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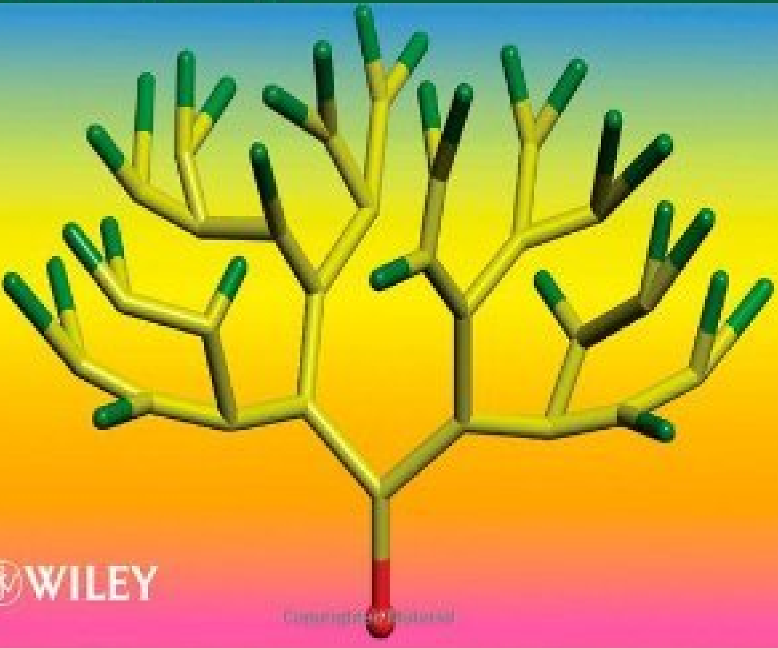
HYPERBRANCHED POLYMERS

Synthesis, Properties, and Applications

Edited by Deyue Yan, Chao Gao, and Holger Frey



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Preface

Since the first works on the fundamental principles of polymerization reactions by Hermann Staudinger in the early 1920s, numerous types of linear polymers have been synthesized and commercialized. This area has now become a mature field, as is demonstrated by the vast applications of such materials in our everyday life.

A novel kind of dendritic polymer architecture emerged in the 1980s. The so-called "dendritic polymers," which mainly comprise the "hyperbranched polymers" and the perfectly branched "dendrimers," are macromolecules with highly branched, three-dimensional globular topology. Normally, dendrimers have to be prepared in demanding multistep syntheses in a classic organic approach. In pronounced contrast, the randomly cascade-branched hyperbranched polymers are obtained in a typical polymer approach at the expense of polydispersity with regard to both molecular weight and branching structure.

Because of to their unusual structures, specific properties, and potential applications, hyperbranched polymers have attracted the increasing attention of both scientists and engineers over the last two decades and the field has become a cutting-edge area in polymer research. Hyperbranched polymers resemble dendrimers in many physical and chemical properties, such as low viscosity, excellent solubility, and large number of functional groups. Yet, they can be readily prepared by one-step polymerizations on a large scale. The first monograph on dendritic macromolecules was published by Wiley-VCH in 1997. Since then, several books on dendrimers and dendrons have been published; however, until now a comprehensive book on hyperbranched polymers does not exist.

Owing to the many facets of synthesis methodologies, characterization of the relevant parameters such as degree of branching (DB) and molar mass, and kinetic theories for various hyperbranched polymerization systems, as well as the increasing number of publications, it has been quite difficult to organize the first monograph on hyperbranched polymers. Invited by Dr. Edmund H. Immergut, a consulting editor for Wiley and Wiley-VCH publishers, we started to conceive and organize the edition of this book since May, 2005. In 2005 and 2006, Chao and Holger met at Mainz, Bayreuth, and Freiburg, Germany several times to discuss the details of this project face-to-face. In July, 2009 when the project was drawing to an end, Deyue and Holger met at Ludwigshafen for further improving the manuscripts. During the Chinese New Year holiday of 2010, Chao, Deyue, and Holger made the final revisions.

This book is targeted to become a comprehensive and useful volume for anybody working in the area of polymer science and polymer engineering, as well as in functional materials. For "newcomers" it will be a valuable source of information on the synthesis, theory, and application of hyperbranched polymers. The book is potentially useful also for readers who work in the fields of organic chemistry, physical chemistry, surface chemistry, theoretical chemistry, supramolecular chemistry, combinational chemistry, pharmaceutical chemistry, medicinal chemistry, environmental chemistry, biochemistry, and bioengineering. There is also a strong link to nanoscience and nanotechnology.

Leading scientists, invited from both academic and industrial fields, contributed chapters covering basic concepts, synthesis, properties, characterizations, theories, modifications, and applications of hyperbranched polymers. So, this book is appropriate as a textbook for courses including polymer chemistry, polymer physics, nanopolymers, biopolymers, functional materials, biomaterials, nanomaterials, and nanochemistry. It is also an interdisciplinary frontier reference book for undergraduates, graduates, teachers, researchers, and engineers.

Even though we have tried our best to bring together the state of the art of hyperbranched polymers, many important articles were not included in this book, partly because the reports on hyperbranched polymers are related to too many other topics and subjects, and partly because this field is still rapidly developing. Also, this book might contain some errors and overlapping content in definitions, classifications, descriptions, and comments. We hope that the readers will give us their valuable comments and advice, so that the book can be further modified in the next edition.

We would like to thank all the authors who have contributed to this book, for their valuable work, patience, and understanding. It is their contributions that have laid the foundation of this book. We also wish to express our sincere gratitude to the editors, Edmund H. Immergut, Jonathan T. Rose, and Amy R. Byers, for their great support, constructive suggestions, and long-term effort. It was their continuing encouragement that helped us to finish this five-year project.

The twentieth century has witnessed the birth, development, and resplendence of conventional linear polymers. It is expected that the twenty-first century will witness the thrive and prosperity of dendritic polymers. As the saying goes, a single flower does not make a spring. We hope that the publication of this primary book will attract more researchers, engineers, students, teachers and enterprisers to grow, irrigate, and cultivate molecular "trees" and make them further bloom and flourish in the near future.

DEYUE YAN, CHAO GAO, and HOLGER FREY
March, 2010

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Chapter 1

Promising Dendritic Materials: An Introduction to Hyperbranched Polymers

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1.1 IMPORTANCE OF BRANCHING

In nature and universe from living to nonliving things, branching occurs anywhere and anytime, such as the Crab Nebula, forked lightning, river basins, trees, nerves, veins, snow crystals, nervures, and proteoglycan ranging from light-years to kilometers, and to microscale and nanoscales (see Figure 1.1 for selected branching patterns). Hence, branching is a general and important phenomenon that could result in faster and more efficient transfer, dissipation, and distribution of energy and/or matter.

1.2 POLYMER ARCHITECTURE

The past century has witnessed pioneering work and blossoming of polymer science and industry, for which various star scientists like Staudinger, Flory,

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

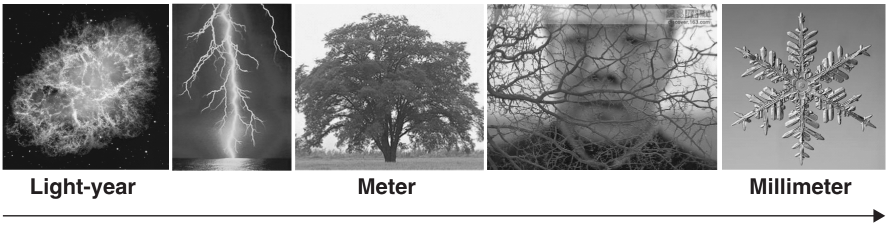


Figure 1.1 Selected branching patterns observed in universe and nature (from left to right: Crab Nebula, forked lightning, tree, vascular network, snow crystal). The images were obtained from the Internet.

Ziegler, Natta, de Gennes, Shirakawa, Heeger, MacDiarmid, Noyori, Sharpless, Grubbs, and others have made great contributions. Notably, their focus has mainly concentrated on linear chains. Since the first beacon publication of "Über Polymerisation" (on Polymerization) in 1920,[1] and the definition of "macromolecules" as primary valence chain systems in 1922 by Staudinger,[2] numerous types of macromolecules with various architectures have been synthesized successfully. Figure 1.2 shows besides linear polymers that seem to approach a period of fatigue nowadays,[3] new paradigms including chain-branched, cross-linked, cyclic, starlike, ladderlike, dendritic, linear brush-like (or comblike), cyclic brush-like, sheetlike, tubal, and supramolecular interlocked architectures keep coming to the fore, promising an unlimited future for and sustainable development of polymer science and technology. Except the linear, cyclic, and interlocked polymers, all other architectures possess branched structures, also indicating the significance of branching in the molecular construction.

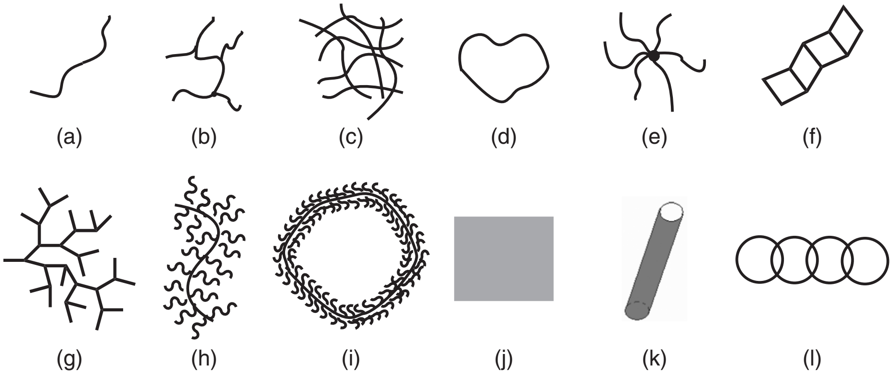


Figure 1.2 Architectures of synthesized macmolecules: (a) linear, (b) chain-branched, (c) cross-linked, (d) cyclic, (e) starlike, (f) ladderlike, (g) dendritic, (h) linear brush-like, (i) cyclic brush-like, (j) sheetlike, (k) tubelike, and (l) interlocked.

1.3 DENDRITIC POLYMERS

In the 1980s, a kind of highly branched three-dimensional macromolecules, also named *dendritic polymers*, was born, and gradually became one of the most interesting areas of polymer science and engineering. Despite the 12 architectures shown in Figure 1.2, dendritic architecture is recognized as the main fourth class of polymer architecture after traditional types of linear, cross-linked, and chain-branched polymers that have been widely studied and industrially used.[4] Up to now, eight subclasses of dendritic polymers have been developed: (i) dendrons and dendrimers, (ii) linear-dendritic hybrids, (iii) dendronized polymers, (iv) dendrigrafts or dendrimer-like star macromolecules (DendriMacro), (v) hyperbranched polymers (HPs), (vi) hyperbranched polymer brushes (HPBs), (vii) hyperbranched polymer-grafted linear macromolecules, and (viii) hypergrafts or hyperbranched polymer-like star macromolecules (HyperMacro) (Figure 1.3), of which the first four subclasses have the perfect and ideally branched structures

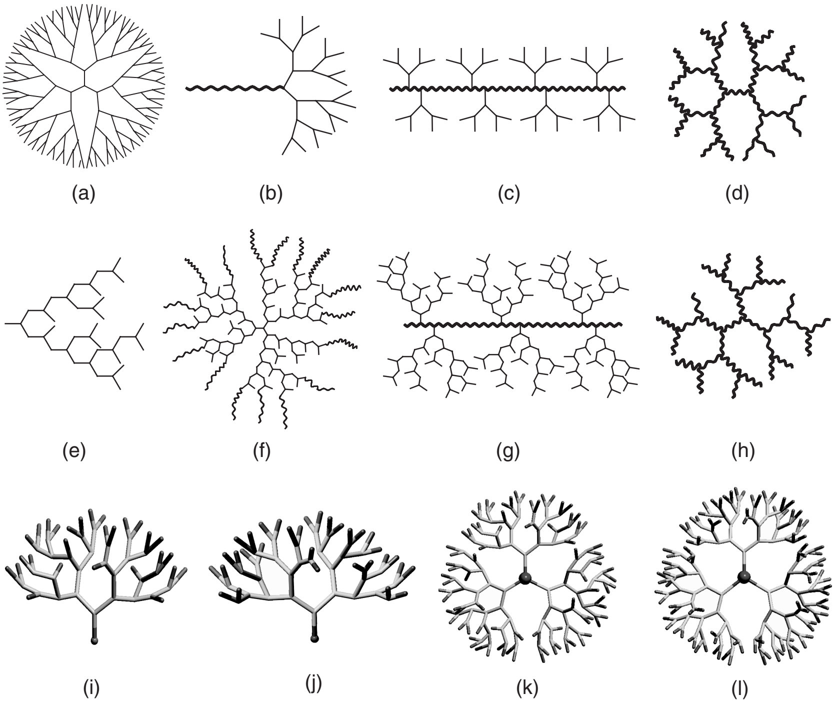


Figure 1.3 Dendritic polymers with different structures. (a) Dendrimer, (b) linear-dendritic hybrid, (c) dendronized polymer, (d) DendriMacro, (e) hyperbranched polymer, (f) multiarm star polymer or hyperbranched polymer brush, (g) HP-grafted polymer, (h) HyperMacro, (i) 3D model of HP with initial unit, (j) 3D model of dendron, (k) 3D model of HP with a core, and (l) 3D model of dendrimer.

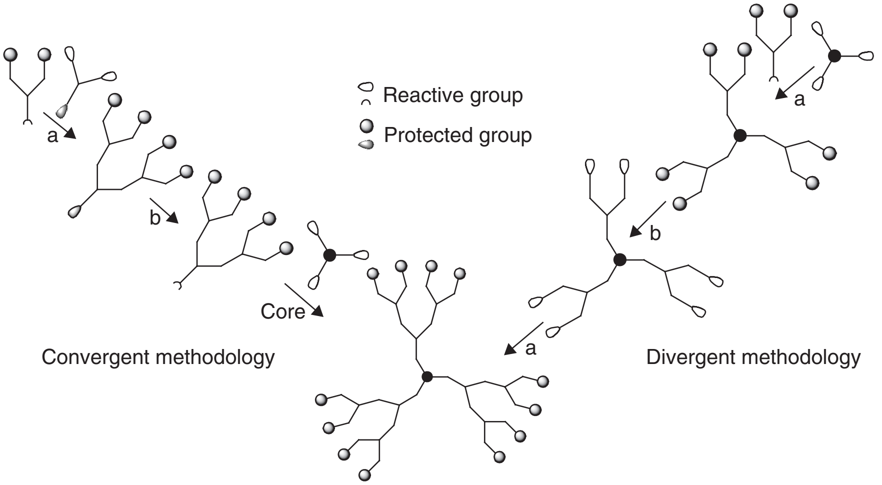


Figure 1.4 Convergent and divergent methodologies for synthesis of dendrimers.

with the degree of branching (DB) of 1.0, and the latter four exhibit a random and irregular branched configuration with lesser DB (normally, 0.4–0.6).[5] Dendrimers and HPs have been extensively studied as the representative regular and irregular dendritic polymers, respectively.

Dendrons and dendrimers can be synthesized by divergent and convergent methodologies (Figure 1.4).[4,6] Generally, step-by-step synthesis, purification, protection, and deprotection are needed for accessing dendrimers with controlled molecular structure, shape, size, and functions and functional groups. Nevertheless, the employment of "click" chemistry, especially the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition between azides and acetylene derivatives (also called *azide–alkyne click chemistry*)[7] and thiol-ene click chemistry possessing the merits of specificity, fast reaction, tolerance to common functional groups and water, greatly furthers the progress of dendrimer synthesis because the tedious protection/deprotection and chromatography-based purification steps are not required any more.[8] There is no doubt that the facile availability of dendrimers would boost their real applications. However, the accessible varieties and structures through click chemistry are still limited at present.

A backbone of linear polymer attached with high density of side dendrons is called a dendronized polymer, which can be prepared by four approaches: direct polymerization of dendron–monomer (macromonomer approach), grafting dendrons to a linear polymer (attach to approach), divergent step-growth from a core of linear polymer (divergent approach), and their combinations (Figure 1.5). The cylindrical dendritic polymers can be easily visualized and manipulated using atomic force microscopy (AFM), affording the chance for the fabrication of complex structures via molecular fusion techniques.[9]

Dendrigrafts[10] and hypergrafts[11] are highly branched star polymers constructed with linear polymeric blocks via controlled and random branching

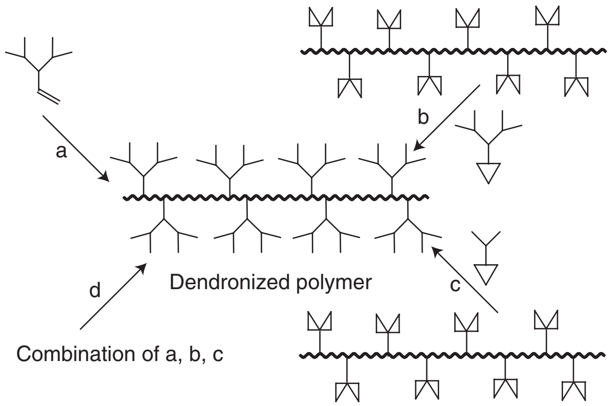


Figure 1.5 Synthesis approaches to dendronized polymers: (a) macromonomer approach, (b) attach to approach, (c) divergent approach, and (d) combination of a, b, and c.

approaches, respectively. They can be prepared through three strategies: divergent "grafting onto," divergent "grafting from," and convergent "grafting through." The sizes of both kinds of macromolecules can range from tens to hundreds of nanometers, which is 1–2 orders of magnitude larger than their counterparts of dendrimers and HPs. Because of the building blocks of linear polymers, dendrigrafts and hypergrafts may show crystallization behavior, which is also essentially different from the classic dendrimers and HPs, which are normally amorphous due to the lack of chain entanglements.

More details on dendrimers, dendronized polymers, and dendrigrafts can be obtained from relevant review papers and books. This book will focus on synthesis, characterization, properties, and applications of HPs.

1.4 HYPERBRANCHED POLYMERS

1.4.1 Concept and History

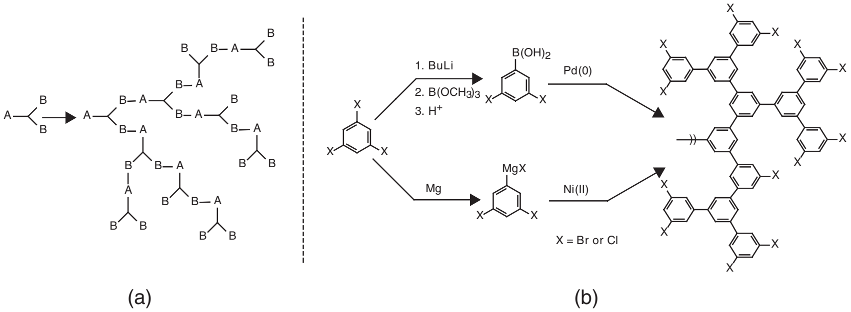
It is known that the DuPont researchers, Kim and Webster, coined the term *hyperbranched polymers* to define dendritic macromolecules that have a random branch-on-branch topology prepared by single-step polycondensation of AB_2-type monomers in the late 1980s.[12–16] The first intentional preparation of the HP (hyperbranched polyphenylene) was warranted as a patent in 1987,[12] and presented to the public at the 1988 American Chemical Society Meeting at Los Angeles.[13,16] Around this period, Tomalia[17] and Fréchet *et al.*[18] also reported their work on highly branched structures independently. But the history of HP is quite long and complex (Table 1.1); it can be dated to the end of the nineteenth century, the gestation period of the synthesized polymer, when Berzelius reported the formation of a resin from tartaric acid (A_2B_2-type monomer) and glycerol (B_3-type monomer).[5,19] In 1901, Watson Smith attempted the reaction of

Table 1.1 History of Hyperbranched Polymers[5]

Year	Case	Lead Authors	Reference
Before 1900	Tartaric acid + glycerol	Berzelius	[19]
1901	Glycerol + phthalic anhydride	Smith	[19]
1909	Phenolic + formaldehyde	Baekeland	[22]
1929–1939	Glycerol + phthalic anhydride	Kienle	[19–21]
1941	Molecular size distribution in theory	Flory	[23–27]
1952	AB_n polymerization in theory	Flory	[28]
1982	$AB_2 + AB$ copolymerization	Kricheldorf	[29]
1987–1991	AB_2 homopolymerization	Kim/Webster	[12–16]
		Odian/Tomalia	[17]
		Fréchet/Hawker	[18]

phthalic anhydride (latent A_2-type monomer) or phthalic acid (A_2-type monomer) and glycerol (B_3-type monomer).[19] Following his report, Callahan, Arsem, Dawson, Howell, and Kienle *et al.* investigated that reaction further, obtaining some interesting results.[19–21] Kienle showed that the specific viscosities of samples prepared from phthalic anhydride and glycerol were lower than those of linear polymers (e.g., polystyrene) given by Staudinger.[20] In 1909, Baekeland produced the first commercial synthetic plastics and phenolic polymers, in his Bakelite Company through the reaction of formaldehyde (latent A_2 monomer) and phenol (latent B_3 monomer).[22] Notably, the soluble precursors of phenolic thermosets obtained just prior to gelation would have the randomly branched topology.

In the 1940s, Flory *et al.* introduced the concepts of "degree of branching" and "highly branched species" when they calculated the molecular weight (MW) distribution of three-dimensional polymers in the state of gelation.[23–27,30] In 1952, Flory pointed out theoretically that highly branched polymers can be synthesized without the risk of gelation by polycondensation of a monomer containing one



Scheme 1.1 Flory's theoretical model of highly branched polymer prepared by polycondensation of AB_2-type monomer (a)[28] and Kim-Webster's hyperbranched polyphenylene prepared by Suzuki polycondensation of AB_2 monomer (b).[13]

A functional group and two or more B functional groups capable of reacting with A (ABg-type monomer, $g \geq 2$) (Scheme 1.1).[28] This work, primarily, lays the theoretical foundation of highly branched polymers. Intrigued by the stronger mechanical property, higher heat-resistant temperature, and other better strentgh-related performance of highly-branched polymers, the subsequent three decades have led to the witnessing of the fast and incredible development of linear polymers, cross-linked plastics, and chain-branched polymers. Accompanying the focus shift from strength to functionality in polymer science and technology, cascade molecules or dendrimers were successfully synthesized via multistep reactions by Vögtle,[31] Tomalia *et al.*,[32] Newkome *et al.*,[33] and Fréchet *et al.*[34] Following the discovery of dendrimers with regular branched units, another kind of dendritic polymer, the HP with random branched units, was prepared by one-step polycondensation of AB_2-type monomer in the late 1980s (Scheme 1.1), as mentioned above.[12–16] Prior to Kim's definition, Kricheldorf and coworkers even prepared highly branched copolymers by one-step copolymerization of AB- and AB_2-type monomers, in 1982.[29] Since the pioneering work of Kim and Webster, HPs have drawn much attention of both scientists and engineers, and has become one of the hottest fields in polymer science and engineering, as demonstrated by the increasing number of related publications (Figure 1.6), due to their unique properties, highly reactive and numerous terminal groups, and wide range of potential applications.[5,35] Till date, various HPs have been prepared, comparable with the library of linear polymers, including polyesters, polyethers, polyamides, polyimides, poly(ether ketone)s, polystyrenes, polyacrylates, polyolefins, and so forth. The details will be discussed in the subsequent chapters of this book.

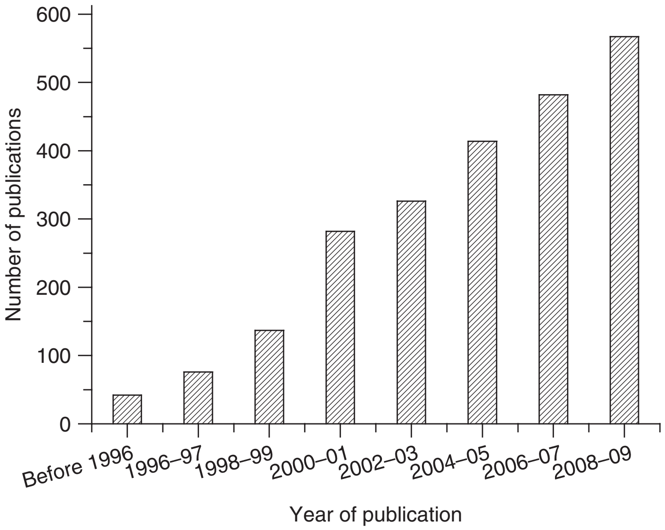


Figure 1.6 Publication numbers during 1988 and 2009 with the topic of "hyperbranched polymers" searched by ISI Web of Science.

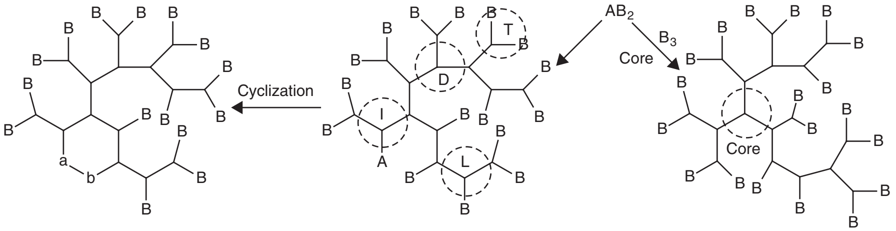


Figure 1.7 Schematic structure of hyperbranched polymer prepared from AB$_2$-type monomer. Reprinted with permission from Ref. [36].

1.4.2 Structure and Properties

Generally, there are initial (I), linear (L), dendritic (D), and terminal (T) repeating units in a hyperbranched macromolecule prepared from an AB$_2$-type monomer.[36] After polymerization, A HP contains, at most, one A group at the initial unit that could be converted into another bond (e.g., *ab* bond) by reaction either with intramolecular B group via cyclization or with extra-added multifunctional core molecules (Figure 1.7). The units with one unreacted B group, two reacted B groups, and two unreacted B groups represent linear, dendritic, and terminal units, respectively. Two types of linear units may exist for a HP prepared from an asymmetric AB$_2$ (or ABB$'$) monomer.

To correlate the units of HP and describe the structure of HPs quantitatively, Fréchet and coworkers gave an equation for the DB at first, as shown in Eq. (1.1).[18]

$$\mathrm{DB} = \frac{\text{(no. of dendritic units)} + \text{(no. of terminal units)}}{\text{total no. of units}} = \frac{D+T}{D+T+L} \tag{1.1}$$

Here, D is the total numer of dendritic units, T the total number of terminal units, and L the total number of linear units. For a HP with large MW, the number of terminal units (T) is very close to that of dendritic units (D). Accordingly, Eq. (1.1) can be simplified as Eq. (1.2).[36]

$$\mathrm{DB} = \frac{1}{1 + L/2D} \tag{1.2}$$

Equation (1.2) is quite useful since L/D or L/T could be easily calculated from the corresponding nuclear magnetic resonance (NMR) spectrum, whereas it is always difficult to know the exact numbers of units.

From the theoretical point of view, Frey, Müller, and Yan *et al*. obtained more strict expressions of DB as a function of conversion (Eq. 1.3) upon the condition of equal reactivity of all B groups,[37,38] which is very helpful in the prediction of DB at a given MW or degree of polymerization (DP).

$$\mathrm{DB} = \frac{2x}{5-x} \tag{1.3}$$

Here, x is the conversion of the A group. When the reaction approaches completion, x would be approximately equal to 1, and thus DB would approach 0.5. The detailed calculations will be discussed in Chapter 13. Most of reported HPs prepared from AB_2 monomers have DBs close to 0.5, indicating the coincidence of theory and experiments.

On the other hand, DB could be altered or even tuned to some extent.[39] To increase DB, the five methods can be attempted: (i) enhancement of the reactivity of the functional group associated with linear units;[40] (ii) addition of multifunctional core molecules (B_f) to the polymerization system of AB_n;[41] (iii) polycondensation of dendrons without linear units;[42] (iv) postmodification of the formed HPs to convert linear units to dendritic ones;[43] and (v) using special catalyst.[44] Through these techniques, DB could be obviously higher than 0.5 or even approach 1 in some cases.[44–48] Attentively, HPs still contain many isomers with different MWs even though DB is equal to 1, which is different from dendrimers that have the same MWs. For tuning DB, four methods can be attempted: (i) copolymerization of AB_2 and AB monomers with different feed ratios;[49] (ii) changing the polymerization conditions such as temperature, feed ratio of monomer to catalyst, and solvent;[50–52] (iii) host–guest inclusion of AB_2 or multifunctional monomer;[53] and (iv) combination of the above ones.

DB is one of the most important parameters for HPs because it has a close relationship with polymer properties such as free volume, chain entanglement, mean-square radius of gyration, glass-transition temperature (T_g), degree of crystallization (DC), capability of encapsulation, mechanical strength, melting/solution viscosity, biocompatibility, and self-assembly behaviors.[54–62] Hence, the properties of HPs can be controlled to some extent by adjusting DB. For instance, Yan and coworkers found that T_g decreased almost linearly and DC decreased exponentially with the increase of DB of poly[3-ethyl-3-(hydroxymethyl)oxetane] (PEHMO) (Figure 1.8).[56–58] Frey and coworkers revealed that hyperbranched polyglycerol (HPG) showed much higher capacity in supramolecular encapsulation of guest dyes than its linear analog.[61] Haag *et al.* demonstrated that a moderate DB (0.5–0.7), rather than too low or too high, is beneficial to gene transfection in the gene delivery using the carrier of

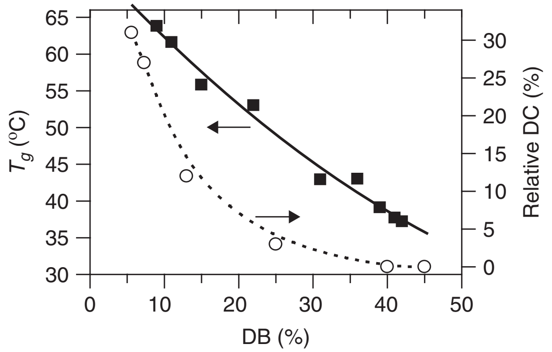


Figure 1.8 Relationship between glass-transition temperature (T_g) or relative degree of crystallization and degree of branching (DB) for poly[3-ethyl-3-(hydroxymethyl) oxetane]s.[56–58]

Table 1.2 Average Degree of Polymerization and Polydispersity Index of Polymers Prepared from AB_g-Type Monomers ($g \geq 1$)[63,64]

Monomer Type	AB	AB_2	AB_g
P_n	$1/(1-x)$	$1/(1-x)$	$1/(1-x)$
P_w	$(1+x)/(1-x)$	$(1-x^2/2)/(1-x)^2$	$(1-x^2/g)/(1-x)^2$
PDI	$1+x$	$(1-x^2/2)/(1-x)$	$(1-x^2/g)/(1-x)$

modified hyperbranched poly(ethyleneimine) (PEI).[62] The correlation of DB and properties will be explained in detail in Chapter 12. So the research on this aspect would be a promising direction, which will discover the essential difference and intrinsic similarity among linear polymers, HPs, and dendrimers. The uncovered rules can be then used to design new materials with desirable applications.

MW is another important parameter for HPs. Theoretically, the equations of number- and weight-average degrees of polymerization (P_n and P_w) and the polydispersity index (PDI) for polymers prepared from AB_g-type monomer ($g \geq 1$) are calculated as Eqs. (1.4)–(1.6).[63,64]

$$\overline{P_n} = 1/(1-x) \tag{1.4}$$

$$\overline{P_w} = (1-x^2/g)(1-x)^2 \tag{1.5}$$

$$\text{PDI} = \overline{P_w}/\overline{P_n} = (1-x^2/g)/(1-x) \tag{1.6}$$

Here, x is the conversion of A group. If $g = 1$ or 2, we obtain the corresponding equations of linear polymers prepared by polycondensation of the AB monomer or the HP prepared from the AB_2 monomer, as shown in Table 1.2.

Therefore, we can see that PDI increases linearly for linear polymers but exponentially for HPs with increasing the conversion (x). So, the PDI of HP would be much higher than that of linear polymers, especially when the reaction approaches completion (i.e., x approaches 1). If $x = 0.99$, for example, the theoretic PDI approximates to 50 for HPs prepared from AB_2 monomers, while PDI is only about 2 for linear polymers. In experiments, nevertheless, PDI is usually smaller than the calculated value because residual monomers and oligomers might be removed from the product during the purification. The HPs with a broad PDI could be used as plasticizers to improve the processability of other polymers. On the other hand, the PDI could be narrowed by the techniques of (i) slow addition of monomers during polymerization,[65–69] (ii) polymerization in the presence of core molecules,[67–73] and (iii) classification of HPs via precipitation or dialysis.

The relationship between MW and viscosity for various polymer topologies is schematically depicted in Figure 1.9.[74] The intrinsic viscosity of HP is normally lower than that of its linear analog but higher than that of dendrimers.

For comparison, the characteristics and properties of HPs are summarized in Table 1.3 with both linear polymers and dendrimers as shown in Ref. [36]. Usually, HPs show ellipsoid-like 3D architecture, randomly branched structure

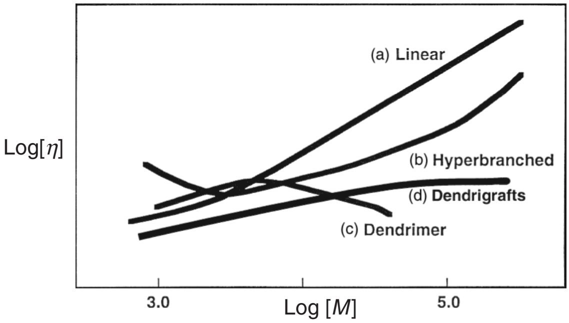
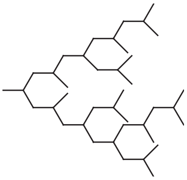
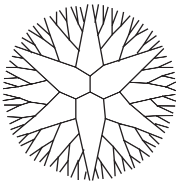


Figure 1.9 Schematic plots for the relationship between intrinsic viscosity (log[η]) and molecular weight (log[M]) for various polymer topologies. Reprinted with permission from Ref. [74].

Table 1.3 Comparison of Hyperbranched Polymer with Linear Polymer and Dendrimer[36]

Polymer	Linear	Hyperbranched	Dendrimer
Structure			
Topology	1D, linear	3D, ellipsoidal	3D, globular
Synthesis	One-step, facile	One-step, cost-effective	Multistep, laborious
Purification	Precipitation	Precipitation	Chromatography
Scaling-up	Already, easy	Already, easy	Already, difficult
MW	Mixed MWs	Mixed MWs	Same MW
PDI	>1.1	>3.0	1.0 (<1.05)
DB	0	0.4–0.6	1.0
Molecular cavity	No	Reversible box	Irreversible box
Entanglement	Strong	Weak	Very weak or no
Viscosity	High	Low	Very low
Solubility	Low	High	Very high
Functional group	At two ends	At linear and terminal units	At terminal units
Reactivity	Low	High	Very high
Strength	High	Low	Very low

with DB < 1.0 (normally 0.4–0.6), wide polydispersity of MW (normally, PDI > 3.0), little molecular entanglement, low viscosity, high solubility, and plenty of functional groups linked at both the linear and terminal units; dendrimers exhibit globular architecture, perfectly branched and regular structure with DB 1.0, extremely narrow polydispersity of MW (ideally, PDI $= 1.0$; normally, PDI < 1.05), no molecular entanglement, very low viscosity, high solubility, and plenty of functional groups at the terminal units. Thus, dendrimers, synthesized via multistep controlled manner, are more close to pure molecules with precise molar mass and exact chemical units and bonds, while HPs, prepared by one-step polymerization, are more close to conventional polymers with distributions of MW and DB. Despite the differences, HPs have very similar properties such as low viscosity, high solubility, weak strength, highly reactive functional groups, and good capacity of encapsulation for guest molecules to dendrimers. On the basis of their cost-effective and large-scale productivity, HPs are preferred in industrial applications as compared with dendrimers.

1.4.3 Synthesis Philosophy

From the philosophy viewpoint, HPs can be accessed via three avenues: bottom up (i.e., polymerization of monomers), top down (i.e., degradation of giant networks or biomacromolecules), and middle upon (modification of as-prepared hyperbranched polymeric-precursor), as illustrated in Figure 1.10.[36] Figuratively, a tree is grown from a sapling (like bottom up), cuttings of branches (like top down), or grafting new branches on a tree (like middle upon) (Figure 1.10b). Most HPs are prepared through the bottom up avenue and modified as amphiphilic polymers, multiarm star polymers (or HPBs), and other polymers with dendritic architecture through the middle upon avenue.[5]

Four methodologies have been developed to prepare HPs via the bottom up ideology: (i) polycondensation of AB_g-type monomers, $(g \geq 2)$

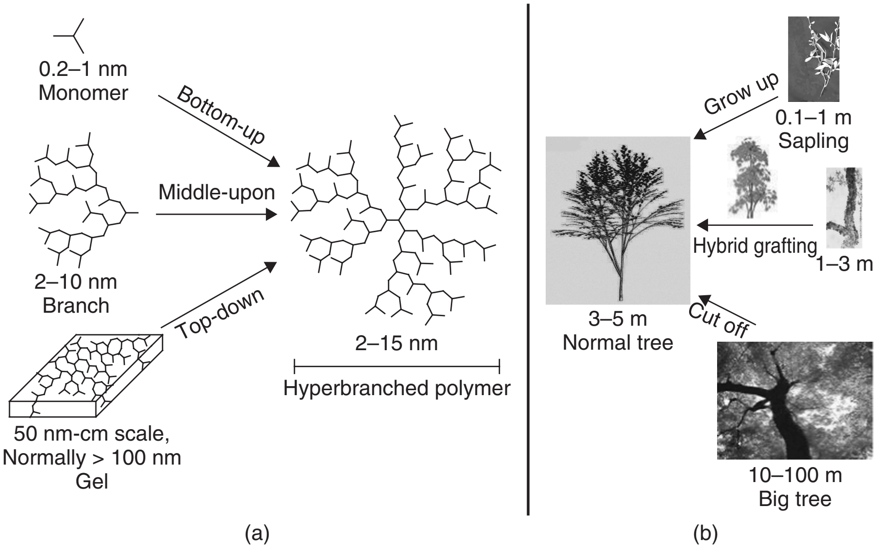


Figure 1.10 Three avenues to obtain hyperbranched polymers (a) and three manners to get a tree (b). Reprinted with permission from Ref. [36].

(ii) self-condensing chain-growth polymerization of AB*-type (latent AB_2) monomers, (iii) polycondensation of symmetric monomer pairs of A_2 and B_3 monomers under the rule of Flory's equal reactivity, and (iv) polymerization of asymmetric monomer pairs (coupling-monomer methodology, CMM) with the principle of nonequal reactivity (Table 1.4). The first two methodologies can also be ranged as "single-monomer" strategy, and the last two ranged as "double-monomer" strategy.[5] The details will be shown in the following chapters respectively. Polycondensation of AB_g-type monomers gave rise to various HPs without the risk of gelation.[5,75] However, most of AB_g monomers are not commercially available, limiting the large-scale production of HPs. Alternatively, polymerization of AB* monomers including vinyl and cyclic molecules can result in HPs capable of controlling DB by employing self-condensing vinyl polymerization (SCVP),[76] atom transfer radical polymerization (ATRP),[77–81] ring-opening polymerization (ROP),[82–86] and proton-transfer polymerization (PTP)[87] techniques. Polycondensation of A_2 and B_3 monomers may achieve soluble HPs with the advantage of commercial availability of monomers.[88,89] But it should be noted that high risk of gelation exists during reaction, and special skills such as slow addition

Table 1.4 Synthesis Approaches for HPs via Bottom Up Ideology

Strategy	Methodology	Approach	Lead author	Year	Reference
Single-monomer	AB_g polymerization	Condensation model	Kim/Webster	1987	[12–14]
		Addition model	Hobson/Feast	1997	[75]
	AB* polymerization	SCVP	Fréchet	1995	[76]
		ATRP	Matyjaszewski	1997	[77–80]
		ROP	Suzuki	1992	[82]
			Penczek	1999	[83]
			Hult	1999	[84]
			Frey	1999	[85]
			Yan	1999	[51,86]
		PTP	Fréchet	1999	[87]
Double/multiple-monomer	Symmetric monomer pair	$A_2 + B_3$	Jikei/Kakimoto	1999	[88]
			Emrick/Fréchet		[89]
	Asymmetric monomer pair (CMM)	$AA' + B'B_2$	Yan/Gao	2000	[92]
		$AA' + B'_2 + B'B_2$	Gao/Yan	2000	[94]
		$A_2 + CB_g$	Gao/Yan	2001	[95–97]
		$ABA_2 + CD_g$	Gao/Yan	2001	[95,98]
		$A^* + CB_2$	DSM Research	2001	[99]

of A_2 monomers to the diluted solution of B_3 and moderate catalysts are needed to delay the gelation point.[90,91] In the CMM, based on the rule of nonequal reactivity of functional groups in specific monomer pairs such as AA' and $B'B_2$, AB_2-type intermediate would predominantly form *in situ* in the initial stage of polymerization if the reactivity of A' is faster than that of A or the reactivity of B' is faster than that of B; further reaction would produce hyperbranched macromolecules without gelation.[5,92–95] More than 10 families of HPs including hyperbranched poly(sulfoneamine)s, poly(ester-amine)s, poly(amidoamine)s, poly(amido-ester)s, poly(urethane-urea)s, and polyesters have been prepared via CMM in various research groups and companies.[96–99] Most recently, the kinetic analysis was also done for the reaction system of "$A_2 + CB_2$", obtaining theoretical results that are in accordance with the experiments.[100] The newly developed CMM possesses both the merits of commercial availability of monomers and no risk of gelation, facilitating the large-scale production and industrial application of HPs.

Through the middle upon ideology, various new polymers derived from HPs can be obtained by the "attach to," "grafting from," "grafting through," and "building block" approaches (Figure 1.11).[5,36] The details have been published in a comprehensive review.[5] Modification of HPs by the "attach to" approach could dramatically change the nature of the polymer such as the T_g and thermal decomposition temperature (T_d) values, because of the significant

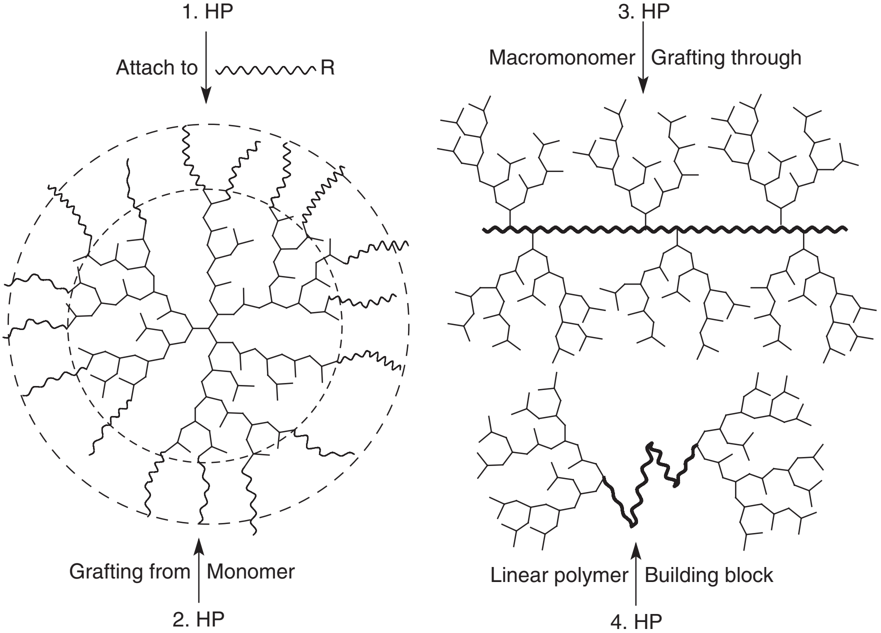


Figure 1.11 Four approaches to modify HPs and construct complex dendritic structures via middle upon ideology.[36]

effect of terminal groups on the properties of HPs. For instance, T_g of hyperbranched polyphenylene can be varied over a wide range, from 96 °C for the polymer with α-vinyl phenyl end groups to 223 °C for the polymer with p-anisol end groups.[15] Through the "attach to" approach, functional HPs such as liquid crystalline,[101] fluorescent HPs,[102,103] and amphiphilic HPs[61,104] were prepared by immobilization of mesogenic, fluorescent molecules, and suitable molecules or chains with opposite polarity on HPs, respectively. Amphiphilic HPs can play the role of a dendritic box to load guest compounds such as dyes and drugs.

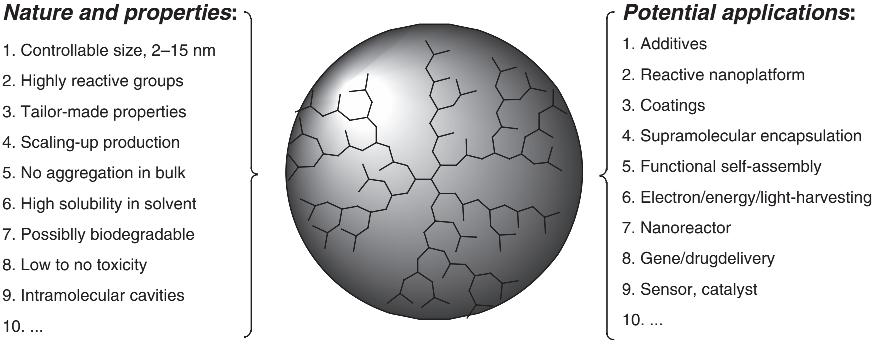
HPBs are accessible by *in situ* polymerization of monomers with HPs as macroinitiators, via the "grafting from" or the "terminal grafting" approach. The physical properties such as polarity, solubility, and flexibility as well as the self-assembly capability of HPs, can be readily tailored by selection of desired monomers. The techniques of controlled radical polymerization such as ATRP, anionic polymerization, and cationic polymerization have been introduced to make HPBs via reaction processes of macromolecular initiator-first and *in situ* one-pot grafting.[105–112] The generally used HP macroinitiators include HPG, PEHMO, hyperbranched polyester of Boltorn, PEI, and so on.

The "grafting through" approach refers to polymerization of hyperbranched macromonomers to prepare cylindrical HPs or HP-grafted combburst polymers.[113] Alternatively, with HPs as building blocks, more complex macromolecules can be constructed.[114] After the pioneering work of Fréchet *et al*. on multibranched polystyrene,[115] Frey and coworkers have studied complex branched polymers comprehensively.[116–119] However, more efforts are required to further their remarkable development in terms of synthesis, purification, properties, and applications, as compared with dendronized polymers.

1.4.4 Applications

On the basis of their unique structures and properties aforementioned, HPs are promising in many applications such as additives, coatings, gene/drug carriers, nanoreactors and nanocapsules, and multifunctional platforms, as listed in Figure 1.12, of which bio- and nanorelevant applications will be discussed in Chapters 15 and 16, respectively.[36]

Recently, the application of HPs in supramolecular chemistry is arousing the tremendous interest of researchers. For one thing, just like birds and nests in a tree, core-shell amphiphilic HPs can be used in supramolecular encapsulation to load guest molecules owing to their intramolecular cavities (Figure 1.13). Dyes, drugs, metal–ion complexes, and inorganic nanoparticles have been successfully filled into hosts of amphiphilic HPs including HPG,[61,120–122] poly(amidoamine) (PAMAM),[123] poly(sulfoneamine),[124] PEI,[125] and poly(ester amide).[126] For the loading of dyes and drugs into the mixture of water and oil, phase transfer occurs generally with the indicative change of the color getting thinner for the guest phase and thicker for the host phase (Figure 1.13). Thus, the loading capacity (C_{load}) can be easily obtained from the UV–vis measurements for either the



***Nature and properties*:**

1. Controllable size, 2–15 nm
2. Highly reactive groups
3. Tailor-made properties
4. Scaling-up production
5. No aggregation in bulk
6. High solubility in solvent
7. Possiblly biodegradable
8. Low to no toxicity
9. Intramolecular cavities
10. ...

***Potential applications*:**

1. Additives
2. Reactive nanoplatform
3. Coatings
4. Supramolecular encapsulation
5. Functional self-assembly
6. Electron/energy/light-harvesting
7. Nanoreactor
8. Gene/drugdelivery
9. Sensor, catalyst
10. ...

Figure 1.12 Characters and potential application fields of HPs.

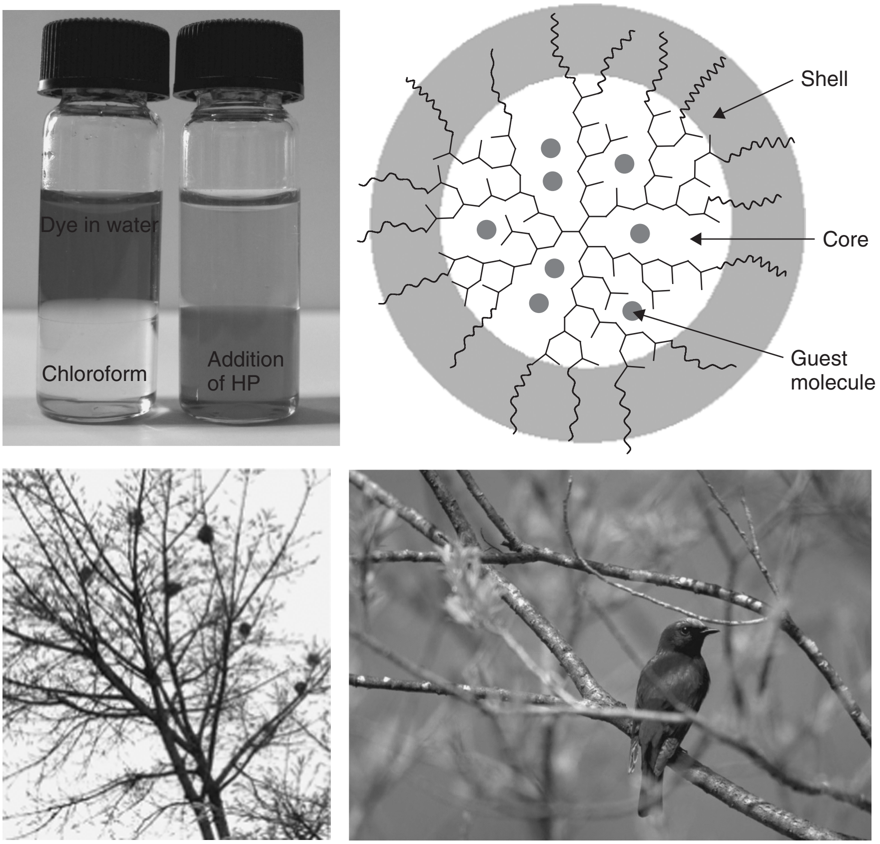


Figure 1.13 Supramolecular encapsulation of hyperbranched polymer to guest molecules (top), and photographs of nests and a bird in a tree (bottom). The bottom photographs are obtained from Internet.

water or the oil phase. By design of special structures, HP hosts can be used to selectively trap particular guests from mixtures and then release them under certain surroundings, declaring that HPs are a promising option in the separation and purification of mixtures as well as in the collection of wastes and in environmental protection.

Besides single-guest encapsulation, double or multiple-guest encapsulation, especially synergistic encapsulation, was found by Gao and coworkers, suggesting that the C_{load} of one sort of guests can be considerably increased in the presence of other sorts of guests.[123] Such a synergistic encapsulation indicates the unicity and complexity of HP-based host–guest chemistry as compared with the relatively smaller hollow hosts such as cyclodextrins, cucurbiturils, and calixarenes. It has been found that the C_{load} of HPs is dependent on the factors of (i) polarity difference between core and shell layers (the larger difference, the higher C_{load}), (ii) size or MW of the HP core (the bigger size, the higher C_{load}), (iii) DB (usually the greater the DB, the higher the C_{load}), (iv) degree of modification (a moderate modification facilitates guest loading, and either too high or too low is unfavorable), and (v) interaction force between the host and the guest (polyelectrolyte host promotes the loading of guests with opposite charges), etc.[36]

Supramolecular self-assembly of HPs highlights the research progress of this subject, as demonstrated in a recent feature article from Zhou and Yan.[127] Classically, only regular molecules such as surfactants and polymers with well-defined structures such as block copolymers with narrow PDIs and dendrimers could self-assemble into ordered objects. On the contrary, HPs possess irregular structures and randomly branched units, implying that it would be difficult for HPs to perform supramolecular self-assembly behaviors. Nevertheless, HPs have been actually demonstrated recently as a versatile materials to show miraculous assembly behaviors after the landmark work of Yan and coworkers who discovered the macroscopic molecular self-assembly by using poly(ethylene oxide) (PEO)-grafted hyperbranched PEHMO.[128] Up to now, assembly objects covered from macroscopy to nanoscale have been achieved with various morphologies and functions, as shown in Figure 1.14,[36,129–136] not only greatly enlarging the extension and intension of supramolecular chemistry, but also opening a promising new field. Being novel building blocks or precursors of self-assembly, HPs have several advantages over conventional molecules: (i) the cavities associated with HPs endow enough room for the adjusting of molecular configuration to form ordered structures; (ii) the multiarms or multifunctional groups afford strong multivalent interactions among primary assemblies making the resulting structures ultrastable; (iii) the globular topology favors the aggregation of macromolecules from any direction; and (iv) the functional groups at linear units may provide extra force for assembly by hydrogen bonding. Owing to the combined merits of big size, stable and flexible structures, the vesicles of multiarm HPs could be used as model membranes to mimic the fusion and fission behaviors of cells under optical microscopy in aqueous solution,[137] advancing the development of bionics that may give the answer for the highlighted question of "how far can we push chemical self-assembly" presented by Science in its 125th anniversary issue.[138]

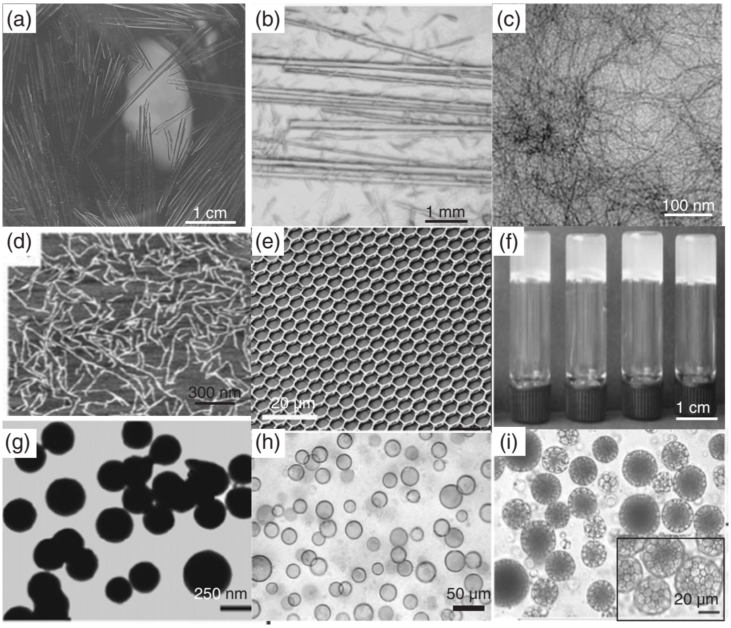


Figure 1.14 Selected self-assembled structures of amphiphilic hyperbranched polymers: macroscopic tubes (a),[128] mesoscopic tubes (b),[129] microscopic tubes (c),[130] nanoscale fibers (d),[131] honeycomb films (e),[132] physical gel (f),[133] spherical micelles (g),[134] vesicles (h),[135] and composed vesicles (i).[136]

Furthermore, Liu *et al*. reported an interesting work by the combination of supramolecular encapsulation and self-assembly of HPs to fabricate large-area honeycomb-like films with strong fluorescence via self-assembly of dye-loaded hyperbranched PAMAM.[132] The emission color or wavelength can be readily tuned by the encapsulated dyes, demonstrating the versatility and flexibility of the supramolecular chemistry of HPs.

Most recently, Gao *et al*. studied the self-assembly of miktoarm HPBs for the first time.[139] As shown in Figure 1.15, the dendritic brushes were synthesized by self-condensing atom transfer radical polymerization (SC-ATRP) of clickable initiator–monomer (click inimer), 3-azido-2-(2-bromo-2-methylpropanoyloxy) propylmethacrylate, followed by one-pot orthogonal multigrafting of PEO and poly(methyl methacrylate) (PMMA) heteroarms via click “attach to” and ATRP “grafting from” approaches, respectively. Self-assembly of the brushes with weight-average molecular weight (M_w) of 204,500 and PDI of 2.62 in DMF and water resulted in spherical micelles with diameters of 150–300 nm. In DMF and methanol, large assembled sheets can be observed. Significantly, the polymerization can be extended to copolymerization of click-inimer and 2-hydroxyethyl methacrylate (HEMA), affording HP with heterofunctional groups of azido, bromo, and hydroxyl. Further one-pot modification of the

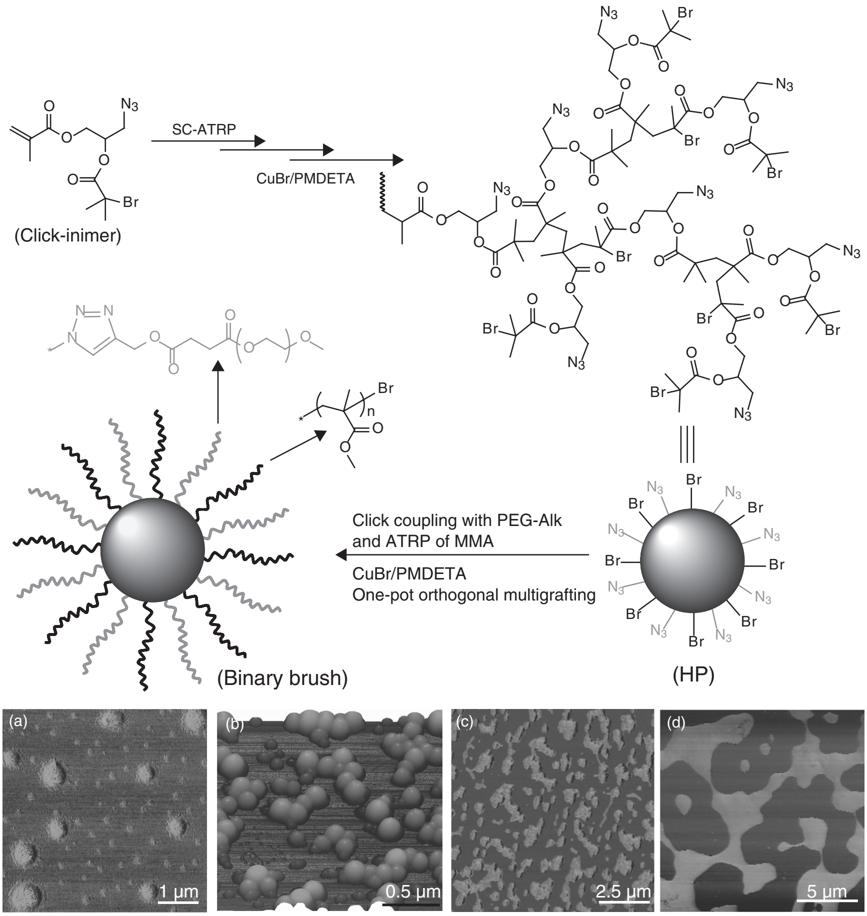


Figure 1.15 Synthesis of miktoarm hyperbranched polymer brushes by SCVP of click-inimer (top), and their dynamically self-assembled structures (bottom) in DMF/water system (a, b) and DMF/methanol system (c, d). Reprinted from Ref. [139] with permission.

multifunctional HP by click chemistry, esterification, and ATRP techniques gave rise to trinary hyperbranched brushes with hydrophilic PEO chains, and hydrophobic aliphatic and poly(*tert*-butyl acrylate) chains. In the DMF and water system, the trinary brushes can self-assemble dynamically into the dendritic tubes with dimensions of hundreds of micrometers. The dynamic assembly mechanism was speculated by the measurements of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and NMR-tracing. The self-assembly of miktoarm HPs opens the door for construction of complex superstructures that may have multiple functions.

In addition, HPs showed great potential in bioapplications. Owing to its water-solubility and biocompatability, HPG has been widely researched as a drug carrier.[122] The MW could be improved to around half a million with controlled anionic polymerization in solution[140] and on solid surfaces,[141] showing fascinating potential in bionanotechnology. After coating HPG on CdTe quantum dots (QDs), the cytotoxicity of QDs was remarkably decreased, and the biostability of QDs significantly improved since the fluorescence of HPG-grafted QDs could be clearly observed after incubating with cells for 24 h, whereas naked QDs were almost completely faded (Figure 1.16).[142] Hyperbranched PAMAM is another promising material that could possibly replace the famous PAMAM dendrimer in bionanotechnology, as it shows nontoxicity and high efficiency in gene transfection when modified with phenylalanine as compared with PEI (Scheme 1.2).[143] Hyperbranched polyphosphates[144] (Scheme 1.3) and polylysines[145] were also reported for potential bioapplications.

Besides the aforementioned potential fields, various new applications can be extended and explored in terms of different demands on the foundation of unique structures and special properties of HPs.

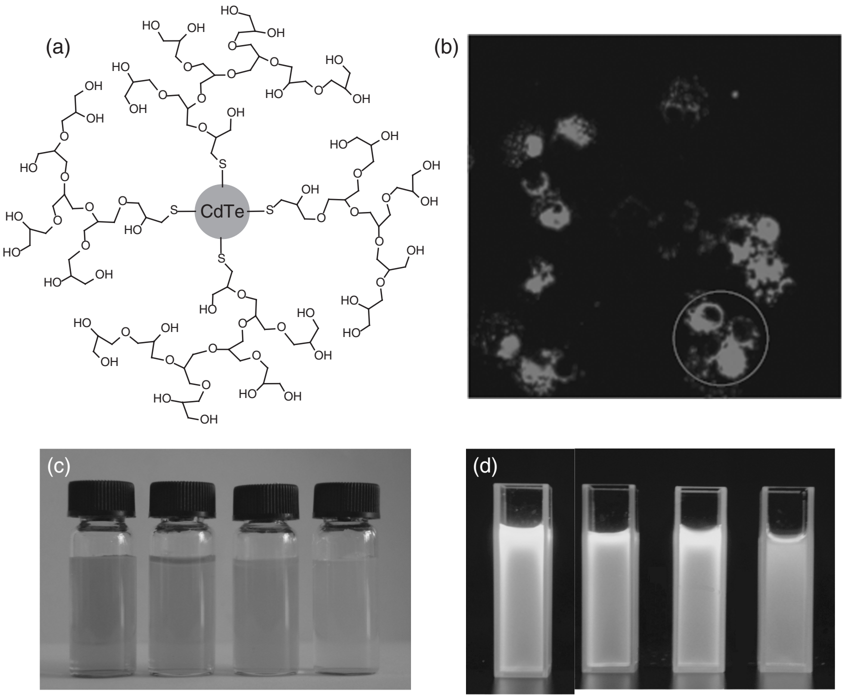
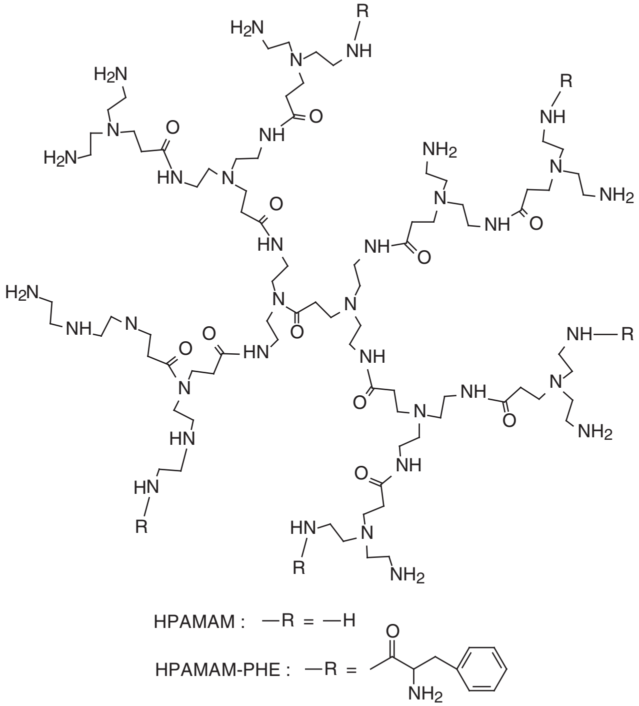


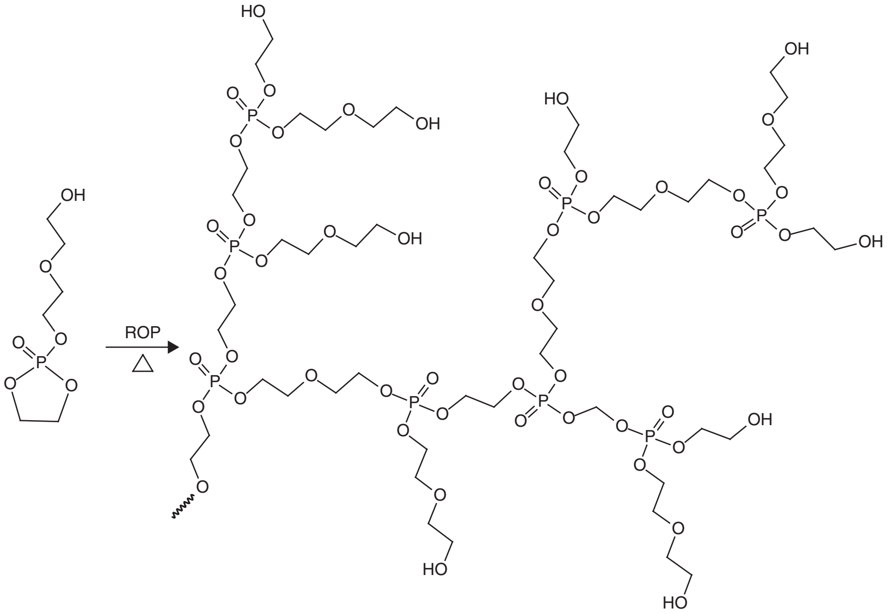
Figure 1.16 Schematic structure of hyperbranched polyglycerol-grafted CdTe quantum dot, QD@HPG (a), confocal microscopy image of A375 cells incubated with QD@HPG (at 2 mg/mL for 8 h) (b), photographs of pristine QDs and QD@HPGs with different amounts of HPG in aqueous solution under daylight (c), and irradiated at 365 nm (d). Reprinted from Ref. [142] with permission.



Scheme 1.2 Chemical structures of hyperbranched poly(amidoamine) (HPAMAM) and HPAMAM modified with phenylalanine (HPAMAM-PHE).[143]

1.5 CONCLUSIONS

HPs are one of the major subclasses of dendritic architecture following linear, cross-linked, and chain-branched ones. Even though HPs have irregular structures with random branched topology, they still possess properties similar to dendrimers, such as low viscosity, high solubility, and large number of functional groups. From the philosophy viewpoint, the imperfect structure partly furnishes HPs with unlimited space for modification, functionalization, control over topology, tuning of DB, adjusting of MW and PDI, and hybridizing by copolymerization and terminal grafting, and so on. Such a flexibility makes the vitality of HPs inexhaustible. Hence, the progress of HPs can not only push the development of polymer science and engineering as well as related subjects, but can also inspire the thoughts of researchers and spread much wider the application realm than the prediction. Despite the limited products of commercialized HPs at present, we believe that more and more industrial applications would be achieved for HPs with their fast development in future, as linear polymers have exhibited in the past century.



Scheme 1.3 Synthesis of biocompatible hyperbranched polyphosphates by thermal ring-opening polymerization (ROP).[144]

Acknowledgment

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Chapter 2

Polycondensation of AB$_x$ Monomers

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2.1 INTRODUCTION

The polycondensation of AB$_x$ monomers is the most widely studied method to prepare hyperbranched polymers, as shown in Scheme 2.1. The A, B, and ab in Scheme 2.1 represent unreacted functional groups (A, B) and reacted ones (ab), respectively. Theoretically, each resulting molecule has one unreacted A group. However, the A group is hardly observed by spectroscopic measurements by increasing the molecular weight for most hyperbranched polymers. The number of the B functional group is equal to $(x + 1)$ for the x-mer molecule prepared from an AB$_2$ monomer. It is well known that the chemical modification of the B group changes the properties of the hyperbranched polymers. This chapter describes the polycondensation of AB$_x$-type monomers, mainly from the synthetic point of view. After a brief discussion on the statistical aspects, the polymerizations are classified into the type of the propagation reactions.

2.2 STATISTICAL CONSIDERATION

2.2.1 Polymerization Behavior

The reactions applied for the self-polycondensation of AB-type monomers are potentially useful for the propagation reactions for AB$_x$-type monomers.

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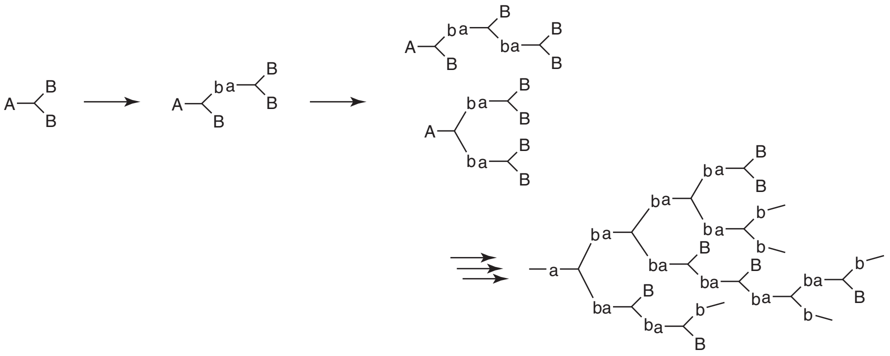


Scheme 2.1

A branching point is usually incorporated in the monomer structure, and an imino group and an aromatic ring are often used for the branching point. The branching point can be prepared during the polymerization in some cases.

As Flory pointed out over 50 years ago,[1] the formation of infinite network is not statistically allowed in the self-polymerization of AB_x-type monomers. However, gelation may occur experimentally when undesired side reactions are involved in the polymerization process. The side reactions may also make the products insoluble in organic solvents. The gel formation would be also observed when intermolecular interaction, such as hydrogen bonding, of propagating molecules is strong enough to form three-dimensional networks. Dilution of the monomer in solution polymerizations might be effective in avoiding gelation caused by the intermolecular interaction. On the other hand, side reactions in the early stage of the polymerization inhibit the formation of polymers having a high molecular weight, especially, when the A functional group in AB_x molecules is consumed by the side reactions such as ring formation to form cyclic oligomers. It has been reported that AB_x monomers composed of flexible chain segments, such as long alkyl chains and siloxane chains, often form cyclic oligomers during the self-polycondensation.

The relationship between the degree of polymerization and the conversion of the functional groups of an A-R-B_{f-1} monomer is described in Table 2.1.[1] The polydispersity, denoted by DP_w/DP_n, of the polymers from AB_x monomers becomes much larger than that of the polymers from AB monomers. The polydispersity of hyperbranched polymers determined experimentally is often large in comparison with that of linear polymers, but smaller than the calculated ones. This is a major drawback for the polymerization of AB_x monomers, and the several attempts to narrow the polydispersity of the resulting hyperbranched polymers have been reported, which involve slow addition of monomers during the polymerization and the polymerization in the presence of core molecules.

Table 2.1 Degree of Polymerization and Polydispersity of Condensation Polymer from A-R-B_{f-1}-type Monomers

Monomer type	A-R-B_{f-1}[a]	AB_2[a]
DP_n	$\frac{1}{1-p}$	$\frac{1}{1-p}$
DP_w	$\frac{1-p^2/(f-1)}{(1-p)^2}$	$\frac{1-p^2/2}{(1-p)^2}$
DP_w/DP_n	$\frac{1-p^2/(f-1)}{1-p}$	$\frac{1-p^2/2}{(1-p)^2}$

[a] p: conversion of A function

2.2.2 Degree of Branching

Hyperbranched polymers are composed of partially branched repeating units which are called *linear units* in addition to fully branched (dendritic) and terminal units. Figure 2.1 shows the schematic architecture of the hyperbranched polymer prepared from AB_2 monomers. When the x in AB_x monomers is more than 2, the resulting polymers have several kinds of partially branched units which are called *semidendritic units*.

In 1991, Fréchet defined the degree of branching (DB) as a factor to explain the structure of hyperbranched polymers, as described in Eq. (2.1).[2] DB can be used as an indicator in order to compare the structure of hyperbranched polymers

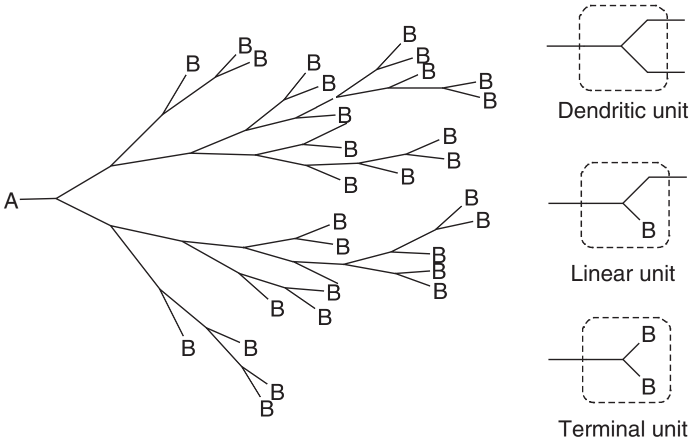


Figure 2.1 Schematic architecture of the hyperbranched polymer prepared from an AB_2 monomer.

with the corresponding dendrimers and dendrons.

$$\text{Degree of branching (DB)} = \frac{D+T}{D+T+L} \tag{2.1}$$

where D is the number of dendritic units, T is the number of terminal units, and L is the number of linear units. Frey has reported the modified definition of DB based on the growth directions, as shown in Eq. (2.2).[3]

$$\mathrm{DB} = \frac{2D}{2D+L} = \frac{D+T-N}{D+T+L-N} \tag{2.2}$$

where N is the number of molecules. Equations (2.1) and (2.2) give almost the same DBs for the hyperbranched polymers with a high molecular weight since N in Eq. (2.2) can be negligible in such cases. Frey also pointed out that DB statistically approaches 0.5 in case of the polymerization of AB_2 monomers.[3] Most of hyperbranched polymers reported in the literature have actually DBs close to 0.5. It should be noted that hyperbranched polymers possess many isomers even if DB is equal to 1. If propagation reactions proceed symmetrically and DB of the polymer is equal to 1, the architecture of the hyperbranched polymer is eventually the same as that of the corresponding dendron.

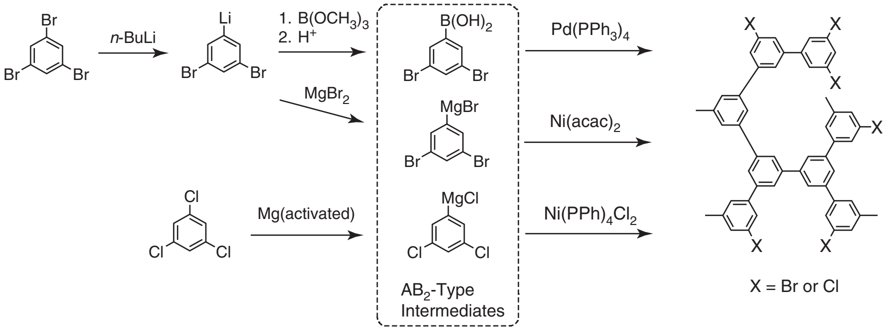
NMR spectroscopy is a powerful tool to determine the DB of hyperbranched polymers. In addition to ^{1}H NMR, ^{13}C, ^{15}N, ^{19}F, and ^{29}Si NMR spectroscopic measurements have been used to determine the DB for various hyperbranched polymers. When the polymer is composed of degradable linkages such as esters and carbonates, the DB could be calculated by the quantitative analyses for the products after degradation.

2.3 POLYMERIZATION OF AB_x-TYPE MONOMERS

2.3.1 C–C Coupling Reactions

2.3.1.1 Metal-Catalyzed Cross Couplings

Metal-catalyzed cross couplings are apparently one of the most important and useful condensation reactions for polymer syntheses, especially for π-conjugated polymers. The incorporation of a hyperbranched structure can improve the poor solubility of the highly conjugated polymers. In 1990, Kim reported hyperbranched polyphenylenes by the one-step polycondensation of (3,5-dibromophenyl) boronic acid.[4,5] The polyphenylenes are the first hyperbranched polymers which are prepared as alternatives to dendrimers. The synthetic strategy is described in Scheme 2.2. The AB_2-type intermediates were not stable and used immediately for the polymerization. The polymerization resulted in the formation of the hyperbranched polyphenylenes whose molecular weights (M_n) determined by GPC with polystyrene standards were in the range



Scheme 2.2

5000–35,000 with the polydispersity (M_w/M_n) less than 1.5. In the ^{1}H NMR spectra, the peaks corresponding to aromatic protons became broad, which suggested that the polymer contained many isomeric structures. The ^{13}C NMR spectra gave the information for the branching efficiency of the hyperbranched polyphenylenes. Statistically, the ratio of C_1 carbon connected with phenyl rings and C_4 carbon located between carbons connected with halogens, described in Figure 2.2, becomes 0.25 when the degree of polymerization is larger than 24 and halogens are located only on the peripheral phenyl rings. The branching efficiency based on the deviation of the ratio of C_1 and C_4 from 0.25 was 70% in the case of the polymerization catalyzed by palladium, which implied that the resulting polymer contained one-substituted linear units, as shown in Figure 2.2.

The hyperbranched polyphenylenes were soluble in organic solvents, such as *o*-dichlorobenzene, tetrachloroethane, and tetrahydrofuran, although the main chain of the polymer was only composed of rigid aromatic rings. The lithiation of the Br-terminated hyperbranched polyphenylene and the subsequent reactions with electrophiles provided the modified (70–80%) polymers with various functional groups on the periphery. When nonpolar functions such as methyl and trimethylsilyl groups were introduced, the modified polymers were soluble in diethyl ether and showed the glass transition temperature at 152 °C, which was lower than the original transition temperature at 238 °C. On the other hand, the

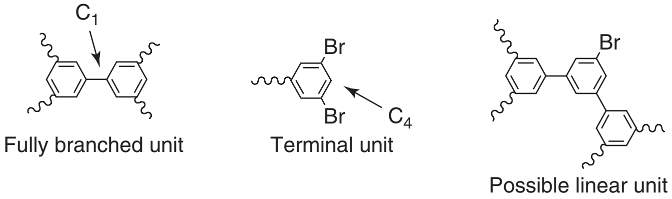
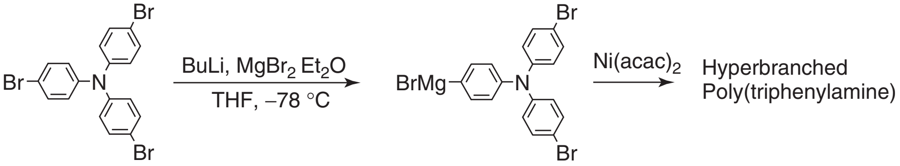


Figure 2.2 Possible repeating units for the hyperbranched polyphenylene.

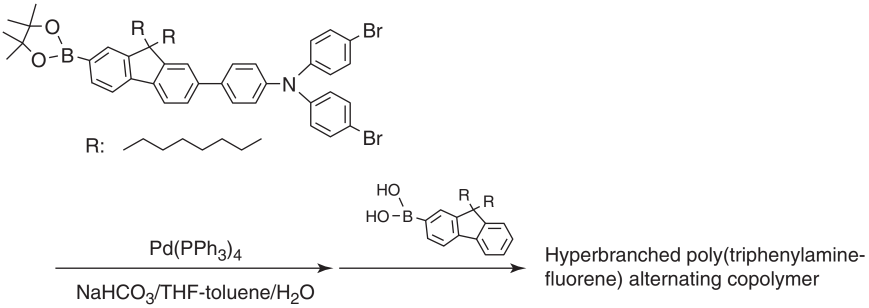
polymer became soluble in water by the formation of micelle when carbon dioxide was used as an electrophile to convert the B functional group into lithium carboxylate. The hyperbranched polyphenylenes were examined as multifunctional initiators for the preparation of star polymers.

Organic and polymeric materials based on triphenylamine are one of the promising compounds as components for organic electroluminescence diodes due to their stability, electrical conductivity, and hole-transporting ability. Hyperbranched poly(triphenylamine)s were prepared by the Ni(II)-catalyzed cross-coupling of the AB_2-type Grignard reagent, as shown in Scheme 2.3.[6] The resulting polymer had an average molecular weight of 4000 and was soluble in organic solvents, such as tetrahydrofuran (THF) and chloroform. The polymer showed a new transition band at 360 nm, possibly brought about by the conjugation between biphenylene units and nitrogen atoms. Hyperbranched poly(triphenylamine-fluorene) alternating copolymers with high molecular weight were also prepared by the one-pot Suzuki coupling of the AB_2 monomer carrying flexible alkyl chains, as shown in Scheme 2.4.[7] The dialkyl fluorene group improved the solubility of the resulting polymers to form the high molecular weight copolymer. The weight-average molecular weight and the polydispersity (M_w/M_n) of the copolymer calibrated with polystyrene standards were 169,000 and 1.16, respectively. Both the absorption and emission spectra of the copolymer red-shifted in comparison with those of the starting monomer.

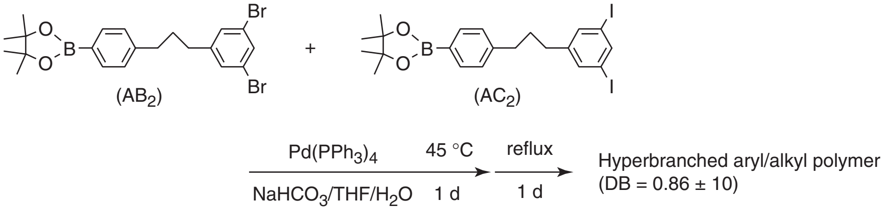
Hyperbranched aryl/alkyl polymers with a high DB were prepared by the one-pot Suzuki coupling reaction of AB_2 and AC_2 monomers, as shown in



Scheme 2.3



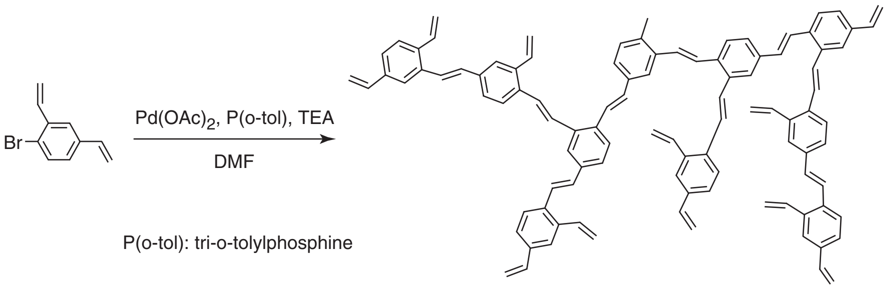
Scheme 2.4



Scheme 2.5

Scheme 2.5.[8] It is well known that iodoaromatics react with arylboronic acids under mild condition in comparison with bromoaromatics. Therefore, the polymerization was carried out in a one-pot and two-step temperature program. The AC_2 monomer should be consumed during the first stage to form multi B functional oligomers. The DB of 86 ±10% was achieved by the polymerization of the AB_2 and AC_2 monomers, while the homopolymerization of the AB_2 monomer resulted in the formation of the polymer with a DB of 56 ± 10%. The dramatic decrease in the peak intensity of the linear unit was observed in their ^{13}C NMR spectra.

Hyperbranched poly(phenylene vinylene)s were prepared by palladium-catalyzed Heck reactions.[9–11] Hyperbranched poly(1,2,4-phenylene vinylene) was prepared from 5-bromo-1,3-divinylbenzene, as shown in Scheme 2.6.[9] Since both the 1,2- and 1,4-connectivity can contribute to the extension of the conjugation length, the conjugation of the hyperbranched poly(1,2,4-phenylene vinylene) should be extended and be dependent on the degree of polymerization in contrast to hyperbranched poly(1,3,5-phenylene vinylene). It was indeed observed that the UV–vis absorption and photoluminescence spectra red-shifted and depended on the molecular weight of the resulting polymer. The red-shifted emission over 490 nm and the lack of the emission at 410 nm also indicated an efficient energy transfer and funneling process from the higher bandgap



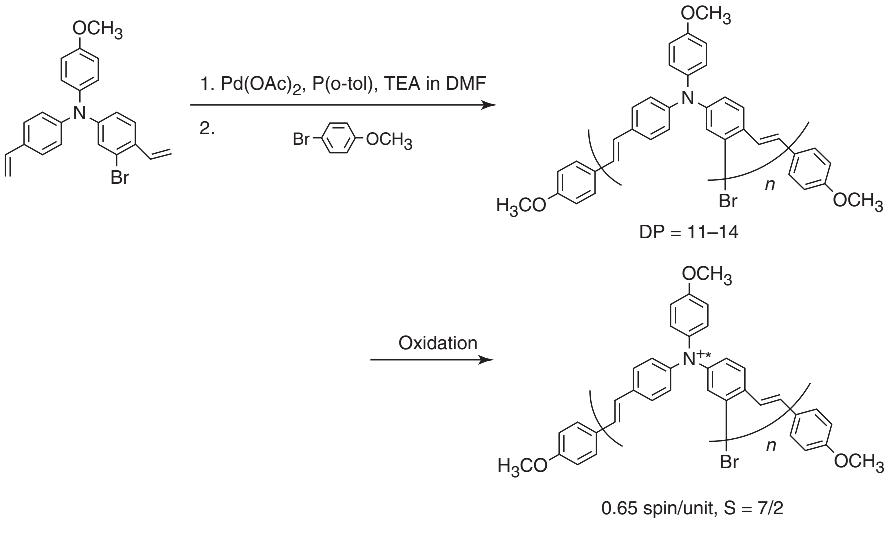
Hyperbranched poly(1,2,4-phenylene vinylene)
(M_w: 2800–20,500)

Scheme 2.6

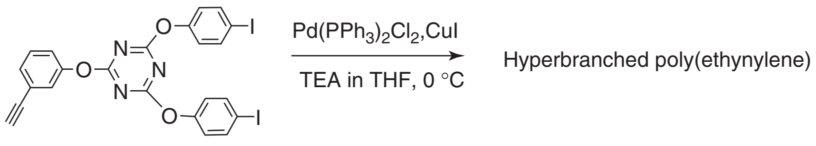
1,2-linking branches to the lower bandgap 1,4-linking backbones. Nishide reported the preparation of hyperbranched poly(1,2,4-phenylene vinylene anisylaminium) as a stable high-spin polymer (Scheme 2.7).[11] The aminium polyradical was generated by electrochemical or chemical oxidation. It was observed that the spin concentration based on the titration with *n*-tetrabutylammonium iodide was 0.65 spin/unit and the average spin quantum number was 7/2 even at 70 °C.

Hyperbranched poly(ethynylene)s were prepared by Pd-catalyzed C–C coupling reactions of the AB_2 monomer, which possess one aryl ethynyl and two aryl iodide units, as shown in Scheme 2.8.[12] The hyperbranched poly(ethynylene)s were soluble in organic solvents, and the M_w determined by GPC ranged from 6000 to 10,000 with the polydispersity (M_w/M_n) of 1.6–3.0. Spectroscopic measurements indicated that the polymer contained diacetylenic moieties (ca. 25%) formed by the oxidative coupling of two aryl ethynyl units in addition to the desired aryl ethynylene units.

Since acetyl groups activate both the ortho C–H bonds for the addition reaction to olefins catalyzed by ruthenium complexes, acetophenone derivatives



Scheme 2.7



Scheme 2.8

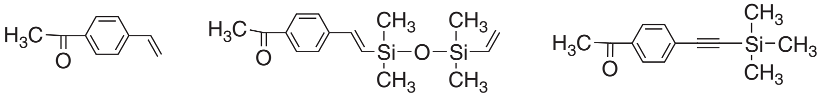
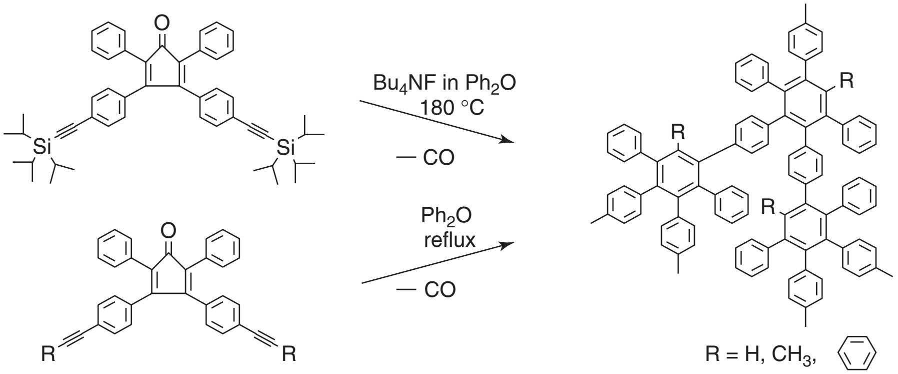


Figure 2.3 AB_2 monomers for Ru-catalyzed self-polycondensation.

which have a vinyl or an ethynyl group should be suitable AB_2 monomers for the corresponding hyperbranched polymers. Figure 2.3 shows the list of AB_2-type monomers reported for Ru-catalyzed polycondensations.[13–15] The ruthenium hydride complex ($[Ph_3P]_3RuH_2CO$) and its coordinately unsaturated complex prepared by the hydrogenation of styrene were found to be effective for the polymerization. The hyperbranched polymer prepared from 4-acetylstyrene had the molecular weight in the range 3700–13,900 (M_w by GPC) and showed good solubility in THF and toluene but was insoluble in methanol.

2.3.1.2 Diels–Alder Reactions

Diels–Alder reactions are inherently reversible, but the reversibility is prevented by the removal of the small molecules from the reaction mixture, which is preferred as a propagation reaction for polycondensation. Müllen has reported the synthesis, properties, and applications of dendritic and hyperbranched polyphenylenes prepared by Diels–Alder cycloaddition reactions (Scheme 2.9).[16,17] The AB_2-type molecules have one cyclopentadienone and two triple bonds as a diene and dienophiles, respectively. The triisopropylsilyl-protected monomer was heated in the presence of tetrabutylammonium fluoride to form the deprotected dienophiles *in situ*. The weight-average molecular weight of the polymer determined by size-exclusion chromatography (SEC) measurements ranged from 3000 to 107,500 and the 18-mer was detected by matrix-assisted laser disoorption/ionization time-of-flight (MALDI-TOF) mass



Scheme 2.9

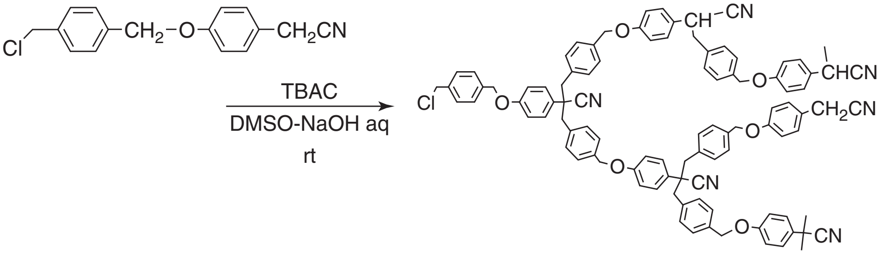
spectroscopy. The resulting hyperbranched polyphenylenes were soluble in toluene and benzene, whereas the polymers were composed of extremely dense packing of benzene rings.

2.3.1.3 Nucleophilic Substitution by Activated Methylenes

The methylene group activated by electron-withdrawing groups can be used as a difunctional nucleophile. The AB_2-type monomers which have an activated methylene and a chloromethyl group were reported as starting materials to form hyperbranched polymers.[18,19] The polymerization of 4-(chloromethyl)phenylacetonitrile proceeded in dimethylsulfoxide (DMSO) in the presence of NaOH aqueous solution. The activated methylene units are changed to branching junction during the polymerization. The polymerization in the presence of tetra-*n*-butylammonium chloride (TBAC) as a catalyst resulted in gelation, although the molecular weight of the polymer prepared without catalysts was not high enough. The polymerization of 4-(4′-chloromethylbenzyloxy)phenylacetonitrile proceeded in a DMSO−NaOH(aq) medium in the presence of TBAC without gelation in high yield, as shown in Scheme 2.10.[19] The M_n determined by ^1H NMR spectrum was 9,100, and GPC measurement suggested a broad molecular weight distribution. The resulting hyperbranched polymers were soluble in organic solvents, such as dimethylformamide (DMF), DMSO, and THF.

2.3.1.4 Electrophilic Acylations

Electrophilic acylations of carbonyl compounds to activated aromatic rings are also useful reactions for the preparation of hyperbranched poly(ether ketone)s. Shu reported the preparation of hyperbranched poly(ether ketone)s from AB_2 and A_2B monomers shown in Figure 2.4.[20,21] The polymerization was carried out in the presence of phosphorus pentoxide/methanesulfonic acid as the condensing agent and solvent. The soluble hyperbranched poly(ether ketone)s were isolated in good yield. The functional groups on the periphery dramatically affected the solubility and glass transition temperature. It was reported that the ammonium



Scheme 2.10

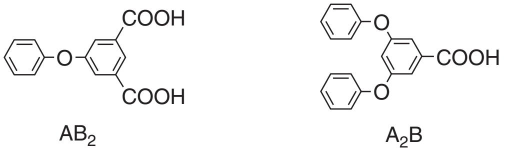
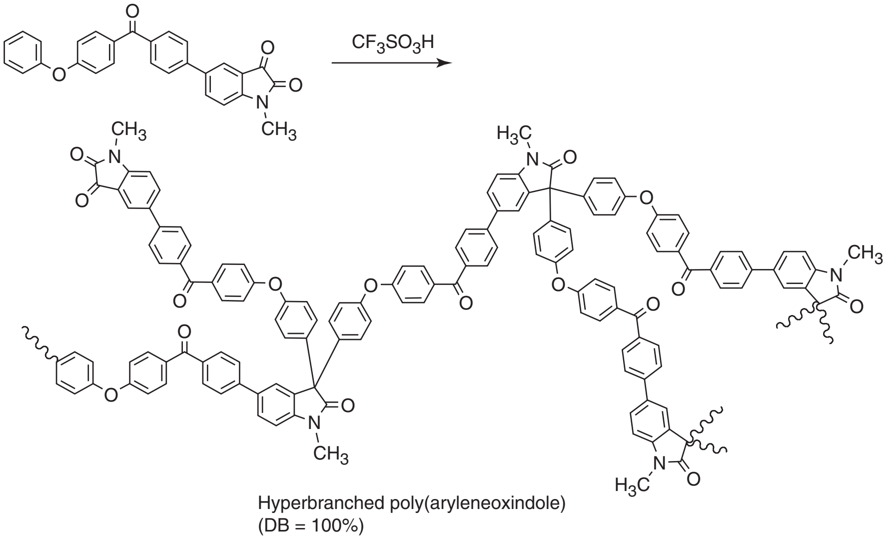


Figure 2.4 AB_2 monomers for hyperbranched poly(ether ketone)s through electrophilic acylation.

salt of the hyperbranched poly(ether ketone) from the AB_2 monomer was soluble in water and behaved as a unimolecular micelle. It should be noted that hyperbranched poly(ether ketone)s can also be prepared through the nucleophilic substitution of phenoxides to aromatic halides, as described in Section 2.3.2.1.

The condensation of isatins with aromatic compounds in the presence of triflic acid proceeds quantitatively to form 3,3-diaryloxindoles. Hyperbranched poly(aryleneoxindole)s were prepared through the superacid-induced condensation, as shown in Scheme 2.11.[22] Since the isatin ring in the monomer quantitatively reacts with two equivalent of the aromatic ring, the hyperbranched poly(aryleneoxindole) with a DB of 1.0 (100%) should be formed by the self-polycondensation. The polymerization was carried out in triflic acid at 60 °C. The resulting polymers were soluble in organic solvents and had the molecular weight of 20,000 (M_w by GPC). All NMR spectroscopic data indicated the DB of 100%, as no traces of linear units could be observed. The chemical modification of the terminal isatin ring in the hyperbranched poly(aryleneoxindole) was also reported.



Scheme 2.11

2.3.2 C–O Coupling Reactions

2.3.2.1 Nucleophilic Substitution Reactions by Phenoxides or Alkoxides

The self-polycondensation through nucleophilic substitution reactions by phenoxides or alkoxides gives hyperbranched polyether derivatives. Figure 2.5 shows the typical design of monomers for the self-polycondensation. Electron-withdrawing groups are generally required for the activation of aromatic halides, whereas aryl bromides can react with phenoxides in the presence of copper catalysts (Ullmann-type reactions). Alkyl halides can react with phenoxides or alkoxides without activation. Depending on the electron-withdrawing group, the resulting polymers are hyperbranched poly(aryl ether)s, poly(ether ketone)s, poly(ether sulfone)s, poly(ether amide)s, poly(ether phosphine oxide)s, poly(ether imide)s, and poly(ether quinoxaline)s.

In 1993, Miller and Neenan first reported the preparation of hyperbranched poly(aryl ether)s by the nucleophilic aromatic substitution, as shown in Scheme 2.12.[23] The resulting polymers are recognized as dendritic analogs of engineering plastics such as poly(ether ketone) and poly(ether sulfone). The fluorides located at the para position are activated by the other fluoride groups connected at the same phenyl ring or the electron-withdrawing spacer group (X). The weight-average molecular weight of the resulting polymers determined by SEC versus polystyrene standards was in the range 11,300–134,000, which was dependent on the structure of the spacer group. The resulting polymers were soluble in common organic solvents such as chloroform and THF, although the polymers were composed of aromatic rings and short spacer units. Thermal gravimetric analyses under nitrogen revealed that the hyperbranched polyethers retained over 95% of their mass up to 500 °C and had high thermal stability, similar to linear poly(ether ketone)s and poly(ether sulfone)s. Glass transition temperature was observed in the range 135–231 °C but melting points were

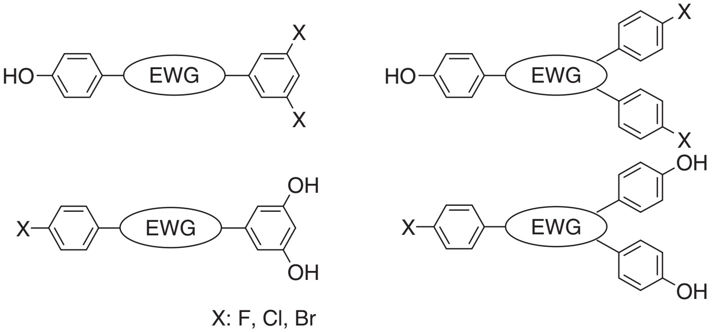
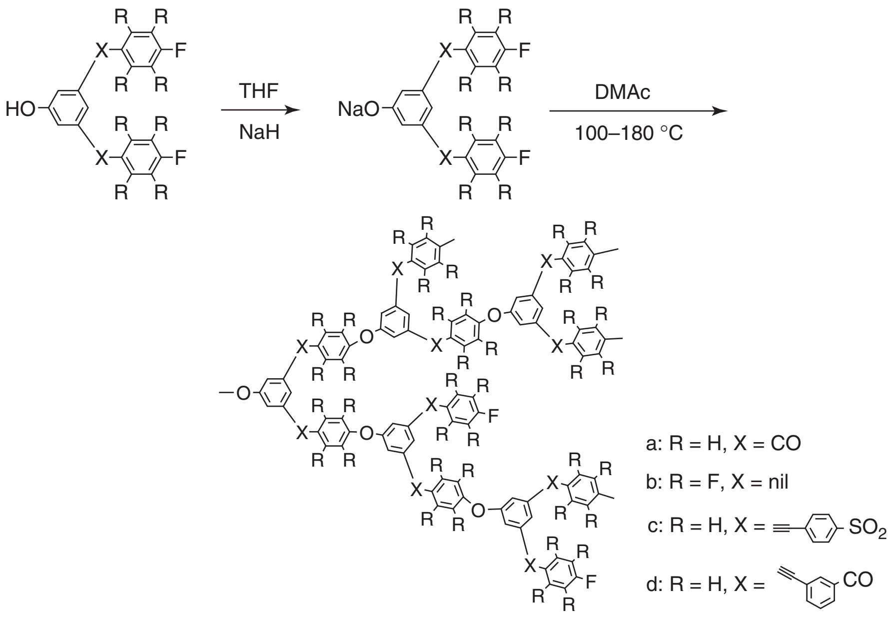


Figure 2.5 Design for AB_2 monomers for hyperbranched polyethers through nucleophilic aromatic substitutions by phenoxides.



Scheme 2.12

not detected. Hult investigated the hyperbranched poly(fluorinated aryl ether) for optical waveguide applications.[24] It was reported that the hyperbranched poly(fluorinated aryl ether) had very low losses in the near-infrared (NIR), 0.1 dB/cm at 1550 nm, and the refractive index in the range 1.450–1.638 depending on the structure of the terminal functional group.

Hawker reported a systematic study for the synthesis of hyperbranched poly(ether ketone)s by nucleophilic aromatic substitution of AB_2, AB_3, AB_4, and A_2B monomers listed in Figure 2.6.[25,26] The self-polymerization was carried out in N-methylpyrrolidone in the presence of potassium carbonate with an azeotropic distillation of water with toluene. Soluble hyperbranched poly(ether ketone)s were isolated in good yield with the M_n in the range 20,000–55,000. The DB for the polymer prepared from the A_2B monomer was 0.15, whereas that for the polymer prepared from the AB_2 monomer was 0.49. The AB_3 and AB_4 monomers having prefabricated dendritic units gave the polymer with a higher DB. Solubility of the hyperbranched poly(ether ketone)s was highly dependent on the terminal unit arising from B functional groups. The hydroxy-terminated hyperbranched poly(ether ketone) was soluble in aqueous alkaline solutions. In the case of the hyperbranched poly(ether ketone)s, the thermal properties were independent of macromolecular architecture, that is, DB, but depended remarkably on the nature of the chain end functional groups, with a glass transition temperature in the range 97–290 °C. The hydroxy- and fluoro-terminated hyperbranched poly(ether ketone)s were stable up to 480 °C under nitrogen with 10% weight loss above

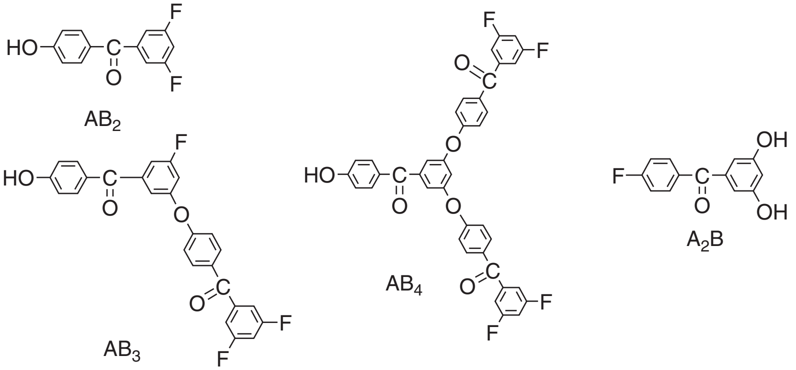


Figure 2.6 AB_x monomers for hyperbranched poly(ether ketone)s reported by Hawker.

500 °C. All the hyperbranched poly(ether ketone)s were completely amorphous although their linear analogs have a high degree of crystallinity.

Various hyperbranched poly(aryl ether)s have been prepared from the AB_2-type monomers having electron-withdrawing spacer groups. The AB_2 monomers reported in the literature are listed in Figure 2.7.[27–38]

Some of the heterocyclic groups act as efficient electron-withdrawing groups for nucleophilic aromatic substitutions. Moore reported the preparation of hyperbranched poly(ether imide)s from the AB_2 monomer, as shown in Scheme 2.13.[39–41] The imide ring activates the fluoride, and the silylated phenols are deprotected during the polymerization. The *tert*-butyldimethylsilyl (TBDMS) group was less labile than trimethylsilyl groups and, therefore, allowed thorough purification of the monomer by recrystallization. The DB of the hyperbranched poly(ether imide) determined by ^1H NMR measurement was 0.66, which agreed well with the DB estimated from a study of a model compound.[42] The prolonged heating caused a transetherification reaction, which lowered the DB to 0.42. The M_n's determined by GPC in N-methyl-2-pyrrolidinone (NMP) containing lithium bromide with light scattering calibration were in the range 51,600–85,000. The hyperbranched poly(ether imide) was soluble in common organic solvents. The temperature for 10% weight loss in air was 530 °C, which implies that the polymer is one of the most thermally stable hyperbranched polymers. The effect of the terminal functional groups of the hyperbranched poly(ether imide) on the glass transition temperature, solubility, film-forming ability, and wettability was investigated.[43] Figure 2.8 shows the other AB_2-type monomers for the preparation of hyperbranched poly(ether imide)s by the nucleophilic aromatic substitution.[44–46] It should be noted that hyperbranched poly(ether imide)s can be prepared by the formation of imide rings, as described in Section 2.3.3.1. Hyperbranched poly(aryl ether phenyl quinoxaline)s[47–50] and hyperbranched poly(ether benzoxazole)s[51] were also prepared by the same strategy from the AB_2 monomers having electron-withdrawing heterocyclic groups.

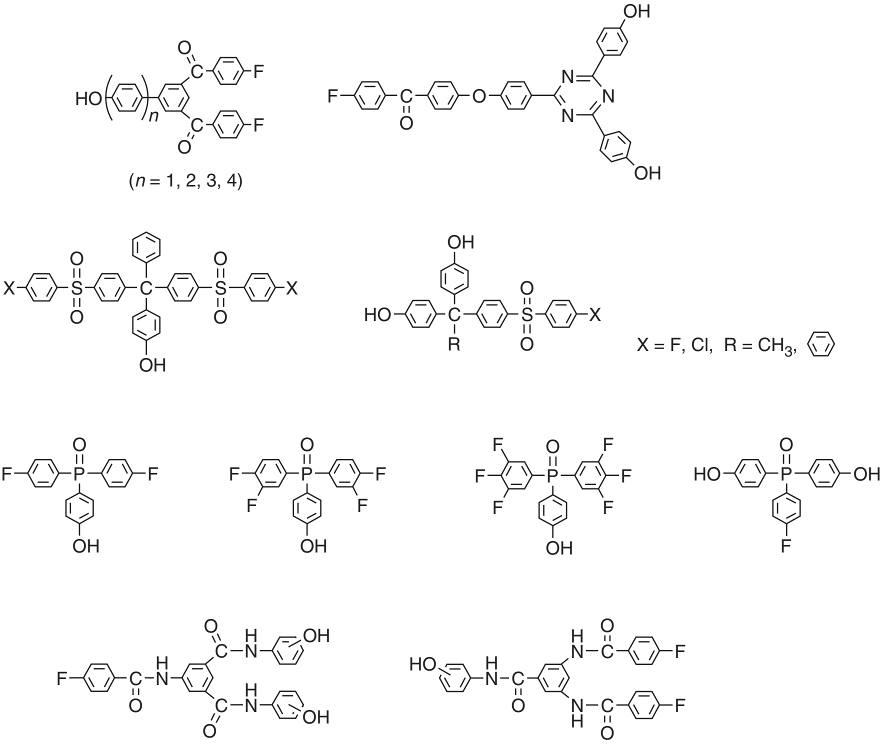
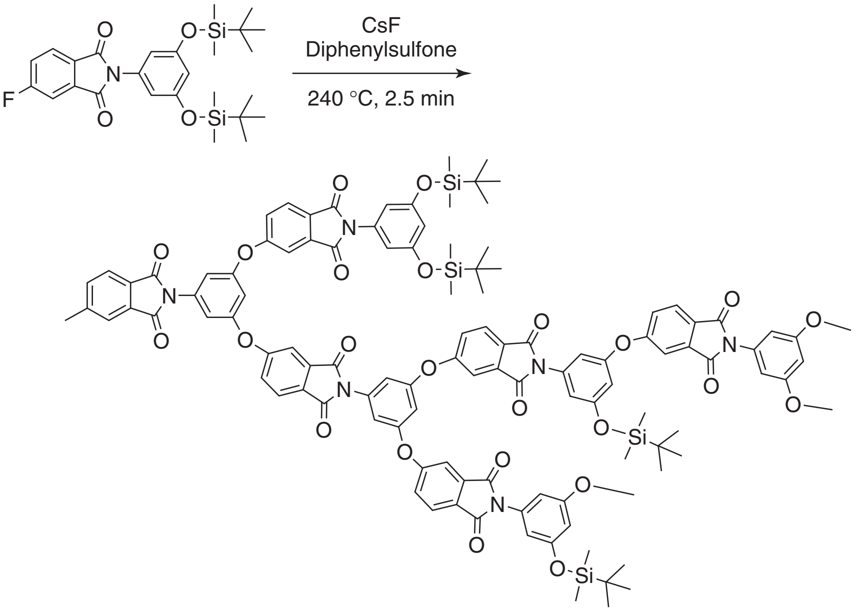


Figure 2.7 AB$_2$ monomers having various spacer groups for hyperbranched polyethers through nucleophilic aromatic substitution.

Ullmann couplings in the presence of copper catalysts were also applied for the preparation of hyperbranched poly(aryl ether)s. The reported AB$_2$-type monomers for the Ullmann polycondensation are shown in Figure 2.9.[52,53] The weight-average molecular weight determined by GPC with polystyrene standards was in the range 2230–8000. The terminal functional groups influenced the solubility and thermal properties of the hyperbranched poly(aryl ether)s. The bromo- and alkoxy-terminated polymers were soluble in chloroform and THF. The carboxylate-terminated polymer, prepared by the reaction of bromo-terminated polymer with *n*-BuLi, and then carbon dioxide, was soluble in water and showed the characteristics of a unimolecular micelle as a host for nonpolar guest molecules.

Aromatic–aliphatic hyperbranched polyethers whose main chains are composed of benzyl ether linkages were prepared through the nucleophilic reaction of the phenolate with benzyl bromide, as shown in Scheme 2.14.[54] The hyperbranched polyether is an analogue for Fréchet-type dendrimer, which is one of the most extensively studied dendrimers. The polymerization was carried out in the presence of K_2CO_3 and crown ether (18-crown-6) in acetone. It was found



Scheme 2.13

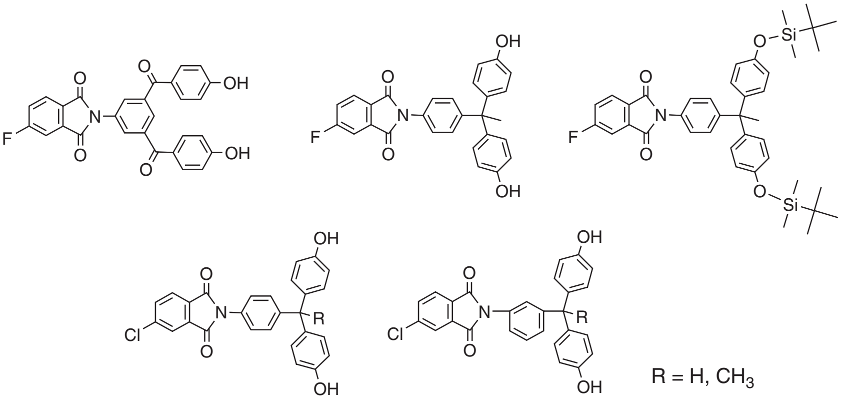


Figure 2.8 AB_2 monomers for hyperbranched polyimides through nucleophilic aromatic substitution.

that the resulting polymers contained C-alkylated methylenes up to 30% of the polyether structure in addition to O-alkylated benzylic methylenes. The M_w of the hyperbranched polyethers, determined by SEC-low angle laser light scattering (LALLS), exceeded 10^5, which was 3–5 times higher than the value calibrated by polystyrene standards. The glass transition temperature could be controlled from 311 to 343 °C by the chemical modification of phenolic chain ends.

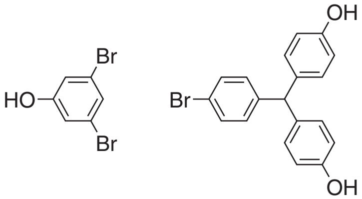
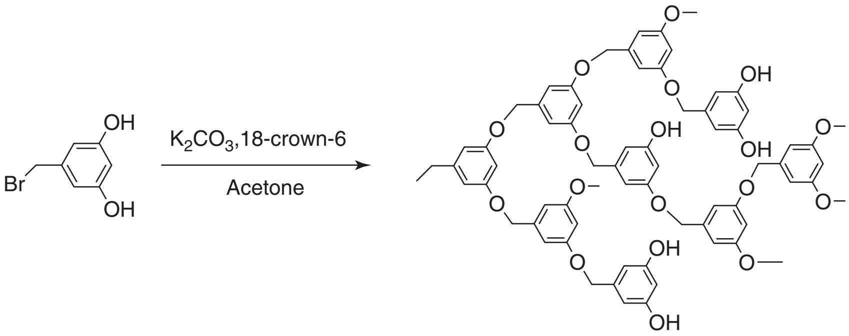


Figure 2.9 AB_2 monomers for hyperbranched polyethers through Ullmann-type coupling.



Scheme 2.14

The hyperbranched poly(benzyl ether)s containing tetrafluorinated phenylene units were prepared from the AB_2 and AB_4 monomers, as shown in Figure 2.10.[55] The self-polycondensation was promoted by deprotonation of benzylic alcohol by sodium particles in THF. The polymerization in the presence of sodium particles less than 1 mm resulted in the formation of the polymer with a low molecular weight in high yield. In contrast, the use of sodium particles larger than

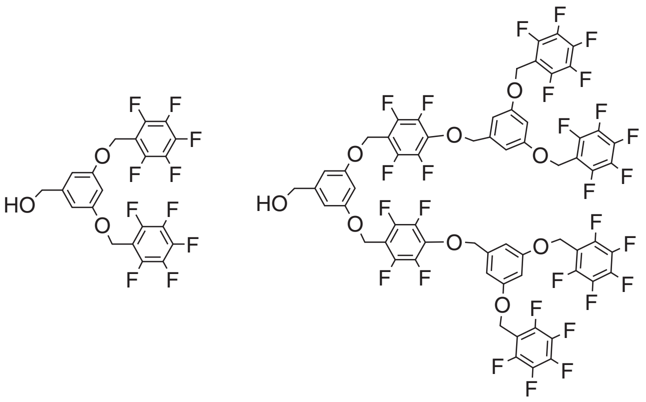


Figure 2.10 AB_2 and AB_4 monomers for fluorinated hyperbranched poly(benzyl ether)s.

1 mm led to low yields of high molecular weight polymer. Cyclized components were detected by MALDI-TOF mass spectroscopy.[56] The resulting polymers were soluble in common organic solvents, such as THF, DMF, methylene chloride, chloroform, toluene, and acetone. Contact angle measurements for water and hexadecane on films of a pentafluoro-terminated hyperbranched polymer as well as trifluoroethoxy-substituted and $1H,1H,2H,2H$-perfluorodecanoxy-substituted derivatives indicated a high degree of hydrophobicity and lipophobicity. The $1H,1H,2H,2H$-perfluorodecanoxy-substituted polymer led to a more than twofold decrease in the coefficient of friction and adhesive force.

Liquid-crystalline hyperbranched polyethers were prepared from the AB_2-type monomers containing rigid mesogens, two phenolic hydroxyl groups, and an alkyl halide, as shown in Figure 2.11.[57,58] The polymerization was carried out in an aqueous solution of *o*-dichlorobenzene and NaOH (10 N) in the presence of tetrabutylammonium hydrogen sulfate. The resulting polymers were isolated after endcapping reactions of phenolic terminal groups with alkyl halides at the end of the polymerization, which gave soluble hyperbranched polyethers. The molecular weight of resulting hyperbranched polymers was relatively low compared to those of linear polymers prepared from the corresponding AA and BB monomers since intramolecular cyclization occurred during the polymerization. The gauche conformer favors the synthesis of the dendritic architecture, while its anti conformer favors the formation of a conventional nematic liquid-crystalline phase. Some of the hyperbranched polyethers indeed exhibited an enantiotropic nematic mesophase derived from anti–gauche isomerization, as shown in Figure 2.12. The temperature range of the nematic mesophase was dependent on the structure of the mesogen and the end functional groups. A stable nematic phase in the range of 50–132 °C was observed for the polymer composed of terphenylene as the mesogen unit and octyl ether as the end group.

Hyperbranched poly(ether amide)s were prepared through nucleophilic ring-opening polymerization of 2-oxazoline-containing AB_2 monomer, as shown in Scheme 2.15.[59] The number-average molecular weight determined by GPC based on polystyrene standards was 47,500. MALDI-TOF mass measurements indicated that the polymer was composed of the repeating unit of 179.3 Da, which was in agreement with the proposed structure. Glass transition temperature and decomposition onset of the poly(ether amide) were 176 and 330 °C, respectively. The hydrolysis of some oxazoline groups as a side reaction was observed during the polymerization when the polymerization was carried out in tetramethylene sulfone or in bulk.

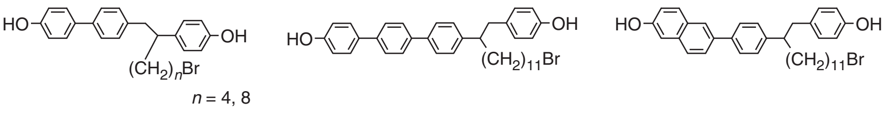


Figure 2.11 AB_2 monomers for liquid-crystalline hyperbranched polyethers.

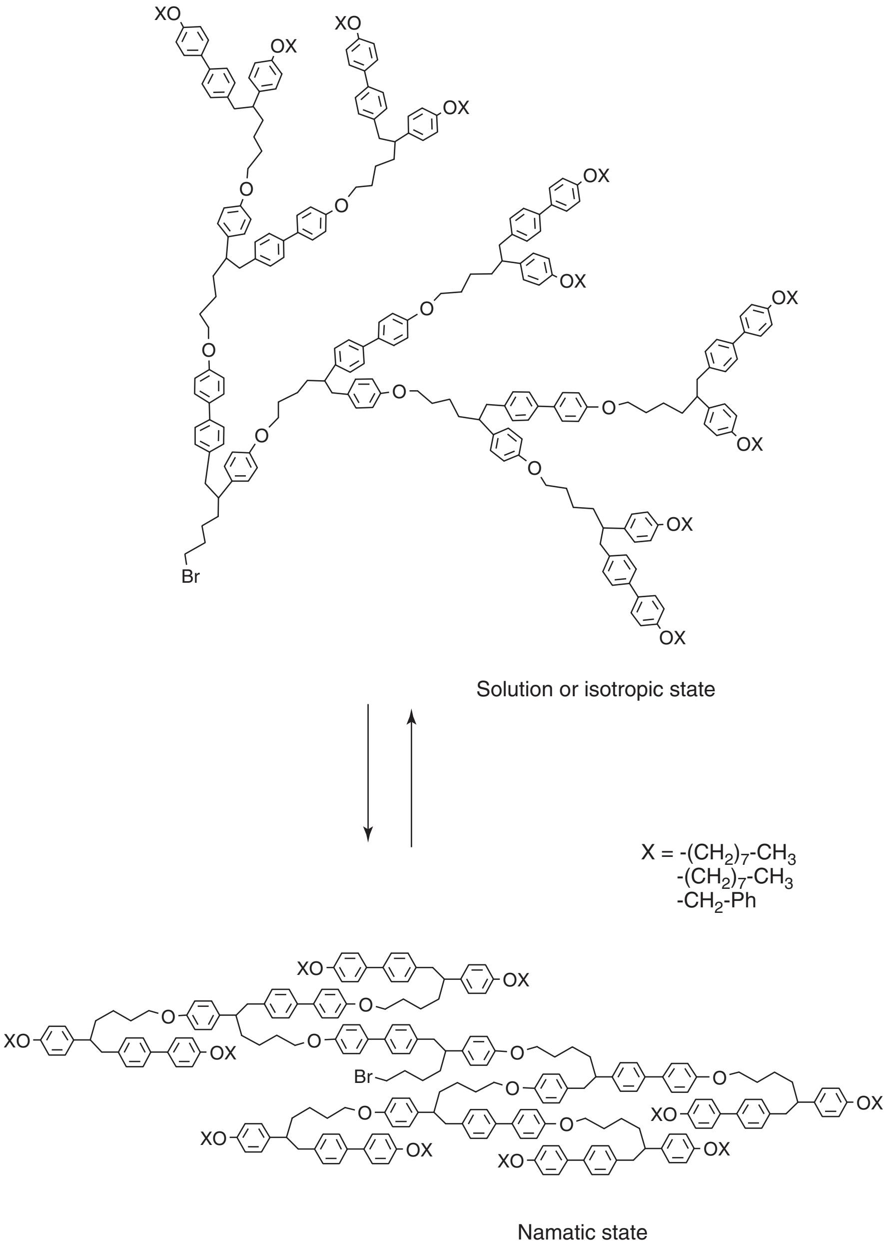
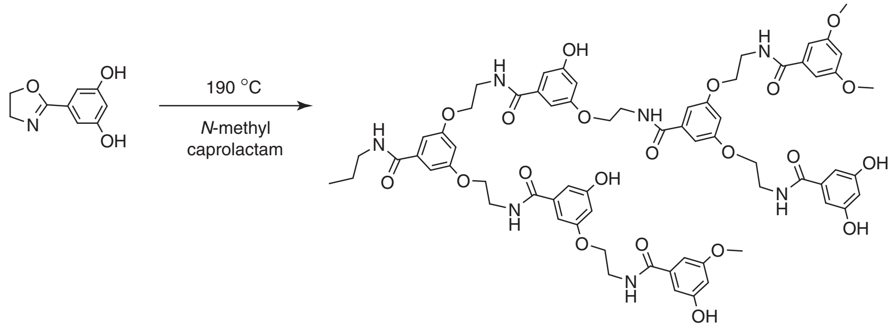


Figure 2.12 Anti–gauche isomerization of the liquid-crystalline hyperbranched polyether.



Scheme 2.15

2.3.2.2 Esterification of Carboxylic Acid Derivatives

The polycondensation reactions of AB_x-type monomers through the esterification of carboxylic acid derivatives produce hyperbranched polyesters and polycarbonates. Most of the propagation reactions involve the condensation between hydroxy and carboxyl groups associated with appropriate activation processes.

Many kinds of hyperbranched polyesters have been prepared from 3,5-dihydroxybenzoic acid or 5-hydroxyisophthalic acid as raw material. Some of the AB_2-type monomers are listed in Figure 2.13. Hydroxy groups are often activated by acetylation or trimethylsilylation. Carboxyl groups are often converted

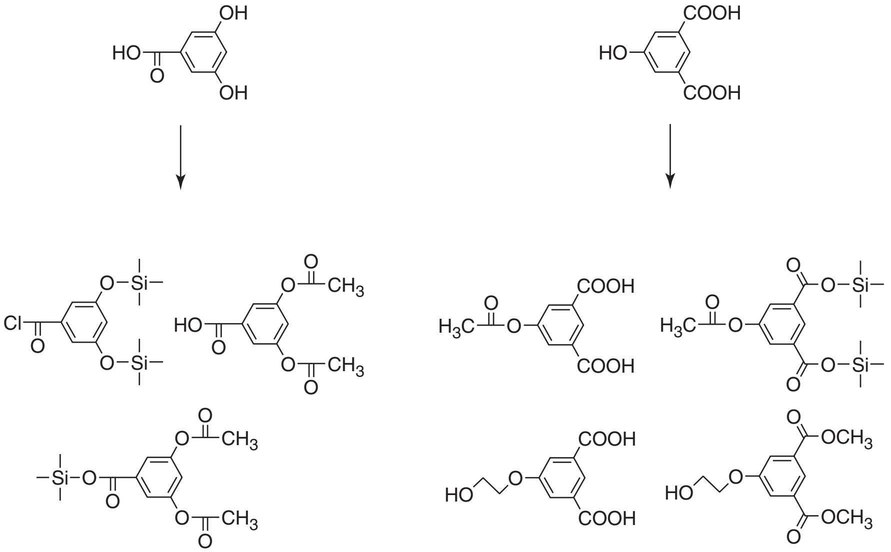
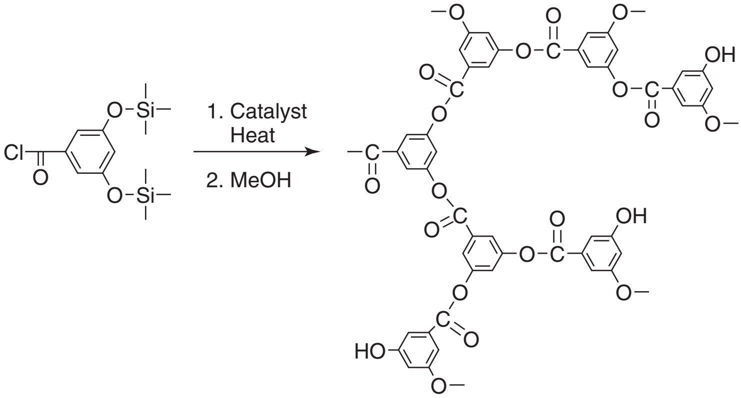


Figure 2.13 AB_2 monomers derived from 3,5-dihydroxybenzoic acid or 5-hydroxyisophthalic acid.

to acetyl or trimethylsilyl esters for the activation. The use of unmodified hydroxy and carboxyl groups has also been reported in the literature. Melt polymerizations in the presence of appropriate catalysts seem to be convenient routes to produce hyperbranched polyesters, while solution polymerizations have also been applied for some hyperbranched polyesters.

3,5-Bis(trimethylsiloxy)benzoyl chloride was first used as an AB_2-type monomer for the synthesis of aromatic polyester copolymers by Kricheldorf in 1982,[60] and then the successful homopolymerization of the AB_2 monomer was reported by Fréchet in 1991,[2] as shown in Scheme 2.16. Bulk polymerization of the AB_2 monomer was carried out in the absence or presence of catalysts such as trimethylamine hydrochloride and DMF. It was reported that a small amount of impurity gave an insoluble product even though the reaction temperature was lower than 200 °C.[61] Hydroxy-terminated hyperbranched polyesters were isolated after pouring the solution of the crude product into methanol to hydrolyze trimethylsiloxy groups. The M_w of the hyperbranched polyester, determined by GPC-MALLS, was about 80,000, which was dependent on the reaction conditions.

This hyperbranched polyester is the first example for the characterization of the branching structure by DB. As shown in Figure 2.14, the resulting hyperbranched polyesters are composed of dendritic, linear, and terminal units. The ratio of each unit determined by ^{1}H NMR measurements gave a DB of 0.55–0.60. The hydroxy-terminated polymers were soluble in common organic solvents such



Scheme 2.16

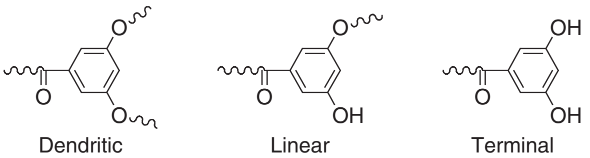


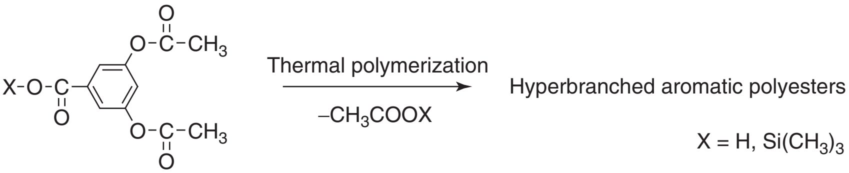
Figure 2.14 Dendritic, linear, and terminal units for the hyperbranched polyester.

as acetone, THF, and DMF, and were thermally stable up to 400 °C with a glass transition temperature (T_g) of 197 °C. T_g dramatically decreased to 6 °C when the hydroxyl groups were protected by monobenzyl adipic acid ester.

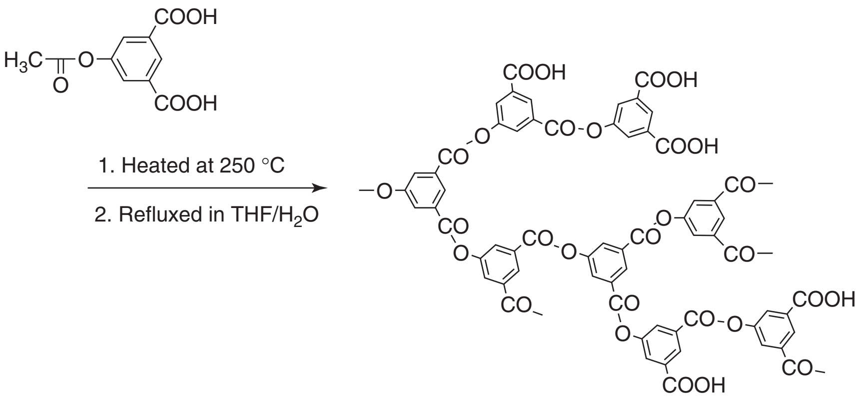
The acylation of 3,5-dihydroxybenzoic acid also gave the AB_2 monomers for hyperbranched aromatic polyesters, as shown in Scheme 2.17.[62,63] 3,5-Diaceoxybenzoic acid required a higher reaction temperature (250 °C) in order to achieve high molecular weight in comparison with the polymerization of 3,5-bis(trimethylsiloxy)benzoyl chloride. The bulk polymerization of 3,5-diacetoxybenzoic acid at 250 °C gave a soluble hyperbranched polyester with $M_w > 1{,}000{,}000$ as determined by SEC. The relationship between intrinsic viscosity and molecular weight of the resulting polyesters suggested a highly branched structure and α in the Mark–Houwink equation was found to be less than 0.5. Kricheldorf reported that the thermal polymerization of trimethylsilyl 3,5-diacetoxybenzoate gave a perfectly soluble product even at the reaction temperature of 280 °C.[64]

Several kinds of hyperbranched polymers, such as hyperbranched poly(ester amide)s,[65,66] poly(ester imide)s,[67] and their copolymers,[68,69] were also prepared through the esterification reactions of trimethylsilylated or acetylated AB_2-type monomers. Triacetylated gallic acid (3,4,5-triacetoxybenzoic acid) can be used as an AB_3-type monomer to prepare hyperbranched polyesters and their copolymers.[70,71] The hyperbranched polyesters containing coumarin groups as chromophores were also prepared through the esterification of an acetylated AB_2-type monomer.[72]

5-Acetoxyisophthalic acid is an another starting material for AB_2 monomers in order to prepare hyperbranched aromatic polyesters. The product prepared by the melt polymerization of 5-acetoxyisophthalic acid at 250 °C was insoluble in organic solvents because intermolecular dehydration between carboxyl groups occurred during the melt polymerization. Hydrolysis of the crude product gave a soluble hyperbranched polyester having carboxyl groups as a terminal function, as shown in Scheme 2.18.[73] The SEC trace of the trimethylsilylated polymer suggested a broad molecular weight distribution. The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) calculated by universal calibration using coupled differential viscometry were 42,900 and 3.69, respectively. The DB determined by ^1H NMR spectrum was about 0.5, which was similar to the case for the hyperbranched polyesters prepared from AB_2 monomers originating from 3,5-hydroxybenzoic acid. The carboxyl-terminated hyperbranched polyesters were



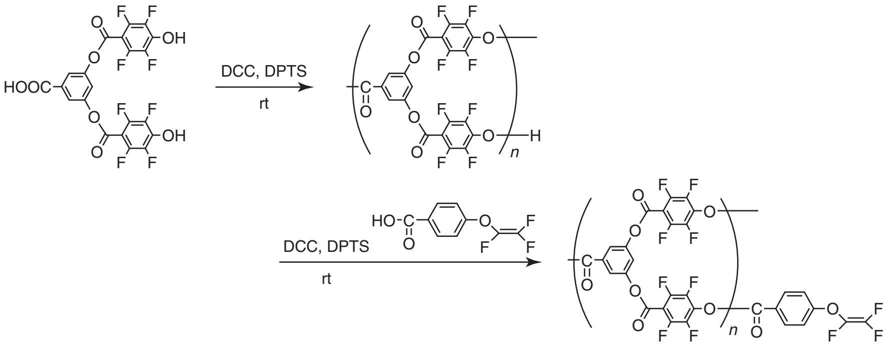
Scheme 2.17



Scheme 2.18

easily converted to ammonium or sodium salts and the salts became soluble in water. The viscosity of the aqueous solution was dependent on the concentration of the polymer and inorganic salts, similar to conventional polyelectrolytes.

Although many hyperbranched aromatic polyesters have been prepared through melt polycondensations, the high reaction temperatures may lead undesirable side products, such as cyclic oligomers. The room-temperature polycondensation of an AB_2 monomer in the presence of condensation agents was reported for the preparation of a hyperbranched aromatic fluoropolyester, as shown in Scheme 2.19.[74] The polymerization proceeded at room temperature in THF/dichloromethane in the presence of dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) as the condensation agents. The weight-average molecular weight of the hyperbranched polyester functionalized with *p*-trifluorovinyloxy benzoic acid, determined by GPC with polystyrene standards, was 17,800 with a polydispersity of 1.55. After the



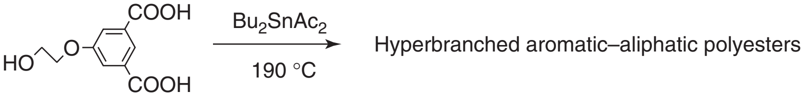
Scheme 2.19

thermal cross-linking reaction of the terminal trifluorovinyl group, the resulting polymer showed a low optical loss of 0.58 dB/cm at 1310 nm and good thermal stability up to 470 °C.

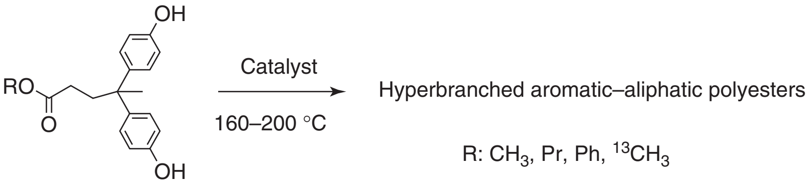
The preparation of hyperbranched aromatic polyesters through the CO insertion reaction catalyzed by palladium was also examined.[75] Although CO insertion can be used as a propagation reaction for linear aromatic polyesters, the polymerization of 3,5-dibromophenol as an AB_2 monomer resulted in the formation of an insoluble product. On the other hand, a soluble product with a low molecular weight was isolated from the polymerization of A_2B-type monomers, 5-bromoresolcinol and 5-iodoresolcinol. The side reactions at the "B" function of the monomers, such as aryl–aryl coupling and dehalogenation, would occur during the polymerization and affect the solubility and the molecular weight of the resulting polymers.

Introduction of alkyl chains into the backbone of monomers causes decrease in glass transition temperature of the resulting hyperbranched polymers, which enables melt polycondensations at lower temperature. An ethoxy group was easily introduced by the reaction of dimethyl 5-hydroxyphthalate and ethylene oxide. The melt polymerization of 5-(2-hydroxyethoxy)isophthalic acid at 190 °C in the presence of organic tin catalyst proceeded efficiently to form a hyperbranched aromatic–aliphatic polyester, as shown in Scheme 2.20.[73] Intermolecular dehydration to form anhydrides was avoided since the reaction temperature was lower than that required for the polymerization of 5-acetoxyisophthalic acid. The T_g of the hyperbranched polyester lowered to 150 °C in comparison with all aromatic hyperbranched polyesters.

Hawker reported the polycondensation of 4,4-(4′-hydroxyphenyl)pentanoic acid esters and determination of DB from degradation products, as shown in Scheme 2.21.[76,77] The bulk polymerization of the phenyl ester in the presence of cobalt acetate as a catalyst gave the highest molecular weight of 128,000 (M_w by GPC-MALLS). The DB determined by the hydrolysis of the resulting



Scheme 2.20



Scheme 2.21

hyperbranched polyesters was 0.49, which was independent of the ester groups of the starting AB_2 monomers. ^{13}C labeled NMR experiments revealed that the extent of cyclization during the polycondensation was less than 5%.[77]

Aromatic–aliphatic polyesters composed of rigid segments (mesogens) and flexible segments often show liquid-crystalline phases. Liquid-crystalline hyperbranched polyesters were prepared through the esterification reactions of the AB_2 monomers listed in Figure 2.15.[78–80] A cholesteric mesophase was observed for the hyperbranched polyester composed of biphenyl unit as a mesogen and an alkyl chain as a flexible spacer after the endcapping reaction with a chiral functional group.[78]

Hyperbranched poly(ester amide)s are commercially available hyperbranched polymers and their propagation reactions are composed of the esterification of the AB_2-type compounds formed *in situ* (Scheme 2.22).[81] A carboxylic anhydride and a dialkanolamine are used as starting materials. The first reaction step is the addition of the anhydride to an excess of diisopropanolamine through slow addition technique to prepare multifunctional monomer units. The subsequent polycondensation proceeds through esterification via oxazolinium ions to form hyperbranched poly(ester amide)s. The poly(ester amide)s have a glass transition temperature in the range of 10–100 °C depending on the ratio of monomers and the type of anhydride used. In addition, the terminal groups of the hyperbranched poly(ester amide)s can be easily functionalized with various acids such as unsaturated fatty acids, maleates, fumarates, and methacrylates.

Both thermal and solution polycondensation can be applied for the synthesis of hyperbranched aliphatic polyesters. Hult reported the melt polymerization of 2,2-bis(hydroxymethyl)propionic acid as an AB_2 monomer in the presence of a core molecule 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, as

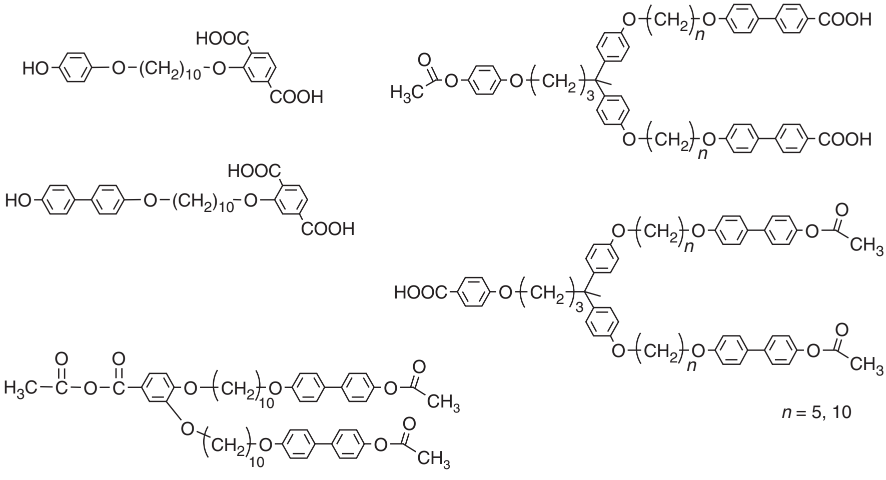
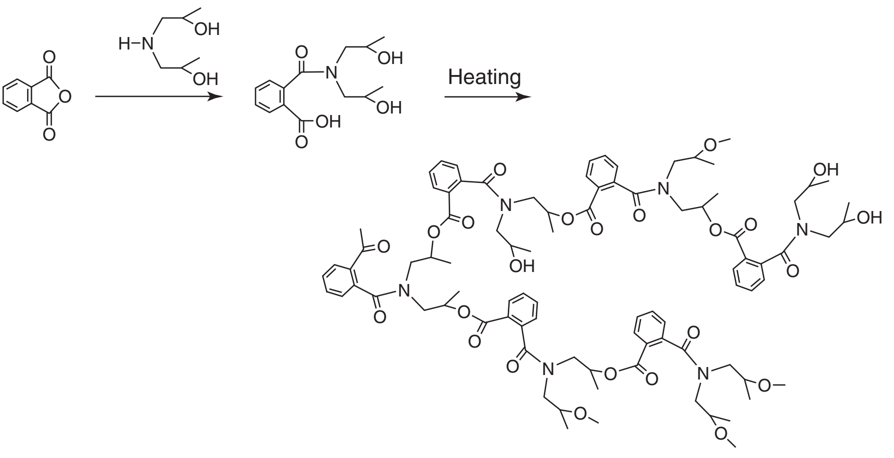
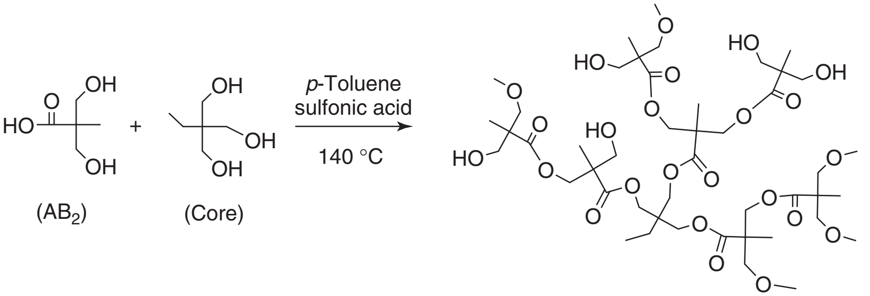


Figure 2.15 AB_2 monomers for liquid-crystalline hyperbranched polyesters.



Scheme 2.22



Scheme 2.23

shown in Scheme 2.23.[82,83] The polymerization was carried out at 140 °C in the presence of *p*-toluenesulfonic acid as a catalyst. The molecular weight of the resulting polymer depended on the molar ratio of the AB_2 monomer and the core molecule. The deviation from theoretical molecular weight became large over 10^4. High DB values in the range 0.83–0.96 were achieved by the polymerization in the presence of the core molecule. The hyperbranched polyesters had T_g's of about 40 °C and good thermal stability up to ca. 300 °C.

Combburst-like hyperbranched polyesters can be prepared from AB_2-type macromonomers, which are prepared by the reaction of oligomeric linear chains and a branching unit such as 3,5-dihydroxybenzoic acid and 2,2′-bis(hydroxymethyl)propionic acid. The AB_2 macromonomers reported in the literature are listed in Figure 2.16.[84–86] The properties of resulting polymers are usually dependent on the linear chains. In 1996, Hawker first reported the polymerization of AB_2 macromonomers to produce hyperbranched poly(ethylene

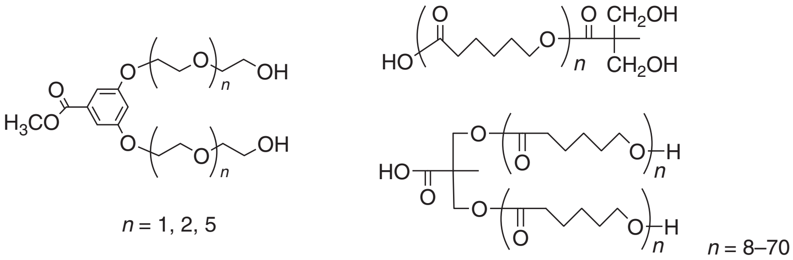


Figure 2.16 AB_2 macromonomers for hyperbranched polyesters.

glycol)s through the transesterification reaction.[84] Crystallization of ethylene oxide chains was inhibited by the introduction of the branching unit and the T_g of the polymers depended on the number of each ethylene oxide unit in the range of 234–268 K. The complex formation of a lithium cation with ethylene oxide chains of the polymer ($n = 5$) was confirmed by the relationship between T_g^{-1} and the concentration of $LiClO_4$. An ionic conductivity of 10^{-5} S/cm was obtained at 30 °C for a concentration of lithium perchlorate of 0.62 molecule per repeat unit. Hedrick reported larger AB_2-type macromolecules composed of oligo(ε-caprolactone)s and 2,2′-bis(hydroxymethyl)propionic acid as the branching point.[85,86] Monodispersed oligo(ε-caprolactone) chains were prepared by “living” ring-opening polymerization of ε-caprolactone initiated by aluminum benzyloxide or tin octate. The esterification of the AB_2 macromonomer was carried out in the presence of DCC and DPTS as condensation agents. The DB of the hyperbranched polyesters was found to be 0.37 ± 0.03 and was independent of the molecular weight of the macromonomer. The thermal properties depended on the degree of polymerization of the macromonomer.

Hyperbranched aromatic polycarbonates were prepared by the polycondensation of the AB_2-type monomers derived from 1,1,1-tris(4′-hydroxyphenyl)ethane listed in Figure 2.17.[87,88] The polymerization was carried out at 70 °C in the presence of AgF led to a precipitate, leaving the imidazolide anion as a salt. After

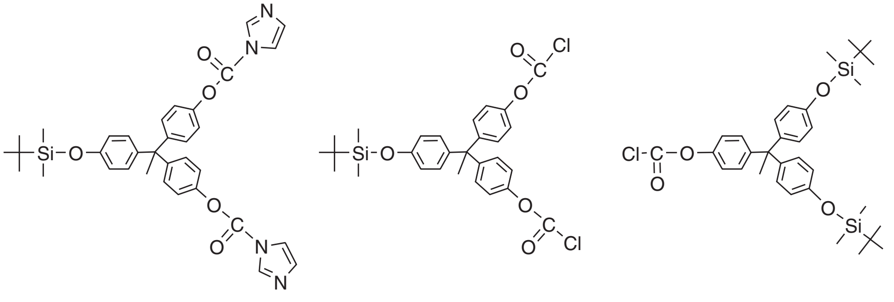
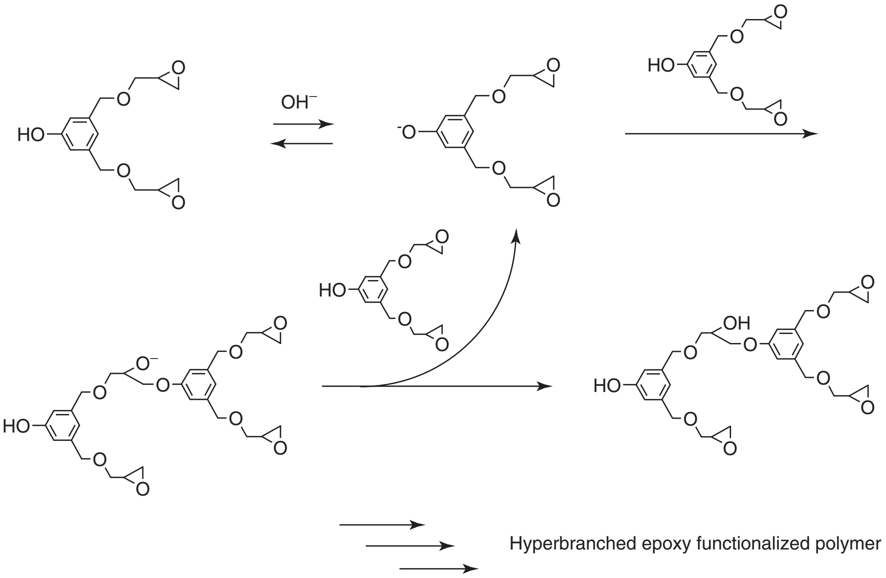


Figure 2.17 AB_2 monomers for hyperbranched polycarbonates.

hydrolysis of carbonylimidazolide chain ends, phenol-terminated hyperbranched polycarbonates were isolated. The hyperbranched polycarbonate was soluble in common organic solvents such as THF and acetone. The DB of the polycarbonate was 0.53, which was determined by the quantitative analysis of the degradation products of the carbonate bonds by reaction with lithium aluminum hydride. The hydroxy-terminated polycarbonate was thermally stable up to 350 °C and had a T_g of 205 °C.

2.3.2.3 Ring-Opening Reaction of Epoxides

The ring-opening reaction of an epoxide by phenoxides generates an ether linkage and a secondary alkoxide. Fréchet reported the preparation of hyperbranched poly(hydroxyether)s from the AB_2 monomer composed of two epoxide and one phenolic hydroxyl groups, and termed it *proton-transfer polymerization*.[89] As described in Scheme 2.24, the polymerization is initiated by the addition of a base to abstract the phenolic hydrogen and, then, the nucleophilic addition of the phenolate anion to an epoxide ring proceeds to form a dimer containing a secondary alkoxide. The activated dimer undergoes a proton exchange reaction with another AB_2 monomer to produce the phenolate anion and a neutral dimer. The much lower pK_a (ca. 10) of the phenolic group relative to that of the secondary alkoxide (pK_a ~ 17) enables the fast proton transfer from the phenolic proton to the secondary alkoxide. The colorless and soluble polymers were isolated from the polymerization in THF at 70–75 °C in the presence of KOH as a base.



Scheme 2.24

The molecular weight increased with reaction time up to 206,000 (M_w by GPC-MALLS), and the portionwise addition of the monomer to the polymerization mixture was effective to narrow the polydispersity to 2.4.

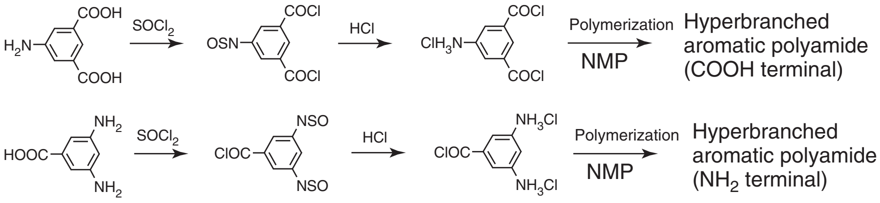
2.3.3 C–N Coupling Reactions

2.3.3.1 Condensation of Amines and Carboxylic Acid Derivatives

Hyperbranched polyamides, polyimides, and polybenzoxazoles have been prepared through amidation reactions of AB_x-type monomers.

In 1992, Kim first reported the preparation of hyperbranched aromatic polyamides through low-temperature polycondensation of amines and acid chlorides, as shown in Scheme 2.25.[90] 5-Aminoisophthalic acid and 3,5-diaminobenzoic acid were used as starting materials. The polymerization of the acid chlorides was carried out in NMP with or without $CaCl_2$ at 0 °C. The polymerization of sulfinyl amino acid chloride of 5-aminoisophthalic acid in the presence of 1 equiv. of water was also reported. Both carboxyl- and amino-terminated polyamides were soluble in amide solvents such as DMF, NMP, and dimethylacetamide (DMAc), while the amino-terminated polyamide was soluble in water because the amino groups were converted to their hydrochloride salt during the polymerization. The GPC analysis of the resulting hyperbranched polyamides in a DMAc/LiBr/H_3PO_4/THF mixture showed that the molecular weight ranged from 24,000 to 46,000 with the polydispersity of 2.0–3.2, based on polystyrene standards. The NMP solution containing more than 40 wt% of the carboxyl-terminated hyperbranched polyamide exhibited a nematic liquid-crystalline phase and did not lose birefringence up to 150 °C. On the other hand, the amino-terminated polyamides did not show birefringence.

The direct polycondensation in the presence of condensation agents to activate carboxylic acid groups *in situ* is the other attractive route to synthesize hyperbranched polyamides. The potential advantage for the direct polymerization is the stability of the monomers at room temperature in contrast to the low-temperature polymerization of acid chlorides. Some of the AB_2 monomers for hyperbranched aromatic polyamides reported in the literature are listed in Figure 2.18.[91–96] Triphenyl phosphite/pyridine and diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate/triethylamine have been reported as efficient condensation agents



Scheme 2.25

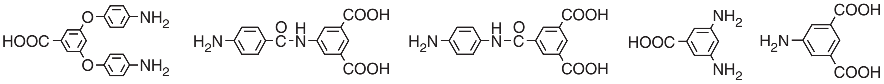
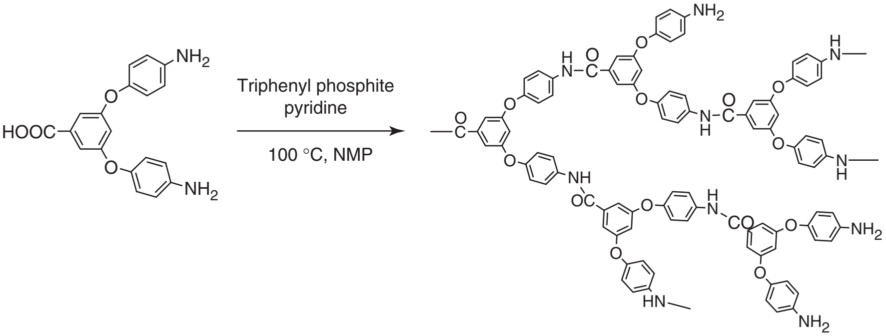


Figure 2.18 AB_2 monomers for direct polycondensation to form hyperbranched aromatic polyamides.

for the polymerization. All the hyperbranched polyamides prepared from the AB_2 monomers listed in Figure 2.18 were soluble in amide solvents, and the solubility and thermal properties were dependent on the nature of end functional groups. In addition, the inherent viscosity of the resulting polymers was low, in the range 0.1–0.4 dL/g, similar to other hyperbranched and dendritic polymers in the literature.

Scheme 2.26 shows the polymerization of 3,5-bis(4-aminophenoxy)benzoic acid in the presence of triphenyl phosphite and pyridine as a representative example of direct polycondensation.[91,92] The polymerization proceeds homogeneously in NMP, similar to the case for linear aromatic polyamides. The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) determined by GPC-MALLS were 98,000 and 2.3, respectively. The DB of the hyperbranched polyamide determined by quantitative ^{13}C NMR measurements was 0.48. This implies that the propagation reaction proceeded statistically without severe steric hindrance or reactivity change during the polymerization. The shape factor (α) in the Mark–Houwink equation ($[\eta] = KM^{\alpha}$), determined by the relationship between intrinsic viscosity and molecular weight in DMF was 0.35. The glass transition temperature of the hyperbranched polyamide was 200 °C and was lowered to 164 °C by the endcapping reaction of amino groups with heptanoyl chloride.

The effect of the structure of AB_x monomers on the DB of hyperbranched aromatic polyamides was reported by Kakimoto and coworkers.[96] The DB of the polymer prepared from 3,5-diaminobenzoic acid was 0.32, which is much lower than the statistical expectation of 0.5. The low DB might have been caused by



Scheme 2.26

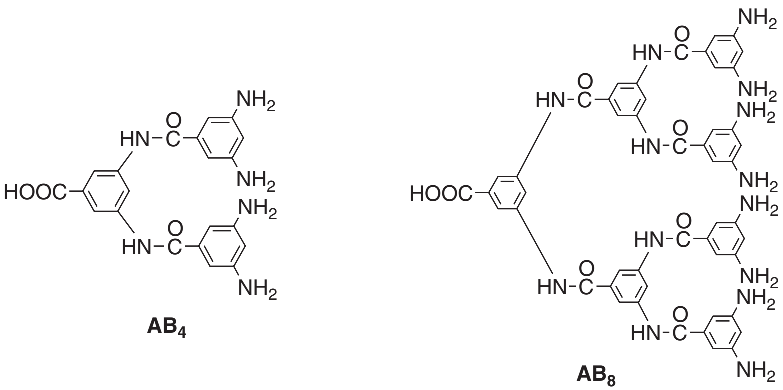
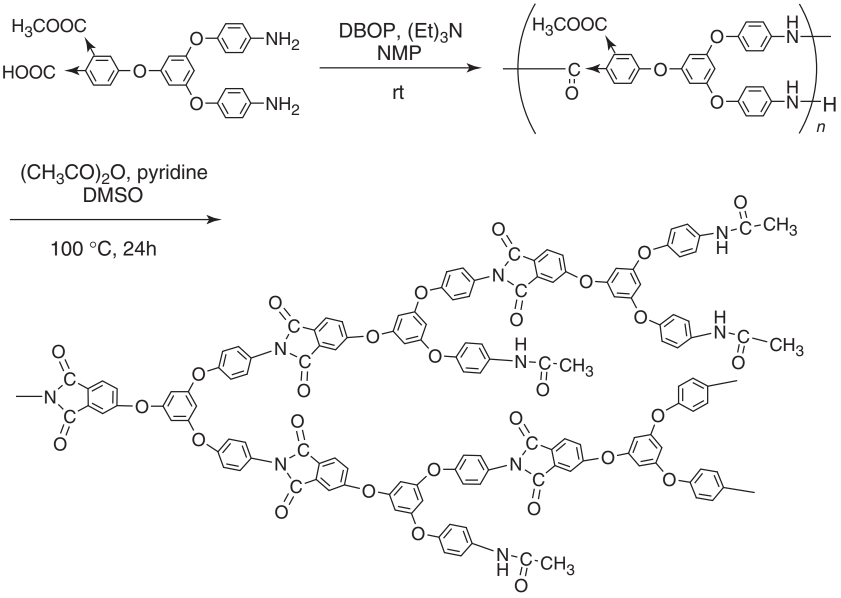


Figure 2.19 AB_4 and AB_8 monomers for hyperbranched aromatic polyamides.

the steric hindrance during the polymerization. The polymerization of AB_4 and AB_8 monomers, shown in Figure 2.19, resulted in the formation of polymers with higher DBs (0.72 for the AB_4 and 0.84 for the AB_8 monomers). It should be pointed out that the increase in the DB is mainly caused by the prefabricated dendritic units and is not directly related to the formation of spherical molecules. The DBs could be also controlled continuously from 0.3 to 0.7 by the copolymerization of the AB_2 and AB_4 monomers. Although any noticeable influence by enhancing DBs of the hyperbranched polyamides was not observed, the DB difference must result in the formation of a different architecture and potentially affect the properties of the polymers, such as an encapsulation effect.

Direct polycondensations of amino groups and carboxyl groups can be applied for the preparation of precursors for heterocyclic polymers. Kakimoto reported the synthesis of hyperbranched poly(ether imide) through the corresponding poly(amic acid) ester precursor, as shown in Scheme 2.27.[97–99] The polymerization proceeded in the presence of diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) and triethylamine at room temperature. Subsequent imidization of the resulting precursor gave a hyperbranched poly(ether imide) quantitatively. Chemical imidization in the presence of acetic anhydride and pyridine resulted in the formation of the soluble polyimide endcapped with an acetamide group. The hyperbranched polyimide had a DB of 0.48 and an M_w of 188,000 determined by GPC-MALLS. Differential scanning colorimetry (DSC) and thermogavimetris analysis (TGA) measurements revealed a T_g of 193 °C and a 10% weight loss at 470 °C in air. This polymer was soluble in aprotic polar solvents and had a low inherent viscosity, similar to other hyperbranched polymers. It was also found that the film of the hyperbranched polyimide endcapped with 4-methylphthalimide showed a lower dielectric constant, lower birefringence, and shorter cutoff wavelength than a film of poly(4,4′-oxydiphenylene pyromellitimide).[98] The looser packing architecture of the hyperbranched polyimide might be affecting these properties. It should be



Scheme 2.27

noted that hyperbranched poly(ether imide)s can be prepared by the etherification reactions, as described in Section 2.3.2.1.

Hyperbranched poly(benzoxazole)s were also prepared by the direct polycondensation of the AB_2 monomers to prepare hyperbranched poly(*o*-hydroxyamide)s as precursors and the subsequent cyclization of the precursors.[100–103] The AB_2 monomers examined are shown in Figure 2.20. The chemically cyclized hyperbranched poly(benzoxazole)s were soluble in organic solvents, such as THF. The positive- or negative-working lithographic performance was evaluated for the hyperbranched poly(benzoxazole)s after the chemical modification of the precursors.

Although thermal polymerization is a well-known process for the preparation of aliphatic polyamides with a high molecular weight, it is generally difficult to obtain aromatic polyamides having high molecular weight by the

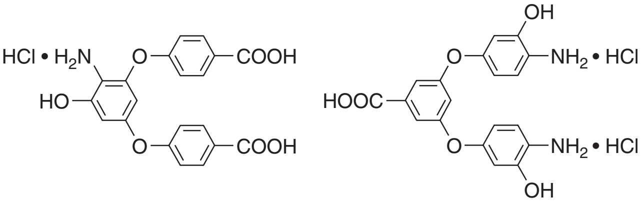


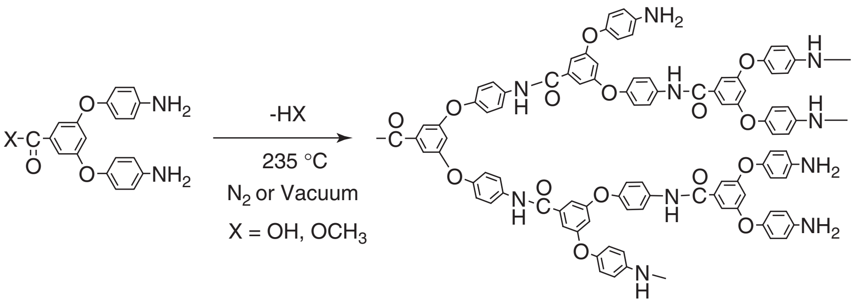
Figure 2.20 AB_2 monomers for hyperbranched polybenzoxazoles.

molten polycondensation method. However, melt polycondensation is applicable for some AB_2-type monomers to prepare hyperbranched aromatic polyamides with a reasonably high molecular weight, as shown in Scheme 2.28.[104] The thermal polymerization of 3,5-bis(4-aminophenoxy)benzoic acid at 235 °C proceeded in stable molten state and gave a glassy solid after cooling to room temperature. Pouring the DMF solution of the glassy product into methanol containing lithium chloride precipitated a white polymer. The weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) determined by GPC-MALLS were 74,600 and 2.6, respectively, which were equal to the values obtained for the polymer prepared by direct polycondensation. Thermal polymerization of the corresponding AB monomer, 3-(4-aminophenoxy)benzoic acid, failed because the melt phase advanced to a nontransparent solid quickly. The molecular weight of the linear product was found to be low by end-group analysis. The amorphous state and low viscosity due to the high DB of the hyperbranched polymers seem to be suitable for the thermal polymerization.

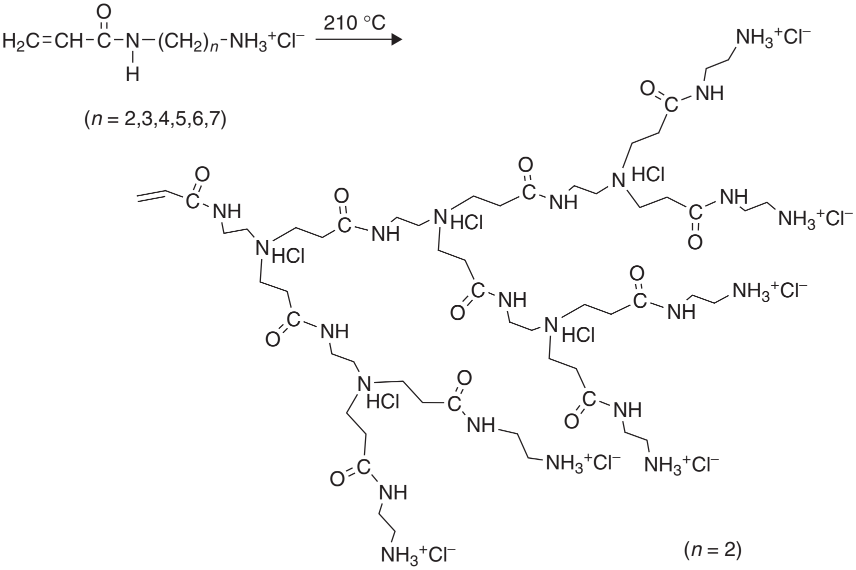
2.3.3.2 Nucleophilic Addition of Amines

This section deals with the preparation of hyperbranched polyamines through the nucleophilic addition of amines, which involves Michael-type addition and palladium-catalyzed C–N coupling reactions.

A series of AB_2 aminoacrylate hydrochloride monomers gave hyperbranched poly(amidoamine) through Michael addition chemistry, as shown in Scheme 2.29.[105–108] Heating the hydrochloride salts resulted in consumption of the acryloyl group and formation of new methylene units. The polymer had the same elemental composition as the monomer used, which indicated that no hydrogen chloride was lost during the polymerization. On the other hand, the thermal polymerization of the free amine or the *t*-Boc-protected one gave insoluble products. It was presumed that the propagation reaction involved the addition of the free amine to the acryloyl unit since the alkyl ammonium ions were not sufficiently nucleophilic for the Michael addition. Spectroscopic measurements indicated the formation of the proposed structure,



Scheme 2.28

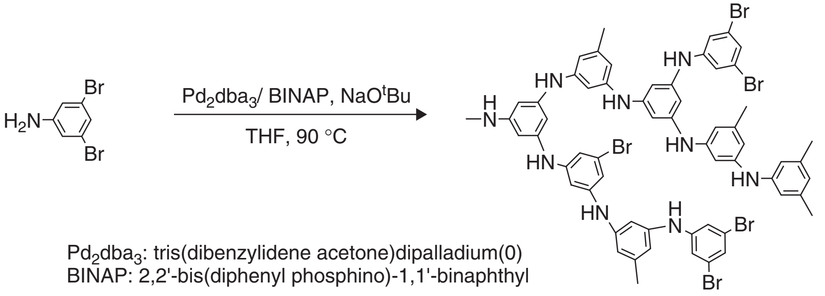


Scheme 2.29

and MALDI-TOF mass analysis ruled out intramolecular cyclization during the polymerization as a significant reaction pathway. The number of methylene unit affected both the reactivity of the monomer and properties of the resulting polymers. *N*-Acryloyl-1,2-diaminoethane hydrochloride ($n = 2$) showed high reactivity for the polymerization and gave a polymer with a DB greater than 0.9. The glass transition temperature of the polymers increased with increasing the internal CH_2 units, with a pronounced odd/even effect. It was also reported that the amino-methacylate monomers showed lower reactivity than the aminoacrylate ones for the polymerization through Michael-type addition.[108]

The copolymerization of *N*-acryloyl-1,2-diaminoethane hydrochloride ($n = 2$) in the presence of a B_6 core molecule tris-(2-aminoethylamine) gave an analogue of the hydrochloride salt of poly(amido amine) (PAMAM) dendrimers. The relationship between the molecular weight calculated from the monomer to the core ratio, as well as the intrinsic viscosity of the copolymer, suggested the formation of unique topologies characteristic of dendrimers in the solution.[106] The intrinsic viscosity decreased with increasing the molecular weight of the AB_2/B_6 copolymer over a certain molecular weight. The trend is similar to the case of PAMAM dendrimers, while the "one-pot" synthesis gives rise to the distribution in both molecular weight and structure.

Palladium-catalyzed C–N coupling reactions have been developed since 1990s and are applicable for the preparation of hyperbranched polymers. Hartwig first reported the preparation of triphenylamine dendrimers by stepwise reactions,[109] and then Meyer reported the polymerization of 3,5-dibromoaniline to prepare hyperbranched *m*-polyaniline through the palladium-catalyzed

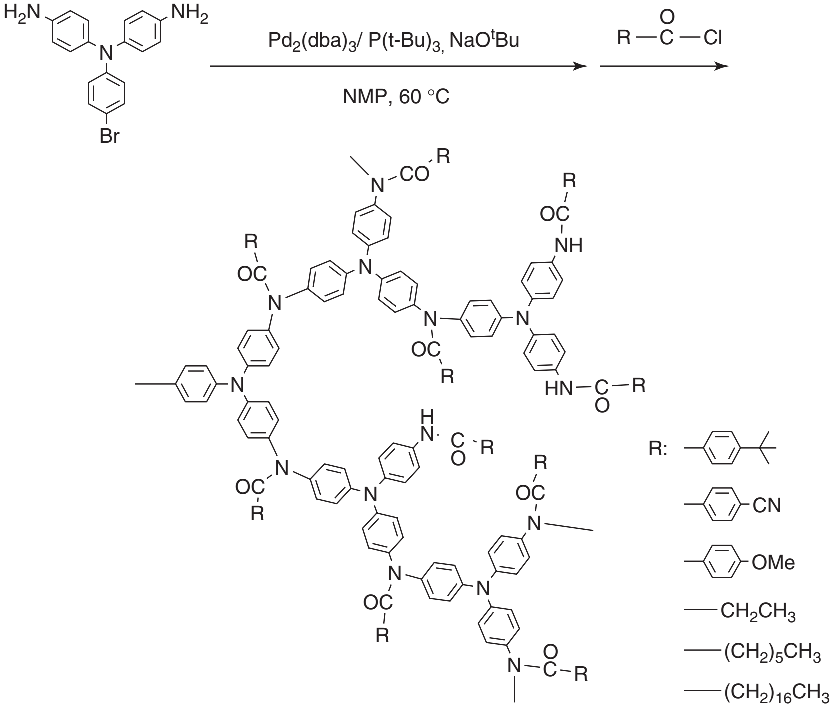


Pd$_2$dba$_3$: tris(dibenzylidene acetone)dipalladium(0)
BINAP: 2,2'-bis(diphenyl phosphino)-1,1'-binaphthyl

Scheme 2.30

coupling (Scheme 2.30).[110] The polymerization of 3,5-dibromoaniline proceeded in the presence of the palladium catalyst 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) as a ligand and sodium *t*-butoxide as a base in THF at 90 °C. The resulting hyperbranched polyaniline was soluble in organic solvents and the M_w determined by GPC in THF was 7000.

Hyperbranched poly(triphenylamine)s were also prepared through the palladium-catalyzed C–N coupling reaction, as shown in Scheme 2.31.[111]



Scheme 2.31

Since the amino-terminated hyperbranched poly(triphenylamine)s was unstable, presumably due to the oxidation by air, the endcapping reaction by various acid chlorides was carried out in order to isolate the soluble hyperbranched polymers. The properties of the hyperbranched poly(triphenylamine)s, such as solubility, thermal properties, and ionization potential, were dependent on the end functional groups. The multilayered electroluminescence (EL) device composed of indium tin oxide (ITO)/hyperbranched poly(triphenylamine)/Alq_3/Mg−Ag was fabricated in order to evaluate the hole-transporting property of the hyperbranched poly(triphenylamine). The device performance was improved when the alkyl group (hexyl or heptadecyl) was introduced at the end of the hyperbranched poly(triphenylamine). It should be noted that the preparation of hyperbranched poly(triphenylamine)s has also been reported by the metal-catalyzed cross-coupling reactions, as described in Section 2.3.1.1.

2.3.3.3 Other C−N Coupling Reactions

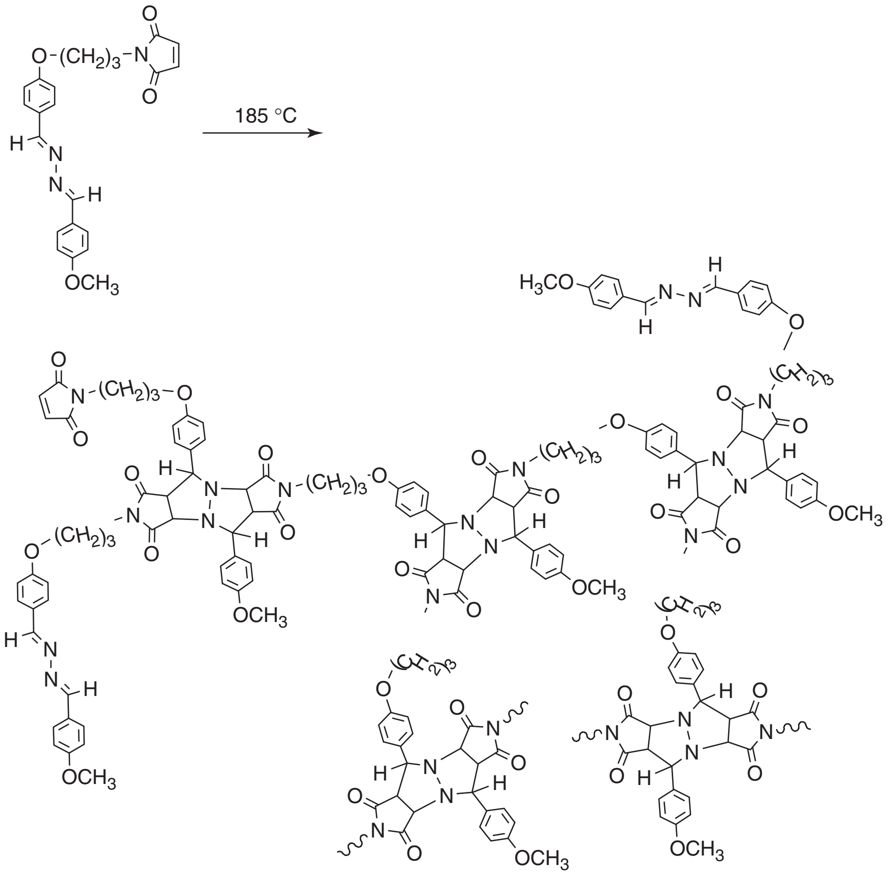
The 1,3-cycloaddition between aromatic aldehyde azines and unsaturated compounds proceeds quantitatively in the ratio 1:2 since the unstable intermediate formed by the first cycloaddition reacts with another unsaturated compound quickly and quantitatively. The thermal polymerization of 4-(3-maleimidopropoxy)—4′-methoxybenzaldehyde azine was reported as an approach to prepare the hyperbranched polymer without linear units, as shown in Scheme 2.32.[112] The resulting polymer prepared at 180 °C for 15 min was soluble in organic solvents, such as chloroform and THF. The number-average degree of polymerization of the resulting polymer was determined to be 8 by the ^{1}H NMR measurement and 14 by the GPC measurement. The ^{13}C NMR measurement suggested the formation of the hyperbranched polymer without linear units.

The azo-coupling reaction was also applied for the preparation of hyperbranched polymers, as shown in Scheme 2.33.[113] The clear solution of the diazonium salt prepared from *N*,*N*-bis[2-4-aminobenzoyloxy)ethyl]aniline was added to DMF and stirred at 0 °C. The isolated azo polymer had the number-average molecular weight of 7100 with the polydispersity of 1.5. The characteristic absorption attributed to the azo group was observed in the UV−vis spectrum.

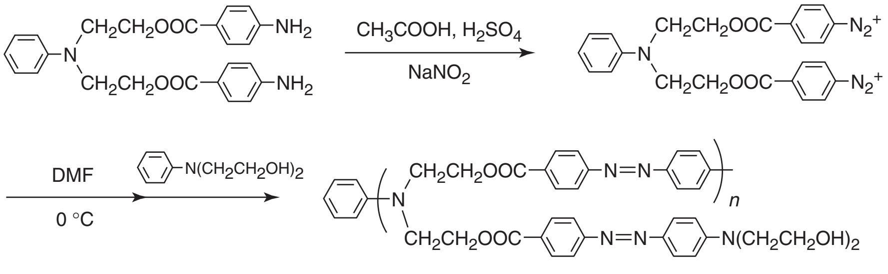
2.3.4 Si−C or Si−O Coupling Reactions

2.3.4.1 Hydrosilylation Reactions

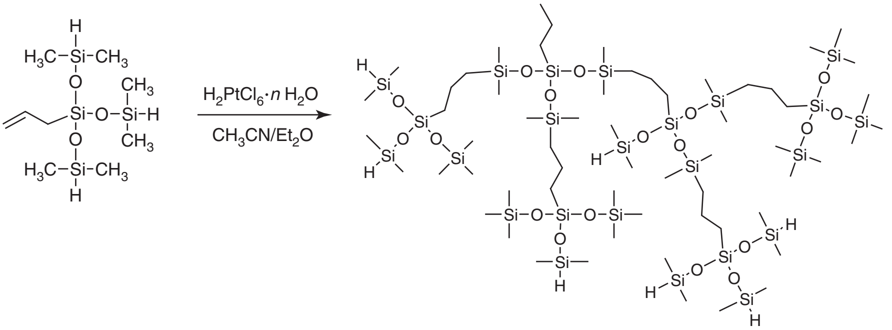
The hydrosilylation between a double bond and a Si−H group is a useful propagation reaction to prepare hyperbranched polysilanes. In addition to the desired β-addition, α-addition was also observed, and the β/α selectivity depends on the structure of the monomer and reaction conditions. Intramolecular cyclization often competes with the propagation reaction since the main chains are composed of flexible segments.



Scheme 2.32



Scheme 2.33



Scheme 2.34

Mathias first reported the preparation of a hyperbranched poly(siloxysilane) through the hydrosilylation, as shown in Scheme 2.34.[114] The polymerization was carried out in a mixture of acetonitrile and ether under nitrogen at 52 °C in the presence of hydrogen hexachloroplatinate hydrate as catalyst. IR and ^1H NMR spectra of the resulting polymer indicated the consumption of vinyl groups and presence of Si–H groups located at chain ends. SEC measurements in THF gave an M_w of 19,000 based on polystyrene standards. It was pointed out that the intramolecular cyclization to form six-membered cyclic products occurred during the polymerization.

Rubinsztajn reported the self-polycondensation of the AB_3 monomers, shown in Figure 2.21, through hydrosilylation.[115,116] The possible five-membered cyclic products have a high ring strain energy of about 10 kcal/mol more than the six-membered cyclic product, which favors intermolecular reactions rather than intramolecular cyclization. The polymerization of the AB_3 monomers proceeded in the presence of a heterogeneous platinum catalyst to form hyperbranched poly(siloxysilane)s in good yield. The resulting polymer prepared by the slow addition of AB_3-I had a high molecular weight ($M_w = 53{,}000$) and a broad molecular weight distribution ($M_w/M_n = 5.6$). ^{13}C NMR measurements revealed

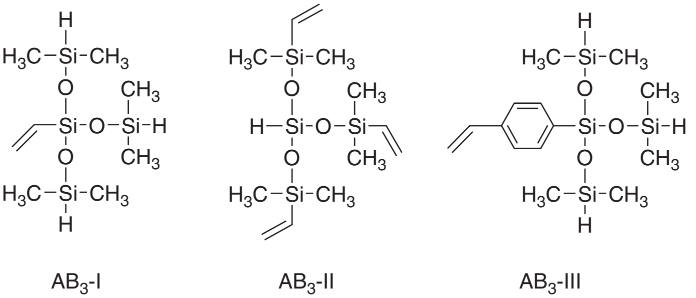


Figure 2.21 AB_3 monomers for hyperbranched poly(siloxysilane)s reported by Rubinsztajn.

that the α-addition to the double bond occurred in the range 10–20% during the polymerization apart from the β-addition. The reactivity of AB_3-II for the polymerization was much lower than that of AB_3-I, which might have been caused by the chelating ability of the double bonds in AB_3-II to the platinum catalyst. Since silicon hydride moieties are known to be thermally unstable and easily undergo some thermal rearrangement, the endcapping reaction with vinyltrimethylsilane was carried out to improve the thermal stability of the hyperbranched poly(siloxysilane)s. The onset temperature of the polymer prepared from AB_3-I after the endcapping reaction improved to 401.5 °C. The polymerization of AB_3-III, an aromatic analogue of AB_3-I, in the presence of platinum catalyst was also carried out in the same manner. ^{29}Si NMR measurements suggested that the ratio (β/α) of silicon hydride addition to vinyl group was 60/40. The glass transition temperature of the polymer from AB_3-III ($T_g = -58\,^\circ C$) was substantially higher than the T_g of the polymer from AB_3-I ($T_g = -100\,^\circ C$).

Fréchet reported the polymerization of the AB_2, AB_4, and AB_6 monomers, shown in Figure 2.22, to form hyperbranched poly(siloxysilane)s.[117,118] The polymerization was carried out at 50 °C in the presence of platinum-on-active-charcoal as catalyst. The isolated yield of the resulting polymers after removal of low molecular weight products was in the range 55–70%. According to ^{1}H NMR, IR spectra, and GPC traces, the polymerization was accompanied by significant intramolecular cyclization reactions in all cases. The weight-average molecular weight determined by GPC with polystyrene standards ranged from 5800 to 8900. It was reported that the progressive, slow addition of the AB_2 monomer into the polymerization mixture resulted in the significant increase in molecular weight up to 86,000. The resulting polymers were soluble in organic solvents, such as hexane, halogenated alkanes, and ethers, but insoluble in polar solvents, such as methanol or acetonitrile. For the polymer prepared from the AB_2 monomer, the relative integration of the α and β signals in ^{1}H NMR spectrum indicated that the

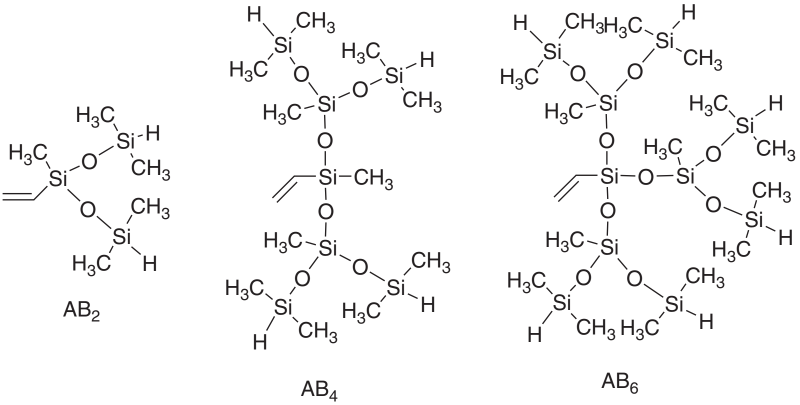


Figure 2.22 AB_2, AB_4, and AB_6 monomers for hyperbranched poly(siloxysilane)s reported by Fréchet.

α addition occurred in ca. 30%. The chemical modification of silicone hydride groups allows controlling the properties of hyperbranched poly(siloxysilane)s. The glass transition temperature of the modified polymers ranged from −126 to −2 °C, depending on the nature of the end groups.

Other hyperbranched poly(siloxysilane)s have been prepared by the same strategy through hydrosilylation. The AB_2 monomers reported for hyperbranched poly(siloxysilane)s are listed in Figure 2.23. UV-curable hyperbranched poly(siloxysilane)s were prepared by the polymerization of the AB_2 monomer containing two vinyl or allyl groups, or the endcapping reaction of the Si–H terminated polymer.[119] The degradable hyperbranched poly(alkoxysilane)s was also prepared from the AB_2 monomer containing alkoxysilane groups, which can be easily hydrolyzed under acidic conditions.[120]

Frey reported the polymerization of a triallylsilane through the hydrosilylation to form hyperbranched poly(carbosilane)s, as shown in Scheme 2.35.[121–123] The complete conversion of the Si–H functionality was confirmed by ^{1}H NMR spectroscopy. The isolated hyperbranched poly(carbosilane)s were soluble in common organic solvents regardless of the molecular weight. GPC trace of the hyperbranched poly(carbosilane) showed trimodal molecular weight distribution, and the fraction for the highest molecular (500,000) weight might be formed by the side reactions, such as cross-linking reactions. The addition of a B_1 molecule, 2-(10-decen-1-yl)-1,3-oxazoline, allowed controlling the molecular weight of the resulting polymers in the range 17,000–800 (M_w by GPC with polystyrene standards). The possible repeating units of the poly(carbosilane), dendritic (D), semidendritic (sD), linear (L), and terminal (T) are described in Figure 2.24. The integration of each resonance in the ^{29}Si NMR spectrum gave the DB of 0.48 ± 0.05, which agreed well with the statistically obtained value (DB = 0.44).[3] The oxazoline-anchored hyperbranched poly(carbosilane) can be

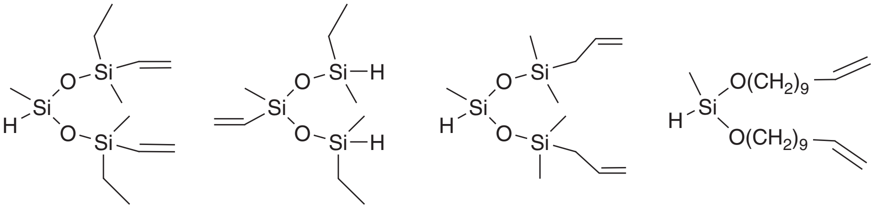
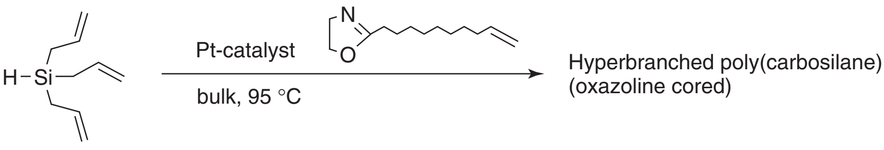


Figure 2.23 AB_2 monomers for hyperbranched poly(siloxysilane)s through hydrosilylation.



Scheme 2.35

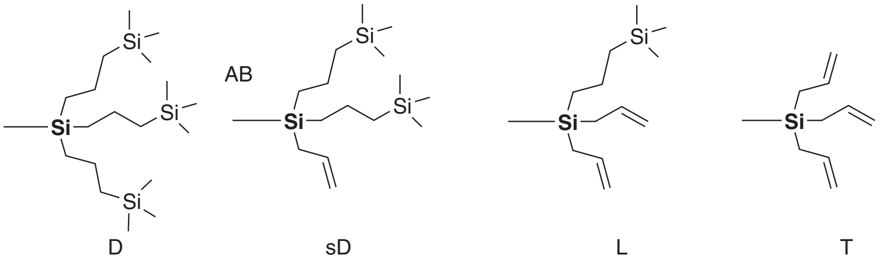


Figure 2.24 Possible repeating units for the hyperbranched poly(carbosilane) reported by Frey.

recognized as a macromonomer for further chemical reactions. The coupling with a core molecule, ring-opening polymerization of the oxazoline group, copolymerization with 2-phenyl-1,3-oxazoline, and chemical modification of vinyl groups resulted in the formation of various macromolecular architectures.[122]

The spacer groups between the double bond and the Si–H group influence the polymerization behavior through the hydrosilylation. The hydrosilylation of methyldivinylsilane, methyldiallylsilane, triallysilane, and methyldiundecenylsilane, shown in Figure 2.25, was carried out in order to prepare hyperbranched poly(carbosilane)s with various spacer groups.[124] Methyldivinylsilane, methyldiallylsilane, and triallysilane did not yield high molecular weight polymers when the reaction mixture was diluted by a solvent. The bulk polymerization of the short-chain monomers often resulted in the formation of cross-linked products, which might be caused by the rearrangement of the terminal double bonds and reductive elimination reactions to form disilanes. The cross-linking reactions could be avoided by keeping the reaction temperature and catalyst concentration low. On the other hand, high molecular weight polymers were readily obtained by the polymerization of methyldiundecenylsilane where the distance between the double bond and the silicon atom was essentially enlarged. The molecular weight of the hyperbranched poly(carbosilane) could be controlled by the subsequent addition of further monomer to the polymerization mixture.

Hyperbranched poly(carbosilarylene)s were synthesized through the same strategy as aliphatic poly(carbosilane)s. The AB$_3$ monomers examined are listed in Figure 2.26.[125] The glass transition temperatures of the hyperbranched poly(carbosilarylene)s depended on the structure of starting monomers in the

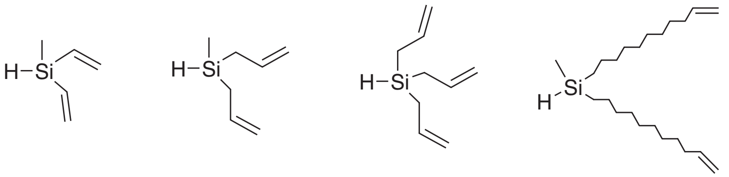


Figure 2.25 AB$_x$ monomers having the alkyl spacer groups between the double bond and the Si–H group.

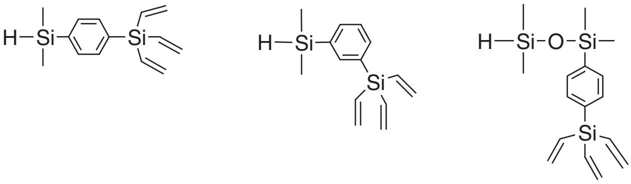


Figure 2.26 AB_3 monomers for hyperbranched poly(carbosilarylene)s.

range −45–12 °C and are higher than those of aliphatic poly(carbosilane)s. Hyperbranched poly(carbosilane)s having furan or thiophene rings were also prepared from the corresponding AB_2 monomers through hydrosilylation.[126]

Hyperbranched poly(silylene vinylene)s were prepared through hydrosilylation in the presence of platinum or rhodium catalysts from the AB_x monomer having triple bonds, as shown in Figure 2.27.[127–130] The unique π-to-σ charge transfer was observed for the hyperbranched poly(silylenephenylene vinylene) prepared from bis(4-ethynylphenyl)methylsilane and *m*-bis[dimethylsilyl] phenylacetylene.[129,130]

2.3.4.2 Condensation Reactions

The condensation reactions of silanol groups to form siloxane linkages were applied for the preparation of hyperbranched poly(siloxane)s. Kakimoto reported the preparation of a hyperbranched poly(dimethylsiloxane) from an AB_2 monomer, as shown in Scheme 2.36.[131,132] The stable AB_2 molecule was used as the starting compound and activated *in situ* for the polymerization. The molecular weight of the hyperbranched poly(dimethylsiloxane) was ca. 10,000 which was determined by vapor pressure osmometry. The polymer endcapped

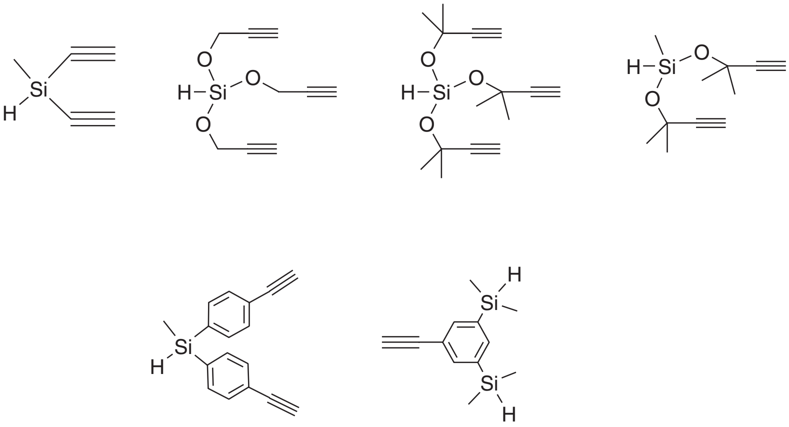
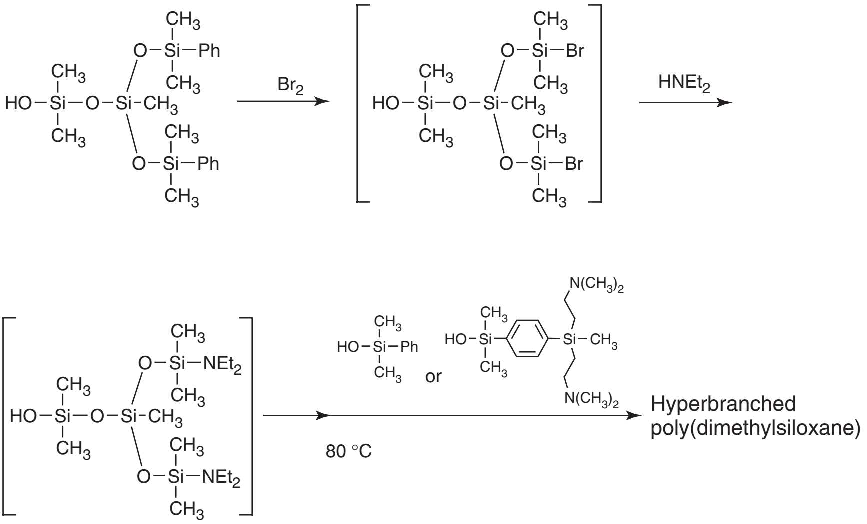


Figure 2.27 AB_x monomers for hyperbranched poly(silylene vinylene)s.



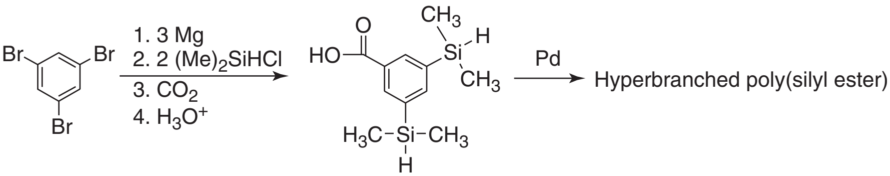
Scheme 2.36

with dimethylphenylsilanol was soluble in organic solvents, such as THF. When the silanol having dimethylamino groups was reacted as an endcapping agent, the resulting polymer became soluble in acidic aqueous solution and showed the amphiphilic property to encapsulate hydrophobic molecules. The UV–vis measurements indicated that the hyperbranched poly(siloxane) solubilized about five molecules of 1,6-diphenylhexatriene which is known as a hydrophobic dye.

The preparation of hyperbranched poly(ethoxysiloxane)s from tetraethoxysilane (TEOS) as starting compound was also reported.[133,134] In the initial stage, TEOS was reacted with ethanol or acetic anhydride to form the AB_3-type monomer and the following polymerization was carried out without isolation of the AB_3 monomer. Although the main structure of the resulting polymers is composed of hyperbranched architecture, the formation of internal loop was also observed by NMR and MS measurements.

2.3.4.3 Other Si-Containing Reactions

Hyperbranched poly(silyl ester)s were prepared through cross-dehydrocoupling catalyzed by palladium, as shown in Scheme 2.37.[135] The polymerization was carried out at 100 °C for one day in the presence of palladium on activated carbon. The weight-average molecular weight and the molecular weight distribution based on polystyrene standards were 23,000 and 6.8, respectively. The DB determined by the ^1H NMR measurement was 0.51. The hydrolytic degradation of the hyperbranched poly(silyl ester) exhibited a slow initial molecular weight loss, followed by rapid cleavage.



Scheme 2.37

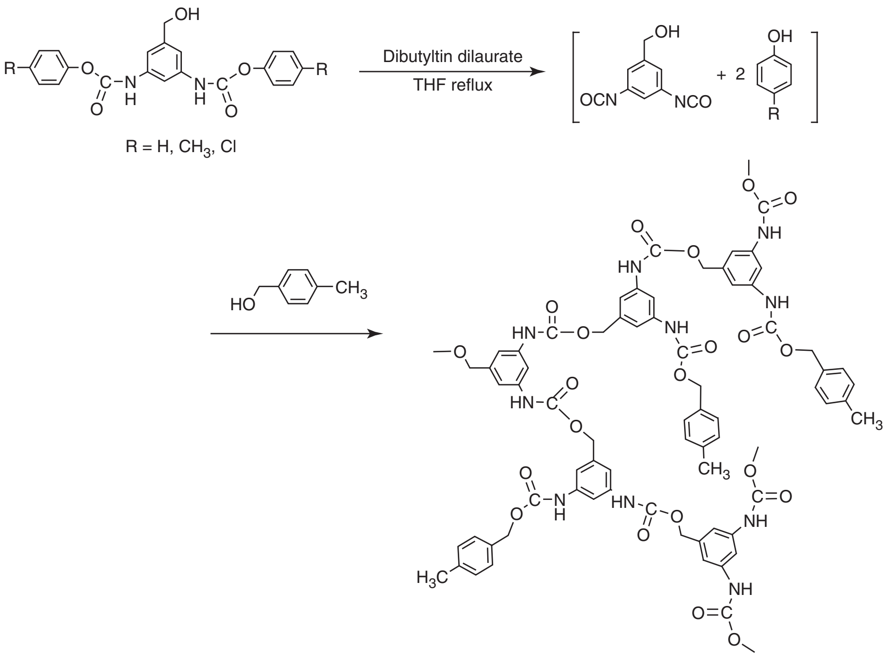
2.3.5 Other Coupling Reactions

2.3.5.1 C–O or C–N Coupling Reactions of Isocyanates

Isocyanate groups form urethane linkages by the reaction with alcohols or from urea linkages by the reaction with amines. The isocyanate groups in the self-condensing monomers must be protected since they are highly reactive against nucleophiles. Deprotection is usually carried out *in situ* during the polymerization process. The preparation of hyperbranched polyurethanes and polyureas from the AB_2 monomers having protected isocyanate groups has been reported as described below.

Aryl–aryl carbamate groups are useful for the protection of aromatic isocyanates since the carbamate bonds are easily cleaved by heating. Hyperbranched polyurethanes were prepared from the AB_2 monomer, which has one alkyl hydroxyl group and two protected isocyanate ones, as shown in Scheme 2.38.[136] The polymerization proceeded in refluxing THF in the presence of dibutyltin dilaurate as a catalyst. The soluble polymer with an M_w of 34,000 was isolated by the polymerization at a monomer concentration of 1 mol/L. Further increase in the concentration resulted in the formation of a cross-linked network, which might be caused by the side reactions of isocyanate groups such as dimerization and trimerization. The polymerization of the AB_2 monomer in the presence of an aliphatic alcohol resulted in the formation of the endcapped polyurethanes. The endcapped polyurethanes were thermally stable up to 200 °C, whereas the polymers isolated without the endcapping reactions were not stable above 120 °C. Glass transition temperature of the polymers ranged from 119 to 57 °C, depending on the end functional group. All the endcapped polymers were soluble in THF, DMF, and DMSO, with the decyl-capped polymer also being soluble in a diethyl ether/chloroform mixture.

The thermal decomposition of carbonyl azides also generates isocyanates. Wholly aromatic hyperbranched polyurethanes were prepared by the self-polycondensation of the AB_2 and A_2B monomers having carbonyl azides, as shown in Figure 2.28.[137,138] Although both the AB_2 monomer and the resulting polymer are insoluble in toluene, the polymerization was carried out in refluxing toluene, which is considered as dispersion polymerization. The M_w determined by GPC based on polystyrene standards was 9100, and the DB determined by ^1H NMR was 0.59. The polymerization of 5-hydroxyisophthaloyl azide as



Scheme 2.38

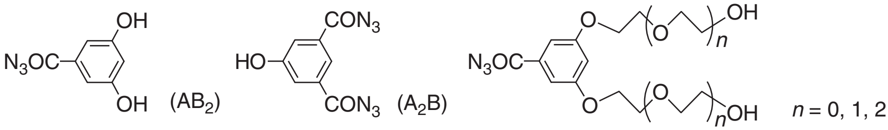


Figure 2.28 AB$_2$ monomers having carbonyl azides as protection groups for isocyanates.

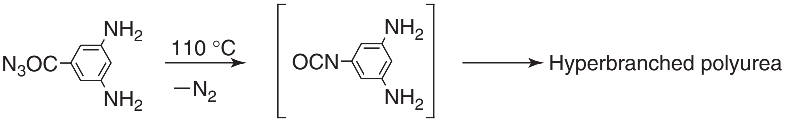
an A$_2$B monomer gave a carbamate-terminated polyurethane after endcapping reaction with ethanol before isolation. The resulting polyurethane was found to be insoluble in most of organic solvents, which was probably due to the side reactions of isocyanate groups. Soluble polymers were isolated when the polymerization of the A$_2$B monomer was carried out in the presence of an equivalent amount of an alcohol. Melt polymerization was applicable for the AB$_2$ monomer containing oligoethyleneoxy segments. The inherent viscosity of the hyperbranched polyurethanes increased with increasing length of the oxyethylene segments and ranged from 0.20 to 0.30 dL/g in DMSO. Glass transition temperature decreased remarkably by the introduction of oxyethylene units in the range 106–13 °C. The oxyethylene units improved the thermal stability by about 100 °C in comparison with the corresponding wholly aromatic polyurethane.

Hyperbranched polyurea was prepared by the self-polycondensation of the AB_2 monomer containing a carbonyl azide and amino groups, as shown in Scheme 2.39.[139] The thermal decomposition of 3,5-diaminobenzoyl azide in NMP at 110 °C generated the corresponding 3,5-diaminophenyl isocyanate *in situ*. Rapid evolution of N_2 was observed during the initial stage of the reaction, and subsequent heating resulted in the formation of a wholly aromatic hyperbranched polyurea in high yield. The DB determined by ^{1}H NMR spectrum was found to be 0.55. The M_w and M_w/M_n determined by GPC based on polystyrene standards was 19,500 and 1.56, respectively. The wholly aromatic hyperbranched polyurea was soluble in organic solvents such as DMSO, NMP, and DMF, whereas the linear analogues were almost insoluble in any organic solvents.

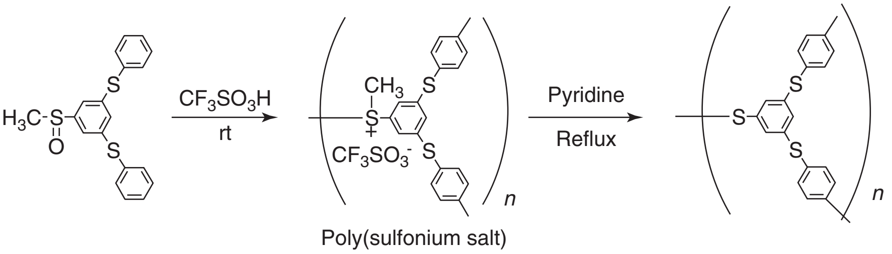
2.3.5.2 C–S Coupling Reactions

The preparation of hyperbranched poly(phenylene sulfide)s and poly(phenylene sulfone)s through electrophilic or nucleophilic substitution reactions has been reported in the literature.

It was reported that the linear poly(phenylene sulfide) with a high molecular weight was formed by the reaction of sulfoxide monomers through the electrophilic substitution in the presence of trifluoroacetic acid.[140,141] By adopting the strategy to an AB_2 monomer, Kakimoto first reported the preparation of a hyperbranched poly(phenylene sulfide), as shown in Scheme 2.40.[142] The poly(arylsulfonium cation) formed in the first stage through electrophilic substitution was converted to hyperbranched poly(phenylene sulfide) by refluxing in pyridine. The weight-average molecular weight and the molecular weight distribution determined by GPC-MALLS were 25,700 and 1.45, respectively. The



Scheme 2.39

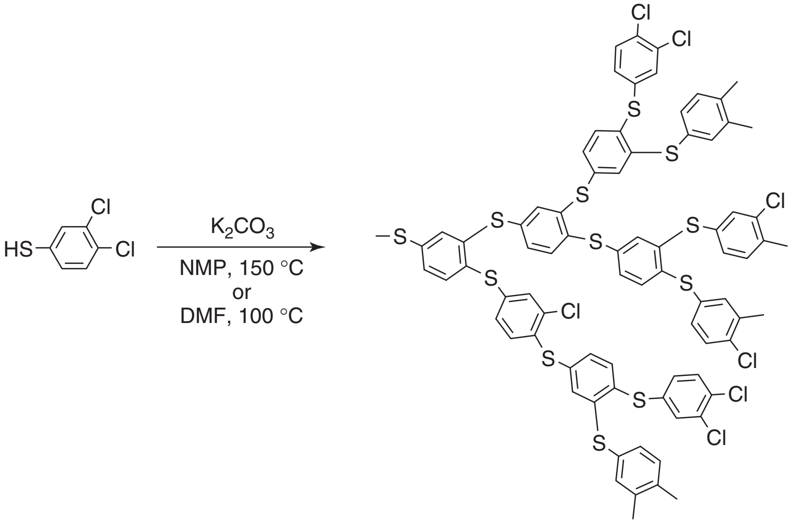


Scheme 2.40

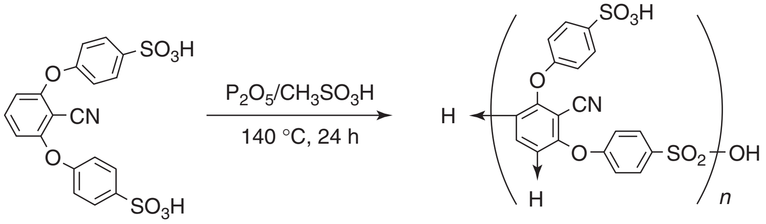
hyperbranched poly(phenylene sulfide) was amorphous and soluble in organic solvents such as chloroform, although linear poly(phenylene sulfide), known as a crystalline polymer, is almost insoluble in any organic solvents at room temperature.

Hanson reported the preparation of hyperbranched poly(phenylene sulfide)s through nucleophilic aromatic substitution reactions, as shown in Scheme 2.41.[143] The polymerization was carried out at 150 °C for 1 h in NMP or 100 °C for 24 h in DMF. The precipitate was observed at longer polymerization times. The polymers isolated before the precipitation were soluble in THF and amide solvents. The weight-average molecular weight and the polydispersity determined by GPC-LS were 17,000 and 2.0, respectively, for the polymer prepared in DMF. The addition of a trivalent core, 1,3,5-trichlorobenzene, reduced the molecular weight and polydispersity. The oxidation of the hyperbranched poly(phenylene sulfide) resulted in the formation of the hyperbranched poly(phenylene sulfone). The oxidation reaction was confirmed by elemental analysis. The hyperbranched poly(phenylene sulfone) was insoluble in organic solvents in contrast to the original hyperbranched poly(phenylene sulfide). The glass transition temperature of the hyperbranched poly(phenylene sulfide) was in the range 60–90 °C and increased by the oxidation to form the hyperbranched poly(phenylene sulfone) (155 °C).

Hyperbranched poly(ether sulfone)s were also prepared by the aromatic sulfonation reactions of the AB_2 monomer, as shown in Scheme 2.42.[144] The polymerization proceeded in phosphorus pentoxide and methanesulfonic acid as the condensing agent and solvent, respectively, to form the hyperbranched



Scheme 2.41



Scheme 2.42

poly(ether sulfone) with many terminal sulfonic acid groups. The sulfonic acid-terminated polymer was soluble in DMSO and water. The weight-average molecular weight of the polymer terminated with anisole was 44,000, based on GPC with polystyrene standards. The onset temperature of the thermal decomposition of the hyperbranched poly(ether sulfone)s terminated with sulfonic acid or anisole was 275 and 285 °C, respectively. The blend film of the sulfonic acid-terminated polymer with polyvinyl alcohol exhibited proton-transporting ability, which might be useful for thermally stable electrolyte films for fuel cells.

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Chapter 3

Synthesis of Hyperbranched Polymers via Polymerization of Functionally Symmetric Monomer Pairs

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3.1 INTRODUCTION

AB_n type monomers that contain one "A" functional group and n"B" functional groups undergo self-polycondensation or copolymerize with AB type monomers to generate hyperbranched polymers.[1,2] However, the limited commercial availability of functionally nonsymmetric AB and AB_n type monomers has precluded industrial implementation. Polymerization of functionally symmetric monomer pairs such as A_2 and $B_x (x \geq 3)$ has emerged as an alternative approach to the classic AB_n type polymerization to synthesize hyperbranched polymers.[3–6] Various combinations of functionally symmetric monomer pairs are possible, including A_2 and B_4, A_3 and B_3, and A_2 and B_3; however, A_2 and B_3 polymerization, also termed as "$A_2 + B_3$," has received significant attention in the last decade as a more facile approach to synthesizing hyperbranched polymers. Several types of difunctional (A_2) and trifunctional monomers (B_3) are commercially available, or much less effort is required to synthesize A_2 and B_3 monomers compared to AB_n monomers. The wide range of commercially available A_2 and B_3 monomers also allow tailoring the polymer structure because

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

of various choices of monomer pairs and provide more facile routes to many families of hyperbranched polymers. Moreover, the risk of premature polymerization in some AB and AB_n type monomers is insignificant in the polymerization of separate functionally symmetric monomer pairs.[7]

According to Flory's well-established theory, the direct polymerization of A_2 and B_3 monomers is a cross-linking strategy that results in a sol–gel system based on the A_2:B_3 molar ratio and functional group conversion.[1,2] Despite the high risk of gelation, the potential for $A_2 + B_3$ polymerization in many industrial applications has encouraged scientists to devote significant attention to the determination of reaction parameters to avoid gelation. The first two pioneering reports that described the synthesis of hyperbranched polymers using the $A_2 + B_3$ polymerization appeared in 1999. Kakimoto and coworkers reported the synthesis of hyperbranched aromatic polyamides that were derived from commercially available aromatic diamines (A_2) and trimesic acid (B_3).[3] In addition, Fréchet and coworkers demonstrated the synthesis of hyperbranched polyether epoxies via proton-transfer polymerization from 1,2,7,8-diepoxyoctane (A_2) and 1,1,1-tris(hydroxymethyl)ethane (B_3) using various molar ratios of A_2 and B_3.[4,5] Stopping the reactions immediately prior to gelation resulted in soluble, network-like products with reasonable molar mass and high degrees of branching, which resembled hyperbranched polymers.

After these two pioneering reports, several families of hyperbranched polymers, such as aromatic polyamides,[8–10] polyimides,[11–18] poly(ether sulfone)s,[19] poly(arylene ether)s,[20] polyesters,[21–23] and polycarbonates,[24] were reported via $A_2 + B_3$ polymerization. $A_2 + B_3$ addition reactions were also reported for the preparation of various hyperbranched polymers via Michael addition.[7,25,26] In addition, highly branched copolymers, such as poly(ether ester)s,[27,28] poly(arylene ether)s,[29] poly(phosphate ester)s,[30] and segmented polyurethanes/poly(urethane urea)s[31–35] were reported using $A_2 + B_3$ polymerization and a functionally symmetric oligomeric precursor in place of either the A_2 or B_3 monomer. The term *highly branched*, rather than *hyperbranched*, was used to describe the branched polymers synthesized using an oligomeric precursor as these polymers possess less branching per unit mass. The classic $A_2 + B_3$ approach was altered with monomer pairs such as $AA^* + B_3$, $A_2 + B^*B_2$, or $AA^* + B^*B_2$ to control the hyperbranched structure formation, where A and A^* or B and B^* were the same or similar type of functional groups exhibiting different reactivities.[36–41] These types of monomer pairs are not solely functionally symmetric and are, therefore, excluded from this report.

Many researchers have asserted that various factors account for avoiding gelation and generating fully soluble, hyperbranched products. These factors include the formation of reactive intermediates that resemble the AB_2 type monomers,[3] partial conversion of functional groups,[4,5] slow addition of one monomer to another,[11,21] significant levels of cyclization reactions,[19] and reactivity differences between identical functional groups within the same molecule.[13,23] If one or more of these factors arise, $A_2 + B_3$ polymerization deviates from ideal cross-linking conditions and the polymerization results in high molar mass, highly branched structures. In this review, the theoretical treatment of $A_2 + B_3$ polymerization and synthetic methods for preparing various gel-free hyperbranched polymers from functionally symmetrical monomer pairs are reported. Moreover, the influence of reaction parameters and the factors that mitigate gelation for new families of gel-free hyperbranched polymers are discussed.

3.2 THEORETICAL TREATMENT OF $A_2 + B_3$ POLYMERIZATION

Flory first introduced the theory of gelation for nonlinear polymers in 1952.[1,2] According to this theory, polymerizations that contain multifunctional monomers (monomer units with functionalities higher than two) generate a three-dimensional network at a certain monomer conversion for a given stoichiometric ratio of functional groups. Therefore, according to this theory, treatment of $A_2 + B_3$ polymerization and determination of the gel point are essential to synthesize gel-free hyperbranched polymers. In a nonlinear polymerization system such as $A_2 + B_3$, a branching coefficient, α, is defined as the probability that a given functional group of a branch unit (B_3) is linked to another branch unit. In general, α can be calculated from the ratio of the "A" and "B" functional groups and the extent of reaction at a given time. In the case of an $A_2 + B_3$ polymerization, α can be calculated using Eq. (3.1):

$$\alpha = r \times p_\mathrm{A}^2 = p_\mathrm{B}^2/r \tag{3.1}$$

where r is the ratio of A to B groups (A:B), and p_B and p_A are the fractions of A and B groups that have reacted. Another important term is the critical branching coefficient (α_c), which defines the gel point. For a given r value, α increases as a function of the extent of reaction. An infinite network is formed when α reaches a critical value, α_c. The critical branching coefficient (α_c) is calculated as

$$\alpha_\mathrm{c} = \frac{1}{(f-1)} \tag{3.2}$$

where f denotes the average functionality of multifunctional monomers in the system.

Therefore, α_c becomes 0.5 for an $A_2 + B_3$ polymerization because only trifunctional monomer is present as a multifunctional monomer. During polymerization, a fully soluble product is present when $\alpha < \alpha_\mathrm{c}$, and a sol–gel mixture begins to appear when $\alpha > \alpha_\mathrm{c}$. As calculated from Eq. (3.1), the maximum α value is equal to one, which resembles a fully cross-linked system. The value of α can also be correlated to the degree of branching (DB) of a product, which apparently increases as a function of monomer conversion. In addition, the weight fractions of sol–gel are proportional to α in the $\alpha_\mathrm{c} < \alpha < 1$ regime. In an $A_2 + B_3$ polymerization, it is important to calculate the critical conversion of A and B groups (p_Ac and p_Bc) at the gel point for various r values, based on Eqs. (3.1) and (3.2).

Table 3.1 Calculation of Gel Point in $A_2 + B_3$ Polymerization ($\alpha_c = 0.5$) for Various Monomer Ratios Using Eqs. (3.1) and (3.2)

A_2:B_3	$r =$ A:B	p_{Ac}	p_{Bc}
0.75:1.00	0.50	1.000	0.500
0.90:1.00	0.60	0.913	0.548
1.00:1.00	0.67	0.866	0.577
1.25:1.00	0.83	0.775	0.645
1.50:1.00	1.00	0.707	0.707
2.00:1.00	1.33	0.612	0.816
3.00:1.00	2.00	0.500	1.000

Table 3.1 summarizes the critical conversion of A and B groups for various A to B ratios. As the molar ratio of A to B functional groups is increased, the gel point is reached sooner, at a lower monomer conversion, and gelation becomes more difficult to avoid.

It should be noted that Flory's well-established theory on gelation is based on the following assumptions: (i) the reactivity of the functional groups remains constant during polymerization; (ii) the reactions do not involve cyclization; and (iii) the polymerization is restricted to the reaction between A and B groups. As discussed later, deviations from these assumptions may shift the gel point to higher conversions and avoid gelation, resulting in high molar mass, highly branched structures.[12]

Other than Flory's theory for gel formation, there are few significant reports on the theoretical treatment of $A_2 + B_3$ polymerizations. Voit and Schmaljohann reported a theoretical simulation of structural development and reported the influence of several factors such as composition, kinetics, and monomer addition on the resulting hyperbranched polymer via the $A_2 + B_3$ polymerization.[42] Seven types of different structural units, such as substructures of linear, dendritic, and terminal units, were identified based on different monomer sequences and adjacent groups of each structural unit. Initial monomer composition played an important role in determining the ratio of these structural units in the final product. The structural units and monomer sequences as predicted in theoretical calculations were also reported using detailed NMR spectroscopic analysis.[8]

Determination of the DB is an essential metric for hyperbranched polymers. Several equations were developed earlier to define the structure of hyperbranched polymers based on the self-condensation of AB_2 monomers.[10,43] The DB was described as the ratio of the sum of fully branched and terminal units to the total number of units[44]

$$\mathrm{DB} = (D + T)/(D + T + L) \tag{3.3}$$

where D, T, and L correspond to the total number of dendritic, terminal, and linear units, respectively, and $D + T + L = 1$. Alternatively, Frey and coworkers defined the DB according to Eq. (3.4).[45] In most cases, these equations are also

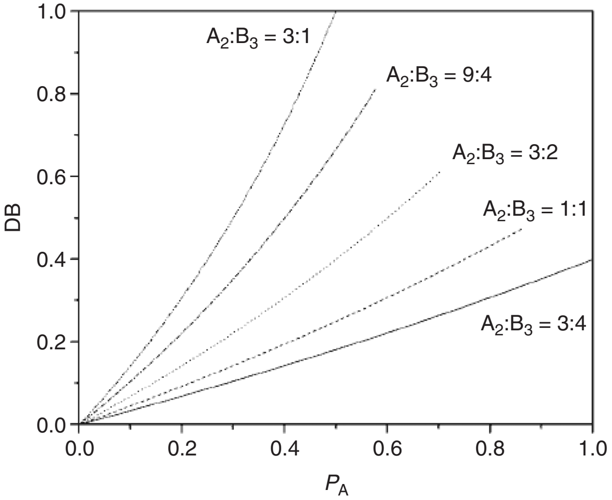


Figure 3.1 Theoretical simulation of DB versus conversion of A functional groups (p_A) for various A_2:B_3 monomer ratios.

applicable to the products of $A_2 + B_3$ polymerization:

$$\mathrm{DB} = 2D/(2D + T) \tag{3.4}$$

Voit and Schmaljohann reported theoretical calculations at various monomer compositions demonstrating that higher degrees of branching (based on Eq. (3.4)) are achieved at higher A_2 to B_3 monomer ratios. Gelation occurs at p_A values as the A_2 to B_3 monomer ratio increases (Figure 3.1).[42] The discontinuity in each plot indicates the gel point at a corresponding p_A.

Differences in the reaction rate constants for the conversion of the A_2 monomer influenced the DB, and slow addition of either both monomers or just the B_3 monomer had the strongest effect on the resulting higher DB. In all cases, higher rate of conversion without gelation was critical for high molar mass products.

Recent reports in our laboratory provided a comparative study of experimental results and theoretical simulations for the synthesis of highly branched, segmented poly(urethane urea)s (HB-PUUs), where a dilute solution of an A_2 oligomer (polyether diisocyanate) was slowly added to a B_3 (triamine)solution.[32] The HB-PUU molar mass increase was monitored as a function of A_2 addition using size exclusion chromatography (SEC) analysis. The experimental procedure was modeled using Monte Carlo (MC) simulations to better understand the molar mass increase and structure development. Similar to the experimental procedure, N molecules of A_2 were sequentially added into N molecules of B_3. When MC simulations were employed in the absence of cyclization, reactions between A and B groups on the same molecule were not allowed. However, as discussed later, cyclization is a very important factor that accounts for deviations from

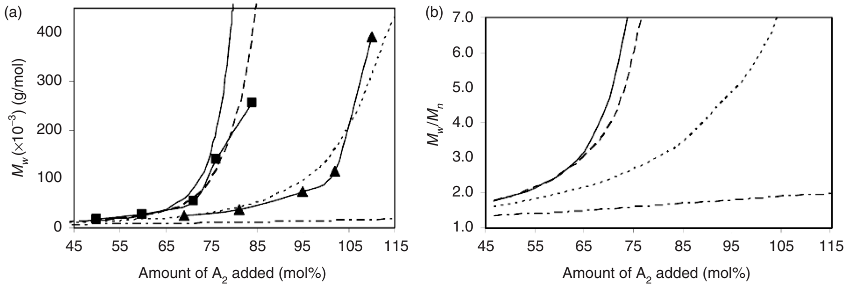


Figure 3.2 Comparison of experimental and simulation results on the development of (a) weight average molar mass and (b) polydispersity as a function of A_2 addition and cyclization ratio. Experimental data: Molar masses from SEC analysis. Polymerization conducted in (■) 25 wt% and (▲) 10 wt% by solids. Simulation data: (—) $\gamma = 0$, (– – –) $\gamma = 0.01$, (- - -) $\gamma = 0.1$, and (–·–·–) $\gamma = 1$.

theoretical assumptions and a significant shift in the gel point during the synthesis of hyperbranched polymers.[19,46–49] It is well known that dilute solutions favor cyclization reactions and cyclic macromolecules are generally prepared under very dilute conditions (approximately below 5% solids).

In an attempt to simulate experimental conditions, a cyclization parameter (γ) was introduced based on the selected probabilities for the reaction between A and B groups within the same molecule. The value of γ varied between 0 (no cyclization) and 1 (highest cyclization ratio), and the structural characteristics such as the molar mass, polydispersity, DB, and number of cycles per molecule were monitored. The experimental and theoretical molar mass data are plotted in Figure 3.2.[32] The experimental values for the polymerizations at 25% solids in Figure 3.2(a) agree fairly well with the simulations at low cyclization ratios ($\gamma = 0 - 0.001$). At lower concentrations (10% solids) that are known to promote cyclization, experimental values agreed very well with the theoretical data at a higher cyclization ratio ($\gamma = 0.1$). Figure 3.2(b) shows that cyclization also plays an important role in the polydispersity of the final products. MC simulations suggest that higher polydispersities are achieved at lower cyclization ratios. In summary, MC simulations with a cyclization parameter f clearly demonstrated that cyclization reactions have a great influence on the final polymer product in the slow addition of an A_2 monomer to a B_3 monomer.

3.3 POLYMERIZATION OF SYMMETRICAL MONOMER PAIRS

3.3.1 Polycondensation of A_2 and B_3 Monomers

3.3.1.1 Polyamides

Kakimoto and coworkers reported the direct polycondensation of aromatic diamines (A_2) and trimesic acid (B_3) as a new approach to synthesize

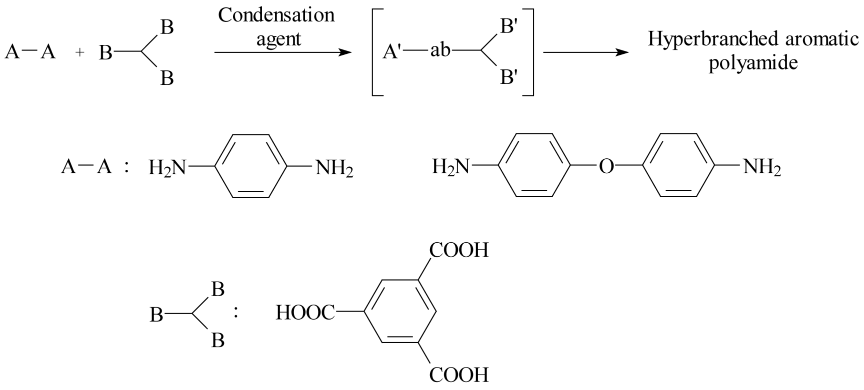


Figure 3.3 Synthesis of hyperbranched aromatic polyamides from aromatic diamines (A_2) and trimesic acid (B_3).

hyperbranched aromatic polyamides as shown in Figure 3.3.[3] Equimolar amounts of diamines and trimesic acid were polymerized (A_2:B_3 = 1:1, A:B = 2:3) in the presence of triphenyl phosphite and pyridine as the condensation agents and NMP (*N*-methyl pyrrolidone) as the solvent. While the reaction mixture with a 1:1 molar ratio of monomers was expected to cross-link at $p_{\mathrm{Ac}} = 86.6\%$, no gelation was experimentally observed. This apparent discrepancy was explained by the formation of an A'-ab-$(B')_2$ type intermediate when the reaction was kinetically controlled, and the first condensation reaction of A_2 and B_3 was faster than subsequent propagation (Figure 3.3). This intermediate resembled the common AB_2 type molecule, and the polymerization of this intermediate proceeded without gelation.

Gel-free products were prepared only in dilute solutions (as low as 4 wt%), and gelation was inevitable when the amount of solvent was reduced. Jikei and Kakimoto compared the structural features of hyperbranched aromatic polyamides that were prepared using both $A_2 + B_3$ and AB_2 polymerizations.[10] ^{13}C NMR spectroscopy revealed that although both polymers had similar DB values, hyperbranched polyamides from $A_2 + B_3$ had a larger number of dendritic units relative to terminal units, whereas the number of dendritic and terminal units was nearly equal in hyperbranched polyamides from AB_2 polymerization. Therefore, $A_2 + B_3$ polymers had higher inherent viscosities than the more conventional AB_2 polymers.

Russo, Voit, Komber, and coworkers subsequently reported the synthesis of hyperbranched aromatic polyamides via $A_2 + B_3$ polymerization and studied the influence of various reaction parameters such as initial monomer ratio on gel formation and final polymer structure.[8,9,50–54] When the polymerizations were stopped prior to gelation for A_2:B_3 = 1:1(A:B = 2:3) and A_2:B_3 = 3:2(A:B = 1) ratios, the number and nature of endgroups, as well as the DB, varied. Stopping the reaction immediately prior to gelation resulted in partial monomer conversion. Therefore, final products possessed both amine (A) and carboxylic acid (B) endgroups, and the relative number of these endgroups depended on the initial ratio of A_2 and B_3.

Detailed ^1H, ^{13}C, and 2D NMR spectroscopic analyses were used to characterize the microstructures present in a hyperbranched aromatic polyamide.[8] Various structural units were assigned to a hyperbranched aromatic polyamide, based on the monomer sequence and the nature of the endgroups as shown in Figure 3.4. In the early stages of the polymerization, only AB_2, A_2B, and A_3 type structures form (Figure 3.4, top row). The reaction of an A group in the top row with a B functionality transforms this group to A′, which connects two B_3 units. In general, products from $A_2 + B_3$ were similar to products of AB_2 polymerization in terms of intrinsic viscosity and thermal properties, but possessed different ratios of structural units. DB also varied and deviated from the classic 50% value for AB_2 polymers due to differences in the structural units with varying A_2:B_3 ratio. Finally, polymerization of A_2 and B_3 monomers in a ratio of 0.71:1.00 (A:B = 0.5) yielded only low molar mass oligomers with a low fraction of dendritic units.

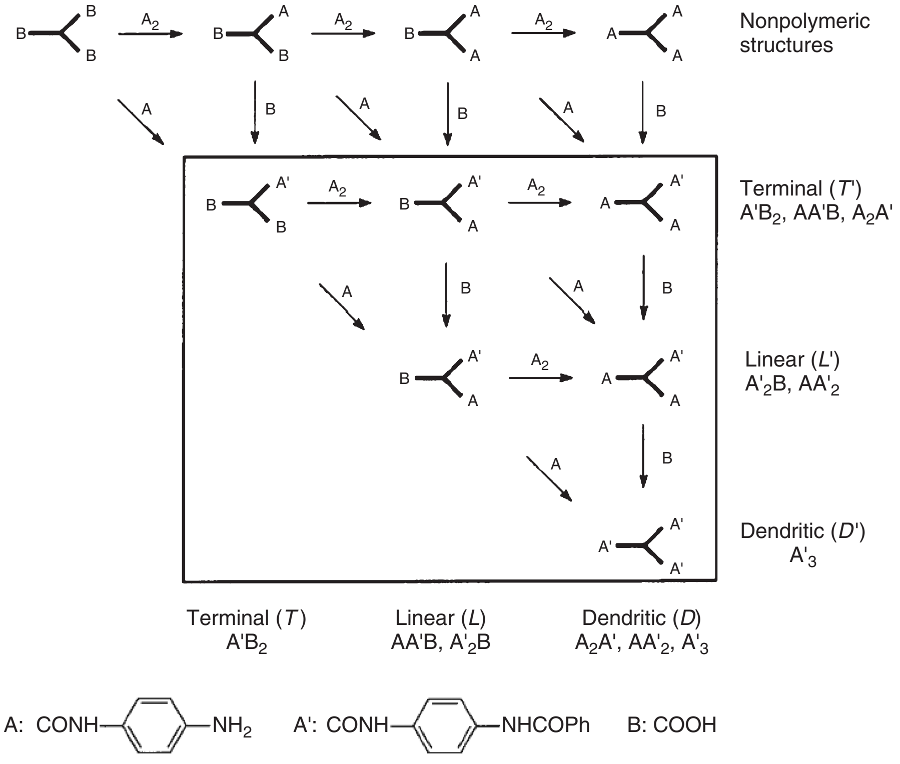


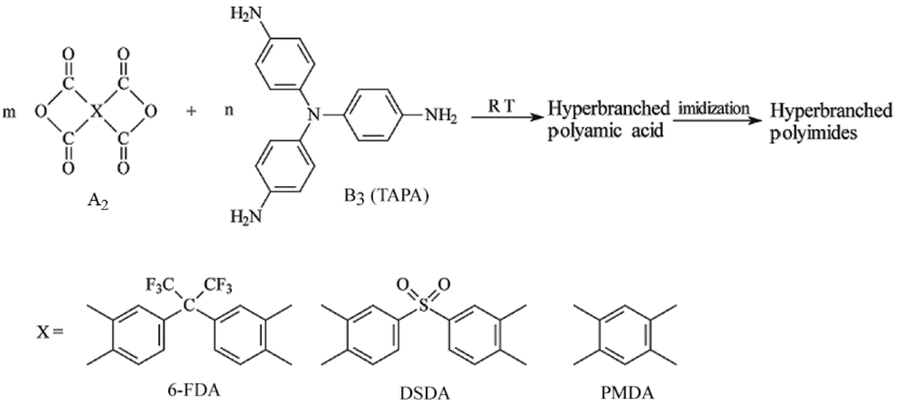
Figure 3.4 Structural units and reaction pathways for the polycondensation of *p*-phenylenediamine (A_2) and trimesic acid (B_3).

Hyperbranched aromatic polyamides were evaluated as potential supporting materials for protein immobilization[51] and palladium nanoparticles.[52–54] When the hyperbranched polyamides were used as the polymeric matrix in a solution containing Pd nanoparticles, the interaction between the amine endgroups and the metallic precursor ($PdCl_2$) tailored the stability of the solution. The number of amine groups affected the extent of nanoparticle stability in the solution. The Pd nanoparticle solutions were stable up to five months under optimized conditions using an $A_2 + B_3$ hyperbranched polyamide as the polymeric matrix.

3.3.1.2 Polyimides

Synthesis of hyperbranched aromatic polyimides using A_2 and B_3 monomers (Figure 3.5) was reported by Okamoto *et al.* for the first time using a series of commercially available dianhydrides (A_2) and a triamine, tris(4-aminophenyl)-amine (TAPA, B_3), synthesized from tris(4-nitrophenyl)amine in one step.[11] Earlier, preparation of wholly aromatic hyperbranched polyimides using the conventional AB_2 polymerization was not feasible because of the high reaction rates between anhydrides and amines. A functionally nonsymmetric monomer that possesses two complementary reactive sites such as anhydride and amine would not exist due to premature reaction.

In the polymerization of dianhydrides (A_2) and triamines (B_3), different orders of monomer addition resulted in hyperbranched polymers with different endgroups. In the first approach, a dianhydride (A_2) solution was added to a TAPA (B_3) solution in a 1:1 molar ratio, resulting in an amine terminated hyperbranched polyimide with DB values ranging from 64% to 72% depending on the dianhydride selection. The final product that was derived from 6-FDA (2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, Figure 3.5) had a



m/n = 1/1 (when a dianhydride was added to TAPA solution)
2/1 (when TAPA was added to a dianhydride solution)

Figure 3.5 Synthesis of wholly aromatic hyperbranched polyimides from A_2 and B_3 monomers.

weight average molar mass of 37,000 and a polydispersity of 5.8. Slow addition of a TAPA (B_3) solution into a dianhydride (A_2) solution at A_2:B_3 = 2:1(A:B = 4:3) ratio resulted in wholly branched, anhydride-terminated polyimides. The final product that was derived from DSDA (3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride, Figure 3.5) had a weight average molar mass of 150,000 and a polydispersity of 18. Gelation occurred immediately when the rate of monomer addition was too fast, or when the monomers were mixed at the onset of the reaction. In both approaches, higher monomer concentrations in the solution resulted in gelation and so were maintained below a critical concentration value to avoid gelation.

Despite the fact that slow addition of one monomer into another at an optimized molar ratio seemed to avoid gelation, significant effort was not devoted to understand the apparent discrepancy with Flory's theory behind the formation of fully soluble products. Kakimoto *et al.* subsequently reported a nonideal $A_2 + B_3$ polymerization approach to prepare hyperbranched polyimides using a more convenient polymerization strategy.[12–14] Two novel B_3 monomers, tri(phthalic anhydride) and tri(phthalic acid methyl ester), were synthesized for this purpose (Figure 3.6).

Polymerization of 1,4-phenylenediamine (A_2) and tri(phthalic anhydride) (B_3) resembled an ideal $A_2 + B_3$ polymerization; however, it was difficult to assess the preferred monomer addition strategy, that is, mixed monomers at the onset or A_2 monomer addition into B_3 due to high reactivity.[12] The final products had limited solubilities in common organic solvents. Therefore, a nonideal $A_2 + B_3$ system was preferred to prepare hyperbranched polyimides from 1,4-phenylenediamine (A_2) and tri(phthalic acid methyl ester) (B_3) in the presence of a condensation agent (DBOP, diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate). The presence of the condensation agent effectively prevented the carboxylic acid groups from reacting with amine nucleophiles at once; two different competing active intermediates that were reactive toward

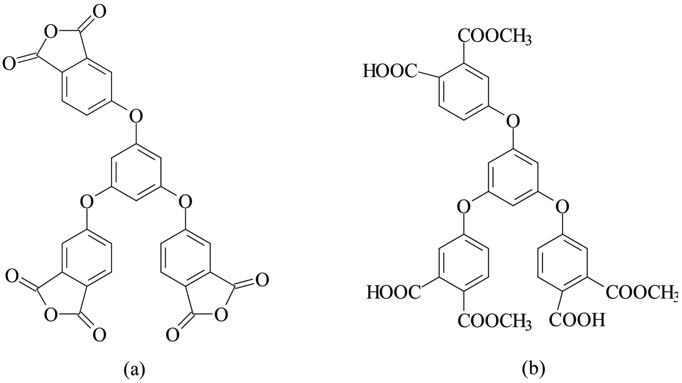


Figure 3.6 B_3 monomers used by Kakimoto *et al.*: (a) tri(phthalic anhydride) and (b) tri(phthalic acid methyl ester).

amine nucleophiles were formed early in the polymerization, of which one had a lower tendency for reaction.

Deviation from the assumption that functional group reactivity remains constant during polymerization clearly avoids gelation in a nonideal $A_2 + B_3$ polymerization. Monomer concentration was effectively optimized to obtain polyimides with a high DB. The content of dendritic units increased as the monomer concentration was increased, and above a critical concentration (0.08 g/mL), high molar mass products with high DB (above 50%) were obtained.

Two hyperbranched polymers, one derived from nonideal $A_2 + B_3$ monomer pairs and the other derived from an AB_2 monomer, had the same repeating unit, but distinct physical properties.[13,14] Hyperbranched polymers from the nonideal $A_2 + B_3$ polymerization had a much higher inherent viscosity and formed self-standing films with superior mechanical properties relative to the AB_2 self-condensation product.

These studies revealed that chain entanglements were present to some extent in the nonideal $A_2 + B_3$ polymerization.[14] As shown in Figure 3.7, this was attributed to the formation of linear oligomers at early stages of nonideal $A_2 + B_3$ polymerization, resulting in loose packing and a lower branching density compared to the AB_2 self-condensation product.[14]

3.3.1.3 Polyethers

Kricheldorf *et al.* studied the $A_2 + B_3$ polymerization and used matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) as a powerful tool for the analysis of these complex reaction mixtures. Detailed

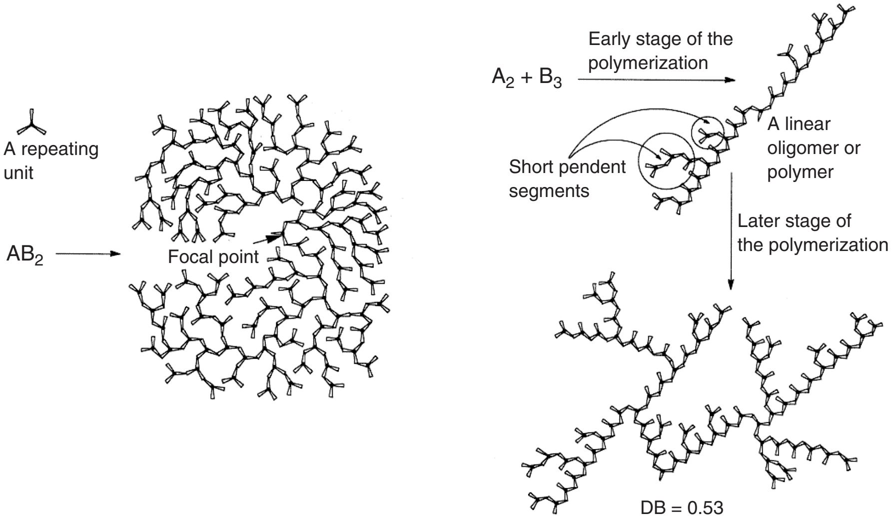
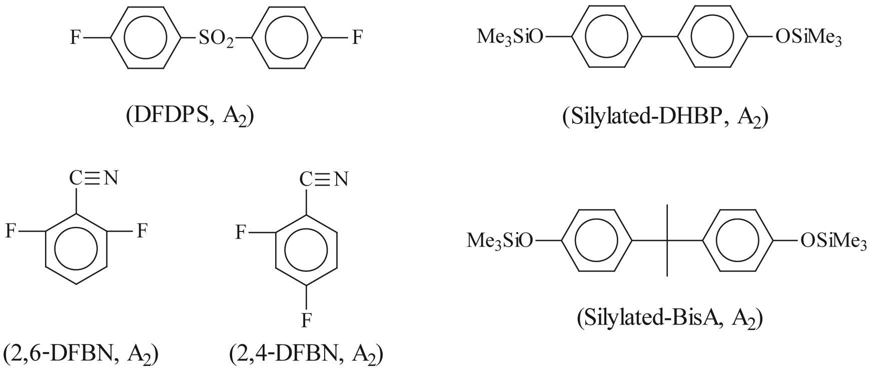


Figure 3.7 Molecular topologies of hyperbranched polyimides by AB_2 self-condensation and nonideal $A_2 + B_3$ polymerization.



(DFDPS, A_2)

(Silylated-DHBP, A_2)

(2,6-DFBN, A_2)

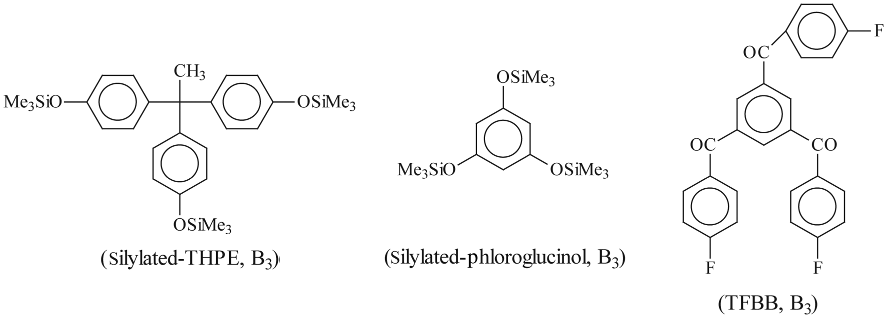
(2,4-DFBN, A_2)

(Silylated-BisA, A_2)

Figure 3.8 Chemical structure of A_2 monomers commonly used by Kricheldorf *et al.*

MALDI-TOF/MS studies on various step-growth polymers, such as polyesters, polyamides, polyimides, polycarbonates, poly(ether sulfone)s, and poly(ether ketone)s, demonstrated that cyclization competes with chain growth during all stages of a step-growth polymerization (even for linear polymers) and at all concentrations.[46] MALDI-TOF/MS characterization revealed that the final structure of the $A_2 + B_3$ polymerization products is very sensitive to cyclization reactions. Extensive cyclization during the $A_2 + B_3$ polymerization avoids gelation, and produces branched polymers with cyclic building blocks or a mixture of branched and multicyclic polymers.[19,46–48]

When 4,4′-difluorodphenyl sulfone (DFDPS, A_2, Figure 3.8) and 1,1,1-tris(4-hydroxyphenyl)ethane (THPE, B_3, Figure 3.9) were polymerized in a 1:1 molar ratio to prepare poly(ether sulfone)s, gelation was avoided, and MALDI-TOF/MS detected significant fractions of cyclic components.[19] An excess of 10 mol% DFDPS (A_2) resulted in gelation when polymerized with THPE (B_3), while polymerization of DFDPS (A_2) with silylated-THPE (B_3, Figure 3.8) at molar ratios of A_2:B_3 = 1.0:1.0 or 1.1:1.0 did not result in gelation. As expected, the

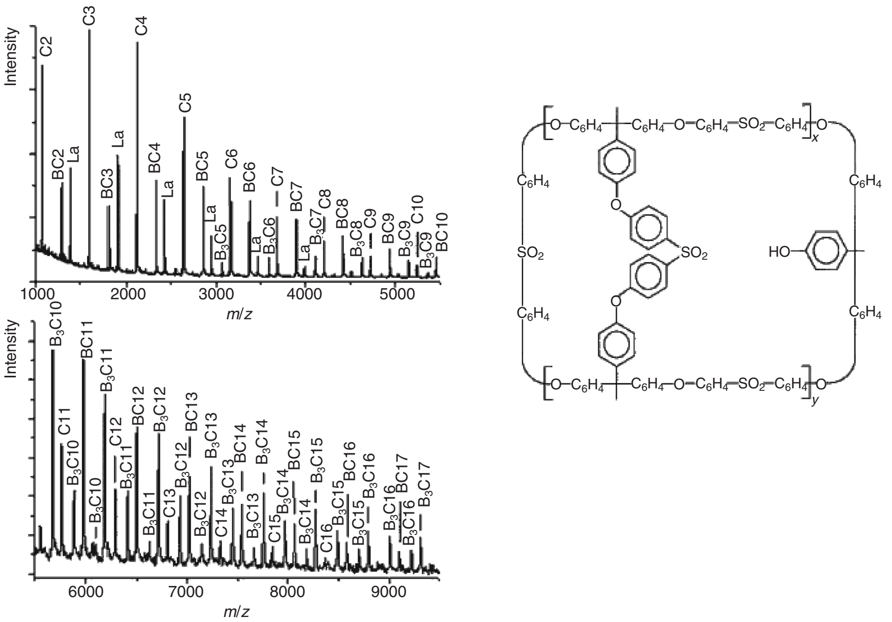


(Silylated-THPE, B_3)

(Silylated-phloroglucinol, B_3)

(TFBB, B_3)

Figure 3.9 Chemical structure of B_3 monomers used by Kricheldorf *et al.*



(a) (b)

Figure 3.10 (a) Typical MALDI-TOF/MS of a hyperbranched poly(ether sulfone) from DFDPS (A_2) and silylated-THPE (B_3) with A_2:B_3 = 1.1:1.0. (b) Proposed bridged cyclic (bicyclic) oligo(ether sulfone)s detected (labeled as BC).

A_2:B_3 = 1.1:1.0 ratio yielded products with higher molar mass. An increase in the A_2:B_3 ratio to 1.2:1.0 resulted in gelation.

MALDI-TOF/MS revealed the presence of significant fractions of cyclic components detectable up to a degree of polymerization of 16 (C16) (Figure 3.10a).[19,46] More complex cyclic structures, such as bicyclic oligo(ether sulfone)s (Figure 3.10b), were also detected using MALDI-TOF/MS. Kricheldorf and coworkers also established a nomenclature, BxCY, in order to denote the number of "bridge units" (x) and total number of repeating units (Y).[19] In a similar manner, MALDI-TOF revealed a high degree of cyclization and a significant fraction of multicyclic product that was derived from a 1:1 ratio of DFDPS (A_2, Figure 3.8) and silylated phloroglucinol (B_3, Figure 3.9). Gelation was observed when 30 mol% excess of DFDPS (A_2) was added. The final branched and cross-linked polymers mainly consisted of cyclic building blocks.[47]

The influence of chain stiffness also plays an important role on the extent of cyclization.[48] 1,3,5-Tris(4-fluorobenzoyl)benzene (TFBB, B_3, Figure 3.9) was polymerized with silylated diphenols (4,4′-dihydroxybiphenyl, DHBP, and bisphenol-A, BisA, as A_2, Figure 3.8) of varying chain stiffness to synthesize poly(ether ketone)s.[48] Polymerization of TFBB (B_3) with silylated-DHBP showed a lower cyclization tendency and resulted in partially cross-linked products even at a 1:1 ratio of A_2:B_3, whereas cyclic and multicyclic poly(ether ketone)s were obtained up to a 1.3:1.0 = A_2:B_3 ratio without gelation when silylated-BisA was used. Kricheldorf *et al.* also reported the influence of structural isomerism on cyclization in $A_2 + B_3$ polymerization.[55] Polycondensation of silylated-THPE (B_3, Figure 3.9) with either 2,6-difluorobenzonitrile (2,6-DFBN, A_2) or 2,4-difluorobenzonitrile (2,4-DFBN, A_2) (Figure 3.8) in a 1:1 molar ratio produced completely soluble polyethers. Gelation was observed with a 10 mol% increase in 2,6-DFBN, whereas completely soluble products were obtained even with a 50 mol% excess of 2,4-DFBN. Such a difference in cyclization tendency was attributed to the different isomer conformations favored by energy minimization.

Czupik and Fossum reported the synthesis of a series of hyperbranched poly(arylene ether phosphine oxide)s (HB-PAEPOs) via the polymerization of a variety of bisphenols (A_2) and tris(4-fluorophenyl)phosphine oxide (TFPO, B_3, Figure 3.11).[20] The influence of various reaction parameters, such as A_2 monomer reactivity, A:B ratio (A_2:B_3), addition mode, solvent, and concentration, on the final molar mass, polydispersity, and DB was studied. The B_3 monomer, TFPO, was synthesized to provide a spectroscopic handle (^{31}P NMR) to study the development of branching during the reaction. Polymerization of BisA (A_2, Figure 3.11, 2a) with TFPO (B_3) in toluene/NMP at an A_2:B_3 = 1:1 molar ratio yielded products with weight average molar mass values as high as 220,000 g/mol. When the A_2:B_3 ratio was increased, a significant decrease in the time required to reach the gel point was observed.

Monomer concentration in the solution also affected the final properties of the products. Decreasing the concentration from 0.176 to 0.050 mol/L resulted in low molar mass products and a gel point was not reached, which is indicative of extensive cyclization reactions that are promoted in dilute solution. When a BisA (A_2) solution was added to a TFPO (B_3) solution for 6 h to achieve an A_2:B_3 = 1:1 ratio, the weight average molar mass increased to 299,000 g/mol

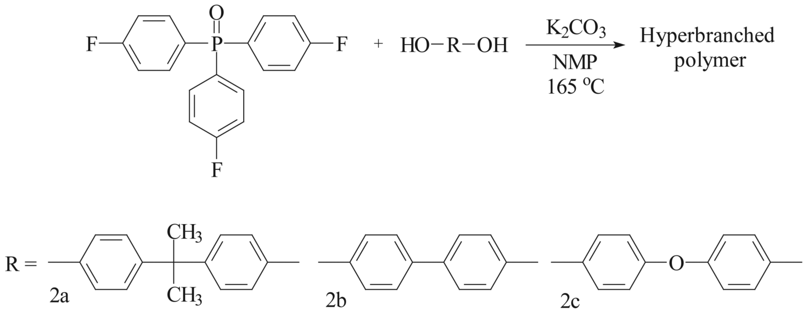


Figure 3.11 Synthesis of hyperbranched poly(arylene ether phosphine oxide)s (HB-PAEPOs) via the polymerization of a variety of bisphenols as A_2 and tris(4-fluorophenyl)phosphine oxide (TFPO) as B_3.

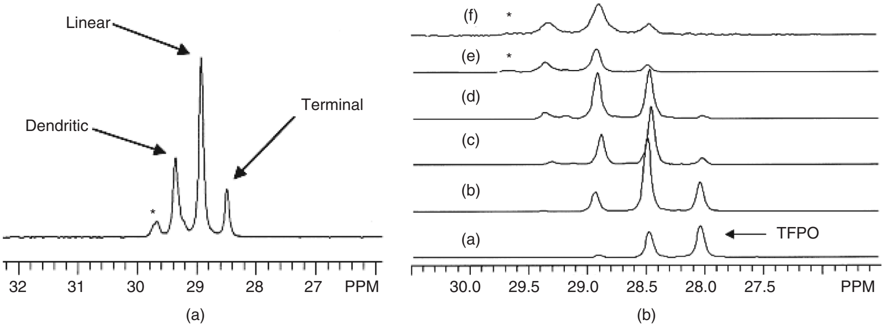


Figure 3.12 (a) Typical ^{31}P NMR spectrum of an HB-PAEPO and (b) ^{31}P NMR spectra at various reaction times of HB-PAEPO synthesized via the slow addition of A_2 into B_3.

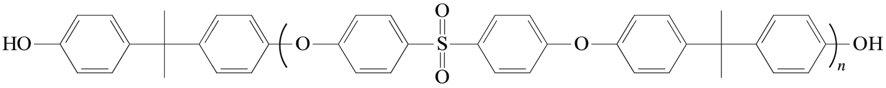
with a polydispersity of 24. In contrast, only 85% of TFPO (B_3) solution could be added to the BisA (A_2) solution before the gel point was reached.

As depicted in Figure 3.12, ^{31}P NMR allowed the investigation of the branched structure of the final products. When A_2 was added to B_3, DB was monitored over time using ^{31}P NMR spectroscopy. The final polymeric product had a DB value of 54%. In contrast, the final soluble product obtained from the slow addition of B_3 to A_2 had a DB value of 70% when only 80% of B_3 was added. Reactions under more dilute conditions also resulted in similar DB values; however, the presence of a downfield signal was more significant (Figure 3.12B (f)) and attributed to intermolecular cyclization products.

Long *et al.* synthesized branched poly(arylene ether)s via the polymerization of phenol-terminated telechelic poly(arylene ether sulfone) oligomers (A_2, Figure 3.13) with TFPO (B_3).[29] The molar mass of the A_2 oligomer allowed the synthesis of poly(arylene ether)s of various architectures, such as hyperbranched, moderately branched, slightly branched, and linear.

3.3.1.4 Polyesters

Long *et al.* reported the synthesis of hyperbranched aromatic polyesters via the slow addition of a dilute BisA (A_2) solution into a dilute 1,3,5-benzenetricarbonyl trichloride (BTC, B_3) solution at room temperature.[21] The molar ratio of A_2:B_3 was maintained at 1:1 and the maximum final monomer



A_2 oligomer (n = 3, 6, 8, 16)

Figure 3.13 Phenol-terminated telechelic poly(arylene ether sulfone) oligomer (A_2) to obtain branched poly(arylene ether sulfone)s.

concentration was ~0.08 mol/L to obtain gel-free products. The residual acid chloride functional groups (B) were further made to react with methanol to obtain methyl ester–terminated hyperbranched aromatic polyesters. ^{1}H NMR spectroscopy revealed a DB value of ~50% with the aid of model dendritic, terminal, and linear compounds for chemical shift assignments. Final products had moderate molar masses with polymodal SEC traces, which is a characteristic of hyperbranched polymers. In a similar manner, synthesis of highly branched poly(ether ester)s was reported by Long *et al.* via the polymerization of A_2 oligomers with B_3 monomers (Figure 3.14).[27] A dilute solution of various

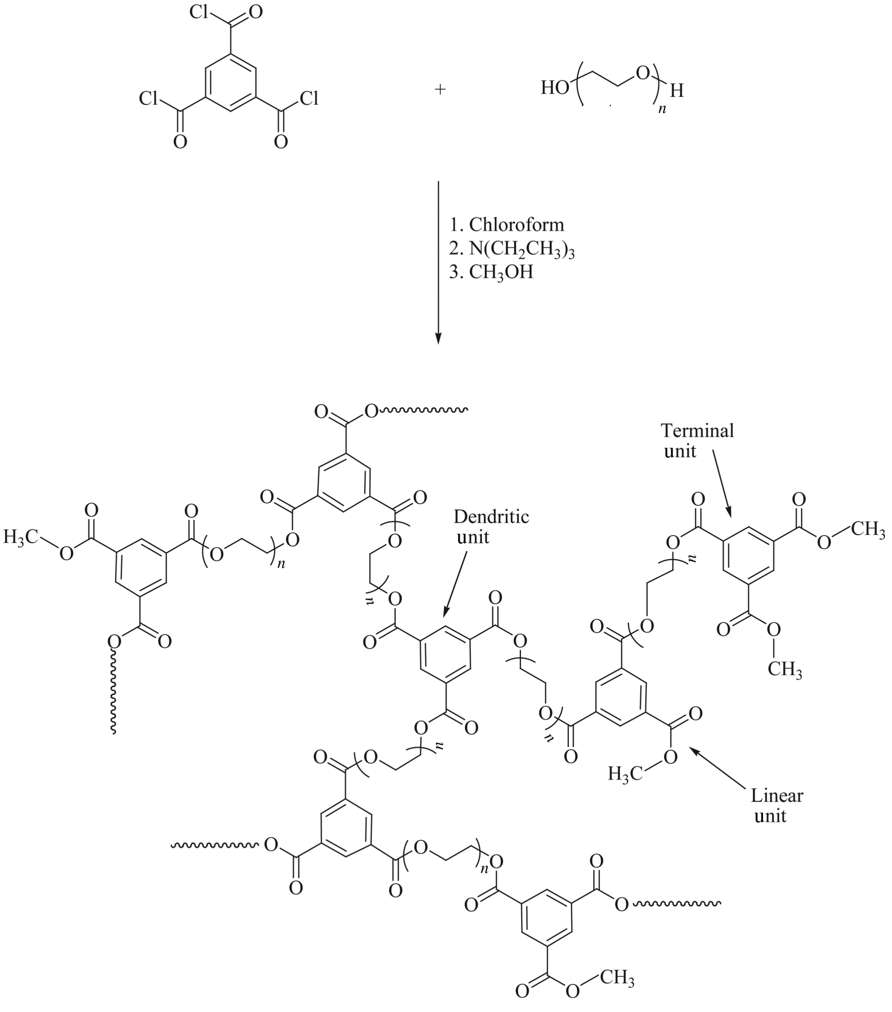


Figure 3.14 Synthesis of methyl ester–terminated highly branched poly(ether ester)s via polymerization of A_2 oligomers and B_3 monomers.

molar mass poly(ethylene glycol)s was slowly added into a dilute solution of BTC at a critical monomer concentration to prepare gel-free, highly branched products. Although the reaction methodology was similar to the polymerization of low molar mass A_2 and B_3 monomers, the DB was effectively tailored via the molar mass of the A_2. Thus, macromolecules with a range of branched topologies were prepared without AB or AB_n monomers. Moreover, the final products exhibited a well-defined distance between B units due to the use of relatively narrow molar mass distribution oligomers as A_2 monomers. The high M_z values and very broad polydispersities obtained from SEC analysis revealed that the final products were a mixture of high molar mass branched polymers and low molar mass cyclic components. Both the SEC traces and the MALDI-TOF/MS indicated the presence of low molar mass cyclic oligomers, which were presumed responsible for the lack of gelation at an A_2:$B_3 = 1$:1 ratio.

The Mark–Houwink equation ($[\eta] = kM^a$) was used to analyze the relationship between the intrinsic viscosity and molar mass of the highly branched poly(ether ester)s. The Mark–Houwink constant, a, provides insight on the globular shape or random coil conformation of the polymer chains in dilute solution. The value of a ranges from 0.65 to 0.75 for linear random coils in a good solvent and approaches 0.25 for hyperbranched structures.[56,57] This value was in the range of 0.55–0.62 for linear poly(ether ester)s. On the other hand, highly branched poly(ether ester)s that were derived from PEG-200 had much lower a values, approaching 0.25, which indicated a more compact or highly branched structure. As the distance between the B_3 units was increased using PEG-600 and PEG-2000 as A_2 oligomers, the values increased and approached the values of linear analogs, indicating the branching density decreases as the length of the A_2 oligomer is increased. Finally, functionalization of the peripheral acid chloride endgroups with 2-hydroxyethyl acrylate and subsequent photo-cross-linking reactions in the presence of a photoinitiator resulted in tack-free, self-standing films of cross-linked poly(ether ester)s.[27]

While the vast majority of hyperbranched polymers as shown in the literature is synthesized in solution, a few studies report $A_2 + B_3$ polymerization in the melt phase.[4,5,22,23] Synthesis of hyperbranched aliphatic polyesters via the melt polymerization of adipic acid (A_2) and glycerol (B_3) is an example of a nonideal $A_2 + B_3$ system.[23] Molar ratios of A_2:B_3 from 1:1 to 2:1 were utilized to obtain hyperbranched products, and the molar mass increased with increasing A_2:B_3 ratio. The absence of gelation even at A_2:$B_3 = 2$:1 suggests a distinct difference in the reactivity between the primary and the secondary alcohols on glycerol (B_3), and hence glycerol acts as a B_2B^* type monomer.

Long *et al.* studied the melt polymerization of A_2 oligomers and B_3 monomers for the synthesis of highly branched poly(ether ester)s. Melt polymerization overcomes the need for large quantities of polymerization solvent and limits the presence of low molar mass products and cyclization reactions. Highly branched poly(ether ester)s were synthesized via the melt condensation of poly(propylene glycol) (A_2 oligomer) and trimethyl 1,3,5-benzenetricarboxylate

(TMT, B_3 monomer).[28] The conversion of each monomer was monitored during the polymerization to understand the onset of gelation in the melt phase. When a 1:1 molar ratio of A_2 and B_3 was mixed at the onset, the polymerization displayed a classic step-growth behavior with a dramatic increase in molar mass after $p_A = 80–85\%$ (Figure 3.15); however, gelation occurred at 90% conversion of A groups ($p_A = 90\%$ and $p_B = 60\%$).

Close agreement between gel points obtained experimentally and theoretically indicated that there were negligible cyclization reactions that would have accounted for a delayed gel point. Moreover, ester-interchange reactions allowed the introduction of a monofunctional comonomer, which effectively avoided gelation at >98% monomer conversions, but did not influence branching in the $A_2 + B_3$ polymerization. It was suggested that a nonideal $A_2 + B_3$ system was formed, where a B_3 monomer reacted with an endcapping reagent and formed a B_2B^* type intermediate (B^* denotes the reacted B group that undergoes ester interchange at a lower rate). Thus the polymerization was similar to the previously reported nonideal $A_2 + B_3$ systems, and resulted in random, highly branched polymers.

The branching index (g'),[58] which was derived from SEC viscometric data, was used to characterize branching more efficiently. The value g' provides a direct comparison of the hydrodynamic volume of a branched molecule with a linear analog and is calculated as $g' = [\eta]_{\text{branched}}/[\eta]_{\text{linear}}$ where $[\eta]_{\text{branched}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of branched and linear polymers of equivalent weight average molar mass. The g' values are closer to unity for linear polymers and decrease as branching increases. Monitoring g' provided an understanding of branched structure formation during $A_2 + B_3$ polymerization. Figure 3.15 shows that branching increases as a function of monomer conversion and follows a similar trend as molar mass.

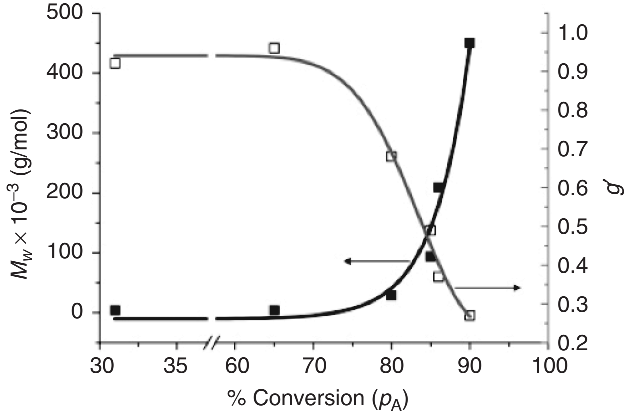


Figure 3.15 Weight average molar mass and branching index (g') as a function of monomer conversion in $A_2 + B_3$ melt polymerization.

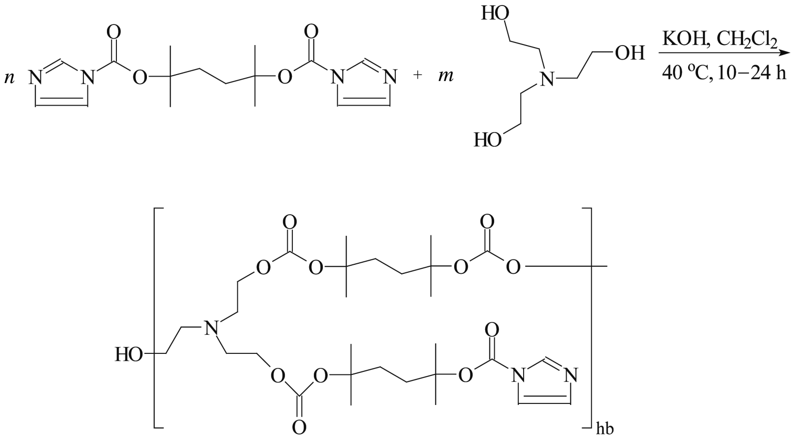


Figure 3.16 Synthesis of a hyperbranched polycarbonate via $A_2 + B_3$ polymerization.

3.3.1.5 Polycarbonates

The reaction of a bis(carbonylimidazolide) (A_2) with triethanolamine (B_3) in the presence of a catalytic amount of KOH resulted in hyperbranched thermolabile polycarbonates (Figure 3.16).[24] ^1H and ^{13}C NMR spectroscopic analyses effectively differentiated reacted and unreacted monomers in the final product mixture. The unreacted B_3 monomer showed different chemical shifts than the bB_2 and b_2B units (Figure 3.16) where b denotes the reacted B group. Similarly, unreacted (A_2), half-reacted (aA), and fully reacted (a_2) bis(carbonylimidazolide) units were differentiated. 2D NMR spectroscopy detected cyclic structures in the final product and the cyclic content increased with decreasing monomer concentration during polymerization. The final product that contained carbonate groups had a T_g of $-14\,^\circ C$ and decomposed completely into volatile products above $200\,^\circ C$. Thus, the decomposition behavior of these compact and globular hyperbranched polycarbonates may find application as templates for the preparation of nanoporous polymeric materials.

3.3.1.6 Polyurethanes

Polymerization of functionally symmetric A_2 oligomers and B_3 monomers allowed the synthesis of highly branched poly(urethane urea) elastomers with improved processibility and a multitude of functional endgroups.[31] Linear soft segments were introduced between each hard segment branch point using A_2 oligomers. A polyether diisocyanate, freshly synthesized from a polyether diol, and a twofold excess of diisocyanate (HMDI, bis(4-isocyanatohexyl)methane) formed the A_2 oligomer (Figure 3.17), whereas various triamines were utilized as the B_3 monomer (Figure 3.18). HB-PUUs were synthesized via the slow addition of A_2 oligomer to B_3 monomer in dilute solution (10–15 wt%).

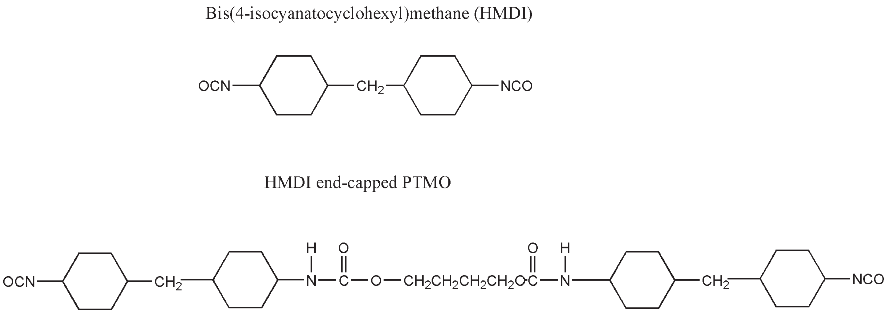


Figure 3.17 Chemical structures of monomeric and oligomeric A_2 reagents in the synthesis of highly branched poly(urethane urea)s.

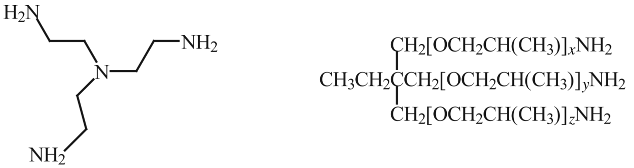


Figure 3.18 Chemical structures of triamines in the synthesis of highly branched poly(urethane urea)s.

Molar mass and polydispersity were monitored as a function of A_2 oligomer addition to understand the branched structure development. The experimental gel point was significantly dependent on the concentration of the solution. Slow addition of a monomeric A_2 solution (HMDI, Figure 3.17) to a B_3 solution (ATA, poly(oxyalkylene)triamine, Figure 3.18) at various concentrations revealed that the extent of cyclization reactions significantly increased and the gel point shifted to higher monomer conversions as the solution concentration was decreased.

When the molar mass was monitored during the slow addition of an A_2 oligomer to a B_3 monomer, a classic step-growth polymerization behavior was observed. The gel point of the 25 wt% reaction mixture was reached at lower monomer conversions relative to 10 wt% reaction mixture (Figure 3.2).[32] The final products that were based on TRIS (tris(2-aminoethyl)amine, B_3) showed acceptable mechanical performance comparable to linear analogs and emerged as a new family of elastomers with unique topologies.[31] Branching did not significantly influence the microphase separated morphology essential to the elastomeric behavior of these novel materials.[33] The stress–strain behavior of poly(tetramethylene oxide) (PTMO)-based highly branched poly(urethane urea)s was comparable to linear analogs due to the strain-induced crystallization of the soft segment phase. The highly branched poly(urethane urea)s that were derived from a 1:1 molar ratio of A_2:B_3 possessed peripheral amine functional groups, and *in situ* functionalization with cyclohexyl isocyanate resulted in urea endgroups.

Stress–strain results revealed that the nature of the endgroups played a significant role on the mechanical performance of these highly branched poly(urethane urea)s, and the introduction of urea endgroups via *in situ* functionalization dramatically improved mechanical performance.

Highly branched poly(urethane urea)s were electrospun from solution and formed elastomeric fibrous mats that had superior elongation, which did not fail at 1300% elongation.[59] Because of lower solution viscosity of highly branched polymers than linear analogs, less solvent was required to electrospin highly branched poly(urethane urea)s; nevertheless, both linear and highly branched fibrous mats had similar mechanical performances. These novel, HB-PUU elastomers offer the improved processibility peculiar to hyperbranched polymers and the advantageous mechanical performance multiphase morphology with linear soft segments between hard segment branch points.

Recently, a new family of highly branched, potentially biodegradable polyurethanes was reported using a polycaprolactone (PCL) triol(B_3) as the soft segment.[34,35] One of the major drawbacks of using PCL as a soft segment in linear, segmented polyurethanes has been the high degree of crystallinity when long segments of PCL ($>$1000 g/mol) are incorporated. Incorporation of longer segments of PCL results in the presence of a crystalline phase and a melting point within the service window, which results in undesirable variations in performance. Therefore, branching was effectively used to incorporate higher molar mass PCL segments (2000 g/mol). The final products derived from PCL triol possessed a completely amorphous soft segment, whereas the linear analogs derived from PCL diols of 2000 g/mol retained the crystallinity. Similar to the previously reported poly(urethane urea)s, highly branched polyurethanes synthesized from a B_3 oligomer displayed mechanical properties comparable to the linear analogs; nevertheless, they possessed a multitude of functional endgroups and a completely amorphous PCL soft segment phase.

3.3.2 Proton-Transfer Polymerization of A_2 and B_3 Monomers

Fréchet and coworkers authored one of the two pioneering reports on the synthesis of hyperbranched polymers via $A_2 + B_3$ polymerization.[4] Hyperbranched aliphatic polyethers containing epoxy chain ends were synthesized via proton-transfer polymerization from A_2 and B_3 monomer pairs, such as a diol (A_2) and a triepoxide (B_3)[5] or a diepoxide (A_2) and a triol (B_3).[4,5] Hyperbranched polymers were obtained before gelation by stopping the reactions prior to full monomer conversion, which otherwise would result in gelation in the bulk. It was also proposed that the $A_2 + B_3$ polymerization of triepoxide (B_3), synthesized from the reaction of a triol (1,1,1-tris(hydroxymethyl)ethane) and excess epichlorohydrin, with a diol (1,4-butanediol, A_2) produced an AB_2 diepoxyalcohol intermediate as depicted in Figure 3.19.[5]

The polymers isolated prior to the gel point had polydispersities greater than 20, and separation of the final product from the residual low molar mass

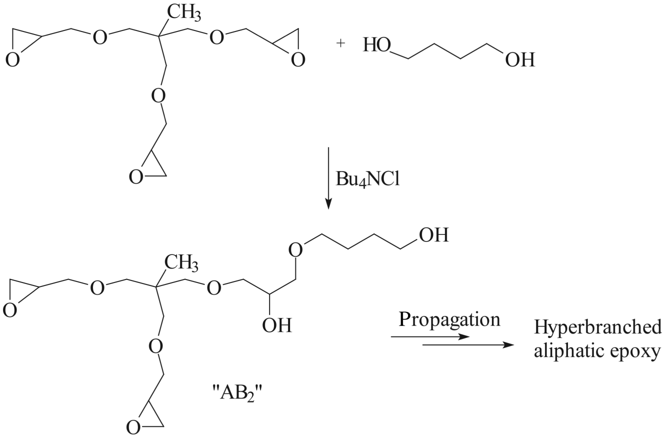


Figure 3.19 Formation of an AB_2-type diepoxyalcohol in the synthesis of hyperbranched polyethers via the proton-transfer polymerization of a triepoxide (B_3) and 1,4-butanediol (A_2).

impurities was infeasible. Thus, the $A_2 + B_3$ polymerization of diepoxides with triols was alternatively reported to prepare hyperbranched aliphatic polyether epoxies.[4,5] In order to achieve epoxy chain ends, the ratio of diepoxide to triol (A_2:B_3) was maintained between 1.5:1 and 3:1. Initially, a secondary alkoxide was formed by the addition of a chloride ion to diepoxide (A_2). Subsequently, a primary alkoxide was generated by proton exchange between the secondary alkoxide and the triol (B_3) as shown in Figure 3.20, followed by propagation to produce hyperbranched aliphatic polyether epoxies.

Step-growth polyaddition kinetics was observed when molar mass was monitored as a function of reaction time. Hyperbranched products derived at a molar ratio of $A_2:B_3 = 3:1$ resulted in the highest DB and possessed epoxide chain ends, with a glass transition temperature of $-20\,^\circ C$. Thermogravimetric analysis showed a thermal degradation onset of $305\,^\circ C$ with a 50% weight loss at $395\,^\circ C$. Furthermore, the hydroxyl groups on the hyperbranched aliphatic polyether epoxies were successfully functionalized to silyl, hexyl ester, and carbamate groups, which resulted in increased hydrophobicity because of the hydrocarbon substituents for each derivatization. Fréchet and coworkers similarly reported the synthesis of a hyperbranched polyether that possessed multiple pendant porhyrin units. A bisphenolic porhyrin served as an A_2 monomer (Figure 3.21) and was polymerized with a triepoxide (B_3) via proton transfer. Porphyrin chromopores offer promise for the construction of optoelectronic devices.[60]

3.3.3 The Michael Addition Polymerization of A_2 and B_3 Monomers

Michael addition reactions between functionally symmetric monomer pairs have been successfully demonstrated to prepare hyperbranched polymers.[7,25,26] Voit

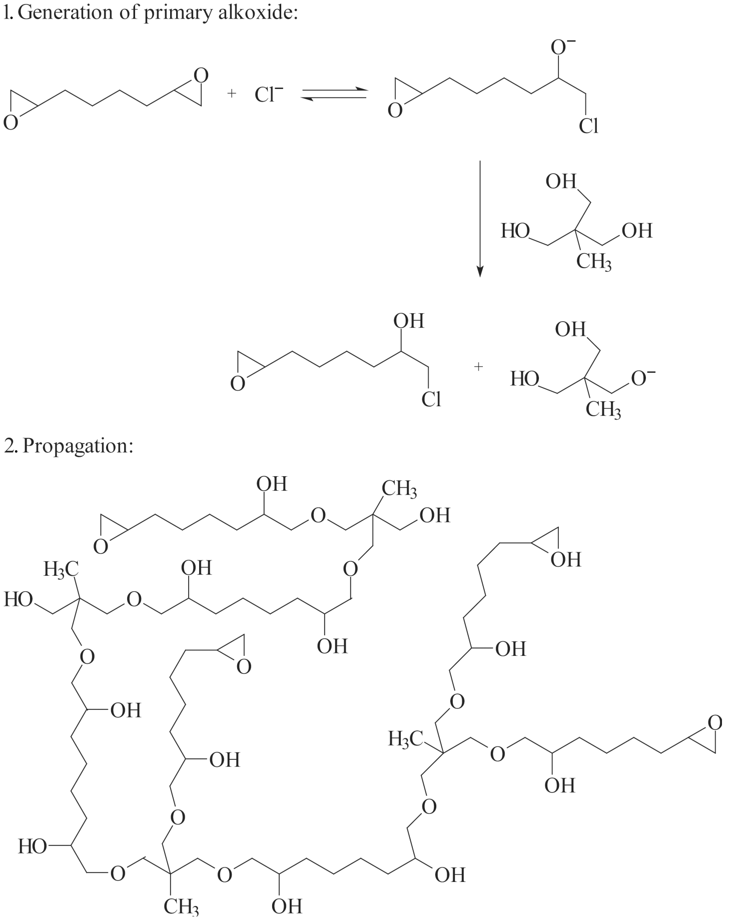


Figure 3.20 Formation of a primary alkoxide by proton-transfer and propagation steps during the $A_2 + B_3$ polymerization of a diepoxide and triol.

and coworkers reported the synthesis of hyperbranched polythioethers via the Michael addition of dithiol (A_2) to a trivinyl compound (B_3, Figure 3.22).[7] Owing to the high reactivity of thiol toward vinyl groups, AB_2 type monomers do not appear suitable for the synthesis of hyperbranched polythioethers. In an $A_2 + B_3$ polymerization of a dithiol and a trivinyl momomer, suppression of gelation was attributed to cyclization reactions resulting in products with crown ether structures suitable for metal salt binding.

Hyperbranched poly(ester amine)s with terminal acrylate groups were prepared via a Michael addition between piperazine (A_2) and trimethyloylpropanetriacrylate (TMPTA, B_3, Figure 3.23).[26] The TMPTA (B_3) solution was added to a piperazine (A_2) solution in an ice bath for 1 h. The reaction temperature was subsequently increased and maintained at 30 °C for 48 h.

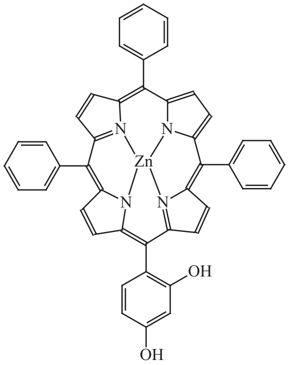


Figure 3.21 Chemical structure of bisphenolic porphryin as an A_2 monomer.

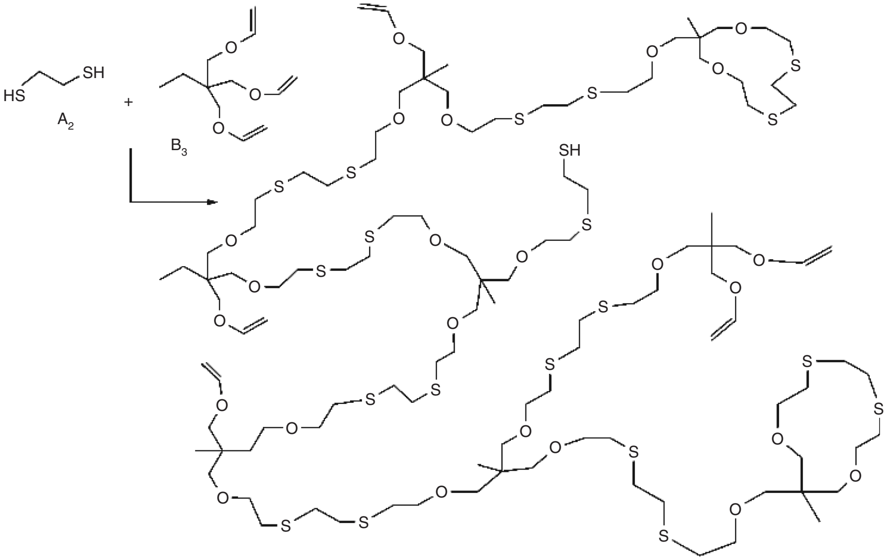


Figure 3.22 Synthesis of polythioethers via the Michael addition.

Fully soluble, hyperbranched products were obtained below 10 wt% monomer concentrations in THF, whereas higher concentrations resulted in gelation in very short reaction times.

The DB, molar mass, polydispersity, and glass transition temperature of the final products systematically increased as the A_2:B_3 ratio was increased. The DB values, based on Frey's definition, increased from 28.7% to 52.5%, whereas the number average molar mass increased from 1820 to 3250 g/mol as the A_2:B_3 ratio was increased from 1:2 to 1.00:1.08. The final products formed stable aggregates in an acetone–acidic water mixture because of their amphiphilic nature, and the terminal acrylate groups were successfully UV irradiated to form cured particles

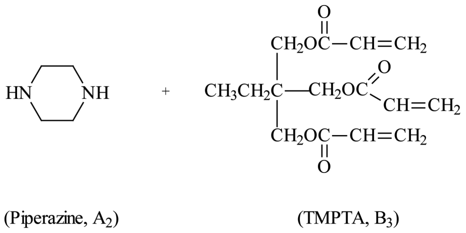


Figure 3.23 Chemical structures of A_2 and B_3 monomers for the synthesis of hyperbranched poly(ester amine)s via the Michael addition.

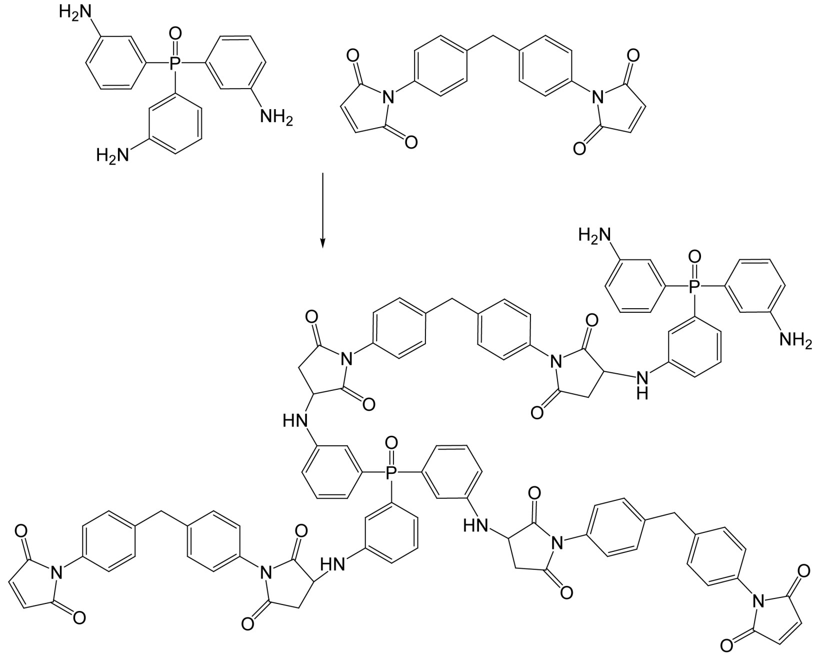


Figure 3.24 Synthesis of hyperbranched polyaspartimides via the Michael addition of A_2 and B_3 monomers.

for potential application as hydrophobic drug capsules and pH-dependent release systems.

Liu *et al.* synthesized hyperbranched polyaspartimides via the Michael addition reaction of bismaleimides (A_2) and triamines (B_3) as shown in Figure 3.24.[40] High monomer concentrations (0.76 M) resulted in a cross-linked product. Therefore, a lower monomer concentration (0.19 M) was selected to avoid gelation. Among the two bismaleimides (Figure 3.24), 4,4'-bismaleimidodiphenyl methane (BMDM) showed a higher reactivity than bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (BEMM) due to steric and inductive effects arising from alkyl substituents.

The DB (Fréchet) ranging from 51% to 69% indicated a hyperbranched structure. Hyperbranched polyaspartimides had glass transition temperatures above 200 °C. Thermogravimetric analysis revealed good thermal stabilities for both products. The hyperbranched polymers derived from tris(3-aminophenyl)phosphine oxide (TAPPO) were thermally stable up to 370 °C under both air and nitrogen and showed high char yields.

3.4 CONCLUSIONS

Polymerization of functionally symmetric monomer pairs such as A_2 and B_3 monomers received great attention in the last decade due to the commercial availability of these monomers, despite the high risk of gelation. Several research groups reported the successful polymerization of A_2 and B_3 monomers and optimized reaction conditions avoided gelation to prepare hyperbranched polymers including polyamides, polyimides, polyethers, polyester, and polycarbonates. In addition, substitution of one of the monomer pairs with functionally symmetric, oligomeric precursor yielded highly branched polymers with a well-defined distance between the branch points. Highly branched polyurethanes and poly(urethane urea)s synthesized via the oligomeric $A_2 + B_3$ polymerization offered acceptable mechanical properties in addition to improved processibility and tailored functionalities. Important reaction conditions to avoid gelation were the solution concentration, A_2:B_3 molar ratio, order of monomer addition, and relative reactivity of the functional groups. Concentration of the polymerization medium played the most important role since the dilute solution conditions promoted cyclization reactions and shifted critical monomer conversion values for gelation to higher values. At an optimized concentration of monomers, gelation was successfully mitigated even at molar ratios A_2:$B_3 = 1$:1. Mixing the monomers at the polymerization onset or slow addition of one onto another influenced the gelation incidence, as well as the final structure of the branched polymers. In addition to the most common polycondensation reactions, other types of reactions such as the proton-transfer polymerization and the Michael addition of A_2 and B_3 monomers were also demonstrated to synthesize hyperbranched polymers. In an attempt to further understand the synthesis and structure–property relationships in $A_2 + B_3$ hyperbranched polymers, this review provided an overview of the recent synthetic approaches to the polymerization of A_2 and B_3 type, functionally symmetric monomer pairs.

LIST OF ABBREVIATIONS

2,4-DFBN	2,4-difluorobenzonitrile
2,6-DFBN	2,6-difluorobenzonitrile
6-FDA	2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride
ATA	poly(oxyalkylene)triamine
BisA	bisphenol-A
BTC	1,3,5-benzenetricarbonyltrichloride

DBOP	diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate
DFDPS	4,4′-difluorodiphenyl sulfone
DHBP	4,4′-dihydroxybiphenyl
DSDA	3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride
HB-PAEPOs	hyperbranched poly(arylene ether phosphine oxide)s
HB-PUU	hyperbranched, segmented poly(urethane urea)
HMDI	bis(4-isocyanatohexyl)methane
MC	Monte Carlo
PCL	polycaprolactone triol
SEC	size exclusion chromatography
TAPA	tris(4-aminophenyl)amine
TFBB	1,3,5-tris(4-fluorobenzoyl)benzene
TFPO	tris(4-fluorophenyl)phosphine oxide
THPE	1,1,1-tris(4-hydroxyphenyl)ethane
TMPTA	trimethyloylpropanetriacrylate
TMT	trimethyl 1,3,5-benzenetricarboxylate
TRIS	tris(2-aminoethyl)amine

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Chapter 4

Synthesis of Hyperbranched Polymers via Polymerization of Asymmetric Monomer Pairs

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4.1 INTRODUCTION

Two methodologies, single-monomer and double-monomer, have been developed to prepare hyperbranched polymers.[1] In the single-monomer methodology (SMM), hyperbranched macromolecules are synthesized by polymerization of an AB_n or a latent AB_n monomer.[2–6] In the double-monomer methodology (DMM), direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers. DMM can be divided into two main subclasses based on the selected monomer pairs and different reaction pathways. The classical one, the polymerization of symmetrical A_2 and B_3 (or $B_n, n > 2$) monomers, can be called the "$A_2 + B_3$" method. This was first adopted intentionally to prepare soluble hyperbranched polymers by Kakimoto[7] and Fréchet,[8] and then developed by Long,[9–17] Yin,[18–23] and other researchers[24–26] to prepare hyperbranched polyimides, polyesters, and segmented hyperbranched polymers. The details are

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excluded in this chapter but described in Chapter 3. The combination of the basic SMM synthetic principle and the multimonomer character of the "$A_2 + B_3$" methodology results in the other DMM, relevant to this chapter: couple-monomer methodology (CMM) based on *in situ* formation of AB_n intermediates from specific monomer pairs due to the nonequal reactivity of different functional groups.[1,27–29] Because the *two* types of raw monomers would preferentially *couple* with each other to generate *one* type of AB_n intermediate *in situ* in the initial stage of polymerization to produce hyperbranched macromolecules without gelation, we call the strategy for preparation of hyperbranched polymers CMM or *couple-monomer strategy* (CMS). CMM was first reported by Yan and Gao[27–29] and DSM Research[30,31] independently, and further developed and extended by several research groups recently.[32–35] Many commercially available chemicals can be used as reactive monomer pairs in the CMM, which should extend the availability and accessibility of hyperbranched polymers with various new end groups, architectures, and properties, without the risk of cross-linking. Up to now, various families of novel hyperbranched polymers such as hyperbranched poly(sulfoneamine)s (HPSA)s, poly(ester amine)s, poly(amidoamine)s (PAMAM)s, poly(amido-ester)s, poly(urethane-urea)s, polyesters, and so on, have been synthesized via CMM. This chapter will focus on the CMM developed in recent years.

4.2 GENERAL DESCRIPTION OF POLYMERIZATION OF ASYMMETRIC MONOMER PAIRS

Flory's gelation theory for the ideal polymerization of A_2 and B_3 monomers is based on three assumptions: (i) equal reactivity of all A or B groups at any given stage of the reaction; (ii) no side reactions, and the reaction restricted to the condensation of A and B groups; and (iii) no intramolecular cyclization and chain termination in the process.[36] If the first assumption is invalid, gelation should be avoided, leading to soluble hyperbranched polymers with high molar mass. This gives the theoretical base for the CMM: nonequal reactivity of functional groups in specific monomer pairs.

The basic principles of SMM, the "$A_2 + B_3$" method, and CMM are schematically illustrated in Figure 4.1. In SMM, polymerization of AB_2 or a latent AB_2 monomer results in oligomers and then macromolecules possessing only one A group in each molecule, at most. Thus, no network structure would be formed and gelation is avoided. When a symmetrically bifunctional A_2 monomer reacts with a trifunctional B_3 monomer, AB_2-type species also forms at first. Further reactions of the AB_2 species with the residual A_2 or B_3 monomer give rise to A_2B, B_4, and then A_xB_y $(x \geq 2, y \geq 2)$ species. Therefore, intramolecular cycles or network structures may form because of the existence of A_xB_y $(x \geq 2, y \geq 2)$ species. After critical conversion of the functional groups, gelation would occur. If the reaction is stopped just before the gelation point, hyperbranched polymer can be obtained. This is the key to prepare soluble hyperbranched polymers by the "$A_2 + B_3$" approach.

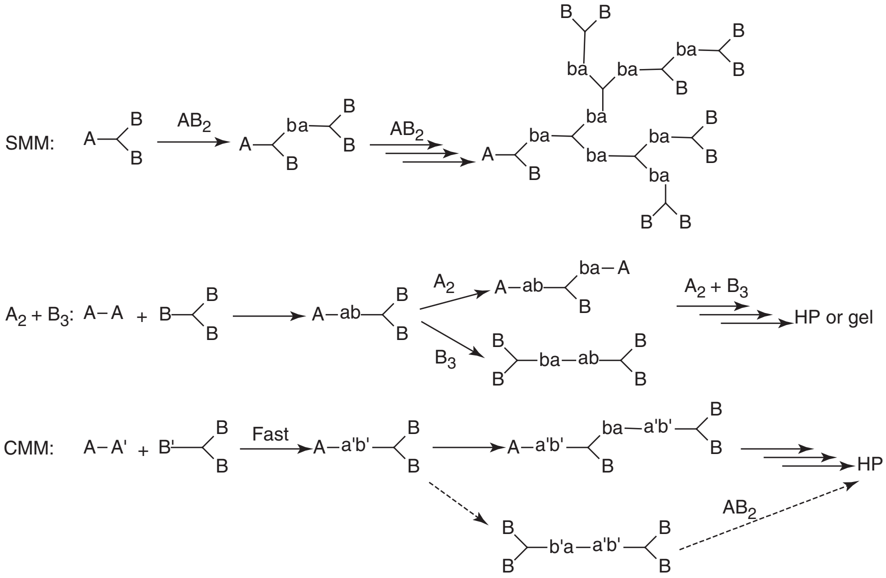


Figure 4.1 Schematic illustration for the preparation of hyperbranched polymers by single-monomer methodology (SMM), "A_2+ B_3" approach, and couple-monomer methodology (CMM).

In comparison with the "$A_2 + B_3$" method, multifunctional asymmetric monomers are used as the raw materials in CMM in order to generate AB_n ($n \geq 2$) type intermediate online. In CMM, choosing a suitable monomer pair is the most important step for the molecular design of a hyperbranched polymer, and the polymerization can be simply understood as one-pot, two-step reaction. For a monomer pair of AA' and $B'B_2$, if A is identical to A' and B is equal to B', CMM degenerates into the "$A_2 + B_3$" polymerization. If A' has a higher reactivity than A, CMM affords "$AA' + B_3$" polymerization; and if B' is more active than B, CMM presents "$A_2 + B'B_2$" and "$A_2 + CB_2$" polymerization systems. When both A and B groups are different from A' and B' groups, CMM means an "AC + DB_2" polymerization. In all designed polymerization systems, dominant AB_2 intermediates will be generated *in situ*, and further reaction of the AB_2 species will result in hyperbranched macromolecules without the risk of gelation. For example, if the reactivity of the B' group in the $B'B_2$ monomer is greater than that of the two B groups, AB_2 intermediates can be formed *in situ* during the initial reaction. Further self-polycondensation of the formed AB_2 species will give rise to hyperbranched polymers without gelation. On the other hand, the molecule containing four B groups should be generated if the formed AB_2 further reacts with a $B'B_2$ molecule as a result of the higher reactivity of the B' group. The species B_4 can play the role of a core molecule in the preparation of hyperbranched polymers and leads to a narrower molecular weight distribution.[37–44] Further polymerization of AB_2 and B_4 generates a hyperbranched macromolecule with a core.

The molecular weight and terminal functional groups of the resulting hyperbranched polymers can be adjusted by the feed ratio of the two monomers. Higher molecular weight product can be obtained if the molar feed ratio of AA' to $B'B_2$ is adjusted from 1:1 to 2:1. When the feed ratio is lower than 1:1, lower molecular weight products with B groups can be made. Products with A groups can be synthesized when the feed ratio is greater than 2:1. If the feed ratio is in the range of 1:1 and 2:1, hyperbranched macromolecules with both A and B functional groups can be synthesized.

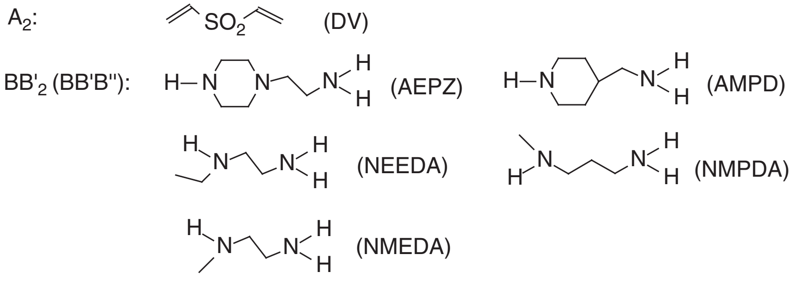
CMM is also essentially different from the conventional method involving polycondensation of AB_2 monomers in the presence of multifunctional core moieties ($AB_n + B_m$ approach). Compared with the "$AB_n + B_m$" method, CMM exhibits three characteristics. First, the AB_n and B_m compounds are generated *in situ* from two or more monomers, which can be commercially available. Second, no clear borderline exists between the formation of AB_n and its polymerization. The polymerization reaction generally occurs as soon as the formation of an AB_n molecule occurs, although the molecule appears only under special conditions. So, pure AB_n or B_m compounds formed *in situ* are not separated. Although the reactivity between A and B' groups is higher than between A and B groups, hyperbranched polymers are prepared in a single step from an A_2-type difunctional monomer and $B'B_2$-type trifunctional monomer. Finally, CMM can be used to design and develop novel hyperbranched polymers with new architectures and structures. Through the new strategy, series of hyperbranched polymers with alternating different units, for example, ab' and ab units, can be easily fabricated. On the contrary, it is very difficult to acquire hyperbranched polymers with the same structure through the conventional "$AB_2 + B_m$" approach or polycondensation of AB_2 monomers.

4.3 HYPERBRANCHED POLYMERS PREPARED BY POLYMERIZATION OF ASYMMETRIC MONOMER PAIRS

The discovery and application of CMM not only makes the large-scale production of hyperbranched polymers cost effective but also greatly enlarges the structure and product diversity of the hyperbranched polymer family. Up to now, a series of novel hyperbranched polymers prepared via CMM have been developed.

4.3.1 Poly(Sulfoneamine)

HPSA is usually prepared by polymerization of divinyl sulfone (DV, A_2) and asymmetric diamine with a secondary and a primary amino group (BB'_2 or $BB'B''$).[27–29] The used monomers are shown in Scheme 4.1. For the BB'_2 or $BB'B''$ monomer, the reactivity of secondary amine and primary amine is different, and AB'_2 or $AB'B''$-type intermediate will be formed when one vinyl group (A) reacts with one hydrogen of the amines. Self-polycondensation of the

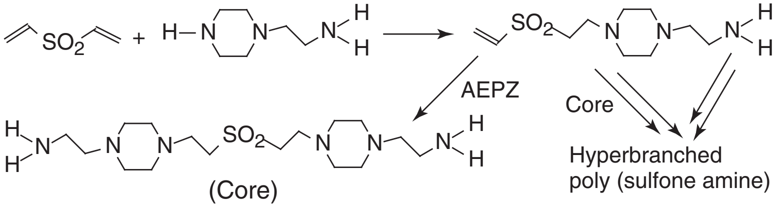


Scheme 4.1

intermediate results in HPSA at high temperature[27–29,45,46] or a slightly branched/linear polymer at low temperature (<20 °C).[47]

Polymerization of DV and 1-(2-aminoethyl)piperazine (AEPZ) is a typical example to prepare HPSA.[27,29] This reaction can be carried out in either water or organic solvents such as chloroform and *N,N*-dimethylformamide (DMF). When the feed ratio of DV to AEPZ was 1:1, no gelation was observed for a total monomer concentration below about 7.0 mol/L. A higher concentration resulted in an extremely fast reaction, and a very high local temperature, resulting in loss of control of the polymerization. The solid-state product rapidly appeared. The solids were generally soluble in aqueous HCl solution, although sometimes they were found to be gel particles, insoluble in any of the solvents tested.

The *in situ* Fourier transform infrared (FTIR) measurements showed that the reaction between the secondary amine of AEPZ and the vinyl group of DV was much faster than that between the primary amine and the vinyl group. Thus, the formation of AB'_2-type species with one vinyl group and two active hydrogens of the primary amine was dominant. Because of the high reactivity between the vinyl group and the secondary amine, the species with two primary amino groups (B'_4) was also formed as AB'_2 reacted with AEPZ. The existence of AB'_2 and B'_4 molecules in the initial reaction stage was verified by mass spectroscopy. Polymerization of AB'_2 in the presence of B'_4, a kind of multifunctional core molecule formed *in situ*, gave rise to HPSA with relatively low polydispersity index (PDI) at higher temperature (>20 °C), as shown in Scheme 4.2.



Scheme 4.2

HPSAs were also successfully prepared from DV and 4-(aminomethyl)piperidine (AMPD), *N*-ethylethylenediamine (NEEDA), *N*-methylethylenediamine (NMEDA), or *N*-methyl-1,3-diaminopropane (NMPDA) at high temperature in either water or organic solvents such as chloroform, *N,N*-dimethylacetamide (DMAc), DMF, and *N*-methyl-2-pyrrolidone (NMP).[29,45,46]

For the reaction systems described above, a product can be obtained by two means: (i) pouring the reaction solution into a mixture of concentrated aqueous HCl and a precipitation agent such as acetone, methanol, or ethyl ether to obtain protonated hyperbranched polycations; and (ii) pouring the reaction solution into ethyl ether and drying the precipitate under vacuum at room temperature to afford hyperbranched polymers with copious active amino groups. Size-exclusion chromatography (SEC) measurements with water as the solvent and poly(ethylene oxide) (PEO) as standard showed that the resulting HPSAs had moderate apparent M_ns (10,000–40,000) and very narrow PDIs (1.2–2.5), which was in agreement with the *in situ* formation of the core molecules in the reaction system.

It is noteworthy that the Michael addition between the vinyl group and the amine is strongly dependent on temperature. At low temperature, the reactivity of the secondary amine formed after the addition of vinyl group and primary amine is normally lower than that of the primary amine, so only linear or slightly branched polymer can be obtained by the Michael self-addition of the AB'_2 species (in this case, AB'_2 functions as AB' or $AB'B''$-type monomer).[47] At higher temperatures ($>20\,^\circ C$), the reactivity of the formed secondary amino group is comparable with or even much higher than that of the primary one. Thus, a highly branched polymer (the degree of branching, DB, can approach 0.5 or be even greater than 0.5) is available.[27–29,48,49]

HPSA made from DV and AEPZ is highly water soluble. After modification with hydrophobic moieties such as valeryl chloride, nonanoyl chloride, or palmityl chloride, the core–shell amphiphilic hyperbranched poly(DV-AEPZ) was obtained.[50,51] The modified polymer can be used to load dyes such as Congo red (CR), methyl orange (MO), and Rose Bengal (RB), from aqueous phase to chloroform phase. The longer the hydrophobic chain, the higher the loading capability (C_{load}) for the same dye. For the palmitoyl-modified HPSA, the average number of dye molecules trapped by per macromolecule reaches 41.8 of CR, 19.4 of MO, and 3.0 of RB.[50] Such a high loading capability is considered to be due to the high water solubility of the HPSA core and the large polarity difference between the hydrophilic core and hydrophobic shell. Interestingly, the loaded dyes can be released from the molecular vessel by mixing its chloroform solution with pure water. The high loading capability associated with the reversible releasing property would pave the way for the use of molecular vessels in applications such as drug transfer/delivery, selective molecular recognition and separation, nanocatalysis, and nanocoating. More interestingly, the amphiphilic hyperbranched poly(DV-AEPZ) showed a synergistic encapsulation effect.[52] This means that C_{load} of one or two dyes increases in the presence of another dye when double or multidyes are used as the guest substances. For the palmitoyl-modified HPSA, the C_{load} of methyl blue (MB) can be raised to a

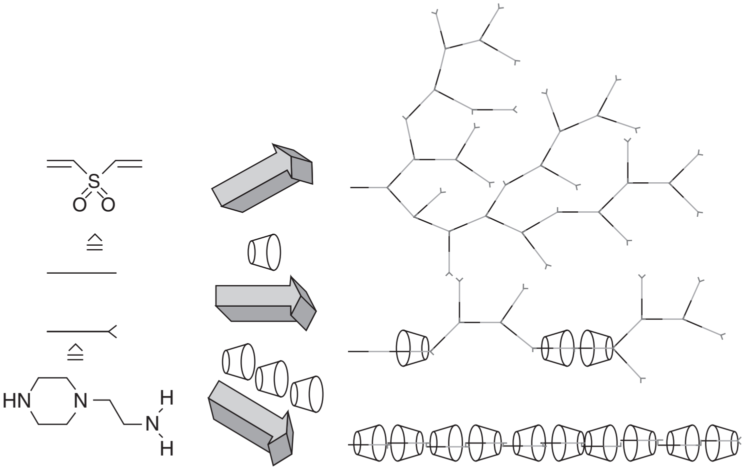


Figure 4.2 Proposed mechanism for an architecturally controlled polymerization. Reprinted with permission from Ref. [56].

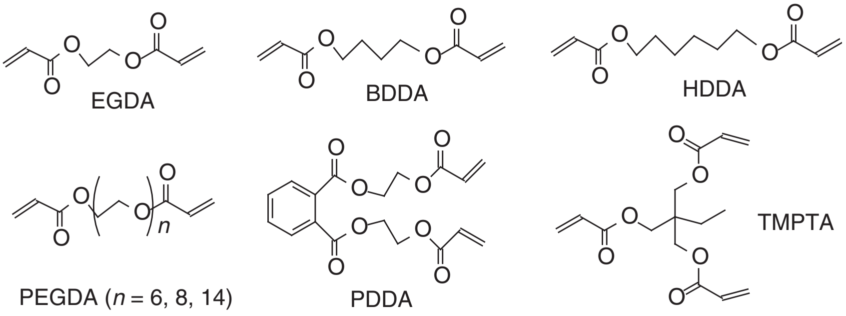
40–100-fold level of single-dye encapsulation without loss of MO. In addition, self-association behavior was observed in water for the HPSA.[53–55]

In addition to the large-scale availability of HPs, CMM possesses another advantage: the architecture of the resulting polymers can be varied by modification of one of the double monomers before polymerization. For example, Zhu and Yan *et al.* reported that DB of the hyperbranched poly(DV-AEPZ) can be controlled by the addition of β-cyclodextrin (CD), since an inclusion complex can be formed between AEPZ and β-CD (Figure 4.2).[56] Only linear units were formed when DV reacted with the AEPZ/β-CD complex monomer because of the strong steric hindrance of β-CD, whereas both linear and dendritic structures were formed when DV reacted with free AEPZ. Thus, DB can be readily adjusted by the feed ratio of AEPZ:β-CD. If the ratio is higher than 1:1, the branched polymer is obtained; if the ratio is equal to or lower than 1:1, only the linear polymer forms.

Through one-pot polymerization of DV, AEPZ, and isocyano-functionalized β-CD, hyperbranched poly(DV-AEPZ) with a DB of 0.41 was successfully grown from the core of β-CD. Around 6.7 primary hydroxyl groups of 7 ones of β-CD were functionalized, and in each arm there are approximately 18 DV and 18 AEPZ units, calculated from nuclear magnetic resonance (NMR) spectra. The hyperbranched polymer-functionalized β-CD preserved the inclusion ability of natural β-CD as revealed by the testing of inclusion of alkaline phenolphthalein.[57]

4.3.2 Poly(Ester Amine)

Similar to the reaction between DV and asymmetric diamines, the commercially available cross-linking agents, diacrylates or triacrylates, instead of DV, can



Scheme 4.3

be used as raw materials to synthesize water-soluble hyperbranched poly(ester amine)s via Michael addition (Scheme 4.3).[29,32,58]

Reaction conditions such as temperature and monomer concentration have a strong effect on the Michael addition polymerization. For the reaction between ethylene glycol diacrylate (EGDA) and the diamines shown in Scheme 4.1, no gelation occurred for polymerization with a 1:1 feed ratio. When the feed ratio was increased to 3:2, cross-linking was not observed in a dilute solution at low temperature. When the reaction temperature was lower than 40 °C, gelation was not observed after 30 days. At higher temperatures, networks formed depending on the monomer concentration: if the feed volume ratio of the two monomers to solvent was greater than 2:1, gelation occurred quickly, whereas the gel did not appear if the volume ratio was lower than 1:2. HCl usually helps in the solubilization and protection of amine-containing compounds, and soluble and stable hyperbranched poly(ester amine)s with terminal amino and vinyl groups can be obtained by precipitating the reaction mixture with acetone and aqueous HCl.

The M_ws for hyperbranched poly(ester amine)s measured by SEC with water as the eluent and PEO as standard ranged from 15,000 to 25,000. Again, their molecular weight distributions were very narrow (1.28–1.40).[58] Similar results were obtained when 1,4-butanediol diacrylate (BDDA) or 1,6-hexanediol diacrylate (HDDA), instead of EGDA, reacted with the diamines.

If a monomer of poly(ethylene glycol) diacrylate (PEGDA), instead of EGDA, is adopted to react with the asymmetric diamines, hyperbranched poly(ester amine)s containing ethylene oxide units in their frameworks can be produced. The number-average degree of polymerization (DP_n) and the molecular weight of the resulting product depend on the monomer purity.

Hyperbranched poly(ester amine)s could be prepared from phthalicdiglycol diacrylate (PDDA) and AEPZ via Michael addition. The polymers were further cured with β-glycidyloxylpropyl trimethoxysilane under ambient condition. The mechanical properties of the cured coatings such as hardness, impact strength and adhesion were measured.[59]

All of the hyperbranched poly(ester amine)s mentioned above are highly soluble in water and certain organic solvents such as chloroform, DMF, DMAc, NMP, DMSO, but are poorly soluble in tetrahydrofuran (THF).

When the feed ratio of the diacrylate to the diamine is 2:1, hyperbranched poly(ester amine) with terminal acrylate groups was obtained.[60] The acrylate groups could be further modified as primary, secondary, and tertiary amines as well as monohydroxyl and diol groups.[61] The water-soluble hyperbranched poly(ester amine)s are degradable under physiological conditions (pH 7.4, 37 °C), in which more than 10% ester bonds were hydrolyzed within 4 h, and can be used as nonviral gene carriers. Hyperbranched poly(HDDA-AEPZ), poly(HDDA-AMPD), and poly(BDDA-AMPD) were shown to effectively condense plasmid DNA into small (~94–135 nm) and positively charged complexes. The polymer/DNA complexes (polyplexes) were able to transfect COS-7 cells *in vitro*. The transfection activity of the polyplexes was preserved in the presence of serum proteins. The transfection level of the poly(HDDA-AEPZ)/DNA polyplex was higher than or comparable to that of polyplexes based on polyethylenimine (PEI) and poly(2-dimethylaminoethyl methacrylate) (PDMA).[62] In addition, photoluminescence (PL) at 456–473 nm was found for the hyperbranched poly(ester amine)s if excited at 372–394 nm.[61]

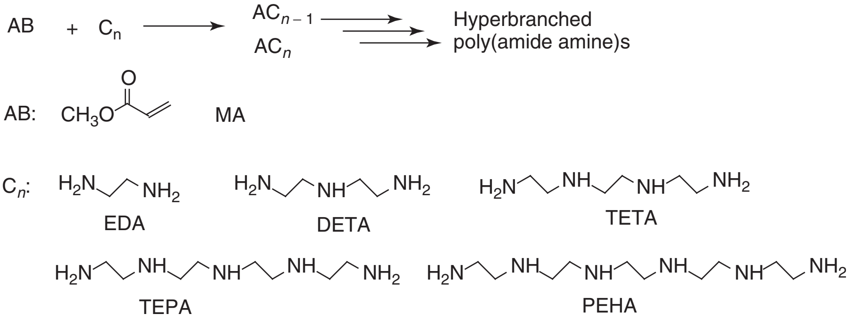
Trimethylolpropane triacrylate (TMPTA) was also used to react with AEPZ to prepare hyperbranched poly(ester amine), which is also degradable and less cytotoxic compared with PEI (25k) and showed transfection efficiency comparable to the PEI for *in vitro* DNA delivery.[63]

Core–shell amphiphilic hyperbranched poly(ester amine)s with terminal secondary amine groups were synthesized by Michael addition between piperazine and trimethylolpropane triacrylate with a molar ratio of 13:6, followed by reaction with aliphatic acid chlorides such as stearoyl chloride, dodecanoyl chloride, and octanoyl chloride. The modified amphiphilic polymers could be used as host molecules to extract the guest acid dye, MO, from the aqueous layer to the organic layer. More MO molecules were extracted by the modified macromolecules at a lower pH because of the quaternization of tertiary amino units. The transfer capability of MO increased with increasing the length of the alkyl chains.[64]

4.3.3 Poly(Amidoamine)

It is well known that the PAMAM dendrimer[65–67] is one of the fastest developing varieties and engaging research efforts in the field of dendritic polymers, and has shown many potential applications, including nanoscale catalysts,[68–70] reaction vessels,[71] and drug carriers.[72] However, it is very difficult to prepare a large-scale product of PAMAM dendrimer in a cost-effective way. Thus, to prepare hyperbranched PAMAM is an alternative way to get dendritic PAMAM readily.

Aliphatic hyperbranched PAMAMs can be easily prepared by the polymerization of methyl acrylate (MA) (AB-type monomer) with polyamines (C_n



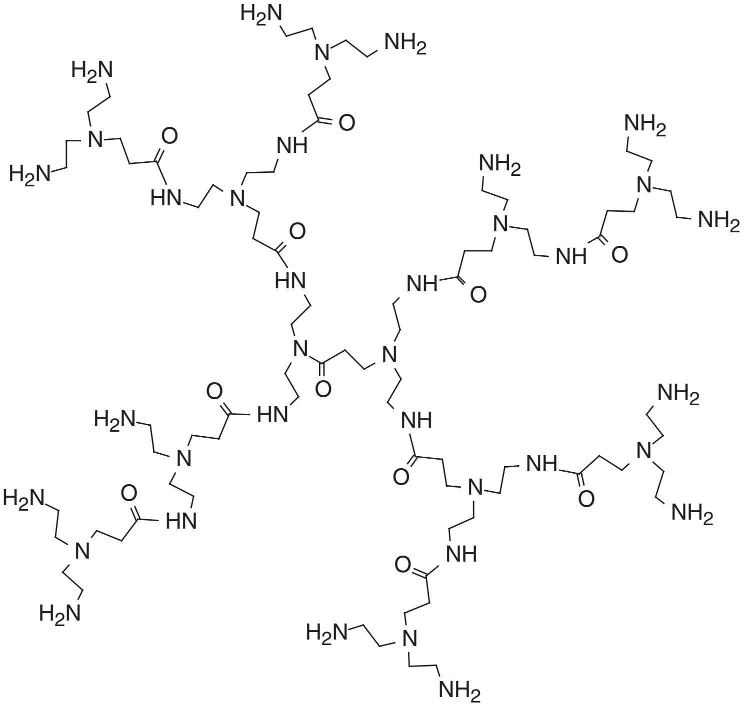
Scheme 4.4

monomers) such as ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA) (Scheme 4.4). The AC_n or AC_{n-1} intermediate can form *in situ* at room temperature for a feed ratio of AB to C_n of 1:1. Hyperbranched PAMAMs could then be prepared by self-condensation of the intermediates at higher temperatures under vacuum. Interestingly, the feed ratio of AB to C_n can be adjusted over a relatively wide range from 1:1 to n:1, resulting in hyperbranched polymers with various terminal groups. Because of their different functional groups, hyperbranched polymers exhibit different properties. Therefore, the structure and property of hyperbranched polymers can be controlled through the feed ratio of AB to C_n.[73,74]

In the reaction, MA was added dropwise to a methanol solution of polyamine. The reaction mixture was kept at room temperature for 24–48 h, and then the solvent was removed from the reaction system under reduced pressure at 60 °C on a rotary evaporator. Under vigorous revolution and vacuum distillation, the mixture was kept at 60 °C for 1 h, 100 °C for 2 h, 120 °C for 2–4 h, and, finally, 135–150 °C for 2–4 h. Pale-yellow viscous solid hyperbranched polymers were produced. Since no extra reagents such as catalyst and condensation agent were added to the reaction mixture, it was not necessary to separate the raw product by reprecipitation, and therefore the yield was very high (>95%). Moderate apparent molecular weights of 7000–12,000 with narrow PDIs of 1.8–2.6 were found using GPC with DMF as solvent and polystyrene (PS) as standards.[74]

Variation of the AB to C_n feed ratio results in a change in the structure and properties of the products. For example, the solubility of the hyperbranched polymer made from MA and DETA in water decreases with an increase in the feed ratio of MA to DETA. The structure of hyperbranched PAMAM made from MA and DETA is shown in Scheme 4.5, which is quite similar to that of PAMAM dendrimer.

All of the hyperbranched PAMAMs with a feed ratio of 1:1–1.5:1 described above are highly soluble in water and polar solvents such as DMF, DMAc, DMSO, and NMP. The water-soluble cationic hyperbranched polyelectrolytes may be useful in the pigments, coatings, and gene delivery or transfection fields.

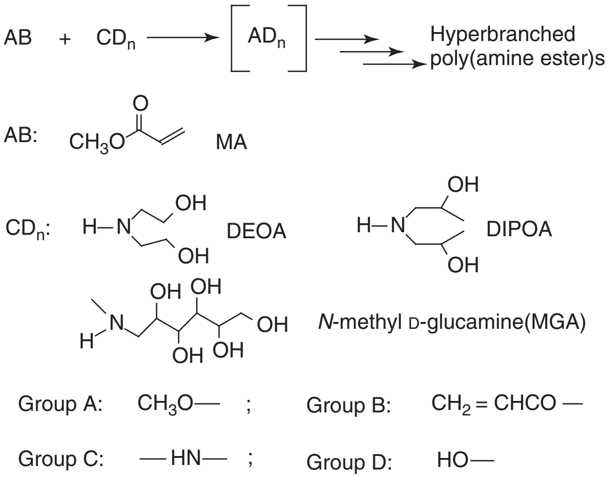


Scheme 4.5

Similar to the HPSA mentioned earlier, the hyperbranched PAMAMs modified with long aliphatic chains such as palmityl chloride can encapsulate dyes with a high capacity. For instance, benzoyl- and palmitoyl-modified hyperbranched poly(MA-EDA)s can load CR with a capacity of 0.3089 and 0.9949 g CR per gram of polymer, respectively. Synergistic encapsulation effect was also observed for the hyperbranched poly(MA-DETA) when MO and MB were used as the guest molecules. The C_{load} of MO can be increased by about 100% with the cooperation of MB.[52]

Similar to the preparation of HPSAs and poly(ester amine)s, hyperbranched PAMAMs can also be synthesized by the Michael addition of the diacrylamide (A_2) *N,N*′-methylene diacrylamide (MDA) with the trifunctional asymmetric diamines AMPD, NMEDA, or AEPZ, by adjusting the feed ratio.[33]

Slightly branched aromatic PAMAMs were prepared from triamine (BB′B″), 2,4,4′-triaminodiphenyl ether, and dicarboxylic acids (A_2) in the presence of 2,3-dihydro-2-thioxo-3-benzoxazolyl phosphonic acid diphenyl ester (DBOP) as a condensing agent. Although the DB was as small as 0.05, their solubility in amide solvents was clearly improved. Strong but brittle films were prepared by casting from DMF solution. The mechanical properties were comparable with those of the corresponding linear polymers.[75]



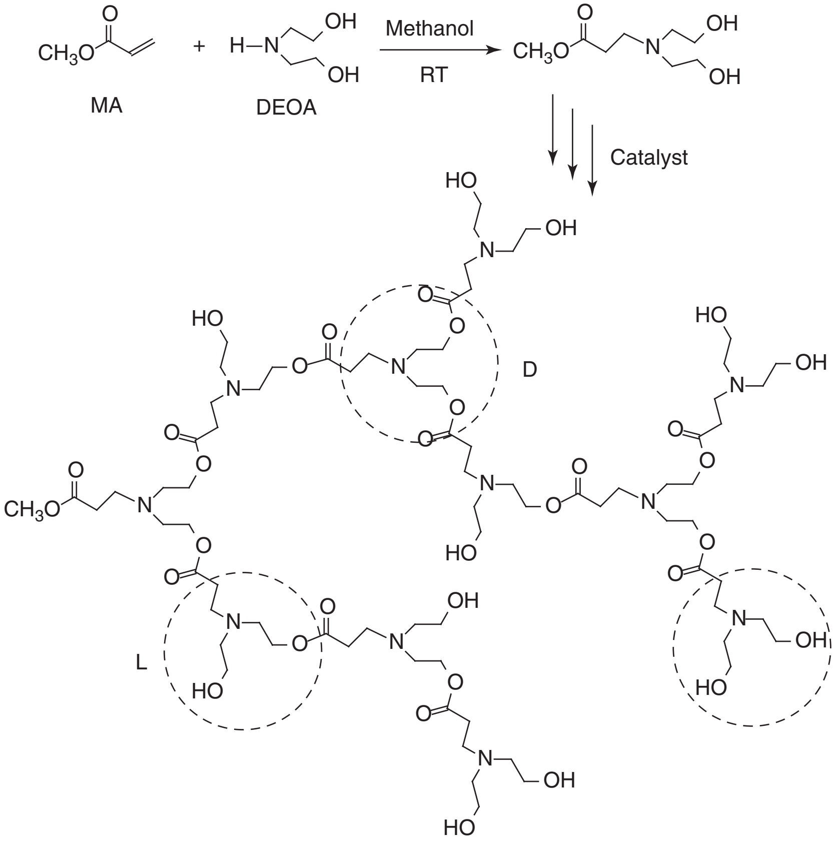
Scheme 4.6

4.3.4 Multihydroxy Hyperbranched Poly(Amine Ester)s

Multihydroxy hyperbranched poly(amine ester)s (HPAEs) can be prepared by polymerization of MA (AB) and the monomer containing one secondary amino group and multihydroxy groups ($CD_n, n \geq 2$) such as diethanolamine (DEOA) and N-methyl D-glycamine (MGA). At mild temperatures, the vinyl group (B) reacts with the amino group (C) via Michael addition to form an AD_n intermediate containing a methyloxy carbonyl ($CH_3OC{=}O$) group and n hydroxy groups. Water-soluble multihydroxy hyperbranched polyesters with tertiary amino units in their backbones can be prepared by self-condensation of the AD_n under stronger conditions (Scheme 4.6).[76,77] The reactions between A and C or D can be suppressed by using methanol as solvent. Measurements of *in situ* ^{1}H NMR with diethylamine and 1,4-butanediol (BDO) as model compounds confirmed that the reaction between the methyloxy carbonyl and the amino or hydroxyl group was negligible under mild conditions.

To improve the conversion ratio of CD_n or MA and shorten the reaction time of the initial stage, the feed ratio of AB to CD_n is a little higher than 1:1 (typically 1.05–1.1:1). The polymerization process is similar to that of hyperbranched PAMAMs from MA and polyamines.

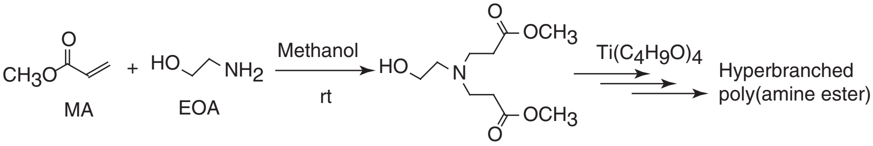
The structure of the hyperbranched poly(amine ester)s made from MA and DEOA is shown in Scheme 4.7. Depending on the reaction temperature and the catalyst, M_n of hyperbranched poly(MA-DEOA) ranged from 10,000 to 260,000 and of poly(MA-MGA) ranged from 38,000 to 66,000, with a narrow molecular weight distribution. The DB of poly(MA-DEOA) calculated from ^{13}C NMR was close to 0.5 (0.52–0.56). Thermogravimetric analysis (TGA) showed that the 5% weight-loss temperature for the poly(amine ester)s is above 200 °C, and the 10% weight-loss temperature is above 250 °C.[76]



Scheme 4.7

There is one ester bond and one tertiary amino group in each repeating unit of the hyperbranched poly(amine ester)s. Such a structure is very attractive in the field of drug delivery. The hyperbranched polymers are degradable in water because of their ester bonds. Owing to the introduction of amino groups, the resulting polymers are easily soluble in water. Furthermore, the acid groups formed in the hydrolysis neutralize the amino groups. So, the pH of the aqueous system of the hyperbranched poly(amine ester)s can be self-adjusted to about 7, which is an important parameter for a good drug-delivery material.[78]

A methoxycarbonyl-terminated hyperbranched poly(amine ester) could be synthesized by the reaction of MA with a compound containing a hydroxyl and one primary amino (e.g., ethanolamine, EOA) or two secondary amino groups (Scheme 4.8). In the presence of $Ti(C_4H_9O)_4$, the polymerization occurred smoothly. SEC measurements with PS as standards showed that the hyperbranched poly(amine ester)s had apparent M_n's of 35,000–70,000. The onset decomposition temperature (T_d) of poly(MA-EOA) was 275–290 °C.



Scheme 4.8

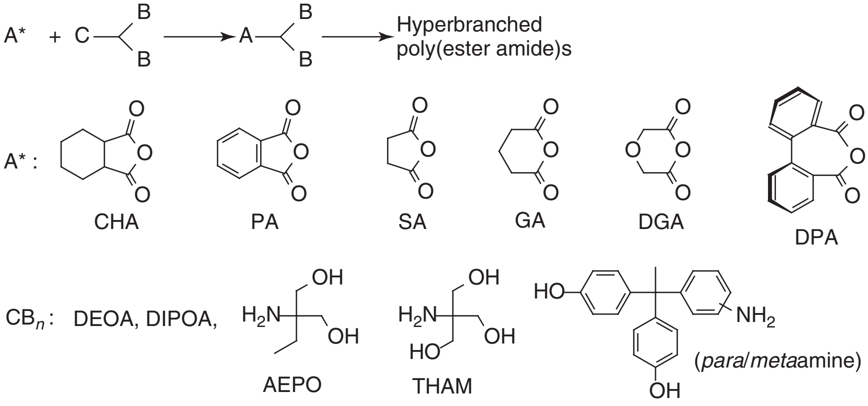
Using 1,1,1-trimethylol propane (TMOP) as a molecular core, multihydroxy hyperbranched poly(amine ester) was synthesized by the polymerization of MA and DEOA with toluene-*p*-sulfonic acid (*p*-TsOH) as catalyst.[79,80] Cross-linked hyperbranched polymer films were prepared by cross-linking the terminal hydroxyl groups of HPAE using glutaraldehyde. The films showed a contact angle of <32.9 °, tensile strength of >0.35 MPa, elongation at break of >9.2%, and swelling degree of >63% in water. Bovine serum albumin adsorption was relatively low.[80] The results indicated that cross-linked films are promising candidates for a wide range of applications, especially in high-performance coatings.

When diisopropanolamine (DIPOA), instead of DEOA, was reacted with MA, hyperbranched poly(amine ester)s were also obtained. These polymers were directly cured with hexamethylene diisocyanate (HDI) in absence of solvent under ambient conditions, forming cross-linked coatings with gel mass fractions higher than 0.90 and an anti-impact strength of 50 cm kg.[81]

4.3.5 Poly(Ester Amide)s

DSM researchers first reported the "$A^* + CB_n$" ($n \geq 2$) approach to hyperbranched poly(ester amide)s.[30,31] In their presentation, A^* and CB_2 were denoted as Aa and bB_2, respectively. They used 1,2-cyclohexane dicarboxylic anhydride (CHA) as the Aa monomer, and di-2-propanolamine as the bB_2 source. Recently, Li *et al.* developed the "$A^* + CB_n$" approach, using dicarboxylic anhydride compounds as A^* (or AA') and multihydroxy amines as CB_n.[34,35] An A^* monomer contains two latent functional groups; one A group will be formed after the reaction of A^* with the C (e.g., amino) group of CB_n, giving rise to an AB_n intermediate. Self-polycondensation of the intermediate results in hyperbranched poly(amide ester)s (Scheme 4.9).

The reaction between CHA and DIPOA has been investigated using electrospray ionization (ESI) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, and SEC in combination with on-line differential viscosimetry detection (SEC-DV).[82–84] The exothermal reaction of CHA and DIPOA normally leads to a species (AB_2) having one carboxylic acid group and two (2-hydroxypropyl)amide groups. Ester bonds were formed through an intermediate oxazolinium–carboxylate ion pair, and hyperbranched macromolecules were generated under reduced pressure (5 mbar) at around 180 °C, without a catalyst (Scheme 4.10).



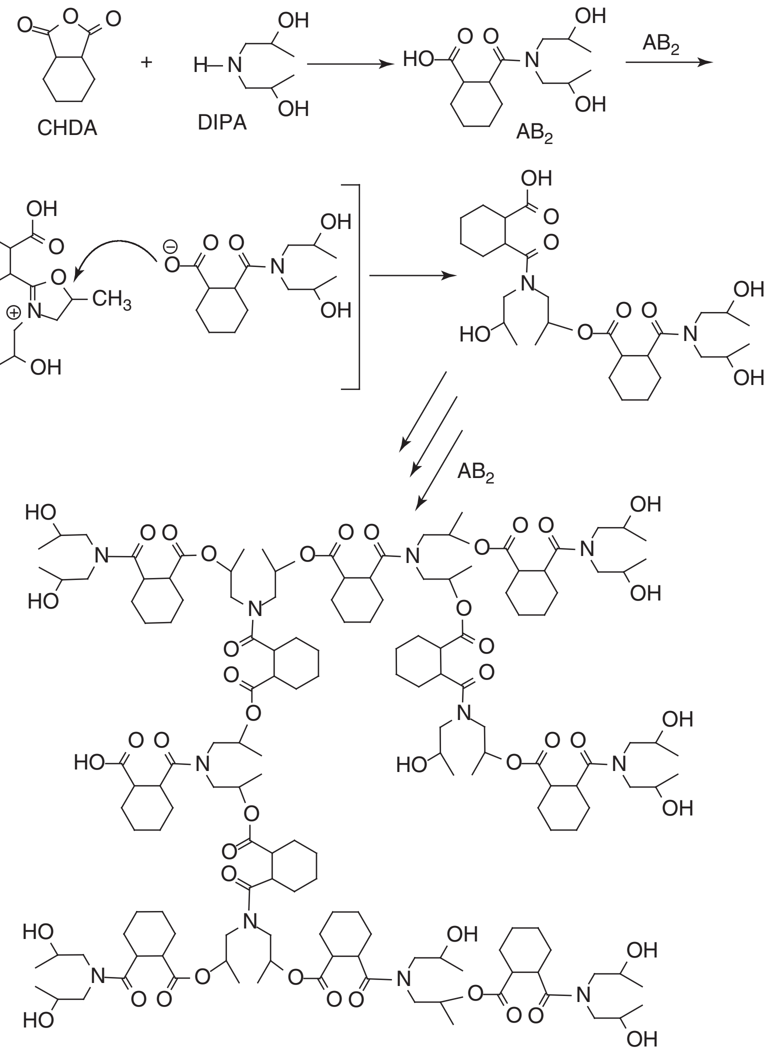
Scheme 4.9

DSM's Hybrane® hyperbranched poly(ester amide) made from CHA and DIPOA has been scaled up to the ton scale.[85] Interestingly, the addition of small quantities of water-soluble Hybrane to paper coating can give an improved control over the rheology of the dispersion at high speeds. This indicates that this kind of hyperbranched polymer can be used in paper coating and related fields.[86]

Other hyperbranched poly(ester amide)s series can be prepared by direct polymerization of phthalic anhydride (PA), succinic anhydride (SA), diglycolic anhydride (DGA), or glutaric anhydride (GA) with DEOA or DIPOA with similar reaction routes and conditions. The M_ns of the hyperbranched poly(ester amide)s detected with SEC-DV by using PS as standard and dichloromethane as solvent and eluent were very low (680–6000).[31,83,84]

Apart from the multihydroxy secondary amines, multihydroxyl primary amines such as tris-(hydroxymethyl)aminomethane (THAM) and 2-amino-2-ethyl-1,3-propanediol (AEPO) can be also used as the CB$_n$-type monomers to react with the carboxyl anhydrides (A*) to produce hyperbranched poly(amide ester)s in the absence of any catalyst and solvent.[34,87] Analysis using ^{1}H and ^{13}C NMR spectroscopy revealed that the DB of the resulting polymers ranged from 0.36 to 0.55. The weight-average molecular weight (M_w) of the polymers ranged from 28,900 to 106,000 with PDIs of 2.11–3.30, using DMF containing 0.05 M LiBr as eluent.[34]

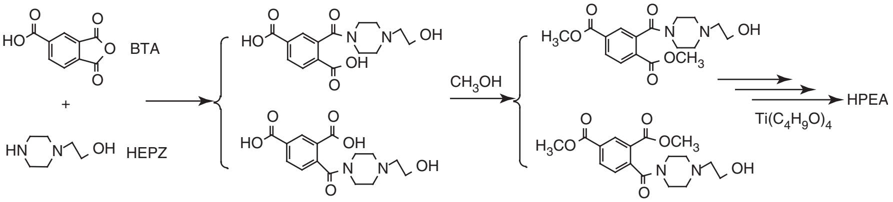
Aromatic or semiaromatic hyperbranched poly(ester amide)s were prepared by polycondensation of 2,2-diphenic anhydrides (A*, DPA) with aromatic or alphatic multihydroxyl primary amines (CB$_x$) such as 1-(4-aminophenyl)−1,1-bis(4-hydroxyphenyl)ethane, 1-(3-aminophenyl)-1,1-bis-(4-hydroxyphenyl)ethane, THAM, and AEPO without any catalyst.[35] The DBs of the resulting polymers were determined to be 0.53–0.63 by ^{1}H NMR or ^{13}C NMR inverse-gated decoupling and distortionless enhancement by polarization transfer (DEPT) spectra. These polymers possess moderate molecular weights (M_w = 6300∼78,500) with



Scheme 4.10

PDIs of 2.15–2.78 determined by SEC using DMF + 0.05 M LiBr as eluent and poly(methyl methacrylate) (PMMA) as the calibration, and can be well soluble in a variety of solvents such as DMAc, DMSO, THF, and chloroform. The decomposition temperatures of the polymers at 10% weight-loss point (T_d^{10}) ranged from 333 to 397 °C in nitrogen.

In addition, hyperbranched poly(ester amide)s can be prepared from benzene-1,2,4-tricarboxylic acid-1,2-anhydride (BTA) or other AA* or A$_2^*$-type monomers with *N*-(2-hydroxyethyl)piperazine (HEPZ) or other CB-type monomers possessing one hydroxyl and one amino groups (Scheme 4.11).[88] The AA* monomer



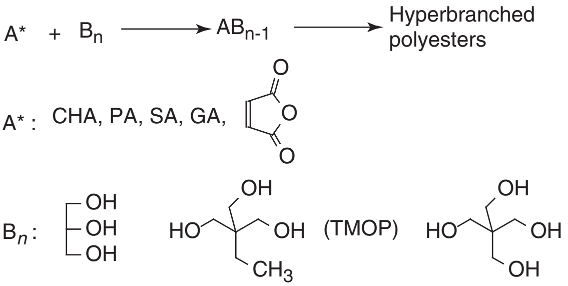
Scheme 4.11

contains one A and one A^* group, and A_2^* contains two A^* groups. As claimed above, one A^* is a latent A_2. In the "AA^*+ CB" approach, the reaction between A^* and C groups generates an A_2B intermediate which can be self-polycondensed to obtain a hyperbranched polymer. Under mild conditions and in the presence of catalysts such as phosphoric acid and tetrabutyl titanate ($Ti(C_4H_9O)_4$), hyperbranched poly(ester amide)s were prepared, with moderate M_n (25,000−50,000) and narrow PDI (1.4−2.5). The prepared hyperbranched poly(ester amide)s were highly soluble in water because of their tertiary amino and amido units.

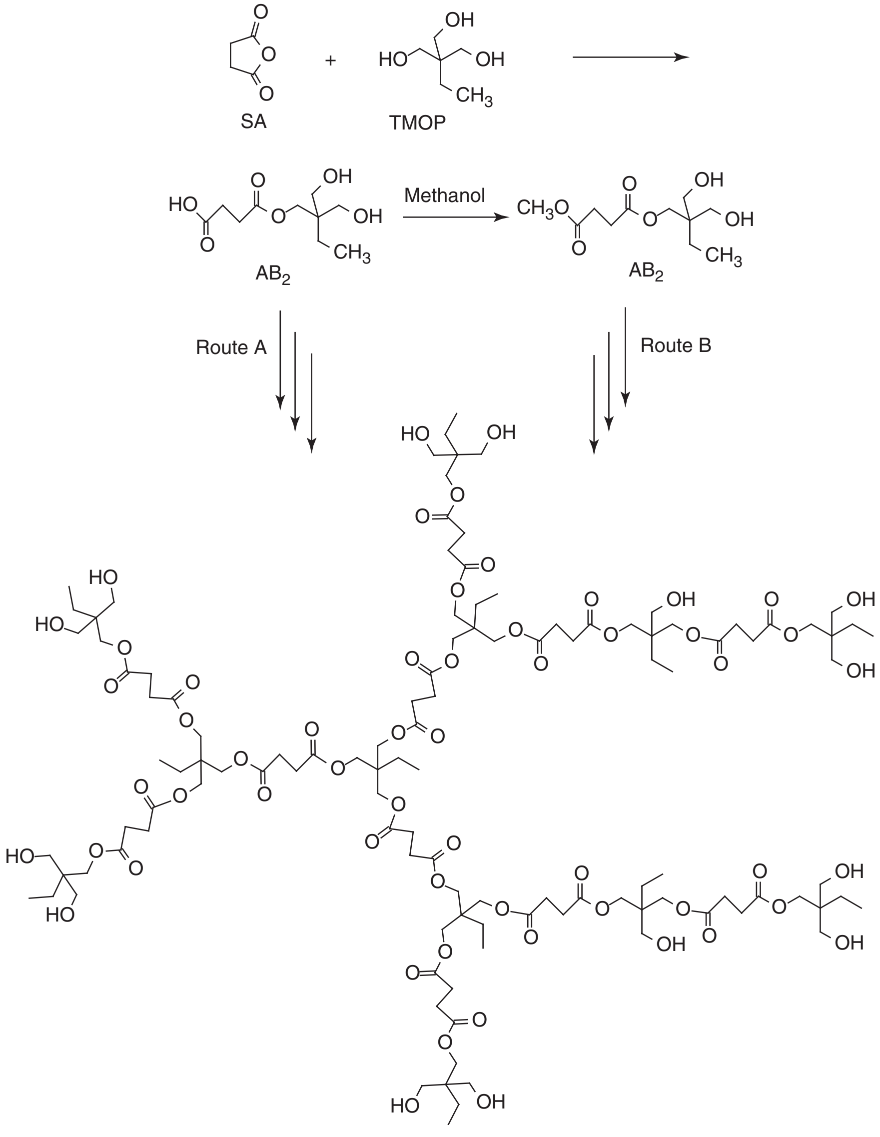
4.3.6 Polyesters

Polyhydric alcohols (B_n) such as glycerol, TMOP, and pentaerythritol can directly polymerize with the aforementioned dicarboxylic anhydrides (A^*), forming hyperbranched polyesters (Scheme 4.12). The reaction between PA and glycerol had been investigated by Kienle *et al.* as early as 1929.[89] However, only low molecular weight products or insoluble materials were obtained at that time. To obtain soluble high molecular weight hyperbranched polymers, it was necessary to reinvestigate the reactions between dicarboxylic anhydrides and polyhydric alcohols or multihydroxy molecules.

Because each hydroxyl group of B_n has almost the same reactivity, gelation occurred easily in the reaction. It is crucial to remove water from the reaction system during the initial stage to avoid network formation. The existence of water in the monomers or solvents leads to the ring opening of the anhydrides, giving difunctional A_2 molecules and leading to insoluble products within several hours.



Scheme 4.12

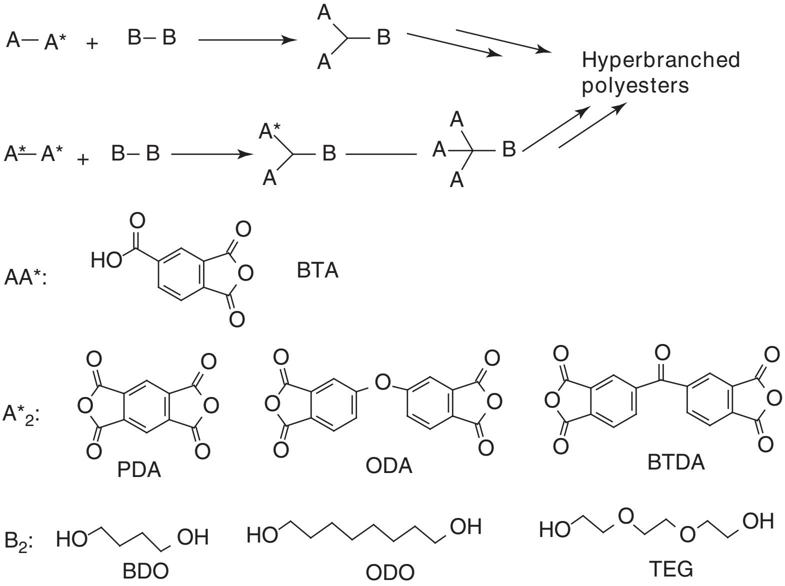


Scheme 4.13

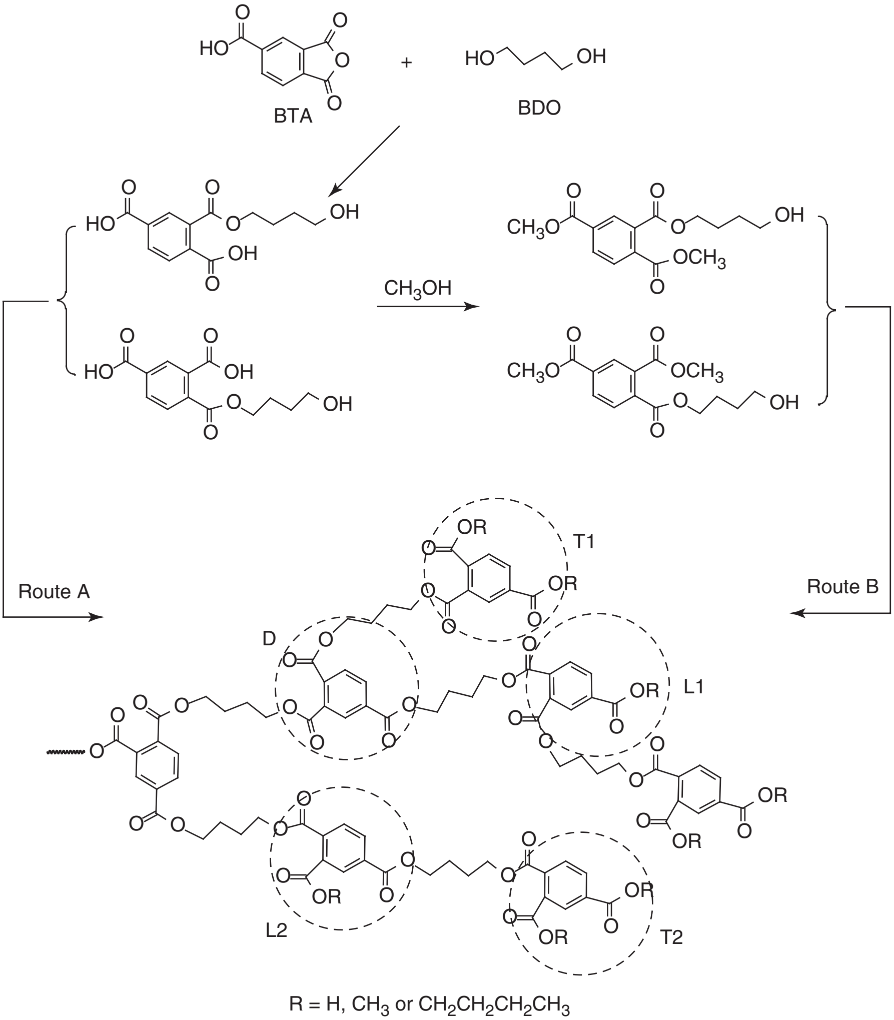
Two routes were employed in the polymerization. Scheme 4.13 describes a typical example. Route A represents direct polymerization of the *in situ* formed AB$_2$ intermediate possessing a carboxylic acid group and two hydroxyl groups. In route B, the AB$_2$ species was modified with methanol in advance to afford the new AB$_2$-type monomer, and then hyperbranched polyesters were prepared by the polymerization of the modified AB$_2$. Only moderate molecular weight product was obtained ($M_n = 5,000–20,000$) via route A, even though the reaction was performed under reduced pressure at 140–150 °C for 10–20 h. The color of the raw product was very deep, indicating that carbonization or oxidization occurred in part of the polymers. As a comparison, the products made through route B had a high M_n (30,000–120,000) and were almost white.[90]

The hyperbranched polyesters made from maleic anhydride (MAH) and polyhydric alcohols have carbon–carbon double bonds in every repeating unit, so the cross-linked membrane can be prepared by UV light irradiation.

Hyperbranched polyesters can be also prepared by the polymerization of AA^* such as BTA and dihydroxy B_2 monomers such as BDO, 1,8-octanediol (ODO), and triethylene glycol (TEG), as shown in Scheme 4.14. Because of the much higher reactivity of the anhydride group over the carboxylic acid group in the condensation, a species with two carboxylic acid groups and one hydroxyl group can be presented. Then, hyperbranched polyesters can be prepared smoothly according to the conventional polymerization conditions and process. Similar to the reaction of AA^* and B_2, the reaction of one of the A^* of A_2^* with one of the B groups in B_2 affords the species AA^*B containing a carboxylic acid group, one anhydride group, and one hydroxyl group. Self-condensation of two AA^*B gives the A_3B species. Hyperbranched polyesters can also be prepared by further polycondensation of the A_3B molecules. The structures of A_2^* monomers such as pyromellitic dianhydride (PDA), 4,4′-oxydiphthalic anhydride (ODA), and benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BTDA) are also given in Scheme 4.14.



Scheme 4.14



Scheme 4.15

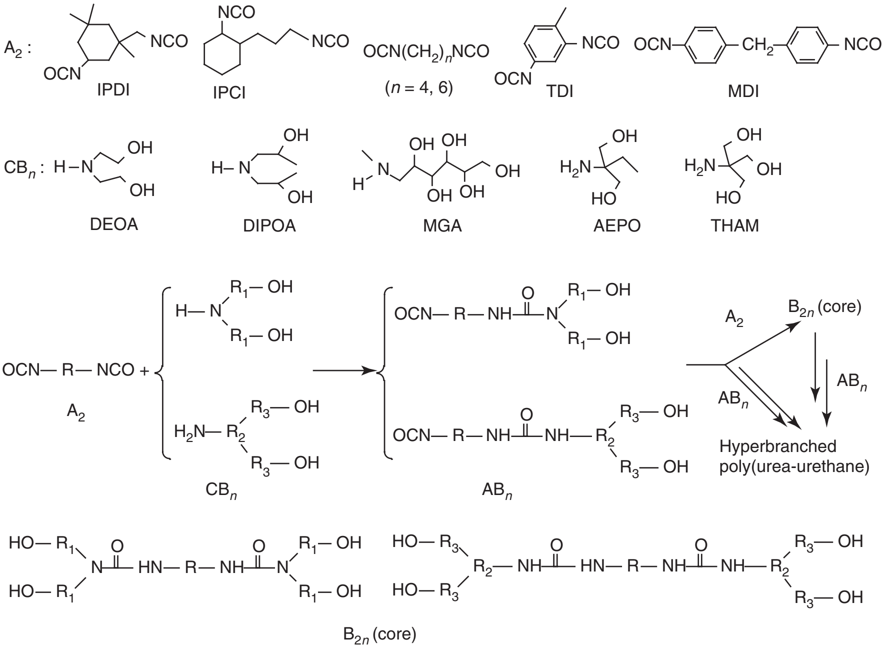
A typical example for the "AA* + B_2" approach to hyperbranched polyesters is described in Scheme 4.15. The first step was conducted at room temperature in chloroform. Two intermediates were formed. Hyperbranched polymers were prepared through two routes: direct polymerization or polymerization of the modified intermediates, as shown in Scheme 4.15. Again, the products synthesized using route B exhibited a higher molecular weight (M_n20,000–120,000) than those synthesized using route A (M_n3000–15,000). The hyperbranched polyesters were further modified with 1-butanol, resulting in the hydrophilic hyperbranched polyesters. It is well known that *n*-butyl phthalate is a good plasticizer for polyvinyl chloride. However, the low molar mass *n*-butyl phthalate is often released from the PVC, which strongly influences the quality of the plasticized product. The modified hyperbranched polyester has a similar structure as *n*-butyl phthalate and a much higher molecular weight, and may be a better plasticizer for PVC or other commercial plastics.

4.3.7 Poly(Urea-Urethane)s

Linear polyurethanes and polyureas are now widely used in rubber, plastics, fiber, and coatings. It is well known that polyurethanes or polyureas can be prepared by polycondensation of diisocyanates with dihydroxyl compounds or diamines. Because of the high reactivity of isocyanato groups (–N=C=O) against the nucleophile, it is hard to obtain an AB_2 monomer with an isocyanato group. Therefore, hyperbranched polyurethanes or polyureas cannot be directly synthesized from AB_2 monomers. Generally, an AB_2 monomer containing a functional group such as a carbonyl azide that can be transferred *in situ* into the isocyanato group is synthesized in advance, and then polymerization of the formed monomers leads to hyperbranched polyurethanes or polyureas.[91–94] However, it is very difficult to apply the prepared hyperbranched polyurethanes or polyureas owing to the complexity of the synthesis and the purification procedures.

Through CMM, hyperbranched poly(urea-urethane)s can be easily prepared by direct polymerization of commercially available diisocyanates (A_2), such as isophorone diisocyanate (IPDI), 2-(3-isocyanato-propyl)cyclohexyl isocyanate (IPCI), 1,4-diisocyanatobutane (BDI), HDI, tolylene 2,4-diisocyanate (TDI), and 4,4′-methylenebis(phenyl isocyanate) (MDI), as well as multihydroxyl amines (CB_n) such as DEOA, DIPOA, MGA, AEPO, and THAM, as shown in Scheme 4.16.[95–101] A CB_n monomer has one amino group (secondary or primary amino) and *n* hydroxyl groups. The fast reaction between the A group and the C group in CB_n affords AB_n and B_nB_n intermediates at mild temperature. Further reactions between isocyanato and hydroxyl groups at higher temperature give rise to hyperbranched polymers with alternating ureido and urethano units.

This reaction process has been monitored with on-line attenuated total reflection (ATR) FTIR spectroscopy. The reaction between the monomer TDI and DEOA was selected as a typical example.[97] It was found that the carbonyl groups (C=O) of the ureido units (–HN*CO*NH–) first rapidly appeared as peaks at 1670 and 1650 cm^{-1}, with a decrease in the absorption band of the isocyanato group at 2265 cm^{-1} during the initial reaction stage. The ureido absorption then stayed constant, and the carbonyl groups of the urethano units (–HN*CO*O–) appeared as a new peak at 1729 cm^{-1}, and gradually increased with decrease of the absorption peak of the isocyanato groups. If more DEOA was added into the reaction system, the ureido absorption band increased fast again, while the urethano band remained constant. This data shows that one isocyanato group of TDI quickly reacted with the amino group of DEOA, resulting in the formation of an B_2

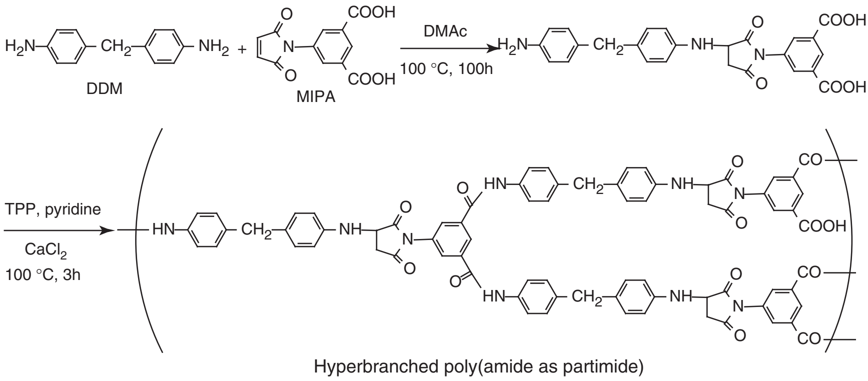


Scheme 4.16

intermediate. Then self-condensation of the intermediate along with other formed species generated the hyperbranched macromolecules with ureido and urethano units. Similar results were obtained for other reaction systems "$A_2 + CB_n$".

The peaks of the AB_n and B_nB_n species formed during the initial reaction period were also detected with mass spectroscopy. Reaction conditions such as temperature, concentration, and monomer feed ratio strongly influenced the reaction. The temperature during the initial several hours should be kept below 25 °C; otherwise, insoluble product would be generated. Gelation was barely observed for the polymerization in a feed ratio of 1:1 (A_2:CB_n) at given conditions. For the reaction with a 3:2 feed ratio (A_2:CB_n), cross-linking mainly depended on the temperature and concentration. Gelation occurred within several minutes in the conditions of high concentration (1.0 mol/L) and high temperature (60–80 °C), whereas at low concentration (0.15 mol/L) and low temperature (20 °C) gelation was not observed. SEC with 0.05 M LiCl in DMAc eluent at 70 °C showed that the resulting hyperbranched poly(urea-urethane)s had moderate M_ws ranging from 18,000 to 130,000, and relatively narrow PDIs with typical values of 1.7–3.5.[95]

Complete structural analysis was carried out using ^1H and ^{13}C NMR for aromatic hyperbranched polymers based on TDI. The values of the terminal, linear, and dendritic subunits were calculated, which were affected significantly by the monomer structure, monomer feed ratio, type of terminator or stopper,



Scheme 4.17

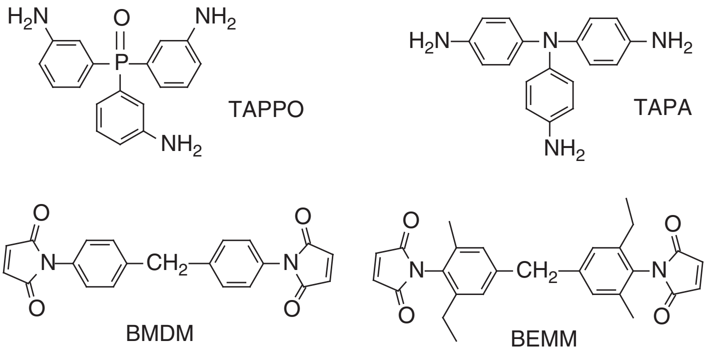
and reaction temperature. DB was found to be >60% for poly(TDI-DEOA)s and 45–48% for poly(TDI-DIPOA)s.[98] The hyperbranched poly(urea-urethane)s are soluble in polar organic solvents such as DMF, DMAc, DMSO, and NMP.

4.3.8 Other Polymers

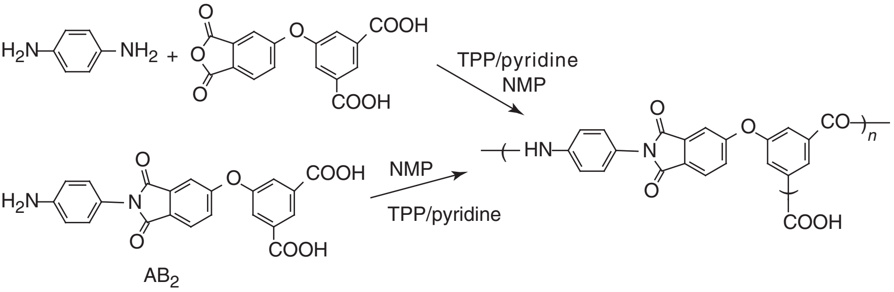
Hyperbranched poly(amide aspartimide)s were prepared through the reaction of 4,4′-diaminodiphenylmethane (DDM) with 5-maleimidoisophthalic acid (MIPA), as shown in Scheme 4.17. The synthesis was performed through a one-pot operation by means of the Michael addition between amine and maleimide groups, followed by the dehydration condensation between amine and carboxylic acid groups in the presence of triphenyl phosphate (TPP)/pyridine, as condensing agents. The AB_2 intermediate containing one amino and two carboxylic acid groups could be isolated from the reaction system and purified. The obtained polymers exhibited fairly good solubility in aprotic polar solvents at room temperature and in pyridine, THF, acetone, and chloroform upon heating. The polymers with moderate M_n (21,300, measured by GPC with PS as standard) show good thermal stability above 290 °C and have DBs of 0.42–0.48.[102]

By comparison, hyperbranched polyaspartimides were prepared from bismaleimides (A_2), 4,4′-bismaleimidodiphenylmethane (BMDM), and bis(3-ethyl-5-methyl-4-maleimidophenyl) methane (BEMM), and triamines (B_3), tris(3-aminophenyl)phosphine oxide (TAPPO), and tris(4-aminophenyl)amine (TAPA), through Michael addition. The monomer structures are shown in Scheme 4.18. DBs ranging from 0.51 to 0.69 were found with the poly(aspartamide)s. The polymers also showed good solubility in common solvents, high T_gs of 256 °C, and excellent thermal stability above 370 °C.[103]

A hyperbranched aromatic poly(amide-imide) was prepared by the copolymerization of 1,4-phenylenediamine, which is an A_2-type monomer, and 4-(3,5-dicarboxyphenoxy)phthalic anhydride, which is a $B'B_2$-type monomer, as shown



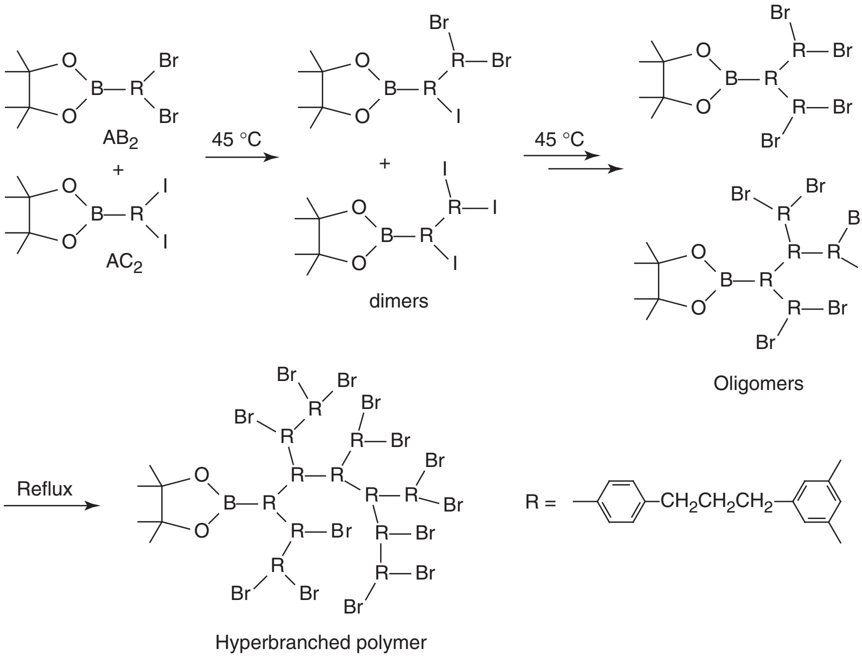
Scheme 4.18



Scheme 4.19

in Scheme 4.19. The rapid reaction between the anhydride and amino groups led to the formation of the dominant imide intermediate which can be regarded as a new AB_2-type of monomer. Further polymerization of the intermediate, without isolation, in the presence of TPP/pyridine, as condensing agents, offered the hyperbranched poly(amide-imide) with carboxylic acid chain ends. This polymer has nearly identical structure with that synthesized by self-polymerization of the AB_2 monomer which was prepared separately. DBs of the hyperbranched poly(amide-imide)s were estimated to be 60–61%.[104]

A bromo-terminated hyperbranched polymer with high DB ($86 \pm 10\%$, calculated from ^{13}C NMR integration) and M_w of 13,500 and PDI of 2.22 (measured by GPC with PS as standards) was prepared by Suzuki copolymerization of two monomers, AB_2 and AC_2, with different reaction rates (Scheme 4.20). At 45 °C, only iodoaromatics undergo the Suzuki coupling, forming oligomers mostly composed of dendritic and terminal units. Under reflux (about 65 °C), bromoaromatic compounds start to react and generate higher molar mass polymers.[105]



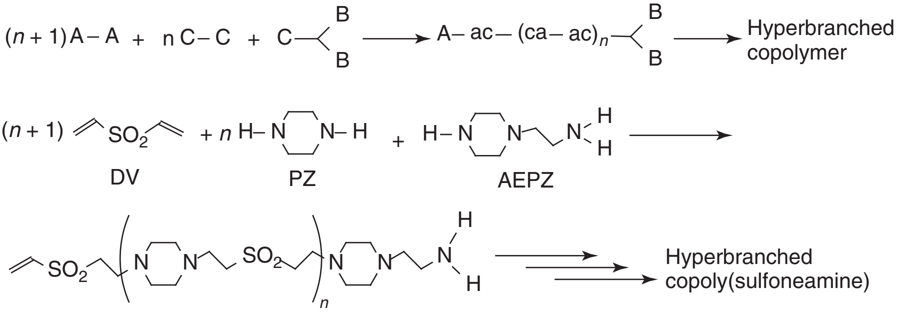
Scheme 4.20

4.3.9 Highly Branched Copolymers

CMM can be extended to prepare highly branched copolymers with different DBs by copolymerization of suitable difunctional monomers with the monomer pairs described above. DBs and some thermal and mechanical properties can be controlled by the feed ratio of the monomers. Here we selected the "$A_2 + C_2 + CB_2$" approach as an example to recount how to control the architecture and properties of the resulting polymers in copolymerization.[58,106–109]

In the "$A_2 + C_2 + CB_2$" approach, the A_2 and CB_2 monomers are the same as those of the "$A_2 + CB_2$" or "$A_2 + BB'_2$" approach described above, and C_2 is bifunctional molecules which can react with A group of A_2 rapidly. During polymerization, the rapid reaction between the A and C groups results in the formation of an AB_2-type intermediate. The linear units formed from the reaction of A and C_2 also are embedded in the AB_2 species, which indicated that the segment between two branching points and the number of linear units can be adjusted by the feed ratio of C_2 to CB_2. On the other hand, the B_4-type species may be formed. Highly branched copolymers with various linear units will be obtained from the further self-condensation of the intermediates (Scheme 4.21).

For the reaction system of divinyl monomers (A_2, e.g., DV, EDA, and EDAm) and asymmetric diamines (BB'_2), the compounds with two secondary amino groups such as piperzine (PZ) and 4,4′-trimethylenedipiperidine (TMDP)



Scheme 4.21

can be selected as the C_2 monomers. For the system of diisocyanates (A_2) and multihydroxyl amines (CB_n), bifunctional diamines such as PZ, TMDP, 1,2-diaminoethane, 1,4-diaminobutane, and so on, can be used as C_2 monomers.

The feed ratio of A_2 to the total C_2 and CB_2 was set as 1:1, and the ratio of C_2 to CB_2 (n) was varied. Thus, the physical properties such as the degree of crystallization, T_g, and architecture (DB) of the resulting polymers can be controlled by the feed ratio of C_2 to CB_2.

When DV (A_2) reacted with PZ/TMDP (B_2) and AEPZ (BB'_2), a homogeneous solution was observed throughout for reactions carried out in strong polar organic solvents such as DMF, DMAc, DMSO, and NMP. Nevertheless, a precipitate was found for B_2 to BB'_2 ratios greater than 3:1 if water or chloroform was used as the solvent. The phenomenon was attributed to the crystallization of the formed macromolecules rather than the appearance of a gel. In fact, the precipitate was soluble in polar solvents such as DMF and DMSO, and the hydrochloride of the polymers was highly soluble in water. No gelation was observed even at a very high concentration of the total monomers (1 g/1 mL of solvent) and at a high temperature (80 °C). The incidence of cross-linking can be easily avoided under general reaction conditions. When the feed ratio of B_2 to BB'_2 is changed from 1:5 to 5:1, DB varied from around 0.5 to 0.1.

The dependence of inherent viscosity (η_{inh}) on DB is also interesting for the branched copolymers with different DBs. Under the same molecular weight, η_{inh} decreases slightly with increasing DB at first, and then decreases dramatically after DB reaches around 0.3. The results suggest that the segment density of a branched polymer increases slightly, and then increases significantly, with the increase of DB after a critical point. Studies on other copoly(sulfoneamine)s show similar behavior, and the critical DB is 0.3–0.35.[106]

The DB also influences the crystallization of a branched polymer. When the feed ratio of B_2 to BB'_2 is equal to 3:1 ($n = 3$), crystallization and melting peaks can be observed in the differential scanning calorimetry (DSC) curves of copolymers made from DV, AEPZ, and PZ.[106] Other branched copolymers made from similar systems showed a similar phenomenon and results.

4.4 CONCLUSIONS

CMM exhibits generality, simplicity, controllability, versatility, and availability in the preparation of hyperbranched polymers. Various commercially available monomer pairs can be employed as the raw materials, and gelation can be effectively avoided even though the monomer conversion is high. Although many new families of hyperbranched polymers have been produced via the novel approaches, CMM is still developing, and more families of hyperbranched polymers and copolymers with application potentials can be prepared through this novel methodology. Most recently, Zhou and coworkers theoretically investigated the polymerization system "$A_2 + CB_2$" with nonequal reactivity,[110] which lays the theoretical foundation for CMM and in turn can provide a guidance for the selection of monomer pairs in experiments.

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LIST OF ABBREVIATIONS

AEPZ	1-(2-aminoethyl)piperazine
AEPO	2-amino-2-ethyl-1,3-propanediol
AFM	atomic force microscopy
AMPD	4-(aminomethyl)piperidine
BDDA	1,4-butanediol diacrylate
BDI	1,4-diisocyanatobutane
BDO	1,4-butanediol
BTA	benzene-1,2,4-tricarboxylic acid-1,2-anhydride
BTDA	benzophenone-3,3′,4,4′-tetracarboxylic dianhydride
CD	cyclodextrin
CHA	1,2-cyclohexane dicarboxylic anhydride
C_{load}	loading capability
CMM	couple-monomer methodology
CR	Congo red
D	dendritic unit
DB	degree of branching

DBOP	diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate
DDM	4,4′-diaminodiphenylmethane
DEOA	diethanolamine
DETA	diethylenetriamine
DGA	diglycolic anhydride
DIPOA	diisopropanolamine
DMA	dynamic mechanical analysis
DMAc	*N,N*-dimethylacetamide
DMAP	4-(dimethylamino)pyridine
DMF	*N,N*-dimethylformamide
DMM	double-monomer methodology
DPA	2,2-diphenic anhydride
DSC	differential scanning calorimetry
DV	divinylsulfone
EDA	ethylenediamine
EG	ethylene glycol
EGDA	ethylene glycol diacryalte
EHBP	epoxy-functionalized hyperbranched polyesters
EOA	ethanolamine
ESI	electrospray ionization
FTIR	Fourier transform infrared
GA	glutaric anhydride
HDDA	1,6-hexanediol diacrylate
HDI	hexamethylene diisocyanate
HEPZ	*N*-(2-hydroxyethyl)piperazine
HPSA	hyperbranched poly(sulfoneamine)
IPCI	2-(3-isocyanato-propyl)cyclohexyl isocyanate
IPDI	isophorone diisocyanate
L	linear unit
C_{load}	loading capability
MA	methyl acrylate
MAH	maleic anhydride
MALDI-TOF	matrix-assisted laser desorption/ionization time-of-flight
MB	methyl blue
MDA	*N,N′*-methylene diacrylamide
MDI	4,4′-methylenebis(phenyl isocyanate)
MIPA	5-maleimidoisophthalic acid
MMA	methyl methacrylate

M_n	number-average molecular weight
MO	methyl orange
M_w	weight-average molecular weight
NEEDA	*N*-ethylethylenediamine
NMEDA	*N*-methylethylenediamine
NMP	*N*-methyl-2-pyrrolidone
NMPDA	*N*-methyl-1,3-diaminopropane
NMR	nuclear magnetic resonance
ODA	4,4′-oxydiphthalic anhydride
ODO	1,8-octanediol
PA	phthalic anhydride
PDA	pyromellitic dianhydride
PDDA	phthalicdiglycol diacrylate
PDI	polydispersity index (M_w/M_n)
PDMA	poly(2-dimethylaminoethyl methacrylate)
PEGDA	poly(ethylene glycol) diacrylate
PEI	poly(ethyleneimine)
PEHA	pentaethylenehexamine
PL	photoluminescence
PMDETA	pentamethyldiethylenetriamine
PS	polystyrene
RB	Rose Bengal
SA	succinic anhydride
SCROP	self-condensing ring-opening polymerization
SCVP	self-condensing vinyl polymerization
SEC	size-exclusion chromatography
SMM	single-monomer methodology
T	terminal unit
T_d	decomposition temperature
TDI	tolylene 2,4-diisocyanate
TEG	triethylene glycol
TEPA	tetraethylenepentamine
TETA	triethylenetetramine
T_g	glass transition temperature
TGA	thermogravimetric analysis
THAM	tris-(hydroxymethyl)aminomethane
THF	tetrahydrofuran
T_m	melting point

TMDP	4,4′-trimethylenedipiperidine
TMOP	1,1,1-trimethylol propane
TMPTA	trimethylolpropane triacrylate
p-TsOH	toluene-*p*-sulfonic acid
TPA	terephthaldehyde
TPP	triphenylphosphine
UV–Vis	ultraviolet-visible spectroscopy
WAXS	wide-angle X-ray scattering

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Chapter 5

Self-Condensing Vinyl Polymerization

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5.1 INTRODUCTION

Several strategies for the preparation of hyperbranched polymers are currently employed. The most common and traditional method is the polycondensation of AB_x monomers containing one "A" functional group and two or more "B" functional groups that are capable of reacting with each other. The reaction involves typical features of a step-growth reaction of multifunctional monomers, resulting in the formation of hyperbranched polymers and oligomers without gelation. A multitude of hyperbranched polymers synthesized via polycondensation of AB_2 monomers have been reported, which are summarized in Chapter 2 of this book.

Vinyl monomers cannot be polymerized via polycondensation of AB_x monomers. Fréchet *et al*. recognized the importance of initiator monomers (later called *inimers*) to synthesize hyperbranched polymers from vinyl monomers, and in 1995 they named the process *self-condensing vinyl polymerization* (SCVP).[1–3] This discovery enabled the use of vinyl monomers for a convenient, one-pot synthesis of hyperbranched vinyl polymers.[2–9] The approach is based on the homopolymerization of AB^*-type monomers, in which B^* is a group capable of initiating the polymerization of vinyl groups, A.

Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

By copolymerizing AB* inimers with conventional monomers, the SCVP technique was extended to self-condensing vinyl copolymerization (SCVCP). Here, highly branched copolymers are formed where the degree of branching (DB) is controlled by the comonomer ratio.[10–15]

Copolymerization of AB*-type monomers with conventional vinyl ones has been performed long before 1995. In attempts to synthesize ω-styrylpolyisobutylene using *m*-/*p*-(chloromethyl)styrene, **AB*18** (Figure 5.1), as an initiator and aluminum alkyls/H_2O as coinitiators, Kennedy and Frisch[16] found significantly less than 100% of vinyl groups in the product. They concluded that copolymerization of the vinyl group of the "initiator" with isobutylene occurred as a "deleterious side reaction." In a similar experiment, Nuyken *et al.*[17] observed the formation of soluble polymers with much higher than calculated molecular weights (MWs) and broad molecular weight distribution (MWD) and attributed this to the formation of branched copolymers. On the other hand, copolymerizations of isobutylene with *p*-(chloromethyl)styrene, **AB*18**, or *p*-(chloromethyl)-α-methylstyrene initiated with boron trifluoride or $EtAlCl_2$ were reported even earlier,[18,19] indicating that **AB*18** acts both as a cationic *ini*tiator and as a mono*mer*. Consequently, the term *inimer* was coined: first by Hazer[20,21] to describe heterotelechelic macromolecules obtained by the capping reaction of hydroxyl groups of polyazoesters with isocyanoethyl methacrylate (*macroinimer*). In a similar way, self-condensing ring-opening polymerization (SCROP) works for heterocyclic inimers. This mechanism is detailed in chapter 6.

This chapter summarizes recent advances in SCVP and SCVCP as an effective method for the synthesis of hyperbranched polymers. Molecular parameters of hyperbranched polymers obtained by SCV(C)P are discussed from a theoretical point of view. An attractive synthetic concept for preparing hyperbranched polymer brushes on various types of surfaces is also described.

5.2 SELF-CONDENSING VINYL POLYMERIZATION

5.2.1 General Principles

Initiator monomers ("inimers") have the general structure AB*, where the double bond is designated as A, and B* is a group capable of being activated to initiate the polymerization of vinyl groups. Examples of such inimers are given in Figure 5.1. In order to initiate the polymerization, the B* group is activated. Scheme 5.1 shows an example of inimer activation where a copper(I) halide or Lewis acid transforms the inactive ("dormant") *p*-(chloromethyl)styrene into an active cationic or radical species, which can then attack the vinyl group of another inimer.

Scheme 5.2 schematically shows the initial steps in SCVP. The initiation occurs by the addition of the activated B* group to the double bond of another inimer, resulting in the formation of the dimer Ab–A*B*. The asterisk indicates

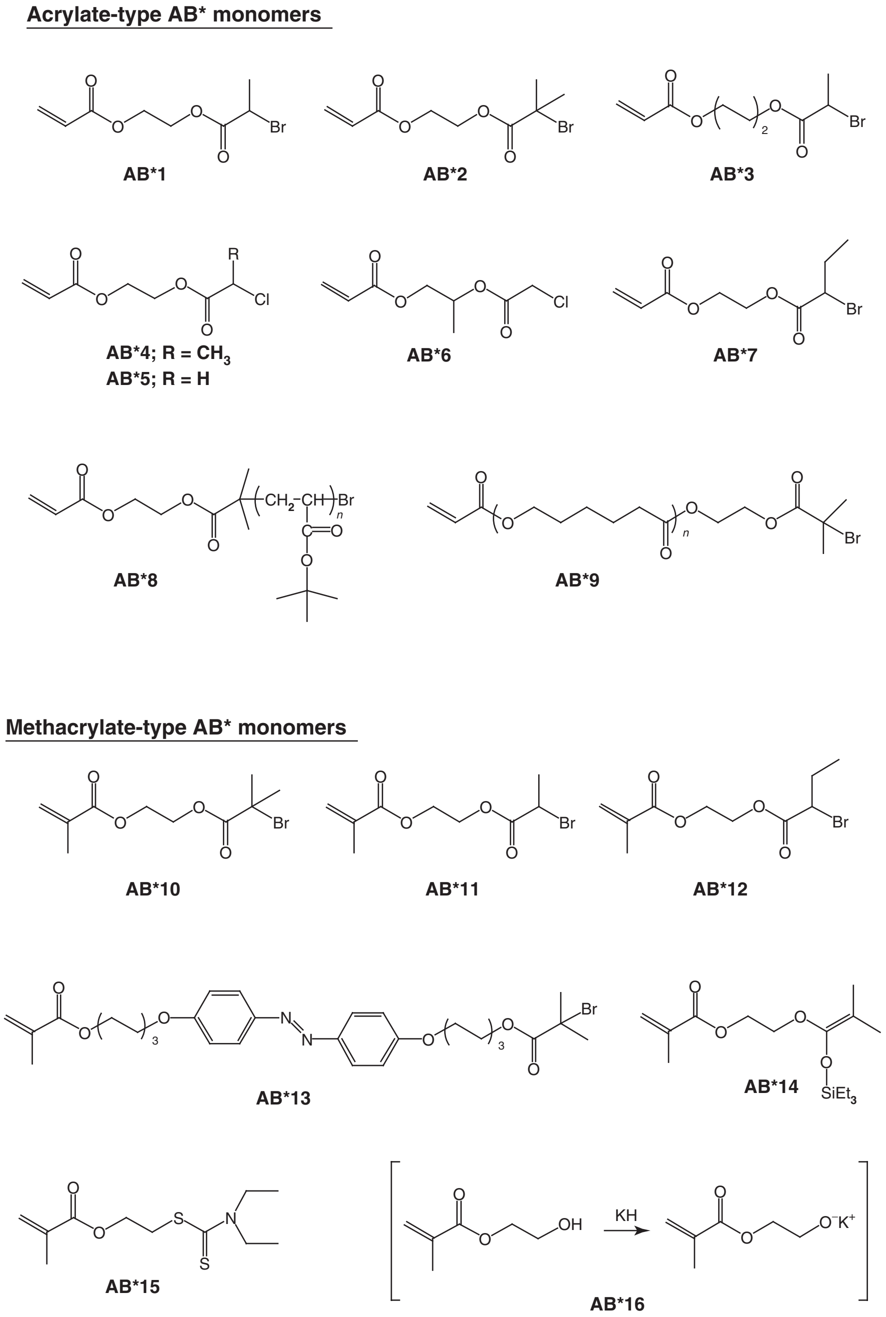


Figure 5.1 AB* inimers used for self-condensing vinyl polymerization (SCVP) and copolymerization (SCVCP).

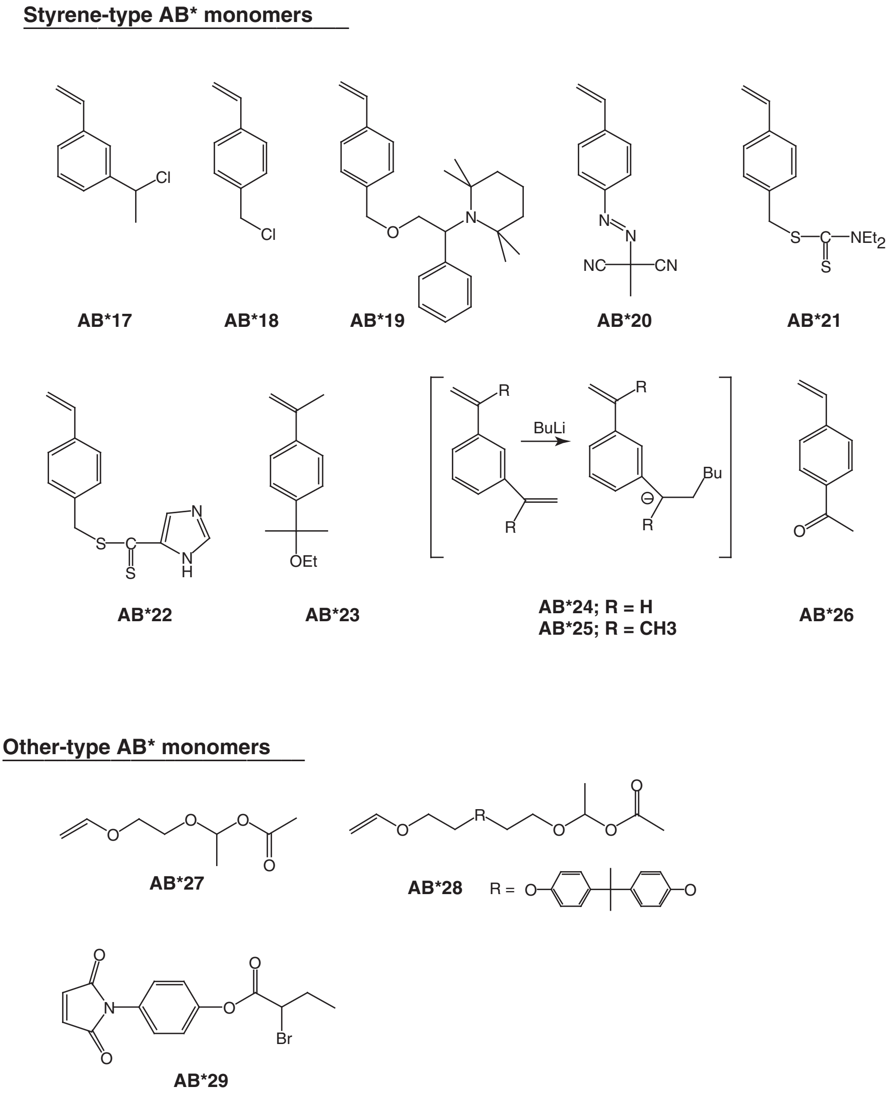
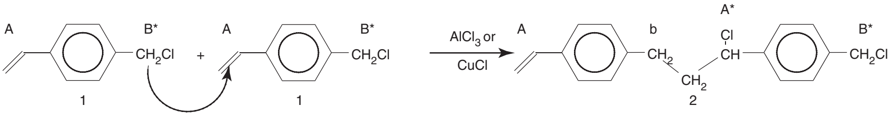


Figure 5.1 (*Continued*)



Scheme 5.1 Initiation step in SCVP of *p*-(chloromethyl)styrene.[22]

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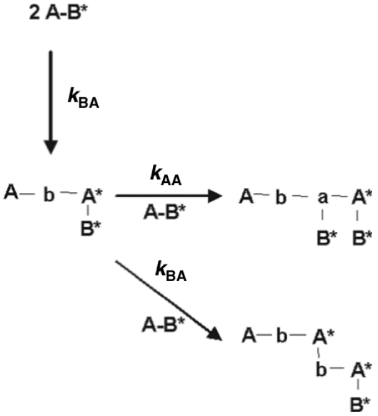

Scheme 5.2 Initial steps in SCVP. Capital letters indicate vinyl groups (A) and active centers (A*, B*); lowercase letters stand for reacted ones (a, b).[24]

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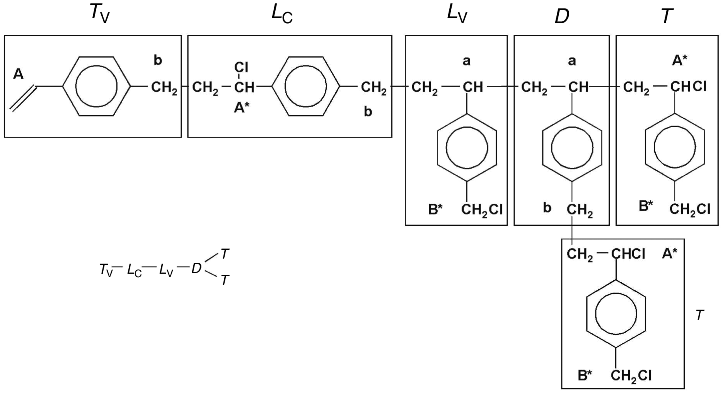
that a structural group can add a monomer; it can be either in its active or dormant form. Lowercase letters indicate that the site has been consumed and can no longer participate in the polymerization. The resulting dimer has two active sites, A* (propagating) and B* (initiating), for possible chain growth besides the vinyl group. Addition of a third monomer unit at either site results in the formation of the trimer that can now grow in three directions. Also, oligomers (e.g., two dimers) or polymers can react with each other, similar (but mechanistically different) to polycondensation. The polymerization can also be initiated by a mono- or multifunctional initiator, leading to better control of MWD and DB, especially when the inimer is added slowly.[23] This will be detailed further below (Section 5.4).

When considering the structure of hyperbranched macromolecules, it is easier to discuss the connectivity of the structural units they consist of rather than



Scheme 5.3 Structure of one possible hexamer obtained from SCVP of *p*-chloromethylstyrene.[25]

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their functional groups. Structural units are composed of a combination of two unlike functional groups. In Scheme 5.3, one of many possible structures of a hyperbranched hexamer is sketched using the two different representations (functional groups and structural units).

The hexamer in Scheme 5.3 contains five different types of structural units. The terminal unit T is made of two active functional groups (A^* and B^*). The T_V unit consists of a vinyl group A and one reacted initiating group b. The branched ("dendritic") unit D is composed of two inactive groups (a and b). Furthermore, the existence of two different types of linear units, L_V (a–B^*) and L_C (A^*–b), respectively, is evident, leading to two different linear analogs. One of these linear polymers is exclusively composed of L_V units and resembles a vinyl polymer. The second linear analog is made of L_C units (exclusive reaction of the initiating groups B^*) and leads to a polycondensate-type structure.

The fraction of branched units is typically expressed as the degree of branching DB. According to the definition first introduced by Hawker *et al.*[26] and Kim[27] and later modified by Hölter *et al.*[28,29] and Yan *et al.*,[25] it reads for a single molecule

$$\mathrm{DB} = \frac{D + T - 1}{D + T + L - 1} \tag{5.1}$$

Note that the symbols given in Eq. (5.1) mean fractions of the respective structural units, and L in our case is the sum of fractions of L_V and L_C units. As an AB^* inimer leads to trifunctional branch points, the number of endgroups exceeds the number of branch points by 1 ($D = T - 1$) and Eq. (5.1) can be rewritten in different ways:

$$\mathrm{DB} = \frac{2D}{2D + L} = \frac{2(T - 1)}{2(T - 1) + L} \tag{5.2}$$

5.2.2 Various Mechanisms of SCVP

In an ideal SCVP process, living polymerization systems are preferred in order to avoid cross-linking reactions and gelation caused by chain transfer or recombination reactions. Cationic,[2,13] anionic,[9] group transfer,[4,30] photo-initiated radical,[31–33] ruthenium-catalyzed coordinative,[34] and controlled radical polymerization processes have been employed. The latter systems include atom transfer radical polymerization (ATRP),[35,36] nitroxide-mediated radical polymerization,[37] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[38,39] More references are given below. Similar to cationic and group transfer polymerizations (GTPs), these systems are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of dormant species; however, they are more tolerant of functional groups and impurities.

AB^* inimers used for SCV(C)P are listed in Figure 5.1. A variety of acrylate-type inimers have been reported, including **AB*1,2**,[5–7] **3**,[40] **4**,[41] **5**,[42] **6**,[43] **7**,[44] **8**,[45] and **9**.[46] In general, Cu-based ATRP was employed for SCVP of these acrylate-type inimers having an acrylate (A) and a bromoester group (B*), capable of initiating ATRP. For example, it was demonstrated that the polymerization of the inimer **AB*1** catalyzed by CuBr/4,4′-di-*tert*-butyl-2,2′-bipyridine at 50 °C provided a hyperbranched polymer (DB = 0.49).[5,6] The significant influence of solubility of the deactivator and of the polymerization temperature, which are closely related to the concentration of Cu(II), on the topology of the resulting polymers has also been reported.[7] However, methacrylate-type inimers **AB*10** and **AB*11** as well as an acrylate-type inimer **AB*2** could not be successfully polymerized by such Cu-based ATRP despite variations in ligand and temperature.[47] It was speculated that the tertiary radical sites generated from methacrylate moieties (A) and/or the 2-bromoisobutyryloxy moieties (B*) coupled rapidly, forming an excess amount of deactivating Cu(II) species, and prevented polymerization. For the preparation of hyperbranched methacrylates, Cu-based ATRP with addition of zero-valent copper for **AB*10** and **AB*11**,[47] Ni-based controlled radical polymerization for **AB*10**,[48] Cu-based ATRP for **AB*12**[49] and **AB*13**,[50] GTP for **AB*14**,[4,30,51] photo-initiated radical polymerization for **AB*15**,[33] and anionic polymerization for **AB*16**[52] have been employed.

For SCVP of styrenic inimers, the mechanism includes cationic (**AB*17**[2] and **AB*23**[13]), atom transfer radical (**AB*18**[8,11]), nitroxide-mediated radical (**AB*19**[3]), RAFT (**AB*22**[53]), anionic (**AB*24**[54] and **AB*25**[9]), photo-initiated radical (**AB*20**[31] and **AB*21**[32,55,56]), and ruthenium-catalyzed coordinative (**AB*26**[34]) polymerization systems. Another example involves vinyl ether–type inimers, **AB*27** and **AB*28**, which undergo cationic polymerization in the presence of a Lewis acid activator, such as zinc chloride.[1,57,58] **AB*29** was employed as a kind of AB* monomer, which comprises heat resistant units of maleimide and benzene ring.[59] The ATRP of the maleimide-type AB* monomer was conducted using the complex of CuBr/2,2′-bipyridine, and the copolymerization with styrene resulted in the formation of hyperbranched polymer.

Note that polymerization of compounds **AB*15**, **AB*20**, and **AB*21** is based either on a dithiocarbamate radical formed by UV radiation or on the methylmalodinitrile radical formed by decomposition of an azo group. These fragments act as reversible terminating/transfer agents, but not as initiators. Hence, these compounds cannot be regarded as initiator monomers, but the mechanism is analogous to SCVP. There are also several accounts of preparing branched polymers from meth(acrylate) derivatives,[60–63] in which polymerization systems can be regarded as SCV(C)P analogs.

5.2.3 Kinetics and MWD

Scheme 5.2 allows us to set up reaction schemes for SCVP. In the simplest case, let us assume that

1. only one double bond is present per molecule;
2. intramolecular reactions are not occurring;

3. there are i active sites of A^* and/or B^* centers in every i-mer; and
4. the intrinsic reactivities of propagating A^* and initiating B^* groups are equal ($k_{AA} = k_{BA} = k$; or, by defining the reactivity ratio $r = k_{AA}/k_{BA} = 1$).

The conversion of vinyl groups (not monomers or inimers!) x follows a first-order relationship on the reduced time, that is, $\tau = kI_0t$ (cf. Figures 5.2 and 5.3 for $r = 1$).

$$-\ln(1-x) = kI_0t = \tau \tag{5.3}$$

where I_0 denotes the initial concentration of the inimer.

Since the number of active centers of a molecule is equal to the degree of polymerization P, its reactivity is proportional to P. Consequently, the average degrees of polymerization read[22]

$$P_n = \frac{1}{1-x} = e^{\tau} \tag{5.4a}$$

$$P_w = \frac{1}{(1-x)^2} = e^{2\tau} \tag{5.4b}$$

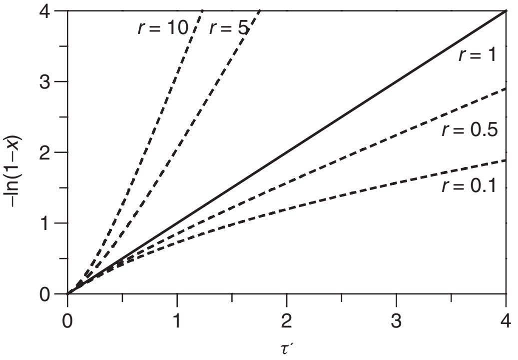

Figure 5.2 First-order plot of conversion of vinyl groups x versus reduced time $\tau' = k_{BA}I_0t$ for SCVP with various reactivity ratios $r = k_{AA}/k_{BA}$.[22]

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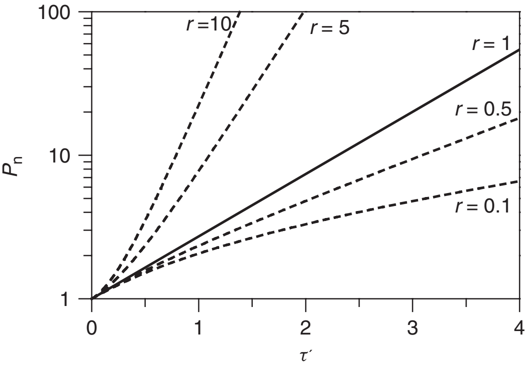

Figure 5.3 Dependence of number-average degree of polymerization P_n on reduced time $\tau' = k_{BA}I_0t$ for SCVP at various ratios of rate constants $r = k_{AA}/k_{BA}$.[22]

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and

$$D = \frac{P_w}{P_n} = \frac{1}{1-x} = \mathrm{e}^{\tau} = P_n \tag{5.5}$$

According to Eq. (5.5) the number-average degree of polymerization equals the polydispersity index. Thus, a hyperbranched polymer prepared by SCVP exhibits an extremely broad MWD, roughly twice as broad as in the polycondensation of an AB_2 monomer.

This feature can be understood on the basis that each growing chain may couple with another chain, in analogy to a polycondensation process. At the same time, the rate at which a given polymer chain adds to another chain is proportional to the number of its functional groups. As this number equals its degree of polymerization, larger molecules will grow at the cost of the small ones, giving an additional increase in polydispersity.

Generally, in SCVP systems, the reactivities of initiating B^* and propagating A^* groups may be different from each other and assumption (4) is no longer fulfilled. Before entering a detailed discussion, however, let us consider the two linear analogs in terms of unequal reactivity of the functional groups (Scheme 5.2). For $k_{AA} \ll k_{BA}$, we obtain only L_C units composed of A^* and b groups, leading to a polymer of structure that resembles a polycondensate.

$$\mathrm{Ab} - [-\mathrm{A}^*\mathrm{b}-]_n - \mathrm{A}^*\mathrm{B}^* \tag{5.6}$$

On the other hand, for $k_{AA} \gg k_{BA}$, we obtain only L_V units composed of a and B^* groups corresponding to a normal vinyl polymer with $[-\mathrm{a}-]_n$ main chain and pendant B^* groups.

$$\mathrm{Ab} - [-\mathrm{a}(\mathrm{B}^*)-]_n - \mathrm{A}^*\mathrm{B}^* \tag{5.7}$$

The kinetic treatment of a system exhibiting unequal rate constants, that is, $k_{AA} \neq k_{BA}$, can be solved only by numerical methods.[22,64] Kinetics and MWD can be represented as a function of a modified reduced time $\tau' k_{BA} I_0 t$.

The corresponding semilogarithmic plot (Figure 5.2) indicates that the kinetics deviates from first order for $r \neq 1$. For $r > 1 (k_{AA} > k_{AB})$, induction periods are observed because of the fact that A^* groups are only formed in the course of the polymerization process. The opposite occurs for $r < 1$ since here the fraction of more reactive B^* groups steadily decreases. Interestingly, the expression for P_n is still independent of the reactivity ratio r; however, its dependence on reaction time $\tau' = k_B I_0 t$ is a function of r (Figure 5.3).

The influence of the reactivity ratio r on the MWD may be exemplified for the limiting case $r = 0$ (i.e., $k_{AA} = 0$). Here, SCVP degenerates into a normal polycondensation of linear polymers with B^* end groups and unreactive A^* groups in the chain, leading to a Schulz–Flory distribution with polydispersity index $P_w/P_n = 1 + x$. For other ratios, the polydispersity index at high conversions, that is, $x \rightarrow 1$, increases from $P_w/P_n = 2$ for $r = 0$ to very large values; $P_w/P_n > P_n$ for $r > 1$ (Figure 5.4). This is surprising since, for $r \gg 1$, nearly linear polymers with a terminal A^* group, few in-chain A^* groups, but mostly

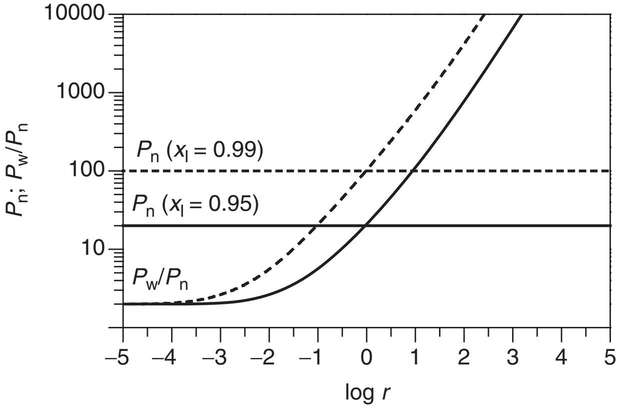

Figure 5.4 Dependence of number-average degree of polymerization P_n and polydispersity index P_w/P_n on reactivity ratio $r = k_{AA}/k_{BA}$ for SCVP at given conversions of vinyl groups $x = 0.95$ (———) and $x = 0.99$ (— — —).[22]

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pendant B* groups, are expected. Since the inimer only has a (nearly unreactive) B* group, we now have a very slow initial phase where active A* centers are formed—a situation entirely different to the case $r = 0$. It should be noted that in the calculated polydispersities the unreacted inimer is included. Since in real experiments the inimer is typically removed in the workup, the corresponding MW averages differ and the polydispersity index becomes lower. Details are given in the original publication.[22]

5.2.4 Degree of Branching

Using a kinetic approach, the corresponding fractions of the functional groups depending on the conversion of inimer, x, are obtained.[25] As the fractions of structural units are identical to the products of the fractions of the functional groups of which they consist, for example, $L_V = a \cdot B^*$, the DB as a function of conversion of vinyl groups reads (cf. Figure 5.5 in case $r = 1$)

$$\mathrm{DB} = \frac{2(1 - e^{-x})(x - 1 + e^{-x})}{1 - (1 - x)(2 - e^{-x})} \tag{5.8}$$

At full conversion of double bonds ($x = 1$), the value of DB_∞ is

$$\mathrm{DB}_\infty = 2e^{-1}(1 - e^{-1}) \approx 0.465 \tag{5.9}$$

Unequal reactivities also affect the DB. Figure 5.5 shows a monotonous increase of DB with conversion for all values of r; however, the initial slopes as well as the final values differ. At all conversions x, the highest values of DB are found at $r \approx 2.59$. The effect of the reactivity ratio r on the DB at full conversion,

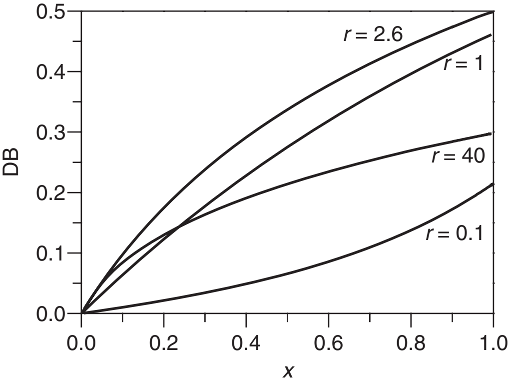

Figure 5.5 Dependence of the degree of branching (DB) on conversion of vinyl groups x for SCVP at various reactivity ratios $r = k_{AA}/k_{BA}$.[25]

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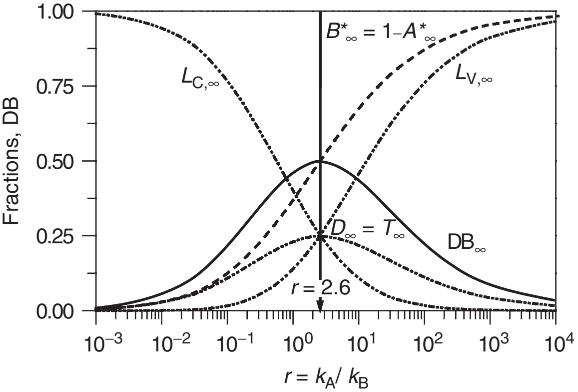

Figure 5.6 Fractions of structural units and degree of branching (DB_∞) as a function of $r = k_{AA}/k_{BA}$ for full conversion, that is, $x = 1$.[25]

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DB_∞, as well as on the fractions of the structural units at full conversion is displayed in Figure 5.6. Obviously, the maximum value of $DB_\infty = 0.5$ is found at $r \approx 2.59$—that is, equal reactivities do not lead to the maximum DB! The fraction of "vinyl-type" linear units L_V increases and that of "polycondensate-type" linear units L_C decreases with r, whereas the fractions of branch points and terminal units exhibit a maximum. Exactly at $r \approx 2.59$, all four structural units have equal fractions, $D_\infty = T_\infty = L_{V,\infty} = L_{C,\infty} = 0.25$, and consequently DB_∞ reaches its maximum value. For $r \ll 2.59$ or $r \gg 2.59$, polymers with predominant linear units, L_C or L_V, respectively, are formed at the expense of branched and terminal ones. At $r = 1$, the fraction of "polycondensate-type" linear units, L_C, significantly exceeds that of the "vinyl-type" ($L_C = 3L_V$) due to the continuous conversion of L_V to L_C units in the reaction with end groups. At the ratio $r \approx 2.59$, this value somehow self-corrects unfavorable statistics and provides polymers with the highest DB.

The fractions of functional groups A^* or B^* can be employed to express r

$$r = \frac{1 - x - B^*}{1 + \ln B^* - B^*} \tag{5.10}$$

or at full conversion of vinyl groups ($x = 1$),

$$r_\infty = \frac{B^*_\infty}{B^*_\infty - \ln B^*_\infty - 1} \tag{5.11}$$

and the reactivity ratio can be determined experimentally (e.g., by NMR). Note, that only one type of group has to be known, as A* and B* are linked.[25] Once r is known, the DB can be obtained using Figure 5.6. It has to be kept in mind, however, that this procedure is still based on assumptions (1)–(3) in Section 5.2.3, which may not be entirely fulfilled in an experiment.

5.2.5 Comparison with Experimental Data

Unfortunately, only a few publications give detailed experimental data regarding the kinetics of the SCVP. For **AB*1**,[5,11]**AB*14**,[51] **AB*17**,[2] and **AB*18**,[6,8] the dependence of MWs on reaction time fits well to the straight line expected from Eq. (5.4b) in a semilogarithmic plot. For extended reaction times, the curve flattens, which may indicate the occurrence of side reactions, for example, cyclization, where the vinyl group of the core unit reacts with an active B* or A* center.[65,66] This side reaction removes the vinyl group from the macromolecules, turning it into a multifunctional initiator. As will be seen below, the presence of the latter decreases the polydispersity. Thus, typically, lower polydispersities are found experimentally than given by theory.

A detailed analysis of the reactivity ratio r and DB is often hampered by the complexity of the hyperbranched polymers' NMR spectra. Using Eqs. (5.10) and (5.11), reactivity ratios have been determined for various SCVP techniques. In ATRP (**AB*1** and **AB*18**)[6,8,11] as well as in GTP (**AB*14**),[30,67] the ratios fall into the same interval: $2.5 \le r \le 126$. For **AB*1**, the effect of ATRP reaction conditions with respect to temperature, catalyst concentration, and catalyst solubility on the reactivity ratio were studied in detail. By optimizing the reaction conditions, a reactivity ratio of $r = 2.5$ was obtained—a value close to the ratio at which the maximum DB is expected, cf. Figure 5.6. Moreover, an increased reactivity of the propagating A* groups seems to be a general feature of SCVP.

5.3 SELF-CONDENSING VINYL COPOLYMERIZATION (SCVCP)

The SCVCP of AB* inimers with conventional vinyl monomers M has a number of benefits compared to a standard SCVP:

1. Conventional monomers are in most cases cheaper and easier to obtain than the corresponding inimers, lowering the expenses of obtaining a hyperbranched polymer.
2. Depending on the chemical nature of the comonomer, different types of functional groups can be incorporated.

3. The polydispersity index can be controlled by the comonomer-to-inimer ratio, $\gamma = \mathrm{M/AB}^*$, and it is expected to be lower compared to hyperbranched polymers prepared by SCVP.
4. Copolymerization allows the control of the DB. Clearly, the DB of the copolymers is expected to be lower than the DB of the corresponding homopolymer; however, the effect on macroscopic quantities such as intrinsic viscosity and radius of gyration should be small.

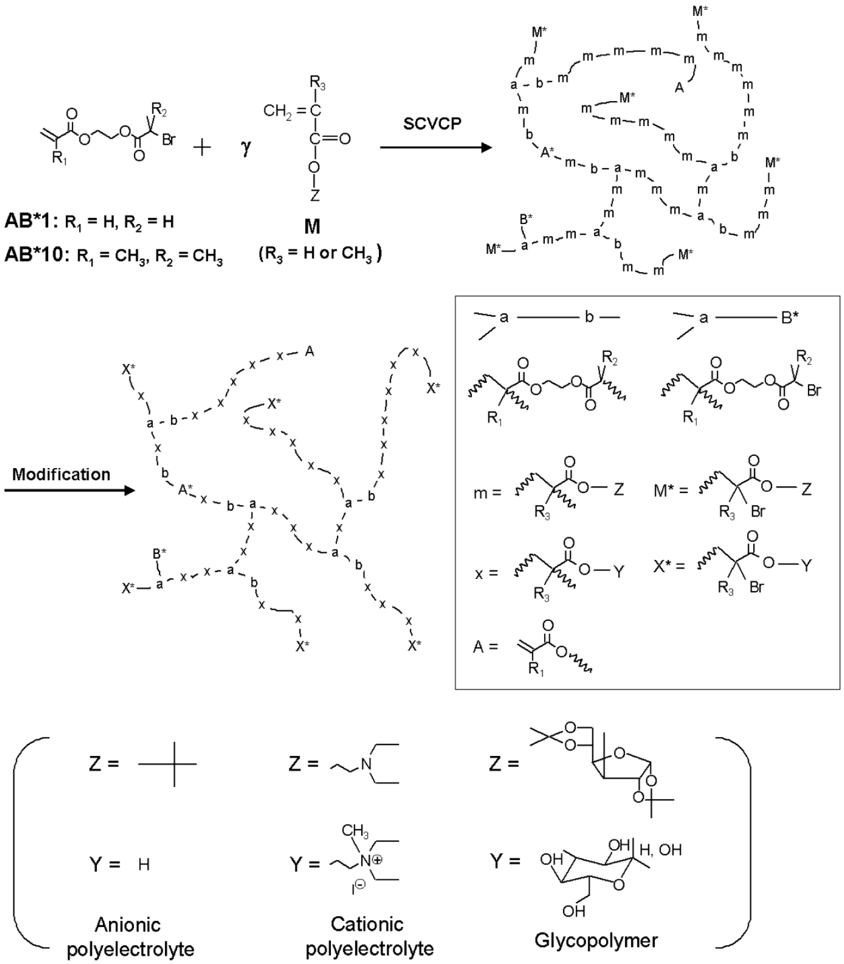
5.3.1 Experimental Data

Several approaches have been reported for the synthesis of hyperbranched (meth)acrylates via SCVCP. Highly branched PMMA was synthesized by SCVCP of MMA, with **AB*14** having a methacrylate group (A) and a silylketene acetal group (B*), capable of initiating GTP.[12] A series of hyperbranched acrylates having different DBs and MWs have been synthesized by SCVCP of the acrylate-type inimer **AB*1** with *tert*-butyl acrylate via ATRP.[15] SCVCP of **AB*1** with methyl acrylate was also reported.[14]

Scheme 5.4 shows the general route to randomly branched functional polymers, which include anionic polyelectrolytes,[15] cationic polyelectrolytes,[68] and glycopolymers,[69,70] by SCVCP via ATRP. Randomly branched (arborescent) cationic polyelectrolytes were synthesized by SCVCP of a methacrylic **AB*10** with diethylaminoethyl methacrylate via ATRP, followed by quaterization.[68] By quaterization with methyl iodide, water-soluble cationic polyelectrolytes with controllable branched structures were obtained, which could provide viable tailored materials with unique properties for various applications, such as chemical sensing and gene delivery systems.

Recently, much attention has been paid to use SCVCP for the preparation of randomly branched polyelectrolytes.[71,72] They are of special interest because of their industrial importance and scientifically interesting properties.[72] One challenge in this field is to produce randomly or regularly branched polyelectrolytes, which are suitable for various applications as well as for quantitative analysis of the relation between the properties and the architectures. The material properties of branched polymers depend not only on the MW and DB but also on the number and type of branching.

Highly branched poly(*tert*-butyl methacrylate) was obtained by SCVCP of the inimer **AB*14** with *tert*-butyl methacrylate, which is a precursor of branched poly(methacrylic acid).[12] Acid-catalyzed hydrolysis of the *tert*-butyl groups and neutralization with NaOH produced a water-soluble, highly branched poly(methacrylic acid) sodium salt.[71] The synthesis of randomly branched poly(acrylic acid) (PAA), which is a weak anionic polyelectrolyte, was conducted by SCVCP of *t*BuA with an inimer **AB*1** having an acrylate (A) and an α-bromopropionate group (B*), capable of initiating ATRP, followed by hydrolysis of the *tert*-butyl groups.[15]



Scheme 5.4 General route to randomly branched functional polymers by self-condensing vinyl copolymerization (SCVCP).

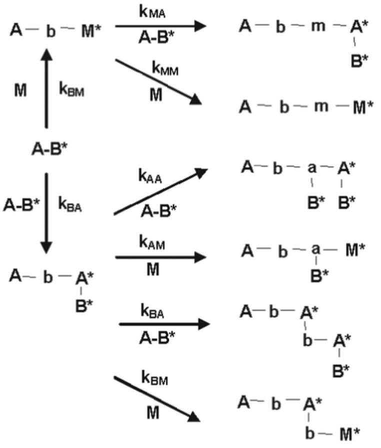
SCVCP of the sugar-carrying monomer with AB* inimer via ATRP provides a straightforward strategy for generating water-soluble hyperbranched glycopolymers and their precursors. Hyperbranched glycopolymers were synthesized by SCVCP of an acrylic **AB*1** inimer with the sugar-carrying acrylate 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-*α*-D-glucofuranoside, followed by deprotection of the isopropylidene protecting groups.[69] This work broadens the scope of facile synthesis of branched glycopolymers by a controlled polymerization technique, in which the architecture can be simply manipulated by the nature and composition of sugar-carrying vinyl monomer used as a comonomer. A similar strategy was applicable for methacrylate-type hyperbranched glycopolymers, and an isopropylidene-protected sugar-carrying methacrylate, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, was selected as a comonomer. Synthesis of methacrylate-type hyperbranched glycopolymers was conducted by SCVCP of the methacrylic **AB*10** inimer with the sugar-carrying methacrylate via ATRP.[70] Deprotection of the isopropylidene protecting groups of the branched polymers resulted in water-soluble glycopolymers with randomly branched architectures. It was found that a suitable choice of the polymerization conditions is required to obtain water-soluble glycopolymers with characteristic highly branched architectures, which can then be manipulated for various biological, pharmaceutical, and medical applications.

An azobenzene-containing inimer **AB*13** was used to prepare hyperbranched homopolymer by SCVP and copolymers by SCVCP with its precursor 6-(4-[4-(6-hydroxyhexyloxy)phenylazo]phenoxy)hexyl methacrylate as a comonomer using ATRP.[50] It was found that the *trans–cis* isomerization of the azobenzene chromophore in the different degree of the branching polymers was markedly different. An attempt to prepare randomly branched poly(*N*-isopropyl acrylamide)s, which show characteristic temperature responsive properties in an aqueous solution, was reported by the polymerization with a styrene derivative having dithioester group **AB*22** as an inimer.[53]

Alternative methods to SCVCP have been developed recently. For example, branched poly(methyl methacrylate)s have been prepared using conventional solution-phase free-radical polymerization of methyl methacrylate in the presence of a branching divinyl comonomer, such as ethylene glycol dimethacrylate and divinylbenzene, with appropriate levels of dodecanethiol chain transfer agent.[73,74] Using mercaptanes as chain transfer agents, cross-linking can be prevented, resulting in the formation of soluble branched polymers in moderate to good yields without gelation. An extension of this concept to controlled radical polymerizations has been recently reported using several systems. Cu-based ATRP or GTP methodologies were employed for copolymerization of methyl methacrylate and ethylene glycol dimethacrylate to yield soluble branched polymers in facile one-pot reactions.[75] Appropriate choice of reaction composition and conditions was required. Highly branched poly(2-hydroxypropyl methacrylate) has been prepared by ATRP using a disulfide-based dimethacrylate branching agent.[76] RAFT polymerization was also used to produce poly(methyl methacrylate) hyperbranched polymers via the one-pot copolymerization of methyl methacrylate and ethylene glycol dimethacrylate as a branching agent, mediated by 2-(2-cyanopropyl) dithiobenzoate.[77] These works demonstrate that the controlled character of the polymerization offers advantages for the synthesis of branched vinyl polymers by not only SCV(C)P using inimers but also facile methods using multifunctional vinyl monomers.

5.3.2 Kinetics and MWD

SCVCP can be initiated by two ways (Scheme 5.5): either by addition of the active B* group in an AB* inimer to the vinyl group A of another AB* inimer



Scheme 5.5 Initial steps in SCVCP. Capital letters indicate vinyl groups (A and M) and active centers (A*, B*, M*); lowercase letters stand for reacted ones (a, b, m).[24]

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forming a dimer with two active sites A* and B*; or by addition of a B* group to the vinyl group of monomer M forming a dimer with one active site M*. Both the initiating B* group and the newly created propagating centers A* and M* can react with any vinyl group in the system. Thus, we have three different types of active centers, A*, B*, and M*, in the dimers, which can react with double bonds A (inimer and macromolecules; each macromolecule contains strictly one double bond) and M (monomer).

The addition of a linear comonomer M also affects the type of structural units of the macromolecule. Besides units already discussed for SCVP ($T_I = A^*B^*$, $T_V = Ab$, $L_C = A^*b$, $L_V = aB^*$, $D = ab$), the comonomer terminal $T_M = M^*$ and linear unit $L_M = m$ have to be accounted for. In consequence, we have six different possible reactions to consider. First let us discuss the simplest case, that is, assumptions (1)–(4) in Section 5.2.3 are fulfilled and all rate constants are equal. Introducing the dimensionless comonomer ratio $\gamma = M_0/I_0$, which corresponds to the theoretical degree of homopolymerization of monomer M initiated by inimer molecules, we obtain the conversion of monomer x_M of the inimer x_I and of vinyl groups x as a function of time.[78]

$$x_M = \frac{M_0 - M}{M_0} = 1 - \exp(-kI_0t) \tag{5.12}$$

$$x_I = 1 - (1 - x_M)e^{-(\gamma+1)x_M} \tag{5.13}$$

$$x = \frac{I_0 - A}{I_0} = x_M \tag{5.14}$$

The time dependencies of the monomer and double bond conversion are described by a first-order law like in a normal living polymerization process. The dependence of inimer conversion on time, however, cannot be expressed in such a simple manner. Figure 5.7 shows that the inimer is used up much faster than the monomer. At very high γ, it is consumed almost instantaneously like

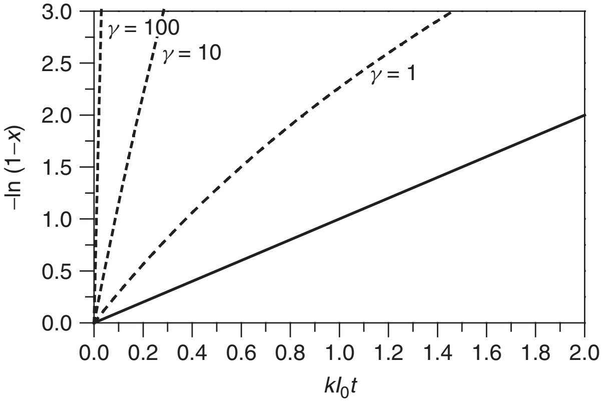

Figure 5.7 First-order time-conversion plot for various ratios monomer/inimer $\gamma = M_0/I_0$; (———) : x_M, x_A; (— — —) : x_I. All rate constants were assumed to be equal.[78]

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a fast initiation process in normal living polymerization. On the other hand, for low γ, the behavior resembles a slow initiation process.

In case we do not assume that the reactivity of all functional groups to be equal, there are six different rate constants to be considered (Scheme 5.5). Of course, it is possible to solve such a system; however, it would lead to an indigestible amount of information. Let us suppose that A* and B* groups are of equal reactivity, although different from that of the M* group.[79] This leads to

$$k_{AA} = k_{BA} \equiv k_{IA} \quad \text{and} \quad k_{AM} = k_{BM} \equiv k_{IM} \tag{5.15}$$

Generally speaking, this assumption is not always true,[7,8,30,67] but in many cases the difference in the reactivity between A* and B* groups is smaller than between former groups and M* groups. That reduces the number of different rate constants from 6 to 4. In analogy to conventional copolymerizations, let us introduce the monomer reactivity ratios[79]

$$r_I = \frac{k_{IA}}{k_{IM}}$$

and

$$r_M = \frac{k_{MM}}{k_{MA}} \tag{5.16}$$

and limit the discussion to an ideal copolymerization case where $r_I r_M = 1$. The detailed discussion of nonideal cases is beyond the scope of this text; the interested reader is referred to the original publication.[79] Instead, let us discuss two special cases: the formation of "macroinimers" and the formation of "hyperstars."

The macroinimer case is met if $k_{IM} \gg k_{IA}$ and $k_{MM} \gg k_{MA}$ ($r_I \ll 1$ and $r_M \gg 1$). The polymerization will proceed in two subsequent steps: First, the inimer will act as an ordinary initiator and add monomer until the latter is completely consumed, cf. Figure 5.8. The "macroinimer" (see Section 5.5 for a more detailed discussion) is composed of one vinyl group A and one active group M*,

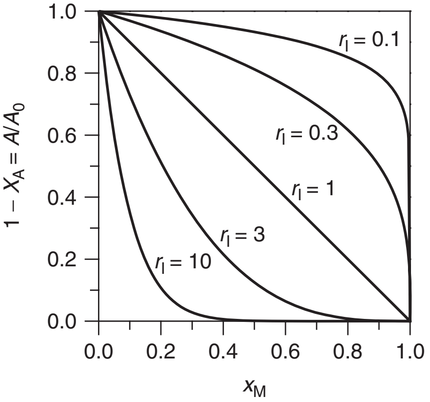

Figure 5.8 Dependence of the concentration of macromolecules on monomer conversion for $\gamma = 10$ and $r_I r_M = 1$.[79]

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and exhibits a degree of polymerization of $P_n = M_0 x_M / I_0 = \gamma x_M$. If the initiation process is fast ($k_{IM} \geq k_{MM}$), the macroinimers should be Poisson-distributed (i.e., $P_w/P_n = 1/P_n$). In case of $k_{IM} < k_{MM}$, the process resembles slow initiation, leading to the Gold distribution[80] with $P_w/P_n \leq 4/3$. Finally, for $x_M \to 1$ these macroinimers will undergo SCVP forming a hyperbranched structure.

"Hyperstars" are created if $k_{IM} \ll k_{IA}$ and $k_{MM} \ll k_{MA}$ ($r_I \gg 1$ and $r_M \ll 1$). Here, inimer molecules will first undergo SCVP and only at very high conversions of inimer and polymer vinyl groups, that is, $x_A \to 1$, they will add monomer M, leading to star-shaped polymers with a hyperbranched core, cf. Figure 5.8 and Refs.[3,67,81]. This will result in a high degree of polymerization and a broad MWD already at small monomer conversion. However, because at higher conversions the polymer vinyl groups' accessibility may be reduced compared to those of monomer, this case may not be probable if vinyl groups of the inimer and monomer have the same chemical nature. It may become important if the vinyl groups of the inimer are much more reactive than those of the comonomer M.

The general effects of different rate constants on the course of polymerization can be deduced from Figure 5.8. Unlike the case of equal rate constants, where the conversions of vinyl groups and monomer are equal, at $r_I < 1$ (or $r_M > 1$) vinyl groups are consumed slower than monomer. At very small r_I, the conversion of vinyl groups A is very small even at x_M close to unity (macroinimer case). If, on the other hand, $r_I > 1$, vinyl groups are consumed faster than monomer (hyperstar case).

As molar masses of monomer m_M and inimer m_I are usually different, it makes more sense to calculate average MWs M_n and M_w rather than average degrees of polymerization. If molar masses are equal or in case $\gamma \gg 1$, the effect of the inimer on the MW may be neglected and both terms can be used. The number-average MW is equal to the ratio of total weight of polymer molecules to the number of macromolecules N. It reads as follows for the case in which all rate constants are equal[78]:

$$M_n = \frac{m_{\mathrm{M}}\gamma x_{\mathrm{M}} + m_{\mathrm{I}}x_{\mathrm{I}}}{x_{\mathrm{I}} - x_{\mathrm{A}}} = \frac{m_{\mathrm{M}}\gamma x_{\mathrm{M}} + m_{\mathrm{I}}(1-(1-x_{\mathrm{M}})\mathrm{e}^{-(\gamma+1)x_{\mathrm{M}}})}{(1-x_{\mathrm{M}})(1-\mathrm{e}^{-(\gamma+1)x_{\mathrm{M}}})}$$

$$\text{for } \gamma \gg 1{:}P_n = \frac{\mathrm{M_n}}{m_{\mathrm{M}}} = \frac{\gamma x_{\mathrm{M}}}{(1-x_{\mathrm{M}})} = P_{n,\mathrm{M}}P_{n,\mathrm{I}} \tag{5.17}$$

Thus, for high γ, P_n is the product of the number-average degree of polymerization generated by the living polymerization of monomer $P_{n,\mathrm{M}}$ initiated by inimer $P_{n,\mathrm{I}}$. The expression for weight-average MW, that is, M_w, for equal rate constants is obtained by solving the kinetic differential equation derived from Scheme 5.5.[78]

$$M_{\mathrm{w}} = \frac{m_{\mathrm{M}}^2\gamma x_{\mathrm{M}}((1-x_{\mathrm{M}})^2 + \gamma x_{\mathrm{M}}) + 2m_{\mathrm{M}}m_{\mathrm{I}}\gamma x_{\mathrm{M}} + m_{\mathrm{I}}^2(1-(1-x_{\mathrm{M}})^3\mathrm{e}^{-(\gamma+1)x_{\mathrm{M}}})}{(1-x_{\mathrm{M}})^2(m_{\mathrm{M}}\gamma x_{\mathrm{M}} + m_{\mathrm{I}}x_{\mathrm{I}})} \tag{5.18}$$

As Eq. (5.18) may be too complicated to be of much use, let us discuss the most important limiting cases. For high conversions, the M_w dependence on x_{M} is governed by the denominator,

$$M_w \propto 1/(1-x_{\mathrm{M}})^2 \tag{5.19}$$

similar to SCVP. For any conversion and high comonomer ratios ($\gamma \gg 1$), the contribution of inimer to M_w can be neglected, and Eq. (5.18) simplifies to

$$M_w = m_{\mathrm{M}}\left(1 + \frac{\gamma x_{\mathrm{M}}}{(1-x_{\mathrm{M}})^2}\right); \text{ or}$$

$$P_w = \frac{M_w}{m_{\mathrm{M}}} = 1 + \frac{\gamma x_{\mathrm{M}}}{(1-x_{\mathrm{M}})^2} \tag{5.20}$$

Hence, the polydispersity index in the limiting case of high conversion and high γ reads for equal rate constants

$$\frac{M_w}{M_n} = \frac{m_{\mathrm{M}}}{M_n} + \frac{1}{1-x_{\mathrm{M}}} \quad \text{or} \quad \frac{P_w}{P_n} = \frac{1}{P_n} + \frac{1}{1-x_{\mathrm{M}}} \approx \frac{1}{1-x_{\mathrm{M}}} = \frac{P_n}{\gamma x_{\mathrm{M}}} \tag{5.21}$$

For high conversion ($x_{\mathrm{M}} \to 1$), that is, for sufficiently high P_n, the first term in Eq. (5.21) can be neglected. Consequently, the polydispersity index is the same as in homopolymerization by a SCVP mechanism, cf. Eq. (5.5), and the dependence of P_w/P_n on x_{M} is not influenced by γ at high conversions. However, P_n increases with γ, cf. Eq. (5.17), and for a given number-average degree of polymerization the polydispersity index decreases with γ, as depicted in Figure 5.9. For high comonomer ratios *and* $x \to 1$, the polydispersity index reaches a limiting value

$$\frac{P_w}{P_n} = \frac{P_n}{\gamma} \tag{5.22}$$

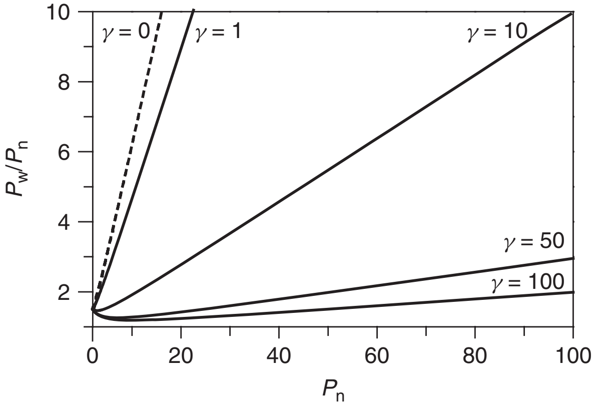

Figure 5.9 Dependence of polydispersity on the number-average degree of polymerization for various ratios monomer/inimer γ. (———) : pure inimer ($\gamma = 0$). All rate constants assumed to be equal.[78]

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In conclusion, for high comonomer ratios, even the SCVCP in the case of equal rate constants can be *formally* regarded as proceeding in two steps: In the first step, monomer molecules add to inimer molecules, forming macroinimers. Because the concentration of monomer is much higher than the concentration of the inimer, this process resembles the initiation process of a normal living polymerization, resulting in a Poisson distribution $P_w/P_n \approx 1 + 1/\gamma$. In the subsequent step, the growth of polymers is mainly driven by linking reactions of the polymeric active groups with double bonds of other macromolecules. This process can formally be described as a normal SCVP of "macroinimers" leading to a broad MWD $P_w/P_n = (1 - x_M)^{-1}$. Clearly, this is only a formal view of the process. In reality, both reactions occur simultaneously.

For nonequal rate constants, the number-average MW can also be described by Eq. (5.17). If we limit the discussion to the case of equal molar masses of monomer and inimer, that is, $m_I = m_M$, Figure 5.10 depicts the dependence of P_n on monomer conversion x_M for a given comonomer ratio $\gamma = 10$.

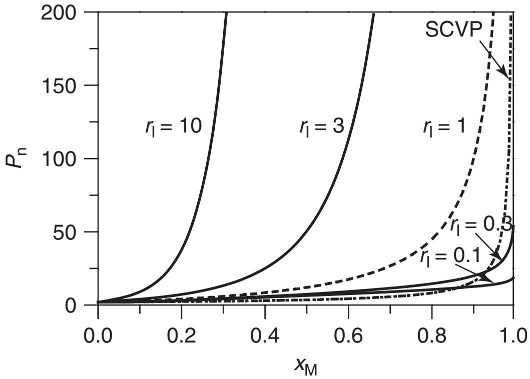

Figure 5.10 Dependence of the number-average degree of polymerization on monomer conversion for various reactivity ratios. $\gamma = 10$. The dash-dotted line corresponds to the SCVP of inimer as a function of x_A.[79]

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Obviously, P_n increases with r_I. At a given r_I, P_n increases almost linearly with γ, similar to the case of equal rate constants. For $r_I \ll 1$, P_n increases with conversion almost linearly up to very high monomer conversion, $x_M < 0.95$, indicating the formation of linear macroinimer. On the contrary, for $r_I \gg 1$, P_n already shows a strong increase at low monomer conversion because inimers are consumed fast, forming the hyperbranched polyinimer via SCVP.

For nonequal rate constants, we find that the polydispersity index increases with increasing P_n, cf. Figure 5.11. The effect of r_I on P_w/P_n is more complex and depends also on γ and P_n. At a given P_n, the polydispersity index as a function of r_I passes a minimum at sufficiently small r_I (for example, for $P_n = 100$ the minimum is reached at $r_I \approx 0.5$ for $\gamma = 10$ and at $r_I \approx 0.1$ for $\gamma = 50$) and then monotonously increases.

5.3.3 Degree of Branching

If assumptions (1)–(4) in Section 5.2.3 are fulfilled (equal rate constants), the DB may directly be derived from Eq. (5.2). As the concentration of all structural units of various types can be calculated,[78] the DB reads

$$\mathrm{DB} = \frac{2(1 - \mathrm{e}^{-(\gamma+1)x_M})\left(x_M - \frac{1-\mathrm{e}^{-(\gamma+1)x_M}}{\gamma+1}\right)}{\gamma x_M + 1 - (1 - x_M)(2 - \mathrm{e}^{-(\gamma+1)x_M})} \tag{5.23}$$

The dependence of DB on conversion for various values of γ is shown in Figure 5.12. It is striking that, for small values of γ, the DB is even higher than in the absence of comonomer. In a SCVP ($\gamma = 0$), a large fraction of A* functional groups at $x = 1$ still remains potentially capable of forming branch points. If small amounts of monomer are present, these may add to the A* groups, resulting in short branches and a monotonous increase of DB with x_M. For higher γ, the monomer will predominantly add to M* groups forming linear units thus

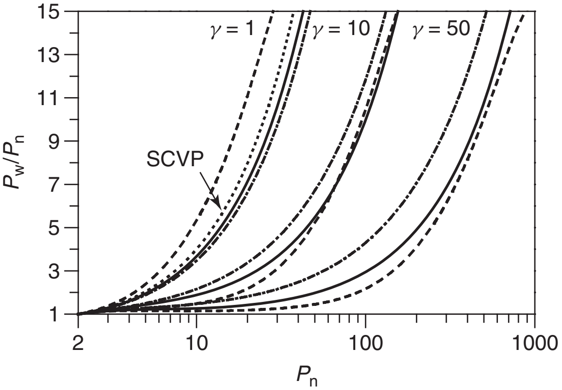

Figure 5.11 Dependence of polydispersity index on number-average degree of polymerization; (– – –) : $r_I = 0,3$; (———):$r_I = 1$; (—·—·—·) $r_I = 3$.[79]

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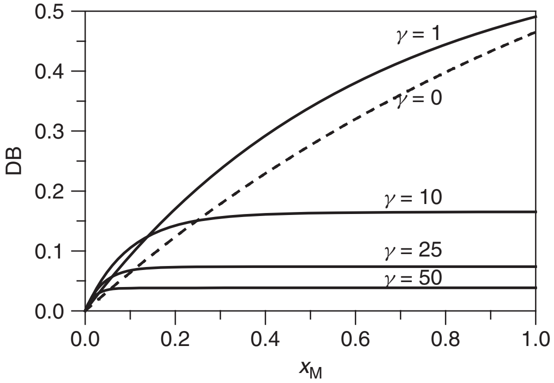

Figure 5.12 Dependence of degree of branching on monomer conversion for various values of γ.[78]

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decreasing DB. For $\gamma \gg 1$, DB very quickly reaches its final value

$$\mathrm{DB} \approx \frac{2}{\gamma + 1} \approx \frac{4\mathrm{DB}_{\mathrm{I},\infty}}{\gamma + 1} \tag{5.24}$$

where $\mathrm{DB}_{\mathrm{I},\infty} = 0.466$ is the final DB obtained in SCVP under conditions of equal rate constants, cf. Eq. (5.9). At full conversion, that is, $x_\mathrm{M} = 1$, Eq. (5.23) simplifies to

$$\mathrm{DB}_\infty = \frac{2(1 - \mathrm{e}^{-(\gamma+1)})(\gamma + \mathrm{e}^{-(\gamma+1)})}{(\gamma + 1)^2} \tag{5.25}$$

Hence, for equal rate constants, DB_∞ exhibits a maximum value of 0.5, which is obtained at a comonomer ratio $\gamma \approx 0.6$.

The DB for nonequal rate constants is strongly influenced by the ratio of rate constants of homopolymerization.[79]

$$a = \frac{k_{\mathrm{IA}}}{k_{\mathrm{MM}}} \tag{5.26}$$

Let us limit the discussion to the dependence of the DB at full conversion, that is, $x_\mathrm{M} = 1$, on the comonomer ratio γ depicted in Figure 5.13. Part a shows an ideal copolymerization, $r_\mathrm{I} r_\mathrm{M} = 1$, for a constant ratio of homopolymerization rate constants $a = 1$ at various monomer reactivity ratios. The effects of a variation of r_M at constant inimer and homopolymerization reactivity ratios, that is, $r_\mathrm{I} = a = 1$, for an nonideal copolymerization are highlighted in Figure 5.13b. In the limiting case of high γ, the DB at full conversion DB_∞ does not differ from the case of equal rate constants, cf. Eq. (5.24) and Figure 5.13. However, if γ is not very high ($\gamma \leq 50$) and a and r_I markedly differ from unity, the difference from the case of equal rate constants may be significant. For various sets of parameters r_I and a (at $r_\mathrm{M} r_\mathrm{I} = 1$, Figure 5.13a), the dependence of DB_∞ on γ passes through a maximum at small $\gamma < 1$ similar to the case of equal rate

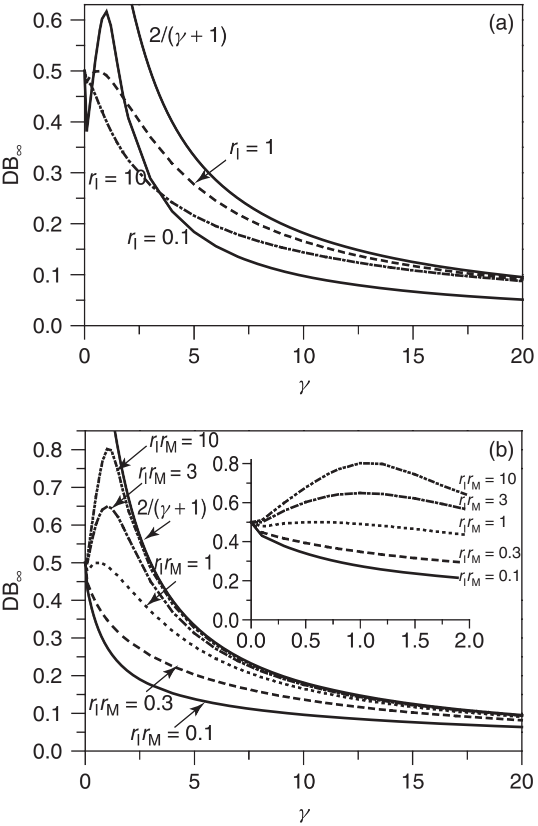

Figure 5.13 Dependence of final degree of branching DB_∞ on γ. (a) $r_I r_M = 1, a = 1$; (b) at $a = 1, r_I = 1$.[79]

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constants. The maximum value of DB_∞ is the higher the value of a (at a given r_I, cf. Figure 5.13a) or the lower the r_I (at a given a, cf. Figure 5.13b).

For $r_I \gg 1$ and $\gamma \gg 1$, star polymers will be formed and the DB becomes meaningless. However, for $r_I \gg 1$ and $2 \geq \gamma > 0$, we will finally obtain a hyperbranched polymer and consecutively short side chains will be added to most L_C and L_V units, leading to a hyperbranched polymer with high DB.

5.3.4 Comparison with Experimental Data

MWs in SCVCP are typically lower than predicted by theory, cf. Eq. (5.24). In case of **AB*14** and MMA, a finite value is reached at complete conversion, which in first approximation is independent of the reaction conditions.[12] This finding is attributed to the cyclization reaction,[65,82] causing the fraction of cyclic x-mers to increase with increasing degree of polymerization P_n and overall conversion. In consequence, the number- and the weight-average MWs do not diverge in the presence of cyclization but remain finite even at complete conversion. When comparing the dependence of the MW averages on the monomer conversion for the

ATRP of **AB*****18** and styrene to the theory for equal rate constants,[11] a very poor fit was observed. Consistent data could be obtained for the nonequal rate constant approach using a parameter set of $a = 1, r_I = 0.3$, and $r_I r_M = 1$ for comonomer ratios $9 \leq \gamma \leq 100$.[79] For even higher comonomer ratios of $100 \leq \gamma \leq 1000$ in the cationic SCVCP of **AB*****23** with isobutylene, a parameter set of $r_I \approx r_M \approx 6$ ($r_I r_M \approx 33$) and $a \approx 2$ gave best fit.[13,79] Again, the predicted polydispersity index exceeded the experimental one—an indication that cyclization was present in this system, too.

The determination of the DB by spectroscopic methods is more challenging due to the low concentration of branch points. Copolymers of **AB*****14** and MMA-d_8 made by GTP and terminated with protons were analyzed by ^{1}H NMR spectroscopy.[12] In the corresponding copolymers, linear monomer units *m* are "invisible" and therefore the protons in A*, B*, and M* centers can be detected even at high comonomer ratios. The DB determined by this approach, $\mathrm{DB_{NMR}}$, agrees qualitatively with the theoretical predictions. In the case of the branched PtBuA obtained by SCVCP of the inimer **AB*****1** with tBuA,[15] the comonomer composition calculated from the ratio of these peaks is in good agreement with the comonomer composition in the feed which corresponds to γ. From these approaches, $\mathrm{DB_{NMR}} = 0.42$ and $\mathrm{DB_{theo}} = 0.49$ can be obtained at $\gamma = 1.1$, respectively. Note that these values represent a rough estimate, as they are calculated on the basis of the assumption of equal rate constants for copolymerization. For low γ values ($\gamma = 0.5$), the DB ($\mathrm{DB_{NMR}} = 0.48$) even exceeds the value for poly(inimer **1**) ($\mathrm{DB_{NMR}} = 0.43$) in accordance with theoretical predictions, cf. Figure 5.12.

5.4 SELF-CONDENSING PROCESSES IN PRESENCE OF INITIATORS

The major drawbacks of hyperbranched polymers are the lack of control of the MW and a broad MWD. Hence, a challenging goal in this field is the development of general AB* polymerization methods that achieve control over DB and narrow the MWD.

5.4.1 Kinetics and MWD

5.4.1.1 Batch Reactions

Based on the discussion of the polymerization mechanism of SCVP, the polydispersity should decrease if we prevent the coupling of two of the polymeric species with themselves. This may be realized by introducing multifunctional core-forming molecules. In SCVP, a multifunctional initiator with *f* functions, J_f, can serve that purpose as it solely reacts with the vinyl group of the inimer.

To account for the ratio of active groups in the initiator to that of the inimer, we shall introduce two new parameters[23,83]:

$$\lambda = \frac{\gamma + 1}{\varepsilon + 1} \quad \text{and} \quad \varepsilon = \frac{fJ_{f0}}{I_0} \tag{5.27}$$

For an SCVP in the presence of multifunctional initiators, we obtain, assuming ideal conditions in the limit of very small initiator concentration, that is, $I_0/J_{f0} = f/\varepsilon \gg 1$, the same expressions like in the absence of initiator, cf. Eqs. (5.4a) and (5.4b), and a polydispersity index equal to P_n. However, in the presence of a core-forming initiator, the average degrees of polymerization approach finite values at $x \to 1$:

$$P_n(x \to 1) = \frac{f}{\varepsilon} = \frac{I_0}{J_{f0}} \tag{5.28a}$$

$$P_w(x \to 1) = \frac{f}{\varepsilon} + \left(\frac{J}{\varepsilon} + 1\right)^2 \tag{5.28b}$$

For high values of P_n, the polydispersity index has a very simple form

$$\frac{P_w}{P_n} \approx 1 + \frac{P_n}{f^2} \tag{5.29}$$

The functionality of initiator does not effect P_n, but it affects P_w and, consequently, the polydispersity index, cf. Eqs. (5.28) and (5.29). At a given inimer/initiator ratio, the use of an initiator with high functionality f significantly decreases the polydispersity index.

For the number-average MW of an SCVCP under ideal conditions (equal rate constants) at full conversion of all comonomers, $x = x_M = x_I = x_A = 1$, and we find

$$M_n(x = 1) = \frac{m_M M_0 + m_I I_0 + m_J J_{f0}}{J_{f0}} \tag{5.30}$$

Consequently, M_n does not diverge as in SCVCP in the absence of initiator, cf. Eq. (5.17) and Figure 5.9, but approaches a final value, which can further be simplified for high comonomer ratios and equal molar masses for the monomer, inimer, and initiator:

$$P_n(x = 1) = \frac{M_0}{J_0} \tag{5.31}$$

Hence, the final value of P_n does not depend on initiator functionality f and is solely defined by the relationship between concentrations of the monomer, inimer, and initiator. In the limiting case of high γ, we obtain for full conversion for P_w[83]

$$P_w(x_M = 1) = \frac{M_0(f^2 J_{f0} + I_0)}{f^2 J_{f0}} \tag{5.32}$$

which leads to the polydispersity index

$$\frac{P_w}{P_n} = 1 + \frac{P_n}{\gamma f^2} \tag{5.32a}$$

Similar to SCVP in the presence of initiator, P_w depends on the initiator functionality f, and the polydispersity index P_w/P_n decreases as f^{-2}, cf. Eq. (5.29).

5.4.1.2 Semibatch Polymerization (Slow Inimer Addition)

The polydispersity can further be decreased if the reaction is performed in a manner in which inimers exclusively react with the preformed core but not with each other. This can be accomplished if the inimer is added slowly enough to keep its concentration infinitesimally low (semibatch conditions). Then, the probability of a reaction of inimer molecules with each other and formation of species P_I ($i > 1$) is negligible. For an ideal system with equal reactivity of all functional groups (assumptions (1)–(4) in Section 5.2.3 are fulfilled; equal rate constants), we obtain the averages P_n and P_w in dependence of the reduced time τ (cf. Eq. (5.3))[23,84]

$$\begin{aligned} P_n &= f(\mathrm{e}^{\tau} - 1) \\ P_w &= 1 + (f + 1)(\mathrm{e}^{\tau} - 1) \\ \frac{P_w}{P_n} &= \frac{1}{P_n} + \frac{f+1}{f} \end{aligned} \tag{5.33}$$

For sufficiently high τ ($\mathrm{e}^{\tau} \gg 1$), that is, for a high degree of polymerization, Eqs. (5.33) can be approximated by[23,84,85]

$$\begin{aligned} P_n &\approx f\mathrm{e}^{\tau} \\ P_w &= (f + 1)\mathrm{e}^{\tau} \\ \frac{P_w}{P_n} &= 1 + \frac{1}{f} \end{aligned} \tag{5.34}$$

and the polydispersity index approaches a limiting value. Interestingly, for the polydispersity index we obtain an expression which is identical to the one given by Schulz in 1937 for coupling of polydisperse macromolecules.[86] Figure 5.14 depicts the dependence of the polydispersity index on the number-average degree of polymerization P_n for various values of the functionality f. Even for the lowest functionality ($f = 1$), the polydispersity is decreased compared to that in a batch process.

This effect may be exemplified if we compare the differences in reactivity caused by various functionalities f under semibatch conditions. As previously mentioned, the overall rate of inimer addition of a hyperbranched molecules is proportional to its number of functional groups. Hence, large molecules grow faster than smaller ones. However, if we aim for a narrow MWD, all species

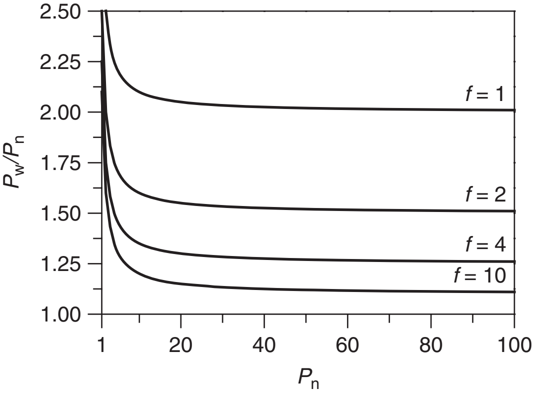

Figure 5.14 Dependence of the polydispersity index on the number-average degree of polymerization P_n for various initiator functionalities f in semibatch mode, assuming equal rate constants.[23]

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should not differ in their reactivity. The step from the pure core to the molecule with degree of polymerization $i = 1$ increases the reactivity relative to the core itself by a factor of 2 in the case of $f = 1$, while, for example, for $f = 4$ and 10, the rate constants increase by a factor of 5/4 and 11/10, respectively. Thus, the higher functionality cores lead to similar reactivities for the first few addition steps, and in turn the MWD stays rather narrow throughout the reaction.

In case of a copolymerization process, we obtain in the limits of high degrees of polymerization[83]

$$M_n = f(m_M\gamma + m_I)e^{\tau} \tag{5.35}$$

$$M_w = (f + 1)(m_M\gamma + m_I)e^{\tau} \tag{5.36}$$

and consequently the polydispersity index is identical to the case of homo-SCVP, cf. Eq. (5.34). As it depends neither on the comonomer ratio γ nor on M_n, we do not obtain a further narrowing of the MWD by employing an initiator in a copolymerization process.

5.4.2 Degree of Branching

The use of an f-functional core requires more general definition of the DB:

$$\mathrm{DB} = \frac{D + T - f}{D + L_C + L_V - f} \tag{5.37}$$

For a monofunctional core, that is, $f = 1$, this expression becomes identical to the original definition, Eq. (5.1).

5.4.2.1 Batch Polymerization

For SCVP, the DB for the batch process in the presence of core-forming molecules does not significantly differ from the DB without them.[23] As their presence affects the evolution of the reaction only at the very end, when the number of species carrying a vinyl group and the number of species without vinyl groups become comparable, the branching statistics can nearly be qualitatively described by the statistics of a conventional SCVP. Hence, we can use the expressions derived in Section 5.2.4, which will lead to $\mathrm{DB}_\infty \approx 0.5$, cf. Eq. (5.9).

In SCVCP, the DB in the limit of full conversion, that is, $x_M = x_I = 1$, approaches that for a batch process in the presence of initiator molecules at high comonomer ratios, $\gamma \gg 1$, $\mathrm{DB}_\infty = 2/(\gamma + 1)$. Note, that for this limiting case the DB depends neither on the initiator concentration J_0 nor on its functionality f; in fact, this is exactly the same result as in the absence of initiator, cf. Eq. (5.24).

5.4.2.2 Semibatch Polymerization

Interestingly, the semibatch process resembles the divergent approach of dendrimer synthesis, as both strategies start with a multifunctional core ($f \geq 2$). Despite the similarities, in SCVP the segments are not added simultaneously but in a statistical process resulting in a nonuniform MWD and a DB < 1. Assuming the long-chain approximation, it reads[23,29,84]

$$\mathrm{DB} = \frac{D + T - f}{i - f} = \frac{2D}{2D + L_C + L_V} = \frac{2(i - 2f)}{3(i - f)} \tag{5.38}$$

For high degrees of polymerization i, we obtain a limiting value of DB = 2/3, significantly exceeding the one of the batch process, cf. Figure 5.6. This variation is caused by a different radial distribution of the structural units throughout the molecule. Whereas the fraction of linear segments in a semibatch process does not show a strong dependence on the generation, branched units are mainly found in lower generations.[23] Hence, the hyperbranched structure possesses a dense core, similar but not identical to dendrimers where any inner generation is exclusively composed of branch points. For the batch process, it is reasonable to assume that the different segment types are distributed nearly equally throughout the molecule, resulting in a lower DB.

In the case of semibatch copolymerization in the presence of initiator, we obtain for a high MW polymer[83]

$$\mathrm{DB}_\infty = \frac{2}{\gamma + 1}\left(\frac{1}{2\gamma + 3} + \frac{\gamma}{\gamma + 2}\right) \tag{5.39}$$

leading to DB = 2/3 for $\gamma = 0$ like in the SCVP case. Hence, DB decreases with increasing comonomer ratio γ, and for sufficiently high γ it approaches $\mathrm{DB}_\infty = 2/(\gamma + 1)$. Compare the result with Eq. (5.24)! It clearly indicates that the use of a multifunctional initiator has no beneficial effects on increasing the DB in SCVP—neither in a batch nor in a semibatch reaction.

5.4.3 Comparison with Experimental Data

Unfortunately, only a very limited number of publications deals with the effect of initiators on the SCV(C)P of inimers. Since the rate of inimer addition cannot be infinitesimally low in a semibatch run, inimer molecules may not exclusively add to initiator molecules and the addition to molecules bearing no initiator unit may also take place. The coexistence of two different types of propagating macromolecules eventually leads to a broadened bimodal MWD.

For SCVP, detailed SEC analysis revealed that the major part of the hyperbranched polymer is initiated by the monofunctional initiator: that is, the concentration of macromolecules not possessing a core-forming unit is low. Contrary to the theoretical predictions, the DB of the semibatch run did not show any differences to a batch polymerization in the absence of initiator.[67] It was speculated that this might be due to unequal reactive of the A^* and B^* centers, which has not been treated quantitatively.

Very few examples of the controlled approach to hyperbranched polymers have been reported. Frey *et al.* reported the controlled chain-growth-type of approach to hyperbranched polymers based on the anionic ring-opening self-condensing polymerization of glycidol, which is another AB^* monomer.[87,88] The MWD of the resulting polyglycerols were reported to be in the range of $M_w/M_n = 1.1-1.3$. On the other hand, Bharathi and Moore recently reported a new hyperbranched procedure (one-step AB_2-type polycondensation) which takes place on an insoluble solid support, providing polymers with low polydispersity and controlled MWs.[89,90] Recently, a series of hyperbranched (meth)acrylates were synthesized by SCVP of the inimers **AB*****7**[49] and **AB*****12**[49] in the presence of a tetrafunctional ATRP initiator capped with bromoisobutyrate, which was used as the core-forming molecule. A decrease of the polydispersity was observed by the addition of the tetrafunctional initiator.

For SCVCP at a given comonomer ratio, the semibatch approach leads to a significant narrowing of the MWD, especially for low ratios of both comonomers to core-forming initiator. The MWD broadens for higher ratios of both comonomers to core-forming initiator, possibly because of an increased formation of polymers without core. Unfortunately, no data on the DB were reported; as similar Mark–Houwink exponents α were found for different comonomer to initiator ratios, no significant changes in polymer structure were anticipated.[12]

5.5 SCVP OF MACROINIMERS

Finally, let us briefly review the case of macroinimers. As already mentioned when deriving the SCVCP in the case of nonequal rate constants, cf. Sections 5.2.3 and 5.3.3, these heterotelechelic macromolecules possess both an initiating and a polymerizable moiety and their reaction may be regarded as a special case of a copolymerization.

First polymerizations of macroinimers were reported by Hazer *et al.*[20,21] They performed a conventional radical polymerization of polyesters with an azo- and a methacrylic function. Due to the noncontrolled character of the polymerization, cross-linked products were obtained. Cheng *et al.* synthesized poly(*tert*-butyl acrylate) with an acryloyl and an α-bromoisobutyrate function, **AB*8**,[45] and Peeters *et al.* a corresponding poly(ε-caprolactone), **AB*9**.[46] ATRP resulted in hyperbranched polyacrylate and polyester, respectively.

Formally, the polymerization process of a macroinimer is identical to that of an AB* inimer. However, here AB* represents a macromolecule with γ linear units, that is, it has a number-average degree of polymerization γ. Let us consider ideal conditions, that is, assumptions (1)–(4) in Section 5.2.3 are fulfilled, and furthermore the macroinimers to be monodisperse (The error in not taking account of a Poisson distribution is negligible for $\gamma \gg 1$.). Now, the averages of the polymacroinimer $P_{\mathrm{n,PMI}}$ and $P_{\mathrm{w,PMI}}$ can easily be derived using Eqs. (5.4a), (5.4b), and (5.5) for SCVP[91]:

$$P_{n,\mathrm{PMI}} = (\gamma + 1)P_{n,\mathrm{SCVP}} = (\gamma + 1)/(1 - x) \tag{5.40}$$

$$P_{w,\mathrm{PMI}} = (\gamma + 1)P_{w,\mathrm{SCVP}} = (\gamma + 1)/(1 - x)^2 \tag{5.41}$$

The polydispersity index of a polymacroinimer reads

$$\left(\frac{P_w}{P_n}\right)_{\mathrm{PMI}} = \frac{P_{w,\mathrm{SCVP}}}{P_{n,\mathrm{SCVP}}} = \frac{1}{(1-x)} = \frac{P_n}{\gamma + 1} = P_{n,\mathrm{red}}$$
$$\text{and for} \quad \gamma \gg 1 \left(\frac{P_w}{P_n}\right)_{\mathrm{PMI}} \approx \frac{P_n}{\gamma} \tag{5.42}$$

The polydispersity index is the same as in SCVP and equals the reduced degree of polymerization. Therefore, for a given P_n, the polydispersity index of a polymer synthesized by reaction of macroinimers is lowered by the factor $\gamma + 1$.

The structural units present in polymacroinimers differ from SCVP (Scheme 5.2) and SCVCP, since vinyl-type additions now lead to a branched rather than a linear unit, that is, $L_\mathrm{V} = >a - \mathrm{B}^*$ becomes $D_\mathrm{V} = >a\text{–}\mathrm{m}_\gamma\ \text{–}\mathrm{B}^*$. Terminal units have the structure $T = \mathrm{A}^*\text{–}\mathrm{m}_\gamma\text{–}\mathrm{B}^*$ and $T_\mathrm{V} = \mathrm{A}\text{–}\mathrm{m}_\gamma\ \text{–b}$, respectively, and no T_M units are present. In the limiting case of complete conversion of double bonds, that is, $x \to 1$, the DB reaches its maximum value

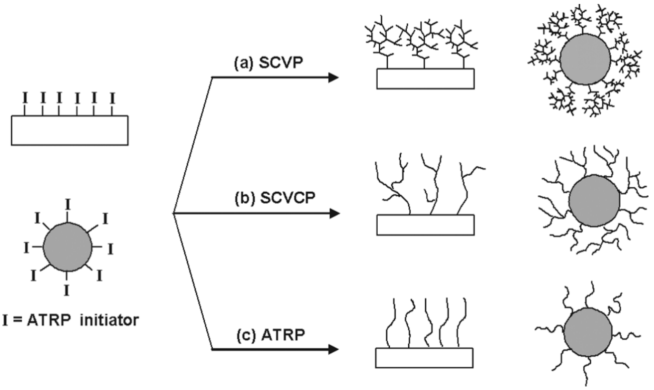
$$\mathrm{DB}_{\infty,\mathrm{PMI}} = \frac{2\mathrm{e}^{-1}}{\gamma + 1} \approx \frac{0.74}{\gamma + 1} \quad \text{and for} \quad \gamma \gg 1\, \mathrm{DB}_{\infty,\mathrm{PMI}}$$
$$\approx \frac{0.74}{\gamma} = 1.68\frac{\mathrm{DB}_{\infty,\mathrm{SCVP}}}{\gamma} \tag{5.43}$$

Due to the denominator $\gamma + 1$ reflecting the presence of the linear units L_M, the value of $\mathrm{DB}_{\infty,\ \mathrm{PMI}}$ is considerably lower than $\mathrm{DB}_{\infty,\mathrm{SCVP}}$. However, if we do not take into account the L_M units ($\gamma = 0$), it is higher by approximately

60%. This is due to the additional D_V units, which are counted as linear L_V units in SCVP. Except for very short linear chains, that is, small γ, the DB obtained by copolymerization exceeds the value for a polymacroinimer. In the polymacroinimer as well as in SCVP at full conversion, there still remains a large fraction of linear units $L_C = \sim A^* - b \sim$, with A^* centers potentially capable of forming branch points. Only in SCVCP these centers can be converted to short branches by addition of small amounts of monomers M. For higher γ, monomer will predominantly add to chain ends $T_M = \sim M^*$ forming linear units, thus decreasing the DB.

5.6 SURFACE-GRAFTED HYPERBRANCHED POLYMERS

Highly branched polymers play an increasingly important role in interface and surface sciences, since their distinctive chemical and physical properties can be used advantageously as functional surfaces and as interfacial materials. Depending upon the substrates, it can be divided into 3D, 2D, and 1D hybrids, which correspond to products grafted on spherical particles, planar surfaces, and linear polymers, respectively.[24] Previously, the synthesis of dendrimers and hyperbranched polymers grafted onto surfaces has been mainly conducted by the "grafting to" techniques.[92–95] A series of repeated "grafting from" steps have been also employed.[96–98] However, both approaches have the disadvantage that many tedious synthetic steps are necessary to reach the defined surface structures. Dendrimers grafted on a linear polymer chain (1D) have been also synthesized.[99,100] Recently, SCV(C)P has been applied as a useful method for the synthesis of 2D and 3D types of surface-grafted hyperbranched polymers (Scheme 5.6).[101]



Scheme 5.6 Synthesis of surface-grafted hyperbranched, branched, and linear polymers.[101]

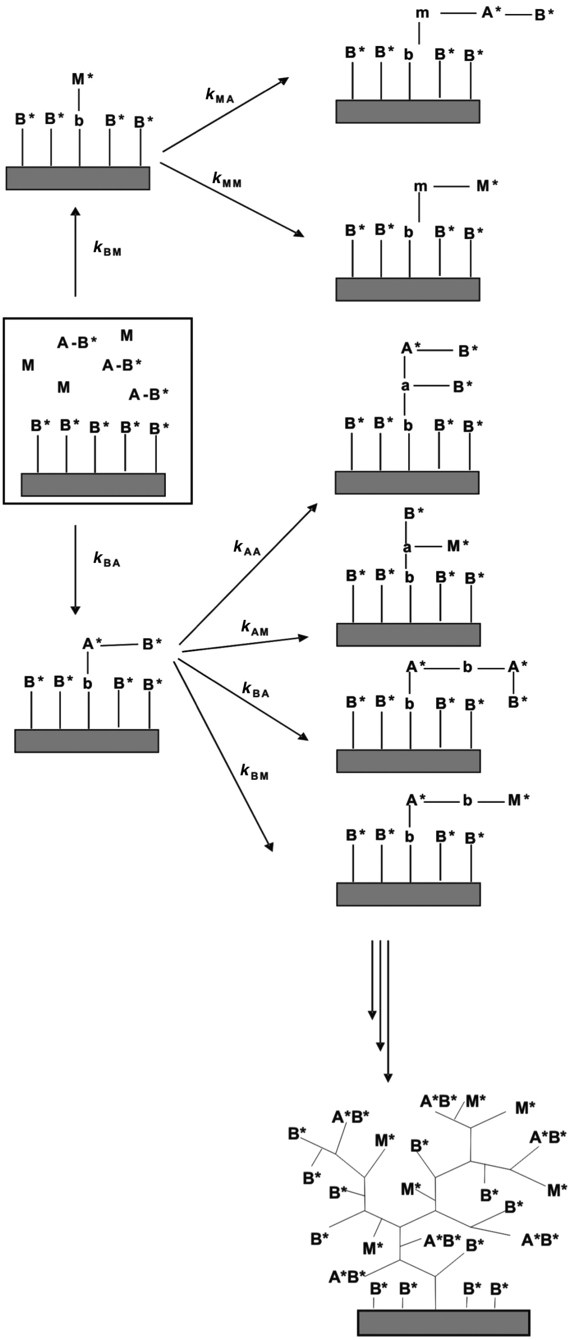
Source: Reprinted with permission from Advincula, R.; Britten, W. B.; Rühe, J.; Caster, C., Eds. *Polymer brushes: From Synthesis to Functional Microstructures*; Copyright 2004. Wiley-VCH.

A novel synthetic concept for preparing hyperbranched (meth)acrylates on a planar surface has been reported, in which a silicon wafer grafted with an initiator layer composed of an α-bromoester fragment was used for SCVP via ATRP.[47] Because both the AB* inimer and the functionalized silicon wafer have groups capable of initiating the polymerization of vinyl groups, the chain growth can be started from both the B* initiators immobilized on the silicon wafer and a B* group in the inimer. Both of the activated B* can add to the double bond A to form the ungrafted or grafted dimer with a new propagating center A*. Further addition of AB* inimer or dimer to A* and B* centers results in hyperbranched polymers. The one-step self-condensing ATRP from the surface can be regarded as a novel and convenient approach toward the preparation of smart interfaces. The mechanism is outlined in Scheme 5.7.

Self-condensing ATRP of the acrylate-type inimer **AB*1** was found to yield polymer films with a high DB and with a characteristic surface topography.[47] The size and density of the nanoscale protrusions obtained on the surface and the film thickness were observed to depend on the polymerization conditions, such as the ratio $[\mathbf{AB^*1}]_0/[\text{catalyst}]_0$. Similar results were obtained by SCVP of the methacrylate-type inimer **AB*10**. The chain architecture and chemical structure could be modified by SCVCP leading to a facile, one-pot synthesis of surface-grafted branched polymers. The surface-initiated SCVCP of a methacrylic **AB*10** inimer with the sugar-carrying methacrylate monomer 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside using a silicon wafer functionalized with monolayers of initiators for ATRP was also employed to synthesize highly branched glycomethacrylates at the surface.[102] The randomly branched glycopolymer surfaces possessed characteristic architecture, topography, and surface tuning properties, and deprotection of the bulky isopropylidene groups resulted in hydrophilic surfaces. Such surfaces can further be modified to yield smart surfaces, which can then be utilized for several biological applications.

Synthesis of hyperbranched polymer–silica hybrid nanoparticles was conducted by SCVP via ATRP from silica surfaces.[103,104] ATRP initiators were covalently linked to the surface of silica particles, followed by SCVP of the inimer **AB*1** (Scheme 5.6). Well-defined polymer chains were grown from the surface to yield hybrid nanoparticles comprising silica cores and hyperbranched polymer shells having multifunctional bromoester end groups. SCVCP of the inimer **AB*1** and tBuA from the functionalized silica nanoparticles created branched PtBuA–silica nanoparticles. The functionality of the end groups on the surface and the chemical composition as well as the structure of the branched polymers grafted on the silica nanoparticles could be controlled by composition in the feed during the SCVCP. Novel hybrid nanoparticles with branched polyelectrolytes, PAA–silica, were obtained after hydrolysis of linear segments of the branched PtBuA.

The SCVP strategy via ATRP was also employed to grow hyperbranched polymers on the surfaces of multiwalled carbon nanotubes.[105] The nanotube surface fixed with ATRP initiators (carbon nanotube–$COOCH_2CH_2OCOC(CH_3)_2Br$) was prepared, and then hyperbranched macromolecules were covalently grafted



Scheme 5.7 General route to the synthesis of surface-grafted hyperbranched polymers.

on the carbon nanotubes by SCVP of **AB*1** via the ATRP process. Characterization of the resulting products showed that the weight ratio of the as-grown hyperbranched polymers on the surfaces reached 80%, and the carbon nanotubes grafted with hyperbranched polymers exhibited relatively good dispersibility in organic solvents such as THF and chloroform.

As discussed in Section 5.4, the presence of multifunctional initiators leads to a considerable narrowing of the polydispersity index, which decreases with increasing initiator functionality f. Thus, the MW and the MWD of the ungrafted polymer obtained in solution might be different from those of the grafted polymer produced by a surface-initiated SCVP. On the other hand, the effect of f-functional initiators on the DB was calculated to be negligible under the batch conditions used here (inimers and initiators grafted on the surface are mixed instantaneously).[23] This indicates that the DB does not depend on whether the polymer is formed in solution or on a surface. Therefore, it is reasonable to suppose that SCVP of inimer **AB*1** with functionalized silica particles (or silicon wafers) provides surface-grafted poly(acrylate) having a highly branched structure, even though the correlation of the molecular parameters of the soluble polymers with the polymers grafted on the surface has not been confirmed experimentally.

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Chapter 6

Ring-Opening Multibranching Polymerization

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6.1 INTRODUCTION

In recent years, ring-opening multibranching strategies have been established as a versatile method for the synthesis of a variety of hyperbranched homopolymers as well as complex macromolecular architectures, such as branched block copolymers or various multiarm star polymers. In this chapter, hyperbranching polymerizations based on ring-opening strategies are summarized. Applications of some of these concepts for the generation of complex hyperbranched topologies are discussed in other chapters.

As demonstrated in other sections of this book, hyperbranched polymers have classically been prepared by polycondensation of AB_m-type monomers.[1,2] In the mid-1990s, the *self-condensing vinyl polymerization* (SCVP) was introduced by Fréchet *et al.*,[3,4] utilizing monomers containing a polymerizable vinyl group along with an initiating moiety, as highlighted in the preceding chapter. Such monomers combining an initiating moiety with a polymerizable moiety have been termed “inimers.” The two aforementioned pathways permit the preparation of a wide variety of hyperbranched polymers but involve the major drawback of leading to broad molecular weight distributions with polydispersities in the range of $DP_n/2$. In contrast, monomers eligible for the pathway covered in this chapter contain a strained, cyclic moiety that generates a branching point only upon ring

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

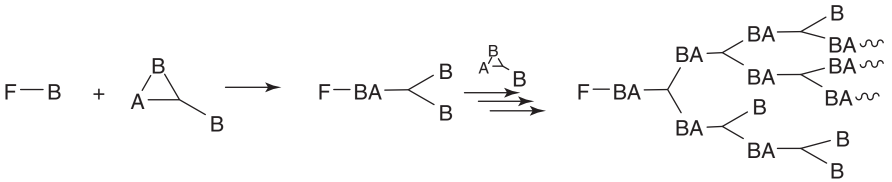
opening in the course of the polymerization. Such monomers are often called "latent AB_m monomers" (Scheme 6.1).

It is obvious that cyclic inimers possess structural analogy with the vinyl inimers employed for SCVP. However, in the case of the cyclic inimers, the driving force for this type of polymerization is the ring-opening isomerization of the cyclic monomer unit. Therefore, this method is now commonly referred to as *ring-opening multibranching polymerization* (ROMBP).

Well before hyperbranched polymers became a matter of broad scientific interest, Sandler and Berg,[5] as well as Vandenberg *et al.*,[6] studied the polymerization of glycidol, a typical cyclic latent AB_2 monomer, aiming at predominantly linear polymer architectures. However, they also observed the formation of undesired branched structures, which were characterized by Vandenberg *et al.* in a seminal paper published in 1985.[6] This interesting work describes the generation of different chain units upon the base-catalyzed polymerization of glycidol (Table 6.1).

Subsequently, both cationic[7,8] and anionic[9–11] ring-opening polymerization techniques were applied to the polymerization of glycidol in the early 1990s by Penzcek, Kubisa, and Dworak in early works in this field. Further progress in this area was made by Frey *et al.*, who established the slow monomer addition (SMA) technique in 1999, leading to polyglycerols with moderate, in some cases narrow, molecular weight distributions. Details of the respective approaches are discussed in the ensuing text.

As early as 1992, Suzuki and Saegusa reported the palladium-catalyzed multibranching polymerization of a cyclic carbamate, another example for a latent AB_2 monomer, leading to hyperbranched polyamines.[12] It is important to note that Suzuki and Saegusa in this paper reported the first *initiated* type of multibranching polymerization, that is, a chain growth mechanism. The low polydispersity ($M_w/M_n = 1.35$) demonstrates the possibility to control the growth of the polymer chains in this system. In all these reactions, the polymerization is typically initiated by a suitable initiating molecule, containing a focal unit F as well as reactive B groups that can react with the cyclic structure under ring opening. For each AB_2 monomer being incorporated into the growing polymer molecule, two new potential polymerization sites are created, while only one is consumed.



Scheme 6.1 General principle of ring-opening multibranching polymerizations. F is the single focal unit, while B depicts the reactive groups of the AB_2 monomer.

Table 6.1 Characterization Data from Vandenberg's Original Paper[a,b]

	Diluent		Catalyst				Polymer							
									Chain units (%)[b]					
Number	Name	Volume (mL)	Name	Weight (g)	Time (h)	Temperature (°C)	Conversion (%)	η_{inh} (dL/g)	I	IB	IA or IIA	II	IIB	III
With R-TMSG														
1	None	—	KOH	2.00	336	22	68	0.013	3	6	33	45	13	ND
With RS-TMSGE														
2	None	—	KOH	2.00	336	22	58	—	4	4	44	44	4	ND
3	None	—	KO*tert*-Bu	0.20	168	75	98	0.036	29	5	56	0	10	ND
4	DMSO	8.8	KO*tert*-Bu	0.20	47	22	89	0.034	16	5	73	5	0	ND
5	DMSO	8.8	KO*tert*-Bu	0.20	1	22	29	0.029	0	0	63	12	0	Trace?
With Glycidol														
6	Ether	10.0	KOH	4.00	22	22	75	0.050	1	7	35	46	10	ND
7	Ether	10.0	KOH	2.00	18	22	19	0.050	4	6	41	38	11	ND
8	CH_2Cl_2	20.0	KOH	4.00	4	0	—	—	—	—	—	—	—	—
	—	—	—	—	22	22	100	0.054	6(6)	6(9)	28(24)	54(55)	6(6)	ND
9	CH_2Cl_2	20.0	Al porphyrin	0.66	4	0	—	—	—	—	—	—	—	—
	—	—	—	—	195	22	88	0.096	4	1	27	48	0	19
10	Ether	10.0	KO*tert*-Bu	0.33	4	0	—	—	—	—	—	—	—	—
	DMSO	6.0	—	—	168	22	100	0.011	5	11	43	38	4	ND
11	CH_2Cl_2	20.0	KO*tert*-Bu	0.33	4	0	—	—	—	—	—	—	—	—
	DMSO	6.0	—	—	168	22	90	0.011	5	5	49	38	2	3
12	Ether	10.0	K hexymethyl disilazane	0.48	4	0	100	0.064	—	—	—	—	—	—
	DMSO	6.0		—	168	22	—	—	10	10	40	37	3	Trace
With TBGE														
13	None	—	KOH	2.00	46	22	58	0.24	—	—	—	—	—	

Source: Ref. [6].

[a] The assignments I and II refer to the different linear units, while IB and IIB represent the dendritic chain units.

[b] IA and IIA belong to the terminal groups and III indicates epoxide end groups.

6.2 CLASSIFICATION OF RING-OPENING MULTIBRANCHING POLYMERIZATIONS

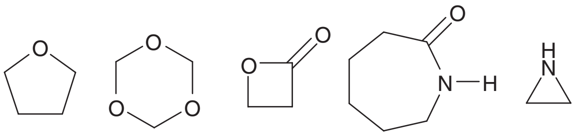
As indicated in the previous paragraph, ROMBP have been carried out under different conditions, utilizing a variety of monomers, initiators, and catalysts. However, all reported approaches are based on the general principle illustrated in Scheme 6.1.

In the following text, a detailed classification of the respective polymerization and branching mechanisms that are important: cationic, anionic, and catalytic ROMBPs, as well as the respective seminal works leading to their development is treated. Within this context, specific prerequisites, synthetic principles, and peculiarities for each particular variant are examined and discussed.

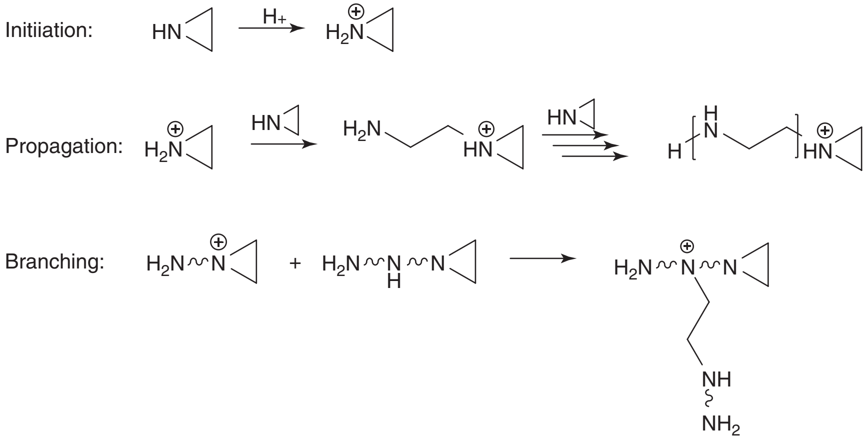
6.2.1 Cationic Ring-Opening Multibranching Polymerizations

In cationic polymerizations, electron-deficient initiators (mostly Brønsted or Lewis acids) react with electron-rich monomers. The active chain end (ACE) bears a positive charge, with the active sites being either carbenium or oxonium ions. Molecular weights are often limited by the inherent sensitivity to impurities, chain transfer, and rearrangement reactions. Suitable monomers for cationic polymerizations are vinyl monomers with electron-donating moieties or cyclic structures containing heteroatoms. The latter case is referred to as cationic ring-opening polymerization. Eligible monomers include cyclic ethers, cyclic acetals, lactones, lactams, and cyclic amines (Scheme 6.2).

In 1969, Hauser first described the ring-opening polymerization of alkyleneimines.[13] It was observed that the polymerization of three-membered imines (aziridines), specifically ethylene imine, leads to a product with extensive branching. Dick and Ham subsequently reported a random distribution of primary, secondary, and tertiary amine groups.[14] Branching results from the formation of tertiary amine groups upon intermolecular nucleophilic attack of secondary amine nitrogens in polymer repeat units on propagating iminium centers (Scheme 6.3). Thus, the long-known polymerization of aziridines in fact represents the oldest known ring-opening polymerization, leading to hyperbranched poly(ethyleneimine)s. The resulting materials have been available for more than three decades and are sold under the trade name Lupasol® on a scale of several 100,000 tons per year.



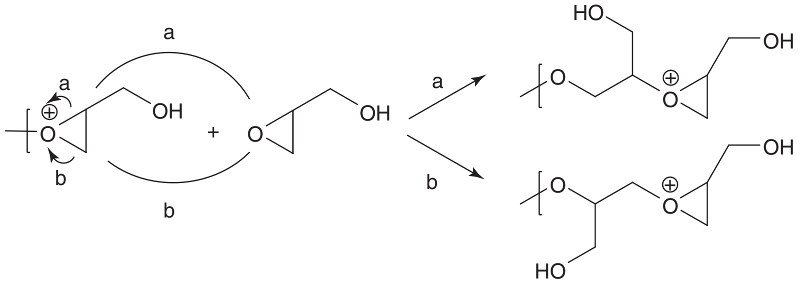
Scheme 6.2 Examples of common monomers for cationic ring-opening polymerizations.



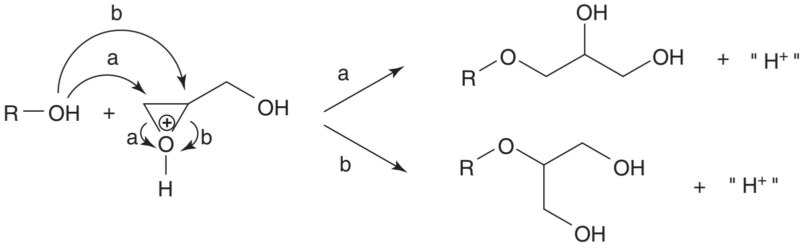
Scheme 6.3 Hyperbranching polymerization of ethylene imine.

Substitution at the aziridine ring impedes polymerization.[15,16] The 1,2- and 2,3-disubstituted species do not polymerize; 1- and 2-substituted aziridines undergo polymerization, but polymer yields and molecular weights are limited.

Oxiranes or oxetanes with attached hydroxyl groups can be potentially polymerized by typical cationic initiators, for example, protic or Lewis acids such as trifluoromethanesulfonic acid (TfOH) or boron trifluoride etherate ($BF_3{\cdot}OEt_2$). In the course of these reactions, branching points are generated. This justifies the term "cationic ring-opening multibranching polymerization." Dworak and Penczek studied the coexistence of *ACE* and *activated monomer* (AM) mechanisms in the cationic polymerization of glycidol (Schemes 6.4 and 6.5). In order to investigate the comparative relevance of both concurrent reaction pathways, hyperbranched polyglycerols with molecular weights of up to 10,000 g/mol were synthesized and characterized. It is obvious that only primary hydroxyl groups would be present as substituents of the polyether chain if the reaction proceeded exclusively by the ACE mechanism.



Scheme 6.4 Active chain end mechanism in the cationic polymerization of glycidol. α- and β-ring opening preserves the CH_2OH substituent.

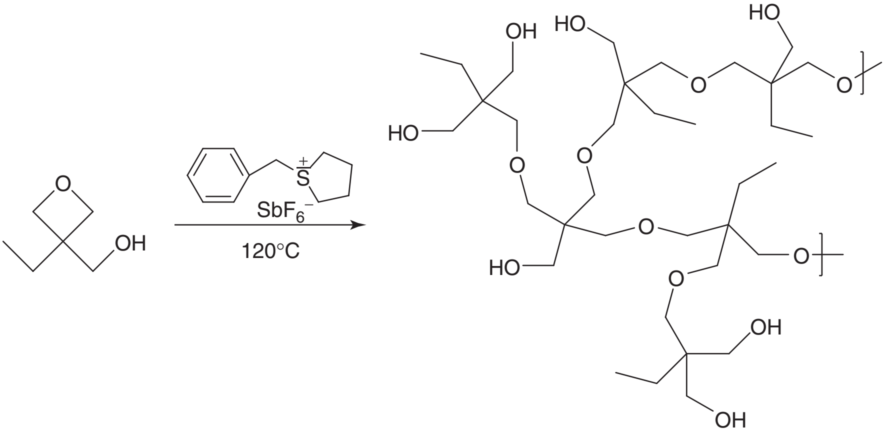


Scheme 6.5 Activated monomer mechanism in the cationic polymerization of glycidol.

In contrast, propagation by the AM mechanism generates two different types of repeating units. R-OH in Scheme 6.5 depicts either the chain end or the side group. In the latter case, branching occurs.

Dworak and Penczek explicitly analyzed the structure of the polymers, which is evidently a consequence of the polymerization mechanism. They found significant contribution of the AM mechanism to the chain growth. Also, within the scope of this elegant work, a direct correlation between the specific initiator and the percentage of secondary hydroxyl groups attached to the polymer backbone was verified. Use of $SnCl_4$ or $BF_3{\cdot}OEt_2$ as Lewis acidic initiators in particular, proved to promote the AM mechanism.

In addition to hydroxyl functional oxiranes, the congruous oxetanes have been studied as monomers in ring-opening polymerizations by Vandenberg *et al.*, who obtained a linear and highly crystalline polymer.[17,18] Additionally, other authors also detailed the synthesis of hyperbranched polyethers from hydroxyfunctional oxetanes.[19,20] Mostly, cationic initiators have been used in the ring-opening polymerization of oxetanes, primarily because of their higher basicity as compared to three-membered oxiranes. The latter are prevalently polymerized anionically. In 1999, Magnusson *et al.*[21] published a study on the cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (EHO). A convenient method for the preparation of the respective hyperbranched polyether by thermally induced bulk polymerization was introduced. The sulfonium salt initiator benzyltetramethylenesulfonium hexafluoroantimonate was used in this approach (Scheme 6.6). Surprisingly, narrow molecular weight distributions ($M_w/M_n = 1.26-1.43$) at molecular weights up to 5000 g/mol were found. Detailed characterization of the hyperbranched polymers by proton-decoupled ^{13}C-NMR experiments showed a correlation between monomer conversion and degree of branching (DB). While at low conversions ($<30\%$) predominantly linear units were formed, increased conversion led to more dendritic units in the polymer structure. Accordingly, the possibility of tailoring the DB of these polymers by controlling the monomer conversion was later reported by Magnusson *et al.*[22] Determination of the number of secondary and tertiary oxonium ions during the reaction provides the ratio of ACE and AM mechanisms upon the polymerization of hydroxy oxetanes. A significant



Scheme 6.6 Synthesis of hyperbranched polyethers via cationic ring-opening multibranching polymerization of EHO.

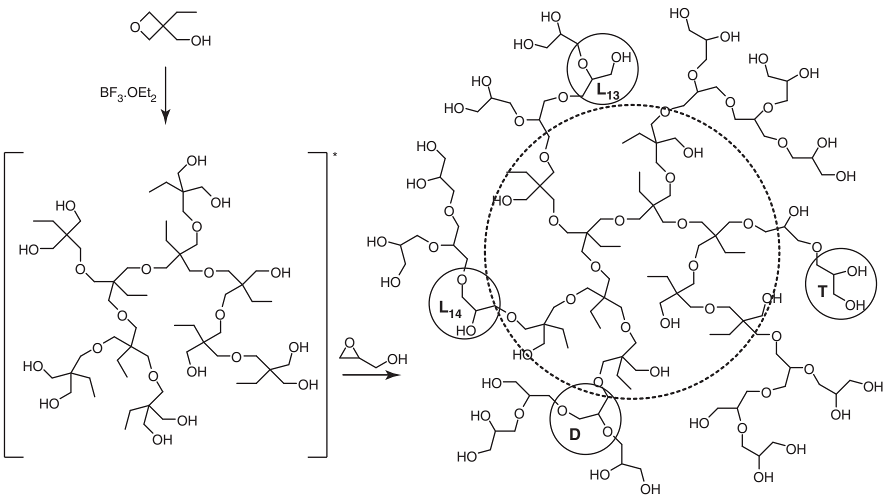
prevalence (90:10) of the AM mechanism was found, leading to highly branched polyethers. However, in no case a DB higher than 0.4 was obtained, which is significantly lower than the theoretical value of 0.5 for polymerizations under entirely statistical conditions. This observation leads to the assumption that upon ring opening of oxetanes, the coexistence of ACE and AM mechanisms adversely affects the generation of branching points.

Gao *et al.* combined the cationic ring-opening polymerization of EHO, initiated by $BF_3 \cdot OEt_2$, with the subsequent addition of glycidol monomer to obtain amphiphilic core–shell polymers with complex hyperbranched–hyperbranched core–shell structures.[23] Expectedly, a higher feed ratio of glycidol monomer led to a higher solubility of the polymer in water (Scheme 6.7).

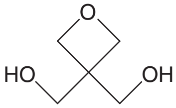
In addition to AB_2 monomers such as glycidol or EHO, conveniently accessible AB_3 compounds such as 3,3-bis(hydroxymethyl)oxetane (BHO, Scheme 6.8) can be used for cationic ring-opening polymerizations.

Farthing,[24] and later Vandenberg *et al.*, polymerized BHO by initiation with a trifluoromethanesulfonic acid catalyst, obtaining a weakly branched polymer of low molecular weight. Interestingly, a more crystalline product of higher molecular weight was obtained when using the trimethylsilyl ether of BHO and $i\text{-Bu}_3\text{Al–}0.7 \cdot H_2O$ cationic catalyst as initiator. Characterization of these polymers with regard to the DB is substantially constricted by the complexity and ambiguity of the respective ^1H- and ^{13}C-NMR spectra. In addition, the strong aggregation of the highly hydroxyl-substituted polymers represents a severe limitation for the further characterization.

Monosubstituted derivatives of tetrahydrofuran (THF) classically have been known to be difficult to polymerize due to thermodynamic reasons.[25] Bednarek and Kubisa recently extended cationic hyperbranching polymerizations to the class of five-membered cyclic ethers containing hydroxyl groups as substituents.[26]

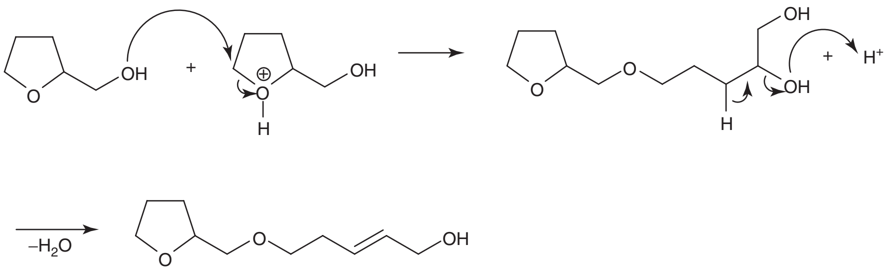


Scheme 6.7 Synthesis of amphiphilic core–shell copolymer by cationic polymerization of EHO and subsequent addition of glycidol. The closed circles depict the terminal, linear, and dendritic units of the hydrophilic polyglycerol shell.



Scheme 6.8 3,3-Bis(hydroxymethyl)oxetane (BHO).

They polymerized 2-hydroxymethyltetrahydrofuran, using a trifluoromethanesulfonic acid initiator. Matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry of the obtained oligomers indicated that elimination of water took place in the course of the polymerization, which is an undesired side reaction. A possible pathway leading to a certain amount of unsaturated units in the polymer structure is given in Scheme 6.9.



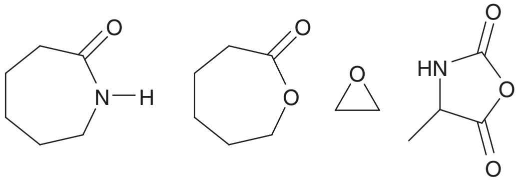
Scheme 6.9 Formation of unsaturated units in the acid-catalyzed polymerization of 2-hydroxymethyltetrahydrofuran.

In order to understand whether this behavior can be ascribed to a more complex mechanism than formerly assumed, the authors studied the polymerization of further THF derivatives and observed elimination of water in all cases. The mechanistic details necessary to explain these results still have to be evaluated. Bednarek and Kubisa suggested a reinvestigation of the polymerizability problems of five-membered cyclic ethers containing hydroxyl groups. Hyperbranched polymers obtained by cationic polymerizations are generally limited in terms of their potential for further academic investigation and potentially also for industrial application, since the number of eligible monomers is limited and other methods have proven to be superior in terms of molecular weights achievable and control over the reaction.

6.2.2 Anionic Ring-Opening Multibranching Polymerizations

Anionic chain polymerizations exhibit many analogous characteristics as cationic polymerizations; however, some distinct differences must be emphasized. Generally, the propagating species are anionic ion pairs or free ions. If termination reactions are absent, further monomer addition will result in continuous chain growth. Hence, these polymerizations are often termed “living polymerizations.” Although anionic polymerizations often proceed rapidly at low temperatures, they are usually not as temperature sensitive as cationic polymerizations. A variety of basic (nucleophilic) initiators have been used to initiate anionic polymerizations, including covalent or ionic metal amides such as $NaNH_2$ and $LiN(C_2H_5)_2$, alkoxides, hydroxides, cyanides, phosphines, amines, and organometallic compounds such as *n*-butyl lithium or phenyl magnesium bromide. The polymerization is initiated by the addition of the base to the monomer, typically vinyl compounds with electron-withdrawing moieties such as acrylonitrile or methyl vinyl ketone. Another group of monomers used in anionic ring-opening polymerizations comprises ring-shaped molecules with electron-deficient carbon atoms such as cyclic amides and esters (lactams or lactones), cyclic ethers (oxiranes), or Leuchs’ anhydrides (Scheme 6.10).

Glycidol, being a latent cyclic AB_2-type monomer containing a highly strained three-membered oxirane ring, represents a monomer that can be polymerized by addition of a nucleophilic initiator. In an early work by Rider and Hill, it was casually mentioned that pyridine polymerized glycidol to a



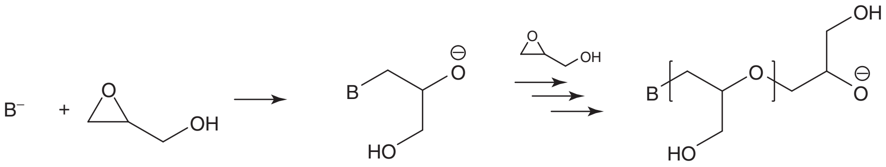
Scheme 6.10 Examples of monomers in anionic ring-opening polymerizations.

water-soluble black tar.[27] Sandler and Berg later observed by chance that glycidol polymerized vigorously in the presence of triethylamine, leading them to a further investigation of the effect of basic catalysts on the rate of polymerization. The belief that the obtained product exhibited an exclusively linear structure (Scheme 6.11) was not challenged until Vandenberg *et al.* characterized a variety of protected and unprotected polyglycerols in the mid-1980s. These polymers were prepared by initiation of glycidol with KOH base catalyst, aiming at a linear chain structure.

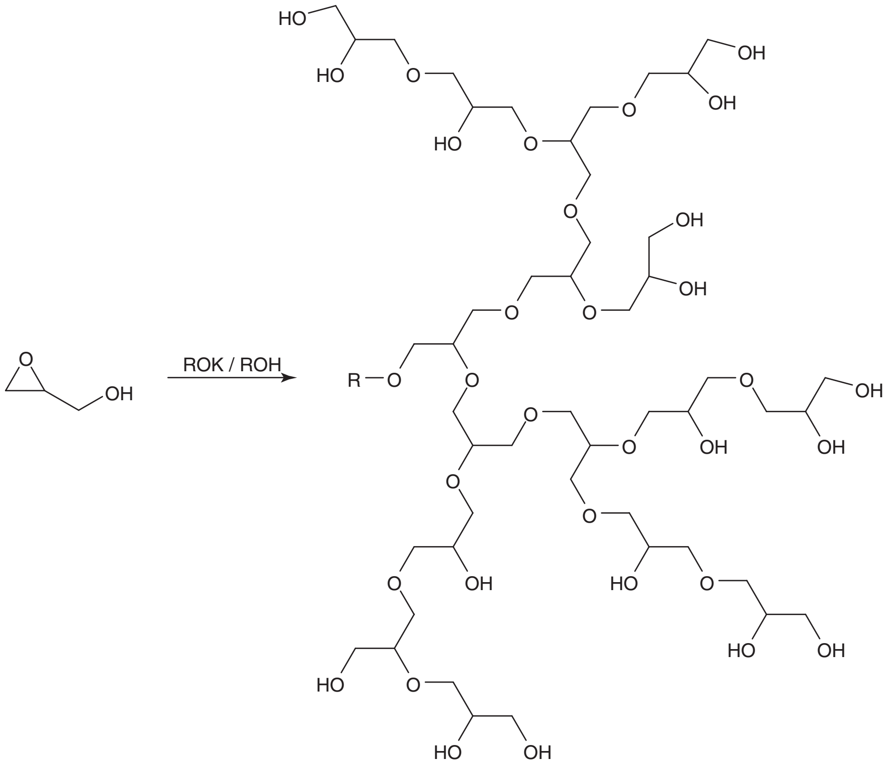
As part of a detailed investigation, analysis of the obtained ^{13}C-NMR spectra provided the authors with initial information about the actual branched structure of polyglycerol (Scheme 6.12).

A 1,4-polymerization pathway involving a proton migration was concluded to be predominant in the base-catalyzed polymerization of glycidol, giving largely poly(3-hydroxyoxetane). Hydroxyl groups (or trimethylsilyloxy groups in case of the protected polyglycerols) are present on both the monomer and the polymer. Easy exchange with the propagating oxyanion was determined to result in chain branching and chain transfer. The processes taking place upon growth of the polyether chain are illustrated in Scheme 6.13. Primary alkoxides are formed after the ring opening due to intra- and intermolecular transfer. Further propagation of these species directly results in branching.

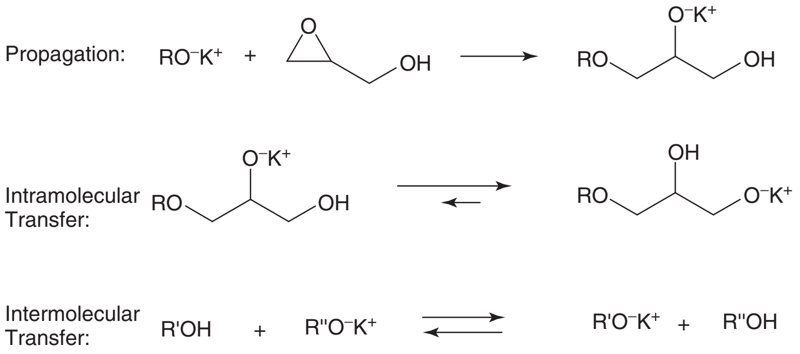
Extensive research involving the synthesis, characterization, and structure of hyperbranched aliphatic polyethers has been carried out by Frey *et al.* since the late 1990s. Analogous to the concepts developed for polymerizations by ATRP[28] and the synthesis of poly(propylene oxide),[29] conventional base initiators were replaced by a partially deprotonated polyfunctional alcohol. Controlled polymerization of glycidol was achieved by applying the SMA approach. 1,1,1-Tris(hydroxymethyl)propane (TMP), bearing three OH groups, has been widely used as a typical multifunctional initiator core. Simultaneous chain growth is essential for obtaining well-defined hyperbranched polyglycerols with narrow molecular weight distributions. Thus, the concentration of active sites in the polymerization (alkoxides) has to be controlled by only partially deprotonating the initiator OH groups, usually by 10% upon addition of a strong base such as potassium methylate as a deprotonating agent, followed by removal of excess methanol. Slow addition of the monomer (SMA) circumvents homopolymerization initiated by deprotonated glycidol as well as any undesired cyclization



Scheme 6.11 Hypothetical formation of linear polyglycerol, as assumed by Sandler and Berg.



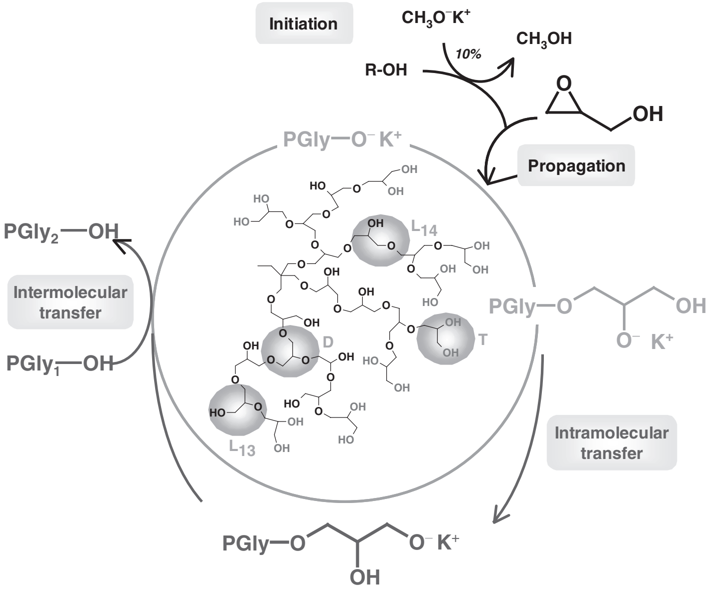
Scheme 6.12 Synthesis of hyperbranched polyglycerol via base-catalyzed polymerization of glycidol.



Scheme 6.13 Mechanism of the anionic polymerization of glycidol.

reactions. Hence this technique further promotes low polydispersities and complete control of the number-average molecular weight by adjustment of the monomer/initiator ratio, when—in the ideal case—every newly formed glycerol unit is attached to the polyfunctional cores or the branched polyols already present in the reaction. The polymerization reaction involves a reversible termination mechanism; nucleophilic attack of the alkoxide takes place at the unsubstituted end of the oxirane ring, leading to a secondary alkoxide. Owing to fast proton transfer equilibria, which are also present in linear epoxide polymerizations, the more stable and more reactive linear alkoxide is formed to a certain extent. Both types of alkoxides are ACEs and therefore lead to the formation of hyperbranched polyglycerols. The fundamental relevance of polyfunctional initiators and the SMA methodology for the formation of well-defined hyperbranched polymers was also shown in an elegant theoretical work for SCVP[30] and by computer simulation.[31] An illustration of the described mechanism is given below. Scheme 6.14 also depicts the different chain units present in the polymer structure.

If the secondary hydroxyl group propagates, the polymer chain is attached to a glycerol unit and a linear 1,3-unit (L_{13}) is generated. A linear 1,4-unit (L_{14}) is formed when the primary hydroxyl group undergoes propagation. Reaction of both hydroxyl groups with monomer leads to the incorporation of a branched, that is, dendritic unit (D). If a monomer unit has been deactivated by proton

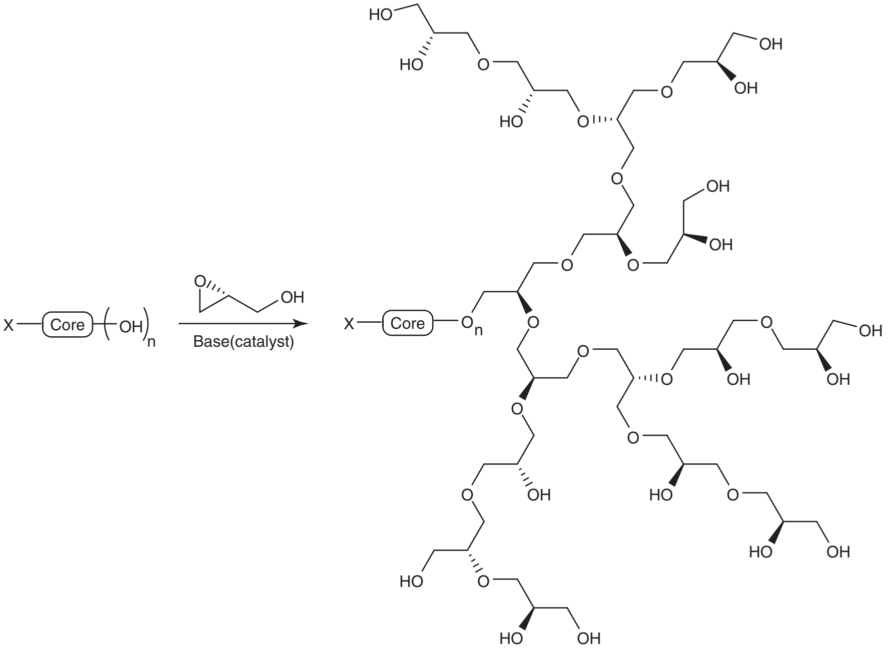


Scheme 6.14 Mechanistic pathway of the base-catalyzed ring-opening multibranching polymerization of glycidol and schematic architecture of the resulting hyperbranched polyglycerol. Examples for terminal (T), dendritic (D), linear 1,3-(L_{13}), and linear 1,4-units (L_{14}) are shaded.

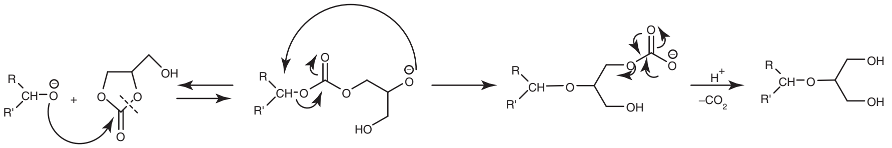
exchange, a terminal unit (T) with two hydroxyl end groups is formed. A detailed structural investigation of these hyperbranched polyglycerols was carried out by Frey *et al.* who analyzed inverse-gated ^{13}C-NMR spectra in order to calculate DBs and degrees of polymerization (DP_n). Incorporation of the TMP core into the polymer and the amount of cyclization occurring during the reaction were studied by MALDI-TOF mass spectrometry. Polymers with molecular weights of up to 10,000 g/mol (significantly higher M_n than for those obtained from the previously discussed cationic polymerizations) were prepared. They exhibited narrow molecular weight distributions ($M_w/M_n < 1.5$, mostly < 1.3) due to the pseudochain growth kinetics. A very interesting recent work in this area was published by Brooks *et al.*, who modified the procedure by adding dioxane as emulsifier. In this case, very high molecular weight polyglycerols with M_n up to 700,000 g/mol have been obtained.[32] These materials exhibit the highest molecular weights obtained for synthetic hyperbranched polymers reported to date. The reason for the formation of high molecular weight polyglycerols possessing narrow polydispersity is not yet clear. Brooks *et al.* tentatively explain the effect on molecular weight by the fast proton exchange in their system. In a further study, Brooks *et al.* have demonstrated excellent biocompatibility and low toxicity for hyperbranched polyglycerols, similar to what has been known for a long time for poly(ethylene oxide) (PEO). This renders the material interesting for biomedical application, potentially as a substitute for PEO.[33]

If only one of the enantiomers of glycidol is used in the polymerization, chiral hyperbranched polyglycerols can be obtained (Scheme 6.15). In analogy to the previously discussed racemic polyglycerols, the respective polymerization of both commercially available glycidol enantiomers has been investigated.[34] The obtained polymers exhibited similar specific optical rotation $[\alpha]$ per monomer unit as the monomer used for polymerization. This is an important observation, since it confirms the expectation that in anionic epoxide polymerization the nucleophilic attack occurs at the least substituted end of the epoxide ring. In this case, the chiral center is not affected. $[\alpha]$ was found to be independent of the DP, since each monomer unit adds one chiral center to the polymer.

Rokicki *et al.*[35] recently reported a promising alternative synthesis of hyperbranched polyglycerol by ROMBP of glycerol carbonate, a benign monomer that can be obtained from the renewable materials glycerol and dimethyl carbonate under mild conditions. The reaction was carried out in accordance with the method established by Frey, for example, TMP was used as a trifunctional initiator core under SMA conditions, leading to the formation of branched polyethers upon CO_2 liberation. Attack of the alkoxide can occur either at the carbonyl or at the alkyl carbon atoms of the cyclic carbonate group. The authors observed an additional ^{13}C-NMR signal that did not appear in the spectra of the polymers obtained from glycidol polymerization. This signal can be attributed to the generation of terminal 1,3-dihydroxy units, which is the result of an intramolecular rearrangement that can take place in the course of the polymerization after formation of an intermediate linear carbonate (Scheme 6.16).



Scheme 6.15 Synthesis of chiral hyperbranched polyglycerol.



Scheme 6.16 Formation of terminal 1,3-dihydroxy units in the polymerization of glycerol carbonate.[35]

The obtained polymers were of low molecular weight and polydispersities ranged between 1.2 and 1.3.

It was highlighted in the previous paragraph that multifunctional oxetanes undergo cationic ring-opening polymerizations resulting in hyperbranched polyol structures analogous to hyperbranched polyglycerols. Oxetanes have been classically considered as monomers that can only be polymerized cationically. However, some anionic polymerizations of unsubstituted oxetane using bulky aluminium-based catalysts with added Lewis acids have been reported.[36,37] It was shown that treatment of substituted oxetanes with extremely strong nucleophiles, such as the azide anion,[38] or redox conditions with lithium 4,4′-di-*tert*-butylbiphenylide[39] result in ring opening, but do not promote polymerization. Smith and Mathias[40] first described the anionic ring-opening polymerization of

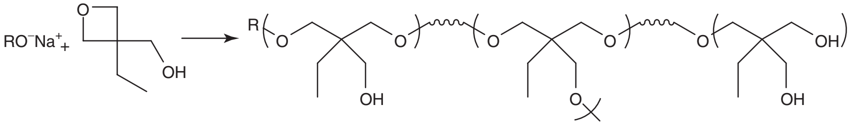
EHO to a hyperbranched polyol using a strong base catalyst (sodium hydride) and TMP as a multifunctional initiator core. The polymerization was carried out under SMA conditions at high temperatures (>100 °C) because of the high activation energy of the ring opening.

The resulting hyperbranched polyols (Scheme 6.17) were of low molecular weight and, in contrast to hyperbranched polyglycerols, dissolved in chloroform and benzene but were insoluble in water. A fraction of the polymers showed solubility in acetone and was found to have a higher degree of branching (DB = 0.48) than the acetone-insoluble fraction (DB = 0.2). On using benzyl alcohol as a monofunctional initiator, the resulting polymer was completely soluble in acetone and NMR spectra indicated a high DB.

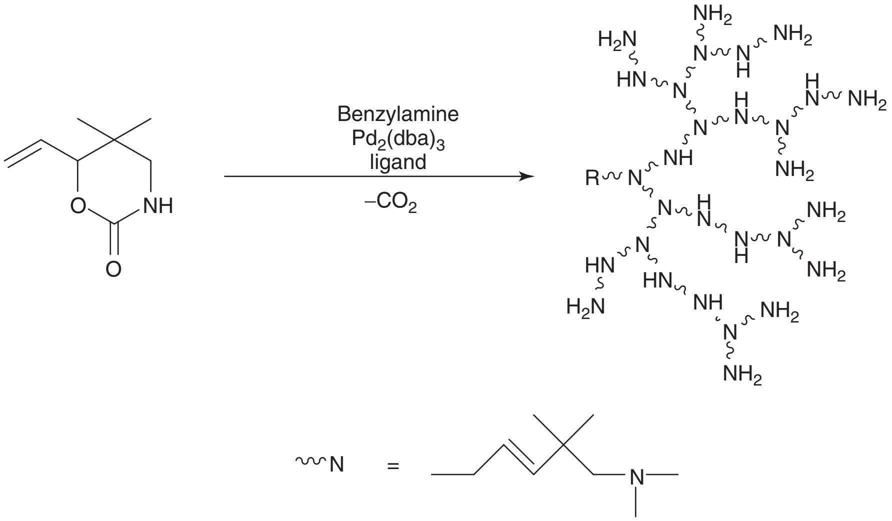
In summary, anionic polymerization techniques represent by far the most common approach in the synthesis of well-defined hyperbranched polymers by ring-opening polymerization at present, particularly in the field of hyperbranched polyols. Numerous research groups are currently engaged in the preparation, modification, and characterization of the respective polymers for a broad variety of applications, ranging from biomedicine to advanced coatings.

6.2.3 Catalytic Ring-Opening Multibranching Polymerizations

A remarkable example of the significance of metal catalysts in polymer science (which won the Nobel Prize in Chemistry jointly for Ziegler and Natta in 1963)[41] can be found in the stereoselective polymerization of α-olefins.[42–44] Further progress in this area, merging the exceptional work of organic, inorganic, and polymer chemists, won the joint Nobel Prize in Chemistry for Chauvin, Grubbs, and Schrock in 2005, for their achievements in the domain of ring-opening metathesis polymerization (ROMP).[45] Ring-opening polymerizations of cyclic lactides and lactones initiated by nucleophiles (i.e., alcohols, amines) in the presence of suitable organometallic promoters have been outlined in numerous publications.[46] The recent impressive progress in the catalytic polymerization of vinyl monomers leading to hyperbranched structures is detailed in Chapter 9 of this volume. The first ROMBP involving a transition-metal catalyst was reported by Suzuki *et al.* in 1992. Pertinent previous studies[47] provided the authors with a concept of combining the catalytic effect of a Pd(0) complex with a suitable monomer structure for ring-opening polymerization. The



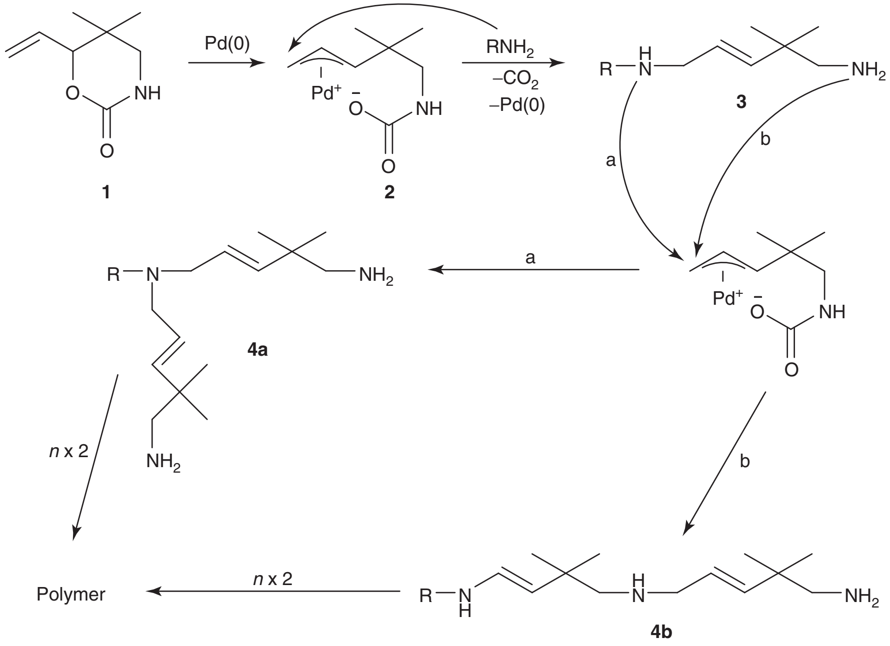
Scheme 6.17 Ring-opening multibranching polymerization of EHO.



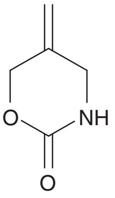
Scheme 6.18 Catalytic polymerization of 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one. The mechanism proposed by Suzuki and coworkers is depicted in Scheme 6.19. It involves the π-allylpalladium complex **2** as the key intermediate. The amine initiator is assumed to attack the electrophilic site of **2** to produce the diamine **3**, releasing carbon dioxide and regenerating a Pd(0) complex. Depending on which of the amino groups of **3** reacts, two different triamines, **4a** and **4b**, are possible.

monomer of choice was the cyclic carbamate 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one (Scheme 6.18). Benzylamine-initiated polymerization with the aid of $Pd_2(dba)_3 \cdot CHCl_3$-2dppe catalyst at room temperature produced a hyperbranched polyamine consisting of primary, secondary, and tertiary amino moieties upon CO_2 evolution. A simplified illustration of the reaction is given in Scheme 6.19.

A peculiarity of this work becomes obvious when the molecular weight distribution of the obtained polymer is considered. After the transformation of secondary amino groups into carbamate groups (to prevent interaction with the polystyrene beads in the gas-phase chromatography (GPC) column), a very low polydispersity of 1.35 was found at a molecular weight of about 3000 g/mol. Since the amount of initiator employed determines the molecular weights obtained, Suzuki *et al.* in fact developed the first case of a controlled ROMBP, avoiding broad molecular weight distributions and undesired side reactions. Paralleling this pioneering work, further studies were carried out utilizing a slightly varied cyclic carbamate structure (Scheme 6.20).[48] 5-Methyleneperhydro-1,3-oxazin-2-one was polymerized by a Pd(0) catalyst of very similar structure. Triphenylphosphine was found to be a better ligand than bis(diphenylphosphino)ethane (dppe) in this case. Narrowly dispersed ($M_w/M_n = 1.3–1.5$) and highly branched polymers with molecular weights between 2000 and 3000 g/mol were also obtained in this work.



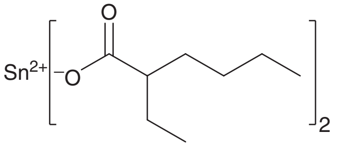
Scheme 6.19 Mechanism of the catalytic polymerization of 5,5-dimethyl-6-ethenylperhydro-1,3-oxazin-2-one.



Scheme 6.20 5-Methyleneperhydro-1,3-oxazin-2-one.

Stannous octoate ($SnOct_2$) (Scheme 6.21) is a widely used catalyst in polylactide synthesis[49,50] as well as in the polymerization of lactones with alcohols.[46,51,52]

The explicit initiation mechanism presumably depends on the temperature and has not been entirely elucidated to date. Two basic types of mechanisms



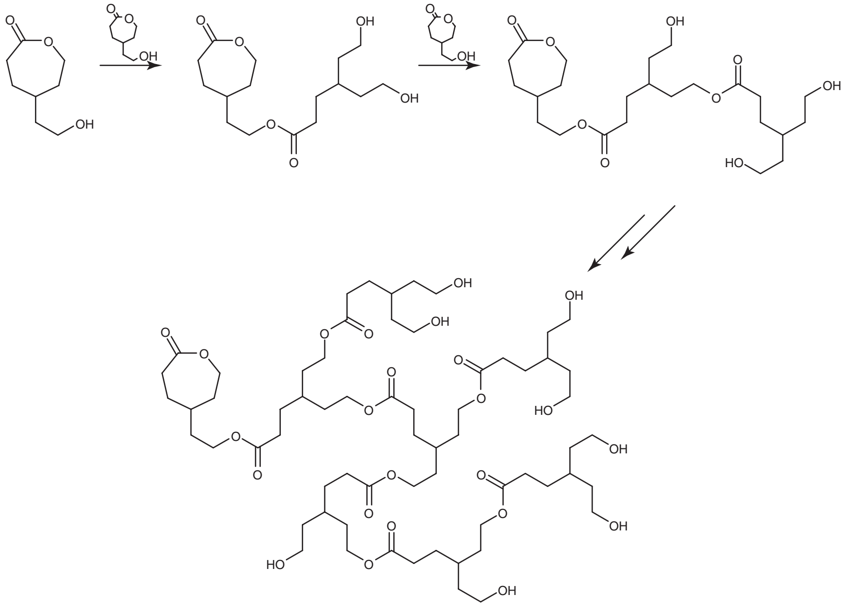
Scheme 6.21 Stannous octoate ($SnOct_2$).

have been proposed in the literature: a direct catalytic type,[53,54] where the catalyst serves to activate the monomer through coordination with its carbonyl oxygen, and monomer insertion type mechanisms,[55–61] involving the catalyst as coinitiator along with either purposely added or adventitious hydroxyl impurities. In the latter case, polymerization proceeds through an activated stannous alkoxide bond.

In 1999, Fréchet *et al.* reported an elegant approach to hyperbranched polyesters of high molecular weight, based on the ring-opening polymerization of a monomer containing an ε-caprolactone ring as well as a primary alcohol group (4-(2-hydroxyethyl)-ε-caprolactone), that is, a lactone-based inimer structure.[62]

Bulk polymerization was carried out at elevated temperature in the presence of a catalytic amount of $SnOct_2$.[63] Scheme 6.22 depicts the pathway of this ROMBP leading to high molecular weight hyperbranched polymers (M_w = 65,000–85,000 g/mol) with a polydispersity of approximately 3.2. Similar to that observed in SCVP, broad polydispersities are in line with expectation for a one-pot synthesis of this type.

The reaction was found to proceed faster when the amount of catalyst was increased. However, smaller amounts of catalyst had a tendency to give polymers with high molecular weights. In agreement with other hyperbranched polymers possessing a large number of hydroxyl end groups, like the previously discussed polyglycerol, the obtained polyester was soluble in polar solvents such as DMSO, DMF, and methanol, but insoluble in THF, CH_2Cl_2, and $CHCl_3$. In



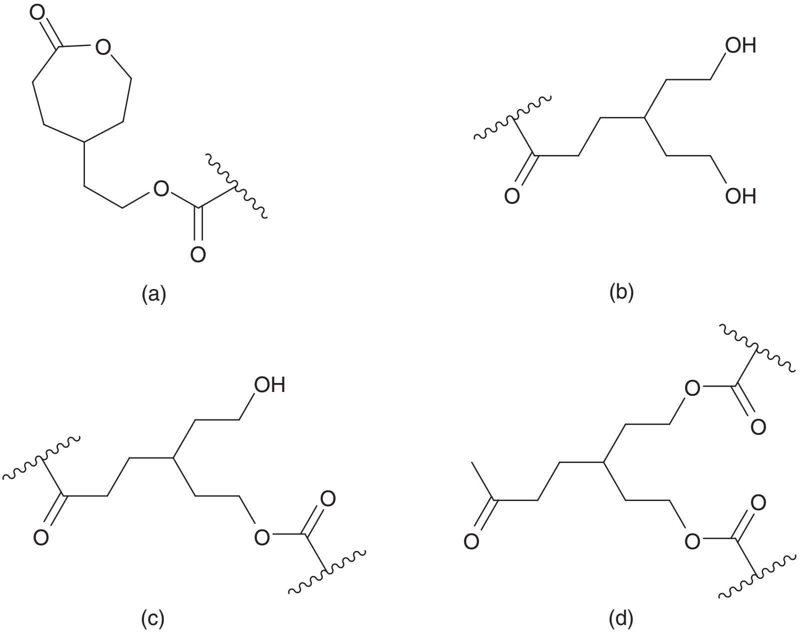
Scheme 6.22 Catalytic polymerization of 4-(2-hydroxyethyl)-ε-caprolactone.[62]

order to determine the relative amount of linear, terminal, and dendritic subunits (Scheme 6.23), ^{13}C-NMR-spectra of the polymer were recorded and compared with spectra obtained from suitable model compounds. The DB was then calculated to be 0.50 according to the definition established by Hawker *et al.* which confirms the hyperbranched structure.[1]

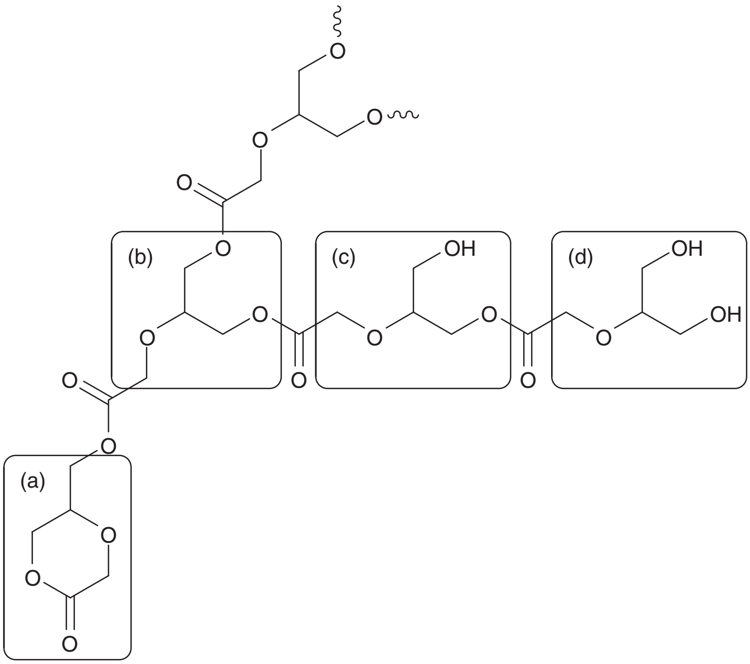
Another hyperbranched polyester was recently prepared and characterized in an elegant work by Rokicki *et al.*[64] They described the synthesis of 5-hydroxymethyl-1,4-dioxan-2-one (5-HDON) and its application for the preparation of hyperbranched polymers by ROMBP initiated by the Sn(Oct)$_2$ catalyst.

The theoretical structure of the obtained polymers and oligomers is shown in Scheme 6.24. Similar to the hyperbranched polyester prepared by Fréchet *et al.*, four main subunits are possible. The polymerization starts at the core unit A. Dendritic subunit B is completely substituted and therefore represents the branching point, while C depicts a linear fragment of the molecule. The terminal units D contain two unsubstituted hydroxymethyl groups.

Characterization by MALDI-TOF mass spectrometry showed a relatively small fraction of polymers containing either hydrolyzed 5-HDON or glycerol as the core unit. Comparably high molecular weights (M_n = 25,000–44,000 g/mol) and low polydispersities (M_w/M_n = 1.7–2.0) were found by GPC analysis. Detailed investigation by NMR spectroscopy revealed that use of an anionic initiator (DBU) lead to the incorporation of more dendritic units into the polymer



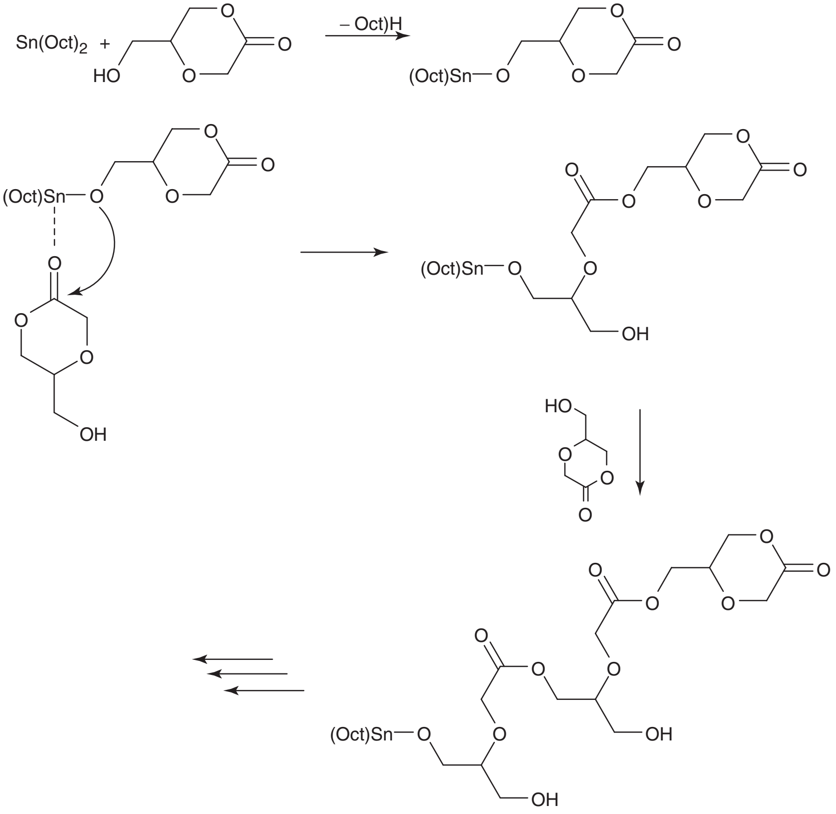
Scheme 6.23 Structure of the possible subunits in the polyester **1**: (a) the focal unit, (b) terminal units, (c) linear units, and (d) dendritic units are depicted.



Scheme 6.24 Theoretical structure of poly(5-HDON).

structure. However, extending the reaction time to 72 h instead of 24 h at increased temperature (110 °C instead of 75 °C) gave highly branched polymers with the $Sn(Oct)_2$ catalyst. These observations appear to confirm earlier assumptions about a temperature dependence of the mechanism in question. The authors therefore suggest the predominance of a coordination–insertion mechanism (Scheme 6.25) at lower temperatures. The respective reaction pathway favors the incorporation of linear subunits (C). Higher temperatures and longer reaction times, however, promote $Sn(Oct)_2$ to act as a transesterification catalyst and hence result in a larger amount of branched structures.

A hyperbranched polyester of closely related structure was prepared by Yu *et al.*, who polymerized 6-HDON with $Sn(Oct)_2$ catalyst at elevated temperatures over periods of 1–8 d.[65] Molecular weights were found in the range of 7,800 to 25,600 g/mol with polydispersities between 2.0 and 3.0. The polymers with high molecular weights were obtained only when the catalyst concentration was fixed at 1/400 (molar ratio to feed). Increasing or decreasing the amount of catalyst resulted in lower molecular weights. DBs were determined by quantitative ^{13}C inverse-gated NMR spectrum analysis and found to be 0.4. The polymerization reaction and the different units of the obtained polyesters are illustrated in Scheme 6.26. Terminal units A and B, linear units C and D, as well as dendritic units E are present in the polymer structure and can be assigned to the respective signals in the NMR spectra. Similar to the polyester prepared by Parzuchowski



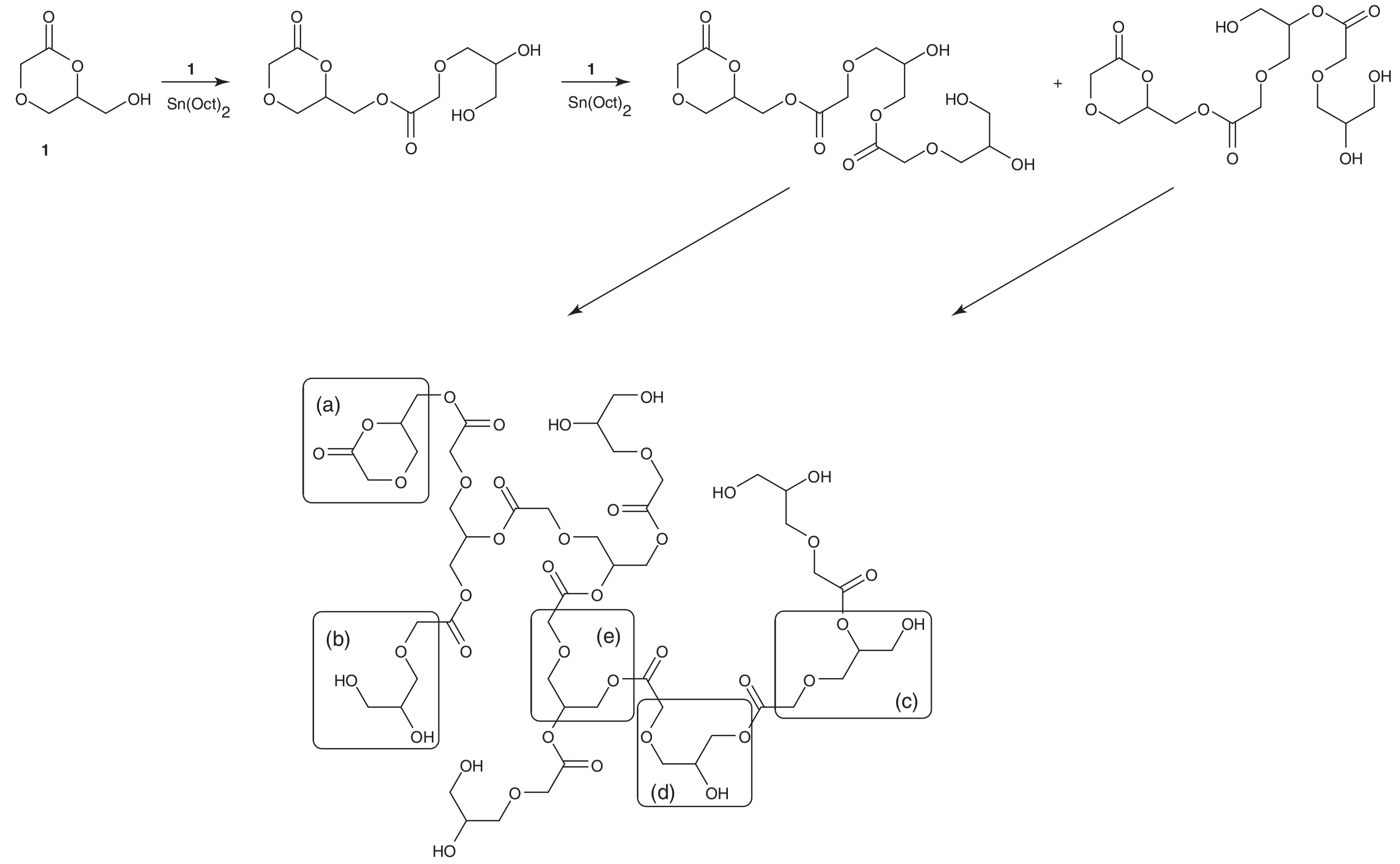
Scheme 6.25 Mechanism of the coordination–insertion polymerization of 5-HDON in the presence of $Sn(Oct)_2$.

et al. (Scheme 6.24), this polymer consists of glycerol and glycolic acid units, which renders it biodegradable and biocompatible.

Catalytic ROMBPs have become a fitting method for the preparation of hyperbranched polyesters with considerable DPs. The associated high molecular weights are often conveniently accessible because the sensitivity to traces of impurities is less distinct than in cationic or anionic polymerization techniques. Furthermore, Pd(0) complexes have been shown to be useful catalysts in the controlled synthesis of hyperbranched polyamines.

6.3 CORE-CONTAINING HYPERBRANCHED POLYMERS BY RING-OPENING MULTIBRANCHING POLYMERIZATION

In this part of the chapter, some recent advances in the synthesis of complex polymer architectures are summarized that capitalize on ring-opening multibranching



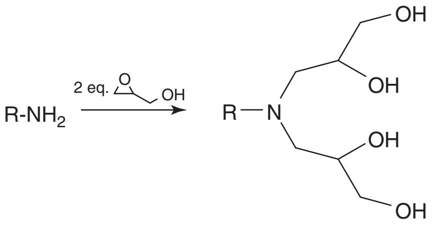
Scheme 6.26 Synthesis and structure of poly(6-HDON).

strategies, such as the incorporation of a functional core moiety. Macromolecular encapsulation in dendritic polymers has received much attention in recent years.[66] Detailed studies on dendrimers have revealed that, at some critical dendrimer generation, the core is encapsulated by the sterically crowded and densely packed branched architecture.[67,68] It has been demonstrated for perfectly branched dendrimers that the site isolation of a core moiety in a dendritic scaffold is of great interest with respect to optical properties and for catalysis. Within this context, Fréchet *et al.* introduced a solvatochromic chromophore (4-(N,N-dimethylamino)-1-nitrobenzene) at the focal point of a polybenzylether dendrimer.[69] It has also been shown that manganese and zinc porphyrins coated by a dendritic structure exhibit better stability and improved regioselectivity in catalytic processes.[70,71] Additionally, dendritic encapsulation of active core moieties has been proposed to serve as a model for the shielding of active centers in naturally occurring enzymes.[72]

Resembling dendrimers in most of their characteristics and being accessible much less tediously, well-defined hyperbranched polymers containing an encapsulated single core moiety have qualified for analogous studies. Tian *et al.* used a modified triphenylamine as core for the synthesis of a conjugated hyperbranched polymer.[73] A direct influence of the hyperbranched architecture on both UV absorption and fluorescence properties of the core was observed. Furthermore, postpolymerization modification of a nitrophenyl ester core, subsequent to the formation of the dendritic structure, has been reported.[74,75]

Competing homopolymerization of the branched monomer is an often disregarded reaction in the synthesis of core-containing hyperbranched polymers. Owing to simple statistical reasons, most hyperbranched macromolecules are unlikely to possess a core unit in a conventional B_n/AB_m-type copolycondensation. In a very elegant study, Žagar and Žigon demonstrated this in 2002 for commercially available hyperbranched polyesters (Boltorn) obtained from an AB_2 monomer and B_3 functional core molecule.[76] Unequivocal evidence of the incorporation of a specific core into all species present in the distribution of a hyperbranched structure can only be given by mass spectrometry, usually MALDI-TOF MS. We recently studied the incorporation of different initiator cores into hyperbranched polyglycerols under the previously described SMA conditions.[77] The employed cores were structurally different, including mono- and bifunctional n-alkyl amines as well as photoactive cores, such as benzylamine and 1-naphthylmethylamine and a typical triplet photosensitizer, 2,2′,4,4′-tetrahydroxy benzophenone $BP(OH)_4$. Bisglycidolization of the amines prior to polymerization (Scheme 6.27) was found to result in improved molecular weight control ($M_n = 1600-8400$ g/mol) and polydispersity ($1.5 < M_w/M_n < 2.5$).

The macromolecules obtained from polymerization of glycidol initiated by the tetra-hydroxyfunctional benzophenone $BP(OH)_4$ were of narrow polydispersity ($1.5 < M_w/M_n < 2$) and exhibited molecular weights between 1500 and 5800 g/mol. The phenolic nature of the initiator hydroxyl groups and the simple deprotonation of this core led to fast and complete incorporation into the



Scheme 6.27 Bisglycidolization of the amine initiator cores.

growing hyperbranched polymers. The applied synthetic strategy is depicted in Scheme 6.28.

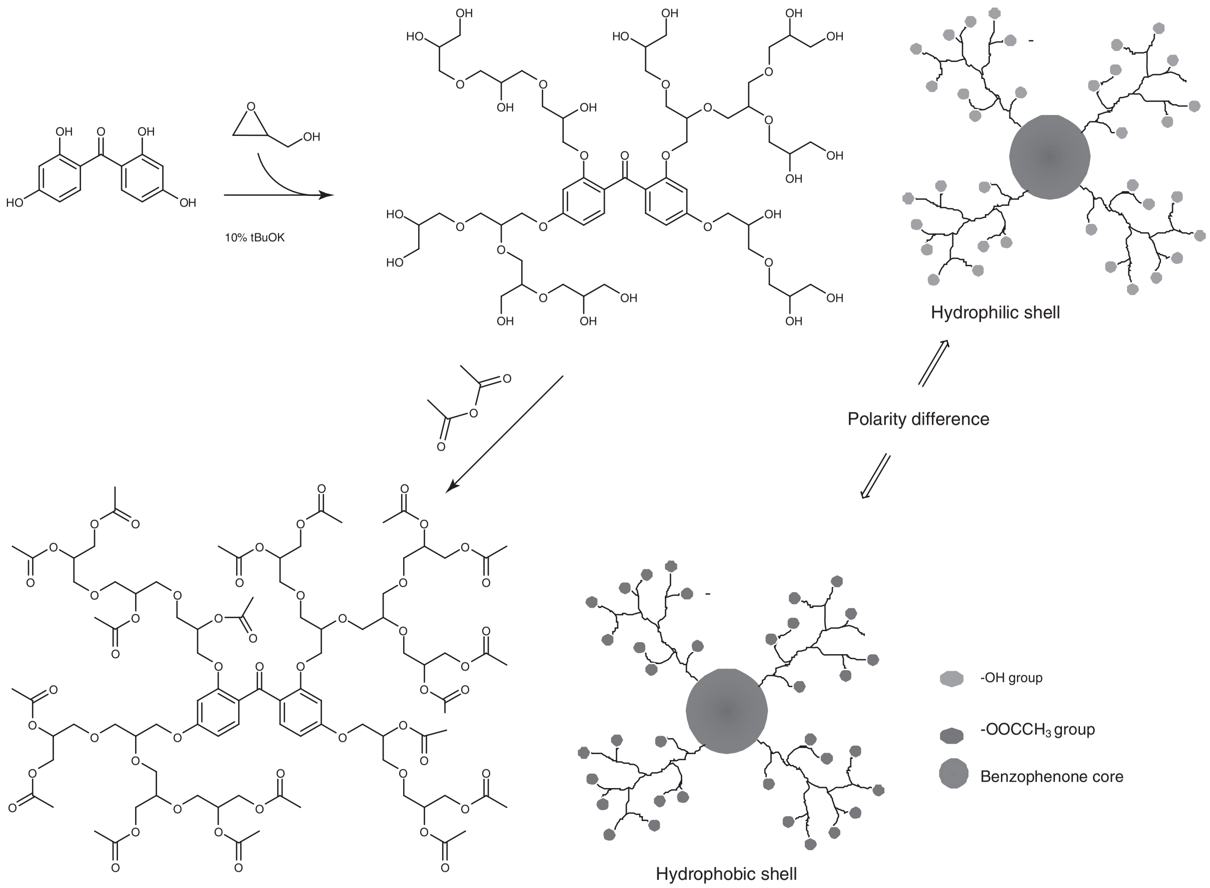
Complete incorporation of the photoactive core moiety into the well-defined hyperbranched structure was conclusively evidenced by MALDI-TOF mass spectrometry. Figure 6.1 shows the central part of the MALDI-TOF mass spectrum (between 500 and 3000 g/mol) of a benzophenone core, containing a polymer with 80 glycidol units.

The molar mass of the glycidol units ($M = 74.1$) is represented by the mass differences between the peaks. The mass of each signal in the molecular weight distribution corresponds to the sum of the mass of the benzophenone core and the mass of the respective number of glycidol repeating units plus one lithium ion (attached to the polymer upon the ionization process in the instrument). Only a single distribution mode can be observed, verifying the absence of masses corresponding to non-core-containing polyglycerol homopolymers thereby proving the quantitative incorporation of the initiator core.

The benzophenones substituted with a hyperbranched polyglycerol PG corona showed high photostability even after prolonged irradiation in methanol. Such polymer-encapsulated benzophenones can be conveniently separated from the reaction media by dialysis or membrane filtration and hence represent very promising materials with respect to application as easily recoverable and reusable photocatalysts.

6.4 CONCLUSION AND PERSPECTIVES

In this chapter, we have demonstrated that ROMBPs are well established as a versatile and often preferential method for the controlled synthesis of well-defined hyperbranched polymers with moderate polydispersity. The heterocyclic monomers discussed in the preceding text generally represent latent AB_m monomers eligible for pseudochain growth (polymerization by ring opening = chain growth, condensation of the pending B group with the heterocycle = step growth). A major advantage of ring-opening polymerizations compared to conventional polycondensations is the generic absence of condensation products. This inherent characteristic allows for the application of cationic, anionic, and catalytic polymerization techniques in the initiated polymerization of suitable cyclic monomers, using functional initiators to achieve remarkable control over



Scheme 6.28 Synthetic approach for the incorporation of a benzophenone core into hyperbranched polyglycerols and peracetylation of the obtained polymer.

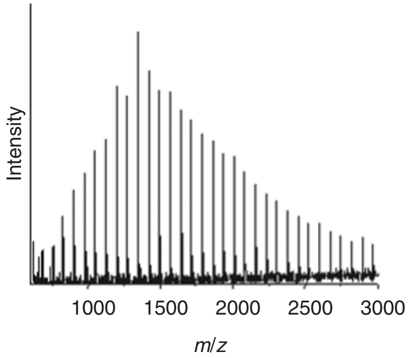


Figure 6.1 MALDI-TOF mass spectrum of benzophenone-cored hyperbranched polyglycerol.

molecular weights and polydispersity. Employing SMA conditions, pseudochain growth was realized for glycidol, permitting a certain extent of control over molecular weights.

Understanding and controlling the branching pattern as well as molar mass represent an important issue for the elucidation of structure property correlations as well as the assembly of more complex polymer architectures using ROMBP. In this context, synthetic principles and detailed examples for the advantages of this strategy are presented in Chapter 11 of this volume.

The characteristics of ring-opening polymerizations also permit us to carry them out in continuous reaction processes. Microstructured reaction systems have recently drawn considerable attention due to their inherent advantages such as high mixing efficiency, excellent heat transfer, and convenient access to large scales of products.[78] Several polymerizations have been carried out in microreactors, in some cases leading to improved control over molecular weight distributions at significantly reduced reaction times.[79,80] Low molecular weight polyglycerols have been recently prepared by ROMBP in a microstructured reactor.[81] This method for the synthesis of low viscosity hyperbranched polymers is very promising in terms of the development of a technically convenient, less time-consuming technique, facilitating access to large amounts of the desired products. As the ring-opening nature of the reactions discussed in this chapter usually renders them highly exothermic, the usage of microreactors is of particular interest because of the high surface-to-volume ratio ensuring very efficient heat removal.

In addition to the development of more efficient reaction systems for existing polymerization procedures, future research involving ROMBPs will certainly include novel cyclic monomers leading to a variety of branched materials that can be obtained under controlled conditions.

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Chapter 7

Hyperbranched Copolymers Synthesized by Cocondensation and Radical Copolymerization

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7.1 INTRODUCTION

Dendritic polymers have emerged as a research area with a huge potential of applications ranging from drug delivery to nano-building blocks, because they have unique properties due to their three-dimensional architecture and high level of functionality.[1–11] Dendritic topology has been recognized as the fourth major class of macromolecular architecture,[12] along with traditional linear, branched, and cross-linked macromolecular structures. This architecture consists of three subclasses related to the degree of structural control, namely, as (i) random hyperbranched polymers, (ii) dendrigraft polymers, and (iii) dendrons/dendrimers.[13] Hyperbranched polymers have the least controlled structures in the dendritic family.

A broad range of dendritic polymers have been synthesized through numerous synthetic strategies in the last decade.[6,12–15] Dendrons and dendrimers, with well-defined size and shape, are usually prepared by solvent-intensive and multistep synthetic pathways, although scientists have made arduous efforts on developing

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

various methods to reduce the synthetic steps. Thus, their commercial development and practical applications have been severely limited. By contrast, hyperbranched polymers can be more easily and effectively synthesized in a one-step reaction by the single monomer methodology (SMM) or the double monomer methodology (DMM).[16] In SMM, the polymerization of an AB_n or latent AB_n monomer leads to hyperbranched macromolecules, such as (i) polycondensation of AB_n monomers (Chapter 2); (ii) self-condensing vinyl polymerization (SCVP) (Chapter 5); (iii) self-condensing ring-opening polymerization (ROP) (Chapter 6); and (iv) proton-transfer polymerization.[16] In DMM, direct polymerizations of two suitable monomers or a monomer pair give rise to hyperbranched polymers. The polymerization of A_2 and B_n ($n > 2$) monomers is a typical example of DMM (Chapter 3). The DMM based on *in situ* formation of AB_n intermediates from specific monomer pairs is designated as *couple-monomer methodology* (CMM) (Chapter 4).

Copolymerization has long been utilized as a tool to modify the chemical and physical properties of polymers. This includes chain growth copolymerization techniques and copolycondensation reactions. This chapter reviews the synthesis of hyperbranched copolymers by one-step cocondensation of AB_n or AB_n intermediates with a comonomer (not including a B_n type core monomer), for example, "$AB_n + AB$" approach, "$AB_2 + AB_2$" approach, "ROP + AB_2" approach, and "$A_2 + B_2 + BB'_2$ (or $B'B_2$)" approach, as well as by self-condensing vinyl copolymerization (SCVCP) via the formation of chain-transfer complex (CTC) inimers, and radical copolymerizations of multifunctional vinyl monomers.

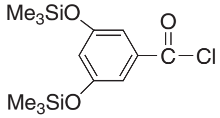
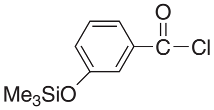
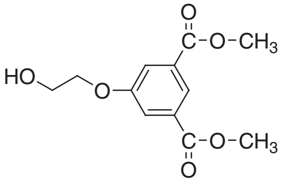
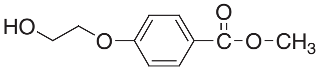
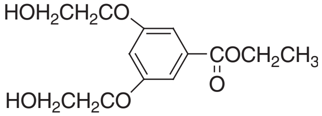
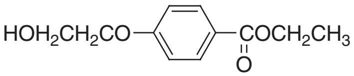
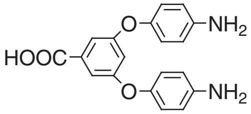
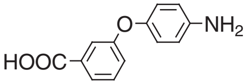
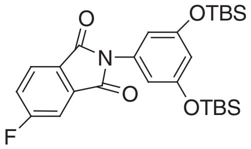
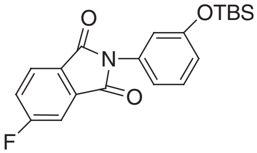
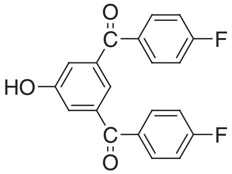
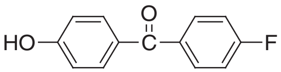
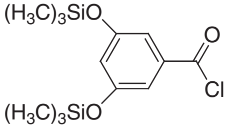
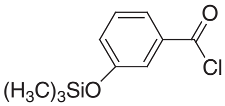
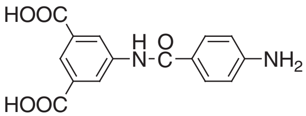
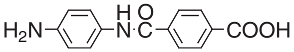
7.2 COCONDENSATION OF AB_n AND A COMONOMER

The step-growth polymerization of AB_n monomer is by far the most intensively studied synthetic route to hyperbranched polymers. AB_2 type monomers are used mostly because of their facile preparation, while AB_3, AB_4, and AB_6 monomers have also been reported as monomers for hyperbranched polyesters and polysiloxanes.[6] Flory was the first to report a statistical study for the polymerization and the infinite network formation of AB_n multifunctional monomer,[17,18] and to propose the concept of the copolymerization.[18] So far, several cocondensation approaches have been used to prepare hyperbranched copolymers by using AB_n and a comonomer.

7.2.1 $AB_n + AB$ Approach

A number of authors have utilized the cocondensation of the "$AB_n + AB$" approach to tune the physical properties of hyperbranched copolymers (Table 7.1), including Kricheldorf *et al.*[19–21] and Kunamaneni *et al.*[22] for polyesters; Jayakannan *et al.*[23,24] for poly(4-ethyleneoxy benzoate) (PEOB); JiKei *et al.*[14,25–28] for hyperbranched aromatic polyamides and polyimides;

Table 7.1 Some Examples of Cocondensation via "$AB_n + AB$" Approach

AB_n	AB	Authors and References
1 	**2** 	Kricheldorf *et al.*[19]
3 	**4** 	Kunamaneni *et al.*[22]
5 	**6** 	Jayakannan *et al.*[24]
7 	**8** 	JiKei *et al.*[25–28]
9 	**10** 	Markoski *et al.*[29,30]
11 	**12** 	Baek *et al.*[31]
13 	**14** 	Frey *et al.*[34]
15 	**16** 	Monticelli *et al.*[35]

Markoski *et al.*[29,30] for poly(etherimide)s; Baek *et al.* for poly(ether ketone) (PEK)s[31] and poly(phenyl quinoxaline)s;[32] and Fossum *et al.*[33] for PEK copolymers. Frey *et al.*[34] have also reported the copolymerization of AB- and AB_n-type monomers via a slow monomer addition (SMA) technique, leading to highly branched polyesters and polyglycerols. The variation of the molar feed ratio of difunctional to trifunctional monomers allows varying the branching density over a broad range, which in turn has an impact on the properties of the resultant polymers including thermal properties, viscosity, and solubility.

In 1982, Kricheldorf *et al.*[19] first reported the copolymerization of AB monomer (3-(trimethylsiloxy)benzoyl chloride) (**2** in Table 7.1) and AB_2 monomer (3,5-bis(trimethylsiloxy)benzoyl chloride, BTBC) (**1** in Table 7.1) to form highly branched aromatic polyester copolymers. Analogous copolyesters having different end groups were also prepared by copolycondensation of 3-acetoxybenzoic acid and 3,5-bisacetoxybenzoic acid. For linear polymers, the end groups have no influence on the physical properties provided that the number-average molecular weight (M_n) of the polymers is above 10^4.[36] The situation is different for hyperbranched polymers because of the large number of end groups. A typical example is the comparison of the glass transition temperature (T_g) of poly(3,5-dihydroxybenzoate)s having acetate or OH end groups and poly(5-hydroxy isophthalate) having COOH end groups. Despite similar molecular weights and polymer chains, their T_gs vary between 140 and 260 °C.[19,20]

The copolymerization of bis-(α-hydroxyethyl) terephthalate (BHET) with AB_2-type ethyl bis-3,5-(2-hydroxyethoxy) benzoate (EBHEB, **5** in Table 7.1) monomer gave rise to branched poly(ethylene terephthalate) (PET).[23] Furthermore, hyperbranched PEOB was prepared by the condensation of ethyl, 4-(2-hydroxyethoxy) benzoate (E4HEB, **6** in Table 7.1) with EBHEB under similar conditions.[24] Various amounts of branching (0–50%) were introduced into the linear polymer by changes in the composition of the comonomers in the feed. The intrinsic viscosity of the copolymers indicated that they were of reasonably high molecular weights. The thermal analysis of the copolymers using differential scanning calorimetry (DSC) showed that both the melting temperatures (T_m) and the percent crystallinity decreased with increasing comonomer content, and the copolymers were completely amorphous when the extent of the AB_2 incorporation monomer exceeded 10 mol%. However, their glass transition temperatures were less affected.

The synthesis and properties of dendritic and hyperbranched aromatic polyamides and polyimides, including the copolymerization of AB_2 and AB monomers, have been reviewed by Jikei *et al.*[14] The one-step cocondensation of AB_2 monomer (3,5-bis-(4-aminophenoxy)benzoic acid) (**7** in Table 7.1) and AB monomer (3-(4-aminophenoxy)benzoic acid) (**8** in Table 7.1) in the presence of condensation agents (triphenyl phosphate (TPP) and pyridine) have been investigated.[25–28] This copolymerization results in the formation of copolymers with low branching density, which can be controlled by the mole ratio of AB_2 and AB monomers.[25,26] The small amount of AB_2 branching points affects the properties of resultant copolymers dramatically, leading to improved solubility.[28] Mark–Houwink parameters of the copolymers are essentially independent of the mole ratio of the monomers. The physical and mechanical properties of the resultant copolymers are influenced not only by the mole ratio of the monomers but also by the structure of the monomers employed. Hyperbranched aromatic polyamide (aramid) copolymers were also prepared by one-step cocondensation of 5-(4-aminobenzoylamino)isophthalic acid (AB_2 monomer, **15** in Table 7.1) with *N*-(4-aminophenyl)terephthalamic acid (AB monomer, **16** in Table 7.1) in the presence of TPP as the condensation agent.[35] The feed ratio of the monomers affects the intrinsic viscosity and the solubility of copolymers in aprotic polar solvents such as *N*,*N*-dimethylformamide, *N*-methylpyrrolidone, and dimethyl sulfoxide. Only high AB_2/AB monomer ratios lead to completely soluble polymers in the above media.

Glycidol as latent branching AB_2 monomer was used in combination with allyl or phenyl glycidyl ethers (AGEs or PGEs) as linear AB comonomers for the preparation of random hyperbranched copolymers with controlled degree of polymerization ($DP_n = 42–72$) and relatively low polydispersity ($PDI < 1.7$).[37] The degree of branching (DB) of the random copolymers of glycidol and AGE as well as PGE was controlled in the range 9–58% by the comonomer ratio. Furthermore, block copolymers of glycidol and AGE, that is, multiarm star polymers, have been prepared by sequential addition of the monomers. The thermal behavior of all materials has been investigated with respect to the copolymer composition.

Random bulk cocondensation and the SMA strategy have been employed for the preparation of hyperbranched aromatic copolyesters, based on BTBC (AB_2, **13** in Table 7.1) and 3-(trimethylsiloxy)benzoyl chloride (AB, **14** in Table 7.1).[34] The monomers were dissolved in dry diglyme, and then this dilute monomer solution was slowly added (within 80 h) by a dispensing pump to a highly concentrated catalyst solution of 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP) in dry quinoline at 200 °C, while the condensation product trimethylsilyl chloride was removed by a slow stream of dry argon. The product in 60–75% yield was obtained after solvent removal, precipitation, and purification. While random cocondensation in bulk yielded limited molecular weights ($M_n = 2900–8400$), considerably higher molecular weight and low polydispersity were obtained under SMA conditions ($M_n = 83{,}000–278{,}000$; $PDI = 1.09–1.49$). Bulk copolymerization of the AB_2 and AB monomers resulted in polymers with controlled DBs in the range 0–0.5; in contrast, using the SMA strategy, the DB of the copolymers was significantly enhanced to above 0.5. A strictly linear dependence of the intrinsic viscosity upon molecular weight was observed for all the copolymers. The Mark–Houwink exponents α clearly decreased with the DB and were in the range 0.18–0.55.

Markoski *et al.*[29,30] reported the copolymerization of a series of AB/AB_2 monomers (**9** and **10** in Table 7.1) with the mole fraction AB monomer content (x_{AB}) ranging from 0 to 1 to study the architecture effect on physical properties. By varying the ratio of the starting monomers, polymers were synthesized ranging from fully hyperbranched (100% AB_2) to fully linear (100% AB). As expected, an increase in viscosity was observed with increasing fraction of AB segments. The data showed small changes in viscosity for copolymers with $x_{AB} \leq 0.80$, suggesting that the molecules in this range have similar highly branched structures. However, at $x_{AB} > 0.80$ showed sharp increases in the viscosity, which suggested the molecular structure becoming more linear and open, resembling long-chain branched molecules. Viscosity changes appeared to directly correlate with calculated distance between branches. These observations suggest that the distance between branches is a key architectural parameter that directly correlates to the rheological property. Glass transition temperatures were found to increase with increasing fraction of AB monomers, indicating an overall decrease in mobility as the chains become more linear. At $x_{AB} \leq 0.75$, small changes in the T_g were observed because the molecular architectures are similar, which are lack of entanglements. On the other hand, in the range of $0.75 < x_{\mathrm{AB}} < 1.0$, a sharp increase in the T_g was observed with the increase in x_{AB} because the structure became increasingly more open, allowing for a higher degree of entanglement formation that reduced mobility, thus increasing the T_g.

The AB_2 monomer (3,5-bis(4-fluorobenzoyl)phenol, **11** in Table 7.1) was synthesized, homopolymerized, and then copolymerized with 4-fluoro-4′-hydroxybenzophenone (AB monomer, **12** in Table 7.1), in weight ratios of 1:3, 1:1, and 3:1 to yield hyperbranched PEK with variable degrees of branching.[31] The 1:1 copolymer had a significantly higher T_g value (212 °C) than both linear and hyperbranched homopolymers. Only the 1:3 copolymer was semicrystalline, displaying melting point at 340 °C, and its wide-angle X-ray scattering (WAXS) pattern indicated that its crystal structure was the same as that of the linear homopolymer.

Kunamaneni *et al.*[22] reported size exclusion chromatography (SEC) and linear shear rheology results for a series of hyperbranched polyesters prepared by cocondensation of AB (methyl 4-(2-hydroxyethoxy)benzoate, **4** in Table 7.1) and AB_2 monomer (dimethyl 5-2-(hydroxyethoxy)isopthalate, **3** in Table 7.1). M_w varied from 3000 to 250,000 but the spacer length between branch points was kept constant by fixing the mole fraction of AB_2 monomers at 43%. The dynamic rheological data were modeled using a dynamic scaling theory for unentangled polymeric fractals based on the Rouse model and an excellent agreement was found. This indicates that these hyperbranched polymers are essentially unentangled. It also demonstrated that rheology is sensitive to small changes in the molecular weight distribution (MWD).

Li and Bo[38] reported the "$AB_2 + AB$" approach based on Suzuki polycondensation (SPC) to synthesize hyperbranched polymers. Two monomers, 7-bromo-9,9-dioctylfluorene-2-boronic acid (BDOFBA) and 3,5-dibromobenzeneboronic acid (DBBZB) (Figure 7.1), were synthesized and copolymerized. The polymerizations were carried out under different feed ratios between BDOFBA and DBBZB in toluene with freshly prepared $Pd(PPh_3)_4$ (0.7 mol%) as the catalyst precursor. Three polymers P5, P15, and P40 were obtained using the molar ratios of BDOFBA and DBBZB as 100:5, 100:15, and 100:40, respectively. Because

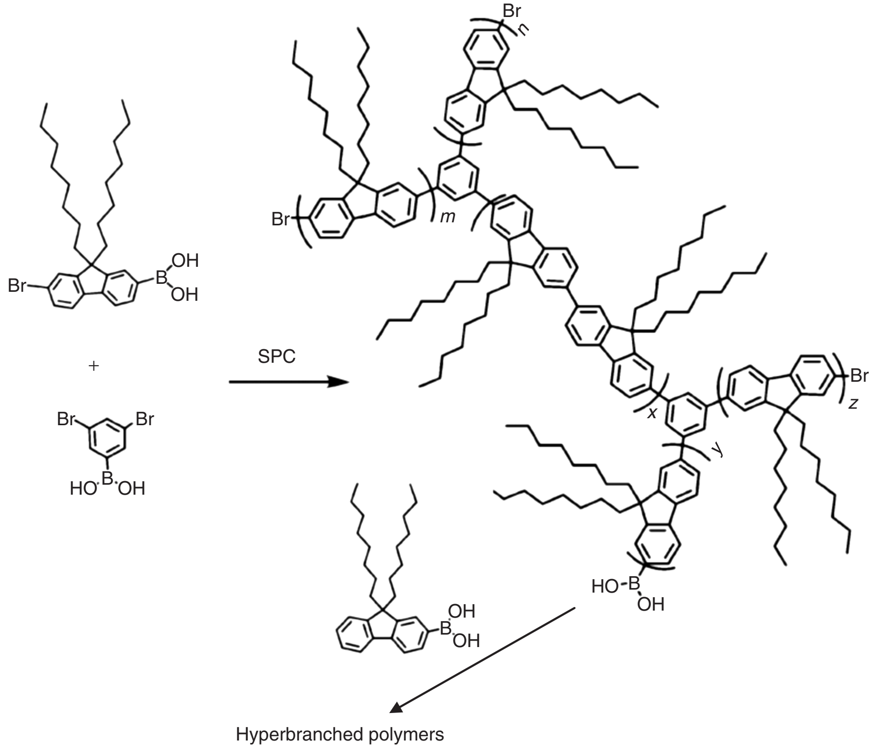


Figure 7.1 Hyperbranched polymers prepared by the "$AB_2 + AB$" approach based on Suzuki polycondensation (SPC).[38]

the random hyperbranched polymer synthesized by one-pot SPC has a large number of bromo end groups that are detrimental for light emitting applications, monofunctional monomer 9,9-dioctylfluorene-2-boronic acid was used to cap the end groups. The hyperbranched polymers synthesized via one-pot SPC were of high molecular weight and good solubility in common organic solvents. P40 film exhibited very good luminescent stabilities, and the blue-green emission band was completely suppressed in its annealed film.

Hydroxyl- and fluorine-terminated hyperbranched poly(phenylquinoxaline)s (HT-HPPQs and FT-HPPQs) were synthesized by copolymerization of AB/AB_2 or BA/BA_2 monomers (Figure 7.2).[32] In the case of HT-HPPQ, the properties of the polymer such as solubility, solution viscosity, T_g, and polymer degradation temperature were greatly influenced by the number of hydroxyl groups on the surface. However, the properties of FT-HPPQ were much less influenced by the number of fluorines on the surface. The copolymers of AB and AB_2 were soluble in most of aprotic and phenolic solvents, with intrinsic viscosities ranging from 0.27 to 1.11 dL/g in *m*-cresol at 30 °C and T_g ranging from 239 to 274 °C. Copolymers of BA and BA_2 were also soluble in most of aprotic and phenolic solvents, with intrinsic viscosities ranging from 1.01 to 1.15 dL/g in *m*-cresol at

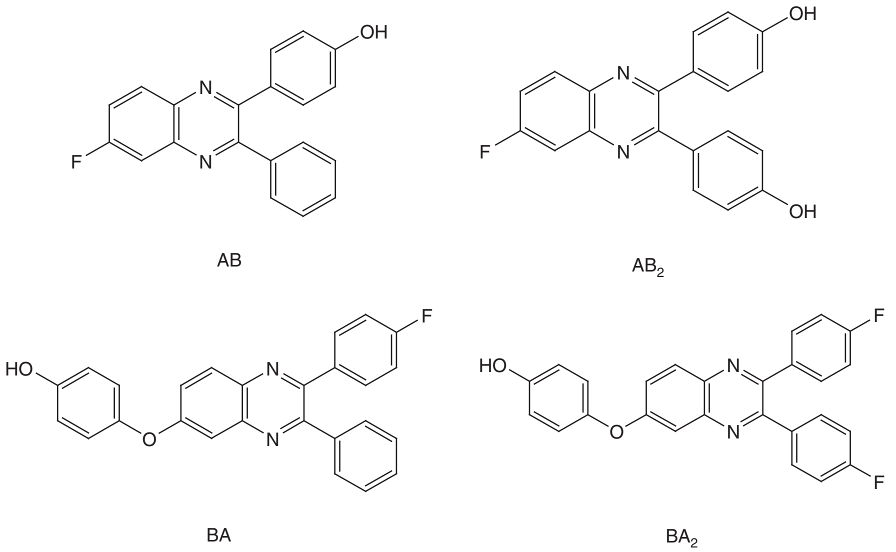


Figure 7.2 AB/AB_2 and BA/BA_2 monomers used for the preparation of hydroxyl-terminated and fluorine-terminated hyperbranched poly(phenylquinoxalines) (HT-HPPQs and FT-HPPQs).[32]

30 °C. FT-HPPQ showed enhanced thermal stability than HT-HPPQs due to the fluorine terminal groups on the macromolecule surfaces.

A series of PEK copolymers were prepared by nucleophilic aromatic polymerization reactions of 4-fluoro-4′-hydroxybenzophenone (AB) in the presence of varying percentages of AB_n monomers based on a triarylphosphine oxide platform, **la** (2F), **1b** (4F), and **1c** (6F) (Figure 7.3).[33] The incorporation of the tetrahedral AB_n comonomers increased the solubility of the resultant materials, relative to linear PEK while decreasing the ability of the PEK segments to crystallize. The crystallinity of the PEK segments was completely suppressed when greater than 5 mol% of **1a** or **1b** was utilized as the comonomer, whereas as little as 3 mol% of **1c** was sufficient to prevent any crystallization. All the samples exhibited excellent thermal stability; 5% weight loss temperatures for the **1a** copolymers (10 mol% of **1a**) were above 500 °C.

The theoretical studies on the copolymerization of AB_n and AB monomers, including calculation of DB and kinetic study of the copolymerizations, have been carried out by Frey[39–41] and Yan[42–44] independently. The DB and the average number of branches per nonterminal monomer unit (ANB) are defined and calculated for random cocondensation of AB_n with AB monomers as well as AB_n with AB_m monomers in general.[39] A new expression has been derived; that is, the dependence of the z-average mean-square radius of gyration on DB for highly branched copolymers made from the AB_2 and AB cocondensations.[42] Yan *et al.*[43] also studied the kinetics of cocondensation polymerization of AB_2 and AB monomers, giving expressions of the two-dimensional MWD function

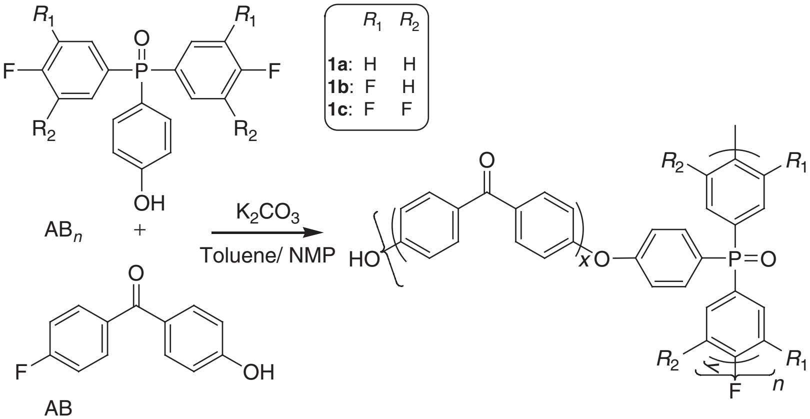


Figure 7.3 Poly(ether ketone) (PEK) copolymers prepared by nucleophilic aromatic polymerization reactions of 4-fluoro-4′-hydroxybenzophenone (AB) in the presence of varying percentages of AB_n monomers based on a triarylphosphine oxide platform, **la** (2F), **1b** (4F), and **1c** (6F).[33]

and the number/weight average molecular weights of the resultant copolymers. (See other chapters for details)

7.2.2 $AB_2 + AB_2$ Approach

As reviewed in the previous section, the copolymerization for the preparation of hyperbranched structures primarily refers to the "$AB_n + AB$" approach. Several others have examined the use of "$A_3 + B_2$" and "$ABB' + A_2$", which are beyond the scope of this chapter. Most of them have focused on improving the preparation methodologies to enhance the branching densities and preclude the formation of cross-linked species. Copolymerizations using two different AB_2-type monomers are rare.

Behera *et al.*[45,46] have undertaken the investigation on the copolymerizations of two types of AB_2 monomers. A series of hyperbranched polyethers containing different types (and lengths) of spacer segments that link the branch points were prepared by a solvent-free melt transetherification methodology.[45] Three types of spacers, that is *n*-alkylene, cycloalkylene, and oxyethylene, were incorporated into the hyperbranched structures to examine the role of spacer length (and flexibility) on the relative compactness of the chain conformation. It showed that the branching density varied in a controlled manner and the relative compactness of the hyperbranched structures diminished with increasing length of the spacer segment. The T_g of the hyperbranched polymers decreased with increasing spacer length, and hyperbranched structures with relatively flexible spacers exhibited lower T_g values when compared to the ones with relatively rigid spacers of similar length.

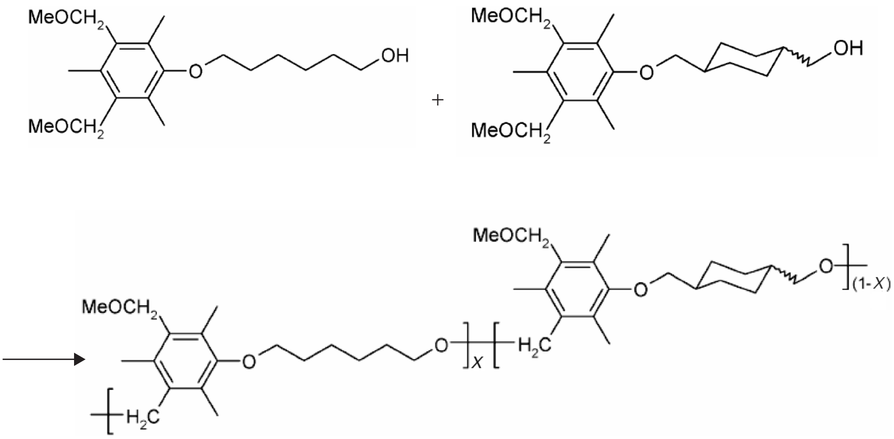


Figure 7.4 Hyperbranched copolymer prepared by two AB_2 monomers having different spacer segments, hexamethylene, and 1,4-cyclohexyldimethylene.[46]

Moreover, a range of hyperbranched copolymers were prepared by the copolymerization of two AB_2 monomers that incorporate spacer segments hexamethylene and 1,4-cyclohexyldimethylene, which have similar lengths but different flexibility (Figure 7.4).[46] The copolymers were also prepared via a solvent-free melt transetherification methodology to yield moderately high molecular weight polymers, ranging from 20,000 to 50,000. The glass transition temperatures of both the hyperbranched and linear counterparts were found to vary in accordance with the Fox equation, which has generally been applied to linear copolymers. However, it was noticed that the hyperbranched copolymers had consistently lower values of T_g compared to their linear analogs. This difference is probably due to the absence of chain entanglements and/or the presence of a very large number of end groups in hyperbranched polymers. Importantly, this study also confirms the applicability of Fox equation to highly branched copolymers, provided that their branching density is maintained constant.

7.2.3 Combined ROP/AB_2 Approach

Hyperbranched polyesters represent a particularly important class of materials that are of interest for coatings and nanostructured networks as well as for numerous biomedical applications. Frey *et al.*[47–49] developed a synthetic method by using a combination of ROP with AB_2 polycondensation, which gives access to a large variety of hyperbranched analogs of aliphatic polyesters.

Firstly, an enzymatic route toward hyperbranched aliphatic polycaprolactone (PCL) copolyesters, based on the combination of ROP and polycondensation of AB_2 monomers, was described.[47] As shown in Figure 7.5, ε-caprolactone (ε-CL) was employed as cyclic AB monomer and 2,2-bis(hydroxymethyl)butyric

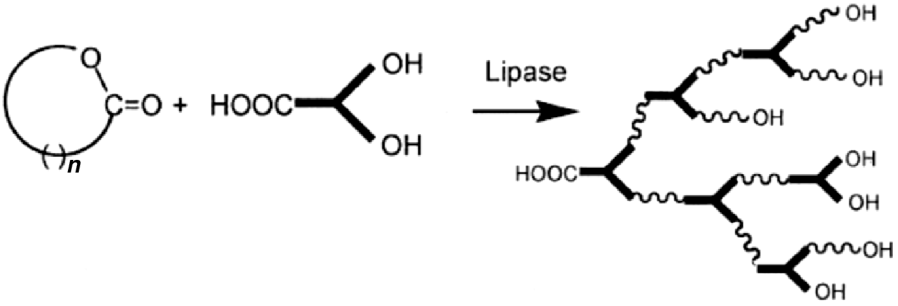


Figure 7.5 The combination of lactone ROP and AB_2 polycondensation.[47]

acid (BHB) was used as AB_2 comonomer, resulting in hyperbranched poly(ε-CL) copolyesters. The reaction was catalyzed by immobilized Lipase B from *Candida antarctica* (Novozyme 435) under mild conditions. By systematic variation of the fraction of the AB_2 comonomer, a series of hyperbranched copolyesters with different DB have been prepared ($0 < DB < 0.33$).

However, there are two limitations for enzymatic strategy: (i) the molecular weights of the resultant copolyesters are limited, particularly at high degrees of branching; (ii) transesterification reactions render direct functionalization of the polyester-polyols impossible.[49] Therefore, Frey *et al.*[49] further utilized two new highly efficient esterification catalysts, $HfCl_4(THF)_2$ and diphenylammonium trifluoromethanesulfonate (DPAT), to prepare hyperbranched aliphatic copolyesters by the copolymerization of ε-CL and BHB (AB_2 monomer). $HfCl_4(THF)_2$ and DPAT were found to exhibit excellent catalytic activity for this combined ROP/AB_2 polycondensation system. DB and, consequently, the density of functional groups of the resultant copolyesters were also controlled by the comonomer ratio in the feed. Slightly higher molecular weights (in the range 22,000–166,000) than the analogs prepared previously by enzymatic catalysis were obtained with apparent polydispersity indices of 1.20–1.95. The DB was in the range 0.03–0.35. The prepared hyperbranched PCLs were used as multifunctional initiators for the ROP of ε-caprolactone, which was also catalyzed by $HfCl_4(THF)_2$, resulting in multiarm star polymers.

Biodegradable and bioadsorbable poly(L-lactide) (PLLA), which is a linear aliphatic polyester and thermoplastic, is usually prepared by ROP of L-lactide. A series of hyperbranched PLLA copolymers were prepared by copolymerization of dilactide with BHB as an AB_2 comonomer via the combined ROP/AB_2 polycondensation (Figure 7.6).[48] All the copolymerization reactions of L-lactide and BHB were carried out at 120 °C for 24 h in bulk, using stannous 2-ethylhexanoate ($Sn(Oct)_2$) as catalyst, which catalyzed both ROP and the concurrent polycondensation of the AB_2 monomer BHB. The apparent molecular weights determined by SEC (polystyrene (PS) standards) were in the range 700–60,000, decreasing with the DB. All the branched copolyesters showed monomodal MWDs with low apparent polydispersities in the range 1.3–2.2. The degree of crystallization of

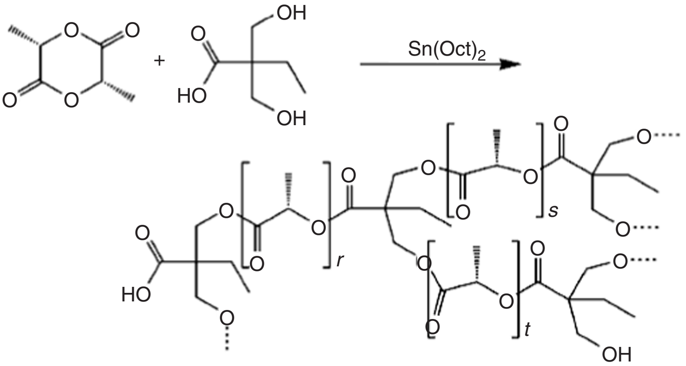


Figure 7.6 Hyperbranched PLLA copolymers prepared by the combination of ROP and AB$_2$ polycondensation.[48]

the materials decreased with increasing DB. With more than 7% incorporation of the BHB monomer, amorphous materials were obtained.

7.3 COCONDENSATION OF $A_2 + B_2 + BB'_2$ (OR $B'B_2$)

Gao and Yan have further extended A_2 and BB'_2 DMM approach (Chapter 4) to prepare hyperbranched copoly(sulfone-amine)s via cocondensation of A_2, B_2 and BB'_2 monomers (Figure 7.7).[50–53] These include hyperbranched copoly(sulfone-amine)s prepared by copolymerization of divinyl sulfone (A_2) with 4,4′-trimethylenedipiperidine (B_2) and *N*-ethylethylenediamine (BB'_2);[50] polyaddition of piperazine (B_2) and *N*-ethylethylenediamine (BB'_2) to divinyl sulfone (A_2),[53] polyaddition of piperazine (B_2) and 1-(2-aminoethyl) piperazine

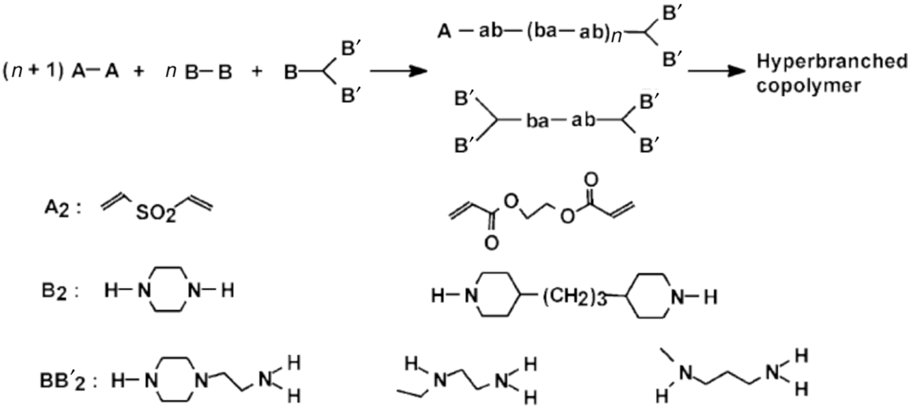


Figure 7.7 Cocondensation of A_2, B_2 and BB'_2 for the preparation of hyperbranched copolymers.[16]

(BB'_2) to divinyl sulfone (A_2),[54] and polyaddition of piperazine (B_2) and *N*-ethylethylenediamine (BB'_2) to divinylsulfone (A_2) without any catalysts.

In the "$A_2 + B_2 + BB'_2$" approach, the A_2 and BB'_2 monomers are the same as those of $A_2 + BB'_2$ approach, and B_2 is the molecule with two secondary amino groups. During polymerization, the rapid reaction between the A and B groups results in the formation of an AB'_2-type intermediate. The linear units formed from the reaction of A and B_2 are also embedded in the AB'_2 species, indicating that the segment between two branching points and the number of linear units can be adjusted by the feed ratio of B_2 to BB'_2.[16] The polymerization mechanism was investigated with FTIR and liquid chromatograph-mass selective detector system (LC-MSD). The results show that the reaction between the secondary amino groups and the vinyl ones was surprisingly fast, within 1 min. The whole polymerization only took 6–10 h in a diluted solution even at room temperature. Therefore, highly branched macromolecules can be approached within several hours. The DB of hyperbranched copolymers, determined by ^1H nuclear magnetic resonance (NMR), varies from around 0.5 to 0.1 when the feed ratio of monomers is changed. It demonstrated that the crystallization behaviors of the resultant polymers are influenced not only by DB and the side groups of a branched copolymer, but also by the stiffness of its main chain.

Skaria *et al.*[47] successfully demonstrated the feasibility of synthesizing hyperbranched polymers by lipase catalysis. However, the monomers they chose required the use of a solvent (toluene–dioxane mixture) to form a monophasic reaction medium. Thus, only low M_w (3500 g/mol) copolymers were obtained after a 24 h reaction at 85 °C. Kulshrestha *et al.*[55] developed a simple one-pot enzymatic synthesis to prepare both linear and hyperbranched copolymers containing glycerol through terpolymerizations of adipic acid (A_2), 1,8-octanediol (B_2), and glycerol ($B'B_2$). Hyperbranched polyesters with octanediol-adipate and glycerol-adipate repeat units were synthesized by bulk cocondensations at 70 °C for 42 h using immobilized Lipase B (Novozyme 435) at mild temperatures. Instead of using organic solvents, the monomers adipic acid (A_2), 1,8-octanediol (B_2), and glycerol ($B'B_2$) were combined to form monophasic ternary mixtures. During the first 18 h of a copolymerization with monomer feed mole ratio (A_2:B_2:$B'B_2$) as 1.0:0.8:0.2, the regioselectivity of Novozyme 435 resulted in linear copolyesters. Hyperbranched copolymers with dendritic glycerol units were formed after extending the reaction to 42 h. The percentage of regioselectivity for esterifications at the primary glycerol positions ranged from 77 to 82 and was independent of glycerol content in the monomer feed. Variation of glycerol in the monomer feed led to hyperbranched copolymers with DB from 9% to 58%.

7.4 SCVCP VIA CHARGE-TRANSFER COMPLEX INIMER

Traditionally, hyperbranched copolymers are prepared by copolycondensation reactions. However, vinyl monomers cannot be polymerized by this approach.

In 1995, Fréchet and coworkers published a new approach, SCVP, to synthesize hyperbranched polymers.[56] This discovery makes it possible to use vinyl monomers for the synthesis of hyperbranched structures. In this approach, a vinyl monomer of the general structure AB was used, where A was a vinyl group and B a functional group which could be converted to an initiating group B* by an external stimulus. Thus, this species combined the features of an initiator and a monomer and was therefore named as an “inimer.”[57,58] The activated species could be a “living” free radical,[59] an electrophilic cationic moiety, or a carbanion.[56] Figure 7.8 shows two examples of such inimers: (a) activation occurs by removing the chlorine to form either a cation[56] or a radical[60]; (b) the silylketene acetal group is activated by nucleophilic catalysts to initiate group-transfer polymerization (GTP).[61,62]

SCVP can be applied to various types of living polymerizations, such as GTP,[63] nitroxide-mediated radical polymerization,[59] cationic polymerization,[64] and atom-transfer radical polymerization (ATRP)[60] for the synthesis of hyperbranched polymers. Moreover, this approach has been extended to synthesize hyperbranched copolymers via SCVCP of a vinyl monomer M and an “inimer” AB*. Matyjaszewski *et al.*[60] synthesized branched copolymers using *p*-(chloromethyl)styrene (PCMS) with styrene (St) via ATRP. Also, hyperbranched fluorocopolymers were synthesized by the atom-transfer radical self-condensing vinyl copolymerization (ATR-SCVCP) of an inimer, either PCMS or *p*-bromomethylstyrene (BMS), with 2,3,4,5,6-pentafluorostyrene (PFS).[65] Muller *et al.*[63] prepared the highly branched polymethacrylates via self-condensing group-transfer copolymerization of the inimer 2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate (MTSHEMA) with methyl methacrylate (MMA) at room temperature, where tetrabutylammonium bibenzoate (TBABB) was used as the catalyst. Yan *et al.*[66] reported one-step synthesis of a series of branched azobenzene side-chain liquid-crystalline copolymers in chlorobenzene solvent by SCVCP of a methyl acrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), with the monomer 6-(4-methoxy-azobenzene-4′-oxy)hexyl methacrylate (M), in the presence of CuBr/N,N,N',N',N'-pentamethyldiethylenetriamine (PMDETA) as a catalyst system. Ishizu *et al.*[67–70] presented a route to hyperbranched PSs by quasi-living radical copolymerization of N,N-diethylaniinodithiocarbamoylmethylstyrene (inimer: DTCS) with St under UV irradiation. Moreover, hyperbranched glycopolymers[71,72] and hyperbranched polyacrylate copolymers[73,74] were also synthesized by SCVCP.

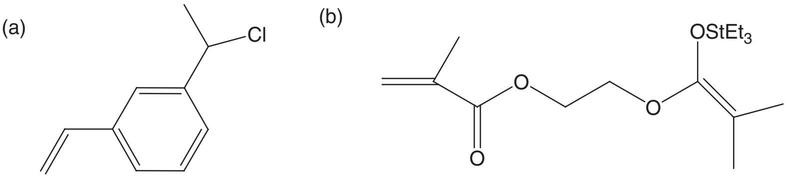


Figure 7.8 Two typical AB inimers.

It is known that a suitable inimer is essential for the synthesis of hyperbranched polymers by SCVCP. However, only a few are available compared to the large variety of conventional vinyl monomers. This is a severe limitation on the number of novel materials that can be prepared by this method. Wang *et al.*[75] reported a versatile approach for the preparation of hyperbranched polymer architectures by combining known inimers with conventional vinyl monomers to form a CTC. This CTC satisfies the AB_2 requirement to produce hyperbranched polymers via SCVP. The hyperbranched fluoro-copolymer of chlorotrifluoroethylene (CTFE) and PCMS was successfully synthesized through this approach (Figure 7.9). CTFE is a typical electron-deficient monomer, which has been incorporated in alternating copolymers with ethylene via a free-radical mechanism.[76] PCMS is an inimer that has been used in the synthesis of hyperbranched polymers by ATRP[60] and is a typical electron-rich monomer, capable of forming a CTC monomer pair with electron-deficient monomers, such as CTFE. This new hyperbranched fluoropolymer is soluble in traditional organic solvents, such as THF and toluene, and has a lower intrinsic viscosity ($[\eta] = 0.042$) than a linear polystyrene of similar molecular weight ($[\eta] = 0.077$). Moreover, DSC analysis shows that it is typically amorphous with a T_g of 88 °C, which is between those of poly(CTFE) (57 °C) and PS (100 °C). These features are a strong indication of its good processability. Yan *et al.*[77,78] also reported hyperbranched alternating copolymers synthesized via living controllable radical copolymerization of the charge-transfer complex made from *N*-phenylmaleimide (NPMI) and PCMS, or PCMS and acrylonitrile (AN), where PCMS was used as an inimer. Star-shaped poly(PCMS-*co*-AN)/poly(MMA) and poly(NPMI-*co*-PCMS)/poly(MMA) block copolymers were then synthesized using these hyperbranched copolymers as functional macroinitiators.

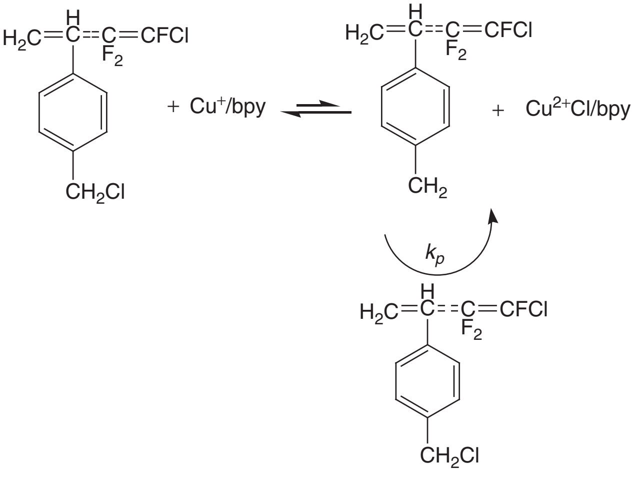


Figure 7.9 Copolymerization of *p*-(chloromethyl)styrene and chlorotrifluoroethylene: mechanism of SCVCP using CTC inimer.[75]

7.5 FREE RADICAL COPOLYMERIZATION OF MULTIFUNCTIONAL VINYL MONOMERS

Multifunctional vinyl monomers generally lead to cross-linked or gelled polymer networks in a free-radical polymerization even at a low concentration. However, highly branched polymers can be obtained if a special synthetic route is adopted to control the chain propagation. In recent years, a few strategies for the preparation of branched polymers from multivinyl monomers have been developed, including chain-transfer controlled radical polymerization used by Sherrington[79–82] and Guan[83] and initiator-fragment incorporation radical polymerization (IFIRP) used by Sato *et al.*[84–96]

Sherrington[79–82,97] and Guan[83] reported chain-transfer controlled free-radical polymerization routes to branched polymers using multifunctional vinyl monomers as the branching species. Gelation was inhibited by the use of thiol or catalytic chain-transfer (CCT) species. However, such chain-transfer agents cannot provide fine control of the molecular weight and branched structure of the polymers because of their nonliving nature. Sherrington and Armes[81] introduced living/controlled polymerization, for example Cu-based ATRP or GTP methodologies, to control the level of the branching multifunctional vinyl monomer employed. Copolymerizations of MMA and ethylene glycol dimethacrylate (EGDMA) were reported, yielding soluble branched copolymers in one-step reactions.[81] However, low concentrations of multifunctional vinyl monomer were required, and the mole ratio of this branching monomer to initiator must be limited to ≤ 1 to form soluble branched polymer and avoid cross-linking. When this ratio exceeds 1, only an insoluble cross-linked network or microgel is produced. Reversible addition fragmentation chain transfer (RAFT) polymerization was also reported for the preparation of PMMA hyperbranched polymers via the one-step copolymerization of MMA and EGDMA mediated by 2-(2-cyanopropyl) dithiobenzoate.[98]

Moreover, it is essential for this strategy that an organic solvent dilutes the whole reaction medium and contributes to the inhibition of cross-linking. However, the use of a solvent in the commercial production of many commodity vinyl polymers would render such processes uneconomic. Remarkably, Sherrington *et al.*[99] have reported the high-conversion copolymerizations of MMA and divinylbenzene (DVB) in aqueous emulsion using sodium dodecyl sulfate as an emulsifier and potassium persulfate as a conventional free-radical initiator. Various thiols have been investigated in order to inhibit cross-linking and hence favor the formation of branched products. Hexanethiol (HT) and benzylthiol (BT) have been found to be particularly effective. The use of appropriate levels of BT allowed mole feed ratios of MMA/DVB up to 100:20 to be employed in producing highly branched products without cross-linking. Typically DVB/BT mole ratios of less than 1 ensure that cross-linking is avoided. Interestingly, Morbidelli *et al.*[100] reported the synthesis of hyperbranched PSs via copolymerization of styrene and DVB in the absence of solvent at high temperatures ($>300\,^{\circ}$C) in a steady-state continuous-stirred tank reactor. Under these conditions, backbiting followed by

β-scission, which was the dominant chain degradation mechanism, was very aggressive. This allowed for the utilization of large amounts of cross-linker, thus producing hyperbranched polymers with high branching density, without the formation of gel.

Sato *et al.*[84] reported a chain-termination-controlled free-radical polymerization route (IFIRP), in which the initiator fragments are incorporated as a main constituent in the resulting polymer. The copolymerization of DVB and ethylstyrene (EtSt) was carried out in benzene with dimethyl 2,2-azobisisobutyrate (MAIB) at high concentrations as initiator in the presence of methyl benzyloxyiminoacetate (MBOIA), a glyoxylic oxime ether, as a retarder. The yield and molecular weight of the resultant copolymers increased with time and then leveled off because of initiator consumption. It is reported that a soluble, hyperbranched copolymer with low intrinsic viscosity as a nanoparticle was formed, which contained a comparable amount (30–40 mol%) of a 1-methoxycarbonyl-1-methylethyl group as a fragment of MAIB to that of DVB.[84] MBOIA (13–16 mol%) was also incorporated into the copolymers through an opening of the C–N bond. Figure 7.10 shows the structure of the resultant polymer.

Following this, Sato *et al.* have carried out further investigations in the IFIRP strategy to homopolymerize DVB,[85,86] divinyl adipate (DVA),[87] and EGDMA.[88] Also, IFIRP has been used to copolymerize various monomer pairs, including DVA/isobutyl vinyl ether (IBVE),[89] EGDMA/α-ethyl β-N-(α'-methylbenzyl) itaconamates,[96] DVB/*N*-isopropylacrylamide (NIPAm),[90] EGDMA/*N*-methylmethacrylamide (NMMAm),[91] EGDMA/1,1-diphenylethylene (DPE),[92] DVB/ethyl acrylate,[93] DVA/ally acetate (AAc),[94] and DVB/ethyl acrylate.[95] Azobisisobutyronitrile (AIBN) was used as an initiator in the copolymerization of DVA with IBVE, and MAIB was the initiator for the rest of the polymerization reactions. In all cases, the intrinsic viscosity of the formed copolymers was reported to be very low, and the results from gel permeation chromatography (GPC), multiangle laser light scattering (MALLS), and transmission electron microscopy (TEM) revealed that individual copolymer molecules were formed as hyperbranched nanoparticles. In the IFIRP approach, high concentration of initiator was required. The use of much higher initiator concentrations

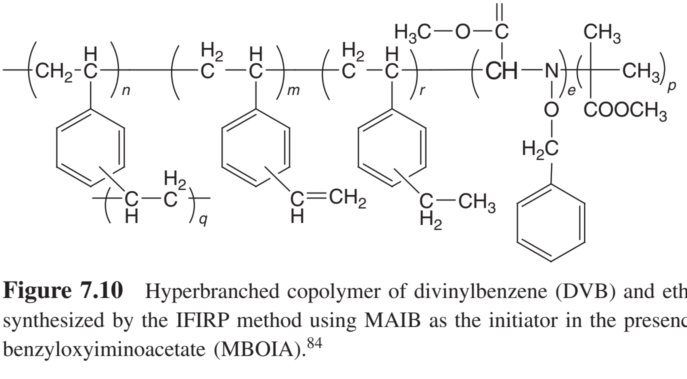


Figure 7.10 Hyperbranched copolymer of divinylbenzene (DVB) and ethylstyrene (EtSt) synthesized by the IFIRP method using MAIB as the initiator in the presence of methyl benzyloxyiminoacetate (MBOIA).[84]

leads to a decrease in the polymer molecular weight so that the resultant hyperbranched polymer becomes soluble and contains a considerable amount of initiator fragments incorporated as terminal groups via initiation and primary radical termination. The decrease of molecular weight and, hence, the increase of solubility are enhanced by the presence of retarder and/or chain-transfer reagent.[89]

Recently, Wang *et al.*[101] developed a "deactivation enhanced" method, which allows the simple use of readily available and inexpensive multifunctional vinyl monomers to synthesize soluble hyperbranched polymers with a high degree of branching and controlled chain structure via homo- and copolymerizations. The key of this strategy is to control the competition between chain growth and reversible chain termination via a deactivation enhanced method. Thus, the polymer chains can grow effectively and the branching is introduced by multifunctional vinyl monomer in a controlled fashion, leading to the formation of hyperbranched polymers rather than crosslinked gel. Unlike conventional ATRP which uses a halogen-Cu^I/Ligand catalyst, Deactivation Enhanced ATRP (DE-ATPR) uses a halogen-Cu^I/halogen-Cu^{II} mixture which enhances the deactivation of polymerisation. Hyperbranched polymers with multitude vinyl functional groups have been successfully prepared via DE-ATRP homopolymerizations of divinyl benzene (DVB) and ethylene glycol dimethacrylate (EGDMA) at a high yield of 60%.[101] DE-ATRP has been further adopted for the synthesis of hyperbranched copolymers to overcome the limitation of multifunctional vinyl monomers involved in the copolymerisations. The copolymerisations of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) (M_n-475), poly(propylene glycol) methacrylate (PPGMA) (M_n-375) and ethylene glycol dimethacrylate (EGDMA) were successfully conducted via this deactivation enhanced ATRP approach. High level of branching monomer EGDMA (up to 30% in feed monomers and the mole ratio of EGDMA to initiator was 30 to 1) was adopted, leading to water soluble hyperbranched PEGMEMA-PPGMA-EGDMA copolymers with a high degree of branching and double bond content (Figure 7.11). However, defect network structures could exist in

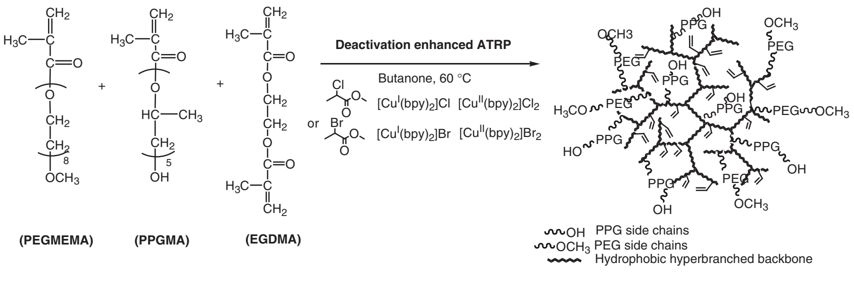


Figure 7.11 Hyperbranched polymer with thermo-sensitive and photo-crosslinkable properties synthesized from copolymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA), poly(propylene glycol) methacrylate (PPGMA) and ethylene glycol dimethacrylate (EGDMA) via deactivation enhanced ATRP (DE-ATRP).[102]

these hyperbranched structures due to internal cyclization or neighbour chain linkage.[102] These hyperbranched PEGMEMA-PPGMA-EGDMA copolymers have thermo-sensitive and photocrosslinkable properties and have demonstrated promising potentials for tissue engineering and drug delivery applications[103] Hyperbranched 2-(dimethylamino) ethyl methacrylate (DMAEMA)/EGDMA copolymer as a highly effective gene delivery vector was also prepared via DE-ATRP in a simple “one pot” reaction.[104] Moreover, an in-situ DE-ATRP was further developed for the copolymerization of PEGMEMA, 2-(2-methoxyethoxy) ethyl methacrylate and EGDMA, where Cu^{II}/Ligand and a small amount of reducing agent L-ascorbic acid (L-AA) were used to generate Cu^{I} in situ.[105] This is to ensure the extra amount of Cu^{II} species remain in the reaction thus lead to the slow chain growth and delayed gelation. It has been demonstrated that the activation/deactivation equilibrium of ATRP could be easily controlled by adjusting the amount of L-ascorbic acid. These PEG-based hyperbranched copolymers also have thermo-sensitive and photocrosslinkable properties and have potentials for tissue engineering and drug delivery applications.[105]

7.6 CONCLUSION

Various hyperbranched copolymers have been prepared not only from AB_n-type monomers but also AB* inimers and multifunctional vinyl monomers by one-step cocondensation, SCVCP, and radical polymerization methods. Recently, the development of new strategies using controlled free-radical polymerization of multifunctional vinyl monomers offers a new approach to synthesis hyperbranched copolymer via a facile route. Although hyperbranched polymers contain fewer branching units, they generally inherit many properties of dendrimers, such as good solubility, low viscosity, and multifunctionality. There are high expectations that these new architectures will be utilized in a variety of fields and the commodity markets.

LIST OF ABBREVIATIONS

AAc	allyl acetate
AGE	allyl glycidyl ether
AIBN	azobisisobutyronitrile
AN	acrylonitrile
ANB	average number of branches per nonterminal monomer unit
ATRP	atom-transfer radical polymerization
BDOFBA	7-bromo-9,9-dioctylfluorene-2-boronic acid
BHB	2,2-bis(hydroxymethyl)butyric acid
BHET	bis-(α-hydroxyethyl) terephthalate
BIEM	2-(2-bromoisobutyryloxy)ethyl methacrylate

BMS	*p*-bromomethylstyrene
BT	benzylthiol
BTBC	3,5-bis(trimethylsiloxy)benzoyl chloride
CMM	couple-monomer methodology
CTC	chain-transfer complex
CTFE	chlorotrifluoroethylene
DB	degree of branching
DBBZB	3,5-dibromobenzeneboronic acid
DMM	double monomer methodology
DPAT	diphenylammoniumtrifluoromethanesulfonate
DPE	1,1-diphenylethylene
DSC	differential scanning calorimetry
DTCS	*N*,*N*-diethylaniinodithiocarbamoylmethylstyrene
DVA	divinyl adipate
DVB	divinylbenzene
EtSt	ethylstyrene
EBHEB	ethyl bis-3,5-(2-hydroxyethoxy) benzoate
EGDMA	ethylene glycol dimethacrylate
E4HEB	ethyl, 4-(2-hydroxyethoxy) benzoate
FT-HPPQs	fluorine-terminated hyperbranched poly(phenylquinoxalines)
GTP	group-transfer polymerization
GPC	gel permeation chromatography
HT	hexanethiol
HT-HPPQs	hydroxyl-terminated hyperbranched poly(phenylquinoxalines)
IBVE	isobutyl vinyl ether
IFIRP	initiator-fragment incorporation radical polymerization
MAIB	dimethyl 2,2-azobisisobutyrate
MALDI TOF	matrix-assisted laser desorption/ionization-time of flight
MALLS	multiangle laser light scattering
MBOIA	methyl benzyloxyiminoacetate
MMA	methyl methacrylate
MTSHEMA	2-(2-methyl-1-triethylsiloxy-1-propenyloxy)ethyl methacrylate
MWD	molecular weight distribution
NMMAm	*N*-methylmethacrylamide
NMR	nuclear magnetic resonance
NPMI	*N*-phenylmaleimide
PCMS	*p*-(chloromethyl)styrene
PEK	poly(ether ketone)

PEOB	poly(4-ethyleneoxy benzoate)
PET	poly(ethylene terephthalate)
PFS	2,3,4,5,6-pentafluorostyrene
PGE	phenyl glycidyl ether
PLLA	poly(L-lactide)
PMDETA	pentamethyldiethylenetriamine
Poly(ε-CL)	polycaprolactone
RAFT	reversible addition fragmentation chain transfer
ROP	ring-opening polymerization
SCVP	self-condensing vinyl polymerization
SCVCP	self-condensing vinyl copolymerization
SEC	size exclusion chromatography
SMA	slow monomer addition
SMM	single monomer methodology
SPC	Suzuki polycondensation
St	styrene
TBABB	tetrabutylammonium bibenzoate
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TMP	2-ethyl-2-hydroxymethyl-1,3-propanediol
TPP	triphenyl phosphate
T_g	glass transition temperature
T_m	melting temperature
WAXS	wide-angle X-ray scattering

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Chapter 8

Convergent Synthesis of Hyperbranched Polymers and Related Approaches

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8.1 INTRODUCTION

One objective of hyperbranched polymer synthesis has been to emulate dendrimers with their low polydispersity and quantitative branching while maintaining a simple one-pot polymerization of AB_n monomers. However, the statistical branching that results from the uncontrolled polymerization of a typical AB_n monomer inherently leads to high polydispersity and incomplete branching. From a synthesis viewpoint, the use of protecting groups in conjunction with a series of protection/deprotection steps and associated purifications in order to control the branching defines a dendrimer synthesis, even though the resulting structure is less than perfect and could itself be considered hyperbranched. The development of AB_n monomers with designed reactivities of the A and B groups that can offer control in a one-pot synthesis, along with procedures that modulate the sequence of branching reactions, is the means to increase the control in a hyperbranched polymerization.

This chapter will focus on a specific technique for the control of hyperbranched polymer synthesis, which can be classified as a convergent method. Polymers derived from the copolymerization of AB_n plus AB monomers will be included in the discussion. While copolymers of this type are not hyperbranched polymers by strict definitions, which require a branching monomer at each repeat

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

unit, these types of copolymers were considered in the original work of Flory.[1,2] The AB sequences between branch points do not alter the essential character of the branching structure, but provide a means of modifying the entanglement, molecular weight, and composition. Most of the results and discussion will be derived from our own work in this area, while some description of related work by others will be presented.

8.2 CONVERGENT CONTROL IN HYPERBRANCHED SYNTHESIS

The synthesis of dendrimers is well known to occur by either divergent or convergent methods.[3–10] In the divergent method, an AB_n monomer is designed with protected or masked B groups. Reaction with a core-forming molecule of the type B_n results in the zeroth generation. Purification and deprotection or conversion of the masked B groups generates a reactive structure that can subsequently be combined with more of the protected or masked AB_n monomer. The reaction sequence continues in order to build structures with an increasing number of B groups. In the complementary convergent method, it is the A group of the AB_n monomer that is masked or protected, and the dendrimer structure is built by first reacting with monofunctional A molecules. After purification and deprotection of the focal A group, reaction with more AB_n monomers having protected A groups can be carried out to build the structure. The branched structure is typically considered a dendron until reaction of the final A group with a multifunctional B_n core.

In contrast, hyperbranched polymer synthesis with AB_n monomers having no protection of reacting groups is typically considered to be neither divergent nor convergent. A clear generational growth distinction cannot be made, and reactions occur in both directions through uncontrolled reaction of both A and B groups. Techniques involving the use of core monomers and slow monomer addition[11–17] can increase the relative amount of divergent growth, improve the polydispersity, or reduce cyclization, but a clear generational growth is not observed.

Because structural control is derived from masking a functional group and ensuring quantitative reactions, a one-pot convergent process in which the focal A group becomes reactive only after reaction of all B groups has occurred would yield ideal control in a hyperbranched synthesis. Such a procedure can be approached by taking advantage of latent AB functional groups in the design of the AB_n monomer. The vinyl group is one example of a latent AB functionality. The vinyl group is reactive with an initiating or propagating center, and subsequently becomes a propagating center only after the addition reaction has occurred. In effect, the addition reaction transforms a vinyl group (in this case considered a B group) into a new functional group (now an A group) that can continue to react with additional B groups. To design an effective AB_n monomer, the non-vinyl B group (or groups) should be more reactive than the vinyl B group. This will ensure high extents of branching under the right conditions. An AB_2

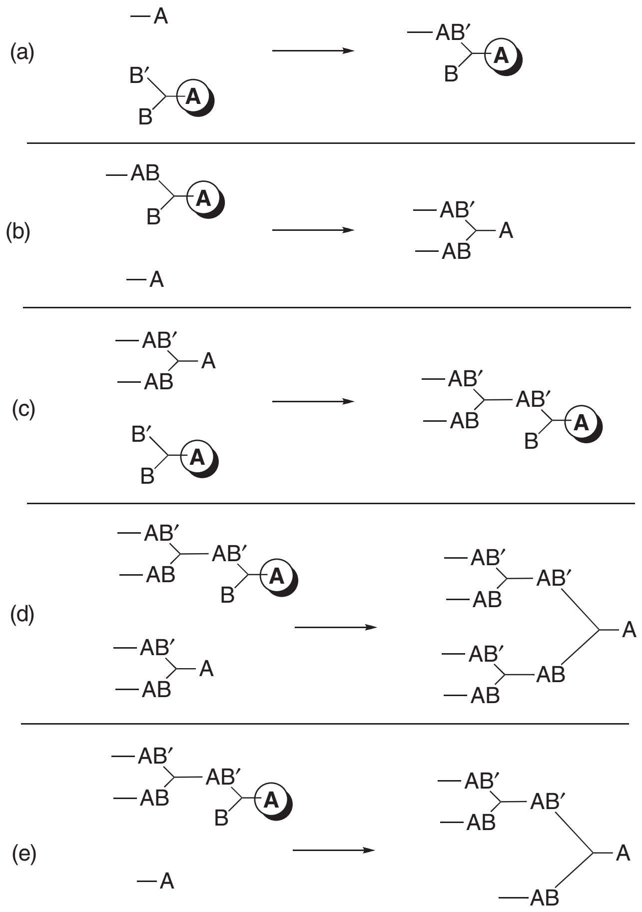
monomer is therefore more correctly considered to be ABB′, where the B′ group is the more reactive non-vinyl group and the A group is the result of addition to the vinyl B group. In the absence of this design, competitive or faster reaction at the vinyl B group relative to the B′ group has the potential to result in cyclization termination reactions and in a tendency toward more linear grafting reactions rather than hyperbranching. Other latent ABB′ monomers can be designed by considering ring-opening monomers as containing latent A groups. A ring-opening monomer is comparable to the vinyl group in that it is a B group until reaction transforms it into a new propagating A group.

Note that the above definition of A and B is the opposite of their designation in self-condensing vinyl polymerization (SCVP) or ring-opening multibranching polymerization (ROMBP), where the vinyl group or ring is considered an A group and becomes a propagating B group after the reaction has occurred (Chapters 5 and 6). The AB_n monomer in SCVP or ROMBP does not direct a convergent reaction as the number of B groups increases with conversion. While the SCVP and ROMBP monomers can be considered “inimers,” by having both initiating and monomer components, the ABB′ monomers for convergent hyperbranched polymerization can be considered “termimers” by having terminating and monomer units.

Given the capability for quantitative reactions in the convergent hyperbranching reaction, effective branching can be accomplished by sequential or slow ABB′ monomer addition to a solution of reactive A groups, and the reaction reaches completion when a stoichiometric equivalent of ABB′ monomer relative to initial A groups is reached. The addition of the ABB′ monomer must be carried out slow enough so that complete reaction with the less reactive B group occurs before the introduction of the next aliquot of monomer. If the addition is faster than the rate of the reaction with the B group, the branching reaction is effectively terminated by reaction with B′, as no new A groups are generated.

The products shown in (a)–(d) of Scheme 8.1 depict idealized reactions of an ABB′ monomer with additional A molecules that occur sequentially. Because the reaction is carried out with an excess of A functional groups relative to B and B′ groups at all times, an A group on any structure can react. This leads to nonideal branched structures such as that depicted in (e) of Scheme 8.1. While this could be a significant defect in the procedure, it will be shown in the Section 8.3 that the amount of this type of branching is minimized by kinetic factors (i.e., the reactivity of all A groups is not constant) and the sequential buildup of structure by the metered monomer addition.

An additional necessary requirement toward regulating the reaction sequence is that there are no side reactions: that is, A groups react only with B or B′ groups. In a vinyl polymerization, this means that there are no termination reactions of propagating vinyl groups other than the reaction with B′. In other words, living polymerization systems are required for the greatest level of control.



Scheme 8.1 Sequence of reactions. Ⓐ represents masked A group. (a) Reaction with B′ group is a faster reaction. (b) Reaction with B group results in the transformation of the masked or latent Ⓐ group into a reactive A group. (c) Branching occurs as the new reactive A group reacts with additional ABB′ monomer. (d) Transformation of the masked or latent Ⓐ group into a reactive A group. (e) Example of non-ideal branching.

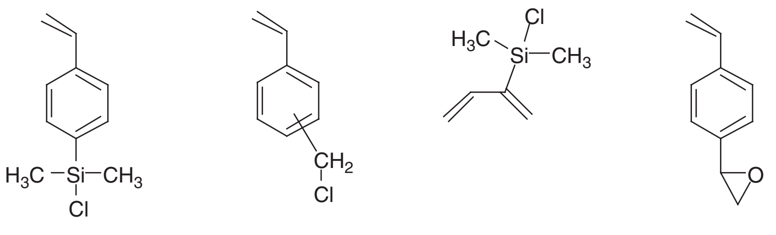
However, even with nonliving polymerizations, the convergent technique described can potentially produce hyperbranched polymers, but with an increased polydispersity. Because any given growing structure contains only one propagating A focal group, termination by coupling with another A group will not lead to cross-linked structures, in contrast to the coupling of multiple B groups in uncontrolled techniques.

8.3 RESULTS

8.3.1 Hyperbranched Polymers by Convergent Living Anionic Polymerization

The above discussion presents the design of the convergent hyperbranched synthesis, but does not describe actual systems. While the technique is generally applicable to any living polymerization, living anionic polymerization of vinyl monomers is an ideal system for study. Living anionic polymerization has been widely studied and described in numerous reviews.[18–22] The reaction can be designed to work well under monomer-starved conditions and shows very slow termination reactions in the absence of added electrophiles. The living chain end can be reacted with a variety of electrophiles in order to effect termination by substitution or addition reactions.[19,23] Examples of useful termination reactions include substitution with silyl halides and alkyl halides and addition reactions with oxiranes and carbonyls.

The design of the reactive ABB′ monomer is important for the overall reaction. As previously described, the rate of reaction of the B′ group is ideally far greater than that of the vinyl B group. This ensures the highest extents of branching given a slow addition of monomer. Figure 8.1 depicts examples of vinyl ABB′ monomers suitable for convergent hyperbranched polymerization by an anionic mechanism. Each of these monomers has been used to varying degrees of success. In **1, 2**, and **3**, the fast reacting B′ group is the silyl halide or benzyl halide, and reaction with a propagating anion (A group) results in coupling via substitution of the halide. In **4**, the oxirane is the B′ group and reaction with a propagating anion results in an addition ring-opening reaction to form an alkoxide that is effectively terminated, as the resulting alkoxide is unreactive with remaining functional groups.



1 **2** **3** **4**

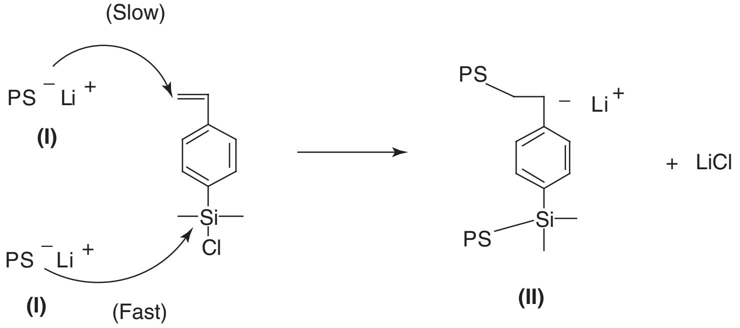
Figure 8.1 Monomers for convergent living anionic hyperbranched polymerization. **1**. 4-(chlorodimethylsilyl)styrene (CDMSS); **2**. vinylbenzyl chloride (VBC); **3**. 2-(chlorodimethylsilyl)-1,3-butadiene (CDMSB); **4**. 4-(vinyl)styrene oxide (VSO).

8.3.1.1 Hyperbranched Polymers from CDMSS and Polystyrene (PS)[24]

Our initial efforts toward the production of hyperbranched polymers focused on living anionic polymerization of styrene and the use of 4-(chlorodimethylsilyl-) styrene (CDMSS) as the ABB′ monomer. The polymerization of styrene and substituted styrenes by alkyllithiums, in particular *sec*-butyllithium, is well studied with a fast initiation.[25] Reaction of CDMSS directly with *sec*-butyllithium can be carried out, but the resulting hyperbranched polymers from slow addition of the CDMSS have relatively broad polydispersities (>2.2) and irregular structures.[26] In this case, the *sec*-butyllithium reactivity is quite different from the reactivity of the styryllithium-like group that results from reaction at the vinyl group of CDMSS, and the strong basicity of the *sec*-butyllithium presents the possibility of significant side reactions.[27] The reactivity of the anion could be mediated by first reacting the *sec*-butyllithium with a few units of styrene before addition of the CDMSS. The polystyryllithium (PSLi) more closely approximates the styryllithium-like group that results from the addition to the vinyl group of the CDMSS. In this way, a similar reactive anion can be maintained throughout the synthesis.

Various lengths of PSLi chains can be used as the initial reactive group, although most of the work has been done with short chains of approximately 10 repeat units with the primary intent to mediate the reactivity of the anion. It has been demonstrated that the reaction of the silyl halide of CDMSS is significantly faster than the reaction of the vinyl group with PSLi.[24,28] Reaction of an excess of CDMSS with an anionic chain can therefore be carried out to produce vinyl-functionalized polymer chains or macromonomers. The faster substitution reaction and formation of macromonomer can be observed by the detection of minimal coupled product from addition to the vinyl group in the reaction of a 1:1 M ratio of PSLi and CDMSS, and no detectable coupled product with an excess of CDMSS.

With the addition of a less than stoichiometric equivalent amount of CDMSS to a solution of reactive PSLi, the macromonomer that forms can subsequently react at the vinyl group of the macromonomer to form a coupled product, (II) in Scheme 8.2, with a reactive anion at the junction point. Product (II) can then participate in reaction with additional CDMSS as it is introduced to the reaction mixture. The same sequence of reactions, that is, the fast reaction at the silyl halide and slow reaction at the vinyl group can subsequently occur. However, since more than one type of anionic species is present in the reaction mixture, multiple types of branched products can be formed in the ensuing steps. Examples of some of the branched structures produced are depicted in Scheme 8.3. The structures depicted are not the only ones that can form. For example, the reaction of PSLi (I) and the first coupled product (II) can react with CDMSS to form product (III) as shown, but the alternative isomer where the polystyrene (PS) anion has reacted at the silyl halide and (II) has reacted at the vinyl group can also result. This increases the diversity of structures that are produced as the



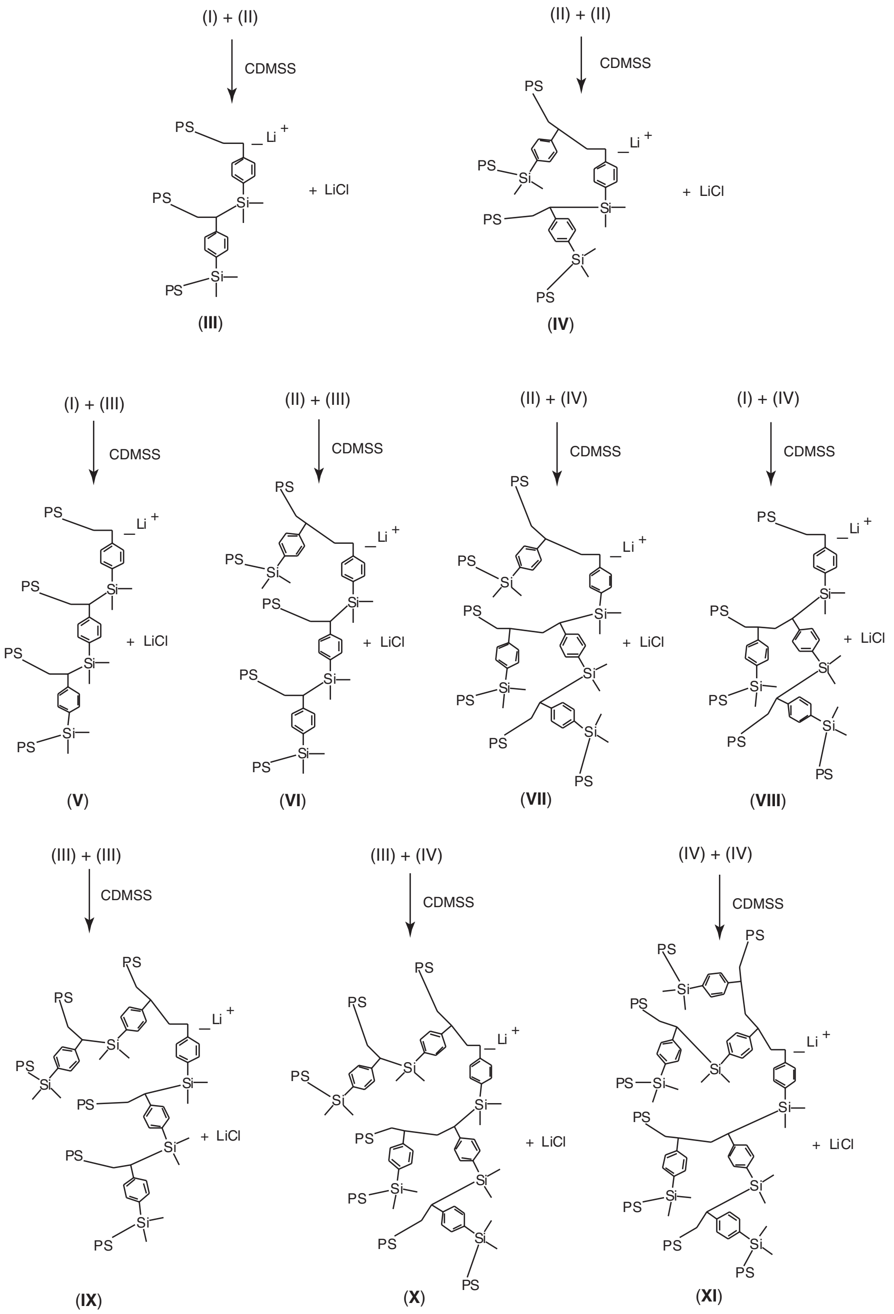
Scheme 8.2 Reaction of PSLi with CDMSS.[29]

various isomers subsequently react with additional CDMSS at either the silyl halide or the vinyl group. The diversity of structures produced is exactly why the polymer is considered hyperbranched rather than a dendrimer.

Each coupling reaction is the result of the termination of one anion and one addition reaction to the vinyl group. The total number of anions therefore decreases in a linear fashion throughout the addition of CDMSS. When half of the stoichiometric equivalent of CDMSS is added, the total number of anions remaining is half of the starting value. At 75% of the CDMSS added, the remaining anions are 25% of the initial amount. The decrease in the number of anions continues until a stoichiometric equivalent of CDMSS relative to initial PS anions is reached. At that point, the final reaction is to terminate the remaining anions with silyl halide and produce a vinyl group at the focal point. In the reaction with PSLi, the decrease in anion concentration can be readily observed, as the PSLi presents a red color in the reaction solution and the color fades as the addition of CDMSS proceeds. When the addition of CDMSS is complete, the reaction becomes colorless.

Unlike other hyperbranched polymerizations that produce linear units due to incomplete reaction of all functional groups, the convergent anionic polymerization of CDMSS leads to quantitative reaction of all silyl halide groups. ^{29}Si NMR confirmed that only one type of Si is present in the structure: that is, a Si attached to a phenyl group, two methyl groups, and a polystyrene-like chain. ^{29}Si NMR spectroscopy is unable to distinguish between a PS chain and the residue from the reaction with the anion from CDMSS, and so, further detail about the branched structure is precluded.

Experiments were performed with rates of CDMSS addition over approximately 5 h, and the reaction was followed by gel permeation chromatography (GPC) to determine the molecular weights and polydispersity. Light scattering detection was used in order to obtain absolute molecular weight data. The molecular weight of the initial PS chains was compared with that of the final products in order to determine the amount of coupling. From this data, the number of PS chains and the number of CDMSS units incorporated could be determined. This was put in terms of an extent of generational growth according to the following



Scheme 8.3 Examples of possible structures produced by addition of CDMSS to PSLi.[29]

equations:

$$M_G = 2^G(M_0 + M_\mathrm{B}) \tag{8.1}$$

$$G = \frac{\log(M_G) - \log(M_0 + M_\mathrm{B})}{\log 2} \tag{8.2}$$

Here, G is equal to the number of generations, and the number of PS chains or number of CDMSS units is equal to 2^G. M_G is the number average molecular weight of the polymer, M_0 is the molecular weight of the initial PS chain, and M_B is the molecular weight of the branch unit from reaction of the CDMSS.

The molecular weight characterization data for a number of samples is reproduced in Table 8.1. Most of the molecular weight of the sample comes from the initial PS chains, and the samples can be considered to be PS stars with a hyperbranched core. The average number of generations of growth is found to be between 3.1 and 3.4 for the samples presented, which corresponds to an average of 8.6–10.6 branch units per molecule, and the molecular weight of the hyperbranched core itself is between 1380 and 1710 g/mol. The polydispersities for all of the samples are quite low, less than 1.20 in each case. The experimental polydispersities and the extent of coupling are dependent on the reaction conditions and purities. Any protic impurities will terminate the anionic polymerization, decreasing the extent of coupling and increasing the polydispersity if the protic impurities are introduced throughout the addition of the CDMSS.

A simple kinetic model was proposed in order to describe the low polydispersities obtained in the convergent synthesis, as actual kinetic data is complicated by the variety of structures formed in the one-pot reaction. The model assumes that the fast reaction at the silyl halide to form a macromonomer can be neglected and therefore only the reaction between the macromonomer and anion is considered. In this case, the kinetics become similar to A-B polycondensation kinetics, as any reactive anion can react with any macromonomer that is present. The branch units are statistically distributed and the polydispersity would be expected to be 2. If the reaction rate of anions with macromonomers is considered to decrease with the size of the molecule, the expected polydispersity also decreases. Using an exponential decrease in the rate constant with size, the polydispersity is expected to be approximately 1.1. The decrease in reaction rate based on size is reasonable and can be related to a steric hindrance of the reactive sites as well as a decrease in the diffusion of the larger molecules relative to the CDMSS.

Table 8.1 Molecular Weight Characterization by GPC Light Scattering[29]

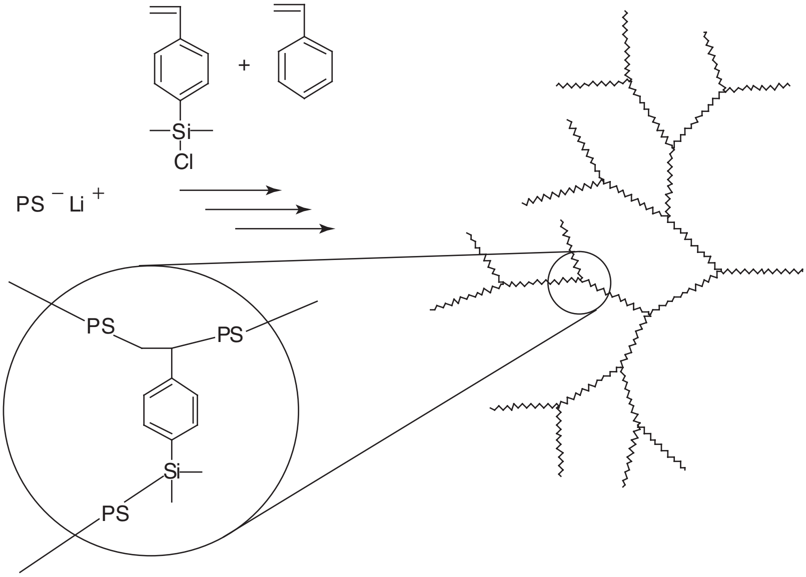
M_n of initial chain (g/mol)	M_w/M_n of initial chain	M_n (g/mol)	M_w/M_n	Average generation number
[a]1690	1.10	15,500	1.17	3.1
[a]1020	1.14	11,300	1.15	3.2
[a]940	1.10	12,000	1.15	3.4

[a] Molecular Weights determined by GPC coupled with Multiangle Laser Light Scattering Detection.

8.3.1.2 Copolymerization of CDMSS and Styrene[24]

Copolymerizations with different molar ratios of CDMSS/styrene were found to increase the molecular weight and the average number of generations. Molar ratios of CDMSS/styrene of from 1:5 up to 1:200 have been investigated. The polymerizations were carried out via slow addition of the monomer mixture over 5 h. The statistical copolymerization of the styrene with the CDMSS results in the same molar amount of styrene units as in the mixture to be distributed around each branch point (Scheme 8.4). The exact distribution of the styrene around the three positions of the branch point could not be determined; however, the average number of styrene repeat units between branch points would be expected to be two-thirds of the molar ratio value based on the random combination of branch units. The hyperbranched core that was produced in the absence of styrene is now spread out, and large dendritic polymers are produced. The increase in generational growth was attributed to the relief of steric hindrance afforded by the relatively flexible PS chain, which allows larger structures to combine, compared to the compact hyperbranched structures from polymerization of CDMSS alone. No cross-linking can occur in the copolymerization because the addition of the AB monomer styrene only extends the hyperbranched structure and the one reactive group at the focal point, either reactive anion or vinyl-functionalized macromonomer, is maintained for each molecule at any time.

The growth of the structures was similarly followed by GPC and light scattering detection. Equations 1 and 2 were used to determine the average number of



Scheme 8.4 Copolymerization of CDMSS and styrene by convergent living anionic hyperbranched polymerization.

generations and the number of branch units with M_B now defined as the molecular weight of the PS distributed around each branch point (i.e., the molecular weight of a styrene repeat unit times the molar ratio of styrene to CDMSS introduced.). Table 8.2 depicts molecular weight characterization results from selected samples using different styrene and CDMSS mixtures.

Low polydispersities (less than 1.5 in almost all cases) result from the copolymerization of styrene and CDMSS. At a ratio of 1:200, a relatively broad and bimodal molecular weight distribution is found. The increased polydispersity is attributed to the partial formation of higher generation structure producing a mixture of molecular weights.

8.3.1.3 Hyperbranched Polymer from VBC and PS[30]

Similar polymerizations have been demonstrated using vinylbenzyl chloride (VBC) with and without additional styrene monomer. The VBC that was used in the hyperbranched polymerizations was a mixture of 3- and 4-isomers. Lower generational growth was observed using VBC as compared to CDMSS. Average generations of 2.4–2.6 were found using VBC alone and 3.2–4.2 using VBC/styrene mixtures of 1:5, 1:10, or 1:15. The polydispersities were also higher than that found in most CDMSS reactions, ranging from 1.20 to 1.88. The decrease in coupling and increase in polydispersity were attributed to the use of the isomeric mixture of VBC, as the reactivity of the macromonomer obtained from substitution of the 3-isomer was proposed to be lower than that of the macromonomer resulting from the 4-isomer. This would effectively result in a termination of growth if the 3-isomer macromonomer did not participate in a vinyl addition reaction on the timescale of the continuous VBC addition. Other causes of the decreased growth and increased polydispersity could be attributed to possible side reactions of the benzyl chloride group—too fast of

Table 8.2 Molecular Weight Characterization by GPC Light Scattering for Dendritic Polystyrene[29]

CDMSS/ styrene ratio	[a]M_n of initial chain	[a]M_w/M_n of initial chain	[a]M_n of dendritic polymer (g/mol)	[a]M_w/M_n	Average generation number[c]
1:5	2130	1.05	62,000	1.13	4.5
1:10	1510	1.10	70,900	1.28	4.8
1:15	1480	1.18	101,000	1.14	5.1
1:20	1480	1.07	176,000	1.21	5.6
1:50	1230	1.02	252,000	1.27	5.3
1:92	1260	1.04	537,000	1.38	5.6
1:137	980	1.07	595,000	1.45	5.3
1:200	1160	1.04	727,000	1.81	5.1

[a] Molecular weights determined by GPC coupled with multiangle laser light scattering detection
[b] Calculated from equation 8.2.

an addition of VBC or VBC/styrene mixtures, or a relatively faster reaction of the vinyl group relative to the benzyl chloride so that termination by cyclization could occur. Reactions over longer time periods were not investigated, nor were reactions with the pure 4-vinylbenzyl chloride isomer.

8.3.1.4 Characterization of Hyperbranched PS

Characterization of the dendritic polymers produced by convergent hyperbranched polymerization confirms the highly branched architecture. Glass transition temperatures (T_g) have been measured, and T_g versus molecular weight plots show that a Fox–Flory chain end free volume theory is followed corresponding to the calculated number of end groups determined by the synthesis procedure.[24,30] Furthermore, measurement of dilute solution viscosity shows a significantly decreased intrinsic viscosity compared to linear polymers of the same molecular weight as would be expected for a highly branched polymer.[24,30]

The radius of gyration (R_g) and hydrodynamic radius (R_h) were determined in toluene by neutron scattering and dynamic light scattering, respectively, for the CDMSS–PS dendritic polymers.[31,32] It was determined that the R_g/R_h value is approximately unity for each of the samples produced with CDMSS/styrene ratios of 1:5–1:200 and an average generational growth of approximately five generations. The actual values ranged from 0.88 to 1.06.[31] The behavior lies between that of flexible polymers with R_g/R_h values of 1.5–1.7 and a hard sphere with R_g/R_h values of 0.78.[33,34] The fact that the R_g/R_h value is practically independent of total molecular weight and the molecular weight between branch points suggests that the polymers with different molecular weight between branch points but the same average number of generations are highly self-similar with constant intramolecular packing densities. Branching ratios ($<R_g^2>/<R_g^2>_{\text{linear}}$) were also determined to be relatively constant, ranging from 0.215 to 0.382. The values were compared to the solution viscosities, which demonstrated a clear difference in viscosity–volume fraction behavior, with the polymer having a larger molecular weight between branch points exhibiting characteristics of a flexible polymer while the polymers with shorter molecular weights between branch points exhibiting colloidal particle-like behavior.

The dependence of R_g on molecular weight for these types of dendritic polymers was compared with dendrimers for which the following dependence was determined:[35]

$$R_g \propto N^{1/5}(G+1)^{2/5}P^{2/5}$$

where P is the number of units between branch points and N is equal to the total number of monomer units. In dendrimer systems, the value of P is typically not varied and the equation reduces to $R_g \propto N^{1/5}(G+1)^{2/5}$. The convergent hyperbranched polymerization allowed the systematic variation of P while maintaining a relatively constant number of generations at ~ 5. By plotting $\log(R_g)$ versus $\log(M_w P^2)$, a relationship of $R_g \propto N^{0.24}$ was determined (Figure 8.2), which favorably agrees with the value of $N^{0.20}$expected for dendrimers.

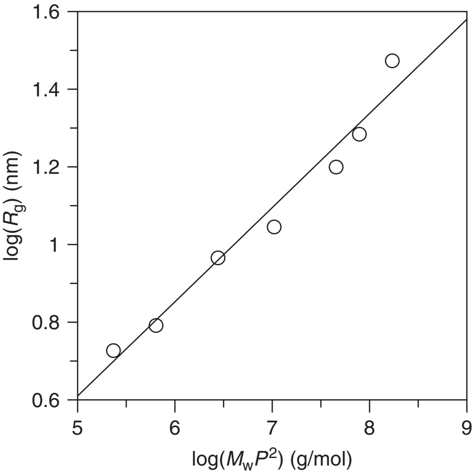


Figure 8.2 Dependence of the radius of gyration on $M_w P^2$.[36]

The melt rheological properties indicate that there is no entanglement in any of the polymers,[32] as would be expected given that the molecular weight between branch points is below PS entanglement molecular weights in all cases.[37] Interestingly, the steady-state shear compliance J_s° increases with the molecular weight and is found to be much larger than for star polymers.

8.3.1.5 Hyperbranched Polyisoprene[27]

A functionalized diene ABB′ monomer, 2-(chlorodimethylsilyl)-1,3-butadiene (CDMSB) (Figure 8.1), was synthesized and examined for its ability to participate in convergent hyperbranched polymerizations.[38] Polyisoprenyllithium (PILi) initial chains were prepared in cyclohexane. Elevated reaction temperatures of 50 °C and slow addition of CDMSB over 10 h resulted in 3.0 generations of growth. The polydispersity of the hyperbranched polymer was determined to be 1.2. This ABB′ monomer demonstrated the ability to undergo similar convergent hyperbranched polymerizations as CDMSS and VBC; however, further investigation of its reaction was abandoned because of the difficulty of the synthetic procedure and handling of the monomer. Instead, hyperbranched copolymers of isoprene and CDMSS were investigated.

Reactions involving PILi chains with CDMSS proceed in a similar fashion to that of PSLi with CDMSS. The reaction of the PILi with the silyl chloride is again the faster reaction compared to reaction at the vinyl group.[28] Once the reaction at the vinyl group occurs, the resulting styryllithium anion can participate in further reaction with additional CDMSS. Relatively low generations of growth occurred, 2.2–3.0, depending on the molecular weight of the starting polyisoprene chains over 4–5 h addition times. The polydispersities remained low at 1.10–1.39.

The use of PILi as the starting chains allowed ^{29}Si NMR spectroscopy characterization to probe the branched structure. In an ideal dendrimer-like structure, the fraction of Si atoms attached to a polyisoprene chain would be equivalent to the fraction of Si atoms that reacted with the CDMSS vinyl group. The NMR spectroscopy results show a ratio of 1.7–1.0 for the relative Si environments, indicating a larger fraction of polyisoprene–Si bonds. This demonstrates that the reaction with the silyl chloride is fast and that the relatively slow crossover from PILi to PSLi[39] from attack at the CDMSS vinyl group is slower than the rate of addition of the CDMSS monomer. In this case, a disproportionate amount of polyisoprene macromonomer is allowed to form before addition to the vinyl group occurs. A more equal distribution would be expected under a slower addition of CDMSS.

Chain-extended hyperbranched polymers were produced by adding a mixture of CDMSS and styrene to the PILi chains. In this case, higher generational growth to 4.2 generations or an average of 18.4 branches was obtained using a 1:5 M mixture of CDMSS/styrene. The structure that is produced is the same hyperbranched CDMSS with PS chains between branch points as previously described, but with a periphery that is polyisoprene rather than PS.

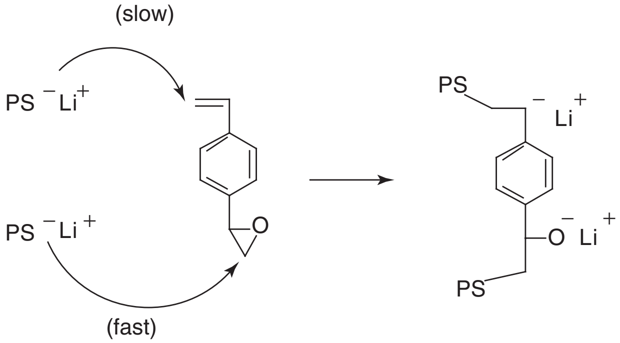
A hyperbranched copolymer of CDMSS with isoprene was investigated to produce a dendritic polymer that was predominately comprised of polyisoprene. PSLi was used as the initial chains and a mixture of CDMSS/isoprene was added in a 1:115 M ratio. The resulting polymer achieved a growth of 4.0 generations (16 branches) and had a molecular weight of 156,000 g/mol from 2180 g/mol PS initial chains. The polydispersity was 1.51 and the slightly higher value compared to previous systems could be due to slow rates of crossover from PILi to PSLi and fast rates of crossover from PSLi to PILi.

8.3.1.6 Convergent Hyperbranching with 4-Vinylstyrene Oxide[40]

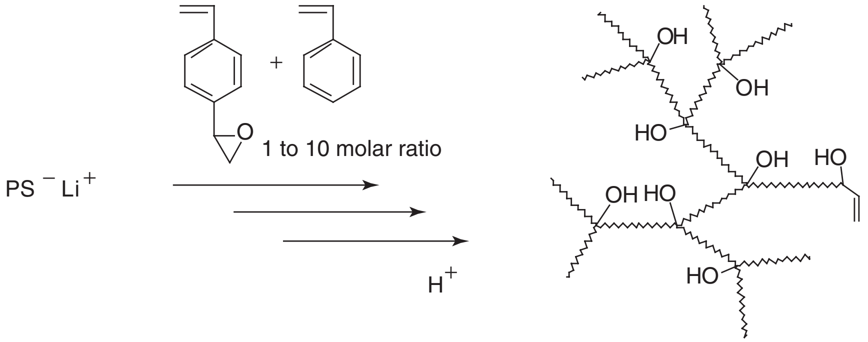
The convergent hyperbranched technique can be used with other ABB′ monomers that can quantitatively terminate by coupling with a reactive anion and form a vinyl-functionalized macromonomer. Addition reactions whereby the resulting anion is unreactive with other functional groups is a mechanism for coupling. 4-Vinylstyrene oxide is an example of a monomer that can form a macromonomer by a ring-opening addition reaction with a carbanion (Scheme 8.5). The resulting lithium alkoxide from ring opening of the pendent epoxide is an effectively terminated chain as it cannot react with the vinyl group or more epoxide. The carbanion, however, can react with the additional 4-vinylstyrene oxide at either the epoxide or the vinyl group, or can react with the additional styrene monomer.

Termination of PSLi with epoxides such as ethylene oxide is well known for alcohol functionalization of chain ends. The resulting lithium alkoxide does not continue to add more ethylene oxide unless long reaction times are used.[42–44] The addition of styrene oxide is less studied; however, it can also quantitatively add one unit to a PSLi chain under the appropriate reaction conditions.[45–47]

Polymerizations were done with 1:10 M mixtures of 4-vinylstyrene oxide/styrene added over the course of 4–6 h to a solution of approximately 1000 g/mol PSLi (Scheme 8.6). Different additives were examined including THF,



Scheme 8.5 Reactions of 4-vinylstyrene oxide in hyperbranched convergent polymerization.



Scheme 8.6 Synthesis of hyperbranched polystyrene with hydroxyl functional branch points.[41]

LiCl, and N,N,N′,N′-tetramethylethylenediamine (TMEDA), with the highest generational growth of 3.8 generations (13.9 branching groups) found for reaction conditions using a combination of 60 equiv. of THF and 5 equiv. of LiCl relative to initial PSLi. The polydispersities depended on the reaction conditions, with the combination of THF and LiCl resulting in a polydispersity of 1.28. Termination of the reaction with acid resulted in a uniquely branched structure with alcohol functional groups at each of the branch points. Titration of the alcohol groups[48–52] provided a measure of the number of branching groups per molecule when combined with molecular weight data. The number of branching groups determined by titration was within 10–15% of that determined using Eqs. (8.1) and (8.2).

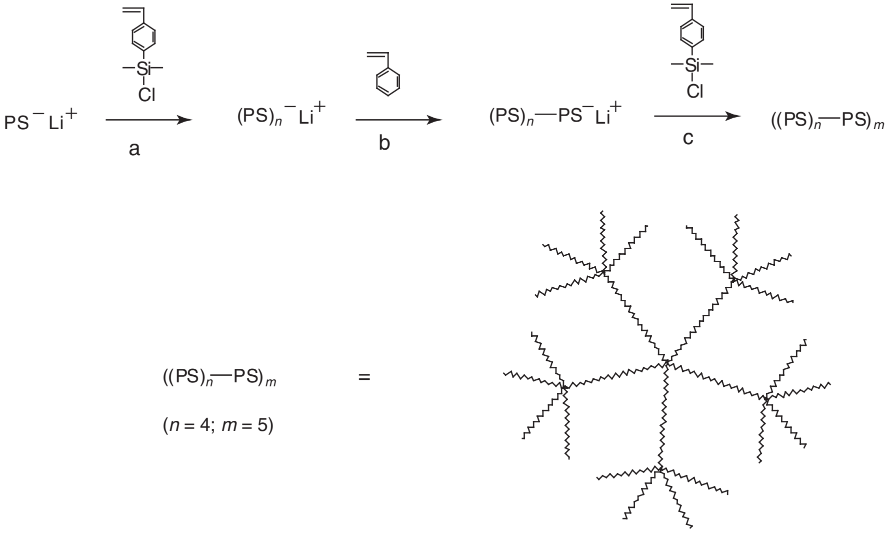
8.3.2 Complex Branching by Convergent Hyperbranched Polymerization

The convergent hyperbranched polymerization technique allows the production of complex branched architectures, and the copolymerization of CDMSS and styrene affords different structures depending on the sequence of addition of the monomer units. Because the convergent method maintains a single reactive group at the focal point of the hyperbranched polymer during all stages of the synthesis, procedures can be designed that modify the branching architecture or produce functionalized hyperbranched polymers for incorporation into larger structures.

8.3.2.1 Hyperbranch-on-Hyperbranch Constructs — $((PS_n)PS)_m$[53]

The slow addition of a stoichiometric equivalent of CDMSS to a solution of PSLi has been demonstrated to produce a hyperbranched polymer with PS chains at the periphery. If a deficiency of CDMSS is added, a reactive anion persists at the focal point. Polymerization can be initiated from the focal anion to grow a linear block from the hyperbranched core. The reactive chain end can then proceed in a subsequent convergent hyperbranched polymerization with more slowly added CDMSS. The overall result is a second-generation dendrimer-like structure that is built from hyperbranched building blocks (Scheme 8.7).

Variation in structure was accomplished by controlling the size of peripheral and interior linear polymer chains and the extent of coupling in the hyperbranched core at each stage of the synthesis. The final product was designated as $((PS_n)PS)_m$ to describe a star-shaped PS (with m number of arms) assembled around a hyperbranched core having stars at the ends of each arm (with n number of arms) assembled around their own hyperbranched cores. The reaction was followed by withdrawing samples at each stage of the synthesis and analyzing by GPC and light scattering characterization. The polydispersity of the product mixture was less than 1.25 in all cases; however, a final fractionation procedure was



Scheme 8.7 Synthesis of dendritic polystyrene by sequential block copolymerization.[54]

performed in order to separate the final product from relatively small amounts of residual material formed by termination at each stage of the reaction. The results from a selection of experiments are reproduced in Table 8.3. The g' values depict the compact nature of the branched architecture.

In a similar fashion, $((PS_n)PX)_m$ copolymers were produced with m equal to 2 and PX corresponding to PS,[55] polyisoprene,[56] or polydimethylsiloxane.[57] The procedure was modified by introducing a different monomer to the hyperbranched macroinitiator and coupling with a difunctional coupling agent rather than more CDMSS.

8.3.2.2 Hyperbranched Macromonomers and Graft Copolymers[58]

The convergent synthesis with CDMSS alone or as copolymerization with styrene monomer ultimately results in a termination of the structure as a vinyl-functionalized macromonomer. The vinyl group is reactive, although sterically hindered. Copolymerizations of the hyperbranched PS macromonomer have been accomplished to produce complex architectures with hyperbranched polymer groups attached to linear polymer backbones. Copolymerizations with styrene or methyl methacrylate were carried out by either free-radical or anionic mechanisms. The extent of vinyl functionalization was determined to be at least 88% for the samples studied, based on the total amount of hyperbranched polymer incorporated into the copolymers.

8.3.3 Related Procedures

Very few procedures have been developed to make use of the convergent hyperbranched methodology outside of our own work. However, a few unique examples that do follow a convergent process and follow similar techniques and/or make use of similarly designed ABB′ monomers are described.

8.3.3.1 Sequential Macromonomer Formation and Polymerization

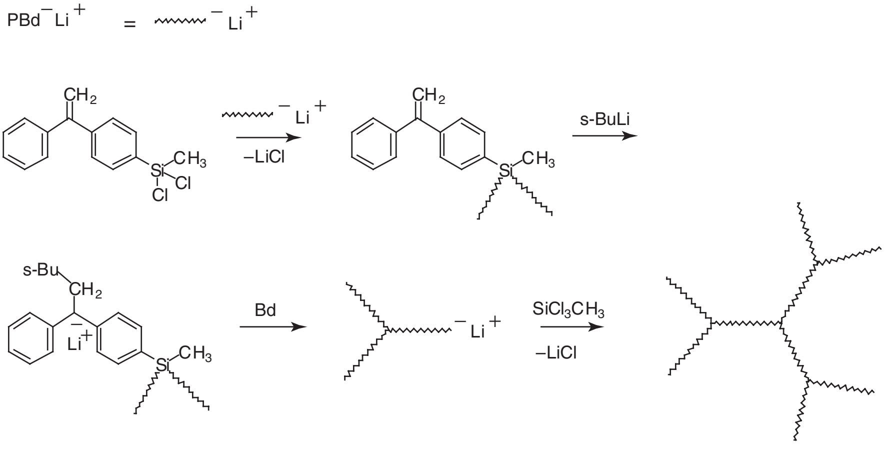
A controlled synthesis procedure has been developed taking advantage of the types of ABB′ monomers described, combined with high-vacuum anionic polymerization techniques.[59] A sequential synthesis was elaborated that modifies the order of reaction of CDMSS monomer and AB comonomers in an attempt to produce more well-defined dendritic structures. In this procedure, vinyl-functionalized macromonomer is synthesized using CDMSS in a 1:1 ratio

Table 8.3 Characterization of $((PS_n)PS)_m$-Type Polymers[54]

M_n of initial chains (g/mol)/ PDI	M_n of $(PS)_n$, initial stars (g/mol)/PDI	N (Average number of exterior chains)	M_n of $(PS)_nPS$, star-b-linear diblock (g/mol)/PDI	M_n of $((PS)_nPS)_m$, radially linked diblock (g/mol)/PDI	m (Average number of core arms)	$g' \left(\frac{[\eta]_{((PS)_nPS)_m}}{[\eta]_{\text{linear}}}\right)$
1,090/1.04	4,320/1.29	3.6	21,300/1.01	121,000/1.16	5.6	0.47
1,090/1.04	3,650/1.26	3.0	19,400/1.01	139,000/1.13	7.2	0.40
1,210/1.10	5,060/1.36	3.8	50,300/1.02	262,000/1.19	5.2	0.58
4,430/1.05	18,900/1.26	4.2	25,000/1.18	145,000/1.15	5.8	0.39
4,430/1.05	18,900/1.26	4.2	59,200/1.03	288,000/1.15	4.9	0.52

with living polymer anions. The solution of macromonomer is then added to a solution of more living polymer anion in a 1:1 M ratio. The resulting coupled polymer with a reactive anion at the junction point is subsequently used as a macroinitiator to polymerize isoprene introduced as an AB monomer. The final step involves coupling the living chain with a multifunctional silyl halide like trichloromethylsilane or tetrachloromethylsilane over 25 days to produce a second-generation dendritic structure. It is reported that the final structure is well defined; however, at least 5% of coupled product is formed during the macromonomer synthesis from competitive reaction at the vinyl group, and this coupled product can participate in subsequent reactions to be incorporated into the final structure. The final reaction mixture contains low molecular weight linear and branched chains from the use of an excess of anions in the final coupling step, and fractionation is required to isolate the desired structure in approximately 50–55% yields. The multistep, multipot procedure follows a convergent synthesis; however, the complexity approaches that of dendrimer synthesis and is therefore not a hyperbranched polymerization in that sense.

Recent expansion of the above procedure uses 4-(dichloromethylsilyl)diphenylethylene (DCMSDPE) as an ABB′B′ monomer.[60] The method again relies on a sequential series of reactions where termination of polybutadienyllithium (PBdLi) chains produces a macromonomer (Scheme 8.8). In this case, the selectivity of the reaction was designed to greatly favor substitution of the silyl halides by the PBdLi rather than attack of the diphenylethylene double bond so that an exact titration of two polymeric anions to one ABB′B′ monomer reportedly prevents addition to the double bond. The latent ethenyl A group is converted into a reactive A group by addition of a small-molecule anionic initiator (*sec*-butyllithium) rather than a polymer. Once the initiation of the diphenylethylene



Scheme 8.8 Sequential macromonomer formation and initiation for the formation of dendritic polymer.[61]

has been accomplished, the addition of butadiene monomer can be carried out to grow a chain from the reactive site. An excess of the first-generation polymeric dendron can then be reacted with trichloromethylsilane over 25 days to effect trimeric coupling and produce a second-generation structure. Alternatively, the procedure was repeated with the addition of first-generation living chains to a solution of DCMSDPE in a ratio of 2:1, followed by reinitiation with *sec*-butyllithium, polymerization of butadiene, and trimeric coupling with a deficiency of trichloromethylsilane over 30 days to produce a third-generation structure. A fractionation procedure is finally applied in order to separate the final structure from any residual excess of reactants or any incompletely coupled product.

8.3.3.2 Hyperbranched Polymers by a Convergent Radical Polymerization

A system that demonstrates some aspects of the convergent hyperbranched synthesis utilizes the ABB′ monomers depicted in Figure 8.3 and controlled radical polymerization by nitroxide-mediated or RAFT techniques.[62–64]

Radical polymerization of styrene initiated with AIBN in the presence of the ABB′ monomers results in branching reactions as the propagating radical can either “terminate” in reaction with the nitroxide radical or dithioester group, or the propagating radical can add through the vinyl group. In comparison to the general technique previously described, the nitroxide or dithioester is considered the B′ group and reacts quickly with the propagating radical to produce a macromonomer. Polymerization through the vinyl group of the macromonomer leads to branching, as demonstrated in Scheme 8.9, using the dithioester ABB′ monomer. However, where this system deviates from the convergent hyperbranched polymerization is that the “termination” or coupling with the B′ group is reversible in each case. The reversible nature of the terminations is the means for controlling the radical polymerization and allows additional monomer to be inserted to increase the molecular weight between branch points. However, the change from a dormant (terminated) state to a reactive (separated) state allows for a shuffling or redistribution of branch molecules as radical chains can recombine at different nitroxide or dithioester sites. The end result of this redistribution

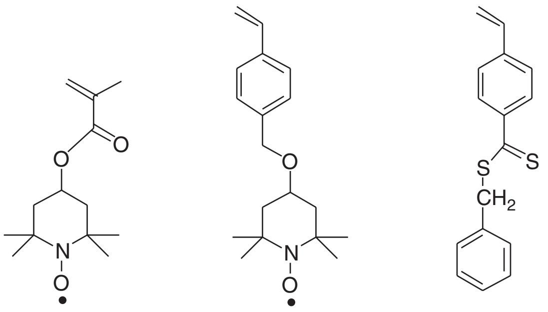
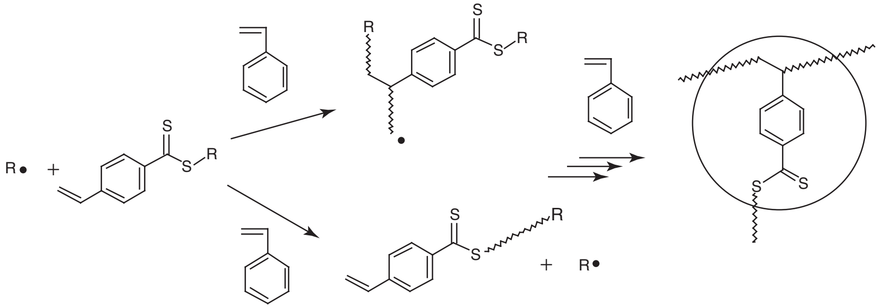


Figure 8.3 ABB′ monomers for controlled radical polymerization.



Scheme 8.9 Hyperbranched polymer by copolymerization of styrene and a polymerizable RAFT agent.

is a random AB_2 hyperbranched polymerization with large polydispersities similar to that obtained with other AB_2 monomers. However, because each branch point is reversibly terminated, reinitiation and polymerization of additional AB comonomers result in a block copolymer produced within the branched structure, that is, between the branch points. Cleavage of the branch points by aminolysis in the case of the dithioester polymerizations or with phenylhydrazine in the case of the nitroxide polymerizations demonstrated that the linear chains between branch points are of low polydispersities, indicative of the well-controlled nature of the AB monomer propagation.

8.4 CONCLUSIONS

The convergent hyperbranched polymerization technique is a useful procedure for effecting control in the formation of hyperbranched and dendritic polymers. The control afforded by the pseudoprotection of the latent vinyl group allows a convergent process to proceed in one-pot reactions without the need for isolation, deprotection, or intermediate purification. Relatively narrow molecular weight distributions can be achieved with the right design of ABB′ monomers and metered addition. Statistical copolymerization or sequential block copolymerization results in chain-extended hyperbranched polymers while maintaining low polydispersities in the products. The use of this technique will increase as new ABB′ monomers are developed, which make use of living anionic and other controlled methods to produce additional hyperbranched and dendritic polymers.

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Chapter 9

Hyperbranched and Dendritic Polyolefins Prepared by Transition Metal Catalyzed Polymerization

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9.1 INTRODUCTION

Polyolefins are an important family of polymeric materials with millions of tons produced every year for broad applications such as fibers, plastics, and elastomers by using inexpensive and abundant olefin monomers obtained from cracking of crude oil.[1] With an excellent balance of physical properties and relatively low costs, the world market share for polyolefins, of the total thermoplastics market, has increased from 20% in the 1960s to about 65% in 2001.[2] One of the major technological driving forces for the polyolefin industry is the transition metal polymerization catalyst technology.[2] Traditionally, polyethylene (PE) and its copolymers with functional monomers were produced by free radical polymerization under high pressure and high temperature.[3] The discovery of Ziegler–Natta catalysts in the 1950s has revolutionized the polyolefin industry,

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

because these transition metal–catalyzed polymerizations can be operated at much milder conditions.[4] Since the 1980s, the well-defined homogeneous versions of Zieglar–Natta catalysts, that is, the early transition metal single-site metallocene catalysts, have been developed rapidly.[5] A number of commercial processes for manufacturing linear low-density polyethylenes (LLDPEs) are based on metallocene and other single-site catalyst technologies. A recent milestone in catalyst development is the discovery of Ni(II)- and Pd(II)-α-diimine catalysts.[6–9] These late metal catalysts are different from the early metal catalysts because of two unique features: (i) these catalysts possess the so-called "chain walking" capability, which leads to the formation of unusual polymer microstructures[6,8,10,11]; and (ii) these catalysts show significantly higher tolerance of functional groups than the early transition metal catalysts.[6,7,9,12]

Despite these important developments, macromolecular branched topologies of polyolefins produced by various catalysts are rather limited. Most polyolefins exhibit simple straight chain topology (such as high-density polyethylene, HDPE), and some possess linear topology with short and few long-chain branches (low-density polyethylene, LDPE; and LLDPE). This is inherently limited by the coordination–insertion polymerization mechanism in which the active growing site is located at the chain end, and the unidirectional monomer addition to the chain end leads to the formation of linear polymers.[3] The need to synthesize polymers with unusual properties has driven the effort of designing polymers with new architectures.[13] Although tremendous progress has been made in synthesizing dendritic[14–17] and hyperbranched polymers,[18–23] a majority of these polymers reported to date are based on condensation polymerization, which is not applicable to polyolefin syntheses. Thus, it is highly desirable to develop methods that can directly polymerize simple olefin monomers to give hyperbranched and dendritic topologies.

Inspired by the recent progress in late-transition-metal polymerization catalysis,[6,7,24–27] we have been exploring the concept of controlling polymer topology using late-transition-metal catalysts with the goal of creating polyolefins with unusual branching topologies from simple olefin monomers.[8,10–12,28–38] Instead of using new monomer approaches, we are pursuing new polymer topologies by controlling the covalent assembly of simple olefin monomers through catalysis. We have succeeded in a few approaches demonstrating this concept. In one strategy, hyperbranched polyolefins were prepared via direct free radical polymerization of divinyl monomers by controlling the competition between propagation and chain transfer using a cobalt chain transfer catalyst (CCTC).[29,30] In another strategy,[8,10–12,33,35,38] the PE branching topology was successfully controlled by regulating the competition between propagation and "chain walking" for ethylene polymerization using a Pd(II)-α-bisimine catalyst.[6] On the basis of studies conducted in others' laboratories and our own, this review summarizes the recent developments in the synthesis of hyperbranched and dendritic polyolefins using transition-metal catalysts.

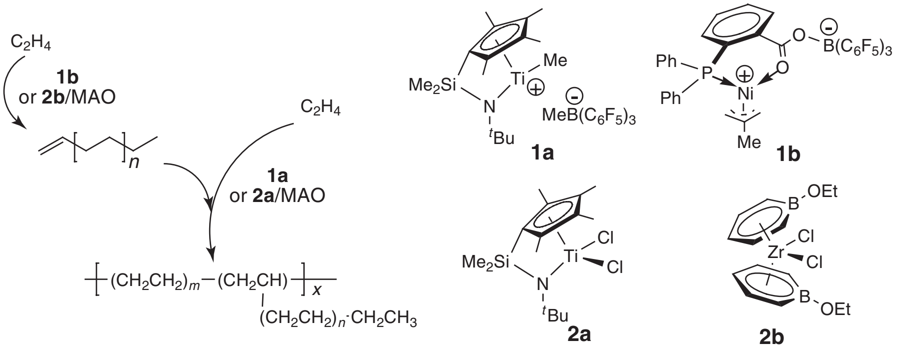
9.2 RESULTS AND DISCUSSION

9.2.1 Branched Polyolefins Made by Radical Polymerization and Early Transition Metal–Catalyzed Polymerization

Polypropylene (PP) possesses a simple linear topology with methyl branches at each repeat unit. For PEs, a few grades (HDPE, LDPE, and LLDPE) with various branching patterns have been manufactured by different polymerization processes.[3] Although these polyolefins exhibit relatively small differences in branching structure, they have a significant impact on the resulting physical properties. For LDPEs obtained from conventional free radical polymerization, the polymer shows a distribution of irregular short- and long-chain branches, which are presumably formed by both intra- and intermolecular radical chain transfer. The combination of long- and short-chain branches enhances the melt processibility; however, the mechanical properties for LDPE are partially sacrificed. For LLDPE obtained by Ziegler–Natta or metallocene catalysts, varying amounts of α-olefin comonomers are copolymerized with ethylene to form polymers possessing regular short-chain branches with controlled length. The introduction of short-chain branches lowers the crystallinity and enhances film formation properties. In some ethylene homo- and copolymerization catalyzed by homogeneous early transition metal catalysts, such as the Dow constrained-geometry single-site catalysts, low levels of long-chain branching has also been reported.[39,40] It is believed that the catalyst can form vinyl-terminated macromonomers *in situ*, which are subsequently incorporated in ethylene polymerization to form long-chain branches. This mechanism will be further discussed in the following section for which multiple catalysts are used to promote branch formation. Another strategy being investigated is to add a small amount of one α,ω-diene to introduce H-shaped branching points.[41,42] This is essentially to add a small amount of cross-linker and the polymerization conditions are controlled not to cross-link but to form branched polymers, instead.

9.2.2 Branched Polyolefins Prepared by Tandem Action of Multiple Transition Metal Catalysts

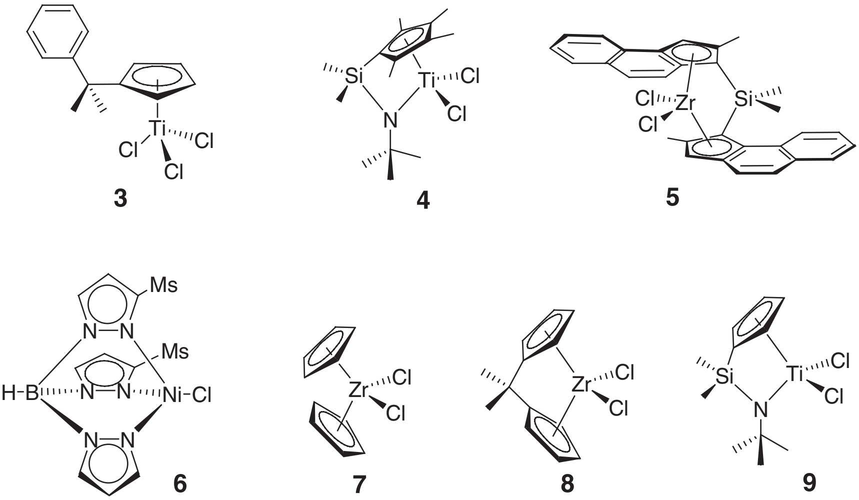
A number of research groups have reported the synthesis of branched PE via tandem action of multiple transition metal catalysts. The general concept is to combine two well-defined homogeneous catalysts with one producing a short α-olefin and other copolymerizing ethylene with the α-olefin produced *in situ* to form a branched PE structure. One representative example is the tandem catalyst system reported by Bazan and coworkers for the synthesis of polyolefins having controlled short-chain branches.[43,44] In the examples shown in Scheme 9.1,



Scheme 9.1 Synthesis of short-chain branched PE via tandem action of multiple catalysts.

complexes **1b** or **2b** oligomerize ethylene into short 1-alkenes, which are further copolymerized with ethylene by olefin polymerization catalysts **1a** or **2a** to form branched PEs. In the **1a**/**1b** system, a Ni(II) complex **1b** oligomerizes ethylene to primarily form 1-butene and 1-hexene, which are then copolymerized by a preactivated catalyst **1a** to afford butene-ethylene and butene-hexene-ethylene copolymers. Similarly, in the **2a**/**2b** system, **2b** upon activation with methylaluminoxane (MAO) oligomerizes ethylene to form 1-alkenes, which are copolymerized with ethylene by **2a**/MAO. Despite the complications that **2b**/MAO produces a statistical distribution of 1-alkenes with different reactivity, it was shown that two independent catalysts could work cooperatively to produce a single product and the polymer properties could be modified by changing the initial mixture of precatalysts. The same concept has also been applied by the same group to a triple tandem catalyst system.[45]

A number of other tandem polymerizations were also reported in the last few years for branched polyolefins. Zhu and coworkers reported the use of homogeneous tandem catalytic systems for the synthesis of ethylene/1-hexene copolymers from ethylene stock as the sole monomer.[46] The reported catalytic systems employ the tandem action between an ethylene trimerization catalyst, $(\eta^5\text{-}C_5H_4CMe_2C_6H_5)TiCl_3$ (**3**)/modified methylaluminoxane (MMAO), and a copolymerization metallocene catalyst, $[(\eta^5\text{-}C_5Me_4)SiMe_2(^t\text{BuN})]TiCl_2$ (**4**)/MMAO or rac-$Me_2Si(2\text{-MeBenz[e]Ind})_2ZrCl_2$ (**5**)/MMAO. During the reaction, **3**/MMAO generates 1-hexene *in situ*, and simultaneously, **4**/MMAO or **5**/MMAO copolymerize ethylene with the produced 1-hexene to generate butyl-branched PE. It was shown that, by the simple manipulation of the catalyst molar ratio and the polymerization conditions, a series of branched PEs with melting temperatures of 60–128 °C, crystallinities of 5.4–53%, and hexene percentages of 0.3–14.2 can be efficiently produced. In the work reported by Casagrande and coworkers, branched PEs were prepared using a combination of catalyst precursors $\{Tp^{Ms}\}NiCl$ (**6**) (Tp^{Ms} = hydridotris(3-mesitylpyrazol-1-yl)) and Cp_2ZrCl_2 (**7**).[47] Marks and coworkers have reported a binuclear complex in which the proximity of catalytic sites was proposed to be responsible for the increased branching level



Scheme 9.2 Other catalysts used in tandem polymerization for the synthesis of branched polyolefins.

in the ethylene homopolymerization.[48] Beigzadeh *et al.* reported both theoretical and experimental work on making polyolefins with long-chain branching using combined early metal catalysts.[49] Finally, Sperber and Kaminsky described a tandem catalytic system composed of $[Me_2C(Cp)_2]ZrCl_2$ (**8**) and $[Me_2Si(N^tBu)(Me_4Cp)]TiCl_2$ (**9**) for producing long-chain branched PE with branch lengths of up to 350 carbons.[50] Compound **8** was used in a first oligomerization step to yield a macro-comonomer, which was incorporated in the subsequent copolymerization with ethylene to form long-chain branches.

The tandem polymerization concept was also applied to systems containing heterogeneous polymerization catalysts. Hu and coworkers reported the combination of 2,6-bis(imino)pyridyl iron catalyst with a traditional Ziegler–Natta catalyst as a tandem catalytic system for the synthesis of branched PE by *in situ* polymerization of ethylene.[51] The branched PE with branches from 8/1000C to 29/1000C was produced by adjusting reaction conditions: the amount of triethylaluminum (TEA), MAO, iron catalyst used, and reaction temperatures. Both the short branches such as ethyl and butyl and the longer branches (hexyl and longer than hexyl) were detected in the products. In another example, Okuda and coworkers described a synthesis of branched PEs by the tandem catalysis of silica-supported, linked cyclopentadienyl-amido titanium catalysts and a homogeneous Ni(II) catalyst having a pyridylimine ligand.[52] In this system, the nickel catalyst produced short α-olefins, which were copolymerized by the titanium catalyst.

It should be noted that, while the PEs made by these tandem catalytic polymerizations have short and/or long branches, their global topology is still linear, because there is no branch-on-branch, that is, hyperbranched structure. This is a general feature limited by the catalytic properties of early transition metal olefin polymerization catalysts. As discussed in the next section, we and other authors have shown that some late transition metal complexes can generate branch-on-branches and thus permit the formation of hyperbranched polyolefins.

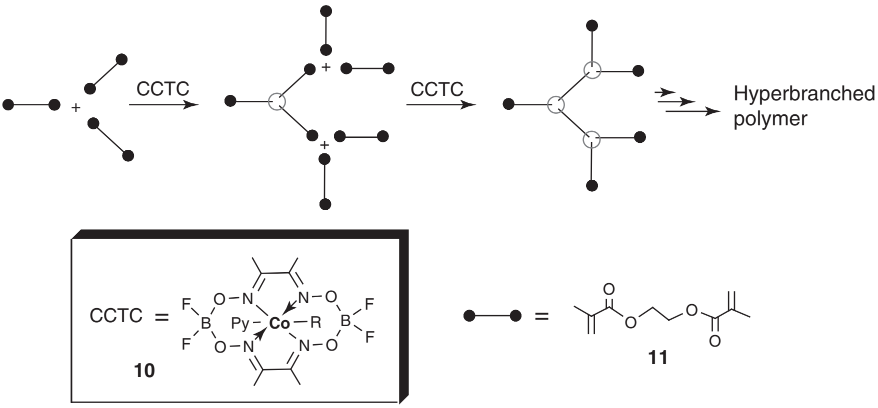
9.2.3 Hyperbranched and Dendritic Polyolefins Made by Late Transition Metal Catalysts

One major research thrust of our group is to develop efficient catalytic synthesis of hyperbranched and dendritic polyolefins using commercial olefin monomers. We have demonstrated a few strategies to control polymer topology using transition metal catalysis. In one strategy, we successfully prepared hyperbranched acrylic polymers via direct free radical polymerization of commercial divinyl monomers by controlling the competition between propagation and chain transfer using a CCTC.[29,30] In another approach, PE topologies were controlled from linear to hyperbranched to globular dendrimer-like by controlling the competition between chain walking and insertion using the Brookhart palladium-bisimine chain-walking catalyst.[8,10–12,33,35,38] The chain-walking polymerization methodology has been successfully applied to the one-pot synthesis of various functional dendritic copolymers. In the following sections, the progress in this area will be reviewed.

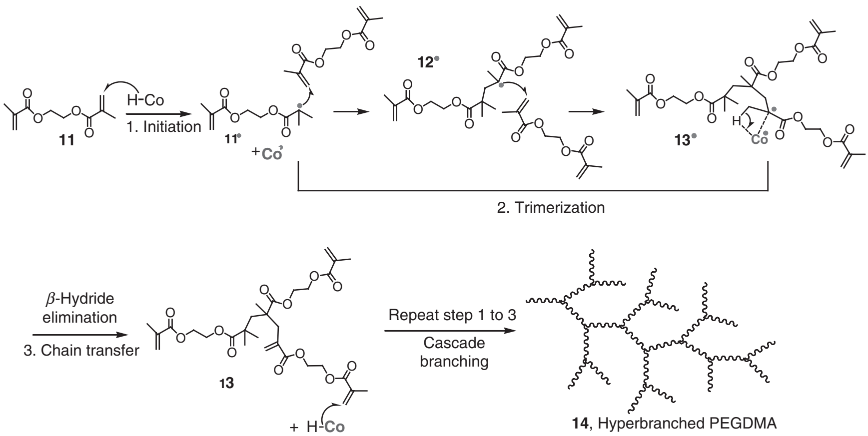
9.2.3.1 Hyperbranched Polyolefins Made by Catalytic Chain Transfer Catalyst

In our first strategy,[29,30] we synthesized hyperbranched polymers through direct free radical polymerization of commercially available divinyl monomers by controlling the competition between propagation and chain transfer using a CCTC. Free radical polymerization is one of the most widely used polymer production methods with major advantages in the generality of monomer choice and the robustness of reaction conditions. However, free radical polymerization usually produces only a limited array of polymer architectures due to the nature of linear radical propagation. It is of both fundamental and practical interest to develop general methods for the preparation of polymers with new topologies by direct free radical polymerization. We used a CCTC **10** to control the propagation of free radical polymerization of a divinyl monomer to afford hyperbranched polymers in one pot (Scheme 9.3).

Previous studies have shown that a series of cobalt complexes afford very efficient catalytic chain transfer reaction to free radical polymerization of vinyl monomers through β-H abstraction.[53] In our study, we used a dimethacrylate monomer and tuned the CCTC concentration for trimerization of methacrylate. The cascade trimerization of a dimethacrylate monomer led to a hyperbranched polymer. Scheme 9.4 shows the radical polymerization of ethylene glycol dimethacrylate (EGDMA), **11**, initiated with an azo initiator and controlled by **10**. The cobalt hydride (CoH) formed in the catalytic cycle initiates



Scheme 9.3 Concept of hyperbranched polymer formation by regulating chain transfer and propagation.



Scheme 9.4 Hyperbranched polymer formation by a cobalt chain transfer catalyst.

a new radical chain, **11**. Because the CCTC concentration was chosen primarily for trimerization, statistically the new chain only propagates twice to form a trimer radical, **13**, which is subsequently terminated by *β*-hydride abstraction by the CCTC. The terminal methacrylate groups of the trimer **13** will be reinitiated by CoH, followed by trimerization and *β*-hydride abstraction to form another branching point. Since every trimerization generates a branching point, the cascade trimerization of EGDMA leads to a hyperbranched polymer.

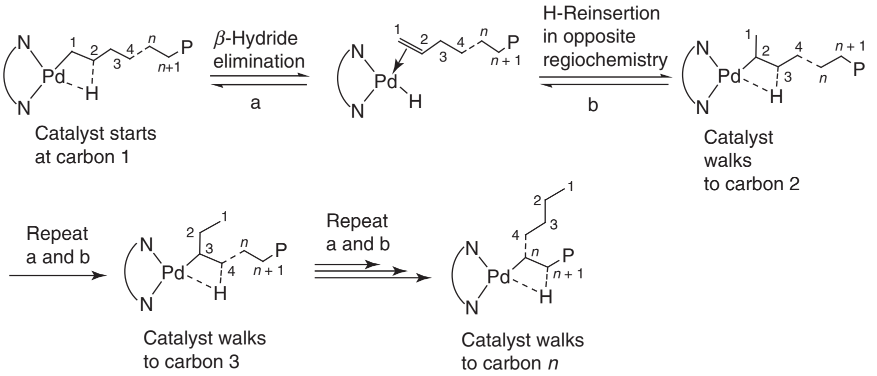
The hyperbranched polymers synthesized were characterized by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS), ^{1}H and ^{13}C NMR, and viscosimetry.[29] The hyperbranched polymers formed exhibit interesting properties such as high surface functionality and low solution viscosity. These unique features, combined with the commercial availability of many divinyl monomers and the robustness of free radical polymerization will make this new approach attractive for the preparation of new functional materials.

9.2.3.2 Hyperbranched Polyolefins Prepared by Chain-Walking Polymerization

9.2.3.2.1 Hyperbranched and Globular Dendrimer-Like Ethylene Homopolymers. In our second strategy,[8,10–12,33,35,38] we successfully controlled the PE topology by regulating the competition between propagation and "chain walking" for ethylene polymerization using a chain-walking catalyst. Our work is based on the discovery of Pd(II)-α-bisimine chain-walking catalysts by Brookhart and coworkers[6,7] Brookhart[6,7] and Fink[54] discovered that when certain Ni(II) and Pd(II) catalysts were used for ethylene polymerization, branched instead of linear PEs were obtained. They also observed a "chain-straightening" phenomenon in α-olefin polymerizations using those Ni(II) and Pd(II) catalysts.

To explain their experimental observations, both Brookhart and Fink proposed that the catalyst could isomerize or "walk along" the polymer backbone during the migratory insertion polymerization. The chain walking of the catalysts is facilitated by a process involving β-hydride elimination and retransfer of the hydride in the opposite regiochemistry (Scheme 9.5).[6,7,54]

Supported by fine mechanistic studies, Brookhart and coworkers showed that the Pd(II)-α-bisimine catalyst can "walk" through a secondary or tertiary carbon but not a quaternary carbon center.[55,56] ^{13}C NMR spectroscopic analysis of the PEs produced by these catalysts provided information on the local-scale microstructure, such as the total branching density, the distribution of short-chain branches, and the shortest branch-on-branches, *iso*-butyl groups.[57,58] Nevertheless, the global branching topology of these polymers was not clear and there



Scheme 9.5 "Chain walking" mechanism proposed by Brookhart and Fink.

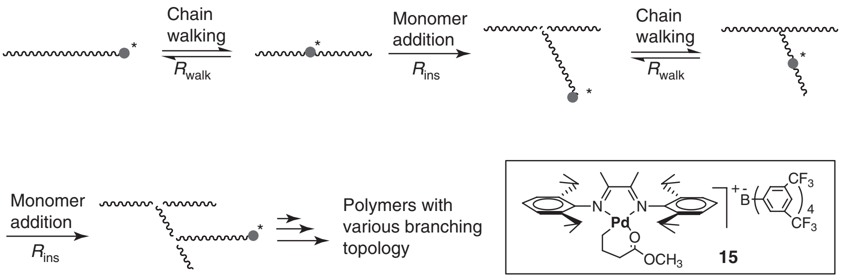
was no attempt to control the PE topology using the chain-walking catalyst prior to our report in 1999.[8]

Following the discovery of the Ni(II) and Pd(II)-α-bisimine catalysts by Brookhart and coworkers, the author was intrigued by the chain-walking mechanism and conceived that this could be used to control PE topology if the competition between chain walking and insertion could be regulated. The concept is shown in Scheme 9.6.[8,10,11] During ethylene polymerization, the chain-walking catalyst isomerizes ("walks") on the polymer chain during propagation, so that the next monomer unit is assembled onto any part of the polymer backbone rather than at the chain end. Instead of introducing branching by monomer structure, here, the branching is introduced by a catalyst that can control the position for the next monomer addition. This nonlinear fashion of chain propagation leads to the formation of branched polymers.[8,10,11]

It was further reasoned that PEs with various branching topologies could be prepared by regulating the competition between the rate of monomer insertion (R_{ins}) and chain walking (R_{walk}).[8,10,11] Using polymerization conditions for which insertion is much faster than chain walking, the catalyst will not walk too far after each insertion; therefore, PEs with a relatively linear topology will be formed. On the other hand, if chain walking is very competitive, the catalyst will walk extensively on the polymer chain after each insertion. This random walk of the catalyst followed by the insertion of ethylene should result in a hyperbranched or a dendritic polymer.

To test the hypothesis, a series of experiments were designed, in which the ethylene pressure (P_{E}) was varied systematically.[8,10,11] Since the insertion rate has a zero-order dependence on ethylene concentration whereas chain walking is inversely dependent upon ethylene concentration, varying the P_{E} should provide the simplest way to control the relative rates of insertion and chain walking. It was expected that at high P_{E}, insertion should be relatively fast because the ethylene concentration is relatively high in the polymerization solution. At low P_{E}, the chain walking will be competitive to the insertion so that the catalyst can walk extensively on the polymer chain between two consecutive insertions.

The initial characterization by quantitative ^{13}C NMR and regular gel permeation chromatography (GPC) of the PEs made at different pressures



Scheme 9.6 Concept of polymer topology control by the chain-walking catalyst.

showed, surprisingly, that they were very similar, as characterized by these methods. The GPC results showed that they exhibit similar molecular weights and the NMR data showed that they are characterized by similar total branching density and distribution of short-chain branches. Without further analysis, we would have fortuitously concluded that these polymers made at different pressures were approximately the same.

However, since the experiments had been purposely designed to examine the polymer topology change with polymerization conditions, more sophisticated analytical tools were utilized to reveal the global topology of the polymers. Specifically, we combined static and dynamic light scattering, solution viscosimetry, neutron scattering and atomic force microscopy (AFM) to investigate the global topology of the PEs generated at different pressures.[8,10,11,28] Through correlation of the local structural information from NMR with the global structural information from the aforementioned studies coupled with statistical modeling, we finally elucidated the global topology of the PEs obtained at different pressures (Figure 9.1).

First, size exclusion chromatography (SEC) equipped with an on-line multiangle light scattering (MALS) detector provided clear evidence that the PEs prepared at different pressures have different topologies (Figure 9.2).[8,28] Because the on-line MALS detector measures both molecular weight (M) and size of the macromolecules (radius of gyration, R_g) for every fraction of polymers eluted from the SEC column, we can compare the R_g at the same M for different samples, which revealed that at constant M the R_g for the PE generated at 34 atm is about three times that of the R_g for the PE prepared at 0.1 atm. For a linear flexible polymer forming a random coil, R_g scales as $M^{1/2}$.[59] Thus, a radius change of a factor of 3 requires nearly an order of magnitude change in M. Without further structural information, the dramatic difference in R_g for PE samples at constant M could in principle be attributed to either a change of the branching density or a change of the branching topology.

However, since the branching density and short-chain distribution stay relatively constant as shown by ^{13}C NMR,[8,28] this large change in R_g can only be

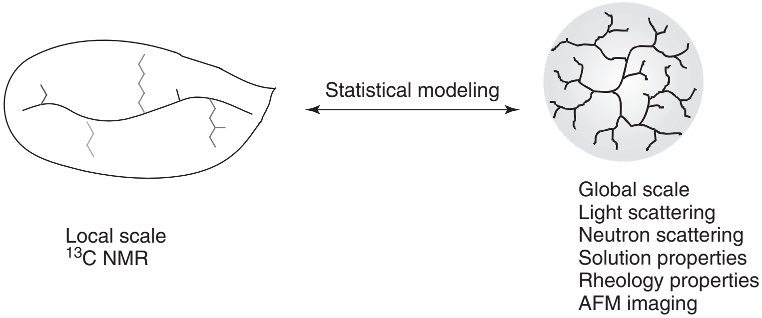


Figure 9.1 Elucidation of PE topology by structural characterization at both local and global scales.

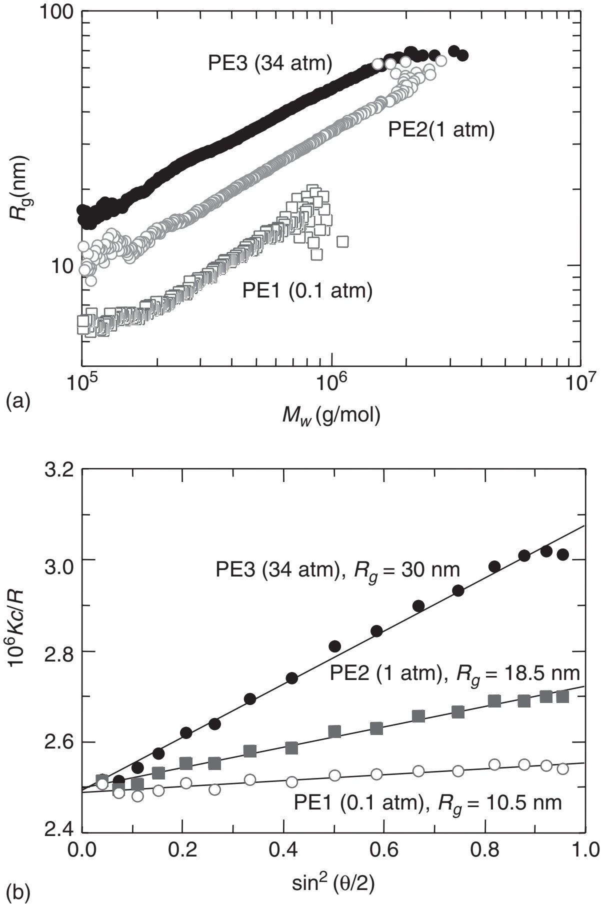
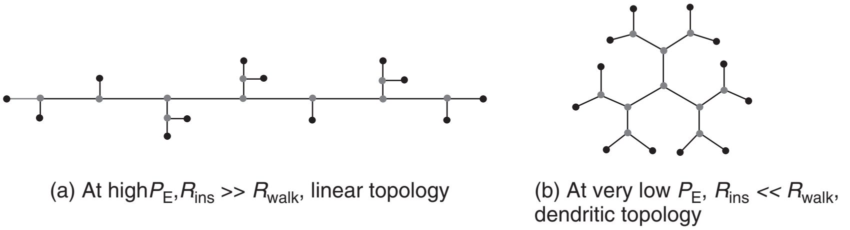


Figure 9.2 (a) Correlation of R_g with molecular weight for the three polyethylene samples generated at 10.1, 101.3, and 3447.4 kPa, respectively. (b) Comparison of Debye plots for the fraction of polymer at the same M_w (400,000 g/mol) for three polyethylene samples synthesized at 10.1, 101.3, and 3447.4 kPa, respectively.

attributed to a change in branching topology. This leads to our unambiguous conclusion that the PE topology changes with the ethylene pressure: as the pressure was decreased, the PE topology became more dendritic.[8] Figure 9.3 shows a simplified model: while the PE formed at high pressure possesses a linear topology with many short branches and even short branch-on-branches, the PE formed at very low pressure exhibits a dendritic topology. The A and B structures in Figure 9.3 feature exactly the same number of branches and should show similar local-scale microstructures by NMR. However, their global topologies are completely different and B should have a much smaller size than A. In our PE samples, the branches will be less uniform, because the branching length has a


(a) At high P_E, R_{ins} >> R_{walk}, linear topology

(b) At very low P_E, R_{ins} << R_{walk}, dendritic topology

Figure 9.3 Models for PEs formed at high pressure (a) and low pressure (b). The blue dots represent the chain ends and the red dots stand for the branching points. Although (a) and (b) are composed of exactly the same amount of chain ends and branching points, they have completely different topologies.

distribution that is governed by the kinetic competition between insertion and chain walking.

Our further investigation of the polymers by dynamic light scattering, solution viscosimetry, rheology, neutron scattering, and AFM revealed more information on the PE topology.[8,28,60,61] The hydrodynamic radius (R_H) was measured by dynamic light scattering. Combining static and dynamic light scattering, the ratio R_g/R_H was obtained, which reflects polymer chain topology and segment density.[62] In general, linear flexible polymers exhibit values of R_g/R_H around 1.5–1.7 in good solvents. A value less than unity, 0.78, is predicted for a hard sphere. Experimental results of less than unity have been reported for multiarm stars,[63] microgels,[64], and dendritic polymers.[65,66] Whereas our high-pressure polymer has a ratio of 1.7, for the lowest pressure sample, this ratio is only, 0.8, indicating that the PE made at the lowest pressure has a compact and globular topology resembling dendrimers.

A recent collaborative study with Colby and Read has provided rheological data in support of the dendritic topology for PEs prepared at very low ethylene pressure.[61] The melt rheology of the dendritic PE formed at low ethylene pressure indicates no entanglement, even though the weight-average molar mass is 370,000 g/mol. PEs produced at higher ethylene pressures with comparable molar masses, however, clearly show entanglement effects in their rheology. The global topology differences in the branching structure account for the rheological features in these branched PEs. The dendritic PE formed at low ethylene pressure is characterized by such a dense branch-on-branch topology that chain entanglement becomes impossible.

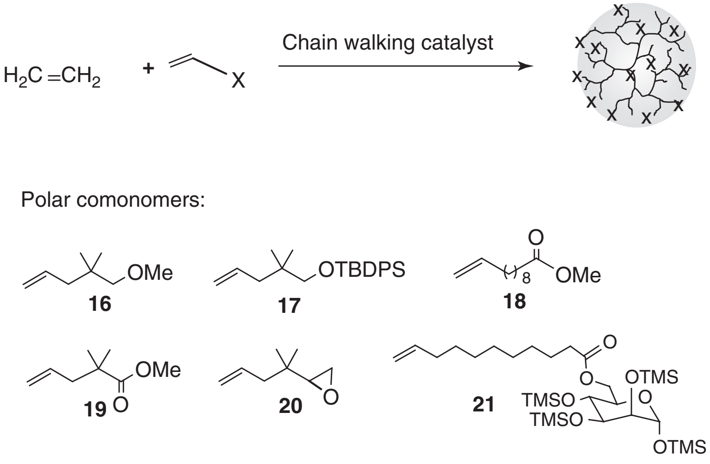
Our neutron scattering experiments further proved a densely packed globular topology for the PE synthesized at the lowest pressure. The Kratky plot for the lowest pressure PE showed a peak.[60] This phenomenon has been observed for dendrimers in previous studies.[67] The intrinsic viscosity of the PE generated at 0.1 atm is only one-eighth of the value for poly(propylene) of comparable molecular weight.[8,28] From all these studies we conclude that the PE made at very low pressures has a very densely packed topology resembling a dendrimer. Recently, Lutz and coworkers[68] have also investigated the structural changes of PEs with polymerization conditions using the chain-walking catalyst, which confirmed our original study.[8,10,11] The recent stochastic simulation results by Ziegler and coworkers[69] and Read and coworkers[61] also support our conclusion. This theoretical work confirmed that with decreasing ethylene pressure the PE topology changes from a linear with short branches to a hyperbranched and finally to a globular dendrimer-like structure.

Whereas hyperbranched vinyl polymers have been prepared by cationic,[70] radical,[71,72], and group transfer[73] self-condensing polymerization of specially designed vinyl monomers (see other chapters of this volume), to our knowledge, our results show for the first time that olefin polymers having a dendritic topology can be prepared by coordination polymerization of a simple olefin monomer like ethylene. This is also the first example of a polymer topology that can be systematically tailored with respect to the degree of branching by simply changing one single experimental parameter like pressure. Although these polymers are not perfect dendrimers because of their polydisperse nature in molecular weight and branching length distribution, their cascade branch-on-branch topology, compact globular structure, and characteristic solution behavior all resemble those of dendrimers. It is reasonable to expect that many physical properties of these dendritic polymers generated by the chain-walking catalyst should be similar to a perfect dendrimer based on the same building block. Because of the ease of synthesis and the availability of many olefinic monomers, these hyperbranched and imperfect dendrimers may find many general applications in which polymer structural precision and uniformity are not critical.

9.2.3.2.2 Functional Hyperbranched and Dendritic Polyolefins. To expand the scope of our strategy, we have recently applied the methodology to functional polymer synthesis via copolymerization of ethylene with polar monomers by taking advantage of the excellent functional group tolerance of late-transition-metal polymerization catalysts. By copolymerizing ethylene with functional monomers at different ethylene pressures, copolymers carrying a variety of functional groups with tunable topologies were obtained (Scheme 9.7).[12] This offers a simple one-pot approach to design functional polymers with a broad range of topologies. Postpolymerization treatment of functional groups can be exploited to introduce different functional groups that are not tolerated by the chain-walking catalysts.

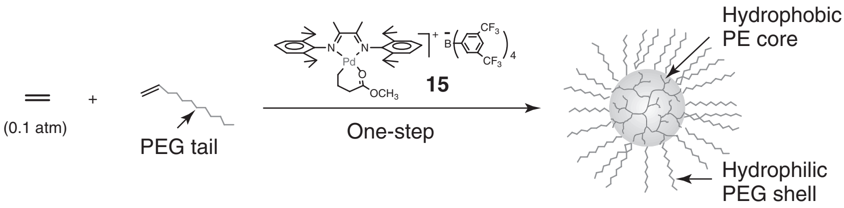
As an example, we have synthesized dendritic copolymers having multiple carbohydrate groups as multivalent ligands for potential biological applications.[12] By applying the chain-walking methodology, simple copolymerization of ethylene with a mannose-containing comonomer **21** at low ethylene pressure and low comonomer concentration resulted in a mannose-coated dendritic copolymer. This provides a simple one-pot synthesis to construct dendritic scaffolds to preferentially present functional groups at the surface of the macromolecules.

9.2.3.2.3 Core–Shell Dendritic Polyolefin Soft Nanoparticles. To further demonstrate the versatility of the chain-walking polymerization strategy, we



Scheme 9.7 Synthesis of functional polymers using a chain-walking catalyst.

developed efficient synthesis of core–shell dendritic polyolefin soft nanoparticles *via* either one-pot or tandem polymerization. In one example, we developed a transition metal catalyzed one-pot synthesis of water-soluble dendritic molecular nanocarriers behaving like unimolecular micelles.[33] Using the palladium-α-diimine chain-walking catalyst, copolymerization of ethylene and an α-olefin containing a poly(ethyleneglycol) (PEG) tail afforded, in one step, an amphiphilic copolymer containing a hydrophobic core and a hydrophilic shell (Scheme 9.8). A much larger amphiphilic core–shell copolymer was also synthesized by a two-step approach: a copolymer having a large number of free hydroxyl groups was first prepared, which was subsequently coupled with PEG to afford the copolymer. Light scattering, fluorescence, and UV–Vis spectroscopic studies with Nile Red in aqueous solution showed unimolecular micellar properties for these copolymers. The dye encapsulation capacity for the core–shell copolymers is nearly proportional to the molecular weight of the hydrophobic core. The unimolecular micellar properties coupled with good water solubility and biocompatibility of



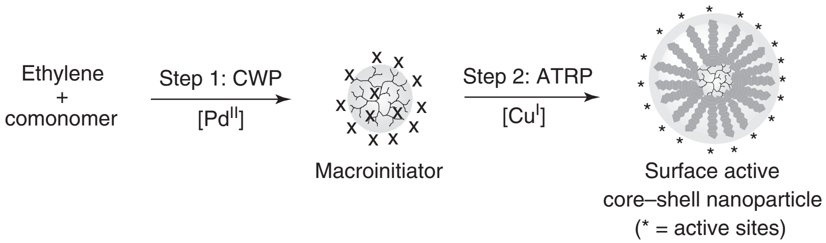
Scheme 9.8 Synthesis of amphiphilic dendritic core–shell polymer via chain-walking polymerization.

the PEG moieties make these molecular nanocarriers promising candidates for many applications including drug delivery and controlled drug release.

Most recently, we have demonstrated a tandem catalytic coordination/living radical polymerization for the efficient synthesis of nanoparticles for bioconjugation.[38] Using a chain-walking palladium catalyst, dendritic macroinitiators bearing multiple radical initiation sites were prepared, which were subsequently used in a Cu^I-mediated ATRP for synthesizing dendritic polymer nanoparticles (Scheme 9.9). The size for both the core and the shell can be controlled precisely in the range of 10–100 nm. Addition of the *N*-acryloyloxysuccinamide (NAS) monomer at the end of the ATRP afforded *N*-hydroxysuccinamide (NHS)-functionalized polymer nanoparticles as convenient scaffolds for bioconjugation. Conjugation with both small dye molecule and ovalbumin demonstrated that these nanoparticles are effective for multivalent bioconjugation. Currently we are preparing nanoparticle conjugates with biologically active proteins for specific biological functions. We are also applying this general methodology to prepare dendritic polymer nanoparticles having other kinds of shell structures.

9.2.3.3 Hyperbranched Oligomers by Transition Metal Catalysts

Concurrent to our studies, Sen and coworkers have reported the synthesis of hyperbranched ethylene oligomers, using a combination of an early or late-transition-metal complex and an excess of an aluminum compound (AlR_xCl_{3-x}).[74,75] These catalyst systems were shown to oligomerize ethylene to form branched oligomers with number-averaged molecular weight (M_n) less than 2000. On the basis of NMR analysis, they proposed that the oligomers formed have hyperbranched structures. While the active catalytic species and the mechanism of branching in these systems remain to be elucidated, the authors proposed that the branching might involve Lewis acid promoted carbocationic rearrangements and oligomerizations. They hypothesize that the transition metal species initially catalyze the formation of short alkenes, which in turn undergo Lewis acid (or H^+) promoted rearrangements and further oligomerizations.

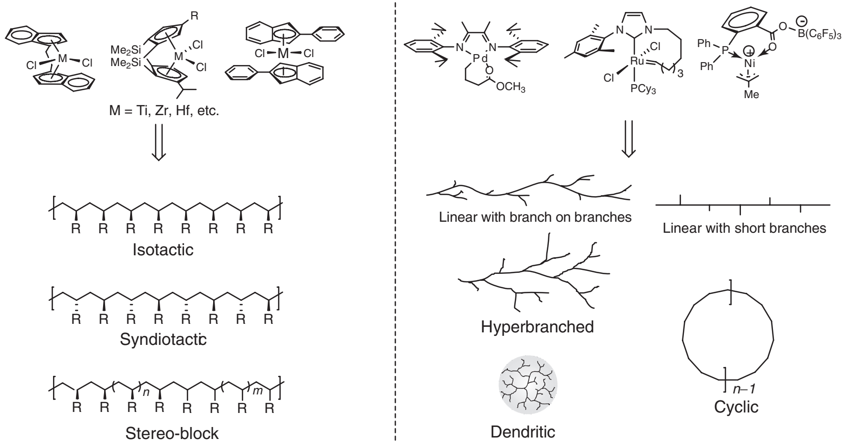


Scheme 9.9 Synthesis of core–shell dendritic nanoparticles via tandem chain-walking polymerization (CWP)-atom transfer radical polymerization (ATRP).

9.3 SUMMARY AND PERSPECTIVE

From the selected few examples highlighted in this article, it is evident that transition metal complexes, especially late metal complexes, are powerful in controlling polymer branching topology. By judicious selection or design of late-transition-metal catalysts, polymers having a broad range of topologies, including linear, short-chain branched, hyperbranched, globular dendrimer-like, and core–shell architectures have been successfully synthesized. A distinctive advantage of the catalyst approaches is that polymers with complex topologies can be prepared in one-pot procedures from simple commercial olefin monomers. A fundamental difference of the catalyst approach as compared with other approaches is that polymer topology is controlled by the catalyst, not the monomer structure. In our own laboratory, we have demonstrated successfully two strategies for controlling polymer topology using late-transition-metal catalysts. In our first strategy, hyperbranched polymers were prepared via direct free radical polymerization of divinyl monomers by controlling the competition between propagation and chain transfer using a CCTC. In our second approach, the PE topology was successfully controlled by regulating the competition between propagation and chain walking by using the Brookhart Pd(II)-α-bisimine catalyst. Although the total branching density and the distribution of short-chain branches are relatively constant, the branching topology changes dramatically with ethylene pressure, varying from predominantly linear with many short branches at high P_E to a densely branched, arborescent globular structure at very low P_E. Polymers synthesized at the lowest pressure exhibited properties similar to dendrimers. Our ability to produce polymers with continuum topologies without changing the chemical structure provides a unique opportunity for many fundamental studies, such as the investigation of topological effects on physical polymer properties. Applying the same methodology, we have developed one-step syntheses of functional dendritic polyolefins and amphiphilic core–shell polymers by combining olefins and functional olefin monomers.

Transition metal catalysts have played and will continue to play crucial roles in the synthesis of important polymeric materials.[76] Whereas early-transition-metal catalysts such as Ziegler–Natta and early-transition-metal metallocene catalysts will remain as the workhorses in the polyolefin industry,[4] significant advances have been made recently in late-transition-metal polymerization catalysts.[24–27] Two most important attributes of late-transition-metal polymerization catalysts distinguish them from early-transition-metal systems: they are powerful in controlling polymer topology[8,10–12,29,30,33,35,38,43–45,74,75] and they possess good functional group tolerance.[6,7,9,12,33,38] The functional group tolerance of late metal complexes can be best illustrated by the fact that olefin polymerization using some Ni(II) complexes can be successfully carried out in aqueous dispersion or emulsion polymerization.[77,78] If the most striking feature of early-transition-metal olefin polymerization catalysts is their capability of



Scheme 9.10 Tacticity control for early-transition-metal metallocene catalysts versus topology control for late-transition-metal polymerization catalysts.

controlling the stereochemistry of α-olefin polymerization,[5,79] the most powerful attribute of late-transition-metal polymerization catalysts must be their versatility for controlling polymer topology (Scheme 9.10).[8,10–12,29,30,33,35,38,43–45,74,75]

The hyperbranched and globular dendrimer-like polyolefins are relatively new and have drastically different properties compared with conventional polyolefins. A few potential applications are discussed here. For simple hyperbranched or dendritic olefin homo- and copolymers, four potential applications are under investigation. As disclosed in a patent, highly branched polyolefins, when incorporated into lubricating oil as an additive, impart improved low-temperature viscosity and thickening efficiency without adversely impacting mechanical shear stability of the formulated oil. Minor amounts of branched polyolefin polymers can impart both detergent and dispersant properties when blended into fuels.[80] Secondly, given the transparency, nontoxicity, and low viscosity for hyperbranched/dendritic ethylene and homopolymers, they can potentially serve as base materials for formulations of pharmaceutical agents and personal care items. It has been disclosed in a patent that hyperbranched polymers and dendrimers offer advantages in this type of applications.[81] The third potential application is their use as a processing aid to improve rheological properties. According to Mackay and coworkers organic nanoparticles can significantly reduce the melt viscosity of linear polymers.[82] It is reasonable to propose that adding our dendritic PE into polyolefins should enhance their melt processibility. Lastly, the hyperbranched or dendritic polyolefins can be blended with conventional polymers to enhance mechanical properties. In a joint study it was discovered that dendritic PE is miscible with linear polystyrene as long as the radius of the dendritic PE nanoparticle is smaller than the radius of gyration of the linear polymer.[82] This finding points to a promising opportunity to prepare many miscible blends of our dendritic PE with various conventional polymers. A recent joint study has shown that addition of a small amount of our globular dendrimer-like PE into polystyrene significantly improves the toughness and modulus of polystyrene.[83]

For functional polyolefins having dendritic and core–shell topologies, many functional applications can be pursued. For example, the amphiphilic core–shell copolymers developed in our laboratory can efficiently encapsulate hydrophobic compounds. Thus, they can be used as nanocarriers for drug delivery or as stabilizers for ink formulation.[33] Multifunctional dendritic nanoparticles can also be used as soft nanoscaffold to conjugate multivalent organic or biological ligands.[38] Many of these applications are currently under pursuit in our laboratory.

The current version of chain-walking catalysts has some limitations that need to be addressed. For example, the thermal stability of Ni(II)- and Pd(II)-α-diimine catalysts is relatively low and the productivity of the Pd(II) catalyst is also quite low. Whereas some of these catalysts can copolymerize polar olefins such as methyl acrylate (MA), the incorporation level for MA is generally low and the productivity of the catalysts is also significantly reduced for copolymerization. To address these challenges, it is imperative to develop the next generation of late-transition- metal catalysts that are more productive, more robust, and more efficient for incorporation of polar olefins. Our own group has recently designed a cyclophane-based α-diimine ligand that can complex to Ni(II) or Pd(II) to form active polymerization catalysts.[34] The Ni(II)-cyclophane catalyst is highly active and has significantly higher thermal stability. At elevated temperatures such as 75 °C, propylene and 1-hexene polymerization using this catalyst still remains living.[36] The Pd(II)-cyclophane catalyst is significantly more efficient in incorporating polar olefins like MA in ethylene copolymerization.[84] Currently we are carrying out further structural modification of the cyclophane catalyst system and also developing new catalysts. We foresee a bright future for the design of new polymeric materials with late-transition-metal catalysts.

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LIST OF ABBREVIATIONS

AFM	atomic force microscopy
CCTC	cobalt chain transfer catalyst
CoH	cobalt hydride
EGDMA	ethylene glycol dimethacrylate
GPC	gel permeation chromatography
HDPE	high-density polyethylene
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
M	molecular weight
MA	methyl acrylate
MALDI-MS	matrix-assisted laser desorption ionization mass spectrometry
MALS	multiangle light scattering
MAO	methylaluminoxane
MMAO	modified methylaluminoxane
M_n	number-averaged molecular weight
NAS	*N*-acryloyloxysuccinamide
NHS	*N*-hydroxysuccinamide
PE	polyethylene
P_E	ethylene pressure
PEG	poly(ethyleneglycol)
PP	polypropylene
R_g	radius of gyration
R_H	hydrodynamic radius
SEC	size exclusion chromatography
TEA	triethylaluminum

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Chapter 10

Hyperbranched π-Conjugated Polymers

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10.1 INTRODUCTION

Academia and industry are intensely endeavoring to design and fabricate new electronic devices—integrated circuits, electroluminescent devices, solar cells, and so on—not from silicon but from semiconducting polymers.[1] These "electronic plastics" are flexible and enjoy the advantages of being cheaper and easier to manufacture in comparison to their silicon counterparts. Research has been focused mainly on linear π-conjugated polymers with poly(p-phenylenevinylene)s (PPVs) as the major players, despite its only moderate stability and delicate processability.[2] Other semiconducting polymers have also been utilized, examples of which include polyacetylenes,[3,4] polyfluorenes,[5,6] polydiacetylenes,[7] poly(p-phenyleneethynylene)s,[8,9] polyanilines,[10] and polythiophenes.[11,12]

Knitting π-conjugated monomeric units together in a linear manner results in the formation of one-dimensional polymers with rigid rod-like structures, which, due to their low solubility and fusibility, are often difficult to process once they reach a certain degree of polymerization.[13] Incorporating branches into the polymer architectures may overcome this obstacle. Natural polymers often take advantage of nonlinear structures: for example, linear cellulose only swells in water, whereas its branched polysaccharide congeners such as glycogen, pectin, and amylopectin readily dissolve.[14]

Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

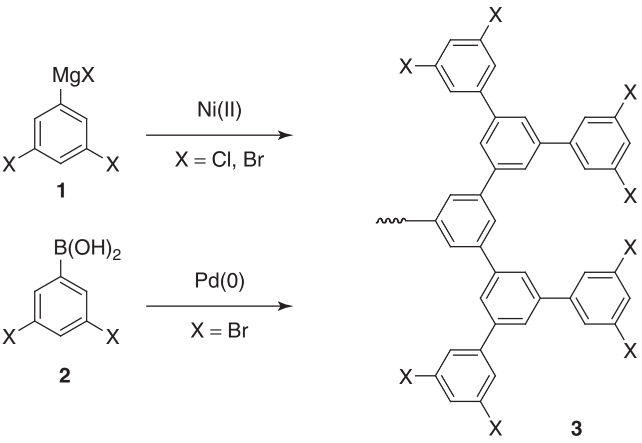
Structurally “perfect” dendrimers and “imperfect” hyperbranched polymers, with branching points at almost every repeating unit, have attracted increasing attention over the past decades due to the expectation that the unique globular structure may impart unusual properties. Compared to their dendritic congeners, hyperbranched polymers are readily prepared in large scales by one-pot, single-step reaction procedures while conserving most of the attractive structurally related features.[15,16] Similar to their linear analogs, most conjugated hyperbranched polymers are prepared by polycoupling protocols. The most commonly adopted approach is self-condensation polymerization of AB_x-type multifunctional monomers with $x \geq 2$, dating back to the theoretical work of Flory in 1952.[17] Due to the limited commercial supply and difficult synthetic access to multifunctional monomers equipped with two or more different functional groups, alternative approaches such as copolymerizations of A_2 monomers with B_n comonomers ($n \geq 3$) have been successfully employed.[18–23] More recently, other methods including self-condensing vinyl polymerizations, initiated by cationic[24] and radical species,[25,26] as well as ring-opening multibranching polymerizations[27–31] have been utilized, however, mainly to synthesize nonconjugated hyperbranched macromolecules.[32–34] In this chapter, we will summarize the latest developments in the field of hyperbranched conjugated polymers together with results from our own research on this exciting new frontier in polymer science.[35,36]

10.2 SCOPE

This review will cover the area of conjugated hyperbranched polymers and their synthesis, properties, and applications. The materials are classified into three categories, namely, poly(arylene)s, poly(arylenevinylene)s, and poly(aryleneethynylene)s. Fused aromatic structures such as naphthalene or fluorene are summarized under poly(arylene)s. Heteroatom-containing polymers such as thiophene, carbazole, and silane are included in the sections with corresponding organic backbones.

10.3 HYPERBRANCHED POLY(ARYLENE)S

Linear poly(*p*-phenylene)s without any substituents such as alkyl or alkoxy groups are normally insoluble in organic solvents. In their search for polymer rheology control agents with thermal stability, chemical robustness, and availability in large quantity, Kim and Webster at the Du Pont Central R&D Laboratories realized the potential of a hyperbranched architecture.[37] In a pioneer effort, they synthesized a hyperbranched poly(phenylene) (**3**) from AB_2-type dihalophenyl monomers containing MgX (**1**) and $B(OH)_2$ groups (**2**) via Grignard and Suzuki couplings, respectively (Scheme 10.1).[38] The polymers were soluble in common organic solvents but had low molecular weights. A water-soluble derivative of

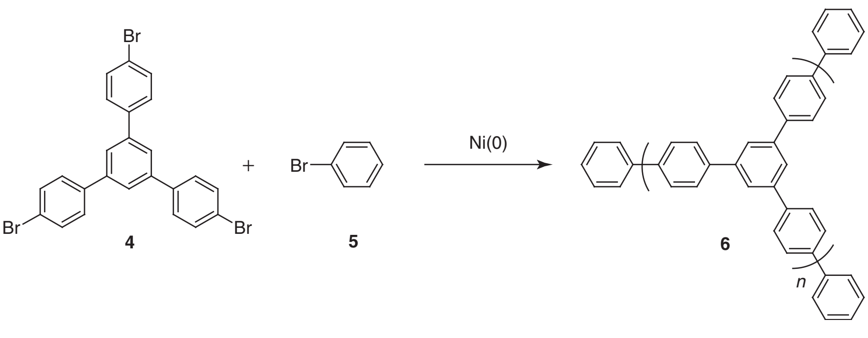


Scheme 10.1

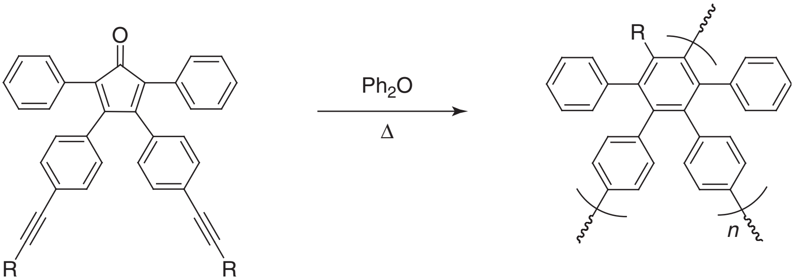
the polymer was prepared by metalation of the terminal bromine groups with n-BuLi followed by quenching with CO_2.

Highly branched defect-free poly(phenylenes) were prepared by Ni(0)-catalyzed dehalogenation of 1,3,5-tris(4-bromophenyl)benzene (**4**) and bromobenzene (**5**; Scheme 10.2).[39] The resulting polymer **6** was highly luminescent, emitting deep blue light (360–380 nm) with quantum yields (QYs) as high as 96%. Interestingly, a linear analogous showed only a QY of 17% with a significant red shift, which were thought to be originated from its structural difference.

Müllen *et al*. utilized the Diels–Alder reaction to prepare high molecular weight poly(phenylene)s with M_w up to 107,000 from ethynyl-, propynyl-, and phenylethynyl-substituted tetraphenylcyclopentadienones (Scheme 10.3).[40] Despite their high molecular weight and numerous phenyl rings, all the polymers showed good solubility in toluene and benzene.



Scheme 10.2



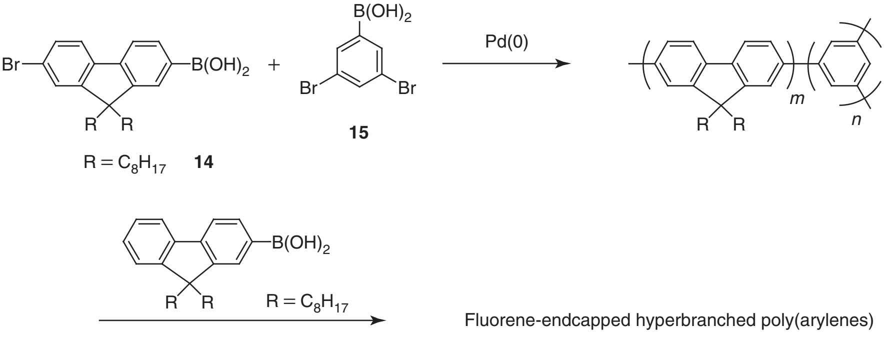
R = H **7**
CH_3 **8**
Ph **9**

R = H **11**
CH_3 **12**
Ph **13**

Scheme 10.3

Linear poly(fluorene)s (PFs) are considered as very promising blue luminescent material for organic light-emitting diodes (OLEDs). However, these rod-like PFs show strong tendency to aggregation in the solid state, associated with excimer formation and hence luminescence quenching. By employing an AB + AB_2 Suzuki-coupling approach of monomers **14** and **15** followed by an end-capping reaction, Bo *et al*. prepared hyperbranched copoly(arylenes) of high molecular weights (Scheme 10.4).[41] They demonstrated, by photoluminescence studies of annealed thin films, that polyfluorene incorporated into the hyperbranched architecture could completely avoid the detrimental excimer emission and show good luminescence stability. Recently, they extended their efforts and utilized the triphenylamine as AB_2 and porphyrins as AB_3 building block in a similar fashion.[42,43]

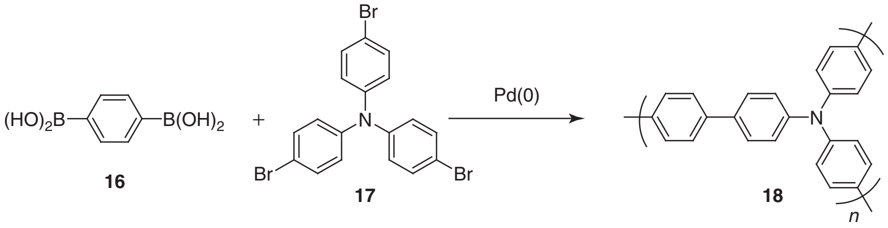
Tanaka *et al*. similarly utilized the Suzuki-coupling reaction and constructed hyperbranched copolymers via $A_2 + B_3$ protocol from benzene-1,4-diboronic acid and tris(4-bromophenyl)amine (Scheme 10.5). Cyclic voltammetry investigations revealed that **18** might be a good charge storage material.[44]



$R = C_8H_{17}$ **14**

15

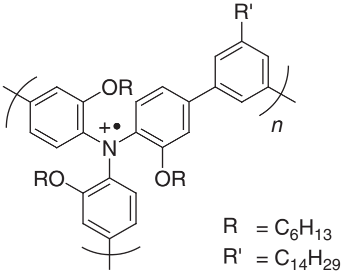
Scheme 10.4



16 **17** **18**

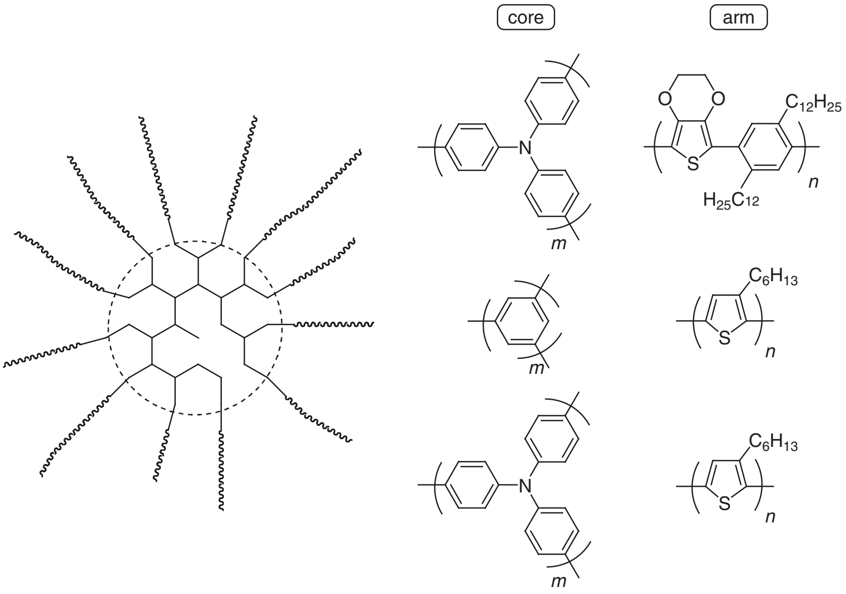
Scheme 10.5

Shiomi *et al*. investigated the molecular magnetism of a polycationic organic high-spin polymer (**19**) by oxidizing a congener of **18**.[45] Their experiments revealed a paramagnetic portion in the oxidized polymer of 17% with dominant spin quantum numbers $S \leq 3$, resulting in a ferromagnetic interaction between adjacent unpaired electrons on the oxidized nitrogen sites.



19

Wang *et al*. attached 3,4-ethylenedioxythiophene (EDOT) together with phenylene groups in an alternating fashion to a hyperbranched poly(triphenylamine) core, yielding a star-branched thermochromic and multicolor electrochromic polymer (**20**), which was able to produce the three basic colors in the RGB system: red, green, and blue.[46] The introduction of the EDOT moiety along the conjugated backbone resulted in a low half-way potential, leading to a fairly clear separation between the oxidation of the conjugated poly(triphenylamine) core and the electroactivity of the whole polymer. According to spectroelectrochemical, switching, and colorimetric measurements, the presence of the poly(triphenylamine) core improved the stability of the optical properties upon switching and conferred a better resistance to overoxidation compared to a linear analog without the hyperbranched core. Earlier, they used the same approach to synthesize star-branched polymers with poly(1,3,5-phenylene) (**21**) and triphenylamine (**22**) cores surrounded by poly(3-hexylthiophene) arms.[47,48] Despite its hyperbranched core, polymer **21** showed a surprisingly high degree of structural order and was able to self-assemble into thin films with morphological, electrical, and optical properties. Polymer **22** consisted of



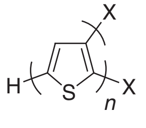
20

21

22

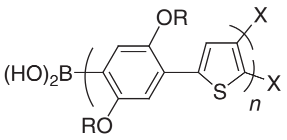
a fully conjugated system, which could be doped to high levels of conductivity and showed redox electroactivity.

Asymmetrical substituted poly(thiophene)s (**23**) were prepared via a Grignard intermediate.[49] However, the solubility was found to be rather low but could be enhanced through the introduction of hexyl groups into the periphery of the polymers. The polymer exhibited an interesting intramolecular conjugation gradient resulting in an efficient energy transfer, which might be useful for light-harvesting applications. Later, hyperbranched poly(thienylenephenylene)s (**24**) were synthesized, and comparison with linear isomeric polymers revealed better solubility.[50]



X = Br or C_6H_{13}

23

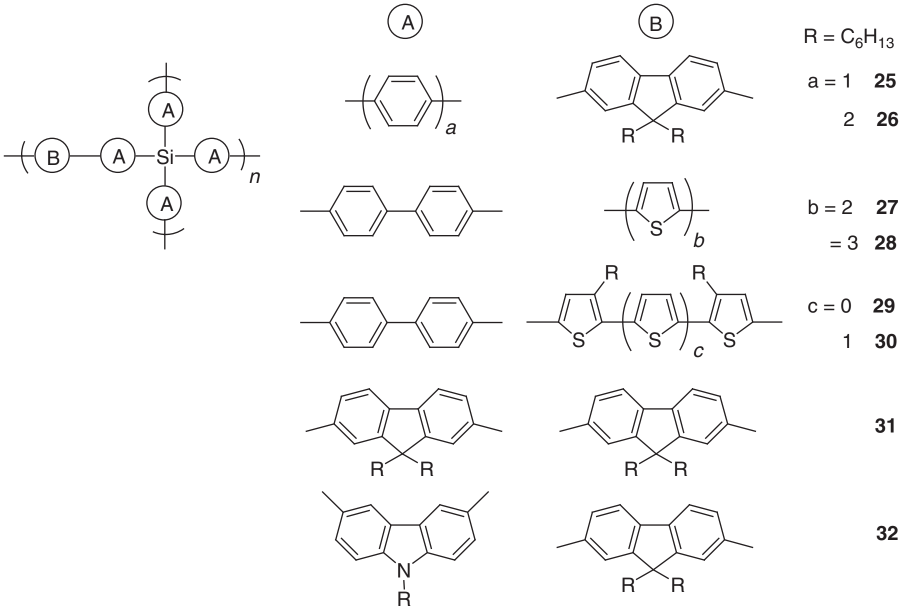


R = C_6H_{13}

X = Br

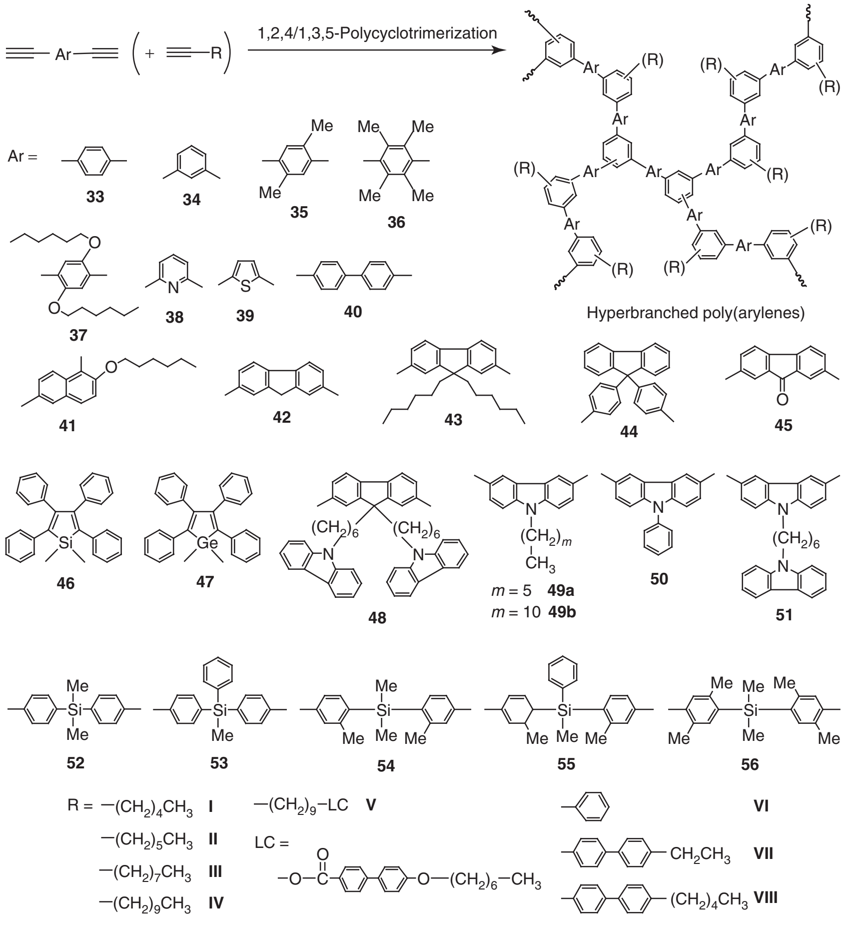
24

He *et al*. prepared a series of Si-containing tetrahedral conjugated hyperbranched polymers (**25**–**32**).[51–54] The materials showed intense and efficient blue to red light emissions in solutions and thin films without excimer formation due to self-aggregation and quenching. OLED devices fabricated from the polymers exhibited narrow and strong blue light emission.



These previously reported polymers were mainly synthesized by Grignard- and Suzuki-type polycoupling reactions. Our group has been interested in developing new methodologies for the construction of hyperbranched polymers from triple-bond building blocks. We have studied transition-metal-catalyzed diyne polycyclotrimerizations to hyperbranched polyarylenes.[55–62] This kind of polycycloaddition involves a single monomer species, suffers no stiochiometic constraints, and can thus potentially produce polymers with very high molecular weights. The resultant polymers are inherently highly branched because of the polycyclotrimerization mechanism, which is intolerant toward the formation of linear repeating units inside the hyperbranched cores. Scheme 10.6 shows homopolycyclotrimerizations of organic diynes as well as their copolycyclotrimerizations with monoynes. The "new" benzene rings of the hyperbranched poly(arylene)s formed by the alkyne cyclotrimerization are interconnected by the "old" aromatic moieties from the monomers via 1,2,4 and 1,3,5 connectivity. This endows the polymers with an extended π-conjugation and interesting electronic properties. For example, copolymers **33/II, 40/I, 42/II, 42/IV**, and **48/II** exhibit fluorescence QY higher than 70%, with **42/IV** showing the highest QY value (98%). The hyperbranched poly(arylene)s are furthermore nonlinear and optically active and strongly attenuate the power of intense 532-nm optical pulses.[55]

During our search for efficient light-emitting materials, we discovered a group of highly emissive molecules called silole (**46**) and germole (**47**). We incorporated the metallole moieties into the molecular structures of the hyperbranched polymers and observed a unique phenomenon of cooling-enhanced light



Scheme 10.6

emission (Figure 10.1).[60] When a dilute dioxane or tetrahydrofuran (THF) solution of copolymer **46/II** is cooled, its photoluminescence intensity increases. This is because the intramolecular rotation of the phenyl rings around the axes of the silacyclopentadiene core are impeded at low temperatures. A similar phenomenon is observed in the system of its congener, **47/II**.[62]

In the previous section, we have described the successful syntheses of hyperbranched polymers by the transition-metal-catalyzed polycyclotrimerizations of aromatic alkynes. All the polymers, however, possess regioirregular structures consisting of 1,3,5/1,2,4-substituted triylphenyl isomers. The structural irregularity may not be disadvantageous for some potential applications and is actually beneficial for the polymer's solubility and processability. On the other hand, it makes it a challenging job to completely characterize the molecular structures of the polymers by spectroscopic analyses. Furthermore, most of the transition-metal

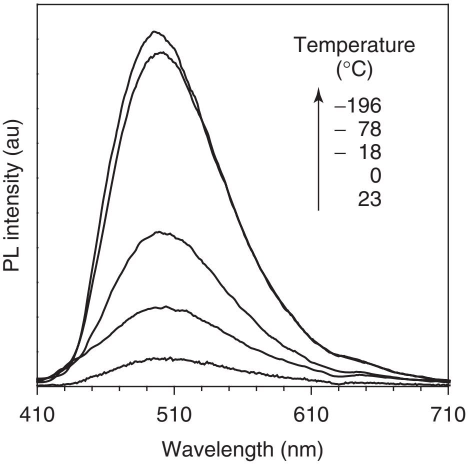
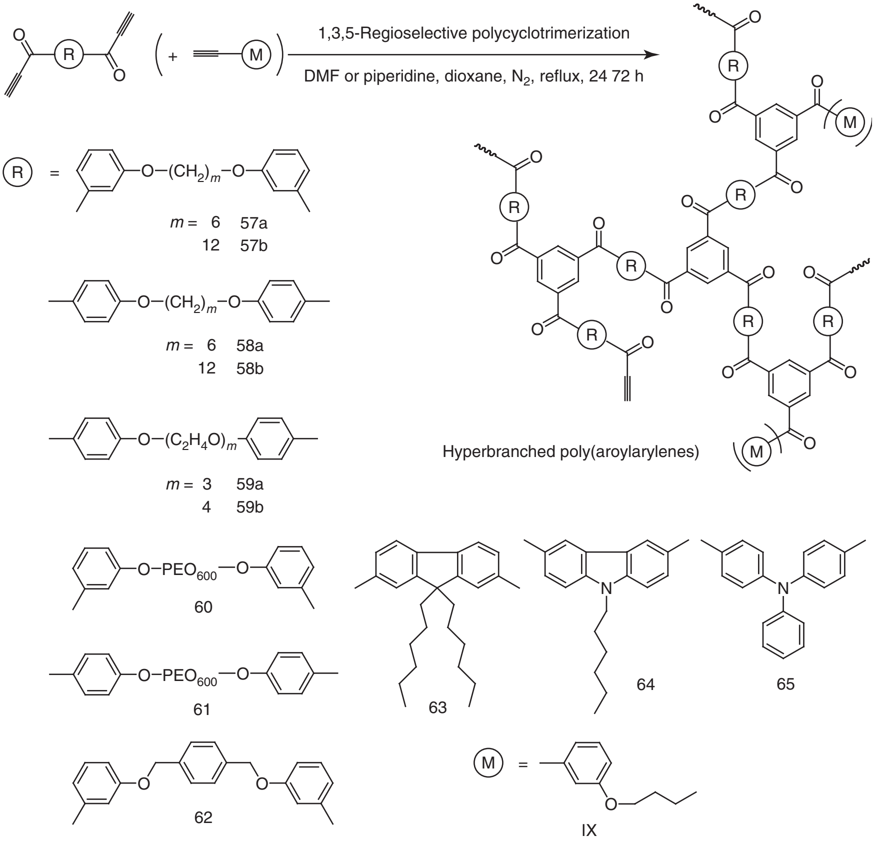


Figure 10.1 Photoluminescence spectra of **46/II** in dioxane at different temperatures; concentration of **46/II**: 10 μM; excitation wavelength: 407 nm. *Source:* Ref. [60]

catalysts are highly moisture-sensitive and intolerant of polar functional groups.[55] Cyclotrimerizations of benzoylacetylenes (monoynes) are known to proceed in a strictly 1,3,5-regioselective fashion due to the involved ionic mechanism.[63,64] Moreover, the reaction is carried out in the absence of transition-metal catalysts. We thus explored the possibility of utilizing this reaction to synthesize hyperbranched polymers from the aroyldiynes-bearing functional groups. We designed and prepared a group of bis(arylethynylketone)s with different organic linkers (R; Scheme 10.7) and studied their polymerization behaviors.[65] Optimization of the polymerization protocol led to the syntheses of high molecular weight polymers in high yield with strict 1,3,5-stereo- and regioregularity. The best results were obtained when piperidine, a secondary amine, was used as catalyst.

Benzophenone has been introduced into natural (e.g., protein) and synthetic polymers (e.g., polyimide) to serve as a photo-cross-linker.[66,67] The hyperbranched poly(aroylarylenes) contain many triaroylbenzene units and may thus show high photo-cross-linking efficiencies. This is indeed the case: for example, a thin film of polymer **62** on a glass plate can be readily cross-linked by the irradiation with a handheld UV lamp at room temperature. The cross-linking may have proceeded via the well-established radical mechanism: one carbonyl moiety abstracts a hydrogen from another benzyl unit, creating a stable benzyl radical.[66–68] Subsequently, coupling of different radicals leads to cross-linking and hence the gel formation.

Figure 10.2 depicts the dose effect on the gel formation of polymer **57a** and **62** films after they have been exposed to a weak UV light (~1 mW/cm^2). Although the photo-cross-linking conditions have not been optimized, both polymers already exhibit much higher sensitivities ($D_{0.5} = 50–180$ mJ/cm^2) than comparable commercial photoresists (650–700 mJ/cm^2).[69] Compared with **57a**, **62** exhibits lower $D_{0.5}$ and higher $\gamma_{0.5}$ (contrast).[70,71] This is possibly due to the faster reduction of the ketone group in **62**, which is attributed to the ease in



Scheme 10.7

abstracting hydrogen from its benzyl unit. This hypothesis is supported by the fact that the intensity of the K band of the triaroylbenzene units of **62** drops much faster than that of **57a**.[65]

Well-resolved patterns with line widths of 1.0 and 1.5 μm are readily obtained when a film of **62** is exposed to a UV dose of 1 J/cm^2 (Figure 10.2b). Patterns with submicrometer resolutions (line width down to 500 nm) are also achievable, as demonstrated by the examples given in Figure 10.2c and 10.2d. Clearly, **62** is an excellent photoresist material.

10.4 HYPERBRANCHED POLY(ARYLENEVINYLENES)

Similar to their linear counterparts, hyperbranched poly(phenylenevinylene)s (HPPVs) have been studied as novel organic semiconductors. The simplest possible HPPV structure is shown in Scheme 10.8 (**68**). It was synthesized via

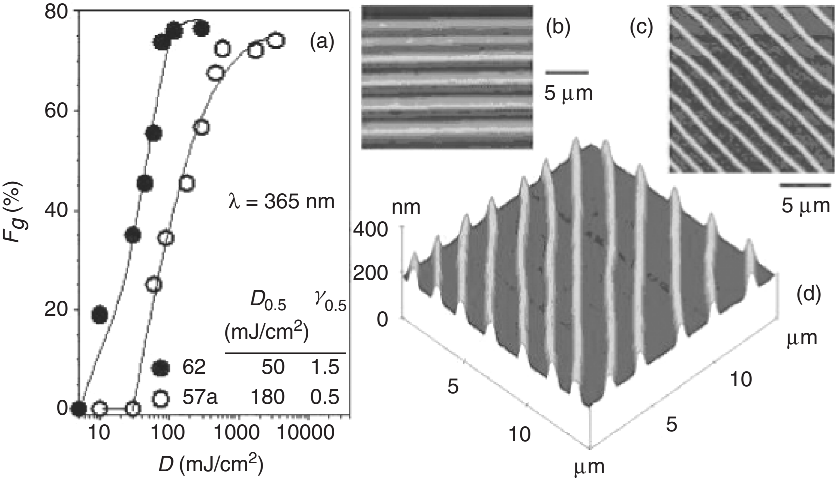
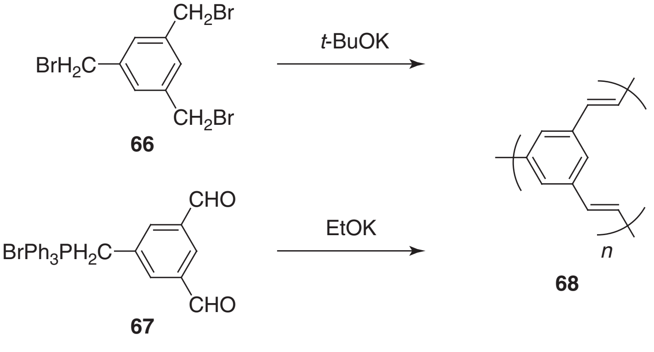


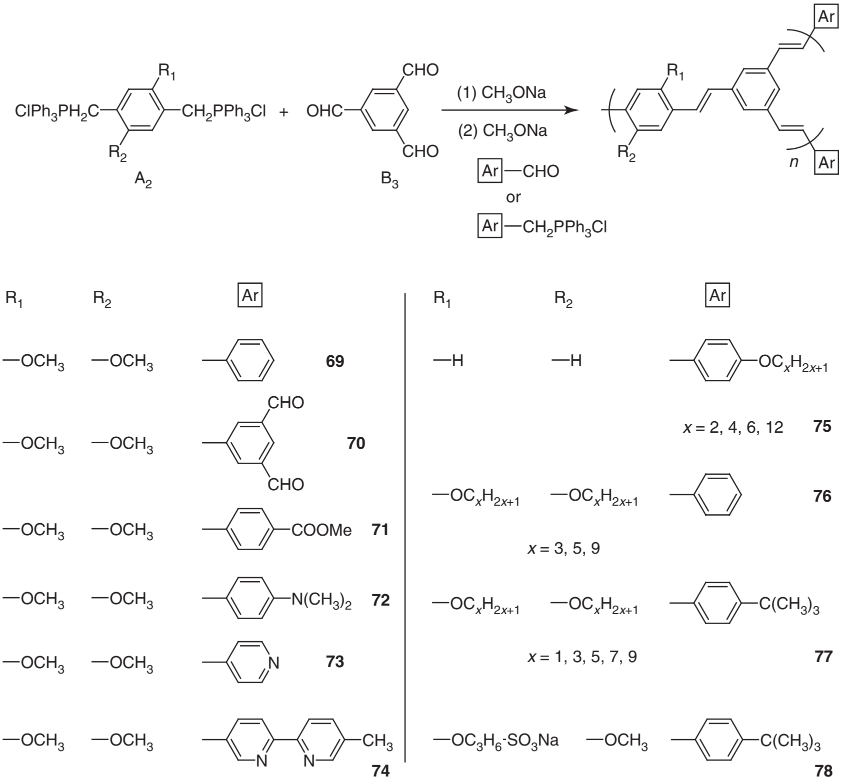
Figure 10.2 (a) Plots of gel fractions (F_g) of **57a** and **62** films versus exposure doses (D). AFM images of (b) micro- and (c and d) nano-scale patterns obtained from the **62** films exposed to 1 J/cm^2 of UV irradiation.
Source: Ref. [65].



Scheme 10.8

a modified Gilch reaction of the trifunctional monomer **66** or a Wittig reaction of AB$_2$-type **67**. However, the molecular weights (M_w) for both reactions, particularly for the Wittig reaction, were very low.[72]

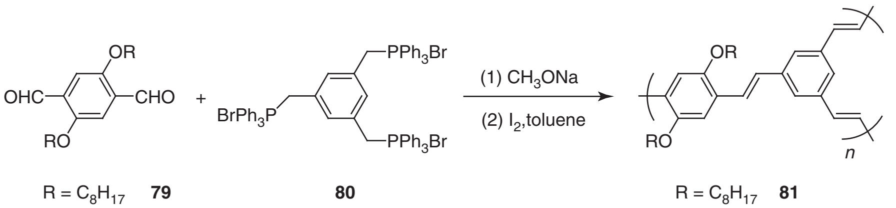
Bai *et al*. successfully prepared a great variety of HPPVs from A$_2$ + B$_3$ monomers via Wittig reaction (Scheme 10.9).[73–80] The molecular weights obtained were up to ~30 × 10^3, depending on the monomers' feed ratio. A ratio of A$_2$:B$_3$ of 1:1, which would correspond to a "AB$_2$" type monomer after the first coupling, gave M_w only up to 5.5 × 10^3, whereas a feed ratio of 2:1 yielded an HPPV with M_w up to 16.6 × 10^3.[74] The obtained HPPVs exhibited



Scheme 10.9

interesting luminescence properties and were utilized for constructing OLEDs. Photovoltaic cells of **71–73** blended with C_{60} showed comparable performances to devices based on common conjugated linear polymers.[79] Furthermore, the interactions of cadmium sulfide (CdS) nanoparticles with HPPVs **76** were studied.[80] Both the association constant and the electron injection rate were related to the chain length of the alkoxy group on the connecting modules, which led to the conclusion that the modification of HPPV at certain substitution sites could control the interaction between HPPV and the nanosized CdS particles. Atomic force microscopy (AFM) images indicated that films with good qualities could be formed on mica substrates and that the presence of the HPPV decreased the self-aggregation of the nanoparticles.

Certain polymers can wrap themselves around singlewall carbon nanotubes(SWNT) and multiwall carbon nanotubes (MWNT) and disrupt the van der Waals interactions that cause the nanotubes to agglomerate into bundles. Star and Stoddart prepared all-trans HPPV by refluxing the obtained polymer in toluene with catalytic amounts of iodine (Scheme 10.10).[81] The resulting polymer **81** efficiently broke up nanotube bundles, and the pockets provided by



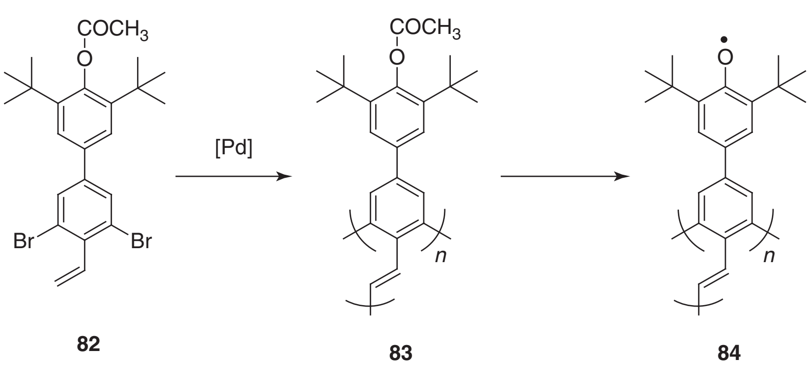
Scheme 10.10

the hyperbranched polymer offered a better fit for the SWNTs compared to its linear congener.

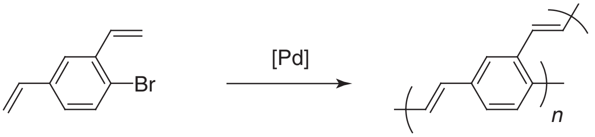
A dibromostyrene monomer **82** bearing a protected phenol ring was polymerized by Pd(0) into high molecular weight **83** (M_w up to 2.4×10^4). Subsequent hydrolysis and oxidation yielded HPPV **84**, which exhibit an alternate but non-Kekulé-type π-conjugation with ferromagnetic connectivity of the unpaired electrons of the pendant phenoxyl group (Scheme 10.11).[82] The spin concentration was found to be 0.4 spins per monomer unit and displayed an average S value of 3.

So far, most reported hyperbranched PPVs comprised 1,3,5-connectivity in the branching unit, which restricts the extension of the π-conjugation length. Park *et al*. demonstrated a modified strategy for obtaining 1,2,4-connected HPPV, which showed increased π-conjugation with growing molecular weight (**86**, Scheme 10.12).[83] Energy transfer and funneling processes caused by the higher bandgap 1,2-linked branches to the 1,4-linked stilbene backbone and associated enhanced fluorescence efficiency were also observed in this HPPV.

Materials with large two-photon absorption (TPA) are attractive for various optical applications. Dimethylamine-terminated HPPV **72** had been tested for its broadband optical limiting and nonlinear absorption properties.[84] It shows an unusually high TPA cross-section δ, which was estimated to be larger than



Scheme 10.11

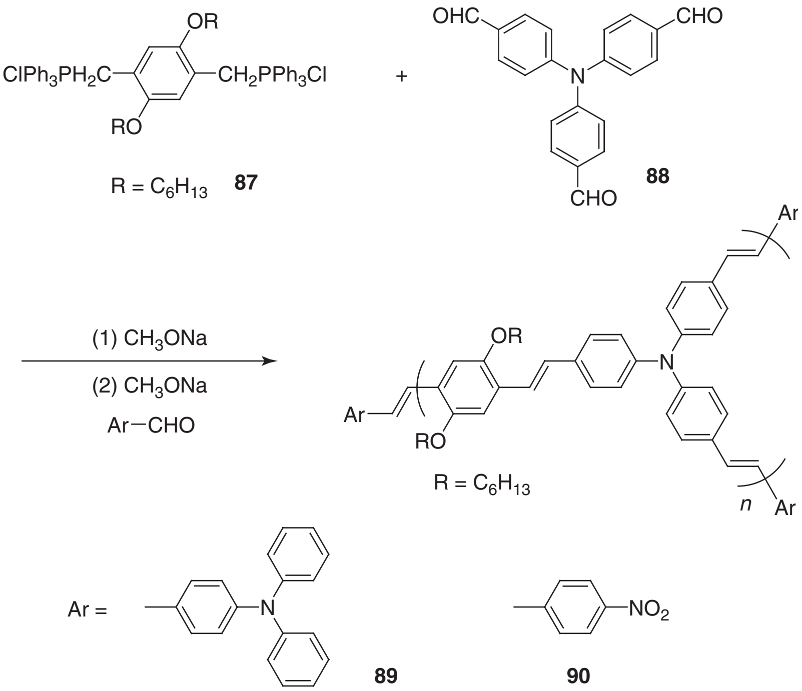


85 **86** **Scheme 10.12**

10^{-16} cm^4/GW or 10^{-44} cm^4/photon/s at 600 nm, resulting in a high optical limiting power.

Tian *et al*. carried out a similar study.[85] They synthesized two triphenylamine-containing HPPVs and studied their TPA properties (Scheme 10.13). The TPA cross section of the triphenylamine (**89**) and nitrophenyl-terminated HPPV (**90**) were determined to be 1.43×10^{-20} and 0.64×10^{-20} cm^4/GW per repeating unit at 800 nm, respectively. Furthermore, chloroform solutions of **89** and **90** exhibit intense frequency-upconverted fluorescence under the excitation of 120-fs pulses at 800 nm with their peak maxima located at 544 and 554 nm, respectively.

An orange-red light-emitting HPPV (**91**) containing 3,5-dicyano-2,4,6-tristyrylpyridine moiety was prepared via palladium-catalyzed Heck coupling. Polymer **91** showed improved electron affinity compared to similar materials.[86]



Scheme 10.13

A double-layer OLED device emitted light of 599 nm, with a brightness of 662 cd/m^2 at 7.0 V and an external quantum efficiency of 0.19%.

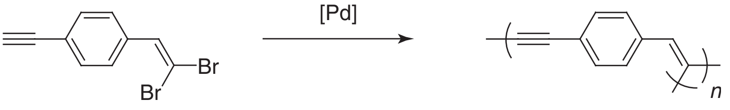
A luminescent conjugated hyperbranched polymer was prepared from β,β-dibromo-4-ethynylstyrene (**92**, Scheme 10.14).[87] Although the resulting polymer **93** was only partial soluble, the structure could be elucidated through spectroscopic methods and with the aid of a model compound. Theoretical calculations revealed a partially disrupted conjugation as a result of the twisted benzene rings.

Weber *et al*. developed an elegant protocol for cross-conjugated hyperbranched poly(arylene/1,1-vinylenes) from the readily obtainable 4-[(trimethy lsilyl)ethynyl]acetophenone (**94**, Scheme 10.15), an AB$_2$ monomer.[88] Ruthenium-catalyzed regioselective addition of the C−H bonds, ortho to the acetophenone functionality, to the C≡C furnished **95** in good yields. The molecular weight, however, was rather low.

Our group carried out polycyclotrimerization of vinylene-containing diynes **96** and **99** (Scheme 10.16).[89,90] The resulting polymers **98** and **100** were soluble in common organic solvents such as THF, toluene, and chloroform; had high molecular weights (M_w up to 30×10^3); and exhibited extended π-conjugation due to the resulting 1,2,4- and 1,3,5-substituted phenyl connections. Both polymers were luminescent and emitted blue-green light, with **100** exhibiting QY as high as 77%.

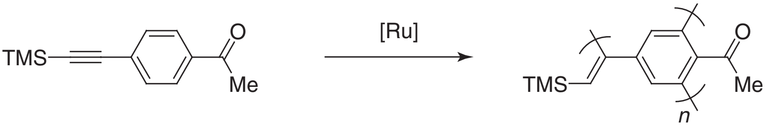
A hyperbranched organosilicon-containing polymer possessing pendant ethynyl groups (**102**) was prepared by hydrosilylation polymerization of methyldiethynylsilane (**101**, Scheme 10.17).[91] The tacky, highly soluble air- and moisture-stable polymer underwent light- and heat-induced cross-linking reactions through the terminal ethynyl groups. Cross-linked **102** exhibited excellent thermal stability as demonstrated by thermogravimetric analysis under nitrogen and in air with char yields of 87% and 62%, respectively, at 1300 °C.

Masuda *et al*. synthesized regio- and stereoregular σ–π-conjugated hyperbranched polymers from silane AB$_2$ monomers (Scheme 10.18).[92,93] Polymer



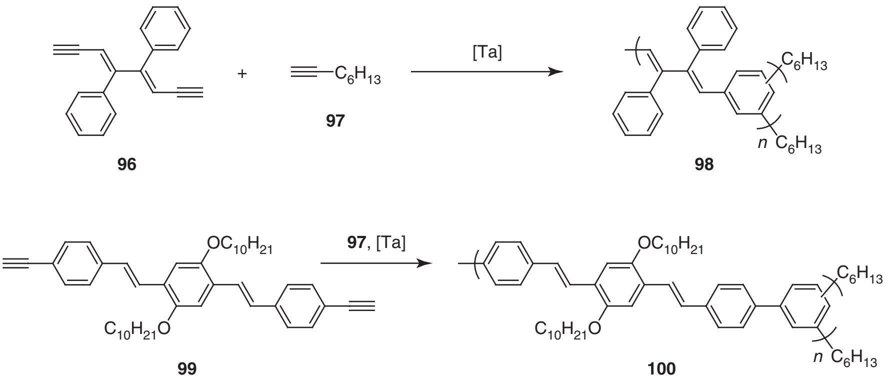
92 **93**

Scheme 10.14

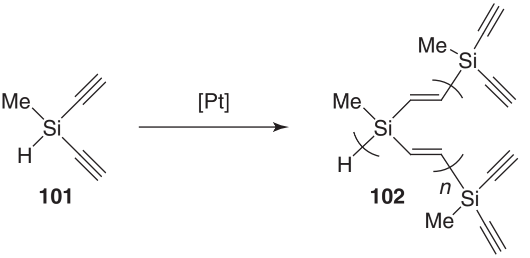


94 **95**

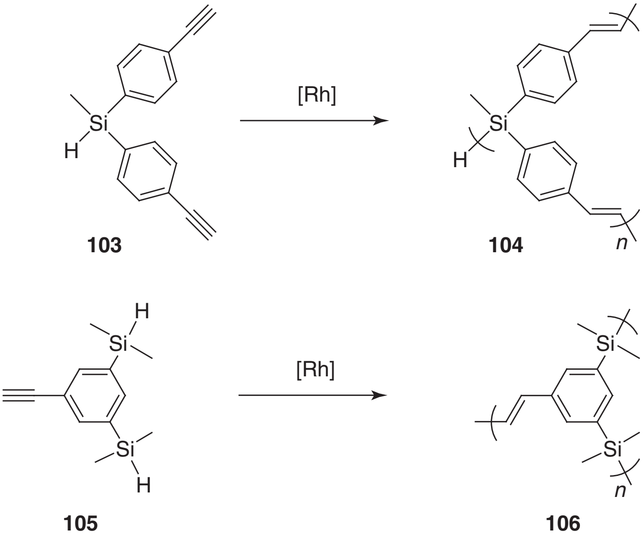
Scheme 10.15



Scheme 10.16



Scheme 10.17



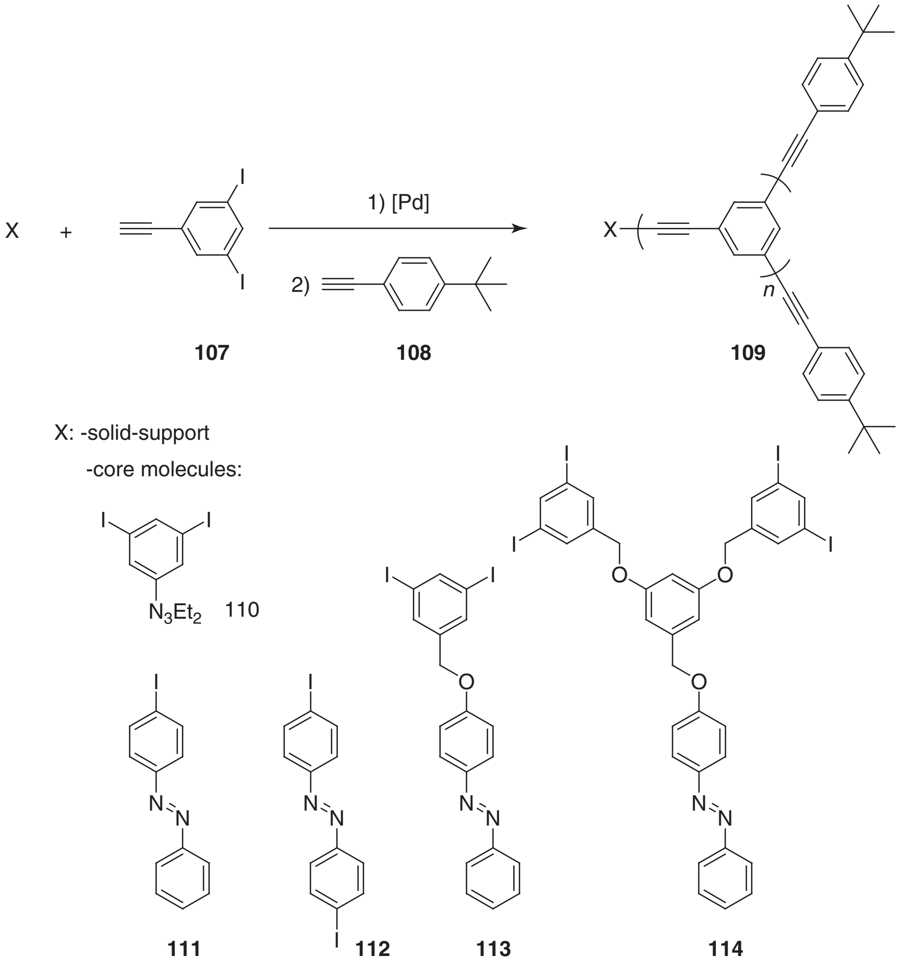
Scheme 10.18

104 contained 95% transvinylene moieties and showed a weight loss of only 9% upon heating to 900 °C under nitrogen. It furthermore displayed a UV absorption at ~275 nm due to $\pi-\pi^*$ transition and a weak absorption at ~330 nm due to π–to–σ charge transfer, which was hardly seen in the corresponding linear polymer. The unreacted terminal silane groups of **106** could either be completely terminated by reacting with excess phenylacetylene or cross-linked by hydrolysis and aerial oxidation. While the first reaction formed a soluble hyperbranched polymer, the latter one furnished a transparent gel through siloxane linkages without any obvious defects such as phase separation or decomposition. The gel film showed a strong resistance against various organic solvents, displayed a weak absorption above 300 nm due to the charge-transfer phenomenon, and emitted an intense blue light. In a similar approach, Yamashita *et al*. utilized a palladium-catalyzed hydrosilylation polymerization to afford soluble silylene-divinylene polymers through an $A_2 + B_2 + B_3$ protocol with 1,3,5-triethynylbenzene and B,B′,B″-triethynyl-N,N',N''-trimethylborazine as branching units.[94] The resulting polymers showed higher thermal stabilities and higher char yields than their linear analogs. The polymers obtained from 1,3,5-triethynlylbenzene showed increased, broad UV absorptions and enhanced fluorescence emissions.

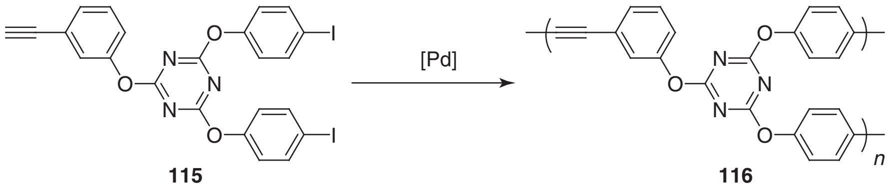
10.5 HYPERBRANCHED POLY(ARYLENEETHYNYLENES)

Poly(phenyleneethynylene)s (PPEs) are the dehydrogenated congeners of poly-(phenylenevinylene)s and have found use in sensory and molecular wire devices.[95] Many papers have been published on oligomers, linear polymers, and perfectly branched dentrimers. In contrast, hyperbranched poly(aryleneethynylene)s (HPAEs), in particular hyperbranched poly(phenyleneethynylene)s (HPPEs), remain virtually unexplored. Moore’s group systematically studied palladium-catalyzed polycoupling reactions of a phenylacteylene monomer, and studied the effect of solid supports[96] and the presence of core molecules[97] on the molecular weights and polydispersity indices (PDIs) of the resulting HPPEs (Scheme 10.19). The polymers obtained on the solid support showed narrow molecular weight distribution but the growth was limited by the nature of the support (e.g., cross-linking density and loading). Slow addition of the monomer to solutions of multifunctional core molecules (**110–114**) resulted in high molecular weight HPPEs with narrow PDIs. Control over the molecular weight was achieved by varying the monomer/core ratio. Interestingly, the PDIs of the hyperbranched polymers were found to decrease with increasing degree of polymerization and with increasing core functionality. The obtained HPPEs also showed interesting properties as precursors to amorphous carbon materials and as dry release layers for microelectromechanical systems (MEMS) fabrication.

Kim *et al*. polymerized a similar AB_2-type monomer containing a 1,3,5-triazine moiety (**115**, Scheme 10.20).[98] However, the resulting HPAE **116** had structural irregularities due to the formation of diacetylene branches.



Scheme 10.19

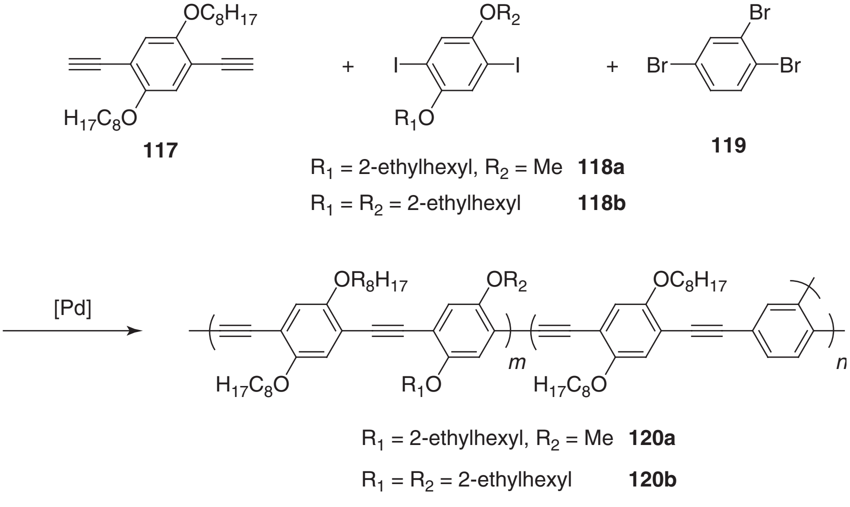


Scheme 10.20

Milli-, micro-, and nanoparticles of cross-linked conjugated polymers were synthesized by palladium-catalyzed cross-coupling polymerization of $A_2 + B_2 + B_3$ in aqueous emulsions (Scheme 10.21).[99,100] The size of the particles was highly dependent on the reaction conditions. For example, micrometer-sized particles (~4.7 μm) were obtained by carrying out the polymerization of monomers **117–119** in a vigorously stirred water–toluene–diisopropylamine mixture, utilizing sodium dodecyl sulfate as a surfactant. The resulting polymer could be precipitated, isolated, dried, and readily redispersed by ultrasonication. Even smaller particles (~50–400 nm) were obtained when the polymerization was carried out with an ultrasonic bath instead of a mechanical stirrer. Preliminary time-of-flight measurements revealed high charge carrier mobility, significantly higher than those of the analog linear polymer, suggesting that the numerous branches and cross-links give rise to improved interchain interactions for this system.

Similar to the hyperbranched poly(phenylene)s and poly(phenylenevinylene)s, our group utilized the cyclotrimerization of arylethynylene-containing diynes for the synthesis of HPAEs (Scheme 10.22).[101–104] Transition-metal catalysts [$TaBr_5$, $NbBr_5$, and $CpCo(CO)_2$] efficiently effected the copolycyclotrimerization between diynes **121–124** and monoynes **II–IV**, yielding soluble, high molecular weight hyperbranched polymers (M_w up to 44×10^3) in quantitative yields. The HPAEs emitted strong deep blue light of ~400 nm and showed high quantum efficiency.

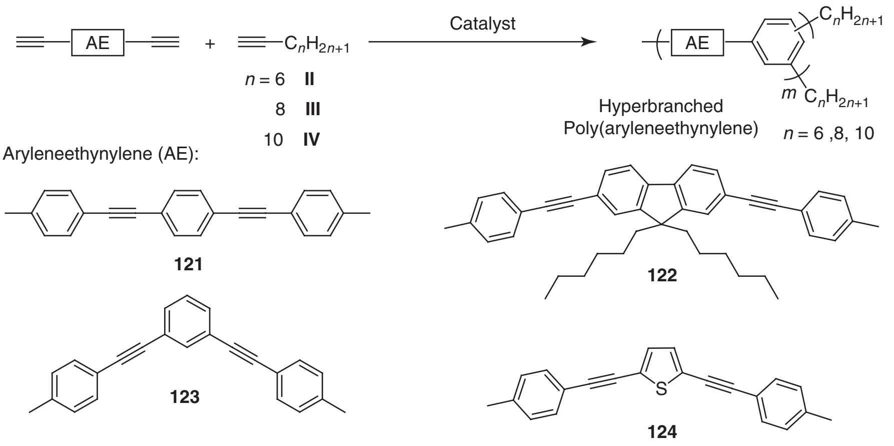
The HPAEs comprise interconnected aromatic rings with extended electronic π-conjugation, which may make them nonlinear optically active.[105] Figure 10.3 shows examples of nonlinear attenuation of the optical power of 532-nm laser pulses by the polymers. The transmitted fluence of **121/IV** initially increases



R_1 = 2-ethylhexyl, R_2 = Me **118a**
$R_1 = R_2$ = 2-ethylhexyl **118b**

R_1 = 2-ethylhexyl, R_2 = Me **120a**
$R_1 = R_2$ = 2-ethylhexyl **120b**

Scheme 10.21



Scheme 10.22

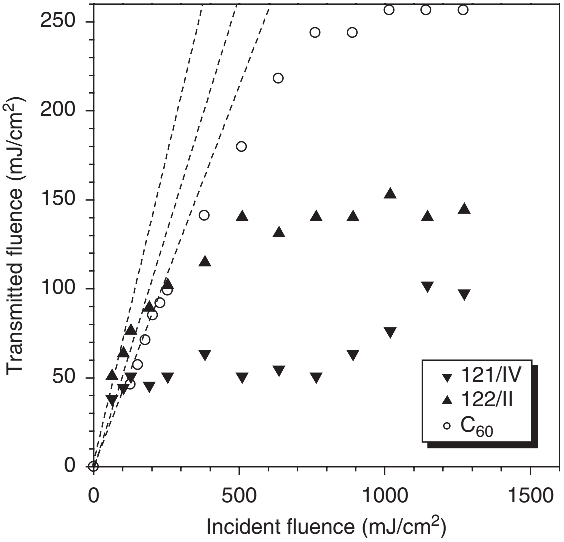
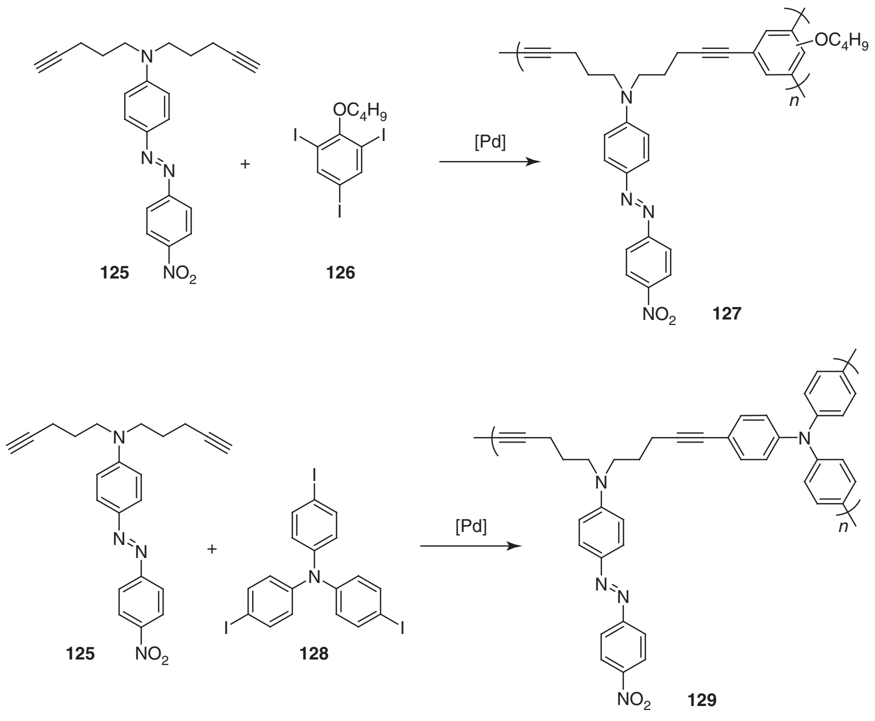


Figure 10.3 Optical limiting responses to 8-ns 532-nm optical pulses of dichloromethane solutions of hyperbranched polyarylenes; concentration: 0.86 mg/mL. Data for a toluene solution of C_{60} (0.16 mg/mL) is shown for comparison.
Source: Ref. [55].

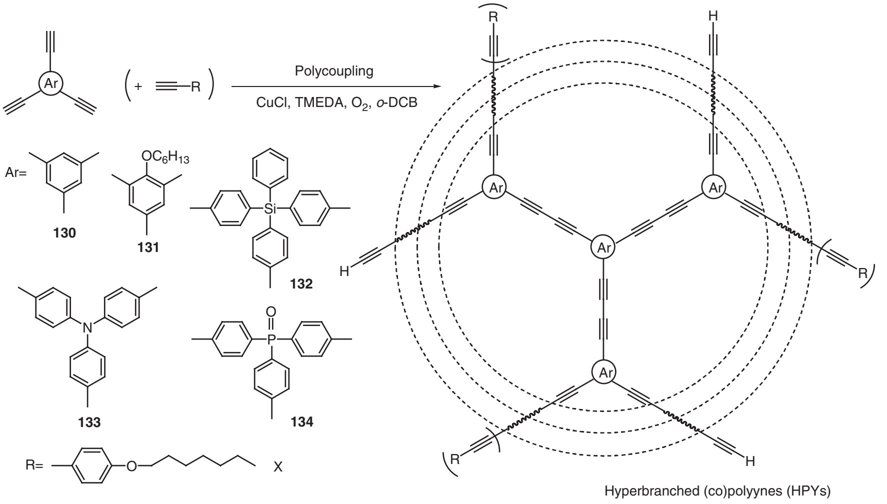
with an increase in the incident fluence in a linear fashion. It commences to deviate from linearity at an incident fluence of about 260 mJ/cm^2 and reaches a saturation plateau of 140 mJ/cm^2. The optical power-limiting performance of **121/IV** is superior to that of C_{60}, a well-known optical limiter.[106] Taking into consideration that fullerene is a three-dimensionally conjugated buckyball, the three-dimensionally conjugated electronic structure of the HPAEs may thus be responsible for their optical nonlinearity. Compared to **121/IV**, **122/IV** is an even better optical limiter (maximum transmitted fluence <100 mJ/cm^2). The optical power-limiting properties of the HPAEs are thus sensitive to changes in their molecular structures, which offers the opportunity to tune their performances through molecular engineering endeavors.

In addition to employing polycyclotrimerization reactions, we have also explored the possibility of synthesizing hyperbranched polymers by polycoupling protocols. Azo-functionalized HPAEs (**127** and **129**) were prepared by palladium-catalyzed coupling of triiodoarenes (**126** and **128**) with a diethynylazobenzene (**125**, Scheme 10.23).[107] The HPAEs were soluble, film-forming, and morphologically stable ($T_g > 180\,^\circ\mathrm{C}$). Their poled films exhibited high second-harmonic generation coefficients (d_{33} up to 177 pm/V), owing to the chromophore-separation and site-isolation effects of the hyperbranched architectural structure of the polymers in the three-dimensional space. The optical nonlinearities of the poled films were thermally stable (no drop in d_{33} when heated to $152\,^\circ\mathrm{C}$) due to the facile cross-linking of the multiple acetylenic triple bonds in the HPAEs at moderate temperatures (down to $88\,^\circ\mathrm{C}$).

Homopolycouplings of aryltriynes $\mathrm{Ar(C{\equiv}CH)_3}$ and their copolycouplings with monoyne $\mathrm{Ar'C{\equiv}CH}$ were effected by CuCl in air under Glaser–Hay oxidative coupling conditions, giving soluble hyperbranched polyynes (HPYs, Scheme 10.24).[108] The HPYs were highly luminescent, with HPY **130** and **130/X** emitting blue light at ~440 nm.



Scheme 10.23



Scheme 10.24

Apart from the luminescence properties, the HPY showed other interesting optical properties. Theory predicts that polymers consisting of groups with high polarizabilities and small volumes can exhibit high refractivities.[109] Owing to its polarizable aromatic rings and slender triple-bond rods, a thin film of HPY **130** showed refractive indexes (n) of 1.861–1.770 in the spectral region of 600–1700 nm (Figure 10.4),[108,110] which are much higher than those of the well-known commercial "organic glasses" such as poly(methyl methacrylate) ($n = 1.497–1.489$), polycarbonates (1.593–1.576),

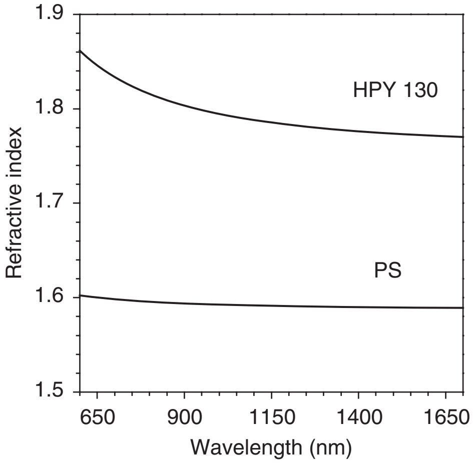


Figure 10.4 Wavelength dependence of the refractive index of a thin film of **130**. Data for a thin film of polystyrene (PS) is shown for comparison.

Source: Ref. [108].

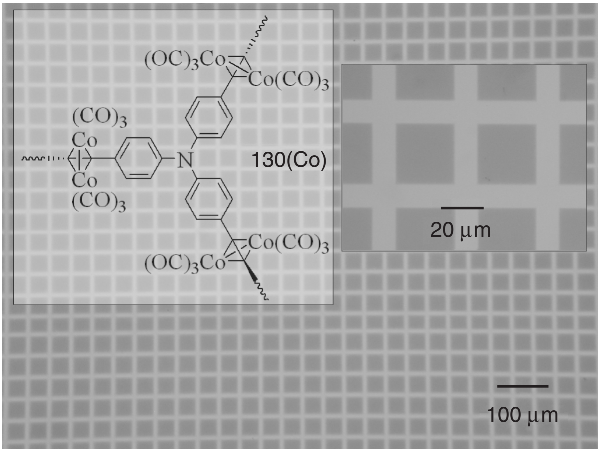


Figure 10.5 Optical micrograph of the photopattern generated by UV photolysis of **130(Co)** through a Cu negative mask. Insets: molecular structure of **130(Co)** and enlarged fraction of the optical micrograph.
Source: Ref. [113].

and polystyrene (1.602–1.589).[111,112] The polyyne film was transparent and showed high transmittance in the long wavelength region.

The carbon-rich polyynes were readily curable (from ~150 °C), thermally stable (T_d up to ~550 °C), and pyrolytically carbonizable (W_r up to ~80% at 900 °C). Complexations with cobalt carbonyls metallified the HPYs, and homogenous brown-colored films of the metallified polymers **130(Co)** could be readily obtained from its freshly prepared complexation solution by spin-coating.[113] Irradiation of the dried films through a Cu-negative mask for 30 min led to photobleaching, leaving behind the pattern of the photomask (Figure 10.5). The enlarged micrograph clearly revealed the sharp edges of the patterns. Interestingly, the illuminated parts and the protected parts have different refractive indices, which makes this material promising for photonic applications such as in holographic devices[114] or as high refractive index optical coatings.[115]

Ceramization of the cobalt–polyyne complex at high temperatures under nitrogen afforded a soft ferromagnetic material with high magnetizability (M_s up to ~118 emu/g) and low coercivity (H_c down to ~0.045 kOe, Figure 10.6).

10.6 CONCLUSION

While hyperbranched polymers have been intensely studied for almost two decades, the three-dimensional features of their conjugated analogs have only recently become the focus of researchers. We have briefly summarized the synthetic efforts so far. A great variety of different structures have already been obtained. Controlled synthesis together with advances in property characterizations will certainly help promote this new frontier in polymer science further.

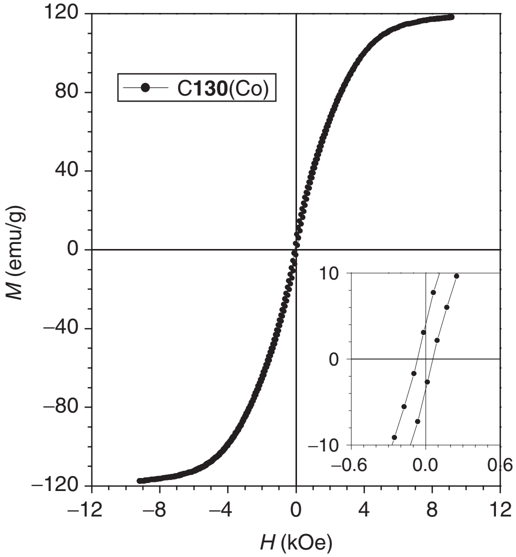


Figure 10.6 Plots of magnetization (M) versus applied magnetic field (H) at 300 K for magnetoceramics **C130(Co)**. Inset: enlarged portion of the M–H plots in the low strength region of the applied magnetic field. *Source:* Ref. [108].

LIST OF ABBREVIATIONS AND SYMBOLS

AE	aryleneethynylene
AFM	atomic force microscopy
Ar	aromatic
D	exposure dose
δ	TPA cross-section
$D_{0.5}$	dose needed for an F_g value of 0.5 (or 50%)
d_{33}	macroscopic second-harmonic generation coefficient
EDOT	3,4-ethylenedioxythiophene
F_g	gel fraction
$\gamma_{0.5}$	contrast
H_c	coercivity
HPAE	hyperbranched poly(aryleneethynylene)
HPPE	hyperbranched poly(phenyleneethynylene)
HPPV	hyperbranched poly(phenylenevinylene)
HPY	hyperbranched polyyne
MEMS	microelectromechanical systems
M_s	saturation magnetization
M_w	weight-average molecular weight
MWNT	multiwall carbon nanotubes
n	refractive index

OLED	organic light-emitting diode
PEO	poly(ethylene oxide)
PDI	polydispersity index
PF	poly(fluorene)
PL	photoluminescence
PPE	poly(phenyleneethynylene)
PPV	poly(*p*-phenylenevinylene)
QY	quantum yield
S	spin quantum number
SHG	second-harmonic generation
SWNT	single-wall carbon nanotubes
T_d	thermal degradation temperature
T_g	glass transition temperature
TPA	two-photon absorption
UV	ultraviolet
W_r	weight residue after pyrolysis

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Chapter 11

Degree of Branching (DB)

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11.1 DEFINITION OF THE DEGREE OF BRANCHING (DB)

Hyperbranched polymers, particularly those obtained in one-pot reaction, consist of macromolecules substantially differing from each other not only in molecular weight, but also in the architecture of their structure. Hence, the molecular weight is by far not a sufficient parameter that characterizes these polymers. Since the number of possible structures becomes very large as the polymerization degree of macromolecules increases, there is a need to characterize also this aspect of hyperbranched polymers. Thus, the term *degree of branching* (DB) was introduced[1–3] as a quantitative measure of the branching perfectness for hyperbranched polymers. Fréchet and Hawker[2] defined it simply as $(1 - a_2)$, where a_2 was the fraction of bifunctional (linear) units in the system. At present, DB is the most commonly used parameter describing the average architecture of highly branched polymers. It has to be distinguished from the *branching coefficient*, a quantity defined by Flory[4] as the probability of a link in a branch unit to lead to another branch unit.

Kim and Webster[5] introduced the *normalized branching factor*, a parameter defined as the ratio of molar fraction of fully branched monomers relative to that of all possible branching sites.[6] The definitions and methods of controlling DB were the subject of analysis in a series of papers by Hölter *et al.*[7–9]

Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

Frey's group defined and measured[10] also another parameter: the *average number of branches* (ANB); that is, the number of branches emanating from units, divided by the total number of units, but without terminal ones.

11.1.1 Single Highly Branched Molecules

For single molecules, the meaning of DB is straightforward as illustrated in Figure 11.1. In a perfect dendrimer, there are only terminal units (open circles) and branched units (filled circles), here of functionality $f = 3$, whereas in the ideal linear chain, there are exactly two terminal units, the rest being linear ones (shaded circles). As follows from the early definition by Fréchet and Hawker,[2] for a perfect dendrimer α_2 is zero and hence DB $= 1$. For the linear chain of polymerization degree n, we have

$$\text{DB} = 1 - \frac{n-2}{n} = \frac{2}{n} \tag{11.1}$$

whose value approaches 0 as $n \to \infty$; it is exactly 0 for a ring molecule of any size.

The more appealing definition of the DB reads

$$\text{DB} = \frac{n_3 + n_1}{n_3 + n_2 + n_1} \tag{11.2}$$

where n_3 (or b), n_2 (or l), and n_1 (or t) stand for the numbers of branched, linear, and terminal units in the molecule, respectively ($n_1 + n_2 + n_3 = n$). Certainly,

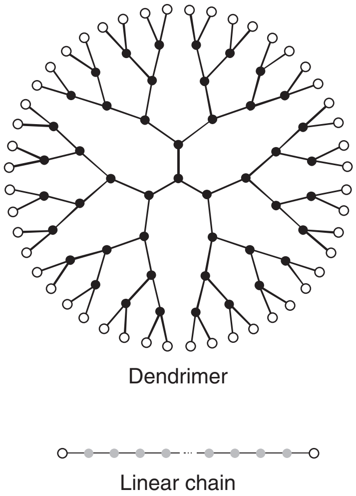

Figure 11.1 Topology of a dendrimer and linear polymer chain.

this equation is fully equivalent to the previous one. The DB defined by Eq. (11.2) is in the literature often referred to as the Fréchet DB.[11–16]

The situation becomes more complicated as branching points of functionality higher than 3 appear in the molecules. Hölter *et al.*[7] proposed to generalize the Kim and Webster[5] factor. They preferred, however, to keep calling it DB. Let the parameter r denote the number of deviations in a unit from linear direction. Thus, $r = 0$ for terminal and linear units, $r = 1$ for a unit from which one branch emanates, $r = 2$ for two branches extending from otherwise linear unit, and so on. DB is then defined as the ratio of the sum of branching parameters of all units in the molecule $R = \sum r$ to the maximal value $R_{\max}$ of such a sum for the most highly branched isomer that could be constructed from the molecule.

In an AB_2-type macromolecule, the sum of branching parameters is simply the number of branching units n_3, whereas $R_{\max}$ is, on average, $n_3 + \frac{1}{2}n_2$, since for a molecule of a certain size, in order to convert it into its isomer with the highest possible number of branched units, one can convert a linear unit into a branched one only at the expense of converting another linear unit into a terminal one.[7] So, only half of the linear units in the molecule can be converted into branching points, and the other half must necessarily be converted into terminal units. Only then would the condition

$$n_3 = n_1 - 2 \tag{11.3}$$

become valid for every AB_2-type macromolecule (see Appendix).

Hölter *et al.*[7] used the incorrect relation $n_3 = n_1 - 1$, since they excluded from considering the focal unit, that is, the unit that had an unreacted A group. The focal unit in any AB_2-type molecule is in fact either a terminal or a linear unit, but the authors considered it always as a branching one.

The generalized DB for a single AB_2-type macromolecule is therefore

$$\mathrm{DB} = \frac{n_3}{n_3 + n_2/2} = \frac{2n_3}{2n_3 + n_2} \tag{11.4}$$

or

$$\mathrm{DB} = \frac{n_3 + n_1 - 2}{n_3 + n_2 + n_1 - 2} \tag{11.5}$$

which becomes the Fréchet and Hawker[2] value (see above) only for large molecules, for which $n = n_1 + n_2 + n_3 \gg 2$. The value defined by Eq. (11.4) is called Frey's DB.[11,13–16]

For polymers of an AB_3 monomer, the maximum branching parameter reads as

$$R_{\max} = 2(n_4 + 2n_3/3 + n_2/3) \tag{11.6}$$

by the same reasoning as above. In order to "convert" a (rather large) AB_3-type macromolecule into its most highly branched isomer, one has to replace units not fully reacted by the highly branched one, but without altering the number of bonds. To obtain a tetrafunctional unit from linear ones, three such units are needed, two of which end up as terminal units. Similarly, one can rearrange links between units in an AB_3-type macromolecule so that two out of three trifunctional units will become fully branched at the expense of one becoming “degraded” to a terminal one. Consequently,

$$\mathrm{DB} = \frac{2n_4 + n_3}{2(3n_4 + 2n_3 + n_2)/3} \tag{11.7}$$

Finally, for a single AB_f-type macromolecule, the generalized DB is

$$\mathrm{DB} = \frac{f \sum_{i=3}^{f+1} (i-2)n_i}{(f-1)\sum_{i=2}^{f+1} (i-1)n_i} \tag{11.8}$$

The other parameter proposed by Hölter *et al.*,[7] i.e., the ANB, is given by

$$\mathrm{ANB} = \frac{\sum_{i=3}^{f+1} (i-2)n_i}{\sum_{i=2}^{f+1} n_i} \tag{11.9}$$

This parameter is less popular and used mostly by the authors from Frey’s group.[12,16,17]

Yet another parameter describing the topology of branched molecules is the Wiener index,[18] defined as the sum of the distances between all pairs of vertices (here: units) in a molecular tree. In the literature,[19] one can find different algorithms for calculating the Wiener index for various molecules. It is high for linear chains and becomes smaller for compact molecules, such as dendrimers. The Wiener index can be related to the square of the radius of gyration of polymer molecules, but only if the links counted by the index are Gaussian subchains. Otherwise, it can be applied to modeling only, since it is a quantity that cannot be measured directly or even indirectly.

11.1.2 A System of Hyperbranched Molecules

The real systems consist of many different macromolecules and any determination of the DB leads to an average value, namely, the number average DB $< \mathrm{DB} >$. This means that the contributions from individual molecules to the average DB are proportional to their number fractions.

For the set of N AB_2 molecules, the average DB is

$$< \mathrm{DB} > = \frac{2N_3}{2N_3 + N_2} \tag{11.10}$$

or

$$< \mathrm{DB} > = \frac{N_3 + N_1 - 2N}{N_3 + N_2 + N_1 - 2N} \tag{11.11}$$

where

$$N_i = \sum_{1}^{N} n_i \tag{11.12}$$

is the sum of units of a given substitution degree ($i = 1, 2, 3$) in all molecules.

Equation (11.10) or (11.11) can be used alternatively, depending on the accuracy of determination of the concentration of units at a given substitution degree. For large molecules, the term $2N$ in Eq. (11.11) is relatively small and can be neglected.

It is important, however, to make sure that unreacted monomer AB_2 is excluded from calculations.[20] In condensation polymerization, only at very high conversion degree of A groups does the concentration of unreacted monomer become small. In determination of DB, the unreacted monomer increases the number of molecules N, and may lead to overestimation of the pendant unit content N_1. The use of definition (11.10) eliminates this danger. The presence or not of the free monomer molecules in the calculations explains the differences between the Fréchet DB from the Frey one quoted by some authors.[12] The latter is usually smaller.

DB is, in principle, insensitive to cyclization, that is, intramolecular reaction between functional groups or sites. In the mean-field modeling of hyperbranched polymerization as well as in Monte Carlo experiments, the number of cycles, at least in the condensation polymerization, is small and can be neglected.[21] The presence of cyclic molecules can be detected, for example, by matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) or electrospray ionization (ESI) mass spectroscopy, and some authors indeed found a considerable content of such molecules in some systems.[22,23] The significance of cyclization in hyperbranched polymerization still remains, however, an open question.

11.2 DETERMINATION OF DB

11.2.1 Direct Determination

Since branching has a dramatic influence on polymer properties, it is important to characterize polymer architecture by experimental techniques. Characterization methods that can distinguish linear, branched, and terminal units in the final products have been employed to determine DB directly. Among these techniques, nuclear magnetic resonance (NMR) spectroscopy has been proven to be the most powerful tool for the determination of DB.

Fréchet *et al.*,[1] in the paper setting out the term *degree of branching*, reported the synthesis of a hyperbranched polyester by self-condensation polymerization of an AB_2 monomer, namely, 3,5-bis(trimethylsiloxy)benzoyl chloride. By characterizing a series of model compounds such as 3,5-dihydroxybenzoic acid and its derivatives on high-resolution one-dimensional ^1H NMR and ^{13}C NMR spectroscopies, the characteristic peaks of branched, linear, and terminal units were assigned respectively, and DB was hence calculated by using Eq. (11.10).

For the hyperbranched polymers with heteroatoms, ^{15}N, ^{19}F, ^{29}Si, and ^{31}P NMR spectroscopies have also been used to measure DB.[24–28] These NMR spectra have usually fewer and less overlapping signals, and therefore the assignment of the signals to various units is much more straightforward.

Now, the quantitative one-dimensional NMR technique (1D NMR) has become the most useful approach to determine DB since it is both practical and convenient. However, in some cases, the resonances from branched, linear, and terminal units are not well separated, hampering determination of DB. Although by using Eq. (11.10) DB can be calculated by just integrating the signals from branched (or, alternatively, terminal) and linear units, there are still many hyperbranched polymers for which the resonances from either branched and linear units or terminal and linear units are not well resolved, yet.[7]

In recent years, two-dimensional NMR techniques (2D NMR) have been greatly enhanced. Compared to 1D technique, 2D NMR improves the spectral resolution by introducing a new frequency dimension, thus allowing the severely overlapping signals in 1D NMR spectra to be resolved into individual peaks in two-dimensional space. Moreover, 2D NMR provides new structural information that is not available from 1D spectrum even at high resolutions.[29] Figure 11.2 gives the ^{13}C, ^1H-HSQC (i.e., heteronuclear single quantum correlation pattern of hyperbranched poly(sulfone amine) made by the copolymerization of 1-(2-aminoethyl) piperazine and divinyl sulfone.[30] Severe overlapping of bands in both ^1H NMR and ^{13}C NMR spectra can be observed. Thus, it is hard to determine the DB using 1D NMR only. Fortunately, by using 2D NMR techniques, the overlapped signals in 1D NMR are well resolved into several individual peaks in the two-dimensional plane, and therefore the DB of hyperbranched poly(sulfone amine) can be determined. With the help of 2D NMR techniques, DB values for some complicated hyperbranched polymer systems have been successfully calculated.[30,31]

On the other hand, for degradable systems, Kambouris and Hawker[32] and Bolton and Wooley[33] proposed a different approach to determine DB. They modified the functional groups of hyperbranched polymers, and then degraded the polymers into different subunits corresponding to branched, linear, and terminal units, respectively. Quantitative chromatographic analysis of the degradation products provided the ratio of these three groups, so that DB could be calculated. The method is applicable to systems that meet certain conditions. First, the hyperbranched polymer must be degradable. Secondly, the degradation of the polymeric backbone should be complete, while the modifying end-groups are well preserved.

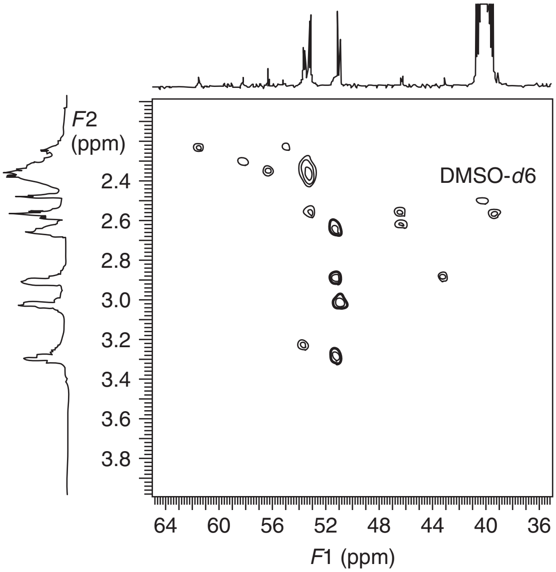

Figure 11.2 ^{13}C, ^{1}H-HSQC pattern of hyperbranched poly(sulfone amine) prepared from 1-(2-aminoethyl) piperazine and divinyl sulfone.
Source: Ref. [30].

Occasionally, other methods such as the Fourier-transform infrared (FT-IR) technique,[34] are also used to evaluate the branching architecture.

11.2.2 Indirect Methods

Indirect methods provide supplemental approaches to evaluate the structure of hyperbranched polymers which have neither well-resolved NMR spectra nor degradable linkages.

Viscometry is the traditional approach to evaluate the branched structure of hyperbranched polymers. As compared to their linear analogs, hyperbranched polymers exhibit much lower intrinsic viscosity and a smaller Mark–Houwink exponent α (Eq. 11.13) because of the compactness of molecules and fewer chain entanglements:

$$[\eta] = KM_v^{\alpha} \tag{11.13}$$

In Eq. (11.13), K and α are the Mark–Houwink constants and M_v is the viscosity-average molecular weight. Generally speaking, α of a randomly coiled linear polymer is in the range 0.5 to 1; and for hyperbranched polymer, it is typically smaller than 0.5.[35,36] In the literature, the intrinsic viscosity contraction factor[37] or the radius of the gyration contraction factor[38] is also used to estimate the architecture of branched macromolecules.

Markoski *et al.*[11] made use of an (A + B)/(A + B_2) low-molecular model reaction strategy to simulate the copolymerization process of AB/AB_2 monomers.

The products had structure similar to the corresponding structural units in copolymers. NMR and high-pressure liquid chromatography (HPLC) were applied to characterize the relative percentage of each unit. The simulated DB was reported to be in good agreement with the value determined directly by the quantitative NMR technique.

Although the aforementioned techniques have been used to determine DB of various hyperbranched polymers with some success, for some complicated systems the determination of DB is still problematic. With the rapid development of the research into hyperbranched polymers, one may expect an impetus to adopt new methods of measuring DB.

11.3 THE VALUE RANGE OF DB

By using simple statistical reasoning, Hölter *et al.*[7] estimated the maximum values of DB that can be arrived at in the random polymerization of AB_f monomers. As reproduced in the Appendix, for $f = 2$, the highest DB was found to be 0.5 at full conversion of A groups. For $f = 3$, at the same conversion, DB approaches 0.44. For these and higher values of f, the dependence of DB on the conversion of A groups is shown in Figure 11.3. As can be seen in this plot, DB grows linearly—or nearly linearly—with conversion and, unfortunately, for random reaction it cannot be improved by increasing the functionality of the AB_f monomer.

In the self-condensing vinyl polymerization, the highest attainable value of DB is even smaller than that in condensation polymerization.[40] The calculated maximum value of DB at full conversion is 0.465.[41] The use of a multifunctional initiator seemed not to improve DB.[42] For the most typical one-batch condensation polymerization, the (Frey) DB was determined to be in the range[43–45] of 0.15 to 0.49.

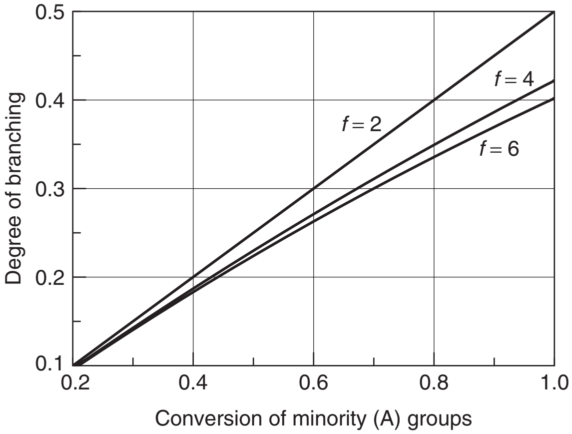

Figure 11.3 Conversion dependence of the degree of branching in one-pot random polymerization of AB_f monomers.

Source: Ref. [39].

A convenient method to assess the range of DB value in hyperbranched polymers is the mathematical modeling of the polymerization process. Yan *et al.*[41] used a kinetic approach to determine DB for both self-condensation vinyl polymerization (SVCP) and AB_2 polycondensation systems. They listed the kinetic differential equations to calculate the fractions of all structural units in the final product, and calculated DB through Eq. (11.14):[41]

$$< \mathrm{DB} > = \frac{2B}{1 - M - 2A'} \tag{11.14}$$

Here, B is the fraction of branching units, M is the fraction of monomer, and A' is the fraction of A groups in the polymer only. For an SCVP system with equal reactivity (i.e., randomly reacting system with $k_A = k_B = k$), the average value of DB can be calculated as

$$< \mathrm{DB} > = \frac{2(1 - e^{-x})(x - 1 + e^{-x})}{1 - (1 - x)(2 - e^{-x})} \tag{11.15}$$

where x corresponds to the conversion of vinyl group. Therefore, DB can be easily obtained when the conversion of monomer is measured.

Kinetic modeling was also used to analyze the effect of reactivity changes of B groups in an AB_2 monomer on DB values.[21] The so-called first shell substitution effect[46] was taken into account. It was assumed that B groups were symmetric and hence reacted in homopolycondensation with equal probability. However, after the first group in a unit reacted the reactivity of the remaining B group changed because of the change in the chemical surrounding of the unit. The reactivity of this second B group either increased (positive substitution effect) or became reduced (negative substitution effect). The substitution effect had a tremendous effect on the value of the average DB, as shown in Figure 11.4. Let the monomer react with positive substitution effect and let the ratio of rate constants, which describes how many times a B group on linear unit reacts faster than it does in the monomer, be higher than, say, 6. Then, as one can see from Figure 11.4, the DB of the resulting polymer exceeds 0.8 at high conversion of the A groups. On the other hand, in a system with negative substitution effect (the ratio of rate constants smaller than 1), the linear fragments of molecules are built preferentially and the DB remains small, even at high conversion of the A groups.

The results of modeling presented in Figure 11.4 may help in selecting a polymerizing system to study and sometimes provide an impetus to try to modify the existing one in order to alter (increase or reduce) the DB. They may also help to understand the limitation or potential of a polymerization system. The modeling might also be quite useful when interpreting the measured data on the DB for the systems with severe signal overlapping in both ^{13}C NMR and ^{1}H NMR spectra.[47]

The intrinsic limitation in the value of DB of polymers prepared in a one-pot synthesis, both by condensation or self-condensing vinyl polymerization, raised the question of under what conditions one could increase the value of DB.

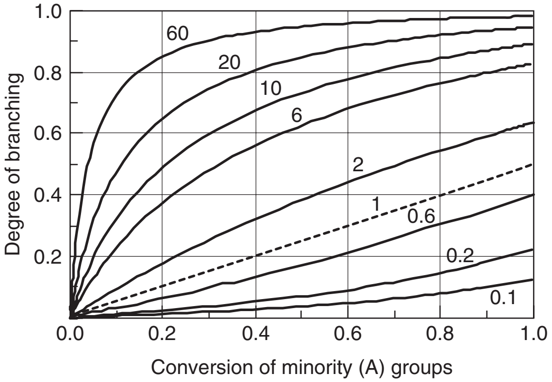

Figure 11.4 The degree of branching as a function conversion of A groups in the polymerization of AB_2 monomer reacting with substitution effect.[21] In the monomer, both B groups react with the same probability. The numbers are the ratios of the rate coefficients at which the "second" B group reacts relative to that of the "first." The heavy broken line corresponds to the random reaction, that is, with the "second" B group reacting at the same rate as the "first" does.

The most straightforward methods of adding a comonomer capable of reacting with AB_2 monomer, namely, with its A groups, that would be either bi- or multifunctional, could not improve the situation as shown already by Hölter *et al.*[8,9]

Several other methods of increasing the average DB of condensation hyperbranched polymers were reported, as follows:

- polymerization of highly branched precursors (dendrons) that contained already preformed dendritic units of high DB[48,49] or postpolymerization modification of terminal functional groups[10];
- polymerization of AB_f monomers in the presence of a multifunctional core monomer,[8,50] possibly with slow addition of AB_f monomer[9,51–53] or introducing it in portions[54];
- selection of monomers with the reactivity of functional groups increasing with conversion,[8] particularly monomers containing groups reacting with the positive substitution effect.[39,55–57]

The most efficient method of improving (increasing) the value of DB seems to be the slow addition of the monomer, both in condensation polymerization and in self-condensing vinyl polymerization. Thus, the calculated maximum value of DB at full conversion increased[51–53] from 1/2 to 2/3 also in the semibatch self-condensing vinyl polymerization.[58]

In the alternative methods of preparing hyperbranched polymers described in previous chapters of the book, the maximization of DB was also one of the targets. Good results were obtained in the case of the so-called criss-cross cycloaddition. Hyperbranched polymers were obtained with no linear units.[24] Hyperbranched polymers of very high DB were also obtained by Suzuki *et al.*[59]

DB was measured also for hyperbranched polymers prepared by off-stoichiometric[60] copolymerization of $A_2 + B_3$ systems.[34,61]

The effect of DB on the rheological and thermal properties for the same polymer, poly[3-ethyl-3-(hydroxymethyl)oxetane], was studied by the Stockholm group,[62] whereas its effect on crystallization was reported by Mai *et al*.[63] The same polymer was used in positron annihilation measurement of free volume and thus the glass transition temperature[64] of this polymer. Thompson *et al.*[65] analyzed the effect of DB on rheological properties of aromatic poly(ether imides). Seiler[13] analyzed the phase behavior of hyperbranched polymers in relation to DB. Aerts[66] modeled intrinsic viscosity behavior of various highly branched macromolecules, with (Fréchet) DB as the topology measure. On the other hand, Widmann and Davies[67] suggested that the Wiener index correlated better with the intrinsic viscosity of hyperbranched polymers than DB. The hyperbranched polyesters with the Fréchet DB of about 0.45 were reported to have macroscopic self-assembly properties.[68] Detailed description of relation between DB and polymer properties is given in the following chapter.

A11.4 APPENDIX

A11.4.1 Numbers of Isomers in Hyperbranched Polymers

In Flory's derivation of the number fraction of hyperbranched molecules consisting of n units, the combinatorial factor reads[4]

$$\omega_n = \frac{(fn - n)!}{n!(fn - 2n + 1)!} \tag{A11.1}$$

and grows very fast with n. It cannot be, however, identified with the number of different isomers of hyperbranched polymers,[6] but with the number of ways the molecules of degree x can be constructed from n monomer molecules.

The actual number of isomers of hyperbranched polymers such as polymers prepared from AB_2 monomers can be calculated by using a recursive procedure developed by Bailey *et al.*[69] Use was made of Polya's counting theorem.[70] If cyclization is excluded, the isomers are, in graph-theoretical parlance, the 3-trees, that is, tree graphs with points of maximum degree (functionality) 3. The numbers of different 3-trees rooted on points of degree 1 or 2 (i.e., on focal unit, the only one with unreacted A group) are provided by the counting functions $R_1(x, y)$ and $R_2(x, y)$, respectively, which are polynomials of the dummy variables x and y. The coefficients at the respective powers of these variables are the numbers of different structural isomers.

Starting from the simplest case of dimer, one can recursively calculate the coefficients at higher and higher powers of dummy variables. The powers have the form $x^n y^{n_1}$, where n is the size of the tree (total number of points) and n_1 is the number of pendant (terminal) points in this tree. For the dimer, the coefficient of x^2y^2 is obviously 1.

The set of counting functions for trees rooted on points of degree 1 (planted trees) and on points of degree 2 reads

$$R_1(x,y) = x^2y^2 + xR_1(x,y) + xyR_2(x,y) \tag{A11.2}$$

and

$$R_2(x,y) = \frac{1}{2xy^2}[R_1^2(x,y) + R_1(x^2,y^2)] \tag{A11.3}$$

respectively.

Their forms, up to octamers, are the following:

$$\begin{aligned} R_1(x,y) &= x^2y^2 + x^3y^2 + x^4y^2 + x^4y^3 + x^5y^2 + 2x^5y^3 + x^6y^2 + 4x^6y^3 + x^6y^4 \\ &\quad + x^7y^2 + 6x^7y^3 + 4x^7y^4 + x^8y^2 + 9x^8y^3 + 11x^8y^4 + 2x^8y^5 \cdots \\ R_2(x,y) &= x^3y^2 + x^4y^2 + 2x^5y^2 + x^5y^3 + 2x^6y^2 + 3x^6y^3 + 3x^7y^2 + 7x^7y^3 \\ &\quad + 2x^7y^4 + 3x^8y^2 + 13x^8y^3 + 7x^8y^4 \cdots \end{aligned}$$

The respective sets of isomers of hexamers with three pendant points are shown in Figure 11.5 Note that there exist only two isomers of 3-trees of size 6 if one does not distinguish the focal unit. The relevant counting function $t(x,y)$ for the number of "free" 3-trees reads

$$t(x,y) = R_1(x,y) + R_2(x,y) + R_3(x,y) - \frac{1}{2x^2y^2}[R_1^2(x,y) - R_1(x^2,y^2)] \tag{A11.4}$$

with the counting function for the number of trees rooted on points of degree 3

$$R_3(x,y) = \frac{1}{6x^2y^3}[R_1^3(x,y) + 3R_1(x,y)R_1(x^2,y^2) + 2R_1(x^3,y^3)] \tag{A11.5}$$

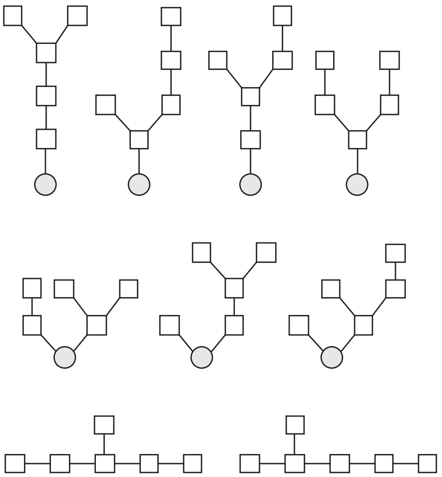

Figure 11.5 All isomers of hexamers of AB_2 polymers represented as 3-trees rooted on the focal monomer or as "free" 3-trees. The numbers of different isomers are the coefficients at x^6y^3 in functions R_1, R_2, and t. Note that each rooted tree in the upper two rows has, in fact, the structure of one of the isomers in the lowest row.

Thus

$$\begin{aligned}t(x,y) = {} & x^2y^2 + x^3y^2 + x^4y^2 + x^4y^3 + x^5y^2 + x^5y^3 + x^6y^2 + 2x^6y^3 + x^6y^4 \\ & + x^7y^2 + 3x^7y^3 + 2x^7y^4 + x^8y^2 + 4x^8y^3 + 5x^8y^4 + x^8y^5 + x^9y^2 \\ & + 5x^9y^3 + 9x^9y^4 + 3x^9y^5 + x^{10}y^2 + 7x^{10}y^3 + 17x^{10}y^4 + 10x^{10}y^5 \\ & + x^{10}y^6 + \cdots\end{aligned}$$

The "free" isomers predicted by term $2x^6y^3$ are also shown in Figure 11.5.

Relevant to this discussion is that the number of pendant units in a 3-tree is the number of branching units plus two. It becomes obvious when one realizes that in every tree of size n, the number of links is necessarily $n-1$. Hence, as the numbers of points of degree 1, 2, and 3 in a tree are n_1, n_2, and n_3, respectively, then

$$n = n_1 + n_2 + n_3 \tag{A11.6}$$

and, taking the links emanating from each point

$$2(n-1) = n_1 + 2n_2 + 3n_3 \tag{A11.7}$$

By eliminating n from these equations, one gets

$$n_3 = n_1 - 2 \tag{A11.8}$$

Analogous relations for 4-trees are

$$\begin{aligned}& n = n_1 + n_2 + n_3 + n_4 2(n-1) = n_1 + 2n_2 + 3n_3 + 4n_4, \text{ yielding} \\ & \quad 2n_4 + n_3 = n_1 - 2\end{aligned}$$

Among the "free" 3-trees, one can distinguish the isomers that are limiting cases of (i) linear chains (all 3-trees with x^iy^2) and (ii) the most highly branched isomers (not necessarily perfect dendrimers). The latter have an even total number of points and the highest number of terminal units (corresponding terms in $t(x,y)$ are $x^4y^3, x^6y^4, x^8y^5, x^{10}y^6, \ldots, x^{2m}y^{m+1}$). For all of them, the generalized DB is 1.

A11.4.2 Number of Units of Different Substitution Degree in Random Polymerization of AB$_f$ Monomer

Use is made of probability generating functions.[71] Thus, let p be the probability of A group in a unit being reacted. Obviously, for random reaction it is equal to the conversion degree of groups A. The probability that B group has reacted in a unit is $p_B = p/f$. The probability generating functions for the links formed by reaction of the respective groups are

$$F_{0,A} = 1 - p + ps \text{ and } F_{0,B} = 1 - p_{\mathrm{B}} + p_{\mathrm{B}}s = \frac{1}{f}(f - p + ps)$$

where s is a dummy variable. Assuming that groups react independently of each other, the probability generating function for the total number of links emanating from a unit selected at random is simply

$$F_0 = F_{0,A} \cdot (F_{0,B})^f \tag{A11.9}$$

or

$$\frac{1}{f^f}[F_{0,A}(f - 1 + F_{0,A})^f] \tag{A11.10}$$

The coefficient at the ith power of s is the probability of finding a unit with exactly i groups reacted (either A or B). For given f, the polynomial has to be expanded to extract the respective coefficients at powers of s. In particular, at $p \to 1$ all $1 - p$ terms vanish and, for $f = 2$, one has the ratio of probabilities at $s^1{:}s^2{:}s^3 = 1{:}2{:}1$, and for $f = 3$, $s^1{:}s^2{:}s^3{:}s^4 = 8{:}12{:}6{:}1$, exactly as quoted by Hölter *et al.*[7] Relation (A11.10) combined with Eq. (11.8) can also be used to verify the linear dependence of DB on conversion of A groups, typical for random polymerization of AB_2 monomers (Figure 11.3).

LIST OF ABBREVIATIONS

ANB	average number of branching
DB	degree of branching
ESI MS	electrospray ionization mass spectroscopy
FT-IR	Fourier-transform infrared (spectroscopy)
HPLC	high-pressure liquid chromatography
HSQC	heteronuclear single quantum correlation (technique)
MALDI-TOF	matrix-assisted laser desorption/ionization-time of flight
NMR	nuclear magnetic resonance
SCVP	self-condensing vinyl polymerization

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Chapter 12

Influence of Branching Architecture on Polymer Properties

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12.1 INTRODUCTION

Benefiting from their highly branched architecture, hyperbranched polymers (HBPs) have the advantages of nonentanglement, low viscosity, good solubility, and a large number of terminal function groups.[1–12] The degree of branching (DB) is one of the most important intrinsic parameters for HBPs, which greatly influences the physical and chemical properties of the polymers.[13–16] Thus, the control of the DB, and the physical and chemical properties is one of the most significant tasks in the study of HBPs. In recent years, various approaches have been developed to control the branching architecture of HBPs, which has been well described in the previous chapters of this book. With the help of these synthesis strategies, a series of polymers with different branching architectures from HBPs to linear polymers have been successfully prepared. Therefore, the systematic researches on the relation between DB and polymer properties become feasible.

Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

12.2 INFLUENCE OF BRANCHING ARCHITECTURE ON POLYMER PROPERTIES

The clarification of the relation between the structure and the property is one of the basic goals in polymer science. Up to now, it has been well understood that the properties of polymer materials can be well adjusted by changing the polymeric structure. Thanks to their highly branching and functionalized architecture, HBPs show many intriguing physical and chemical properties, which are distinct from their linear analogs. In the following sections, the influence of branching architecture on polymer properties is discussed.

12.2.1 Rheological Property

The intrinsic viscosity of polymers depends greatly on the molecular architecture. Generally speaking, the intrinsic viscosity of linear polymers increases steadily with increasing molecular weight, whereas a maximum appears for a dendrimer system.[17] For an HBP, the intrinsic viscosity also increases with increasing molecular weight, but much lower than that of its linear counterpart.[18,19] The relationship of intrinsic viscosity with molecular architecture has been summarized by Fréchet.[20]

The conformational behavior of both uncharged and charged HBPs in dilute solutions was studied by Mulder *et al*.[21] They calculated the radius of gyration (R_g) of the polymers with different DBs, and then discussed the effect of DB on R_g. For uncharged HBPs, the R_g was insensitive to DB variation. However, when the polymers were charged, the R_g showed a decreasing function of DB, suggesting the considerably compact shape of charged HBPs. McHugh *et al*. studied the rheological behavior of hyperbranched poly(ether-imide) with DBs ranging from 0.42 to 0.68 in concentrated solutions.[22] These hyperbranched poly(ether-imide)s showed characteristic Newtonian behavior, and a transition from the Newtonian at the lowest molecular weight to shear thinning at higher molecular weights was observed. The magnitude of the shear viscosity, the onset of the shear thinning, and the rise of normal stress effects directly correlated with the DB. Kannan *et al*. studied the role of architecture on the conformation, rheology, and orientation behavior of linear, star, and hyperbranched polystyrenes.[23,24] The intrinsic viscosity ($[\eta]$), R_g, viscometric radius (R_η), and zero-shear rate viscosity (η_0) were measured. Compared to a linear polystyrene of the same molecular weight, the hyperbranched polystyrene had a significantly lower intrinsic viscosity, Mark–Houwink exponent, and hydrodynamic radius. Interestingly, a new parameter, shrinking factor h, was used to distinguish the effect of branching on the reduced hydrodynamic volume from the effect of molecular perturbation of chain conformation. The experimental data suggested that hyperbranched polystyrene with short branches underwent strong preferential stretches near the center of the molecule, which might be the reason for the partial molecular expansion. When the DB was high and the branch was short, steric hindrance prevented the formation of entanglements, resulting in a linear dependence of η_0 versus molecular weight.

With the aid of computer simulation, Adolf *et al.* studied the rheology of HBPs with different DBs under shear.[25] They found that the HBPs with a low DB revealed a sparse structure, while those with a high DB possessed a very compact structure. Therefore, the conformation change of HBPs under shear flow was quite different. When the DB was small, the HBP was elongated in the direction of shear and was squeezed in the perpendicular direction. However, for an HBP with DB = 0.8, the elongation in the shear direction was small. This result suggested that with the increase of DB, a higher shear rate was needed to initiate shear thinning for practical applications. Subsequently, these authors further discussed the influence of the Wiener index on the $[\eta]$ and R_g of HBPs through the Brownian dynamics simulations.[26] A series of degree of polymerization (N) and DB were adopted, and molecules with different Wiener indices (W) were simulated for each DB and N. Both $[\eta]$ and R_g of HBPs were observed to scale with W at a constant N via a power law relationship.

Besides the solution behavior, the melt properties of HBPs were investigated and a strong relation between the DB and melt rheological properties had been observed. Johansson *et al.* synthesized a series of hyperbranched aliphatic polyethers originating from 3-ethyl-3-(hydromethyl)oxetane.[27] Figure 12.1 gives the rheological curves of complex dynamic viscosity versus temperature for polyethers with different DBs. It can be found that the sample with the highest DB (DB = 0.41) exhibits a completely amorphous behavior and its viscosity decreases rapidly above the glass transition temperature (T_g) without any trace of a rubbery plateau, suggesting the absence of chain entanglement in the melts. On the other hand, those samples with a low DB behave more like a semicrystalline polymer with only a small drop in viscosity at the T_g, together with the presence of a rubbery plateau before the viscosity drop at the crystalline melting temperature. The low viscosity of HBPs makes them excellent modifiers and additives.[28–33] For example, Kim and Webster found that the addition of a small amount of hyperbranched polyphenylene into polystyrene reduced the melt viscosity greatly.[28]

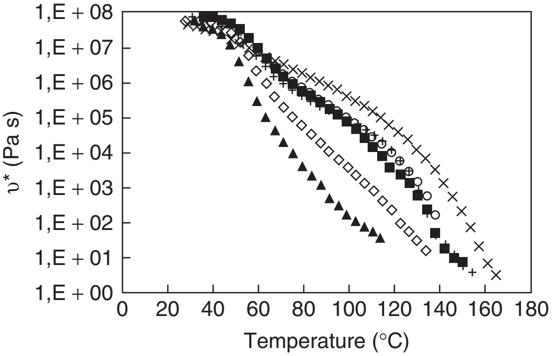

Figure 12.1 Complex dynamic viscosity versus temperature for polyethers with different DBs: 0.41 (▲); 0.32 (◇); 0.30 (■); 0.30 (+); 0.24 (○); 0.11 (×). *Source:* Reprinted with permission from Ref. [27]. Copyright 2002, Elsevier.

12.2.2 Crystallization and Melting Behaviors

The crystallization and melting behaviors of polymers are closely related to their chain architecture. For example, linear high-density polyethylene (HDPE) has a high crystalline melting temperature (135 °C), indicating a strong crystallization ability; by introduction of a slight branching architecture into polyethylene, the obtained low-density polyethylene (LDPE) shows a low melting temperature (115 °C); for the highly branched polyethylene, it is amorphous and the melting peak in the DSC pattern disappears completely.[34] Apparently, the branching architecture has an important influence on the crystallization and melting behaviors of polyethylene.

By changing the ratio of catalyst to monomer or the reaction temperature, Yan *et al*. prepared a series of polyethers with different DBs from the cationic polymerization of 3-ethyl(methyl)-3-(hydroxymethyl)oxetane.[35,36] The differential scanning calorimetry (DSC) melting curves of poly[3-ethyl-3-(hydroxymethyl)oxetane] (PEHO) samples are given in Figure 12.2.[37] It can be found that the hyperbranched PEHO is amorphous and, essentially, the linear sample is partially crystalline. With the decrease of DB, the crystallinity of polyethers increases. Figure 12.3a gives the plot of the relative degree of crystallization (DC) versus the DB of PEHO.[37] It can be seen that the relative DC decreases from 0.31 to 0 when DB increases from 0.06 to 0.40. Apparently, the crystallization ability of PEHO is weakened dramatically with the introduction of the branching structure into the molecular chain. To further clarify the effect of branching architecture on the crystallization behavior, the plots of relative DC versus the content of dendritic (D), terminal (T), and linear (L) units are presented in Figure 12.3b.[37] It can be observed clearly that the crystallinity of PEHO decreases with increasing D and T unit contents, but goes

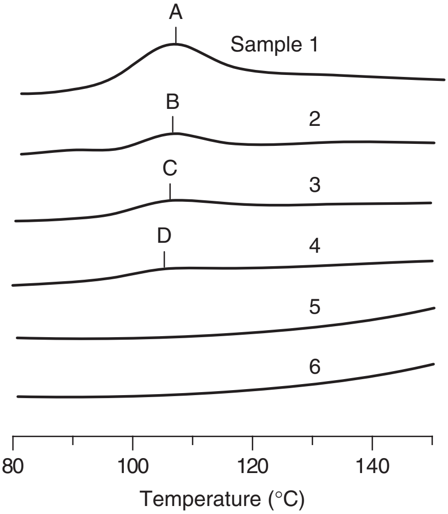

Figure 12.2 DSC melting curves of PEHO samples with different DBs: 1 (0.06); 2 (0.07); 3 (0.13); 4 (0.25); 5 (0.40); 6 (0.45). The temperature of peak A, B, C, D is near 108, 107, 105, and 102 °C, respectively. *Source:* Reprinted with permission from Ref. [37]. Copyright 2005, IOP.

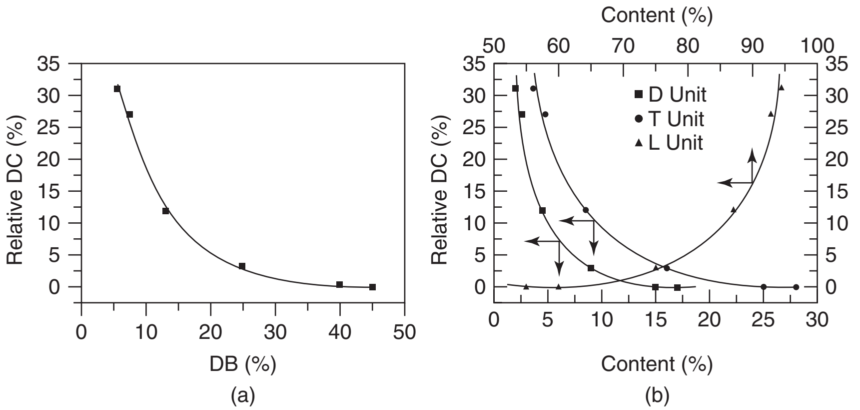

Figure 12.3 Effect of DB on the crystallization behavior of PEHO. (a) Plot of relative DC versus DB; (b) curves of relative DC versus D unit content (■), T unit content (●), and L unit content (▲).

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up with increasing L unit content. Therefore, the crystallization and melting behaviors of polymers can be adjusted by polymer branching architecture.

The effect of DB on crystallization and melting behaviors of hyperbranched polyethers was also studied by Johansson *et al.*[27] It was observed that the crystallinity decreased with increasing DB because of the presence of a branched structure in the polymer. In the meantime, the melting temperature of the polyether was slightly increased for the samples with high crystallinity.

12.2.3 Glass Transition

Glass transition is one of the typical characteristics of polymers. Because of the existence of the highly branched architecture and plenty of end groups, the glass transition of HBPs is quite different from that of their linear counterparts. For a traditional linear polymer, the glass transition originates from long-range segmental motions. However, for an HBP, the glass transition is associated with many cooperative interactions.

Comparing the glass transition temperatures (T_gs) of hyperbranched polyphenylenes with some related small molecules, Kim *et al.* suggested that HBPs had a similar relaxation mechanism with the small molecules.[38] Their research also confirmed the large effect of chain end-groups on thermal relaxation. Subsequently, Hawker *et al.* synthesized a series of hyperbranched poly(ether-ketones)s with a variety of functional end-groups and controllable DBs.[39] The glass transition evaluation of these HBPs showed that thermal stability of polymers was independent of macromolecular architecture, but depended heavily on the nature of functional end-groups. On the basis of the comparison of T_gs of hyperbranched polyglycerols and their esterified derivatives, Frey *et al*. proposed that the T_g of a highly polar HBP with a large number of hydroxyl end-groups was controlled mainly by two factors: the hydrogen bonding of the end-groups and the tendencies of the substituents to form higher ordered phases.[40]

With a copolymerization strategy of linear and branched comonomers, Jayakannan *et al*. synthesized a series of poly(4-ethyleneoxyl benzoate)s with different DBs.[41] They found that the introduction of branching units into linear polymers dramatically affected the glass transition. The variation of T_g with branching exhibited a minimum at a branching content of 10 mmol%, which might be related to the changes of free volume and interacting end-groups simultaneously.

Zhu *et al*. prepared a series of PEHO with variable DBs.[42] In these samples, the molecular weight, molecular weight distribution, and the end-group content were quite similar. Therefore, the direct relationship between the molecular branching architecture and T_g could be disclosed. Figure 12.4 gives the relationship between T_g and DB. For amorphous samples, T_g first increases with DB, then passes through a maximum, and finally decreases sharply. With increasing DB, the large amount of junction points in the PEHO backbone makes the molecule very compact. Therefore, the rigidity of PEHO increases and the T_g of PEHO is enhanced. On the other hand, the free volume contributed from the terminal units also increases with DB, which strengthens the molecular mobility. The competition between the junction density and the free volume of terminal units results in a maximum T_g at an intermediate DB. Following thermal treatments, the hyperbranched polyethers with various DBs exhibit quite different crystallization behaviors, which makes the relationship between the branching architecture and the T_g more complicated. When the samples are crystallized for a long time, the T_g of PEHOs decreases monotonically with DB.[42,43] The positron

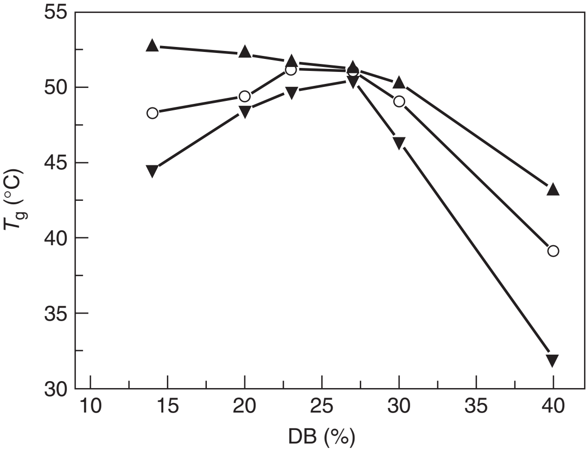

Figure 12.4 The relation between T_g and DB of PEHOs with different thermal treatments (▼: amorphous samples; O: isothermally crystallized at 90 °C for 24 h; ▲: isothermally crystallized at 90 °C for 72 h).

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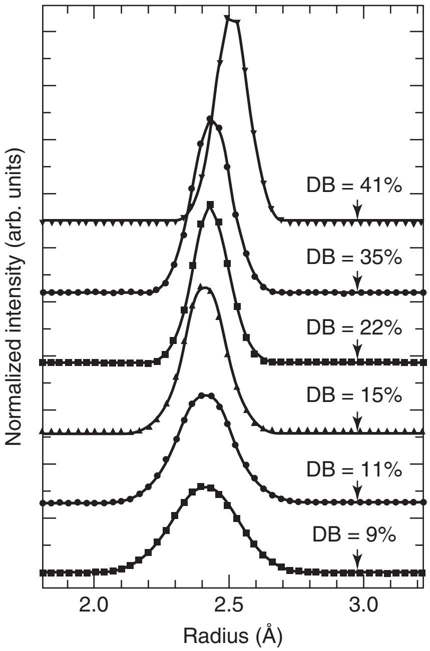

Figure 12.5 Effect of the DB on free-volume size distribution for the hyperbranched PEHO at room temperature. *Source:* Reprinted with permission from Ref. [44]. Copyright 2005, American Chemical Society.

annihilation lifetime measurements in Figure 12.5 show that the enhancement of T_g can be attributed to the low concentration of the free-volume hole.[44]

As stated above, the glass transition of HBP is different from the linear polymer, which can be affected by many factors, such as the content and chemical property of end-groups, branching junctions, compactness of hyperbranched structures, and crystallization ability.

12.2.4 Thermal and Hydrolytic Degradations

The degradation property has become an important performance indicator of temporary materials applied in biomedicine, agriculture, or structural components for reduction of the impact of synthetic functional materials upon the environment.[45–49] By using a phosphazene superbase catalyzed proton transfer polymerization and acid-catalyzed ring opening polymerization, Weber *et al*. prepared the isomeric hyperbranched polysiloxanes and highly regular linear polysiloxanes, respectively.[50] The thermogravimetric analysis of hyperbranched polysiloxane was similar to the linear one, but the former gave a higher final residue about 10% compared with almost zero of the latter. The high thermogravimetric residue might be related to the suppression of volatile cyclics' formation by branching.

Wooley *et al*. compared the hydrolytic degradation processes of linear and hyperbranched poly(silyl-ester)s (DB = 0.51).[51] They found that the degradation behavior of the HBP was very different from that of the linear one. The hyperbranched poly(silyl-ester) exhibited a slow initial molecular weight loss, followed by rapid hydrolytic cleavage. But, for a linear polymer, a rapid initial degradation rate appeared and then followed by an ever-decreasing decomposition rate. The hydrolysis difference of hyperbranched and linear poly(silyl-ester)s might be related to the existence of many silyl ether linkages at chain ends and the formation of macrocycles. Liu *et al*. used the ^{1}H NMR to monitor the hydrolysis of hyperbranched and linear poly(amino-ester)s.[52,53] Compared to the linear poly(amino-ester), the hydrolysis of hyperbranched samples was retarded due to the compact hyperbranched spatial structure preventing the accessibility of water.

12.2.5 Phase Characteristics

In 2002, Iedema *et al*. studied the dynamics of polymer-solvent liquid–liquid phase separation by using the mesoscopic dissipative particle dynamics (DPD) simulation method.[54] They found that the branching structure had a pronounced effect on the R_g and the center of mass diffusion of the polymer. For HBPs, because of a smaller difference in the chemical potential between the collapsed state of the HBP solution and the melt state, the increase in the center of mass diffusion with DB became less pronounced.

Arlt *et al*. systematically investigated the phase behavior of the HBP–solvent and the HBP–solvent–supercritical gas system.[55] After comparing the phase behavior of polymers with different DBs in the same solvent, only a small influence on the vapor–liquid equilibria (VLE) was found. However, because of a comparatively low ethanol activity in the hyperbranched polyglycerol solution, the ethanol adsorption by polyglycerol tended to increase with increasing DB.

12.2.6 Optoelectronic Properties

Conjugated polymers have attracted a great deal of attention due to their unique optoelectronic properties, good film-forming properties, and facile fabrication.[56–59] By changing the molecular architecture, the optoelectronic properties of conjugated polymers, such as emission efficiency, charge transfer, conductivity, energy transfer, and exciton migration, can be readily controlled. Owing to the existence of a strong $\pi-\pi$ interaction, the solubility of traditional linear conjugated polymers is usually poor and the aggregation-induced emission quench happens frequently. To weaken such a strong $\pi-\pi$ interaction, highly branched architecture has been introduced into the conjugated polymer systems to avoid regular molecular stacking.[60–62] On the basis of Suzuki crossing coupling, Wittig coupling, polycyclotrimerizations, and alkine coupling, various hyperbranched conjugated polymers with different branching structures have been successfully synthesized.

Hyperbranched conjugated polymers show several greater advantages than their linear counterparts in terms of high solubility, good processability, less unfavorable interaction, and absent/low crystallization ability. By introducing the branching units into the conjugated polymers, the strong $\pi-\pi$ interaction between the conjugated chains is weakened, which improves polymer solubility greatly. In the meantime, due to the decrease of conjugated length, the hypochromatic shift of maximum absorption peaks can be observed.[63,64] Compared with linear conjugated polymers in solid state, the maximum emission peak of hyperbranched conjugated polymers shows less red-shift in the photoluminescence spectra with higher fluorescence quantum efficiency.[65] This can be explained by the depression of molecular aggregation and excimer formation. After annealing at high temperature, the hyperbranched conjugated polymer shows a stable photoluminescence spectrum.[61] Furthermore, benefiting from the existence of many terminal groups in the hyperbranched conjugated polymers, the optoelectronic properties can be easily adjusted by modifying the functional end-groups or changing the intra- and intermolecular interactions of conjugated polymers.[66–68]

Nevertheless, because of the severe overlap of individual aromatic NMR signals in a very narrow range, the DBs of hyperbranched conjugated polymers are usually difficult to be determined. Therefore, the effect of DB on the optoelectronic properties of conjugated polymers is rarely reported.

12.2.7 Encapsulation Capability

The polymeric micelles of linear amphiphilic block copolymers are generally the multimolecular micelles, which will dissociate at high dilutions. In comparison, amphiphilic HBPs have been widely used as unimolecular micelles and exhibit high stability. Therefore, HBPs are used as the unimolecualr carriers to encapsulate the hydrophobic and hydrophilic guests, such as dyes, metallic ions, and nanocrystals.[69–71] Frey *et al*. prepared the esterified hyperbranched and linear polyglycerols. They found that the esterified hyperbranched polyglycerol could encapsulate the Congo Red dye very well while the linear analog lost the encapsulation capability.[72,73] Brooks *et al*. compared the encapsulation capacity of hyperbranched and linear polyglycidol unimolecular reverse micelles, and also found that the HBP had a higher encapsulation capacity than the linear one.[74] Stiriba *et al*. reported the guest encapsulation capacities of partially amidated hyperbranched and linear poly(ethylenimine)s (PEI)s in solution.[75] The compact core–shell structure in the amidated hyperbranched PEI provided a high encapsulation amount of dye in the polar interior. In contrast, the weak interaction between dyes and the secondary amines in linear PEI resulted in the low loading of dyes. All of these above mentioned results unambiguously demonstrated the crucial role of the hyperbranched topology on the encapsulation capacity.

12.2.8 Self-Assembly Behavior

The self-assembly behavior of amphiphilic HBPs is highly dependent on the DB. Zhou *et al*. synthesized a series of hydrophobic PEHO with variable DBs but similar molecular weights.[36] After that, many hydrophilic poly(ethylene oxide) (PEO) arms were grafted on to the surface of the hydrophobic PEHO core, forming the amphiphilic multiarm copolymer of PEHO-g-PEO. The obtained PEHO-g-PEOs had different branching topologies depending on the DB of PEHO cores. For the hyperbranched core, a core–shell star copolymer was obtained. On the contrary, only a comblike copolymer was formed for the linear PEHO core. If the PEHO had an intermediate DB, the topology of the PEHO-g-PEO was between the star and comb type. Thus, these amphiphilic block copolymers showed different self-assembly behaviors. With the decrease of the PEHO's DB, the self-assembly morphology of PEHO-g-PEOs was changed from vesicles, wormlike micelles, to spherical micelles.[76] Figure 12.6 gives the corresponding self-assembly morphologies.

The self-assembly behavior of plasmid DNA and cationic HBPs can also be affected by the DB.[77] Figure 12.7 gives the atomic force microscopy (AFM) images of DNA condensed by various poly(amidoamine)s (PAMAMs) with DBs from 0.44 to 0.04. Figure 12.7a shows typical plectonemic conformations of supercoiled plasmids deposited onto freshly cleaved mica in the absence of polycation. Keeping the N/P ratio as 2, various morphologies can be observed by only changing the topological structure of cationic polymers. Highly branched PAMAM forms tightly condensed nanoparticles with DNA, as shown in Figure 12.7b. With reducing DB, the particles become looser and looser, and some dendritic or large gorgonlike DNA aggregates appear (Figure 12.7c–e). For the linear PAMAM, only loose circular plasmid DNA exists in the AFM

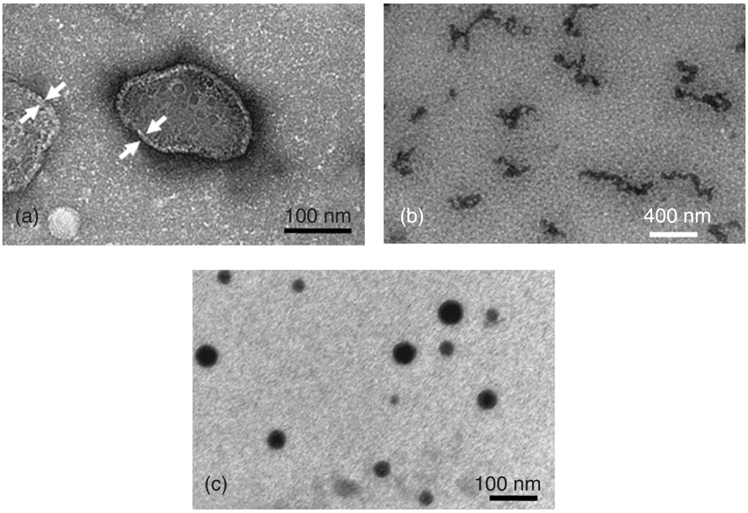

Figure 12.6 TEM photographs of PEHO-g-PEO assemblies. With the decrease of DB in PEHO cores, PEHO-g-PEOs self-assemble into (a) vesicles, (b) wormlike micelles, and (c) spherical micelles.

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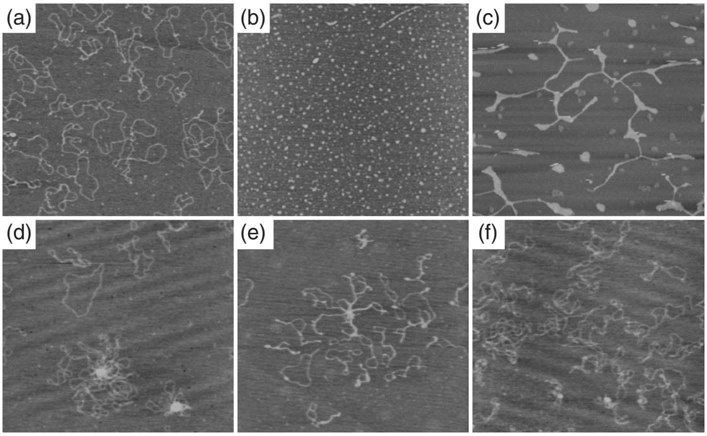

Figure 12.7 AFM images of DNA condensation by various PAMAMs. DNA was bound by polymers at $N/P = 2$. All images were obtained with complexes deposited onto fresh mica surface. Each image represents a 2×2 μm scan. (a) Pure plasmid DNA in Hepes buffer. (b)–(f) DNA binding with various PAMAMs having different branching architectures (DB = 0.44, 0.31, 0.21, 0.11, and 0.04, respectively).

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image (Figure 12.7f). Therefore, by only changing the DB of cationic vectors, the self-assembly behavior of plasmid DNA and cationic polymers can be readily controlled.

12.2.9 Biomedical Applications

Benefiting from their unique topological structure and interesting physical/chemical properties, HBPs exhibit great potential in biomedical applications. By adjusting the branching architecture of polymers, biocompatibility and other related properties will be changed. Zhu *et al*. synthesized a series of cationic PAMAMs with different branching architecture (DBs from 0.44 to 0.04) but with similar compositions and molecular weights.[77] The cytotoxicity of these PAMAMs with variable DBs was evaluated using the [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] (MTT) assay in the COS-7 cell line. It was found that the cytotoxicity of PAMAMs increased with decreasing branching architecture. The low toxicity of a highly branched PAMAM might be related to its small molecular size and compact spatial structure.

Kannan *et al*. conjugated the model drug methyl prednisolone onto a hyperbranched polyol and a PAMAM dendrimer, respectively.[78] Comparing the dendrimer, the drug payload of hyperbranched polyol was higher. More importantly, at short treatment time, the antiinflammatory activity of hyperbranched polyol conjugates was much higher than that of the dendrimer conjugates. It was believed that the imperfect branching polyol was easily uptaken into the lysosome to release the drugs, which improved the antiinflammatory activity.

The branching architecture has a remarkable influence on gene transfer. Through partial degradation of the PAMAM dendrimer into the hyperbranched one, Szoka *et al*. increased the transfection efficiency of the PAMAM dendrimer.[79] They suggested that the high transfection efficiency resulted from the enhanced molecular flexibility of the imperfect branching structure. Zhu *et al*. prepared a series of cationic PAMAMs with DBs from 0.04 to 0.44.[77] *In vitro* transfection studies in Figure 12.8 show that the transfection efficiency is improved for more than three orders of magnitude by increasing the DB of these cationic PAMAMs. On the other hand, both Kissel and Wightman reported that the transfection efficiency of linear PEI *in vitro* was greater than that of hyperbranched one.[80,81] Therefore, systematic studies on the relationship of DB and transfection efficiency are still to be explored.

Eichhorn *et al*. studied the influence of the DB on the protein adsorption potential of hyperbranched polyester films.[82] They found that with increasing DB and hydroxyl end-groups, the protein adsorption increased. To differentiate the influence of branching structure from the functional end-groups, the hydroxyl end-groups were modified. After modification, the protein adsorption behaviors of polyesters with variable DBs were quite similar. It seems to suggest that

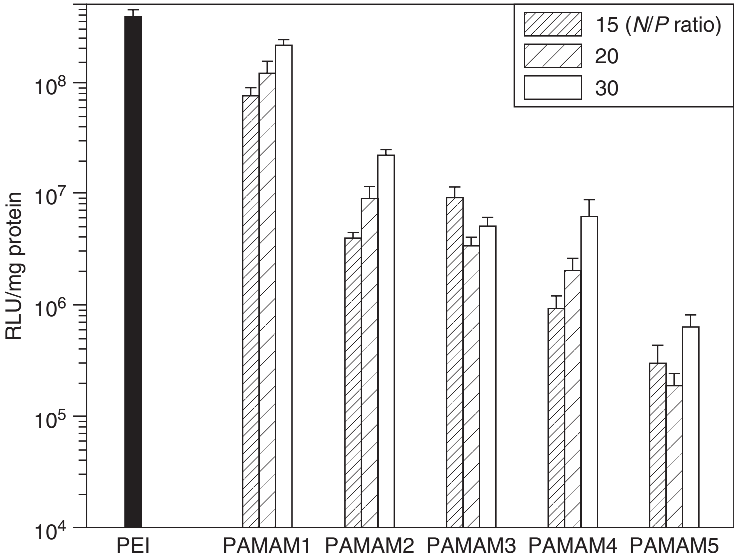

Figure 12.8 Transfection efficiency of PAMAMs (PAMAM1–PAMAM5) with different branching architecture (DB = 0.44, 0.31, 0.21, 0.11, and 0.04, respectively) in COS-7 cells at various N/P ratios. Luciferase expression levels were measured 48 h later. Data are expressed as mean ± standard deviation values of three determinations.

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the DB itself has only a small influence on the protein adsorption. However, the highly branched architecture produces a larger amount of polar end-groups, which dominate the protein adsorption.

12.3 CONCLUSIONS

As the newly emerging polymer architecture following the linear, branched, and cross-linking polymers, HBPs have attracted more and more attention in recent years. Herein, we have summarized the structure–property relationship of HBPs. As shown, many properties of HBPs, including the rheological property; the crystallization and melting behaviors; the glass transition, thermal, and hydrolytic degradations; phase characteristics; optoelectronic properties; encapsulation capabilities; self-assembly behavior; and biomedical applications, are highly related to the branching structures of the polymers. Nevertheless, due to the difficulty in controlling the DB of polymers, the studies on the structure–property relationship of HBPs are still limited. Some relationships have been widely accepted, while some of them are still controversial and need more experimental and theoretical works to support themselves. Obviously, more understanding of the field will build a bridge between the syntheses and applications of HBPs, which will lead to an enhanced controllability of the structures, properties, and applications of such promising polymers.

Acknowledgments

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Chapter 13

Kinetic Theory of Hyperbranched Polymerization

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13.1 INTRODUCTION

There are two major approaches to synthesize hyperbranched polymers from single monomers: the polycondensation of AB_g type monomers[1,2] and the self-condensation addition polymerization of vinyl/heterocyclic inimers.[3,4] In order to control the architecture and the molecular parameters of hyperbranched polymers, it is significant to develop the kinetic models for both AB_g polycondensation and self-condensation addition polymerization.

As early as in 1952, Flory[5] dealt with the polycondensation of AB_g-type monomers by means of probabilistic analysis, giving the molecular size distribution function. Hawker *et al.*[6] and Kim *et al.*[1] coined the definition of the degree of branching (DB) by comparing hyperbranched polymers with their perfectly branched analogs, dendrimers. Frey *et al.*[7] derived the expression of DB by both statistical and kinetic methods for the hyperbranched polymers made from AB_g monomers. Müller *et al.*[8] developed the kinetic theory of AB_2 polycondensation, obtaining the analytical expressions of DB, the molecular weight distribution function, and other molecular parameters. Yan and Zhou[9]

Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

reported the general kinetic model for the polycondensation of AB_g-type monomers. Galina *et al.*[10] theoretically treated the same topic by the mean-field kinetic modeling of polymerization. Beginn *et al.*,[11] Dusek *et al.*,[12] Cameron *et al.*,[13] and Cheng *et al.*[14] have studied the theoretical aspect of the related polycondensation systems as well.

The substitution effect (i.e., the reaction of the first B group in an AB_2 monomer leading to a change in reactivity of the remainder B group) was investigated by Galina *et al.*[15] and Cheng *et al.*[16] The molecular size distribution function and the DB for this case were derived by the authors of this chapter.[17] Taking account of the intramolecular cyclization, Dusek *et al.*,[12] Cameron *et al.*,[13] and Burgath *et al.*[18] have made improvements in the theory.

The molecular weight distribution of the hyperbranched polymers formed in one-pot polycondensation of AB_g-type monomers is extremely broad at high conversion, which is considered to be one of the main drawbacks of hyperbranched materials. This disadvantage can be avoided by adding a small amount of multifunctional core molecules into the polycondensation system to reduce the polydispersity index (PDI) of the resultant hyperbranched polymer according to the kinetic theory,[9,14,19,20] which has been confirmed by the experimental results.[21,22]

The polymerization of conventional AB-type monomers yields linear polymers. To obtain the branched polymer with a certain DB, a branched monomer AB_g ($g > 1$) is needed. Obviously, the DB of the copolymers formed in the copolycondensation of AB_g and AB monomers is expected to be lower than that of the hyperbranched homopolymers made from AB_g monomers, and it is tunable by controlling the feed ratio of AB_g to AB monomers. A series of hyperbranched copolymers with various architectures and rheological behaviors can be designed and prepared by adjusting the feed ratio. Kricheldorf *et al.*[23] first synthesized the highly branched polyester via the copolycondensation of AB and AB_2 monomers. The experimental data show that the properties of the resulting copolymer, such as solubility, viscosity, and glass transition temperature, and mechanical properties, are strongly dependent on the structure and the feed ratio of AB_2 to AB.[24] Generally, a small amount of AB_2 monomers can markedly improve the solubility of the resulting copolymers. Statistical theory of this copolycondensation was first reported by Flory.[5] Frey *et al.*[25] derived the DB for the random copolymerization of AB_2 and AB monomers as well as AB_g and $AB_{g'}$ monomers. The authors of this chapter and their coworkers[26] presented a kinetic analysis for the copolycondensation of AB_2 and AB monomers in detail.

The pioneer work of self-condensing vinyl polymerization (SCVP) was reported by Frèchet *et al.*[3] Then self-condensing ring-opening polymerization (SCROP) was developed simultaneously by several authors.[27] Müller *et al.*[8] theoretically dealt with the kinetics of SCVP, giving the expressions of DB, the molecular size distribution function, and other molecular parameters. Furthermore, Müller *et al.*[19,28,29] investigated the effect of core molecules as well as the self-condensing vinyl copolymerization (SCVCP) of inimers with conventional monomers, obtaining the formulae for molecular size averages.

The molecular size distribution functions for these reaction systems were derived by Yan *et al.*[30,31] Using the generating function, Cheng *et al.*[32] evaluated the influence of trifunctional cores and unequal reactivities on the molecular parameters of the hyperbranched polymers resulting from SCVP.

The vinyl monomers used in SCVP must consist of a double bond and a side group that can be activated by an external stimulus. The activation is assumed to be completed instantaneously. For the convenience of theoretical treatment, an equal feed concentration of stimulus and monomer was adopted in previous work. If the feed concentration of the stimulus is less than that of the monomer, it suggests that both inimers and monomers are present in the reaction system. Experimental data show that molecular parameters of the hyperbranched polymer made from SCVP are related to the feed ratio of stimulus to monomer.[33] The general kinetics of SCVP with stimulus/monomer ≤ 1 was developed by Zhou *et al.*[34]

The difference of reactivities between active sites A^* and B^* in SCVP has a strong effect on molecular parameters of the resultant hyperbranched polymers. The reactivity ratio of B^* and A^* can be determined by measuring the fraction of active groups A^* or B^* at any specified conversion. Taking account of the effect of unequal reactivities, Yan *et al.*[8] calculated the DB by a dummy variable z and the PDI numerically. The molecular size distribution function of such an unequal reactivity system was derived by Zhou *et al.*[35]

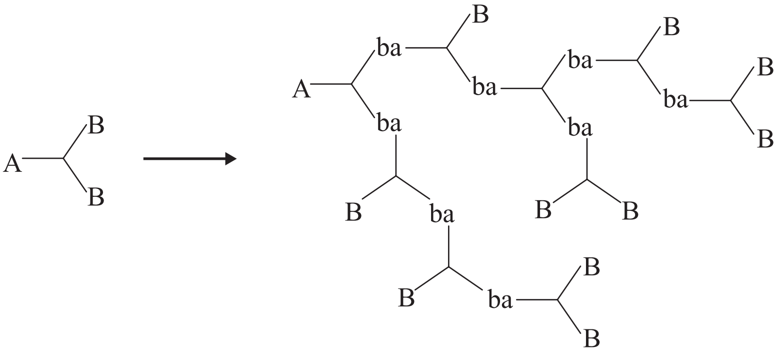
Irzhak[36] has reviewed the kinetics of the formation of hyperbranched polymers (in Russian), with attention to the dependence of critical conversion (gel point) on the kinetic conditions. Ba *et al.*[37] theoretically treated several properties of the SCVP system by the method of statistical mechanics. Two types of canonical partition functions of the system were constructed, by which the expressions of equilibrium free energy and the law of mass action were given.

Computer simulation has also been applied to gain insight into the microstructure of hyperbranched polymers.[38] For example, the change in intrinsic viscosity of hyperbranched polymers with varying topologies was estimated by computer simulation, and the AB_2 polycondensation was investigated with Monte Carlo simulation to numerically calculate the molecular weight distribution curve, the microstructure, and other molecular parameters.

This chapter focuses on the kinetics of AB_2 polycondensation, $(AB_2 + AB)$ polycondensation, and the general model of SCVP. As far as the polycondensation of $AB_{g>2}$ monomers is concerned, the kinetic theory of AB_2 polycondensation can be extended, and readers can refer to the related publications.[5,9] When the ratio of the stimulus to the monomer equals 1, all equations given by the general kinetics of SCVP degenerates into those summarized in Chapter 5. It is expected that a theoretical analysis will facilitate the molecular design of hyperbranched polymers and the control of the polymerization.

13.2 AB_2-TYPE POLYCONDENSATION

Most of hyperbranched polymers were made from AB_2-type monomers.[1,39] Here, AB_2 denotes the monomer with only one A group and two B groups. The A group



Scheme 13.1 Polycondensation of AB_2-type monomers.

can exclusively react with one of the B groups of other molecules. Scheme 13.1 shows the reaction mechanism, where the capital letters (A, B) represent the unreacted groups and the lowercase letters (a, b) stand for the reacted ones.

If the internal cyclization is absent in the polycondensation, an i-mer formed in the reaction system consists of $(i - 1)$ bonds between the reacted a and b groups, with only one residual A group and $(i + 1)$ free B groups. This rule can be found if one counts the numbers of the corresponding bonds and groups in the i-mer. The condensation of two smaller species forming a bigger one can be described as

$$P_i + P_j \longrightarrow P_{i+j}$$

where P_i symbolizes both the species with i structural units in the reaction system and its concentration.

13.2.1 Molecular Size Distribution Function

When an i-mer and a j-mer combine with each other to form an $(i + j)$-mer, the A group can react with one of the $(j + 1)$ B groups of P_j randomly. On the other hand, the A group in P_j can also react with the $(i + 1)$ B groups of P_i randomly. According to the reaction equation given above, one can find the following set of kinetic differential equations for the evolution of various species:

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \frac{k}{2}\sum_{j=1}^{i-1}\left\{(j+1)P_jP_{i-j} + (i-j+1)P_{i-j}P_j\right\} \\ - k\left\{(i+1)P_i\sum_{j=1}^{\infty}P_j + P_i\sum_{j=1}^{\infty}(j+1)P_j\right\}, \quad i = 1, 2, 3, \ldots \qquad (13.1)$$

where k is the rate constant of the reaction between an A group and a B group. The first term on the right side of Eq. (13.1) describes the formation of the species

P_i, and the negative term represents the consumption of the same species. The summation over j in the first term makes every species be counted twice; therefore a factor 1/2 is necessary.

The initial condition of Eq. (13.1) is

$$P_i\big|_{t=0} = \delta_{i,1} M_0 \tag{13.2}$$

M_0 is the initial concentration of the monomer, and $\delta_{i,1}$ is the Kronecker symbol:

$$\delta_{i,1} = \begin{cases} 1, & \text{if } i = 1 \\ 0, & \text{if } i \neq 1 \end{cases}$$

Because every species has only one A group,

$$\sum_{i>0} P_i = A \tag{13.3}$$

where italic A represents the concentration of residual A groups in the reaction system and it is just the total concentration of the molecules including the residual monomers and the polymeric species formed. From the material balance condition, it has

$$\sum_{i>0} iP_i = M_0 \tag{13.4}$$

The conversion of A groups is defined as

$$x = \frac{M_0 - A}{M_0} \tag{13.5}$$

that is,

$$A = M_0(1 - x) \tag{13.5$'$}$$

The A and B groups always react with each other in pairs, so the residual concentration of B groups is

$$B = M_0(2 - x) \tag{13.6}$$

Differentiating both sides of Eq. (13.5′) leads to

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -M_0 \frac{\mathrm{d}x}{\mathrm{d}t} \tag{13.7}$$

On the other hand, the consumption of A groups can be described by

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -kAB = -kM_0^2(1 - x)(2 - x) \tag{13.8}$$

Comparing Eq. (13.7) with Eq. (13.8) yields

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kM_0(1-x)(2-x) \tag{13.9}$$

From this equation, the relationship between A group conversion and reaction time can be derived:

$$x = \frac{2(1-e^{-kM_0t})}{2-e^{-kM_0t}} \tag{13.10}$$

Dividing Eq. (13.1) by Eq. (13.9) and substituting Eqs. (13.3)–(13.4) into it, Eq. (13.1) can be transformed into the following differential equation with x as the variable.

$$\frac{\mathrm{d}P_i}{\mathrm{d}x} = \frac{i+2}{2M_0(1-x)(2-x)}\sum_{j=1}^{i-1} P_j P_{i-j} - \left\{\frac{i+2}{2-x} + \frac{1}{(1-x)(2-x)}\right\} P_i \qquad i = 1, 2, 3, \ldots \tag{13.11}$$

Solving the equation leads to[8]

$$P_i = M_0 \frac{(2i)!}{i!(i+1)!}(1-x)(x/2)^{i-1}(1-x/2)^{i+1} \tag{13.12}$$

It is the molecular size distribution function of the products formed from the polycondensation of AB_2 monomers. From the distribution function, various molecular parameters of the hyperbranched polymers can be calculated.

The kth statistical moment of the size distribution function is defined as

$$\mu_k = \sum_{i>0} i^k P_i \tag{13.13}$$

The zeroth moment (μ_0) and the first moment (μ_1) have been expressed in Eqs. (13.3) and (13.4), respectively. The second moment reads

$$\mu_2 = \sum_i i^2 P_i = M_0 \frac{1-x^2/2}{(1-x)^2} \tag{13.14}$$

The normalized number-, weight-, and z-distribution functions of the products are respectively defined as

$$N(i) = P_i \Big/ \sum_{i=1}^{\infty} P_i, \quad W(i) = iP_i \Big/ \sum_{i=1}^{\infty} iP_i, \quad \text{and } Z(i) = i^2 P_i \Big/ \sum_{i=1}^{\infty} i^2 P_i \tag{13.15}$$

Substituting the distribution function and the corresponding moments into Eq. (13.15), one can get the analytical expressions of the normalized number-,

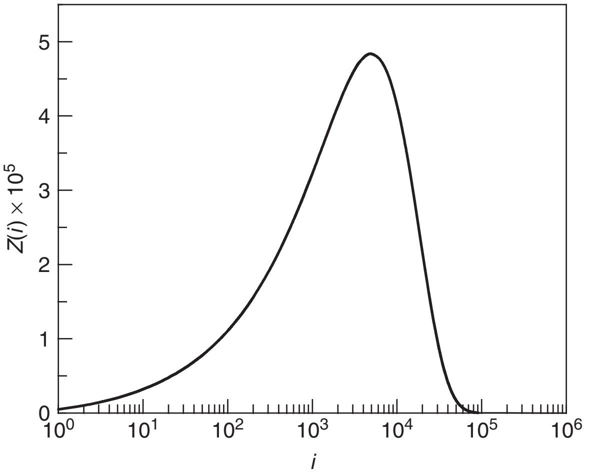


Figure 13.1 z-Distribution curves of the hyperbranched polymers made from AB_2-type monomers with $x = 0.99$.

weight-, and z-distribution functions, respectively:

$$N(i) = \frac{(2i)!}{i!(i+1)!}(x/2)^{i-1}(1-x/2)^{i+1} \tag{13.16}$$

$$W(i) = \frac{(2i)!}{(i-1)!(i+1)!}(1-x)(x/2)^{i-1}(1-x/2)^{i+1} \tag{13.17}$$

$$Z(i) = \frac{i(2i)!}{(i-1)!(i+1)!}(1-x)^3(x/2)^{i-1}(1-x/2)^{i+1}/(1-x^2/2) \tag{13.18}$$

Numeral calculation indicates that both number and weight distribution curves decline monotonously with i without any maximum when $x < 0.99$. Figure 13.1 shows the z distributions at $x = 0.99$, in which a peak appears. The molecular weight distribution is wide according to the figure.

13.2.2 Average Degree of Polymerization and Polydispersity

In accordance with the definitions of number- and weight-average degrees of polymerization and the PDI, we have

$$\overline{P_n} = \mu_1/\mu_0 = 1/(1-x) \tag{13.19}$$

$$\overline{P_w} = \mu_2/\mu_1 = (1-x^2/2)/(1-x)^2 \tag{13.20}$$

$$\mathrm{PDI} = \overline{P_w}/\overline{P_n} = (1-x^2/2)/(1-x) \tag{13.21}$$

Figure 13.2 shows the average degrees of polymerization and PDI of the products versus the conversion of A group (x). It predicates the extremely wide molecular weight distribution for the products when the reaction is close to

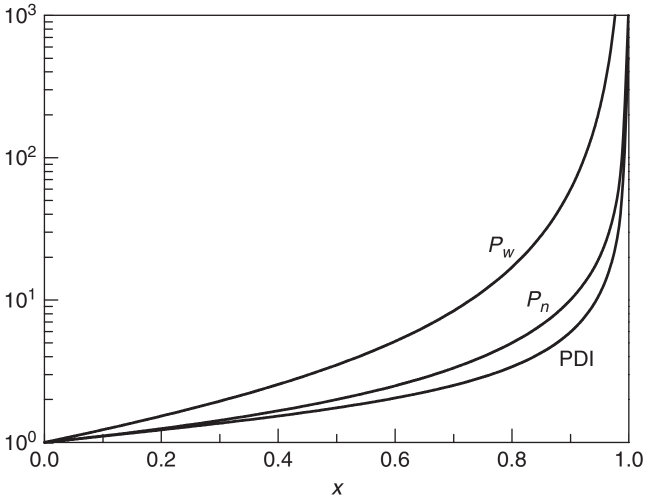


Figure 13.2 Plots of average degrees of polymerization and polydispersity index versus A group conversion for the polycondensation of AB_2-type monomers.

completion. In experiments, the low molecular weight materials (e.g., residual monomers) are usually removed from the products, and the low molecular weight part of the products plays an important role for the PDI. Thus the expressions of the number- and weight-average degrees of polymerization should be revised by subtracting the residual monomer concentration from both the numerator and the denominator:

$$\overline{P_n}' = (\mu_1 - M)/(\mu_0 - M), \quad \overline{P_w}' = (\mu_2 - M)/(\mu_1 - M) \tag{13.22}$$

where M represents the residual concentration of monomers:

$$M = P_1 = M_0(1 - x)(1 - x/2)^2 \tag{13.23}$$

The improved average degrees of polymerization and the PDI may fit the experimental data better.

13.2.3 Substitution Effect

Intuitively, higher reactivity of the B group in a linear unit favors the formation of branched units. The reactivity change after the reaction of the first B group was termed "substitution effect". For the convenience of theoretical treatment, the structural units with only one and two unreacted B groups are denoted as U_1 and U_2, respectively. The former includes AbB and abB units, and the latter is composed of AB_2 and aB_2 units. The rate constant of the reaction between A and U_1 is denoted as k_1 and that between A and U_2 as k_2. Then the reaction equations of AB_2 polycondensation with substitution effect can be set up as follows:

$$P_{i,j} + P_{n-i,l+1-j} \xrightarrow{k_1} P_{n,l}$$

$$P_{i,j} + P_{n-i,l-1-j} \xrightarrow{k_2} P_{n,l}$$

where $P_{n,l}$ denotes the n-mer with l U_1-type units. In every $P_{n,l}$ species, there is only one unreacted A group, and there are l U_1-type B groups and $(n+1-l)$ U_2-type B groups. Evidently, $(n+1-l)$ is an even number because every U_2-type unit has two B groups. If the intramolecular reaction is prohibited, the set of kinetic differential equations adapted to the reaction scheme can be written as

$$\begin{aligned}\frac{dP_{n,l}}{dt} = {} & \frac{k_1}{2}\sum_{i,j}\{jP_{i,j}P_{n-i,l+1-j} + (l+1-j)P_{n-i,l+1-j}P_{i,j}\} \\ & + \frac{k_2}{2}\sum_{i,j}\big\{(i+1-j)P_{i,j}P_{n-i,l-1-j} \\ & + [n-i+1-(l-1-j)]P_{n-i,l-1-j}P_{i,j}\big\} \\ & - k_1\left\{lP_{n,l}\sum_{i,j}P_{i,j} + P_{n,l}\sum_{i,j}jP_{i,j}\right\} \\ & - k_2\left\{(n+1-l)P_{n,l}\sum_{i,j}P_{i,j} + P_{n,l}\sum_{i,j}(i+1-j)P_{i,j}\right\}\end{aligned} \tag{13.24}$$

The index i runs from 1 to $n-1$ in the former two terms, and to infinity in the last two terms. Since $(n+1-l)$ is an even number, $(n-l)$ must be odd. So, the index j should guarantee $(i-j)$ to be odd. The initial conditions are

$$P_{1,0}\big|_{t=0} = M_0 \quad P_{n>1,l\geq 0}\big|_{t=0} = 0 \tag{13.25}$$

The material balance conditions give rise to

$$\sum_{n,l} nP_{n,l} = M_0 \tag{13.26}$$

$$\sum_{n,l} lP_{n,l} = U_1 \tag{13.27}$$

$$\sum_{n,l}(n+1-l)P_{n,l} = 2U_2 \tag{13.28}$$

According to kinetic mechanism it has

$$\frac{dA}{dt} = -(k_1U_1 + 2k_2U_2)A \tag{13.29}$$

$$\frac{dU_1}{dt} = 2k_2 U_2 A - k_1 U_1 \tag{13.30}$$

$$\frac{dU_2}{dt} = -2k_2 U_2 A \tag{13.31}$$

The initial conditions of these equations are

$$A\big|_{t=0} = M_0, U_1\big|_{t=0} = 0, \text{ and } U_2\big|_{t=0} = M_0 \tag{13.32}$$

In order to solve these equations, a dummy variable z is introduced:

$$z = k_2 \int_0^t A dt \quad \text{that is,} \quad \frac{dz}{dt} = k_2 A \tag{13.33}$$

Dividing Eqs. (13.24}, and (13.29–13.31) by Eq. (13.33) and solving the resultant equations yield[17]

$$A = \frac{M_0}{r-2}[(r-1)(2e^{-2z} - 1) + 1 - 2e^{-rz}] \tag{13.34}$$

$$U_1 = \frac{2}{r-2} M_0 [e^{-2z} - e^{-rz}] \tag{13.35}$$

$$U_2 = M_0 e^{-2z} \tag{13.36}$$

$$P_{n,l} = \frac{1 + (-1)^{n-l+1}}{2} \frac{2^l (n-1)!}{l! \left(\frac{n-l-1}{2}\right)! \left(\frac{n-l+1}{2}\right)!} A \left[\frac{e^{(r-2)z} - 1}{r-2}\right]^l \left[\frac{2(e^{-rz} - 1) - r(e^{-2z} - 1)}{r-2}\right]^{(n-l-1)/2} e^{-[(r-1)l + n + 1]z} \tag{13.37}$$

where $r = k_1/k_2$. The relationship between z and x is

$$x = 1 - A/M_0 = \frac{2}{r-2}[(r-1)(1 - e^{-2z}) + e^{-rz} - 1] \tag{13.38}$$

Equation (13.37) is just the molecular size distribution function. Its zeroth moment equals to A, and the first moment is M_0. The second moment reads

$$\sum_{n,l} n^2 P_{n,l} = \frac{(r-2)M_0}{[(1-r)(1-2e^{-2z}) + 1 - 2e^{-rz}]^2} \left\{2 - r + 2(3r-4)e^{-2z} - 4e^{-rz} - \frac{4}{r-2}\left[e^{-rz} - (r-1)e^{-2z}\right]^2\right\} \tag{13.39}$$

Figure 13.3 demonstrates the semilogarithmic weight distribution of hyperbranched polymers generated from AB_2-type polycondensation with various reactivity ratios. When $r < 1$, the semilogarithmic weight distribution has a

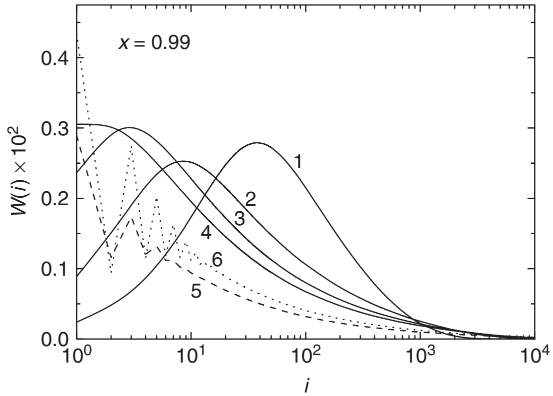


Figure 13.3 Semilogarithmic weight distribution for AB$_2$ polycondensation with substitution effect, $x = 0.99$; (1) $r = 0.01$; (2) $r = 0.1$; (3) $r = 0.5$; (4) $r = 1$; (5) $r = 5$; (6) $r = 10$.

Source: Zhou and Yan.[17]

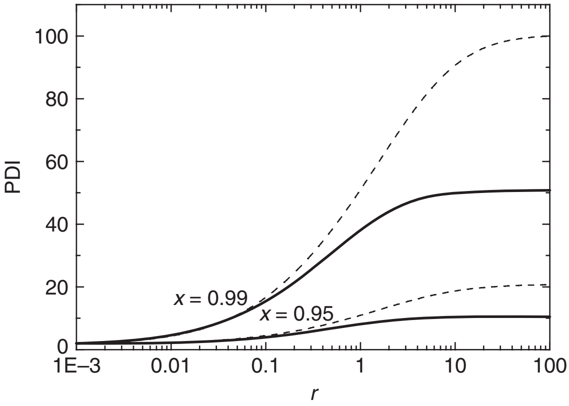


Figure 13.4 Dependence of polydispersity index on reactivity ratio for AB$_2$ polycondensation with substitution effect, dashed lines: containing residual monomers; solid lines: excluding residual monomers.

Source: Zhou and Yan.[17]

maximum, while the number distribution decreases monotonously with i. In the case of $r > 1$, the polymerization system trends to form more dendritic species and the weight distribution curves show an odd–even oscillation for the oligomer part. This is due to the fact that the second B group reacts as soon as the first B group in the same structural unit is reacted if $r > 1$. Therefore, the concentration of the species with an even degree of polymerization is low.

The substitution effect does not affect the number-average size of the products. The weight-average degree of polymerization and the PDI can be readily derived from the moments given above. At a specified conversion of A groups, the PDI of the products enhances with increasing r as shown in Figure 13.4. The reaction system with a much lower r value degenerates into the linear polycondensation and has a low PDI. The higher the value of r, the more the branched units, and the wider the molecular weight distribution.

13.2.4 Degree of Branching

A highly branched structure that contains a large number of terminal groups is the typical characteristic of hyperbranched polymers. The DB is one of the most important molecular parameters that can represent the architecture of hyperbranched polymers. Evidently, the topological structure is related to the physical properties of polymers, such as the glass transition temperature,[40] the crystallinity,[33] and the viscosity in solution or melt. In order to determine the DB, various structural units and their concentration should be examined at first. For the hyperbranched polymers generated from AB_2 monomers, the possible structural units, including linear units, terminal units, dendritic units, and initial units, are tabulated in Table 13.1.

In the case of unequal reactivities of B groups, the structural units in the resulting polymers fit with the following kinetic differential equations respectively:

$$\frac{dI_1}{dt} = 2k_2MA - k_1I_1A - I_1(k_1U_1 + 2k_2U_2) \tag{13.40}$$

$$\frac{dI_2}{dt} = k_1I_1A - I_2(k_1U_1 + 2k_2U_2) \tag{13.41}$$

$$\frac{dT}{dt} = M(k_1U_1 + 2k_2U_2) - 2k_2TA \tag{13.42}$$

$$\frac{dL}{dt} = I_1(k_1U_1 + 2k_2U_2) + 2k_2TA - k_1LA \tag{13.43}$$

$$\frac{dD}{dt} = k_1LA + I_2(k_1U_1 + 2k_2U_2) \tag{13.44}$$

Initially ($t = 0$), the concentration of the all structural units are zero. After a variable transformation by Eq. (13.33), the solutions of these equations can be obtained, which are listed in Table 13.1.

Hawker *et al.*[6] have coined a definition for the DB of hyperbranched polymers made from AB_2 monomers: DB is the ratio of the number of dendritic and terminal units to that of total units. This definition has been widely used to

Table 13.1 Structural Units in Hyperbranched Polymers Made from AB_2 Monomers

Unit	Type of the unit	Symbol	Expression
AbB	Initial unit	I_1	$\frac{2A}{r-2}(e^{-2z} - e^{-rz})$
Ab_2	Initial unit	I_2	$\frac{A}{r-2}(2e^{-rz} - re^{-2z} + r - 2)$
aB_2	Terminal unit	T	$(M_0 - A)e^{-2z}$
abB	Linear unit	L	$\frac{2}{r-2}(M_0 - A)(e^{-2z} - e^{-rz})$
ab_2	Dendritic unit	D	$\frac{M_0 - A}{r-2}(2e^{-rz} - re^{-2z} + r - 2)$

determine the DB in terms of experimental data such as nuclear magnetic resonance (NMR) spectra and chemical analysis results. Strictly speaking, a perfect definition of DB should satisfy the following conditions: (i) DB is unity for a dendrimer; and (ii) DB equals zero for a linear polymer. Evidently, the aforementioned definition does not satisfy the second condition. In fact, the initial AbB unit should be taken as a terminal unit and Ab$_2$ as a linear one for the calculation of DB. Hence a linear molecule should have two terminal groups and they should be ruled out from both the numerator and the denominator: that is,

$$\mathrm{DB} = \frac{(\text{No. of dendritic units}) + (\text{No. of terminal units}) - 2}{\text{Total no. of units} - 2} \tag{13.45}$$

When the all polymer species formed in the reaction system are considered, the average DB is

$$\overline{\mathrm{DB}} = \frac{D + T + I_1 - 2A'}{\sum_{i\,>\,1} iP_i - 2A'} \tag{13.46}$$

where

$$A' = \sum_{i\,>\,1} P_i = A - M \tag{13.47}$$

which is the total number of the polymeric species in the reaction system.

In AB$_2$ polycondensation, if a monomer bonds to a linear unit forming a new dendritic unit, a fresh terminal unit must be generated simultaneously. On the other hand, a linear macromolecule has two terminals ($T + I_1$) without any dendritic unit. In general, the number of terminal units is always equal to the number of dendritic units plus 2 in a macromolecule. Taking account of the all species in the reaction system, it has

$$D = T + I_1 - 2A' \tag{13.48}$$

Besides,

$$\sum_{i>1} iP_i = M_0 - M \tag{13.49}$$

Substituting Eqs. (13.47)–(13.49) into Eq. (13.46) yields

$$\begin{aligned}\overline{\mathrm{DB}} &= \frac{2D}{M_0 - 2A + M}\\ &= \frac{4[(r-1)(1-e^{-2z}) + e^{-rz} - 1](r - 2 + 2e^{-rz} - re^{-2z})}{(r-2)^2\left(1 - \{1 - \frac{2}{r-2}[(r-1)(1-e^{-2z}) + e^{-rz} - 1]\}(2 - e^{-2z})\right)}\end{aligned} \tag{13.50}$$

Shown in Figure 13.5 are the dependence of $\overline{\mathrm{DB}}$ on the reactivity ratio and the conversion of A groups. It reveals that the average DB increases with increasing r. When r approaches zero, a linear polymer can be obtained; if r tends to infinity, $\overline{\mathrm{DB}}$ may reach 1.

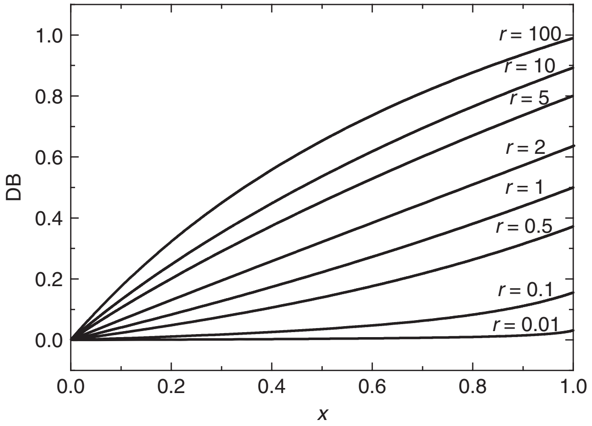


Figure 13.5 Dependence of degree of branching on A group conversion and reactivity ratio in the polycondensation of AB_2 monomers.

In the condition of $r = 1$, the reaction under consideration degenerates into an AB_2-type polycondensation with equal reactivity. Thus the expression of $\overline{\mathrm{DB}}$ is simplified to

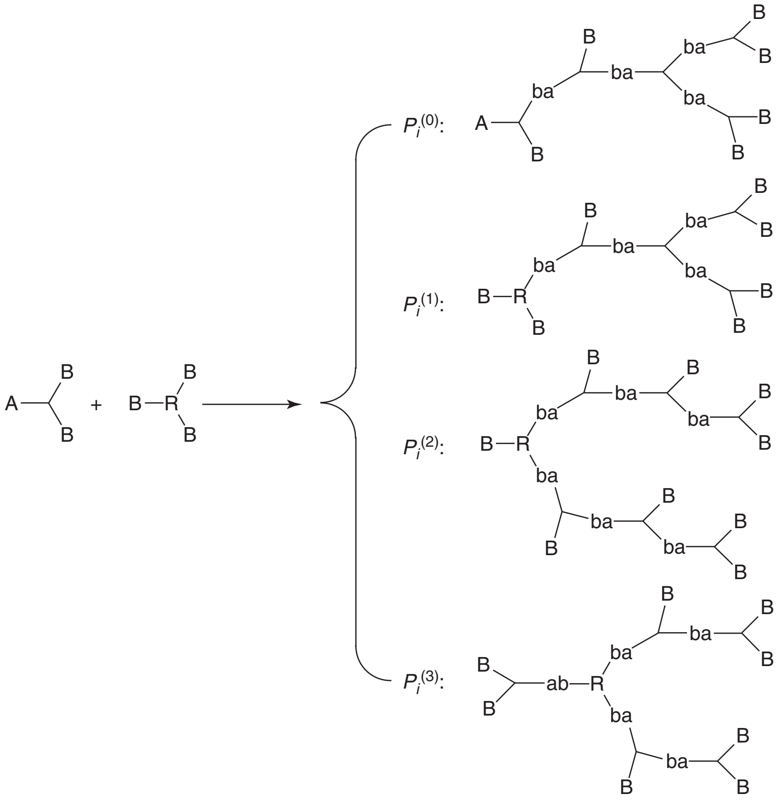
$$\overline{\mathrm{DB}}\Big|_{r=1} = \frac{2x}{5-x}. \tag{13.51}$$

It increases monotonously with increasing x and reaches 0.5 when the reaction is close to completion. It is worth mentioning that Eq. (13.51) is identical with the $\overline{\mathrm{DB}}$ expression given in Ref. [8] if the previously reported one is further simplified.

13.2.5 Effect of Core Molecules

The interest in hyperbranched polymers arises from the fact that they combine structural features of dendrimers with a much simple synthesis. However, the molecular weight distribution of hyperbranched polymers formed from one-pot polycondensation of AB_2 monomers is extremely broad at high conversion. The addition of a small number of multifunctional core molecules into the reaction system can improve considerably the PDI. A comprehensive kinetic analysis for this case has been developed.[9]

In the polycondensation of AB_2 monomers with a small number of multifunctional core molecules (RB_f, in which f is the functionality and R represents the core moiety), there are different types of species with either an initial A group or a core moiety. Scheme 13.2 shows the polycondensation of AB_2 monomers and RB_3 cores. Let $P_i^{(0)}$ represent the species with i structural units and an initial A group, and $P_i^{(l)}$ stand for the one with i structural units and a residual core binding to l branched sectors (i.e., l of the f B groups have reacted in the core molecule). There are $(i + 1)$ unreacted B groups and only one A group in a $P_i^{(0)}$



Scheme 13.2 Polycondensation of AB$_2$ monomers with trifunctional cores.

species and $(i + f)$ free B groups in total in a $P_i^{(l)}$ species, of which there are $(f - l)$ B groups in the core moiety. If the reactivity of all B groups is identical, the set of kinetic differential equations adapted to the polycondensation of AB$_2$ monomers with the core moiety reads as follows:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = -fkR\sum_{i=1}^{\infty} P_i^{(0)} \tag{13.52}$$

$$\begin{aligned}\frac{\mathrm{d}P_i^{(0)}}{\mathrm{d}t} = {} & \frac{k}{2}\sum_{j=1}^{i-1}\left[(j+1)P_j^{(0)}P_{i-j}^{(0)} + (i-j+1)P_{i-j}^{(0)}P_j^{(0)}\right] \\ & - k\left[(i+1)P_i^{(0)}\sum_{j=1}^{\infty}P_j^{(0)} + P_i^{(0)}\sum_{j=1}^{\infty}(j+1)P_j^{(0)}\right] \\ & - kfP_i^{(0)}R - kP_i^{(0)}\sum_{l=1}^{f}\sum_{j=l}^{\infty}(j+f)P_j^{(l)}\end{aligned} \tag{13.53}$$

$$\frac{\mathrm{d}P_i^{(1)}}{\mathrm{d}t} = fkRP_i^{(0)} + k\sum_{j=1}^{i-1}(j+1)P_j^{(1)}P_{i-j}^{(0)} - k(i+f)P_i^{(1)}\sum_{j=1}^{\infty}P_j^{(0)} \tag{13.54}$$

$$\frac{\mathrm{d}P_i^{(l)}}{\mathrm{d}t} = (f-l+1)k\sum_{j=l-1}^{i-1}P_j^{(l-1)}P_{i-j}^{(0)} + k\sum_{j=l}^{i-1}(j+l)P_j^{(l)}P_{i-j}^{(0)}$$
$$- k(i+f)P_i^{(l)}\sum_{j=1}^{\infty}P_j^{(0)} \quad l = 2,3,\ldots,f \tag{13.55}$$

The initial conditions for these equations are

$$R\big|_{t=0} = R_0;\ P_i^{(0)}\big|_{t=0} = \delta_{i,1}M_0;\ P_i^{(l)}\big|_{t=0} = 0, \quad l = 1,2,\ldots,f \tag{13.56}$$

where R_0 and M_0 represents the initial concentrations of the core moiety and of the AB_2-type monomers, respectively. Here the conversion of A groups (x) fit:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\frac{M_0}{\rho}(1-x)(1-\rho x) \tag{13.57}$$

where

$$\rho = \frac{1}{2+f\beta}, \quad \beta = \frac{R_0}{M_0} \tag{13.58}$$

in which ρ is the initial ratio of A to B groups and β is the molar ratio of R_0 to M_0.

Transferring the variable from t to x for these equations and solving them yield the molecular size distribution function:

$$R = R_0(1-\rho x)^f \tag{13.59}$$

$$P_i^{(0)} = \frac{M_0(2i)!}{i!(i+1)!}(1-x)(\rho x)^{i-1}(1-\rho x)^{i+1} \tag{13.60}$$

$$P_i^{(l)} = \frac{R_0 f!(2i)!}{i(l-1)!(f-l)!(i-l)!(i+l)!}(\rho x)^i(1-\rho x)^{i+f}$$
$$l = 2,3,\ldots,f. \tag{13.61}$$

The total concentration of i-mer species is

$$P_i = \sum_{l=0}^{f} P_i^{(l)} \tag{13.62}$$

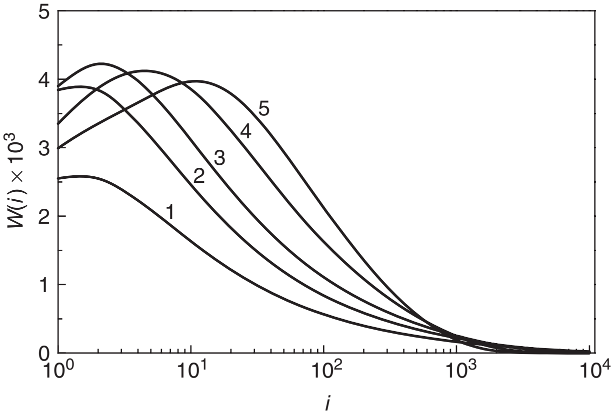


Figure 13.6 Weight distribution curves of hyperbranched polymers generated in the AB_2 polycondensation systems with $\beta = 0.01$ and $x = 0.99$. (1) $f = 0$, (2) $f = 1$, (3) $f = 2$, (4) $f = 4$, (5) $f = 6$.

Source: Yan and Zhou.[9]

The first moment of P_i is M_0, and the zeroth and second moments are, respectively,

$$\sum_{i>0} P_i = M_0(1-x) + R_0[1-(1-\rho x)^f] \tag{13.63}$$

and

$$\sum_{i>0} i^2 P_i = \frac{M_0}{(1-2\rho x)^2}\{1-[2-f(f-1)\beta](\rho x)^2\} \tag{13.64}$$

In the zeroth moment of P_i, the residual core molecules have been excluded. When the reaction approaches completion, the average molecular weight of the resulting hyperbranched polymers becomes large. Thereby the effect of the core moiety on the molecular weight can be neglected if the core is a sort of small molecules. In this case, the definitions of the normalized number-, weight- and z-distribution functions given in Eq. (13.15) are still valid. Shown in Figure 13.6 is the weight distribution curves of the total species generated in the AB_2 polycondensation with various core functionalities. It can be seen that the higher the functionality of the core, the narrower the molecular size distribution.

The number- and weight-average degrees of polymerization and the PDI read, respectively:

$$\overline{P_n} = \frac{1}{1-x+\beta[1-(1-\rho x)^f]} \tag{13.65}$$

$$\overline{P_w} = \frac{1}{(1-2\rho x)^2}\{1-[2-f(f-1)\beta](\rho x)^2\} \tag{13.66}$$

$$\mathrm{PDI} = \frac{1 - x + \beta[1 - (1 - \rho x)^f]}{(1 - 2\rho x)^2}\{1 - [2 - f(f - 1)\beta](\rho x)^2\} \tag{13.67}$$

If the core moiety is large, its molecular weight cannot be ignored, and therefore the average degrees of polymerization have to be replaced with the average molecular weights:

$$\overline{M_n} = \frac{\sum_{i>0} wiP_i^{(0)} + \sum_{i\geq 0}\sum_{l\leq f}(wi + w_R)P_i^{(l)}}{R_0 + \sum_{i>0} P_i^{(0)}} = \frac{\beta w_R + w}{\beta + 1 - x} \tag{13.68}$$

$$\begin{aligned}\overline{M_w} &= \frac{\sum_{i>0} (wi)^2 P_i^{(0)} + \sum_{i\geq 0}\sum_{l\leq f}(wi + w_R)^2 P_i^{(l)}}{\sum_{i>0} wiP_i^{(0)} + \sum_{i\geq 0}\sum_{l\leq f}(wi + w_R)P_i^{(l)}} \\ &= \frac{1}{\beta w_R + w}\left\{\beta w_R^2 + \frac{2ww_R f\rho\beta x}{1 - 2\rho x} + \frac{w^2}{(1 - 2\rho x)^2}\right. \\ &\quad \left.\left[1 - (2 - f^2\beta + f\beta)(\rho x)^2\right]\right\}\end{aligned} \tag{13.69}$$

where w and w_R represent the mass of a monomer unit and a core moiety, respectively. The PDI can be easily obtained from Eqs. (13.68) and (13.69).

Figure 13.7 demonstrates the relationship between the PDI calculated by Eq. (13.67) and the functionality of the core at full conversion. It can be seen that PDI of the final hyperbranched polymers becomes limited even if $f = 1$, while it is

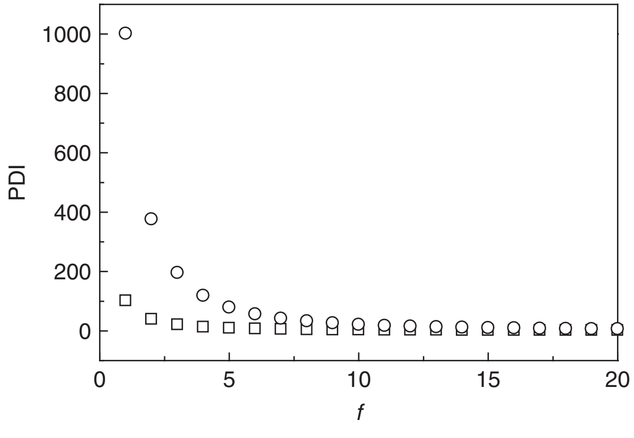


Figure 13.7 Dependence of polydispersity index on functionality of cores for AB_2 polycondensation in the presence of core molecules with $x = 1$. □, $\beta = 0.01$; ○, $\beta = 0.001$.

Source: Yan and Zhou.[9]

infinite when there is no core molecules. Thus the molecular weight distribution can be adjusted by a suitable amount of core molecules with certain functionality.

13.3 COPOLYCONDENSATION OF AB_2- AND AB-TYPE MONOMERS

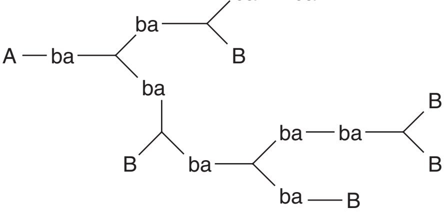
The copolycondensation of AB_2 and AB monomers can generate a highly branched or a slightly branched copolymer, which depends on the feed ratio of AB_2 to AB monomers. Hyperbranched polymers usually have poor mechanical properties because of the absence of entanglement. This is the demerit of hyperbranched materials, besides the broad molecular weight distribution. In order to enhance the mechanical properties, one of the popular approaches is the copolymerization of AB and AB_2 monomers, in which some linear segments can be incorporated into the hyperbranched polymer obtained. Experimental results show that, as the fraction of the AB monomer increases, the DB of the products decreases and the mechanical properties are accordingly improved.[24,41]

13.3.1 Molecular Size Distribution Function

The branched polymers formed by the copolycondensation of AB_2 and AB monomers possess the structure shown in Scheme 13.3. The composition of a copolymer species must be described by two indices n and l: the former is the total number of the units coming from AB_2 monomers; the latter is that from AB monomers. Thus, $P_{n,l}$ represents the concentration of the species with n AB_2 units and l AB units.

Each species $P_{n,l}$ contains an unreacted A and $n+1$ active B groups. If all functional groups have the same reactivity and the intramolecular cyclization is negligible, the set of kinetic differential equations appropriate to the copolycondensation of AB_2 and AB monomers reads

$$\begin{aligned}\frac{\mathrm{d}P_{n,l}}{\mathrm{d}t} &= \frac{k}{2}\sum_{i,j}[(i+1)P_{i,j}P_{n-i,l-j} + (n-i+1)P_{n-i,l-j}P_{i,j}] \\ &\quad - k\left[P_{n,l}\sum_{i,j}(i+1)P_{i,j} + (n+1)P_{n,l}\sum_{i,j}P_{i,j}\right]. \qquad (13.70)\end{aligned}$$



Scheme 13.3 Schematic plot of branched copolymer made from AB_2 and AB monomers.

The initial conditions are

$$P_{1,0}\big|_{t=0} = M_0, P_{0,1}\big|_{t=0} = L_0, P_{i,j}\big|_{t=0} = 0 \ (i + j > 1) \tag{13.71}$$

where M_0 and L_0 are the initial concentrations of AB_2 and AB monomers, respectively.

Let x represent the conversion of A groups still, then

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(M_0 + L_0)(1 - x)(\gamma + 1 - x) \tag{13.72}$$

where γ is the feed fraction of AB_2 monomers, that is

$$\gamma = \frac{M_0}{M_0 + L_0} \tag{13.73}$$

Making a variable transformation for Eq. (13.70) using Eq. (13.72) and solving the resultant differential equations give rise to the molecular size distribution function:[26]

$$P_{n,l} = \frac{(l + 2n)!}{l!n!(n + 1)!} \frac{(M_0 + L_0)(1 - x)(1 + \gamma - x)}{x} \left[\frac{\gamma x(1 + \gamma - x)}{(1 + \gamma)^2}\right]^n \left(\frac{1 - \gamma}{1 + \gamma} x\right)^l . \tag{13.74}$$

Equation (13.74) is a two-dimensional distribution, which depends on two indices n and l (i.e., the numbers of AB_2 and AB units). Because AB_2 and AB units have different molecular weights, we need the expressions of number- and weight-average molecular weights instead of number- and weight-average degrees of polymerization. In order to find the expressions of number- and weight-average molecular weights, we have to know various moments of $P_{n,l}$ in advance. The zeroth moment is $(M_0 + L_0)(1 - x)$. The first moments are $\sum_{n+l\geq 1} nP_{n,l} = M_0$ and $\sum_{n+l\geq 1} lP_{n,l} = L_0$. Its second moments can be derived as follows:

$$\sum_{n,l} n^2 P_{n,l} = \frac{(M_0 + L_0)\gamma}{(1 + \gamma)^2(1 - x)^2}[(1 - x)^2(1 + \gamma)^2 + 2\gamma x(2 + 2\gamma - 2x - \gamma x)] \tag{13.75}$$

$$\sum_{n,l} l^2 P_{n,l} = \frac{(M_0 + L_0)(1 - \gamma)}{(1 + \gamma)^2(1 - x)^2}[(1 - x)^2(1 + \gamma)^2 + 2(1 - \gamma)x(1 + \gamma - x)], \tag{13.76}$$

$$\sum_{n,l} nlP_{n,l} = \frac{(M_0 + L_0)\gamma(1 - \gamma)x}{(1 + \gamma)^2(1 - x)^2}(3 + 3\gamma - 3x - \gamma x) \tag{13.77}$$

The various parameters can be calculated on the basis of these moments:

$$\overline{M_n} = \frac{\sum_{n,l} (nw_2 + lw_1)P_{n,l}}{\sum_{i,j} P_{i,j}} \tag{13.78}$$

$$\overline{M_w} = \frac{\sum_{n,l} (nw_2 + lw_1)^2 P_{n,l}}{\sum_{n,j} (nw_2 + lw_1)P_{n,l}} \tag{13.79}$$

where w_1 and w_2 represent the mass of an AB unit and an AB$_2$ unit, respectively. The PDI is equal to the ratio of $\overline{M_w}$ to $\overline{M_n}$.

13.3.2 Degree of Branching

As tabulated in Table 13.2, in the copolycondensation system of AB and AB$_2$ monomers, there are three types of initial units (Ab, AbB, Ab$_2$), two types of linear units (ab, abB), two types of terminal units (aB, aB$_2$), and only one type of dendritic units (ab$_2$). Besides, there are two types of residual monomers (AB, AB$_2$).

M_1 and M_2 are just the respective $P_{1,0}$ and $P_{0,1}$ defined by the distribution function. The kinetic equations describing the evolution of the structural units can be listed, which are omitted here. The solutions are tabulated in the last column of Table 13.2. Accordingly, I$_1$ and I$_2$ can be regarded as a sort of terminal units, and I$_3$ as a linear unit. Similar to Eq. (13.46), the average DB of a branched copolymer made of AB$_2$ and AB monomers can be defined as

$$\overline{\text{DB}} = \frac{D + T_1 + T_2 + I_1 + I_2 - 2\sum_{n+l>1} P_{n,l}}{(M_0 + L_0) - (P_{1,0} + P_{0,1}) - 2\sum_{n+l>1} P_{n,l}} \tag{13.80}$$

Table 13.2 Structural Units in Hyperbranched Copolymers Made of AB$_2$ and AB Monomers

Unit	Type of unit	Symbol	Expression
AB	Residual monomer	M$_1$	$L_0(1-x)(1+\gamma-x)/(1+\gamma)$
AB$_2$	Residual monomer	M$_2$	$M_0(1-x)[(1+\gamma-x)/(1+\gamma)]^2$
Ab	Initial unit	I$_1$	$L_0x(1-x)/(1+\gamma)$
AbB	Initial unit	I$_2$	$2M_0x(1-x)(1+\gamma-x)/(1+\gamma)^2$
Ab$_2$	Initial unit	I$_3$	$M_0x^2(1-x)/(1+\gamma)^2$
aB	Terminal unit	T$_1$	$L_0x(1+\gamma-x)/(1+\gamma)$
aB$_2$	Terminal unit	T$_2$	$M_0x(1+\gamma-x)^2/(1+\gamma)^2$
ab	Linear unit	L$_1$	$L_0x^2/(1+\gamma)$
abB	Linear unit	L$_2$	$2M_0x^2(1+\gamma-x)/(1+\gamma)^2$
ab$_2$	Dendritic unit	D	$M_0x^3/(1+\gamma)^2$

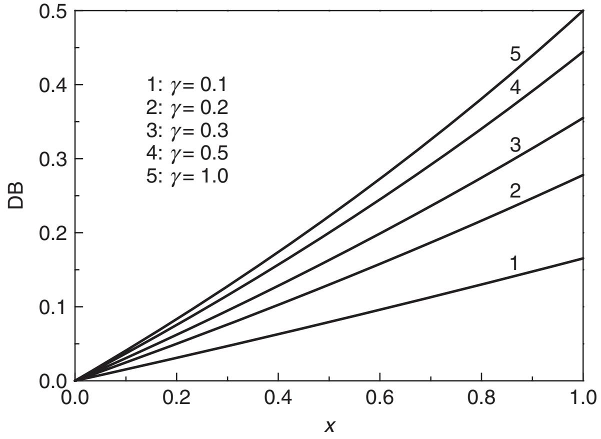


Figure 13.8 Dependence of $\overline{\mathrm{DB}}$ on γ and x for the copolymerization of AB_2 and AB monomers.

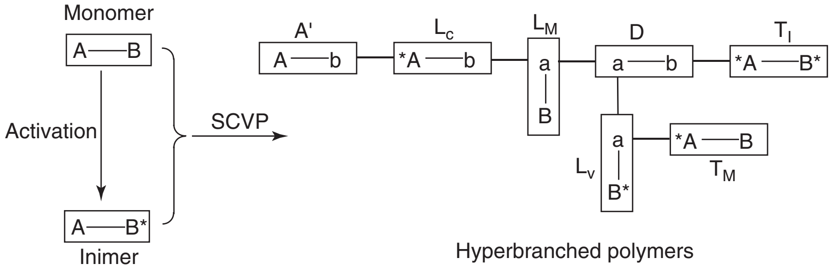
Substituting the corresponding expressions of the structural units in Table 13.2 into the equation yields

$$\overline{\mathrm{DB}} = \frac{2\gamma x}{(1+\gamma)^2 + \gamma(1-x)} \tag{13.81}$$

The $\overline{\mathrm{DB}}$ of a branched copolymer depends on the feed fraction of AB_2 and AB monomers. For the AB polycondensation ($\gamma = 0$), all species obtained are linear ($\overline{\mathrm{DB}} = 0$). In the case of polycondensation of AB_2 monomers ($\gamma = 1$), Eq. (13.81) degenerates into Eq. (13.51). According to Eq. (13.81), a series of branched polymers with various architectures and rheological properties can be designed and manufactured by adjusting the feed fraction. The dependence of $\overline{\mathrm{DB}}$ on both A group conversion and feed fraction of AB_2 monomers is provided in Figure 13.8. At any specified γ value, the $\overline{\mathrm{DB}}$ monotonously increases with increasing x, and finally reaches $2\gamma/(1+\gamma)^2$ at the end of the reaction ($x = 1$). In the meantime, $\overline{\mathrm{DB}}$ also monotonously increases with increasing γ for any x value. These dependences indicate that a moderate addition of AB_2 monomers may result in a considerable improvement in the DB by the end of the reaction.

13.4 SELF-CONDENSING VINYL POLYMERIZATION

Both SCVP and SCROP involve in an AB-type monomer. The A group is a double bond or a hetero-ring, and B is a pendent group that can be transformed into an initiating center by the reaction of B with an external stimulus. Then the AB monomer becomes the AB* type inimer. A scheme of the reaction plots for the general SCVP is given in Scheme 13.4, where A* and B* denote the derivative propagating center and the original initiating site, respectively, and “a” and “b” the respective reacted groups.



Scheme 13.4 Self-condensing vinyl polymerization.

Let M_0 be the initial concentration of AB monomers and α the initial molar ratio of stimulus/monomer. After the activation, the concentration of inimers is $M_0\alpha$ and that of the residual monomers is $M_0(1-\alpha)$. The chain initiation is the addition of active B* groups to double bonds of other inimers or monomers, and then the double bond A becomes a new active site A*. Both the initiating group B* and the newly created propagating center A* can react with the double bonds of other molecules including inimers, monomers, and polymeric species. Further polymerization results in hyperbranched polymers. The B groups attaching to the residual monomers never take part in the reaction and a monomer cannot become a branched point. So the architecture of the resultant polymer depends on the ratio of stimulus/monomer. The hyperbranched species formed in this reaction system are composed of the structural units resulting from both inimer and monomer units. Let $P_{n,m}$ denote the species consisting of n AB* inimer units and m AB monomer units. The chemical equation for the formation of this species reads as follows:

$$P_{i+j} + P_{n-i,m-j} \rightarrow P_{n,m}$$

Examining the species formed from SCVP carefully, one can find the following rules:

1. There is only one vinyl group per molecule in the reaction system.
2. There are n active centers of both A* and B* groups in each of $P_{n,m}$ species.

If the reactivity of various active sites are assumed to be identical and the intramolecular cyclization is absent, the corresponding set of kinetic differential equations describing the evolution of species are

$$\frac{\mathrm{d}P_{n,m}}{\mathrm{d}t} = \frac{k}{2}\sum_{i+j<m+n}[iP_{i,j}P_{n-i,m-j} + (n-i)P_{n-i,m-j}P_{i,j}] - k\left[nP_{n,m}\sum_{i,j}P_{i,j} + P_{n,m}\sum_{i,j}iP_{i,j}\right] \tag{13.82}$$

where k represents the rate constant of the reaction between a double bond and an active site. The initial conditions are

$$P_{1,0}\big|_{t=0} = \alpha M_0,\ P_{0,1}\big|_{t=0} = (1-\alpha)M_0,\ P_{i,j}\big|_{t=0} = 0\ i+j>1. \tag{13.83}$$

The constraint conditions lead to

$$\sum_{n+m\geq 1} nP_{n,m} = \alpha M_0 \tag{13.84}$$

$$\sum_{n+m\geq 1} mP_{n,m} = (1-\alpha)M_0 \tag{13.85}$$

Since every molecule (inimer AB*, monomer AB, or polymeric species) has only one double bond, the conversion of double bonds is defined as

$$x = \frac{M_0 - \sum_{n,m} P_{n,m}}{M_0} \tag{13.86}$$

The total number of molecules (or double bonds) in the reaction system is

$$A = \sum_{n,m} P_{n,.m} = M_0(1-x) \tag{13.87}$$

According to the kinetic mechanism, the consumption of double bonds fits

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -kA(A^* + B^*) = -k\alpha M_0^2(1-x) \tag{13.88}$$

where italic A^* and B^* represent the respective concentration of the two active sites. The total concentration of active groups is always constant and is equal to that of the initial inimers, that is

$$A^* + B^* = \alpha M_0 \tag{13.89}$$

Differentiating both sides of Eq. (13.87) and comparing it with Eq. (13.88) leads to

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k\alpha M_0(1-x) \tag{13.90}$$

Dividing Eq. (13.82) by Eq. (13.90) and substituting the related expressions into it, we can obtain a set of linear differential equations with the new variable x:

$$\frac{\mathrm{d}P_{n,m}}{\mathrm{d}x} = \frac{n}{2M_0\alpha(1-x)} \sum_{i,j} P_{i,j}P_{n-i,m-j} - \left(\frac{n}{\alpha} + \frac{1}{1-x}\right)P_{n,m} \tag{13.91}$$

13.4.1 Distribution Function and Molecular Parameters

Solving Eq. (13.91) rigorously yields the molecular size distribution function of the resulting hyperbranched polymers

$$P_{n,m} = M_0\alpha \frac{n^{n+m-1}}{n!m!}\left(\frac{1-\alpha}{\alpha}\right)^m (1-x)x^{n+m-1}e^{-nx/\alpha} \tag{13.92}$$

Various molecular parameters of the resultant hyperbranched polymers can be calculated from Eq. (13.92). If $\alpha = 1$ ($m \equiv 0$ for this case), it degenerates into the distribution function reported for the SCVP with pure inimers.[8]

Equation (13.87) is the zeroth moment of $P_{n,m}$ and Eqs. (13.84) and (13.85) are the first moments. The second moments can be derived as follows:

$$\sum_{n,m} n^2 P_{n,m} = M_0\alpha \frac{1}{(1-x)^2} \tag{13.93}$$

$$\sum_{n,m} m^2 P_{n,m} = M_0(1-\alpha)\frac{\alpha - 2\alpha x + x^2}{\alpha(1-x)^2} \tag{13.94}$$

$$\sum_{n,m} mnP_{n,m} = M_0(1-\alpha)\frac{x}{(1-x)^2} \tag{13.95}$$

The number distribution function of the hyperbranched polymers is

$$P_i = \sum_{n=0}^{i} P_{n,i-n} = \alpha M_0 \frac{1-x}{x}\left(\frac{1-\alpha}{\alpha}x\right)^i \sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}e^{-x/\alpha}\right)^n \tag{13.96}$$

The second moment of P_i reads as follows:

$$\sum_{i>0} i^2 P_i = \frac{M_0(1-x^2+x^2/\alpha)}{(1-x)^2} \tag{13.97}$$

Correspondingly, the normalized number, weight, and z distributions read as

$$N(i) = \frac{\alpha}{x}\left(\frac{1-\alpha}{\alpha}x\right)^i \sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}e^{-x/\alpha}\right)^n \tag{13.98}$$

$$W(i) = \frac{i\alpha(1-x)}{x}\left(\frac{1-\alpha}{\alpha}x\right)^i \sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}e^{-x/\alpha}\right)^n \tag{13.99}$$

$$Z(i) = \frac{i^2\alpha^2(1-x)^3}{x(\alpha+x^2-\alpha x^2)}\left(\frac{1-\alpha}{\alpha}x\right)^i \sum_{n=0}^{i}\frac{n^{i-1}}{n!(i-n)!}\left(\frac{\alpha}{1-\alpha}e^{-x/\alpha}\right)^n \tag{13.100}$$

For a low α value, there is only a small amount of inimers in the reaction system, and the inimers essentially act as the initiators, which results in slightly branched macromolecules. In this case, all of number-, weight- and z-distribution curves have a maximum. The location of the maximum depends on both α and x values. For a high α, only z-distribution shows a maximum and both number and weight distributions decrease monotonously with the degree of polymerization. Figure 13.9 diagrams the z-distribution with $x = 0.95$ and different stimulus/monomer ratios $\alpha = 0.1, 0.5$, and 1.0, respectively. The higher the value of α, the narrower the distributions.

In accordance with the definitions, Eq. (13.19) is still appropriate for the number-average degree of polymerization here. The weight-average degree of polymerization and the PDI are

$$\overline{P_w} = \frac{\alpha + x^2 - \alpha x^2}{\alpha(1-x)^2} \tag{13.101}$$

$$\text{PDI} = \frac{\alpha + x^2 - \alpha x^2}{\alpha(1-x)} \tag{13.102}$$

The distribution function also contains the information of residual inimers (I) and monomers (M) in the reaction system, of which the concentrations are

$$I = P_{1,0} = M_0\alpha(1-x)e^{-x/\alpha} \tag{13.103}$$

$$M = P_{0,1} = M_0(1-\alpha)(1-x) \tag{13.104}$$

The concentration of the polymeric species in the polymerization system is

$$A' = \sum_{i>1} P_i = M_0\alpha(1-x)(1-e^{-x/\alpha}) \tag{13.105}$$

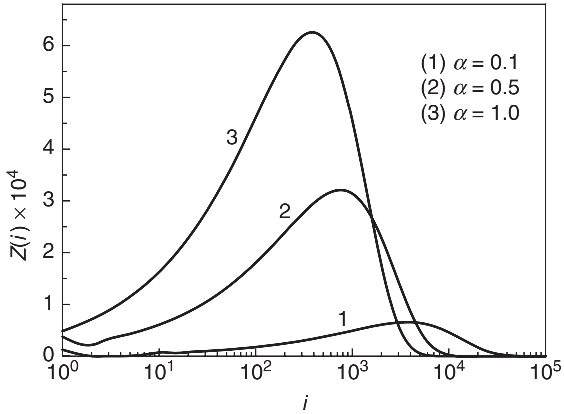


Figure 13.9 z-Distribution curves of the hyperbranched polymers generated from SCVP with $x = 0.95$. (1) $\alpha = 0.1$; (2) $\alpha = 0.5$; (3) $\alpha = 1.0$.
Source: Yan and Zhou.[34]

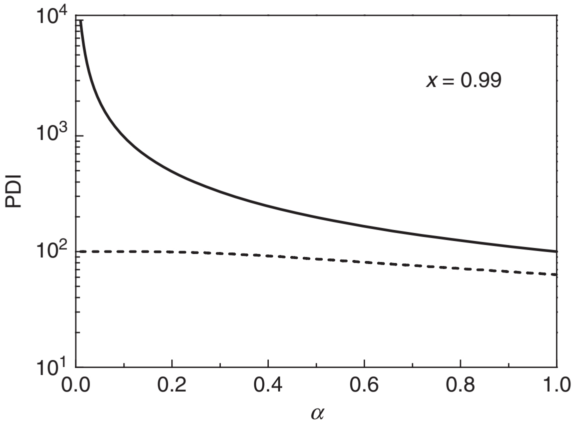


Figure 13.10 Dependence of polydispersity index on the ratio of stimulus/monomer at $x = 0.99$. Solid curve, including residual inimers and monomers; dashed curves, excluding residual inimers and monomers.

Source: Yan and Zhou.[34]

If the residual monomers and inimers are removed from the reaction system, the expressions of the average degrees of polymerization and the PDI can be improved as follows:

$$\overline{P_n{}'} = \frac{\sum_{i>1} iP_i}{\sum_{i>1} P_i} = \frac{1-(1-x)(1-\alpha+\alpha e^{-x/\alpha})}{\alpha(1-x)(1-e^{-x/\alpha})} \tag{13.106}$$

$$\overline{P_w{}'} = \frac{\sum_{i>1} i^2P_i}{\sum_{i>1} iP_i} = \frac{\alpha+x^2-\alpha x^2-\alpha(1-x)^3(1-\alpha+\alpha e^{-x/\alpha})}{\alpha(1-x)^2[1-(1-x)(1-\alpha+\alpha e^{-x/\alpha})]} \tag{13.107}$$

$$\mathrm{PDI}' = \frac{[\alpha+x^2-\alpha x^2-\alpha(1-x)^3(1-\alpha+\alpha e^{-x/\alpha})](1-e^{-x/\alpha})}{(1-x)[1-(1-x)(1-\alpha+\alpha e^{-x/\alpha})]^2} \tag{13.108}$$

The residual inimers and monomers have an important effect on the average molecular weights and the PDI. Shown in Figure 13.10 is the dependence of PDI on the feed ratio of the stimulus/monomer with the specified conversion of double bonds, $x = 0.99$. The solid curve represents the variation of PDI with α including the residual monomers and inimers, while the dashed curve denotes that excluding them. The former decreases with increasing α obviously, while the influence of α on the latter is only modest. $\bar{P}_n$ is independent of α and is equal to $1/(1-x)$, while $\overline{P_w}$ and $\bar{P}_n'$ decreases with increasing α, especially in the range of low α values. The effect of residual monomers and inimers on $\bar{P}_w$ is negligible.

13.4.2 Degree of Branching

The DB of the hyperbranched polymers generated from SCVP is tunable by the ratio of the stimulus to monomer. There are seven types of structural units incorporated in the polymeric species as shown in Scheme 13.4, which include initial units (A′), terminal units (T_I and T_M), linear units (L_c, L_v, and L_M), and dendritic units (D), respectively. Table 13.3 tabulates these units and their symbols. Units A′, T_I, L_c, L_v, and D come from inimers, and T_M and L_M from monomers.

The initial unit (A′) has been defined by Eq. (13.105). In accordance with the reaction mechanism, the evolution of other structural units as well as the active centers (A^* and B^*) fit the following kinetic differential equations, respectively.

$$\frac{dT_I}{dt} = kI(A^* + B^*) - 2kT_I A \tag{13.109}$$

$$\frac{dT_M}{dt} = kM(A^* + B^*) - kT_M A \tag{13.110}$$

$$\frac{dL_c}{dt} = kT_I A + k(A^* + B^*)A' - kL_c A \tag{13.111}$$

$$\frac{dL_v}{dt} = kA(T_I - L_v) \tag{13.112}$$

$$\frac{dL_M}{dt} = kT_M A \tag{13.113}$$

$$\frac{dD}{dt} = kA(L_c + L_v) \tag{13.114}$$

$$\frac{dA^*}{dt} = kAB^* \tag{13.115}$$

$$\frac{dB^*}{dt} = -kB^* A \tag{13.116}$$

Initially, $B^* = M_0\alpha$ and the others are zero.

Dividing these equations by Eq. (13.90) and solving them yield the analytical expressions for the units and active groups. The solutions of structural units are

Table 13.3 Various Structural Units in Polymeric Species of the General SCVP

Structural unit	Type of the unit	Symbol	Expression
A–b	Initial unit	A′	$M_0\alpha(1 - x)(1 - e^{-x/\alpha})$
A^*–B^*	Terminal inimer unit	T_I	$M_0\alpha^2 e^{-x/\alpha}(1 - e^{-x/\alpha})$
A^*–B	Monomer terminal unit	T_M	$M_0\alpha(1 - \alpha)(1 - e^{-x/\alpha})$
A^*–b	Condensation-type linear unit	L_c	$M_0\alpha^2(1 - e^{-x/\alpha})^2$
a–B^*	Vinyl-type linear unit	L_v	$M_0\alpha e^{-x/\alpha}(x - \alpha + \alpha e^{-x/\alpha})$
a–B	Monomer-type linear unit	L_M	$M_0(1 - \alpha)(x - \alpha + \alpha e^{-x/\alpha})$
a–b	Branch unit	D	$M_0\alpha(1 - e^{-x/\alpha})(x - \alpha + \alpha e^{-x/\alpha})$

listed in the last volume of Table 13.3 and those of the actives groups are

$$A^* = M_0\alpha(1 - e^{-x/\alpha}) \tag{13.117}$$

$$B^* = M_0\alpha e^{-x/\alpha} \tag{13.118}$$

Taking the initial unit (A′) as the terminal unit, the average DB ($\overline{\text{DB}}$) can be derived as below:

$$\overline{\text{DB}} = \frac{2(1 - e^{-x/\alpha})[x - \alpha(1 - e^{-x/\alpha})]}{x/\alpha - (1 - x)(1 - e^{-x/\alpha})} \tag{13.119}$$

After a variable transformation, Eq. (13.119) is conformed to that reported by Müller *et al.* for the SCVCP.[29]

The DB of hyperbranched polymers formed in SCVP is related with both α and x. Thus the $\overline{\text{DB}}$ can be controlled by adjusting the feed fraction of the stimulus. Figure 13.11 shows the dependence of $\overline{\text{DB}}$ on α at four specified double bond conversions, $x = 0.1,\ 0.4,\ 0.7$, and 1, respectively. For any specified α, $\overline{\text{DB}}$ increases monotonously with increasing x, while, at a specified x, the dependence of $\overline{\text{DB}}$ on α has a maximum. Interestingly, by a suitable α value, the DB of SCVP containing the linear AB monomer may exceeds 0.465 (the maximum $\overline{\text{DB}}$ of the SCVP with pure inimers) and reaches 0.5. The location of maximum can be found by solving the equation $\partial\overline{\text{DB}}/\partial\alpha = 0$. At the end of the reaction ($x = 1$), it yields

$$\overline{\text{DB}}_\infty = 2\alpha(1 - e^{-1/\alpha})[1 - \alpha(1 - e^{-1/\alpha})] \tag{13.120}$$

when the maximum DB reaches 0.5 under the condition of $\alpha \approx 0.627$.

Let $\alpha = 1$, and Eq. (13.119) reduced to

$$\overline{\text{DB}}\Big|_{\alpha=1} = \frac{2(1 - e^{-x})(x - 1 + e^{-x})}{1 - (1 - x)(2 - e^{-x})} \tag{13.121}$$

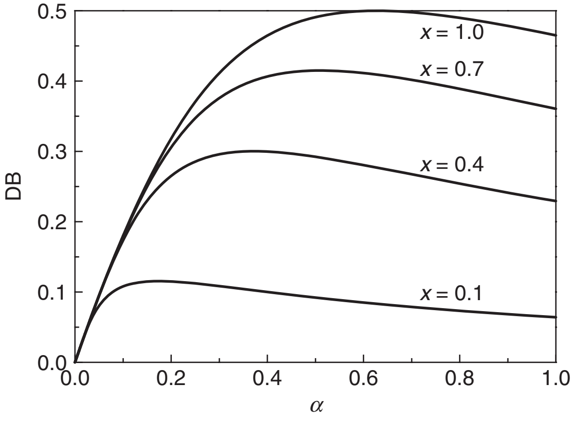


Figure 13.11 Dependence of the average degree of branching on the ratio of stumules/monomer at specified x values, 0.1, 0.4, 0.7, and 1, respectively.

Source: Yan and Zhou.[34]

which is just the DB of the SCVP discussed in Chapter 5. It increases with increasing α monotonously and ultimately reaches about 0.465.

13.4.3 Effect of Core Initiators

To narrow the molecular weight distribution for the hyperbranched polymer made from SCVP, a small amount of multifunctional core initiators (RB_f^*) is added to the reaction system. The strategy is the same as that in AB_2-type polycondensation. Let $P_{i,n}$ denote the concentration of the species consisting of n inimer units and $(i-n)$ monomer units without core, and $G_{i,n}$ denote the concentration of the species with a core initiator, n inimer units, and $(i-n)$ monomer units. If the core initiator is neglected, the degrees of polymerization of both $P_{i,n}$ and $G_{i,n}$ are i. According to the kinetic mechanism, there are exactly a double bond and n active centers ($A^* + B^*$) in every $P_{i,n}$ species, and there are $n+f$ active centers in every $G_{i,n}$ species. If the rate constants of the various active groups are assumed to be identical and the intramolecular cyclization reactions are excluded, the kinetic differential equations for the evolution of species with respect to time are

$$\begin{aligned}\frac{\mathrm{d}P_{i,n}}{\mathrm{d}t} &= \frac{k}{2}\sum_{l<i,j\le l}[jP_{l,j}P_{i-l,n-j} + (n-j)P_{i-l,n-j}P_{l,j}] \\ &\quad - k\left\{nP_{i,n}\sum_{l>0,j\le l}P_{l,j} + P_{i,n}\left[\sum_{l>0,j\le l}jP_{l,j} + \sum_{l>0,j\le l}(f+j)G_{l,j}\right]\right\}\end{aligned} \tag{13.122}$$

$$\frac{\mathrm{d}G_{i,n}}{\mathrm{d}t} = k\sum_{l<i,j\le l}(f+n-j)P_{l,j}G_{i-l,n-j} - k(f+n)G_{i,n}\sum_{l>0,j\le l}P_{l,j} \tag{13.123}$$

where k represents the reactivity between a double bond and an active site.

The initial conditions of species read as follows:

$$\begin{aligned}&P_{1,1}\big|_{t=0} = \alpha M_0, \quad P_{1,0}\big|_{t=0} = (1-\alpha)M_0, \quad P_{l,j}(l>1)\big|_{t=0} = 0 \\ &G_{0,0}\big|_{t=0} = \beta M_0, \quad G_{l,j}(l>0)\big|_{t=0} = 0\end{aligned} \tag{13.124}$$

The constraint conditions can be written as

$$\sum_{i>0,n\le i} n(P_{i,n} + G_{i,n}) = \alpha M_0 \tag{13.125}$$

$$\sum_{i>0,n\le i}(i-n)(P_{i,n} + G_{i,n}) = (1-\alpha)M_0 \tag{13.126}$$

$$\sum_{i\ge 0,n\le i} G_{i,n} = \beta M_0 \tag{13.127}$$

According to the kinetic mechanism, the conversion of A groups fit

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kM_0\lambda(1-x) \tag{13.128}$$

where

$$\lambda = \alpha + f\beta \tag{13.129}$$

Dividing Eqs. (13.122) and (13.123) by Eq. (13.128) and solving the resultant equations yield:

$$P_{i,n} = M_0\frac{n^{i-1}}{n!(i-n)!}\alpha^n(1-\alpha)^{i-n}(1-x)(x/\lambda)^{i-1}e^{-nx/\lambda} \tag{13.130}$$

$$G_{i,n} = M_0\beta\frac{f(f+n)^{i-1}}{n!(i-n)!}\alpha^n(1-\alpha)^{i-n}(x/\lambda)^i e^{-(f+n)x/\lambda} \tag{13.131}$$

These two expressions are just the molecular size distribution function of the species formed from the general SCVP in the presence of multifunctional initiators. If $\beta = 0$, Eq. (13.130) degenerates into the size distribution function reported for the general SCVP (Eq. (13.92)). The various molecular parameters can be obtained from the distribution functions. The zeroth moment of $P_{i,n}$ and $G_{i,n}$ are $\mu_0^P = \sum_{i>0,n\le i} P_{i,n} = M_0(1-x)$ and $\mu_0^G = \sum_{i\ge 0,n\le i} G_{i,n} = \beta M_0$, respectively. The first and second moments can be derived as

$$\mu_1^P = \sum_{i>0,n\le i} iP_{i,n} = M_0\frac{\lambda(1-x)}{\lambda-\alpha x} \tag{13.132}$$

$$\mu_2^P = \sum_{i>0,n\le i} i^2P_{i,n} = M_0\frac{\lambda(1-x)}{(\lambda-\alpha x)^3}[\lambda^2+\alpha(1-\alpha)x^2] \tag{13.133}$$

$$\mu_1^G = \sum_{i>0,n\le i} iG_{i,n} = M_0\frac{f\beta x}{\lambda-\alpha x} \tag{13.134}$$

$$\mu_2^G = \sum_{i>0,n\le 0} i^2G_{i,n} = M_0 f\beta x\frac{\lambda^2+f\lambda x-f\alpha x^2+\alpha(1-\alpha)x^2}{(\lambda-\alpha x)^3} \tag{13.135}$$

The normalized number, weight, and z distributions of the molecular size read

$$N(i) = \frac{\sum_{n\le i}(P_{i,n}+G_{i,n})}{M_0(1-x+\beta)} \tag{13.136}$$

$$W(i) = \frac{1}{M_0}\sum_{n\le i} i(P_{i,n}+G_{i,n}) \tag{13.137}$$

$$Z(i) = \frac{(\lambda-\alpha x)^2M_0}{M_0[\lambda^2+\alpha(1-\alpha)x^2+f^2\beta x^2]}\sum_{n\le i} i^2(P_{i,n}+G_{i,n}) \tag{13.138}$$

Figure 13.12 shows the number distribution of the products, with $x = 0.99, \beta = 0.01$, $\alpha = 0.1$, and several f values, 0, 1, 2, and 5, respectively. A particular feature is that the distribution curve is bimodal when $f > 1$. It means that the products consist of two clusters. One is the group of $P_{i,n}$ species, and the other is that of $G_{i,n}$ species. The total number distribution changes from bimodal to monomodal by increasing the fraction of the stimulus, and there is no peak at high values of α. Shown in Figure 13.13 is the z-distribution curves at $f = 3, x = 0.99, \beta = 0.01$, and for several α values. The lower the α value, the narrower the molecular weight distribution.

The average degree of polymerization and PDI are

$$\overline{P_n} = \frac{1}{1 - x + \beta} \tag{13.139}$$

$$\overline{P_w} = \frac{\lambda^2 + \alpha(1-\alpha)x^2 + f^2\beta x^2}{(\lambda - \alpha x)^2} \tag{13.140}$$

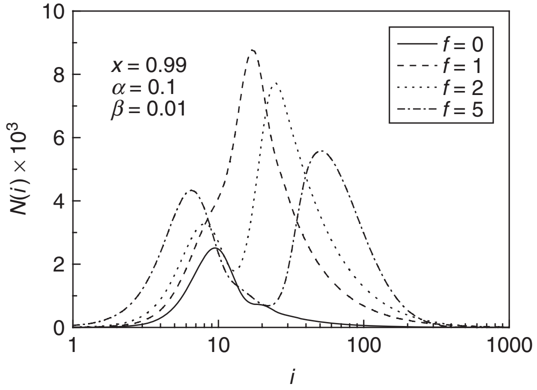


Figure 13.12 The number distributions of the hyperbranched polymers formed from general SCVP in presence of multifunctional cores, with $x = 0.99, \beta = 0.01$, and $\alpha = 0.1$, at the specified values of $f = 0$ (solid line), 1 (dashed line), 2 (dotted line), and 5 (dash-dotted line), respectively.

Source: Yan and Zhou.[34]

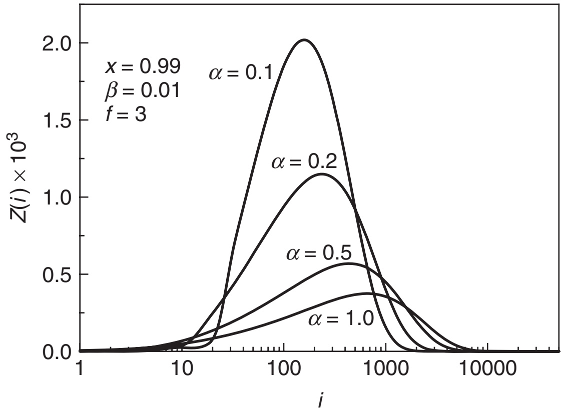


Figure 13.13 The z distributions of the hyperbranched polymers formed from general SCVP in presence of multifunctional cores, with $x = 0.99, \beta = 0.01$, and $f = 3$, at the specified values of α : 0.1, 0.2, 0.5, and 1.0.

Source: Yan and Zhou.[34]

$$\mathrm{PDI} = \frac{(1 - x + \beta)[\lambda^2 + \alpha(1 - \alpha)x^2 + f^2\beta x^2]}{(\lambda - \alpha x)^2} \tag{13.141}$$

Equation (13.139) includes the residual core initiators. The PDI of the products initially increases with increasing x and decreases after a maximum. The location of the maximum depends on the value of α. The lower the value of α, the earlier the maximum appears, as shown in Figure 13.14.

The molecular weight of the $P_{i,n}$ species is $[nw_I + (i - n)w_M]$ and that of the $G_{i,n}$ species is $[nw_I + (i - n)w_M + w_G]$, where w_I, w_M, and w_G denotes the respective mass of the inimer, monomer, and core initiator. Hence, the number- and weight-average molecular weight of the products formed are

$$\overline{M}_n = \frac{\sum_{i,n} [nw_I + (i - n)w_M](P_{i,n} + G_{i,n}) + w_G \sum_{i,n} G_{i,n}}{\sum_{i,n} (P_{i,n} + G_{i,n})} \tag{13.142}$$

$$\overline{M}_w = \frac{\sum_{i,n} [nw_I + (i - n)w_M]^2 P_{i,n} + \sum_{i,n} [nw_I + (i - n)w_M + w_G]^2 G_{i,n}}{\sum_{i,n} [nw_I + (i - n)w_M](P_{i,n} + G_{i,n}) + w_G \sum_{i,n} G_{i,n}} \tag{13.143}$$

At the end of the reaction, the PDI reads

$$\mathrm{PDI} = \frac{1}{f^2\beta}[(2f\beta + 1)\alpha + f^2\beta(1 + \beta)] \tag{13.144}$$

It increases linearly with the increase of α at the specified f and β, and the slope decreases with increasing f. As for the dependence of the PDI on β, it decreases with increasing fraction of core initiator if $\beta < \sqrt{\alpha}/f$. Otherwise, it increases monotonously.

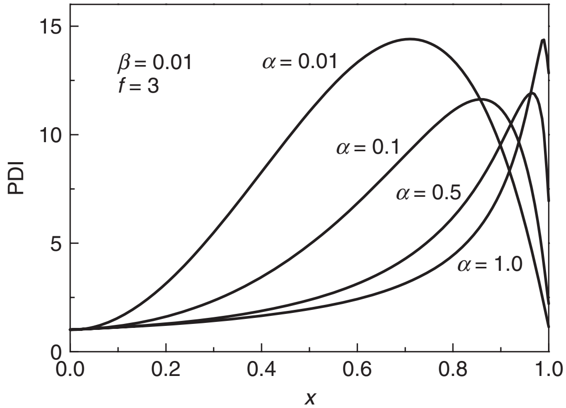


Figure 13.14 The dependence of polydispersity on x with $f = 3$ and $\beta = 0.01$, at the values of $\alpha = 0.01$, 0.1, 0.5, and 1.0, respectively.

Source: Yan and Zhou.[34]

Acknowledgments

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Chapter 14

Grafting and Surface Properties of Hyperbranched Polymers

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14.1 INTRODUCTION

The placement of hyperbranched polymers on solid substrates is required for a variety of prospective applications of these materials for sensing, catalysis, fouling, selective binding, and lubrication. The reorganization of the internal structures of hyperbranched macromolecules deposited/grown on different solid substrates is responsible for variable physical properties of these modified surfaces. Surface composition and, hence, the surface energy, adhesion, friction, and wettability can be "tuned" to a desired physical state by designing proper chemical architecture and component mobility.[1–3] Ultimately, this provides a means for the fabrication of on-demand switchable properties such as self-cleaning abilities and switching from ultrahydrophobic to ultrahydrophilic behavior and back.[4,5]

Stimuli-responsive surfaces can be designed by using a variety of approaches including reversible photoisomerization reaction of grafted photochromic segments, reversible swelling/collapse of water-soluble grafted polymers, and phase separation in mixed polymer brushes or diblock copolymers.[6–8] Recent sophisticated designs resulted in the preparation of surface polymer layers with unique adaptive properties such as reversible switching of surface properties under solvent or temperature treatments.[9–11] For these systems, different conformational

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

changes of dissimilar polymer chains A and B with high molecular weights randomly tethered to a solid surface resulted in dramatic structural reorganization upon exposure to different environments.[12,13] Other examples include self-assembled amphiphilic block copolymers, surfactants, cross-linkable polymers, dendrimers, microemulsions, latex particles, and biomacromolecules.

Surface layers from dendrimers have been fabricated and studied since the mid-1990s.[14–18] More recently, Xiao and coworkers have created thin films from $SiCl_3$-terminated dendrons on mica.[19] The study of dendrimers at interfaces has been expanded in the direction of *in situ* experiments at the liquid–solid interface and the air–liquid interface. Van Duijvenbode and coworkers fabricated surface layers from five generations of 1,4-diaminobutane poly(propyleneimine).[20] Muller *et al.* have used atomic force microscopy (AFM) in liquids to study the adsorption kinetics of high-generation poly(amidoamide) (PAMAM) dendrimers on different substrates.[21] Sui *et al.* used environmental scanning electron microscopy to confirm the edge-on orientation of the amphiphilic dendrimers at the air–water interface.[22] Unlike several studies conducted on dendrimers, very few studies are focused on placing/growing hyperbranched molecules with different core and peripheral groups in order to control and modify the physical properties of the substrates.

This chapter presents the overall review of the existing grafting approaches as applied to hyperbranched polymers and discusses the surface behavior of hyperbranched molecules tethered to various surfaces. We focus on the recently developed strategies for grafting various hyperbranched macromolecules and the corresponding characterization of the resulting surface morphologies and structures.

14.2 SURFACE GRAFTING

The modification of the appropriate surfaces with hyperbranched polymers can be done either by the “grafting from” (Route 1 and 2) or the “grafting to” (Route 3) approaches (Figure 14.1). Both approaches involve either covalent or noncovalent tethering of the hyperbranched macromolecules onto the surface via appropriate linkages (Figure 14.1). All grafting routes start by introducing proper functional groups (X) onto the surface by using a variety of chemical reactions such as oxidation or surface modification with self-assembled monolayers (SAMs). The grafted hyperbranched polymers are typically anchored to a surface by one branch or by the core, such that the whole molecule extends away from the surface (Figure 14.1).

Route 1 is a step-by-step method, which is widely used in the synthesis of highly branched surfaces (Figure 14.1). The procedure starts with the reaction of AB_2 monomers with the X groups (often carboxylic acid or amino groups), followed by the reaction of CD monomers with the B groups attached and repeating the reaction between AB_2 and CD (Figure 14.1). By this method, a large amount and high concentration of the functional groups can be introduced onto the surface. A similar method that involves multifunctional polymers as a monomer is

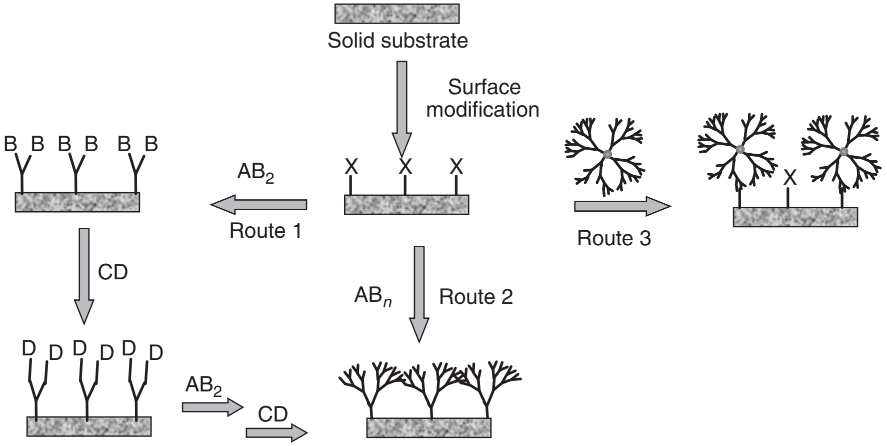

Figure 14.1 General routes of grafting of hyperbranched polymers.

called a *graft-on-graft approach*, which often includes an additional activation step.

The "Grafting from" approach can be used in Route 2, which involves the surface initiating the polymerization (Figure 14.1). Depending upon the nature of the surface, functional groups presented several different polymerization routines that can be exploited. The most popular techniques include step polycondensation, radical polymerization, and ring-opening polymerization (ROP). First two polymerization routines initiate the reaction of the AB_n type (mostly AB_2 or ABB').

On the other hand, Route 3, which represents a "grafting to" approach is used for a covalent or noncovalent tethering of the preformed hyperbranched polymers to a proper functionalized surface (Figure 14.1). Usually, it involves the reaction of the hydroxyl or amino-terminated groups with carboxyl or epoxy groups with the formation of covalent bonds. Alternatively specific and nonspecific interactions such as Van der Waals, hydrogen bonding, or Columbic interactions can be used for relatively weak physical grafting.

14.2.1 "Grafting from" Approach

14.2.1.1 Step-by-Step Methodology

The step-by-step methodology is widely used to synthesize a variety of highly branched polymers on various surfaces. Tsubokawa and Takayama have introduced this approach to functionalize natural polymers such as chitosan.[23] It was found that the hyperbranched PAMAM structure was propagated from the chitosan surface by repeating two steps: (i) Michael addition of methyl acrylate (MA) to amino groups at the surface and (ii) amidation of the resulting esters with ethylenediamine (EDA) (Figure 14.2). Owing to heterogeneous conditions

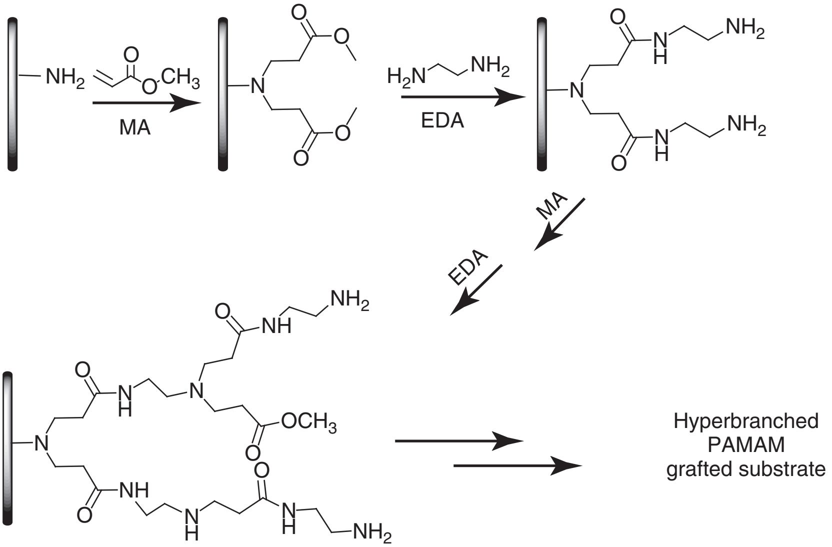

Figure 14.2 General route for the step-by-step grafting methodology for hyperbranched PAMAM surface layer.

and steric hindrances this technique resulted in PAMAM hyperbranched modification of the chitosan. Further postgrafting of the hydrophilic poly(2-methyl-2-oxazoline) and hydrophobic poly(isobutyl vinyl ether) to the hyperbranched grafted layer allowed to control the wettability of the chitosan surface.

Moreover, the step-by-step methodology has been expanded for the functionalization of other inorganic and organic surfaces. For example, Fujiki *et al.* have described the chemical grafting of hyperbranched PAMAM polymers onto highly curved inorganic surfaces such as glass, alumina, and carbon fibers.[24,25] Significant alternation of the wettability of the polymer-grafted inorganic fiber surface was observed in all cases. These researchers also applied this methodology for the grafting of hyperbranched polymers onto silica nanoparticles preliminarily treated with 3-glycidoxypropyl trimethoxysilane.[26,27] Scale-up synthesis of hyperbranched PAMAM grafted onto ultrafine silica nanoparticles was successfully achieved by Murota *et al.* in a solvent-free dry system.[28] Furthermore, the postgrafting polymerization of different monomers onto PAMAM-modified silica nanoparticles resulted in polymer-inorganic nanoparticles with high grafting density, which in some cases was shown to be suitable for solar cell technologies.[29,30]

Finally, Tsubokawa *et al.* have the broadened applications for the grafting of hyperbranched PAMAM by exploring carbon black[31] and polystyrene surfaces.[32] Nakada *et al.*[33] applied a similar approach to the modification of the ultrahigh molecular weight polyethylene (PE). After repeating the grafting cycle several times, they produced an ultathin surface film, which possesses anion exchange capacity and absorbs acid dyes. Similar to the step-by-step method, Gao *et al.* have applied an *in situ* polycondensation approach to functionalize multiwall carbon nanotubes (MWNTs).[34] The polyurea-coated MWNTs showed interesting self-assembling behavior with flower-like morphologies in the solid state. These studies demonstrate the versatility of the step-by-step approach and open new ways for the functionalization of a variety of technologically important surfaces.

14.2.1.2 Graft-on-Graft Technique

The step-by-step technique described in the previous section has significant disadvantages for practical use: one of them being a small increment of the growing thickness of the grafted layer per single step, which limits the overall thickness of the surface layers. To overcome this problem, Crooks *et al.* have developed a new technique by using a single macromolecule as a monomeric unit for growing a hyperbranched film. The synthetic procedure suggested starts with an activation of a gold substrate with a monolayer of mercaptoundecanoic acid (MUA) as an intermediate adhesive layer.[35] The carboxylic acid groups were activated via a mixed anhydride followed by the reaction with a diamino-terminated poly(*tert*-butyl acrylate) (H_2N-P*t*BA-NH_2) (Figure 14.3). This reaction resulted in the grafted polymer layer, whose *t*Bu ester groups were further hydrolyzed to create

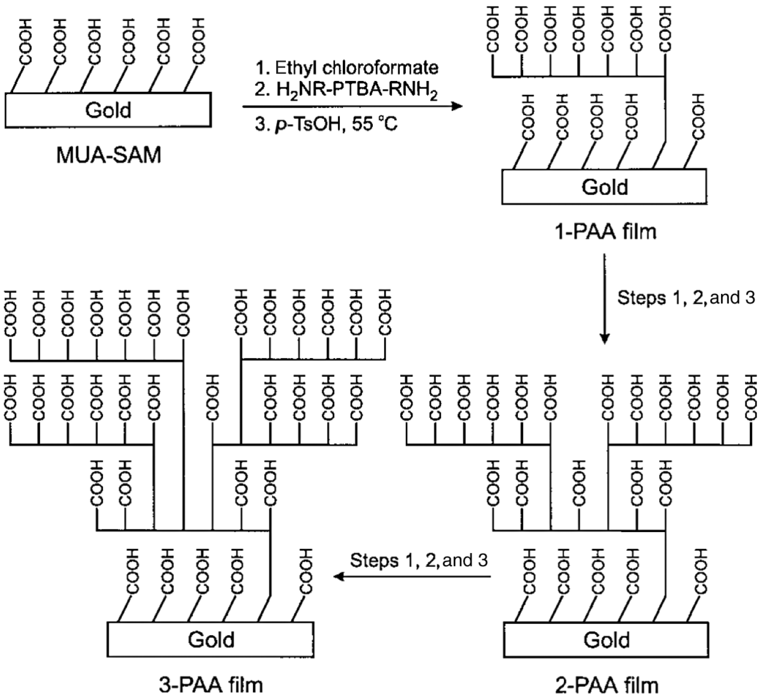

Figure 14.3 The preparation of the hyperbranched PAA surface layer on a gold substrate.[37] *Source:* Reprinted with permission from the American Chemical Society, 1998. Copyright © 2007 by John Wiley & Sons, Inc.

the grafted poly(acrylic acid) (PAA) surface layer. The repetition of these steps yielded additional grafting at multiple sites on each previous graft, leading to a multilayered, hyperbranched polymer film with significant thickness. The PAA film thickness and roughness increased rapidly with the number of grafting steps and following modification.[36]

The substitution of the MUA intermediate layer with $HS(CH_2)_{10}C{\equiv}C{-}C{\equiv}C(CH_2)_{10}COOH$, which polymerizes under UV light, led to the polymer films that are stable even under aggressive external conditions.[38] Further modification of the obtained hyperbranched PAA films through amide or ester linkages could be applied to produce novel films containing a high density of a variety of internal and external functional groups.

In further development, Crooks *et al.* reported the synthesis and the surface passivation properties of hydrophobic surface layers.[39] They have been formed from highly fluorinated, hyperbranched PAA films. These films blocked the electrochemical reactions on gold electrodes, which made them attractive for corrosion-inhibiting coatings.[40] Selective functionalization of the carboxylic groups could also produce the hyperbranched surface films, which are able to reverse sorption of the polyvalent cationic polyelectrolytes.[37] This leads to the formation of ionic nanocomposite polyelectrolyte surface filmsthat can be used as a host matrix in biosensors.[41]

In another twist, Bruening *et al.* applied the graft-on-graft deposition techniques described above to produce hyperbranched PAA membranes on porous alumina supports.[42] They observed that even ultrathin hyperbranched PAA films (40-nm thick) could efficiently cover underlying microscopic pores without filling them.

Bergbreiter *et al.* utilized the graft-on-graft method to build robust and thin hyperbranched PAA films on PE surfaces.[43] Similar to the work described above, diaminopoly(*tert*-butyl acrylate) was attached to the oxidized PE surface with carboxylic acid functional surface groups obtained by the oxidation with $CrO_3{-}H_2SO_4$. The resulting grafted surface film exhibited high efficiency for further modification of PE. Furthermore, it has been demonstrated that by using hyperbranched grafting chemistry the PE particles can be functionalized with carboxyl groups.[44] The modified powders retained the physical properties of the PE material itself. Another approach utilized the polyvalent hyperbranched PAA grafts on the gold surface or the PE surface. A soluble hydrogen bond acceptor polyacrylamides, such as poly(*N*-isopropylacrylamide) was used for a mild hydrogen bond–based grafting method.[45] This hydrogen-bonded polymeric ensemble was stable to extensive washing and addition of an external acid.

In another example, the chemical modification of polypropylene (PP) surfaces by chemical grafting with the hyperbranched PAA surface layer was carried out by using grafting techniques described above for gold, aluminum, silicon, and PE surfaces.[46] Selective treatment of the activated surfaces by pentadecylfluorooctylamine allowed the alternation of the surface properties from initially hydrophilic to completely hydrophobic.

As a next step, Bergbreiter *et al.* have introduced new synthetic methods for modifying the carboxylic acid groups of hyperbranched surface films.[47] Various procedures such as amidation, esterification, reduction, and alkylation reactions of carboxylic acid groups were used to generate functional surfaces not accessible by graft polymerization. Moreover, the oligomerization of covalently attached thiophene monomers with $FeCl_3$ resulted in conjugated fluorescent oligothiophenes within hyperbranched PE grafts.[48] An alternative approach used acrylic acid and Ce(IV) to assist graft-on-graft chemistry.[49] After the functionalization of the oxidized PE surface with the polyhydroxylated oligomer, the hydroxyl surface groups were successively grafted with Ce(IV) and acrylic acid. The resulting carboxylic acid surface groups were converted into hydroxyl groups. The Ce(IV) method appears to be more appropriate for the fabrication of more densely packed surface films. Moreover, the method itself is faster than the graft-on-graft technique and allows producing graft copolymers with a suitable combination of monomers.

Finally, due to the relative simplicity and the reproducibility of the graft-on-graft techniques, a variety of methods were introduced to produce patterned surface films, which could be exploited for the preparation of new sorts of functional nanocomposites for prospective sensor applications. One of the novel methods recently introduced relied on the passivation of the reactive surface on plastic substrates by microcontact printing (μ-CP) followed by polymer grafting to activated surface areas.[50] Another approach particularly useful for the modification of gold-coated substrates is based on the μ-CP of a passivating monolayer (*n*-hexadecanethiol), deposition of the MUA, followed by hyperbranched polymer grafting and subsequent functionalization.[51]

14.2.1.3 Radical Polymerization

Recent advances in control radical polymerization allowed sophisticated synthesis of the well-defined functionalized polymers with different macromolecular architectures grafted onto the solid substrate.[52] Mori and Muller have summarized current developments in the synthesis and characterization of hyperbranched (meth)acrylates at the surfaces.[53] They described a novel synthetic concept for the preparation of hyperbranched polymers on a planar surface (Figure 14.4).

A silicon wafer modified with an initiator layer was used for a self-condensing vinyl polymerization (SCVP) via atom transfer radical polymerization (ATRP).[54] Analysis of the surface morphology with AFM imaging (Figure 14.4) revealed the presence of a large number of nanoscale protrusions with size, density, and the heights dependent upon the conditions of the polymerization and assigned to the grafted macromolecules.

In another development, Nakayama *et al.* have demonstrated a novel strategy to grow multigeneration hyperbranched graft architecture (Figure 14.5).[55]

Two different types of hyperbranched grafts of a third generation were sequentially prepared by photolysis of the benzyl *N*,*N*-diethyldithiocarbamate (DC) group (Figure 14.5). The authors suggested that the increased density of

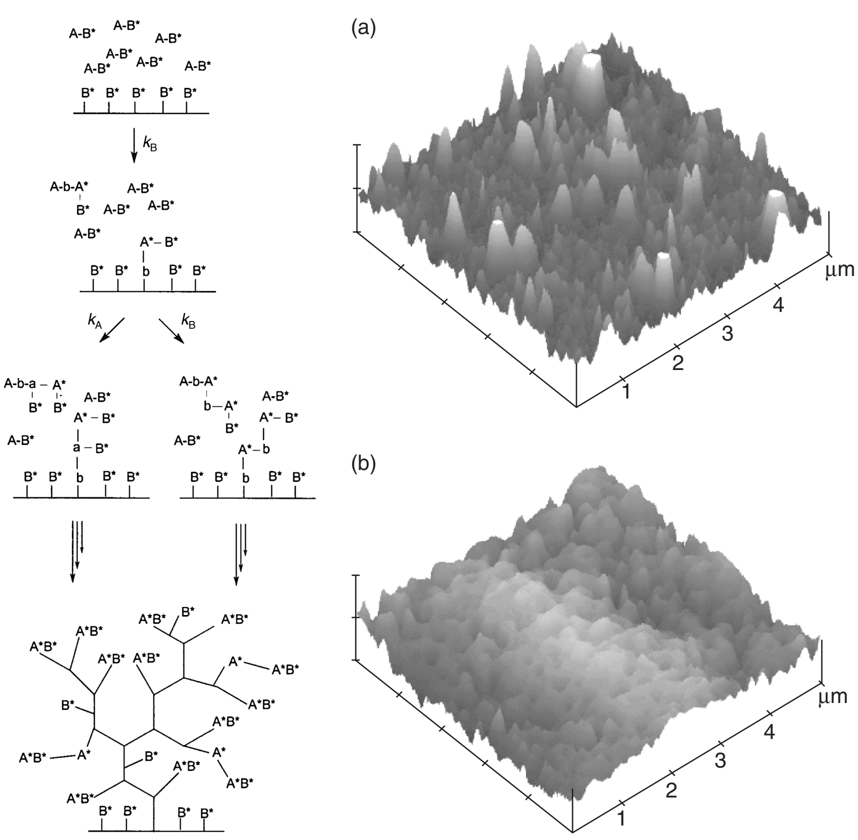

Figure 14.4 The surface-initiated SCVP (left) and 3D topographical images (right) of the grafted polymers obtained from (a) copolymerization of BPEA and *t*BuA and (b) homopolymerization of *t*BuA. The height is 30 nm.[54]

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graft chains, the configuration, or topology of hyperbranched architectures all could control surface mechanical properties, which were expected to be different from those known for grafted linear chains.

Recently, the growing of hyperbranched polymers by SCVP has been expended on highly curved inorganic surface such as silica nanoparticles[56] and MWNTs.[57] Hydrolysis of the ester functional groups of branched poly(*tert*-butyl acrylate) (P*t*BA) chains created novel core–shell nanostructured materials. On the other hand, Tsubokawa *et al.* investigated the grafting of polymers having pendant peroxycarbonate[58] or azo[59] groups onto ultrafine silica nanoparticle surfaces. They found that the chemical grafting of mixed or uniform hydrophilic (poly(2-hydroxyethyl methacrylate), PHEMA and poly(vinyl pyrrolidone), PVP)

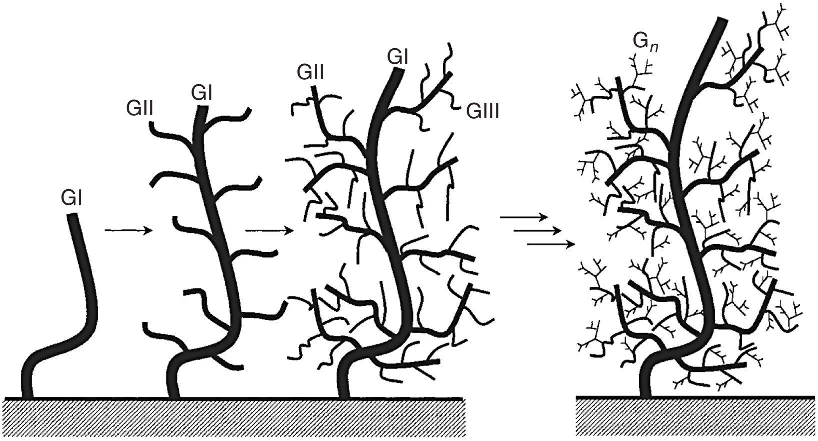

Figure 14.5 Schematics of the first generation (GI) to *n*th generation (G_n) graft architecture.[55] *Source:* Reprinted with permission from American Chemical Society, 2002. Copyright © 2007 by John Wiley & Sons, Inc.

or hydrophobic (poly(methyl methacrylate), PMMA) chains readily controls the surface wettability properties.

14.2.1.4 Ring-Opening Polymerization

Alternative approach to surface grafting involves ROP, which can provide a simple method for growing of hyperbranched polymers in the absence of a catalyst. Kim *et al.* treated amino functionalized silicon substrates with aziridines in order to prepare grafted hyperbranched polymers (Figure 14.6, Path a).[60] AFM indicated that the polymerization is rather regular and that the morphology of the surface does not change significantly after polymerization.[61] Recently, Kim *et al.* have found that hydroxyl groups on the silica solid substrates such as fused silica or silicon wafers with a natural oxide layer are able to initiate the ROP of aziridine, resulting in highly branched poly(ethyleneimine) surface layer.[62] They have shown that the rate of polymerization and the surface morphology of the resulting grafts depend heavily upon the choice of the solvent. For instance, polymerization in toluene results in uniform polymer films with a smoother surface than that in the surface films obtained by the polymerization in dichloromethane.

In another study, Khan and Huck have demonstrated a new procedure to synthesize covalently linked hyperbranched polyglycidol on silicon oxide surfaces via anionic ring-opening (Figure 14.6, Path b).[63] This reaction resulted in the formation of a multibranched glycidol surface layer with the thickness controlled by the reaction temperature. This way, the surface layers from hyperbranched polymers with controlled thickness were formed, and the esterification of the hydroxyl end groups in the postpolymerization reaction was used to tailor their surface properties.

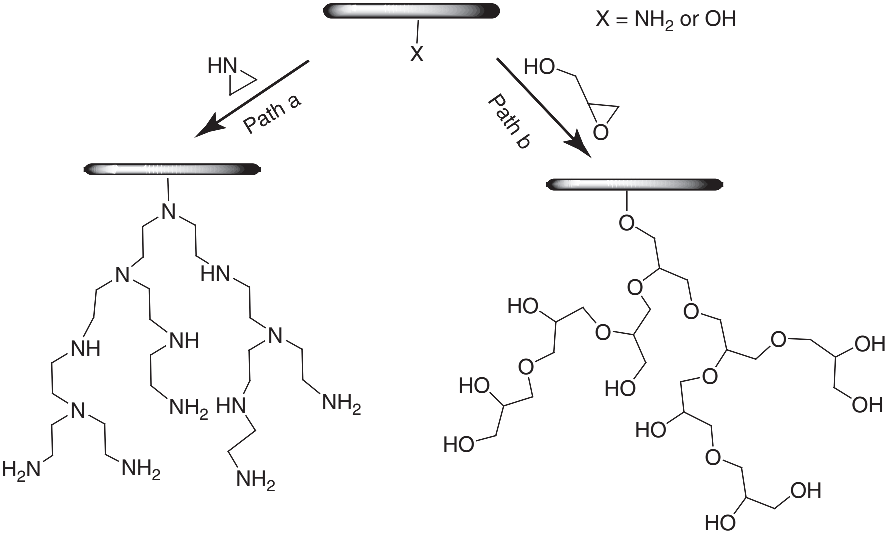

Figure 14.6 Formation of the grafted hyperbranched polymer by ROP.

Another interesting example of ROP was reported for growing multihydroxyl hyperbranched macromolecules on the curved MWNTs' surfaces using 3-ethyl-3-(hydroxymethyl)oxetane (EHOX).[64] Furthermore, additional functionalization of the hydroxyl groups led to the variety of new nanomaterials with advanced properties. Bergbreiter *et al.* reported another example of the synthesis of hyperbranched polymers on silicon wafers by ROP.[65] In this case, a surface-initiated ROP resulted in graft polymerization of 5-vinyl-2-oxazolidinone and the controlled growth of polyamine from the amine functionalized silicon wafer. The surface roughness of the graft polymer films increased with increasing thickness of the polyamine surface layer.

14.2.2 "Grafting to" Approach

A variety of ultrathin (several nanometers) surface layers from functionalized hyperbranched polymers have been fabricated by using the "grafting to" approach which, in many cases, is simpler and more robust than other approaches discussed above. Preference was given to grafting from melt on bare and prefunctionalized surfaces to assure relatively high grafting density. Sidorenko *et al.* have reported the melt grafting of epoxy-functionalized hyperbranched polyesters (EHBPs) to a bare silicon surface by the reaction of secondary epoxy groups with the hydroxyl groups of silicon wafers at elevated temperature (Figure 14.7).[66] They demonstrated that robust, complete, and uniform surface layers with the overall thickness of several nanometers and smooth surface morphology can be firmly grafted to the silicon surface (Figure 14.7).[67] Mikhaylova *et al.* produced ultrathin hyperbranched films by spin coating of hydroxyl and aromatic hyperbranched

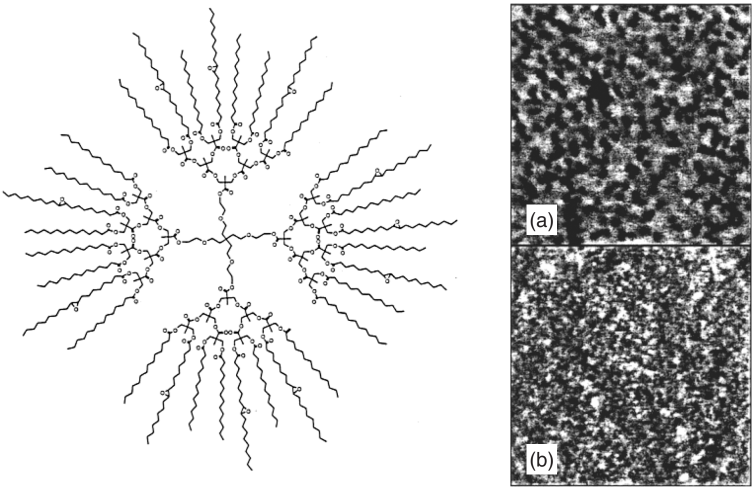

Figure 14.7 Chemical formula (left) and AFM images of grafted monolayers of EHBP with commonly occurring dewetting pattern (a) and uniform monolayer (b) obtained under optimal grafting conditions: scan size 1×1 μm^2.[66]

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polyesters on epoxy-functionalized silicon wafers and subsequently annealing the surface layers above their glass transition temperature.[68]

On the other hand, covalent grafting of the hyperbranched polymers was conducted to glass beads using functionalized SAMs chemistry in a recent study.[69] After selective introduction of carboxyl acid groups into hyperbranched polyols, the residual hydroxyl groups were modified with isocyanate containing silane. A different approach has been used by Shi *et al.* to graft hyperbranched polyesters onto silica nanoparticles.[70] Modified hyperbranched polymers, which possesses 50% end carboxyl groups and 50% end hydroxyl groups and end-capped with octadecyl isocyanate (C_{18}) have been grafted onto 3-glycidoxypropyltrimethoxysilane (GPTS) premodified SiO_2 nanoparticles. The use of photoreactive molecules allows for a unique method to modify polymer films without functional groups through immobilization of other polymers on the film surface. In a different development, Zhai *et al.* have fabricated a novel self-assembled film of hyperbranched conjugated poly(phenylene vinylene) (PPV).[71] The grafting of functional hyperbranched molecules was facilitated through the covalent bonding to a proper hydrophilic substrate (e.g., mica). Interestingly, Haag *et al.* prepared protein-resistant, highly branched polyglycerol (PG) SAMs on gold substrates by a simple chemical modification of these readily available polymers with surface-active disulfide (thioctic acid) linker groups.[72] Owing to the higher thermal and oxidative stability of the bulk PG as compared to the PEG and the easy accessibility of these materials, branched PGs can be considered as promising candidates for biomedical applications.

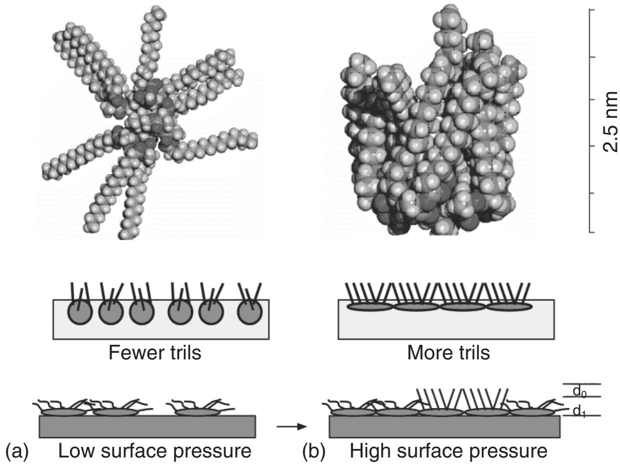

Figure 14.8 Ordering of amphiphilic hyperbranched polymers with different number of alkyl tails at the air–water interface at low (a) and high (b) surface pressures.[76]

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Finally, several examples of weakly attached surface layers of hyperbanced polymers have been reported. For example, Bai *et al.* investigated the influence of the chemical composition of the hyperbranched polymers (different cores, connecting groups, and terminal chromophores) on the optical properties of ultrathin films. These films have been fabricated by spin coating, self-assembly, and Langmuir–Blodgett (LB) deposition.[73]

14.3 SURFACE PROPERTIES OF HYPERBRANCHED POLYMERS

A variety of ordered monolayers have been fabricated from amphiphilic hyperbranched molecules, which are capable of forming stable Langmuir monolayers. Sheiko *et al.* investigated the surface behavior of hyperbranched polymers containing trimethylsilyl or hydroxyethyl end groups in comparison with carbosilane dendrimers.[74] Comparison of the spreading behavior of the OH-terminated dendrimer with that of the hyperbranched polymer with identical chemical composition revealed that the hyperbranched polymer did not show any intramonolayer transitions and exhibited a spreading behavior similar to that of isotropic liquids. In another study, Zakharova *et al.* studied the surface behavior of poly(4-vinylpyridine), hyperbranched perfluorinated poly(phenylenegermane), and their mixtures.[75] They found that changes in the pH of the subphase has no effect on the surface pressure isotherms of the perfluorinated poly(phenylenegermane). However, lower pH significantly increased the stability of the Langmuir monolayer of mixed films.

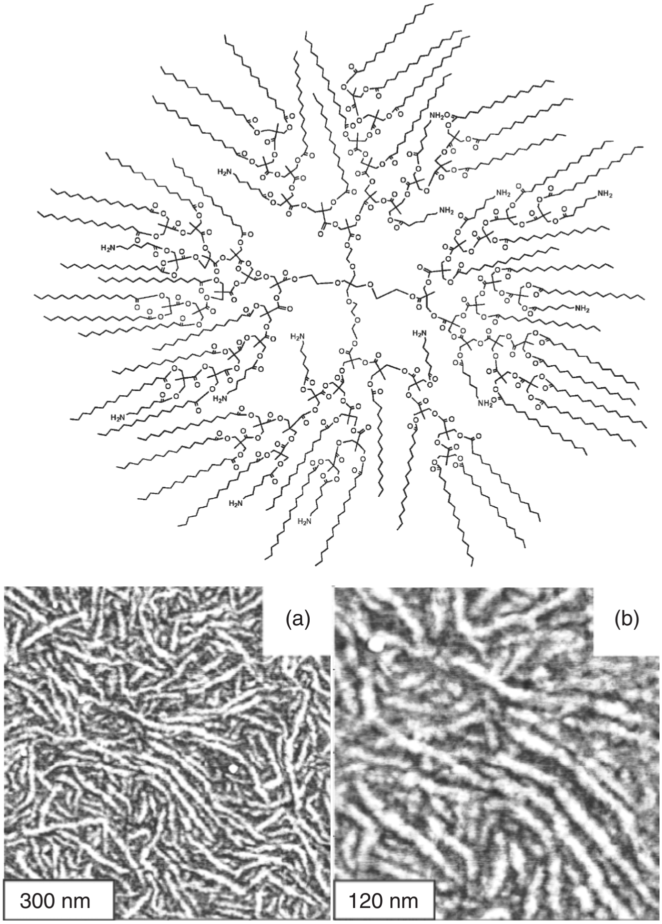

Figure 14.9 Chemical structures (top) of the modified hyperbranched polymer and high-resolution AFM phase images of its nanofibrillar assembles at surface pressure of 20 mN/m.[77]
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The surface behavior of a series of second-generation hyperbranched polyesters with a variable composition of alkyl-terminated groups have been reported by Zhai *et al.* (Figure 14.8).[76] Comprehensive study of the surface properties of the Langmuir monolayers with X-ray reflectivity revealed that organized monolayers could be formed at the air–water interface if the number of alkyl tails is higher than two per hyperbranched core. Similar to regular dendrimers, the alkyl tails of hyperbranched molecules at modest surface pressure formed intramonolayer ordering of the quasi-hexagonal type with well-developed short-range order. Finally, at high surface pressure, the alkyl tails became arranged in an upright orientation with flexible hyperbranched cores adopting a proper shape to accommodate the dense packing of the alkyl tails (Figure 14.8).

In a related development, Ornatska *et al.* investigated the surface properties of the amphiphilic hyperbranched polymers of higher generation with different substitutions of the terminal palmitoyl and 6-aminohexanoic groups.[77] They observed that the amplification of weak multiple interactions between numerous peripheral branches of irregular, flexible, polydisperse, and highly branched molecules can facilitate their self-assembly into well-organized nanofibrillar micellar structures at the hydrophilic solid surfaces (Figure 14.9).

Finally, Shi *et al.* have studied the microtribological properties behavior of the C_{60}-polystyrene hyperbranched polymer.[78] Monolayer and multilayer films from this polymer were prepared on mica using an LB technique. AFM data revealed that the films were uniform and highly ordered and the surface was relatively smooth facilitating a reduced friction coefficient.

14.4 CONCLUSIONS

Despite the fact that a variety of hyperbranched polymers with different chemical compositions and architectures have been demonstrated to date, their surface and interfacial behavior was rarely addressed. The surface properties of hyperbranched films were the subject of only a handful of recent investigations. Despite these muted activities, it has been already demonstrated that hyperbranched polymers can be grafted/grown/deposited onto a wide variety of solid surfaces by both grafting to and grafting from approaches achieving complex nanocomposite structures with rich internal and surface functionalities. However, to date, very little is known about the actual properties of surface layers formed from functionalized hyperbranched molecules. The vast majority of studies on the fabrication of the surface structures from hyperbranched molecules is limited to the synthetic strategy with very little data available for surface morphology and microstructure, let alone multiscale surface properties.

Acknowledgment

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LIST OF ABBREVIATIONS

AFM	atomic force microscopy
PAMAM	poly(amidoamide)
SAM	self-assembled monolayer
MA	methyl acrylate
EDA	ethylenediamine

MWNT	multiwall carbon nanotube
MUA	mercaptoundecanoic acid
PAA	poly(acrylic acid)
PE	polyethylene
PP	polypropylene
BPEA	2-(2-bromopropionyloxy)ethyl acrylate
*t*BuA	*tert*-butyl acrylate
SCVP	self-condensing vinyl polymerization
ATRP	atom transfer radical polymerization
DC	*N*,*N*-diethyldithiocarbamate
P*t*BA	poly(*tert*-butyl acrylate)
PHEMA	poly(2-hydroxyethyl methacrylate)
PVP	poly(vinyl pyrrolidone)
PMMA	poly(methyl methacrylate)
ROP	ring-opening polymerization
EHOX	3-ethyl-3-(hydroxymethyl)oxetane
EHBP	epoxy-functionalized hyperbranched polyester
GPTS	3-glycidoxy-propyltrimethoxysilane
PPV	poly(phenylene vinylene)
PG	polyglycerols
PEO	poly(ethylene oxide)
LB	Langmuir–Blodgett

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Chapter 15

Biological and Medical Applications of Hyperbranched Polymers

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15.1 INTRODUCTION

Just as in the case of dendrimers,[1–3] many potential biomedical applications have been suggested for hyperbranched polymers. The main biomedical fields in which hyperbranched polymers are likely to find applications are gene delivery, drug delivery, biodegradable materials, modification of surfaces (biocompatibilization, antifouling, etc.) and bulk materials, and applications related to biointeractions. These applications are based on the typical characteristics of hyperbranched polymers: low (melt) viscosity, high density of functional groups, presence of end groups as well as internal functional groups, and a compact structure. An additional promising feature is their ability to act as a host for smaller molecules in various ways. Although similar applications have been suggested and explored for dendrimers, their high cost and very limited availability will obviously favor the application of hyperbranched polymers over their structurally perfect analogs. Many of the suggested potential applications, however, have hardly been explored to date. In many of these studies, commercially available hyperbranched polymers, such as poly(ethyleneimine) (PEI), Boltorn® (a hyperbranched aliphatic polyester), Hybrane® (a hyperbranched polyesteramide), and polyglycerol (a hyperbranched polyether) have been used. Presumably, besides availability, the fact that certain features of these materials can be controlled quite effectively

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

(e.g., their fairly low polydispersity) has motivated their further exploration. The main areas in which these hyperbranched polymers have actually been studied with respect to biomedical application can be summarized as follows:

1. The use of hyperbranched polymers as gene delivery carriers or drug delivery systems, either by covalent or noncovalent drug loading.
2. The coating of materials to make them biocompatible or induce antifouling properties.
3. The enhancement of the biodegradability of (linear) polymers by incorporation of branches or by blending with hyperbranched polymers.
4. The use of hyperbranched polymers for the formulation of superior dental composites.
5. The study of the modifications of the interaction between biomolecules, presented as a conjugate onto hyperbranched scaffolds, and their ligands.

In what follows, only research that is obviously related to biomedical applications is cited and discussed. Basically synthetic or physical papers in which the possibility of biomedical applications is only suggested without actually being investigated, have been omitted.

15.2 GENE DELIVERY

15.2.1 Linear and Hyperbranched Poly(ethyleneimine) as Nonviral Gene Vectors

Among the numerous potential biomedical applications of hyperbranched polymers, at present, their use as gene delivery agents is one of the most widely explored. Gene delivery is a promising technique allowing *in vivo* transfer of nucleic acids into cells.[4] Therefore, it is necessary to protect the nucleic acid from enzymatic degradation by nucleases, to facilitate uptake into specific cells and transfer the DNA or RNA into the nucleus or cytoplasm, respectively. It is hoped that gene transfer eventually will be useful for curing severe diseases such as cancer,[5] AIDS,[6] and different hereditary disorders.[7–10] At present, research has advanced to the stage of clinical trials, mainly in oncology.[5] The use of polymers for gene delivery has the advantage of not causing immunogenic and inflammatory responses, which are commonly observed upon use of viral vectors and preclude repeated administrations. Further disadvantages of the latter are the risk of insertional mutagenesis, the limited loading capacity, and problems in large-scale production of viral vectors.

In the field of nonviral vectors, cationic polymers are very promising. PEI, in particular, has been found to display transfection efficiencies similar to those of viral vectors.[11,12] The complexation of nucleic acids with PEI increases their stability in the extracellular environment, improves uptake in the cell by electrostatic interactions of the polycation with the negatively charged cell surface, and promotes endosomal release, presumably due to the so-called proton-sponge effect.[11] This effect consists of the rupture of endosomes as a consequence of the massive uptake of protons by PEI, giving rise to the increase in free chloride concentration and hence, osmotic pressure. It is believed that it is mainly the tertiary amine groups present in the PEI structure that are responsible for this proton buffer effect. The complexation of DNA with PEI is thought to be mediated by electrostatic interaction and is mainly entropy driven by the release of counterions.[13] In order to facilitate cellular uptake, the complex particles formed should be sufficiently condensed and not exceed sizes of around 150–250 nm.[14] The binding between the cationic polymer and DNA occurs in a ratio of nearly 1:1, although a slight excess of the polycation is necessary to provide a positively charged corona around the particles so as to keep them in solution and promote interaction with the negatively charged cell wall, prior to endocytosis.[15]

Although transfection agents based on linear PEI are already commercially available (e.g., ExGen500®, jetPEI®), it has been found that hyperbranched PEI may have certain advantages over the linear polymer. More densely branched PEI usually displays stronger complexation capability and hence superior transfection properties. This effect can be explained on the basis of the presence of more primary amine groups with increasing DB (degree of branching), since it is well known that primary amines favor complex formation due to their higher degree of protonation at a given pH.[16–20] There is also evidence that the high polydispersity and the random character of hyperbranched polymers may increase their transfection efficiency as compared to the structurally analogous dendrimers. It has been shown that the transfection efficiency of PAMAM (poly(amido-amine)) dendrimers was improved dramatically after partial degradation by heat treatment, presumably due to more efficient complex formation by the resulting partially degraded macromolecules.[21] On the other hand, reducing the linear-to-branched ratio of commercial PEI (BPEI, $M_n = 9.5$ kDa, GPC, ratio of secondary to tertiary amines of 1.17) by successive additions of ethyleneimine moieties resulted in highly efficient transfection agents as well as reduced toxicity (Figure 15.1).[22] (In general, higher transfection efficiency is accompanied by higher toxicity.) The modified PEI derivatives were obtained by stepwise alkylation of the commercial BPEI with 2-chloroethylamine, yielding HD2 (hyperbranched dendron), HD3, and HD4 with molar masses (determined by GPC) of 11.7, 13.7, and 15 kDa, corresponding to the addition of approximately 50, 98, and 128 ethyleneimine groups, and decrease of the ratio of secondary to tertiary amines of 1.06 over 0.90 to 0.70, respectively. The fact that a more stable complex results in higher transfection efficiencies was also illustrated by the observation that the transfection efficiency of a DNA–PEI complex showed an eightfold increase upon storage for three weeks, presumably due to the formation of a more compact complex over time (Figure 15.1).[22]

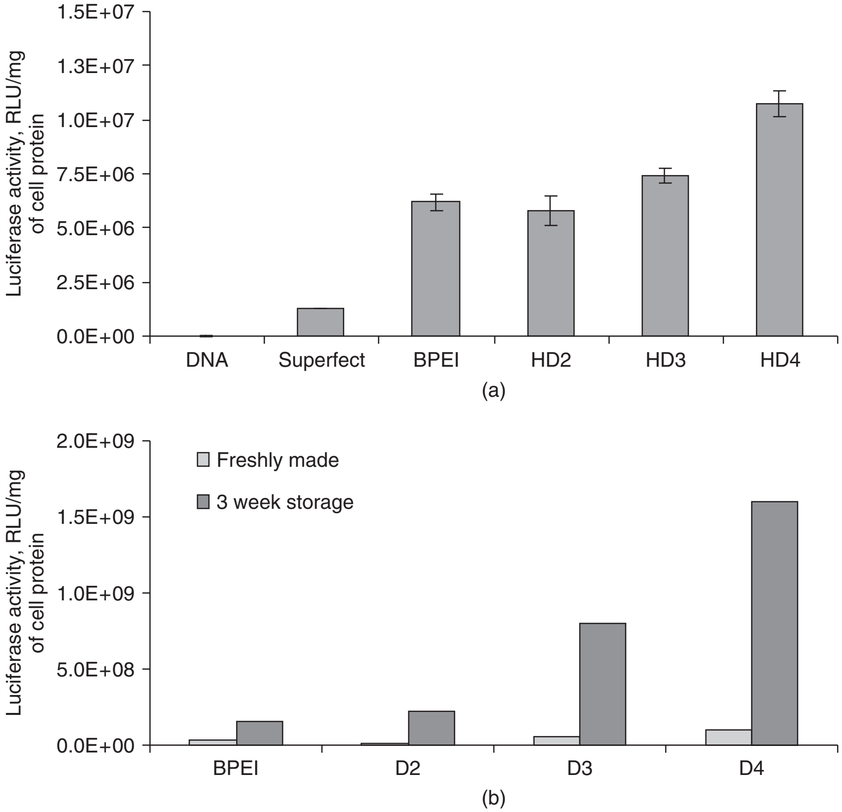


Figure 15.1 (a) *In vitro* luciferase expression in COS-1 cells after transfection using hyperbranched poly(ethyleneimine) BPEI and modified analogs HD2, HD3, and HD4, and Superfect. (b) *In vitro* luciferase activity in COS-1 cells using complexes that were either freshly prepared or stored for three weeks at 4 °C before use.

15.2.2 Modification of Poly(ethyleneimine) and Use of Adjuvant Polyglycerol

In order to improve upon important issues such as biocompatibility and water solubility and reduce immunogenicity, and in certain cases, to induce specificity, PEI has been modified extensively. The attachment of PEG (poly(ethylene glycol)) chains to PEI has been explored in many studies, as it forms a hydrophilic shell that provides steric shielding of the PEI–DNA complex, improving complex solubility[23] and aggregation behavior.[24] In addition, PEGylation has been found to result in decreased interaction with proteins,[21] reduced activation of the complement system,[25] and enhanced circulation time in the blood.[26] PEGylated PEI species also tend to be less toxic than their unmodified analogs.[27,28] Interestingly, the attachment of low molar mass PEI (800 and 2000 Da) to PEG stars was found to result in similar superior complexation behavior as in the case of PEGylated PEI.[29] Presumably, these systems are sufficiently flexible to allow complexation of the external PEI moieties without preventing the "internal" PEG residues from forming a shielding shell around the polyplex. Also, poly-[*N*-(2-hydroxypropyl)methacrylamide] has been used to modify PEI for similar purposes.[30] Modification of branched PEI (in contrast to linear PEI) with dextran polymers has been shown to increase biocompatibility. However, the DNA compacting activity of this conjugate was much lower than in the case of the unmodified analogs.[31] Similarly, functionalization with transferrin led to a marked decrease of nonspecific interactions with erythrocytes and at the same time, allowed cell-specific targeting to a certain extent.[32] Cyclodextrin-modified PEI allowed fine-tuning of the modification of the PEI/DNA particles by complexation with adamantane-functionalized PEG.[33]

Modification of PEI with apolar groups or with a combination of apolar and polar residues sometimes results in a surprisingly good transfection efficiency in combination with low toxicity.[4] Among this type of modifications, especially vectors based on PEI modified with Pluronic 123® display interesting properties. (Pluronics are a type of commercially available ABA copolymers consisting of PEO (poly(ethylene oxide)) as the A block and PPO (poly(*p*-phenylene oxide)) as the B block.) PEI modified with Pluronic 123 as such did not perform very well. However, mixing this conjugate with an excess of the latter resulted intransfection efficiency that was higher than that of PEI 25 kDa[34] (which is usually referred to as the standard). Moreover, cell-specific targeting may also be introduced. In an experiment with oligonucleotides it was found that while PEG(8 kDa)–PEI(2 kDa), a star-shaped conjugate of PEG onto PEI, accumulated in the kidney, P85®-*g*-PEI(2 kDa), the analog in which the PEG was replaced by a Pluronic, was mainly directed to the hepatocytes.[35] Presumably, intermolecular association of the hydrophobic parts of the free Pluronic entities on one hand with the covalently linked chains on the other, assist in the protection of the complexed oligonucleotide. Even more specific cell targeting has been achieved by modification of PEI with carbohydrates, folate receptors, integrin or transferrin, and antibodies.[4]

The increased efficiency observed upon mixing Pluronics to the actual transfection agent may be attributed to the lipid bilayer–disturbing effect of amphiphiles such as Pluronics. In this context, another interesting study comparing the interaction of Pluronics, polyglycerols, and polyglycerol conjugates with cells should be mentioned.[36] It is believed that the sensitizing effect exhibited by Pluronics on tumor cells is due to the inhibition of P-glycoprotein, which is responsible for drug efflux from the cell. Pluronics-induced changes in the cell membrane may be responsible for the observed decrease in activity of this enzyme, which is able to protect tumor cells from the action of anticancer drugs. In this study, both the kinetics of migration of the fluorescent phosphoethanolamine lipid NBD-PE (labeled with a fluorescing nitrobenzoxadiazole moiety) between the two leaflets of the membrane bilayer (this phenomenon is referred to as flip-flop) and the kinetics of transmembrane doxorubicin

(DOX) permeation were monitored as a function of the concentration of the different polyethers investigated. As this was done on liposomes, the behavior in real cells having membranes with numerous biomacromolecules embedded in them may be different. However, these results might be of help for rational design of functional cell-penetrating agents in the future. It was found that the rate of flip-flop increased with the length of the PO (propylene oxide) block and decreased with the length of the EO (ethylene oxide) blocks in the used Pluronic. Interestingly, a PO–polyglycerol conjugate with an oligoglycerol residue ($PO_{30}EO_6G_2$) displayed a threefold higher effect on the flip-flop rate than the analog Pluronic $EO_2PO_{30}EO_2$. Analogously, polyglycerols prepared from a core bearing a hexadecyl tail ($C_{16}H_{33}$-G_{10} and $C_{16}H_{33}$-G_{64}), were generally found to have a more pronounced effect on the flip-flop rate than their Brij analogs ($C_{12}H_{25}EO_4$, $C_{16}H_{33}EO_{10}$, and $C_{12}H_{25}EO_{24}$) in spite of their more voluminous hydrophilic part. Hence, it could be concluded that the presence of hyperbranched polyglycerol in the conjugates increases their membrane-disturbing potential, which highlights the scope for further investigation in this area.

Obviously, the biocompatibility of hyperbranched materials is of great importance in this context. A recent study by Brooks and coworkers evaluated the biocompatibility of linear ($M_n = 6400$ g/mol) and branched ($M_n = 6400$ g/mol) polyglycerol *in vitro* and *in vivo*.[37] They investigated its hemocompatibility based on the assessment of the effects on coagulation, complement activation, red blood cell aggregation, and whole-blood viscosity measurements. *In Vitro* cytotoxicity experiments were also conducted. In all these tests, linear as well as branched polyglycerols displayed low toxicity, comparable to PEG and hetastarch, both polymers commonly used in a variety of clinical settings.

Modified PEI has also been used to investigate the role of the DB on transfection efficiency by measurements of the β-galactosidase activity.[38] Haag and coworkers investigated, first, the transfection efficiency of PEI derivatives (that were commercially available as well as samples synthesized by the authors) with molar masses ranging from $M_w = 800$ to 600,000 and DB between 65% and 75%. Depending upon the cell line investigated, the optimum molecular weight for the PEI was in the range of 6000–25,000 g/mol, for which the transfection efficiency was comparable to Superfect®. The cytotoxicity increased with the molar mass. In a second approach, the PEI samples were modified in two different ways. First, PEI with $M_n = 25$ kDa was treated with acrylonitrile in a Michael addition and subsequently reduced. In this way, PEI analogs modified with a PPI (poly(propyleneimine) shell were obtained. By adjusting the ratio of the reactants, PEI/PPI analogs PEI25PPI58, PEI25PPI72, and PEI25PPI100 with a DB of 0.58, 0.72, and 1, respectively, could be obtained. The transfection efficiency generally decreased with increasing DB (Figure 15.2), which could be explained on the basis of the lower flexibility of the more densely branched analogs, presumably lowering the proton-sponge effect. In general, the transfection efficiency and the cytotoxicity of the PEI/PPI was lower than in the case of the parent PEI derivatives. In a second approach, PEI/PAMAM analogs were

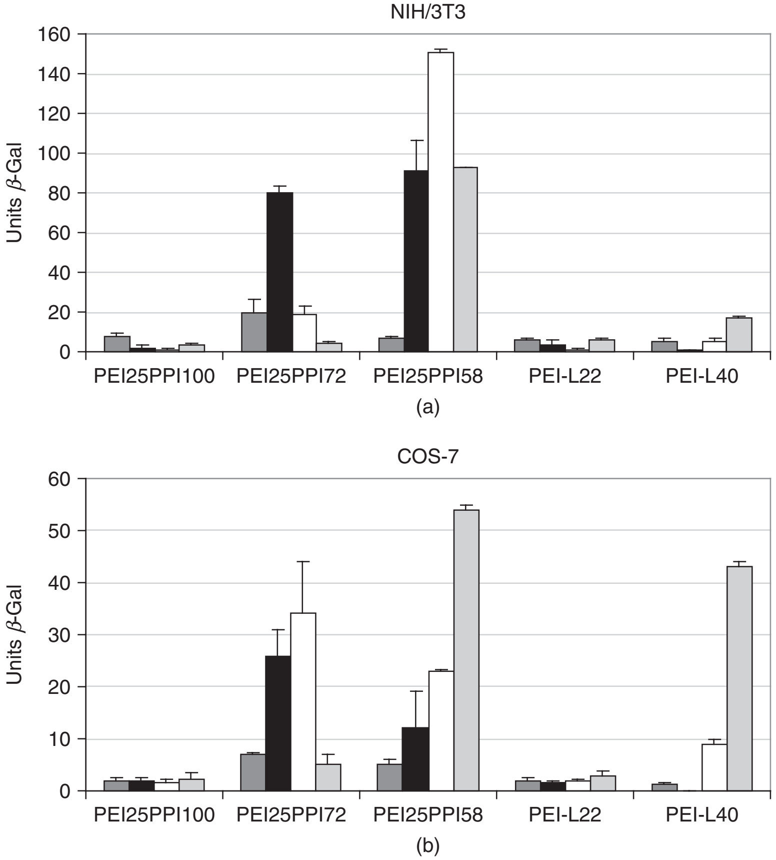
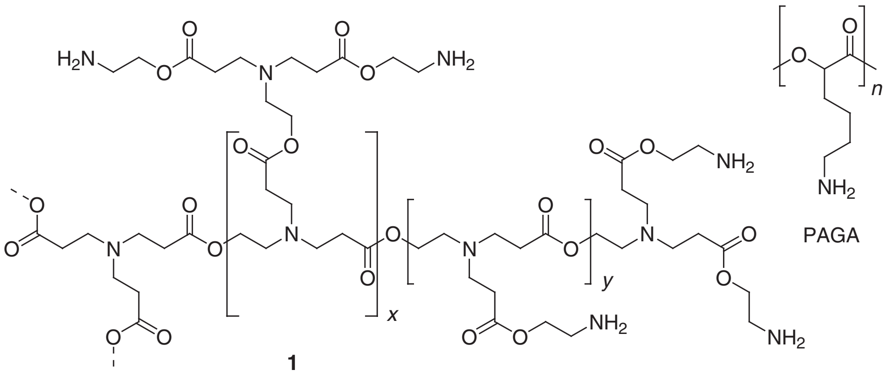


Figure 15.2 Transfection efficiencies of PEI25PPI hyperbranched polymers with different degrees of branching (DB = 100%, 72%, and 58%, respectively) and linear PEI (PEI-L, $M_n = 22$ and 40 kDa respectively) with different molecular weights in NIH/3T3 (a) and COS-7 cells (b).

prepared by reaction of PEI ($M_w = 5000$ and 25,000, respectively) with methyl acrylate followed by amidation with ethylenediamine. In contrast to the PEI/PPI derivatives, DB could not be controlled in this way. This approach resulted in transfection efficiencies comparable to that of Superfect, depending on the cell line, when a PEI core with an $M_w = 25{,}000$ g/mol was used, while again a significant decrease in toxicity was observed.

15.2.3 Hyperbranched Alternatives for Poly(ethyleneimine) as Gene Vectors

An important drawback of PEI gene delivery carriers is their relatively high toxicity. Even upon modification, for example with PEG, this toxicity is still problematic. In order to reduce toxicity, while preserving sufficient transfection



1

PAGA

Figure 15.3 Hyperbranched poly(amino ester) **1** and a linear analog PAGA.

efficiency, investigations have been carried out to synthesize and evaluate PEI analogs which are readily biodegradable.[39–45] The biodegradability may also support the release of DNA after uptake in the cell. Therefore, a cored hyperbranched poly(amino ester) **1** has been synthesized via transesterification of AB_n monomers containing a tertiary amine, followed by conversion of the terminal ester groups into primary amines (Figure 15.3).[42] The molar masses of these compounds were found to be $M_n = 12{,}000$ g/mol by size exclusion chromatography (SEC) in tetrahydrofuran (THF) upon calibration with linear polystyrene standards and $M_n = 29{,}000$ g/mol upon calibration with PAMAM dendrimers. Hence, these compounds combine the essential features of PEI: high density of primary amines for nucleotide complexation and tertiary amines for the proton-sponge effect (Section 15.2.1), with biodegradability due to the hydrolyzable ester linkages. The toxicity of this polymer was very low as compared to PEI and the transfection efficiency was around two orders of magnitude lower. However, this result was still considered promising, because the transfection efficiency was one order of magnitude higher than that of poly[α-(4-aminobutyl)-L-glycolic acid] (PAGA), which was considered a linear analog of the hyperbranched polymer used in this study and lacked the tertiary amines which are necessary for the proton-sponge effect.

Network-type analogs of hyperbranched polymer **1** have been synthesized via A_nB_m and $A_n + B_m$ polycondensation. Both transesterification of the type giving rise to **1** and Michael addition of amines onto acrylates have been applied; the latter displaying higher density of amine groups, even without further modification of the polymer. As an example of an A_nB_m strategy, monomer **2** (Figure 15.4) was subjected to polycondensation, after which the residual alcohol groups of the polymer were esterified with 6-aminohexanoic acid, resulting in the introduction of the required primary amino groups.[44] Poly(amino esters) with rather low apparent molar masses were obtained ($M_n = 3500$ g/mol, GPC, linear polystyrene) Again, these compounds were found to combine a relatively low toxicity with

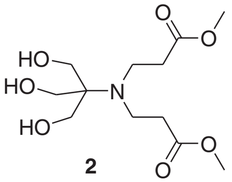


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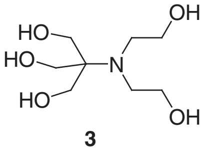
Figure 15.4 Monomer **2** for A_nB_m transesterification polycondensation strategy toward network-type hyperbranched poly(ester amine)s.



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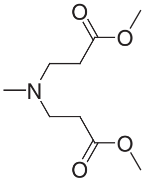

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Figure 15.5 Monomers for $A_n + B_m$ transesterification for the preparation of network-type hyperbranched poly(ester amine)s.

transfection efficiencies that were even higher than that of PEI, especially in the presence of serum.

Concerning $A_n + B_m$ polycondensations, several combinations of monomers have been polymerized, yielding networks of poly(amino esters) by transesterification. The combination of monomers **3** and **4** was found to afford the most effectively transfecting polymers ($M_n = 40 \times 10^3$ g/mol, GPC MALLS i.e., gel permeation chromatography/multiangle laser light scattering photometer) after partial modification of the terminal alcohol groups as 6-aminohexanoates (Figure 15.5).[40] Although a polymer with a primary amine group content of 9.3 nmol/μg was found to be more effective than an analog with only 5.3 nmol/μg primary amine groups, the former, not surprisingly, also displayed an increased toxicity. Again, the performance of these polymers was preserved remarkably well in the presence of serum.

Another approach toward biodegradable poly(amino esters) is the polycondensation by Michael addition of amines to acrylates. Polymerization of a 1:1 mixture of **5** and several diacrylates has been found to result in almost exclusively linear polymers.[41] This was explained on the basis of the far higher reactivity of the piperazine secondary amine when compared to the secondary amine formed by addition of the ethylamine residue on the acrylate due to steric hindrance.[46] However, as these polymers displayed encouraging transfection properties, branched analogs have been prepared by reaction of **5** with triacrylate **6** (in a 2:1 molar ratio)[43] and diamines **7** with triacrylate **8**, respectively (Figure 15.6).[44] In the latter case, the terminal hydroxyl groups were converted to the 6-aminohexanoates or lysine esters.

Interestingly, the unmodified polymer from **7** and **8** (22 kDa, GPC MALLS), possessing no primary amine groups, was found to display very good DNA condensing properties. However, its transfection efficiency was very low, suggesting

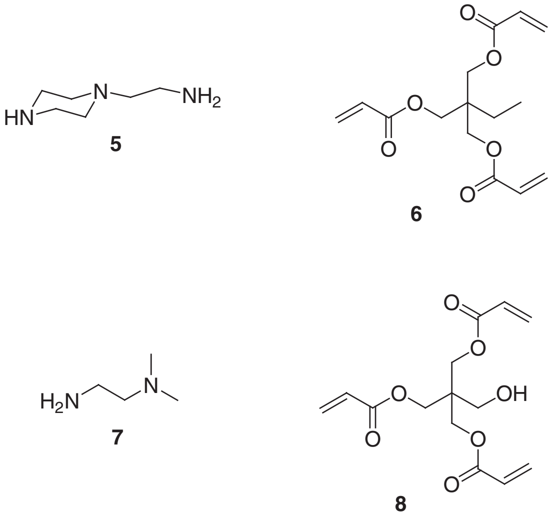


Figure 15.6 Different monomers giving rise to poly(amino esters) by polycondensation by Michael addition.

that primary amines may play an active role in this process in addition to improving complex formation with DNA. Depending upon the type of cells used for the assessment, the lysine ester or the aminohexanoate derivatives showed the best transfection/toxicity ratio.

Recently, an easy and versatile route toward hyperbranched poly(L-lysine) and its copolymers with L-alanine and L-glutamic acid has been described.[45] The interest in the potential of these compounds for use in gene delivery is motivated by their biodegradability and biocompatibility. Dendrimer analogs have already been shown to combine high transfection efficiencies with low toxicity.[47–51] The transfection efficiencies of the hyperbranched analogs remain to be investigated.

In another recent study,[52] hyperbranched PEG-functionalized polyglycerol was modified with tris-(2-aminoethyl)amine, yielding a network-type polymer PG–PEG–amine ($M_n = 116.700$, GPC MALLS) that combined the features of polyglycerol and PEI (Figure 15.7). This polymer was alkylated with ethyl bromide to yield samples with degrees of quaternization of 18%, 44%, and 100%, respectively. These polymers are highly biocompatible as shown by their insignificant effects on hemolysis, erythrocyte aggregation, complement activation, platelet activation, and coagulation. Moreover, they show much lower cytotoxicity than standard cationic polymers such as PEI. A high affinity of these polymers for DNA was demonstrated by ethidium bromide displacement assays, showing binding affinities in the nanomolar range. These polymers condensed plasmid DNA to one of the smallest sizes reported and formed stable nanoparticles, which justifies further investigation of their role as gene carriers. Higher degrees of quaternization resulted in higher toxicity, but high DNA-binding affinities were achieved at low degrees of quaternization. The feasibility of application of these polymers in gene or drug delivery still remains to be investigated.

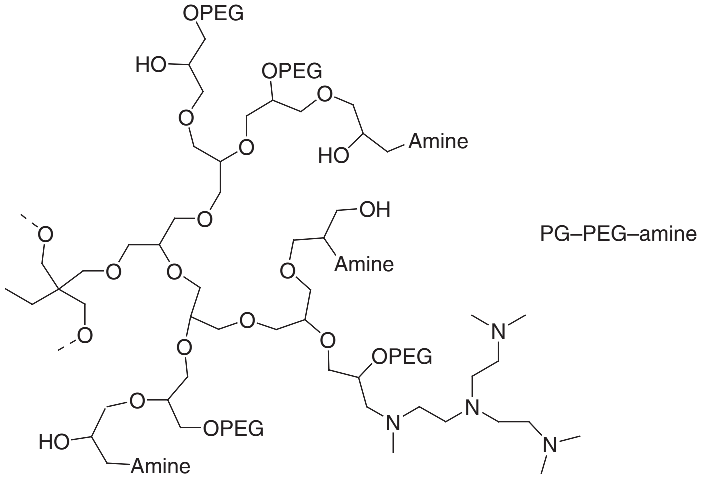
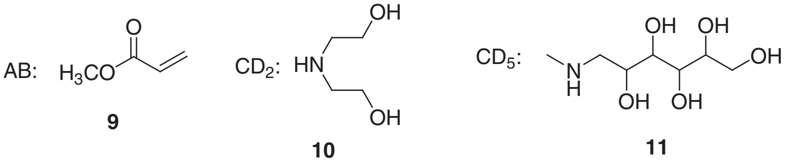


Figure 15.7 The hyperbranched polymer PG–PEG–amine, combining features of polyglycerol and PEI.

15.3 DRUG DELIVERY

15.3.1 Drug Encapsulation and Conjugation

Following dendrimers, several types of hyperbranched polymers have been suggested as candidates for drug delivery applications. In comparison to the well-established linear biodegradable polyesters, such as poly(lactic acid), poly(glycolic acid) and especially their copolymer poly(lactic-*co*-glycolic acid), hyperbranched polyesters might offer the opportunity for fine-tuning to adjust the polymer degradation and erosion rate. Water-soluble, degradable hyperbranched polyesters, obtained from commercial monomers **9, 10**, and **11** by a combination of Michael addition and transesterification in an AB + CD_n approach, have been proposed as promising candidates (Figure 15.8).[53] However, only little research has been carried out exploring the actual feasibility of the use of hyperbranched polymers as drug carriers. The few examples that have been explored in more detail, however, clearly show that in this field, hyperbranched polymers can



9 **10** **11**

Figure 15.8 Commercial monomers for the AB + CD_n approach toward degradable, water-soluble hyperbranched polymers.

be strong competitors for dendrimers. Mainly commercially available (in some cases modified) hyperbranched polymers such as Boltorn, Polyol, Hybrane, and polyglycerol have been used for this purpose.

A comparative study on drug complexation, *in vitro* release, and cellular entry of hyperbranched polymers and dendrimers was performed by Kannan *et al*. In a first paper, the interaction of ibuprofen with PAMAM-G3-NH_2, PAMAM-G4-NH_2 (both dendrimers), and Polyol-G5-OH (a hyperbranched polymer purchased from Perstorp, Sweden, $M_n = 15 \times 10^3$ g/mol, with a hypothetical average of 128 hydroxyl terminal groups was compared.[54] The dendrimers were found to incorporate a higher number of ibuprofen molecules per macromolecule than the polyol (32 and 78 for G3 and G4, respectively, and 24 for the polyol). This was explained on the basis of the different mechanisms of incorporation, being mainly complexation between the carboxylic acid–functionalized ibuprofen by the terminal amine groups in the case of the PAMAM dendrimers and mainly encapsulation in the case of the polyol, which lacked the amine groups. In another paper by the same researchers, the dynamics of cellular entry of dendrimers and hyperbranched polymers into A549 human lung epithelial carcinoma cells and their complexes with ibuprofen were compared.[55] Not only regular PAMAM-G3-NH_2, PAMAM-G4-NH_2, and Polyol-G5-OH but also PAMAM-G4-OH- and PEG-2000-modified PAMAM-G3 with a molar mass of 72 kDa were used. The latter star-shaped polymer displayed a higher drug load than the parent dendrimer, but uptake in cells was found to be much slower. The amino-terminated PAMAM dendrimer complexes showed the fastest uptake into the carcinoma cells, presumably due to favorable interactions of the positively charged dendrimers with the epithelial cells, which are known to bear a negative charge. Although the hyperbranched polyol showed the lowest drug load in combination with a moderate uptake rate, the activity of ibuprofen in the cells, as assessed by cyclooxygenase-2 (COX-2) suppression, was the highest of all the investigated systems. All these drug delivery systems showed a faster COX-2 suppression effect than ibuprofen itself, probably due to the much more efficient uptake of complexed ibuprofen in comparison with the free drug. Not surprisingly, the hyperbranched polyol also showed a significantly lower toxicity than the PAMAM dendrimers, although all systems investigated were found to be only minimally toxic at the concentrations required for the observed drug delivery effect. It should be mentioned that tumor cells have been observed to show a higher degree of permeability than normal cells, which may result in a passive targeting behavior.[56]

More directed targeting can be achieved by folate functionalization of the periphery of dendritic structures, as it is known that a variety of cancer cells significantly overexpress folate receptors.[57] This approach was explored using hyperbranched polyglycerol that had been modified by PEG 5000.[57] Introduction of PEG chains is known to result in prolonged circulation in the blood. As compared to the parent polyglycerol ($M_n = 5000$ g/mol) used, the encapsulation of the hydrophobic anticancer drug tamoxifen, as monitored by the solubility of this compound in aqueous 1 mM solutions of the respective polymers, was enhanced by one order of magnitude. Folate functionalization of the PEG chains resulted in another order of magnitude increase in solubility of tamoxifen. Furthermore, increasing the NaCl concentration of the aqueous solution from 0 to 0.6 M resulted in a decrease in solubility of tamoxifen from 10 to 3×10^{-6} M in the 1 mM PG solution, from 12 to 6×10^{-5} M in the 1 mM solution of the PG–PEG, and only from 2.5 to 2×10^{-3} M in the 1 mM solution of PG–PEG–folate. This observation is important because Na^+ is known to interact with PEG and as the NaCl concentration in the extracellular fluid is 0.142 M, premature release could be expected due to replacement of drug molecules by Na^+. However, the observed fact that at a NaCl concentration of 0.142 M only 6% of the complexed tamoxifen was released is definitely encouraging for further experiments with this system for drug delivery devices.

Kannan *et al*. also explored the potential of covalent conjugates of hyperbranched supports and drug molecules.[58] Polyglycerol ($M_n = 5000$ g/mol) and Perstorp polyol ($M_n = 15 \times 10^3$ g/mol) were used as the hyperbranched carriers. Ibuprofen molecules were covalently attached to the terminal alcohol groups of the polyglycerol by esterification with dicyclohexylcarbodiimide (DCC). Covalent attachment has the obvious advantage that no leaking occurs as long as no degradation of the ester bond takes place. Once in the cell, lysosomal enzymes are expected to cleave off the ibuprofen moieties. High average loads in the order of 50 ibuprofen units per hyperbranched polymer molecule were obtained. Comparison of the bioactivity of ibuprofen administered to cells in the free and conjugated forms was achieved by monitoring the inhibition of COX-2. Administration of free ibuprofen did not result in significant inhibition after 30 min, whereas 5% of inhibition was observed in the case of administration of the polyol conjugate, and even 30% in the case of the polyglycerol conjugate. This result was in agreement with the observed faster uptake of fluorophore-labeled hyperbranched molecules (conjugated or not with ibuprofen) compared to free ibuprofen. After 60 min, no difference between free and conjugated administration could be observed anymore. The difference observed between polyglycerol and polyol conjugates was explained on the basis of the higher hydrophobicity and higher steric hindrance in the latter, decreasing the rate of hydrolysis, and consequently, the release rate of ibuprofen from the polymer. Also, the higher loading of ibuprofen in polyglycerol (70% vs 42%) was assumed to contribute to the activity difference.

In a study aiming at the investigation of the influence of the loading technique for a drug carrier system based on hyperbranched polymers, Boltorn H3200 ($M_n = 4600$ g/mol) and three different poly(ester amide)s, Hybrane 1690, 1500, and 1200, were used.[59] Hybrane 1690 and 1500 are rather hydrophilic, whereas Hybrane 1500 is rather hydrophobic. Acetaminophen (paracetamol) was used as a model drug. For Boltorn, different drug encapsulation techniques were explored, namely gas antisolvent precipitation (GAS), coacervation (C), and the so-called PGSS technique (particles from gas saturated solution). For Hybrane, solid dispersions were prepared by the so-called solvent method. More details about these methods can be found elsewhere.[60–62] From infrared (IR) and differential thermal analysis (DTA), it was concluded that the drug is partly dissolved in the polymer matrix and partly crystallized outside the matrix. It was found that both the properties of the polymer and the encapsulation technique are of high importance for the release characteristics of the system. The release behavior of acetaminophen-loaded Boltorn 3200 microparticles depended on the microencapsulation methods employed. Particles produced by GAS (Bol-GAS) and coacervation processes (Bol-C) show biphasic release: the predominant burst release due to unincorporated drugs and a slower, constant release of the incorporated guest molecules. The release behavior of acetaminophen from particles obtained by PGSS is characterized by the diffusion process since the drug is better dispersed in the polymer matrix. In the case of acetaminophen-loaded Hybrane, the hydrophilic H1690 and H1200 derivatives resulted in fast release, whereas the hydrophobic H1500 showed a biphasic release profile similar to that of Bol-GAS and Bol-C. Hence, it was concluded that mainly H1500 and Bol-GAS and Bol-C are suitable for controlled release applications, if issues of toxicity and biocompatibility will turn out to be favorable as well. On the other hand, the hydrophilic Hybrane 1690 and 1200 were believed to offer some opportunities for other emerging applications such as the modification of drug excipients. These polymers could certainly be expected to increase the hydrophilicity of drug excipients upon blending.

An alternative approach was explored by Shi *et al.*[63]: they modified Boltorn H20 (hydroxyl alcohol groups) with succinic anhydride. The introduced terminal acid groups were then further converted into methacrylates by reaction with glycidyl acrylate, yielding methacrylate-functionalized Boltorn. This compound was found to form nanoparticles in water (critical association constant = 7.4×10^{-3} g/L), which could be loaded with daidzein, a hydrophobic traditional Chinese medicine. In the presence of the enzyme Lipase PS, the drug-loaded nanoparticles degraded in a random one-by-one manner and released the drug over a few days. However, the uptake of daidzein was rather low, as shown by the fact that its solubility in water went up from only 1.7×10^{-6} g/mL in the absence of hyperbranched polymer to 4×10^{-5} g/mL in the modified Boltorn solution at 5×10^{-3} g/mL.

The feasibility of using conjugates of PEI (25 kDa) and PEG (550 or 5000 g/mol, respectively) to protect oligonucleotides including ribozymes, a particularly unstable type of oligonucleotides, has also been evaluated.[64] The latter compounds are promising candidates in the search to modify gene expression in cells, but due to their instability are very difficult to administer properly. The PEI-*g*-PEG copolymers with the short PEG chains showed very good oligonucleotide condensing and protecting properties, comparable with PEI itself, though at far lower levels of complement activation.

Another approach involving delivery of oligonucleotides, at the same time aiming at direct targeting, was explored by Scaria *et al.*[65] They investigated the potential of PEI conjugated with an Arg-Gly-Asp (RGD) peptide via a PEG spacer to take up and deliver siRNA (small interfering RNA) specifically to tumor cells. The siRNA used is able to suppress angiogenesis in tumor cells, and hence inhibits tumor growth. The RGD peptide-conjugated PEI-*g*-PEG showed very good specificity for the relevant gene expression in tumor cells, in contrast to

PEI-*g*-PEG without the RGD sequence. The latter showed comparable activity in different types of healthy cells and much higher activity in lung cells than in the tumor cells.

15.3.2 Controlled Release of Pesticides

A somewhat related application of hyperbranched polyesters could also be mentioned here. Heiden *et al*. investigated the application of poly(vinylpyridine) (PVP) as a matrix for the encapsulation of hydrophobic fungicides (chlorothalonil, tebuconazole) for wood protection.[66] This allows the use of aqueous emulsions of the fungicide-loaded nanoparticles for conventional pressure treatment of wood and hence avoids the common hydrocarbon oil, which prohibits the use of the treated wood for many applications. The encapsulation of the fungicide into the polymer particles could also result in controlled release, enhancing the efficiency of the fungicide. As the release rate of the fungicide is very important for its activity against the fungi that attack the wood, it is highly desirable that this release rate should be fine-tuned. The hypothesis of this research was that addition of Boltorn polyols G2, G3, G4, and G5 to the PVP matrix was expected to increase the porosity of the matrix and consequently, to enhance the release rate of the fungicide. (It should also be noted here that the abbreviation used (Gn, referring to the generation number in the case of dendrimers) may be confusing as these polyols do not differ from each other to the same extent as the generations of dendrimers.) The measured release rates showed a definite increase as a function of the molar mass of the added polyol. It is, however, not clear whether this is a consequence of enhanced porosity or of the higher polarity of the matrix, decreasing the affinity for the rather hydrophobic fungicide. The activity of wood protection of the polymer-encapsulated fungicide was assessed by monitoring the weight loss of the wood after 55 days of exposure to the brown rot fungus *Gloeophyllum trabeum*. No real correlation between the release rate and biological efficiency could be found, suggesting that all the release rates observed exceed the minimum threshold to protect the wood sufficiently. Significant levels of biological efficacy were seen at very low levels of fungicide loading, suggesting that significant amounts of biocide are lost when not applied via a polymer matrix.

15.4 BIOMATERIALS

Two main areas of application for hyperbranched polymers in the field of biomaterials have been suggested. The first is their use as coatings or monolayers to modify the interactions and compatibility of various materials in a biological environment. The second is the modification of the properties of materials for use in biological environments or as biodegradable polymers. This can be achieved either by addition of the hyperbranched macromolecules to the bulk of the material or by direct introduction of branches in the parent linear polymer.

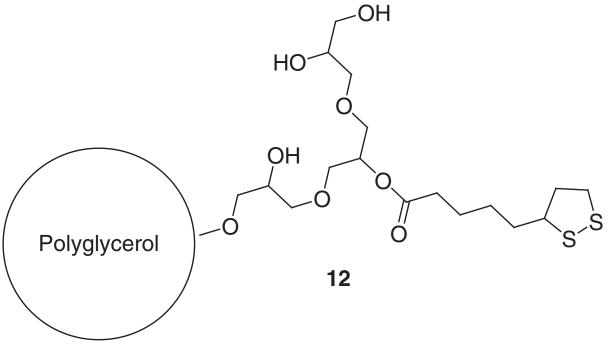


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Figure 15.9 A dithiolane-functionalized polyglycerol for the modification of gold surfaces.

15.4.1 Surface Modification

The monolayer approach to modify surfaces in order to decrease their susceptibility to protein adsorption was explored by Haag *et al*., using a gold surface modified by the functionalized hyperbranched polyglycerols **12** (Figure 15.9).[67] In order to induce sufficient affinity for the gold substrate, the polyglycerol had been functionalized with a 1,2-dithiolane moiety via an ester linkage to the free alcohol groups (with an average of 0.6–2.2 dithiolane units per macromolecule). Four different types of hyperbranched polyglycerol were used: one with $M_n = 5000$ g/mol and a trifunctional core (trimethylolpropane); one with $M_n = 2500$ g/mol and one with $M_n = 5000$ g/mol, both with a pentaerythritol core; and finally, a polyglycerol initiated from glycerol and an $M_n = 5000$ g/mol with 88% of the terminal alcohol groups transformed into methyl ethers. This set of polyglycerols permits the investigation of the influence of the molecular weight, the initiator multiplicity, and the functionalization of the hydroxyl end groups. The latter issue was of particular importance, since a detailed investigation of the protein-repelling properties of small molecules had revealed that the presence of hydrogen-bond acceptors increased protein adhesion.[68] All of the dithiolane-functionalized polyglycerols reduced the adhesion of fibrinogen on the gold surface to an extent similar to the well-known $HS\text{-}(CH_2)_{11}EG_3OH$. Small differences were found between polyglycerols with a trimethylolpropane core and those with a pentaerythritol core, the latter performing slightly better. This was explained on the basis of the better space-filling properties of the more globular, tetrafunctionally cored derivatives. Unlike in the previously mentioned literature,[68] the methyl ether derivative was found to be slightly more adhesive. The use of hyperbranched polyglycerol was found necessary, as a control experiment with a monolayer of thioglycerol revealed hardly any protein repellency. The main advantage of the investigated hyperbranched polyglycerol with respect to the well-known oligo(ethylene glycol) derivatives may be its higher thermostability. The onset of thermal decomposition of PG_{5000} under nitrogen was seen at

395 °C (225 °C under air), which is 115 °C higher than that of PEG_{2000} (110 °C under air). This is considered to be of great importance, as elevated temperatures are typically used for sterilization of biomedical devices.

A more common and widely applied approach for the modification of surfaces is coating. Hyperbranched polymers, in general, possess interesting properties that are of use in coatings, such as high end-group density and low melt viscosity. In the studies by Wooley *et al.*,[67–71] a coating of **13** was covalently fixed to a glass surface via silicate linkages (Figure 15.10). The coating itself consisted of a highly fluorinated aromatic polyether which was cross-linked by nucleophilic aromatic substitution with varying amounts of polyethylene glycol diamino derivatives (14%, 29%, 45%, and 55% weight). The adsorption of several biomolecules to these surfaces was monitored using fluorescent bovine serum albumin, lipopolysaccharides from *Salmonella minnesota* and *Escherichia coli*, and the lectin form *Codium fragile*. The coatings with 45% and 55% of PEG were found to be the least adhesive for these biomacromolecules. Surprisingly, neither the pure PEG nor the pure fluorinated hyperbranched polymer displayed

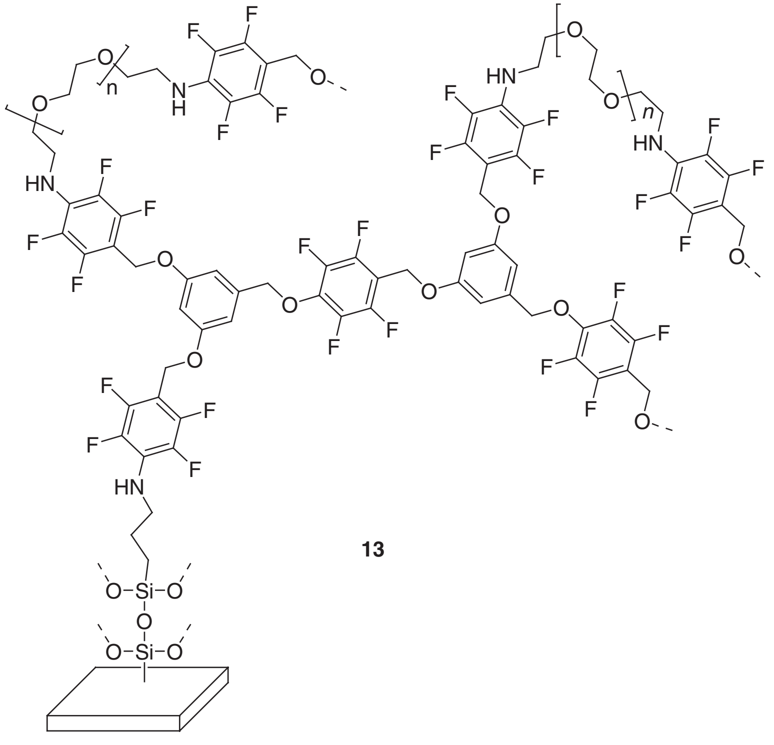

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Figure 15.10 Hyperbranched coating, consisting of a perfluorinated aromatic polyether cross-linked with polyethylene glycol, displaying antifouling properties.

the same potency in this respect. Increasing the PEG content resulted in a higher surface free energy. Both the pure hyperbranched fluorinated polymer with the lowest surface free energy and the PEG coating, well known for its optimal protein resistance, were ineffective in preventing fouling by biomacromolecules since they possessed varying affinities toward hydrophobic and hydrophilic surfaces. The antifouling properties of the coatings were evaluated by investigating the settlement of the green alga *Ulva*. In this case, the coating with 45% of PEG was found to be far superior to others. These findings suggest that not only the surface free energy but also the surface compositional and morphological heterogeneity are highly important for this kind of application. AFM and DSC experiments clearly showed that phase separation occurred at the surface and revealed that the coating with 45% of PEG exhibited multiple melting temperatures, reflecting an inherent morphological heterogeneity that was expected to be reflected in surface topography and composition.

15.4.2 Modification of Bulk Materials

The introduction of branching can be applied to modify the properties of biodegradable polymers. Since poly(L-lactide) (PLA) shows good biocompatibility and biodegradability, high mechanical strength, and excellent shaping and molding properties, it has long been one of the most important materials for biomedical applications. Its high crystallinity, however, can be a problem due to the resulting brittleness of the material and poor compatibility with soft tissues. The introduction of branching in the polymer chain could be a strategy to overcome this problem. In recent work by Frey *et al*., a series of PLLA (poly(L-lactic acid), **14**) was obtained by copolymerization of L-lactide with different ratios of the AB_2 monomer 2,2′-bis(hydroxymethyl)butyric acid (BHB) (Figure 15.11).[72] In this way, the DB could be varied between 0 and 0.47. A similar approach was developed for ε-caprolactone, which was polymerized by enzyme or metal catalyis.[73,74] Ouchi also investigated copolymerization of lactide with mevalonolactone in a fixed 9:1 ratio.[75] In all cases, it was found that the degree of crystallinity decreased with increased branching. For PLLA modified with BHB, no crystallinity was observed from an AB_2 monomer content of 8% onwards. It can be expected that lower crystallinity leads to increased biodegradability, as well as better compatibility with soft tissues.

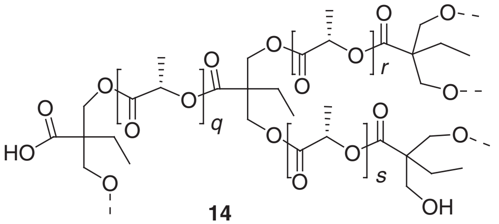

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Figure 15.11 Hyperbranched poly(L-lactic acid) formed by copolymerization of L-lactide with an AB_2 monomer.

Blending of Boltorn H30 ($M_w = 3500$ g/mol) to composite materials composed of PLLA and flax fibers was found to improve the mechanical properties of these biodegradable composites.[76] In particular, the fracture toughness improved (increased by more than 100% upon blending 30% of Boltorn) without compromising the static and dynamic mechanical properties. This was attributed to the better wetting of the flax fibers by the matrix, in presence of the hyperbranched hydroxyl group–terminated hyperbranched polymer. Moreover, the T_g and the crystallinity of the bulk material went down significantly with increased proportion of Boltorn. On the other hand, the presence of the hyperbranched polymers was found to facilitate the crystallization process, probably due to the lower T_g and hence, the higher mobility in the melt. Similar results were also obtained in another study at lower blending ratios.[77]

15.4.3 Modification of Dental Resins

Hyperbranched polymers have also been explored as components or additives of superior composite materials for dental repair. Composite materials used for this purpose containing low molecular weight multifunctional (meth)acrylates usually undergo significant shrinkage during curing, resulting in microfractures in the materials and sometimes, in enamel edge cracks.[78] Secondary caries may get promoted as a consequence of these defects. The use of (meth)acrylates with higher molar mass could reduce this shrinkage, but usually also increases viscosity, which is disadvantageous for convenient use of the formulation. The use of hyperbranched polymers with (meth)acrylate end groups can help to solve this problem because of their relatively high molar mass, inherently low viscosity, and high degree of functionalization.

Klee *et al*. evaluated the shrinkage and mechanical strength of composites containing trimethylolpropane-cored poly-(2,2-dihydroxymethylpropionic acid) ($M_n = 1900$ g/mol, based on NMR) of which the terminal hydroxyl groups had been esterified with different mixtures of methacryloyl chloride and isobutyric acid chloride (with molar ratios of 1:4 and 1:1 respectively).[78] Polymerizable mixtures were prepared on the basis of these hyperbranched methacrylates (74–81% weight) and the smaller triethylene glycol dimethacrylate (TEGDMA) and trimethylolpropane triacrylate (TMPTA), respectively. Camphoroquinone and *N*,*N*-dimethylamino-*p*-benzoic acid ethyl ester (DMABE), common additives for visible-light-curable resins, were added. The final resins were prepared by mixing these polymerizable mixtures with an appropriate filler (73–74% weight) being TPH glass (barium alumino silicate glass, Dentsply De Trey) or Dyract glass (strontium alumo sodium fluoro phosphoro silicate, Dentsply De Trey), respectively. The mechanical strength of these composites after curing was found to be inferior to commercially available analogs such as Spectrum® (Dentsply De Trey). However, significantly lower shrinkage ratios of 0.53–1.55% compared to 3.35% were observed in the case of Spectrum.

In other studies, Boltorn hyperbranched polyols (H20, $M_n = 1500$ g/mol; H30, $M_n = 2200$ g/mol; H40, $M_n = 2600$ g/mol) were fully esterified at the periphery by treatment with methacryloyl chloride, and the resulting esters (H20-MMA, H30-MMA, and H40-MMA) were blended with a dental resin system consisting of bisphenol A glycidyl dimethacrylate (bisGMA) and TEGDMA in a 1:1 ratio.[79,80] Upon addition of 10% of the hyperbranched methacrylate to this resin formulation, shrinkage upon curing decreased by almost 50%, and the mechanical strength increased on the order of 15%, whereas the viscosity of the blend increased only to a minor extent. Biocompatibility assessments revealed that monomer leaching from the cured resins was lower than in the case of the unblended resin and that human gingival fibroblasts showed equal viability on this modified resin.[81]

In a slightly different approach, 1:1 mixtures of TEGDMA and H30-MMA derivatives were investigated.[82] Methacrylate ester attachment to the terminal hydroxyl groups was achieved either by direct esterification (resulting in **15a**) or by reaction with isocyanatoethyl methacrylate, resulting in urethane linkages within the polymer structure **15b** (Figure 15.12). Blending of the latter polymer with TEGDMA in a 1:1 ratio resulted in slightly higher viscosity, but more importantly, it was the only blend that was found to be of superior mechanical strength with respect to the control resin consisting of bisGMA and TEGDMA in a 1:1 ratio. The use of H30 esterified with mixtures of acetic acid and methacrylic acid resulted in around 50% lower viscosity and in the order of 40% shrinkage reduction, both with respect to the control mixture. It was shown that these H30 methacrylates performed comparably well for all ratios of methacrylate to acetate that were higher than 50%.

Poly(methyl methacrylate) (PMMA)-based dental resins could be significantly reinforced by addition of as little as 1% of methacrylated Boltorn E03000 16 as shown by fracture assessments (Figure 15.13).[83] However, further increase of the methacrylated hyperbranched polymer **16** content resulted in a decrease of fracture toughness. For a 5% content of **16**, the fracture toughness was again similar to that of the unmodified PMMA, and a 10% content resulted in a 20% decrease of the fracture toughness with respect to the unmodified PMMA. A polyether was used instead of polyester due to its anticipated superior hydrolytic stability.

Analogous results were found in a study exploring the addition of unmodified Hybrane polyesteramide to a dental composite formulation based on bisGMA

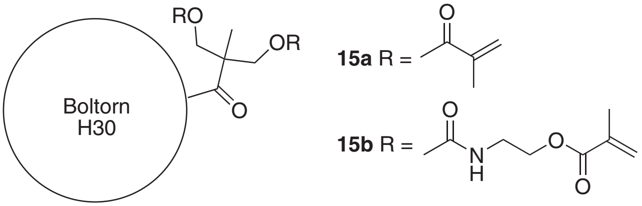
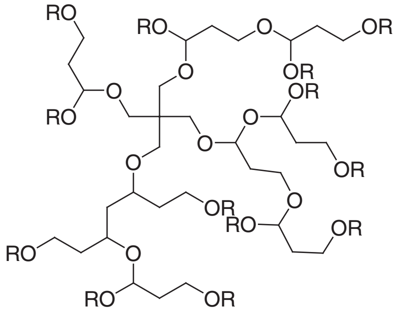


Figure 15.12 Methacrylate-functionalized Boltorn by either direct esterification (**15a**) or by urethane linkages (**15b**).



16 $R = CH_2{=}CHCO$

Figure 15.13 Methacrylated Boltorn E03000 **16** for modification of PMMA resins.

(14%), 2-hydroxyethyl acrylate (HEMA) (7.5%), and TEGDMA (6.5%) as the polymerizable substances and 71.5% of filler (97% silanized glass and 3% colloidal silica).[84] The optimal amount of Hybrane to be added was found to be as low as 0.3%, resulting in increased shear strength, minimal shrinkage, and enhancement of the bond durability of the resins for a variety of dental surfaces.

15.5 BIOINTERACTION

Since hyperbranched polymers possess numerous end groups, which can readily be functionalized, they could be of interest for the presentation of ligands to biomolecules or for the immobilization of enzymes, maybe inducing enhanced affinity through cooperative effects. A further advantage could be the protection of the conjugated biomolecules from potentially harmful physicochemical parameters of the environment.

15.5.1 Hyperbranched Polymers as Supports for Ligand Presentation

Hyperbranched aramides prepared by polycondensation of AB_2 monomers **17** and **18** and network-type analogs derived from polycondensations based on A_n+B_m strategies (monomers **19–24**) have been evaluated as supports for enzyme immobilization (Figure 15.14).[85] On the terminal carboxylic groups of these hyperbranched structures, α-amylase was covalently attached by activation with EDC (1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide). In general, high loads around 70–80% were obtained. k_m (a measure for the enzyme affinity for the substrate) and k_{cat} (a measure for the catalyst efficiency) were determined for these immobilized enzymes. In samples with a larger distance between the branching points, a higher affinity was observed, whereas the catalyst efficiency was found to be lower. This could mean that a less compact structure makes the interaction between the active site of the enzyme and the substrate easier, but does not

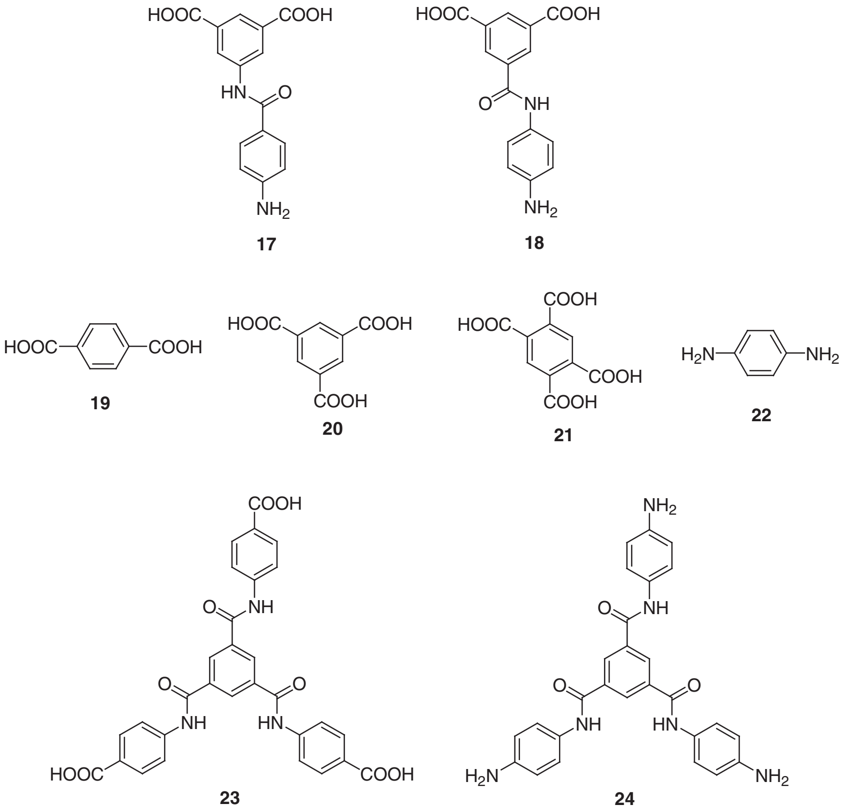


Figure 15.14 Different AB_2, A_n, and B_m monomers for the synthesis of network-type hyperbranched aramides for protein immobilization.

provide improved enzymatic activity. Like the unmodified form, the immobilized enzyme had its optimum at pH 6.5. However, at pH 9, the residual activity in most conjugated samples was significantly higher than that of the unmodified form. This could point in the direction of a protecting effect of the hyperbranched scaffold on the immobilized enzyme.

A somewhat related study investigated the interaction of Boltorn hyperbranched polymers H20 (16 OH terminal groups theoretically) and H30 (32 OH terminal groups theoretically) modified with sugar moieties with a lectin from *Lens culinaris*.[86] This was done in order to explore the potency of these hyperbranched polyethers as multivalent and nontoxic scaffolds for the presentation of different biologically important carbohydrates to their receptors. Mannose moieties were coupled via an aminoethoxy spacer to the hyperbranched polyesters modified with a carboxylic acid-terminated spacer. NMR studies based on saturation transfer difference experiments clearly showed that the interaction of the mannose conjugates with the *L. culinaris* lectin (LCA) exclusively occurred via the mannose moieties and not via the spacers or the hyperbranched scaffold itself. Furthermore, no significant toxic effects of the mannose-modified hyperbranched polyesters were observed up to a concentration of 3 mM on cell cultures of COS-7 and 293-T cells. Only a slight decrease in viability was seen at a concentration of 30 mM.

Precipitation assays were carried out in order to evaluate the binding efficiency with respect to LCA. Solutions of different concentrations of the sugar-modified hyperbranched polymers to be evaluated were mixed with a buffered 25-μM solution of LCA. The precipitate was isolated and redissolved in a 1-M methyl-α-D-mannopyranoside solution and the concentration of LCA was determined by UV spectrometry at 280 nm. It was found that, from a concentration of the mannose-modified hyperbranched polyester of 2 μM onwards, a marked precipitation could be observed, whereas no precipitate was formed with the free aminoethoxy-modified mannose up to concentrations of 1 mM. With the unfunctionalized hyperbranched scaffold, only very little precipitate was observed in the 1 mM concentration region. No significant difference could be detected between the behaviors of the H20- and H30-based systems. (This is consistent with their rather similar molar mass and end-group number.) These findings clearly point to the obvious importance of the multivalence of the hyperbranched conjugate to induce precipitation, but as the maximum amount of LCA that could be precipitated was in the order of 30% of the initial amount, they also suggest that the crowded presentation of the mannose moieties might not be favorable for the interaction with LCA.

15.5.2 Other Applications

Besides their use as drug or gene carriers, hyperbranched polymers can also be expected to act as drugs on their own. In this respect, Haag, Alban, and coworkers compared the potential of unmodified polyglycerol, carboxylated polyglycerol, and polyglycerol sulfates as antithrombotic agents.[87] The most commonly used antithrombotic at present, the natural sulfated polysaccharide heparin, suffers from several disadvantages associated with its biological origin such as limited availability, structural heterogeneity, and risk of contamination. Recent developments such as fondaparinux and ximelagatran circumvent many of these problems. However, these specifically acting antithrombotics lack the other biological activities of heparin such as complement inhibition as well as antiinflammatory, antiangiogenic, antimetastatic, antiatherosclerotic, antiproliferative, antiadhesive, and antiviral effects. Unmodified polyglycerol and carboxylated polyglycerol displayed neither anticoagulant nor anticomplementary activity. However, for sulfated polyglycerol, activities between 5% and 35% of unfractionated heparin were found. Moreover, the ratio of anticomplementary to anticoagulant activity is in the order of 80 to 300 times higher than for heparin. For the latter, the therapeutic utilization of the relatively weak anticomplementary activity is limited by the potential bleeding risk. Polyglycerol sulfates exhibit an improved efficacy–risk ratio, allowing the administration of efficient anticomplementary doses without inducing a high bleeding risk.

Finally, a remarkable study in which the crystallization of $CaCO_3$ at the solid–liquid interface was investigated should be mentioned.[88] The formation of biominerals by living organisms is governed by soluble and insoluble macromolecules with peculiar interfacial properties. Most of the studies on mineralization processes involve model systems that only account for the existence of one organic matrix and thus disregard the interaction between the soluble and insoluble organic components. In this study, a model system was set up consisting of a matrix surface, namely a self-assembled monolayer (SAM), and a soluble component, hyperbranched polyglycerol. In this study, a gold layer, coated on a glass substrate via a chromium connecting layer, was covered with a SAM consisting of alkane thiols terminated with methyl, hydroxyl, or a carboxylic acid groups. $CaCO_3$ crystals were grown on these surfaces from a $CaCl_2$ solution by diffusion of $(NH_4)_2CO_3$. In general, the more thermodynamically stable calcite is formed in most circumstances. This was also the case on SAMs consisting of all the alkane thiols mentioned in the absence of hyperbranched polyglycerol. However, in the presence of polyglycerol, the alcohol-functionalized SAM was found to induce the growth of pure aragonite, the less stable form of crystalline $CaCO_3$. The best results were obtained with polyglycerol molar masses in the range of 500–5000 g/mol. It was reasoned that the less polar (interior) part of the polyglycerol molecule is taken up by the apolar monolayer, resulting in the exposition of the terminal alcohol groups at the interface in a disordered way. The importance of this random exposition was confirmed by the observation that merely calcite was formed on alcohol-terminated monolayers, thus exposing hydroxyl groups in a highly ordered way to the water solution. The use of a carboxylic acid–terminated SAM in the presence of polyglycerol also resulted in calcite formation. Presumably, polyglycerol is attached to the carboxyl groups of this layer by its hydroxyl groups, exposing the internal, more hydrophobic part and not the required alcohol groups to the water phase, making the interface unsuitable for aragonite formation.

15.6 CONCLUSIONS

Clearly, it has been shown that hyperbranched polymers do possess a lot of potential for applications in the biological and biomedical field. However, suggestions have been far more numerous than actual research and *a fortiori* than proofs of usefulness. On the basis of the current state of the art, it is expected that a great deal of potential still remains to be explored, mainly in the field of gene delivery. The main issue continues to be the realization of a gene vector that is highly efficient, highly specific, and less toxic. However, applications such as dental resin, modification of surfaces for biocompatibilization, and modification of biodegradability of bulk materials may definitely merit further investigation.

For many of these (potential) applications, it is anticipated that the less well-defined structure of hyperbranched polymers, as compared to dendrimers, will hardly be a drawback. Obviously, the broad polydispersity can complicate the characterization of hyperbranched polymers as well as their evaluation for (biomedical) application. However, for most of the suggested and investigated purposes, this is only an inconvenience which is largely overruled by the easy accessibility of hyperbranched polymers as compared to dendrimers. In certain studies, even a positive effect of the typical, randomly branched structure was observed. On the other hand, for several types of hyperbranched polymers such as Boltorn and polyglycerol, rather well-defined structures can be obtained with reasonable polydispersity. Therefore, it may be expected that hyperbranched polymers could play an even more important role in biomedical sciences than imagined so far.

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Chapter 16

Applications of Hyperbranched Polymers in Coatings, as Additives, and in Nanotechnology

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16.1 INTRODUCTION

Today, hyperbranched polymers (HBPs) are discussed and widely used today in different applications. Certainly, a major use of these highly branched materials that have already been commercialized as reactive components in coatings and resin formulations. In addition, potential applications as additive compounds in linear polymers, especially for improving rheological, flow, and surface properties as well as thermal stability and modulus, is also a major reason for the development of hyperbranched macromolecules as specialty polymers. These application fields relate to the major features of HBPs: a highly branched, dense, but irregular structure which leads to excellent solubility; low solution viscosity; and modified melt rheology behavior, in combination with the chance to introduce a high variety of reactive end functionalities.[1–4]

Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

Besides these rather well-documented applications, new fields have been explored where the dendritic structure on the nanometer scale plays a significant role, with the possibility of a specific confinement of functional units, formation of cavities, and interesting molecular dynamics. For example, as thin films in sensorics and diagnostics, as porogens for nanofoams, or as carriers for additives, catalytic species, and drugs.[5–9]

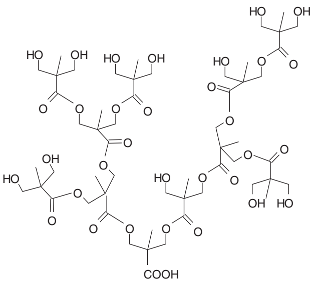
While biomedical and encapsulation applications (Chapter 15) as well as surface properties (Chapter 14) of HBPs and HBPs as novel materials with specific optical and electronic properties (Chapter 10) are covered in other chapters of this book, here we will focus on the use HBPs in coatings and resins, as additives for linear polymers and composites, in nanotechnology, and in thin film and sensor applications.

16.2 HYPERBRANCHED POLYMERS IN COATING AND RESIN APPLICATIONS

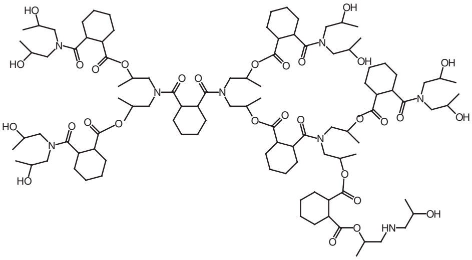
HBPs are particularly interesting for technical applications, because they resemble dendrimers but can be produced more easily on a larger scale at a reasonable cost. They are characterized by a highly branched backbone, which gives access to a large number of reactive groups. Their structure gives them excellent flow and processing properties, which have attracted a great deal of attention for application in coatings and formulations; for example, for powder coatings,[10,11] high-solid coatings,[12] flame retardant coatings,[13], and barrier coatings for flexible packaging.[14,15] The preparation of thermosets based on HBPs, which also makes use of the reactive end groups, has attracted considerable interest.[16–20]

The first HBPs studied in this field were the aliphatic polyesters based on bis-hydroxymethyl propionic acid (BHMPA) as described by Hult[4] and commercialized by Perstorp under the trade name Boltorn™ (Scheme 16.1).[17,21–31] A variety of reactive groups, such as acrylate, methacrylate, and epoxy functions, had been introduced to allow their use in coatings and resins, often in combination with long alkyl chains which provide the right flow and viscosity properties and also allow their use in powder coatings.[32] Shi and Ranby[30] reported early on also on the use of suitably acrylate-modified hyperbranched polyesters in photocuring formulations. Dusek[33] described in detail how the dendritic structure of hyperbranched precursors influenced the final network structure in cross-linked materials.

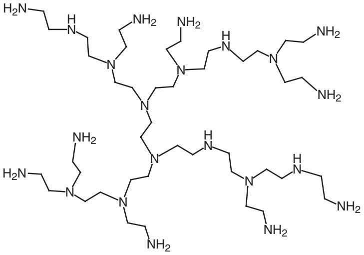
By now, a variety of HBPs with acrylate, vinyl ether, allyl ether, or epoxy functions have been studied as multifunctional cross-linkers in coatings and thermosets, using thermal- as well as UV-curing methods.[10–16,33–37] However, polyesters still dominate the field, with the Perstorp "Boltorn" products leading in technical studies and with hyperbranched polyesters based on the relatively easily available bis(4-hydroxyphenyl) pentanoic acid (BHPPA) often used in academic studies. Further examples for HBPs specially suited for commercial coatings and resin application include the commercialized poly(esteramide)s from DSM under



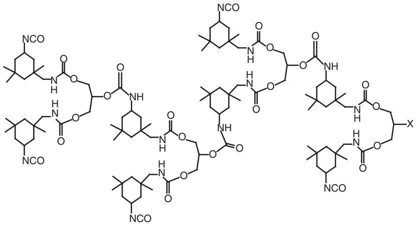
Boltorn™ (Perstorp)



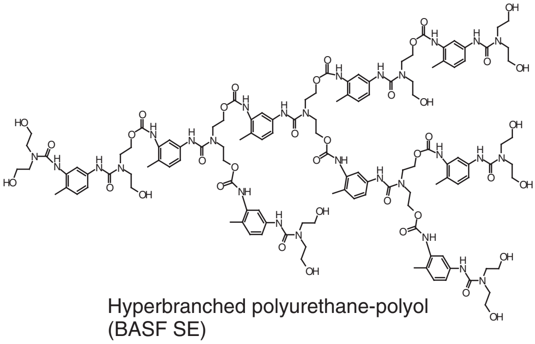
Hybrane™ (DSM)



Lupasol™ (BASF SE)



Hyperbranched polyurethane-polyisocyanate (BASF SE)



Hyperbranched polyurethane-polyol (BASF SE)

Scheme 16.1 Hyperbranched polymers of commercial interest.

the trade name Hybrane™ (Scheme 16.1),[3] polyethyleneimines from BASF SE under the trade name Lupasol™, and polyurethanes (PUs)[38,39] and polyesters,[40] developed by BASF (Scheme 16.1).

16.2.1 Hyperbranched Polyesters in Reactive Formulation Application

The most prominent use of hyperbranched polyesters is as polyols or reactive multifunctional components or additives in coating and resin formulations.[17,21,29–31,34–38,41–45] Hyperbranched polyesters with OH, acrylate, methacrylate, vinyl ether, allyl ether, oxetane or epoxy functions were studied as multifunctional cross-linkers in coatings and in thermosets, using thermal- as well as UV-curing methods. For example, Boltorn found commercial application in thermoset resins,[45] UV-curable coatings including dental applications,[17,46,47] and others in paper coatings.[10,34,36] In general, the advantageous features of the use of these HBPs in reactive formulations are an adapted viscosity,[45,48] a high reactivity in combination with low volatility, and often, an improved toughness,[20,48] without affecting either the viscosity of the uncured coatings or the thermomechanical properties of the cured material. In addition, there is the chance for adapted multifunctionality in the hyperbranched component, for example, combination of the reactive epoxy group and the long alkyl group. Some examples will be outlined in the following section.

For example, in a first attempt, Voit *et al.* modified aliphatic–aromatic hyperbranched polyesters based on BHPPA with UV-curable vinyl ether groups.[41] These molecules react extremely fast in UV formulations to rapidly convert vinyl groups; however, a 1:1 mixture with a difunctional reactive diluent (triethylene glycol divinylether) is necessary to achieve high conversion rates of the functional groups (Figure 16.1). Otherwise, the formulation solidifies so fast that no complete conversion is possible. The resulting coatings show good adhesion to aluminum and exhibit good mechanical properties and hardness; nevertheless, the modification of the hyperbranched polyester with vinyl ether functions requires an expensive Mitsunobu reaction which makes the process unattractive for commercialization.

More recently, it was found that the phenolic end groups of the hyperbranched BHPPA polyesters themselves are rather active as transfer reagents, for example, in the cationic photocuring process of epoxides (Scheme 16.2).[42] It is known that OH-containing molecules can act as transfer agents in the photoinitiated reaction.

Thus, by adding 5–20% of the hyperbranched polyol (*p*BHPPA (core)) to the bis-cycloaliphatic diepoxy resin 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexyl carboxylate (CE, Scheme 16.2), it was possible to increase the

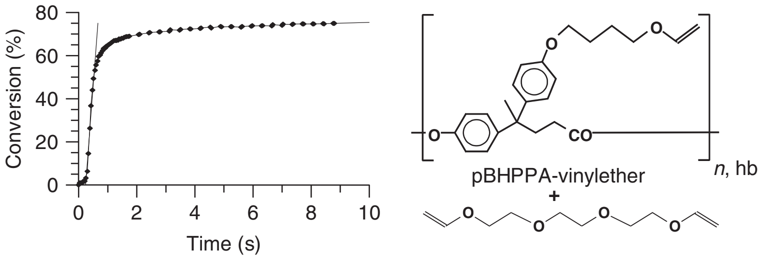
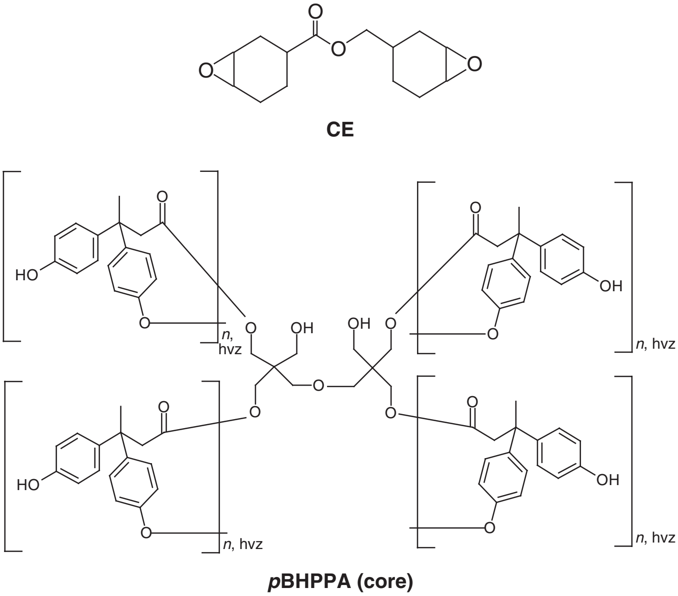


Figure 16.1 Conversion of vinyl ether groups in the coating versus UV irradiation as monitored by rapid scan in-line FT-IR spectroscopy (*p*BHPPA-vinyl ether modified/triethylene glycol divinylether 1:1, 2% UV initiator).[41]



Scheme 16.2 Coating formulation of an epoxy component (CE) and a hyperbranched, aliphatic polyester (*p*BHPPA, modified by using a core molecule).[42]

conversion and speed of the cross-linking reaction (Figure 16.2). Furthermore, higher gel points were achieved with full covalent incorporation of the hyperbranched components, and finally a much better toughness of the resulting epoxy coating was obtained. Also, the modulus and thermal stability could be improved by simply adding the unmodified hyperbranched polyester to the coating formulation.

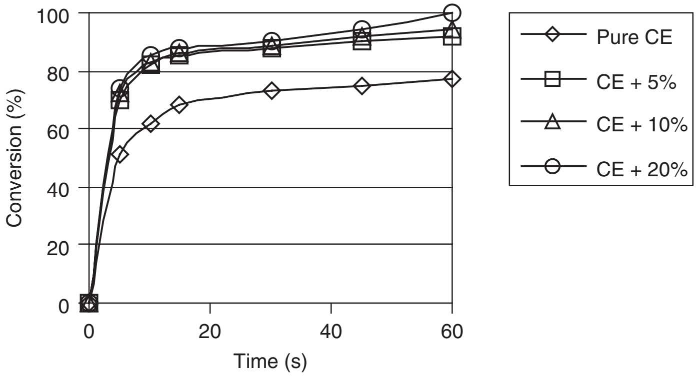


Figure 16.2 Conversion curves (determined from FT-IR spectroscopy) as a function of irradiation time for the system CE + different amounts of hyperbranched polyester *p*BHPPA(core).[42]

A very similar effect was observed when aliphatic, OH-functionalized, hyperbranched polyesters (Boltorn types H20, H30, and H40) were added to a photocurable epoxy coating system. Again, the hyperbranched polyester was incorporated into the network structures and the toughness of the epoxy coating could be improved.[49]

This transferability of OH groups can also be used to chemically bind hyperbranched additives: for example, hyperbranched BHPPA polyesters modified with some long-chain fluorinated end groups into a classical epoxy coating. The remaining unmodified phenolic groups allow chemical bonding with the coating, whereas the fluorinated part is responsible for surface segregation and achievement of low energy surface properties, again without negatively affecting the major coating properties.[44]

Of course, hyperbranched polyesters with OH end groups are also suitable as low volatile polyols in thermally cured coating or thermoset formulations, for example, PU coatings.[35,50,51] For example, the hyperbranched polyester based on BHPPA was applied as polyol in a classical thermally cured PU cross-linking system using 1,6-hexamethylene di isocyanate (HDI) and its trimer (Desmodur™ N3300, Bayer Material Science) as isocyanates.[51] Several effects like those of the solvent, nature of catalyst, and formation of various intermediates were considered in an attempt to elucidate their influence on urethane formation. In contrast to typical PUs, an aromatic OH group was involved in this case, and it is known that the reaction of these phenolic groups is considerably slower than that of the aliphatic hydroxy group. Additionally, it was observed that the reactivity of the phenol group in *p*BHPPA-OH is lower than in 4-ethylphenol of low molar mass, due to steric hindrance in the HBP. But by casting 50% solutions in MPK or diglyme of *p*BHPPA-OH and Desmodur N3300, sheets and films could be prepared and were studied by a number of methods. The studies showed that the HBP *p*BHPPA-OH is a suitable OH-functional precursor for the elevated temperature–curable, two-component, high-solid PU coatings for an application range of 80–100 °C. The surfaces of films are smooth and relatively polar. The effect of the core molecules added during the AB_x polycondensation on the final network properties in PU coatings was studied, and it was found that initially networks are readily formed, but an increase in core functionality also increases the ineffective functionalities within the polymer structure due to loop and cycle formation.[51] Thus, one has to be aware that the high functionality in HBPs might not be transformed completely into effective chain cross-links even when early solidification can be avoided.

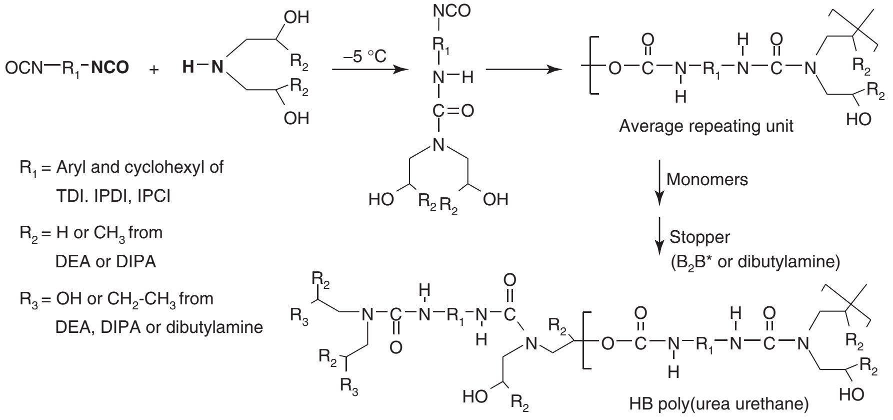
Another field that seems ideal for the use of hyperbranched polyesterols is PU foam formulations.[52] However, since these are highly complex multicomponent systems, one has to be aware that besides the attempted property changes, for example improvement of the flow before curing and increased strength of the final foam, other effects have to also be considered. Thus, modified hyperbranched polyesters (from BHPPA) showed a strong effect on the surface tension of a commonly used polyol in PU foam formulations, even when added in very small quantities.[53]

16.2.2 Hyperbranched Poly(esteramide)s

Hyperbranched poly(esteramide)s have been commercialized by DSM under the trade name Hybrane in 1999.[3] For that polymer, a monomer has been produced from a cyclic anhydride and diisopropanol amine (A_2+ B^*B_2 approach).[54,55] The resulting product, a tertiary amide with one COOH and two OH groups, readily undergoes polycondensation through a reactive oxazolinium intermediate under relatively mild conditions. By varying and combining anhydrides and modifying with several types of end groups, a large variety of structures with different properties and industrial applications have been realized.[3,11,56] The water-soluble product based on succinic acid anhydride and diisopropanolamine proved specially suited to being used as an additive for paper coating due to the resulting ideal control of the rheology of the coating dispersion at high production speed.[57]

16.2.3 Hyperbranched Poly(urea-urethane)s

One prominent example for a newly developed hyperbranched product for coating and resin application is the hyperbranched poly(urea-urethane) as reported by Bruchmann *et al.*[38,58–63] and Gao and Yan.[64] The synthesis involves the combination of $AA^* + B^*B_2$ monomers (Scheme 16.3), similar to the strategy used to prepare Hybrane. Here, the final structure contains both urea and urethane groups and both exist in linear, terminal, and dendritic units. The reaction can be controlled in highly concentrated solutions, resulting in a broad molar mass range in a reasonable and technically feasible time frame.[60] However, the polymer structure contains a large variety of substructures, even more than those determined in AB_x based HBPs. For the aromatic AA* monomer toluylene diisocyanate no reactivity preference of the *o*- and *p*-isocyanate groups toward the



Scheme 16.3 Reaction scheme for the preparation of hyperbranched poly(urea-urethane) polyol via a two-step $AA^* + B^*B_2$ method.

amino function in diethanol amine could be verified—meaning that it is, in reality, an $A_2 + B^*B_2$ system.[60] The resulting HBP is highly soluble, can be prepared as polyol or polyisocyanate for coating applications,[58] and offers, similar to all other HBPs, the potential for end-group modification.[60,61] By this, bulk and surface properties, for example, of coatings and thin films can be governed; however, due to the dominating interactions of the H-bonding urea and urethane groups in the backbone, to a lesser extent as observed, for the hyperbranched polyesters.[61]

Here, first of all the monomers are readily available from PU chemistry and thus are low cost. Secondly, the industry is well prepared with respect to control of reactions pertaining to conversion and to avoidance of gelation as long as common processes can be used: thus, the hyperbranched poly(urea-urethane)s are on the verge of being commercialized by BASF SE.[58,62]

The hyperbranched poly(urea-urethane) structures[60,62] can be applied in thermally curing two-pack coating systems, either as polyisocyanate cross-linkers[39] in combination with standard polyacrylate or polyester binders or as polyol binder in combination with standard isocyanate cross-linkers, for example, 1,6-hexamethylene diisocyanate (HDI) or its trimer (Basonat™ HI100, BASF). Stable, highly cross-linked, free-standing films were obtained which showed good mechanical properties. While the product based on aromatic HB polyol was strong and relatively brittle, the aliphatic HB polyol led to a softer and more elastic network (Figure 16.3).[63]

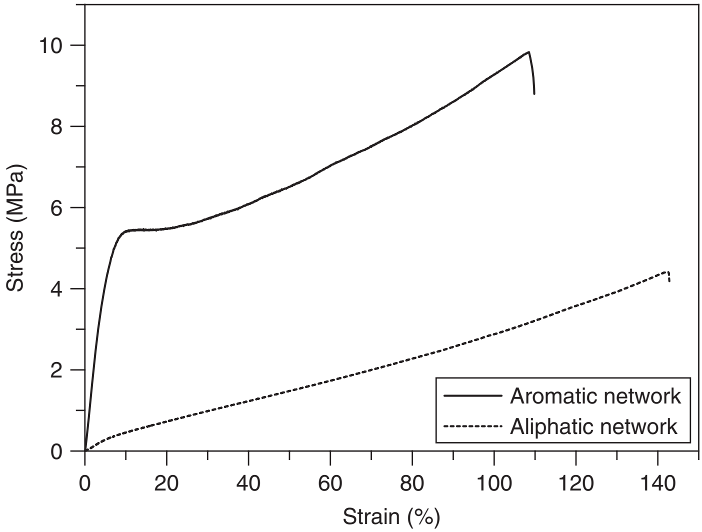


Figure 16.3 Stress-strain curves of thermally cured films of hyperbranched aliphatic (aliphatic network) and aromatic (aromatic network) poly(urea-urethanes) reacted with the trimer of 1,6-diisocyanatohexane.[63]

16.3 HYPERBRANCHED POLYMERS AS ADDITIVES

As already outlined, HBPs are mainly used in formulations for coatings or thermosets as the main reactive components. However, based on their unique properties resulting from their highly branched and compact structure, they are also studied and used as additives for a variety of duromers;[65] for example, as toughening,[18,20,48,66] curing, cross-linking, or adhesive agents[67–69] (some points have already been outlined above). Fluoro- and alkyl-containing HBPs are also used in order to control surface properties[44,70,71] such as antifouling and fouling release performance.[72] Furthermore, hyperbranched poly(esteramide)s (Hybrane) proved very suitable as additives for paper coatings dispersion to reduce friction, as oil field chemicals to suppress crystallization of gas hydrates, and to break azeotrops.[3,6] The use of HBPs as additives in thermoplastics, for example as processing aids, in printing systems, and as stabilizers, will be outlined in greater detail.

16.3.1 Additives for Linear Thermoplastics

The application of HBPs in processing as melt modifiers for thermoplastic polyolefines, polyamides, or polyesters,[73–82] as compatibilizers[19] or as blend components[83–85] is also widespread and has attracted strong industrial interest, especially of late.

Already, Kim *et al.*[85,86] have reported that blends of hyperbranched polyphenylene and linear polystyrene exhibited reduced viscosity at high temperatures and shear rates, and an improved thermal stability when compared to pure polystyrene. When hyperbranched polyesters were blended with linear polyesters, polyamides, and polycarbonates, as described by Massa *et al.*,[83] almost full miscibility was observed due to strong hydrogen bonding. The partially miscible polycarbonate blends exhibited an increase in the tensile strength and compression modulus but loss in toughness. Modified hyperbranched polyesters,[86] polyesteramides,[87] or polyethyleneimines[88] have been used as dye carriers in polyolefine blends. The resulting materials showed a reduced melt viscosity and a homogeneous distribution of the dye in the matrix. The fact that alkyl-modified, hyperbranched polyesters[86,88–90] or polyethers[91] show an amphiphilic character and can act as carrier molecules for physically enclosed organic molecules (e.g., organic dyes) such as in nanocapsules or in the dendritic box,[92] opens many new application fields beyond additive carriers for thermoplastics.

Hong *et al.*[93] found that alkyl-modified aliphatic hyperbranched polyesters have a strong effect on the rheological behavior of polyethylene (LLDPE). Also, melt rheology studies of Nunez *et al.*[94,95] showed drastic viscosity reduction as a function of HBP concentration, in blends based on hyperbranched polyesters and linear polymers. Hsich[96,97] studied the effect of molar mass on the rheological behavior of hyperbranched Boltorn-type polyesters and their blends.

At lower generations hyperbranched polyesters showed shear thinning, whereas at higher generations, a Newtonian dependency was found which was dominant in all studied blends if at least one blend component showed Newtonian behavior. Mulkern *et al.*[98] reported a strong lubricant effect of hyperbranched polyesters in polystyrene or styrene maleic anhydride copolymer blends. Jang *et al.*[99] showed that the crystallization behavior of a semicrystalline polymer was influenced by the presence of an HBP in the blend. However, Wahlen *et al.*[100] observed, that when hyperbranched, fully aromatic polyamides were added during the polycondensation, PA6 was reinforced. The effect of hyperbranched polyaramides on PA6 in solution and melt blending was also studied intensively by Russo *et al.*[101] Here, fully miscible blends were found as indicated by the observed glass transition and the melt rheology behavior. Strong hydrogen bonding between the components was discussed as the cause for the observed material properties. Voit *et al.* studied blends of hyperbranched aromatic–aliphatic poly(etheramide)s[102] with the commercial linear polyamide PA6.[103,104] All blends showed full miscibility. Further, when the concentration was kept below 10 wt%, the HBP had no significant negative influence on the melting and crystallization behavior of the PA6 matrix; the shear storage modulus even increased. But the rheological investigations exhibited an unexpectedly strong reduction in melt viscosity, even when only 0.1 wt% of HBP was added. With regard to the processing of PA6, the reduced melt viscosity without loss of mechanical properties implies interesting application aspects of HBPs as processing aids. The miscibility with the polyamide matrix as well as the resulting material can be controlled by the end groups of the HBP. Acetate and OH end groups allow for a good miscibility with the amorphous phase of the PA6 and when added in small amounts (1 wt%), lead to a decrease in melt viscosity but keep mechanical properties as well as crystallinity of the matrix unchanged. Miscibility is strongly reduced when long alkylester groups are introduced, finally showing phase separation in combination with a reduced melt viscosity, mainly due to a lubricant effect at the mixing aggregate/polymer melt interphase and also with some negative effect on mechanical properties.[104] Reactive end groups can also be applied to allow a chemical reaction between the modified HBP and the matrix polymer during melt mixing.[104] This can lead to a large increase in melt viscosity, accompanied by molar mass buildup; this changes the mechanical values as well as the crystallinity of the matrix significantly. Again, one notices, as in the case of the hyperbranched polyesters, that HBPs with polar end groups show a shear thinning effect which points to a strong internal interaction leading to a kind of a physical network, while alkyl-modified samples show a significantly lower melt viscosity and a classical viscous flow behavior.[104]

In general, one has to state that the effect of HBPs on the properties and flow behavior of linear thermoplastic polymers can be rather complex since besides the individual flow behavior of the HBP and the linear counterpart, changes in crystallinity as well as miscibility, hydrogen bonding, and reactions between the components have to be considered, which might have opposite effects.[105]

Nevertheless, after optimization, HBPs have a strong potential as processing aid and, in some cases, may even improve mechanical properties of the matrix component.

16.3.2 Printing Systems

HBPs can also act as binders or additive components in printing inks for packaging materials, especially for printing on polymer films. Two different systems for printing are currently used in industry: one for printing on polar film materials like polyester or polyamide, the second for printing on nonpolar films like polyethylene or polypropylene (PP). BASF reported a system that works equally well on both groups of polymer materials.[62,106,107]

In a test, a sticky tape was placed on the freshly printed side of the polymer film and removed immediately. If the printing system is poor and the printing ink does not adhere to the polymer material, removing the sticky tape leaves a colorless stripe or smeared area on the polymer surface where the dye came off with the tape. When the printing system containing an HBP was subjected to the sticky tape test, the printing ink was found to adhere equally well to polar and nonpolar polymer films (Figure 16.4).

16.3.3 Stabilizers

A further interesting application where HBPs are used as additives is in the field of stabilizers. An early study published by Dillon *et al.*[108] used aromatic hyperbranched polyesters with benzotriazole end groups as UV light stabilizers or metal chelators. These stabilizers showed improved compatibility and solubility

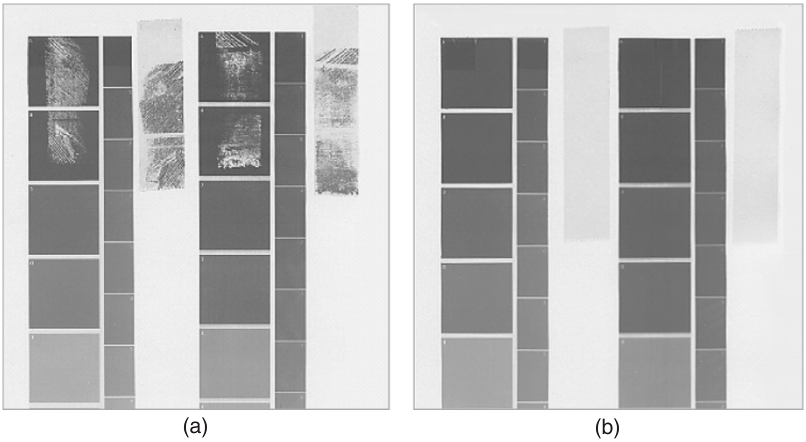

(a) (b)

Figure 16.4 Sticky tape test for comparison of printing systems: (a) poor printing system and (b) poor printing system improved by addition of HB polymer.

within polymer matrices. Thiol-group-containing HBPs and dendrimers were synthesized by Maignan,[109] using these sulfur-containing polymers as antioxidants. Lange a *et al.*[110] developed stabilizers based on poly(alkylene)imine dendrimers or HBPs, where terminally sterically hindered phenols were attached. These systems worked well as thermooxidative stabilizers in segmented polyether–ester copolymers with improved compatibility with respect to the polymer matrix.

A very general approach toward dendritic stabilizers was made by McNamara *et al.*,[111] focusing on UV stabilization, heat stabilization, and antioxidants. The examples are based on polyesters of BHMPA, modified with sterically hindered amines or phenols, benzotriazoles, or triazines. The stabilizers were tested as dyeability promoters for PP, as nonfogging stabilizers for PE, or as dye stabilizers in printed articles.

Hyperbranched phenolic antioxidants based on a BHMPA backbone (Boltorn) were also described by Malmstroem *et al.*.[112] Polyesters of different molecular weights were modified at the outer shell with sterically hindered phenol groups and tested as antioxidants in squalane as well as in PP. Compared to standard antioxidants, the hyperbranched antioxidants showed improved effectivity in squalane but were inferior in PP.

Stabilizers based on PU chemistry were described by Bruchmann *et al.*,[39,113] using hyperbranched PU–polyisocyanates as a backbone for attachment of isocyanate-reactive stabilizing units, such as hindered amines, hindered phenols, or benzophenones. These polymers were tested as stabilizers in thermoplastic PU and styrene copolymers.

16.4 APPLICATIONS OF HYPERBRANCHED POLYMERS IN NANOTECHNOLOGY

16.4.1 Nanocomposites and Nanohybrids

Hybrid organic–inorganic nanocomposites have attracted considerable attention in recent years, because they combine both the advantages of organic polymers (flexibility, lightweight, good impact resistance, good processability) and inorganic materials (high mechanical strength, good chemical resistance, thermal stability, optical properties).[114,115] Many nanocomposites based on conventional linear polymers have been prepared and characterized so far,[114–116] but still very few and recent studies have been reported on the use of HBPs in combination with inorganic nano-objects.[117–119] Moreover, in only some of these, HBP has been employed as the main organic phase and not as an additive in combination with other linear polymers.[119–124] The presence of a large number of functional end groups and the peculiar globular shape of the HBPs seem to be advantageous for the synthesis of nanocomposites, as they can allow a better interaction of the organic phase with the inorganic particles; thus, one can expect that this field will be further exploited.

One of the first reports on the use of HBPs in the field of nanocomposites is by Plummer *et al.*[125–127] and refers to the use of clay modified with OH-functionalized AB_2-type hyperbranched polyesters based on BHMPA (Boltorn) and their integration in PU networks by solution and melt processing. High levels of exfoliation could be achieved, and in addition, a detailed study of the rheological behavior was reported, correlating rheological properties and mechanical response.[127] Ratna *et al.*[123] employed hyperbranched BHMPA-based polyesters in epoxy resins under addition of layered silicate. The toughening effect of the HBP was mainly retained in the resulting nanocomposite, whereas the clay allowed an increase in strength which was only slightly reduced by the presence of the hyperbranched polyester. Russo *et al.*[124] patented the use of layered organophilic clays containing dendritic polymers and quaternary organic salts in thermoplast nanocomposites and the modification of organo clay with hyperbranched polyaramides was reported.[128]

In addition to the use of HBPs as additives to improve exfoliation and toughness in clay-modified resins, the modification of silica composites has also been reported. For that, Shi *et al.*[129] grafted AB_2-type polyesters modified partially with OH, COOH, and octadecyl end groups onto silica nanoparticles (30 nm) using 3-glycidoxy-propyltrimethoxysilane (GPTS) as linkers. The incorporation of the grafted silica particles (3–5%) enhanced the notched impact strength as well as the tensile strength of PP, without affecting the crystallinity. Similarly, Zhao *et al.*[130] observed improvement in toughness and strength of PVC by adding poly(ester amide)-grafted silica nanoparticles. Mori *et al.*[131,132] grafted silica nanoparticles by selfcondensing vinyl polymerization via ATRP, employing an acrylic AB* inimer. Novel core–shell nanomaterials, branched PAA–silica hybrid nanoparticles, were obtained after hydrolysis of the linear segments of the branched P(*t*-BuA).

Also, silica and titanium hybrid materials have attracted considerable attention. Novel polyimide–silica hybrid membranes were investigated by Suzuki and Yamada.[133] The hybrids were prepared using the hyperbranched polyamic acid, water, and tetramethoxysilane (TMOS) in a sol–gel reaction. The CO_2/CH_4 selectivity was found to improve significantly when the silica/hyperbranched polyimide hybrids were prepared as membranes, as compared to linear-type polyimide/silica hybrids. A sol–gel process in the presence of a hyperbranched triethoxysilane-functionalized Boltorn polyester was also used by Lu *et al.*[134] to prepare new SiO_2–TiO_2 hybrid epoxy networks. It was shown that the impact strength of the cured system modified with the hyperbranched polyester was two times higher than that of the neat epoxy. The SiO_2–TiO_2 nanoparticles within the matrix were between 20 and 60 nm in size.

A similar study was reported by DiGianni *et al.*[135] An aromatic–aliphatic polyester (*p*BHPPA), OH-terminated, as well as the same polyester bearing alkoxysilane groups and OH groups, obtained from partial modification of the first one, were used as the matrices for nanocomposite materials containing TiO_2. The TiO_2 nanoparticles were synthesized via an *in situ* sol–gel process in the presence of the HBP, films were prepared from the mixtures, and the polymer was subsequently thermally cured by diisocyanate. TEM analysis, in agreement with AFM and SAXS measurements, showed that in both cases, it is possible to obtain polymer films containing individual nanosized TiO_2 particles. In particular, if the matrix is represented by the modified polymer, due to the strong interaction between the TiO_2 precursor with the $Si(OEt)_3$ end groups of the hyperbranched structure, it is possible to obtain smaller particles with an average size of only 6 nm, compared to those obtained using the unmodified hyperbranched polyester (about 15 nm) (Figure 16.5). DSC analysis also revealed a much stronger interaction between the inorganic nanoparticles and the HBP matrix since a glass transition temperature could no longer be identified. The presence of TiO_2 inside the coating enhances the thermal properties of the coatings with better results when the modified $HBP(OH)-Si(OEt)_3$ is used. Enhanced hardness properties were also achieved by incorporating TiO_2 nanoparticles in the coatings.[135]

Sangermano *et al.*[136] reported the *in situ* preparation of organic–inorganic hybrid coatings from an epoxy-functionalized hyperbranched polyester resin, based on BHMPA in the presence of TEOS as organic precursor of the silica

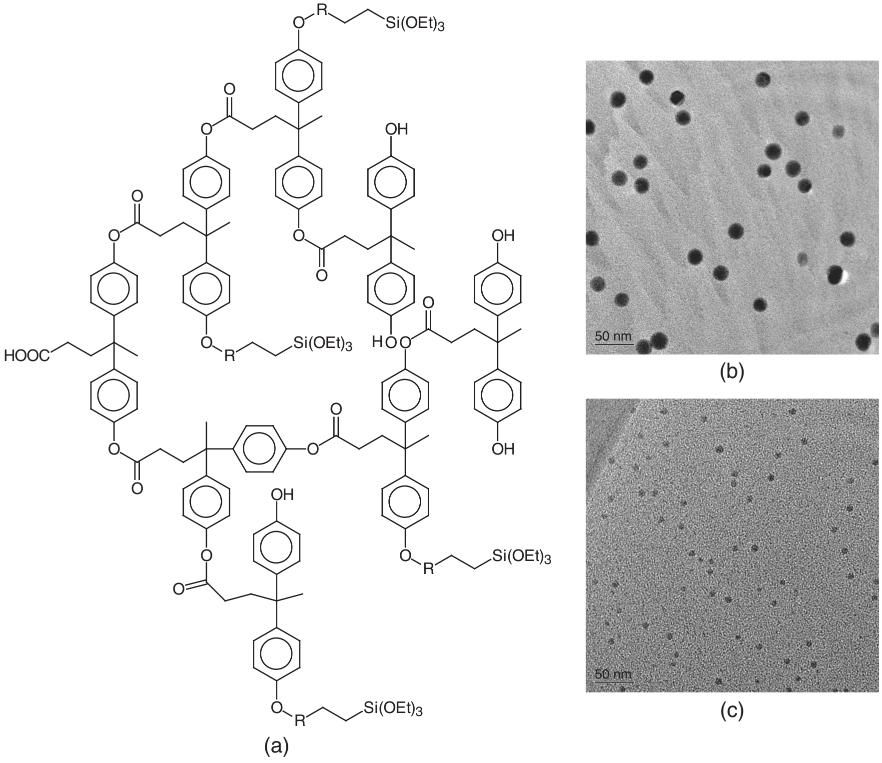


Figure 16.5 TEM images of the coatings obtained from of *p*BHPPA-OH containing 20 wt% of $Ti(iOPr)_4$ (b) and from *p*BHPPA(OH)-$Si(OEt)_3$ (a) containing the 20 wt% of $Ti(iOPr)_4$ (c).[135]

network, and GPTS as coupling agent employing a dual-cure process. After cationic UV curing, the subsequent hydrolysis and condensation reaction was performed by storing the photocured films in an oven at 75 °C for 4 h in a chamber with constant humidity. All the formulations investigated gave rise to photocured films characterized by high gel content values (>98%), indicating the formation of a completely insoluble network and therefore confirming the efficiency of the dual-cure process. The important role of GPTS on reducing the inorganic domain size was demonstrated by TEM analyses. In the absence of GPTS, the SiO_2 particles tend to agglomerate giving rise to the formation of larger size inorganic domains, whereas isolated TiO_2 nanoparticles of only 3 nm were obtained in the presence of GPTS.

Similarly, Zou *et al.* produced new silica hybrid materials by mixing a hyperbranched polyester (OH-functionalized), GPTS or 3-(trimethoxysilyl) propylmethacrylate (for UV curing) as coupling agents, and prehydrolyzed tetraethoxysilane. A much better compatibility between the nanoparticle and matrix was achieved when the hyperbranched polyester was used, as compared to a linear polyester matrix.[120,121]

This concept was further expanded to other nanohybrids. Thus, Zhao *et al.*[137] reported the *in situ* preparation of lead sulfide (PbS) nanocrystallites in a modified hyperbranched polyester matrix by ^{60}Co γ irradiation from sodium thiosulfate at room temperature. TEM analysis proved that isolated PbS nanoparticles of about 8 nm were prepared within the hyperbranched polyester matrix.

Tabuani *et al.*[138] reported the use of hyperbranched polyaramides as stabilizers for palladium nanoparticles and thus, carriers for homogeneous catalysis. It could be proved that the interactions between the polymeric support and the metallic precursor $PdCl_2$ involved only the amino groups of the hyperbranched polyaramides and therefore, the metal nanocluster dimension and stability were strongly dependent on the exact polymer used as stabilizer. A preliminary study of the catalytic performance of the hyperbranched polyaramide-supported Pd nanoparticles in the catalytic hydrogenation of unsaturated compounds proved that the system was efficient, selective, and recyclable.[139]

In order to allow the preparation of more functional nanohybrids, recently, carbon nanotubes (CNTs) have been modified by hyberbranched polymers. Gao *et al.*[140] functionalized multiwalled (MW) CNTs with hyperbranched poly(urea-urethane)s. For this, the CNTs were oxidized to MW-CNT-COOH, converted with thionylchloride into MW-CNT-COCl, and then made to react with excess of diaminohexane to form MW-CNT-NH_2, which was then coupled to different linear and hyperbranched polyureas and poly(urea-urethane)s. The coated MW-CNTs showed interesting self-assembled morphologies. It was also possible to grow multihydroxyl hyperbranched polymers from the surface of MW-CNT macroinitiators (MW-CNT-OH) using the cationic multibranching ring-opening reaction of 3-ethyl-3-(hydroxymethyl)oxetane.[141] Valentini *et al.* reported the grafting of poly(amidoamine) dendrimers on single-walled CNTs in order to enhance the photoelectrical properties of nanocomposites comprising the grafted CNTs and a conducting polymer (poly(3-octylthiophene).[142]

Since nanocomposite and nanohybrid formation is at present a very active field, the list of examples can never be complete. In addition, there are a variety of additional reports that are not so easily classified in the fields of nanocomposites or nanohybrids. Thus, Javaid *et al.*[143] reported the preparation of new nanocomposite membranes by coating octadecyltrichlorosilane, phenyltrichlorosilane, and a triazine-based hyperbranched molecule on porous alumina, achieving significantly higher separation factors.

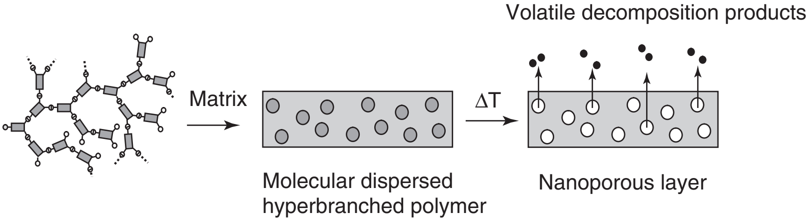
HBPs can also be considered as individual, nanoscale organic particles, similar to dendrimers where one can make use of the peripheral or internal functional (complexing) groups as well as the interior voids and cavities. A more detailed outline of these features will be presented in the chapter on HBPs in medical applications. Just as examples, we would like to mention that Garamus *et al.*[144] used amphiphilic poly(ethylene imine amide)s, prepared from commercial highly branched polyethylene by reaction with methyl palmitate, as unimolecular nanoscale reactors for the preparation of silver nanoparticles. And, like dendrimers,[145,146] HBPs can be used as nanoscale carriers or containers in catalysis[147] or for functional host–guest complexes,[148,149] specific binding of molecules,[150] imprinting,[151] and additives to influence vapor–liquid equilibria.[152]

16.4.2 Nanoporous Materials

As outlined earlier, HBPs can not only be used in nanocomposite and nanohybrid preparations, but they can also themselves be considered as nanoscale particle-like globular macromolecules. This feature was previously used in the preparation of nanoporous materials with highly branched macromolecules, arborescent graft copolymers, star-type block copolymers, HBPs, and dendrimers as templates. This can be of interest for chromatography when preparing areogels or xerogels; hence, Boury *et al.*[153] described the use of dendrimers and arborols with carbosilane cores for the preparation of hybrid xerogels. And in this regard, Muzafarov *et al.*[154] studied the degradation behavior of hyperbranched poly(bis(undecenyloxy)methylsilane)s. The preparation of mesoporous magnetoceramics was reported by Sun *et al.*[155] who used hyperbranched poly[1,1′-ferrocenylene(methyl)silyne] as precursors. During the sintering process at 1000–1200 °C, Fe/Si/C mesoporous electrically conductive ceramics are obtained comprising Fe_2O_3 or Fe_3Si nanoparticles.

But so far, the use of dendritic macromolecules as templates for the preparation of nanoporous inorganic or organic materials has mostly been described in the frame to prepare low dielectric materials for microelectronic applications.[156–159] Here star-type block copolymers,[160] high-temperature-stable hyperbranched polyquinoxalines,[161] or hyperbranched polyesters based on the ring-opening polymerization of an ε-caprolactone derivative[162,163] were used to prepare nanoporous organosilicate networks, a concept which could also be expanded to organic matrices[157,158,164] using arborescent graft copolymers.[165]

To further improve the degradability, specific labile groups have been incorporated into the polyester backbone, for example, labile triazene units.[166,167]



Scheme 16.4 Schematic representation of the formation of nanoporous materials by using hyperbranched macromolecules.[167]

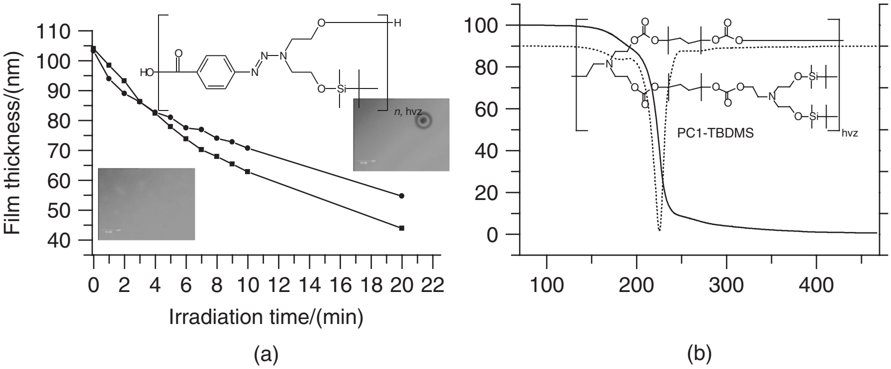


Figure 16.6 (a) Reduction in film thickness as measured by ellipsometry upon UV irradiation of a thin film prepared by pure hyperbranched poly(triazene ester) showing also the films as studied by light microscopy. *Source*: Adapted from Ref. [167]. (b) TGA curve following the thermal decomposition of a hyperbranched polycarbonate.

Source: Adapted from Ref. [168].

These allow the degradation of the hyperbranched polyester in an organic matrix during solidification of the matrix, leaving an increase in free volume and thus a lower dielectric constant (Scheme 16.4). The thermo- and photolabile triazene unit has the further advantage that patterning through UV irradiation can be achieved since UV irradiation also leads to its decomposition into volatiles (Figure 16.6a). HBPs with labile carbonate units within the backbone[168] seem very suitable for that type of application due to a very rapid and nearly quantitative decomposition into volatiles, within a narrow temperature range (Figure 16.6b) once a good compatibility with the organic, temperature-stable matrix can be achieved.

16.5 APPLICATIONS IN THIN FILMS AND SENSORICS

The increasing use of HBPs as specialty polymers in high-tech applications like medical technology, nanotechnology, microelectronics, or in sensors, is a result of their highly branched structure combined with their high functionality as in dendrimers. This renders these materials especially promising for thin-film and sensor applications with the option of increasing sensitivity as well as selectivity. So far, most reports in this field cover the perfectly branched polyamidoamine (PAMAM) or polypropylene imine (PPI) dendrimers, for example, those fixed on the substrate surface as self-assembled monolayers,[169–171] but a variety of other dendrimers with different functional end groups were also employed.[172–174]

On the other hand, imperfect, highly branched, surface-grafted functional materials, such as branched poly(acrylic acid-co-acrylamide) have also been successfully employed as thin layers in different sensors for VOCs.[175,176] Often, the preparation of assemblies or multilayer systems are of interest in order to better control the film thickness and sensor behavior.[177] The field of branched surface-grafted materials has been intensively reviewed recently by Tsukruk *et al.*[178] and is also covered in Chapters 14 of this book. It becomes clear that surfaces modified with highly branched macromolecules may have special features that allow fine-tuning of surface properties, better than when linear polymer or self-assembled monolayers are prepared. Thus, Strumia *et al.*[179] and also Reemers *et al.*[180] report on the surface modification by attachment of dendritic molecules and the potential to prepare active and fine-tuned surface properties with potential use in biomedical application or the preparation of hydrophobic surfaces and/or specific hydrogen bonding capacities. Polyesteramide[179] and PU[180] structures have been used for that purpose. Viville *et al.*[181] compared the surface arrangement of comb graft copolymers versus arborescent graft copolymers. Micropatterning of grafted hyperbranched poly(acrylic acid)/polyethylene films through lithographic processes involving microcontact printing was reported by Crooks *et al.*[182,183] These layers seem to be specially suited to directing the cell growth of mammalian or bacterial cells within hydrophobic corrals with walls covered by the grafted hydrophilic branched polymers, which opens up applications in bioarrays.

Surface properties of hyperbranched polyesters were intensively studied by Voit *et al.*[61,184–188] This involves the studies on thin polymer films regarding specific hydrogen bonding,[187] swelling in aqueous media and buffer solution,[185,186] protein adsorption studies[188] to reveal specific protein interaction with the functional groups of the aromatic hyperbranched polyesters, and a study of the dynamics in very thin films of these polyesters, which differs significantly from that of linear polymers.[189] Kim *et al.*[190] studied in detail the surface properties and swelling behavior of polyglycidol hydrogel films cross-linked with a variety of dialdehydes and diacids.

The direct use of thin films of HBPs in sensor devices is still rarely exploited. Voit *et al.*[184,191,192] reported the use of aromatic hyperbranched polyesters with OH, COOH, or acetate end groups, first as sensitive layers in humidity sensors. The films respond rapidly and repeatedly to water vapor, with a linear dependency between the amount of humidity and the film swelling, and the response significantly depends on the functionality of the polyester. The strongest response for water was found with the hyperbranched polyesters with OH end groups, but the sensitivity changed significantly when different alcohols were used as analytes. The same HBPs could also be successfully employed to detect and quantify different freons.[191] Finally, it was even possible to quantify quaternary mixtures of alcohols in water with a sensor array built up of different films of hyperbranched polyesters.[192] Of late, hyperbranched polycarbosilanes with different end groups have been studied in surface acoustic wave (SAW) sensors, giving a good sensor response for molecules used as models for nerve agents.[193] Hyperbranching carbosilanes with the ability to bond with acid hydrogen were also reported by McGill *et al.* for sensor application.[194,195]

One option to further decrease the response time while increasing the sensitivity is the preparation, for example, of gold nanoparticle/polymer multilayer systems. This concept was successfully employed for fabricating chemiresistor sensors from self-assembled gold nanoparticle/organic composite films, which comprised PAMAM, PPI, and polyphenylene dendrimers as the organic film component.[196–198] In these films, the metal nanoparticles provide electrical conductivity, thereby enabling a straightforward electrical signal transduction. The dendrimer component provides selective sorption sites for interaction with the analyte molecules, while at the same time ensuring mechanical stability of the nanocomposite structure by interlinking the metal nanoparticles in a three-dimensional network. Thus, the presence of suitable functional groups at the periphery of the dendritic macromolecules, which have high binding affinity toward the gold nanoparticles, is essential for the successful formation of the film. Thiol or disulfide groups have been found to be especially suited for that.[196,198] Recently, thiol-terminated hyperbranched polythioethers, synthesized via radical-mediated polyaddition reaction starting from 1,2-ethanedithiol or 1,3-propanedithiol (A_2) and 1-vinyloxy-2,2-bis(vinyloxymethyl)butane (B_3) via an A_2+ B_3 approach, were used as linker molecules in gold nanoparticle composite (AuHP) layers prepared via layer-by-layer self-assembly.[199] The UV–vis spectra of the AuHP films showed a well-resolved plasmon absorbance band at about 550 nm, which evidenced the presence of isolated Au nanoclusters in the layer. Applied in chemiresistor sensors, the vapor-sensing properties of these AuHP nanocomposite films were characterized by measuring the change in their resistance when exposed to vapors of toluene (Figure 16.7), tetrachloroethylene (TCE), 1-propanol, and water. All AuHP sensors responded with fast and reversible increase in resistance upon dosing with solvent vapors with a somewhat higher sensitivity of the nanocomposite layers prepared from the hyperbranched polythioether prepared from propandithiol. The sensitivity to analytes decreased in the order toluene $>$ TCE $>$ 1-propanol $>$ water. The chemical selectivity of the sensors reflects the expected hydrophobic nature of the hyperbranched polythioether linkers.[199]

Besides application in classical sensor devices for VOCs and in liquid media, HBPs increasingly find applications in diagnostics and as biosensors (e.g., Refs. [200–204]), which will be covered in Chapters 14 and 15.

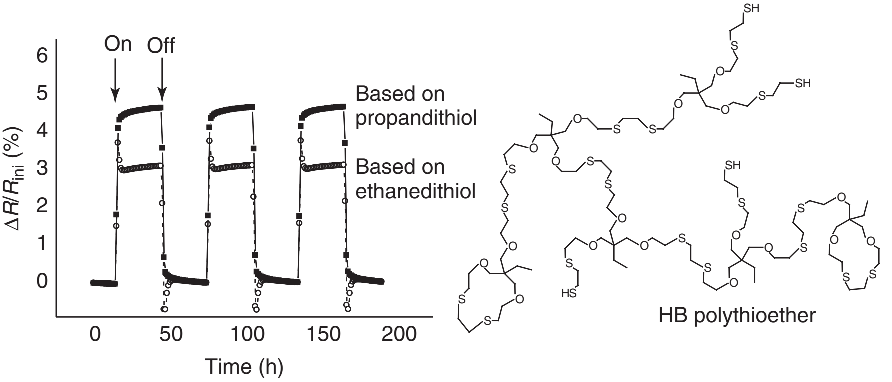


Figure 16.7 Response on 5000 ppm toluene of gold nanoparticle/hyperbranched polythioether nanocomposite (AuHP) layers in a resistivity sensor.

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Chapter 17

Conclusions and Perspective: Toward Hyperbranched/ Dendritic States

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17.1 ACHIEVEMENTS AND PROBLEMS

17.1.1 Ten Main Achievements

As reviewed in the preceding chapters, the last two decades have witnessed the rapid development of the hyperbranched polymer field and many important results have been obtained. In short, the main achievements can be summarized as the following 10 aspects.

1. *Synthesis: Both Polymer Diversity and Synthesis Methodology are Highly Developed.*
   Two methodologies termed *single-monomer* and *multiple-monomer pair* have been presented and widely used to synthesize hyperbranched polymers.[1] As a result, not only AB_x ($x \geq 2$) (Chapter 2) and latent

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Hyperbranched Polymers: Synthesis, Properties, and Applications, by Deyue Yan, Chao Gao, and Holger Frey

AB_x−type (Chapters 5 and 6) monomers but also commercial multifunctional monomer pairs (Chapters 3 and 4) can be employed directly to prepare hyperbranched polymers. This greatly expands their group and makes their large-scale production feasible. In this regard, easy syntheses of hyperbranched polyolefins (Chapter 9); polystyrenes and poly(meth)acrylates, conjugated polymers (Chapter 10); polyurea–urethanes, multihydroxyl polyethers, and water-soluble multiamino polymers are emphasized as compared with the corresponding analogs of linear polymers or dendrimers. Both polymer catalog and polymerization methods are comparable between conventional linear polymers and hyperbranched polymers. In addition to polycondensation, polyaddition, radical polymerization, controlled/living radical polymerization, anionic polymerization, cationic polymerization, coordination polymerization, ring-opening polymerization, reversible addition–fragmentation chain transfer (RAFT) polymerization, and charge-transfer complex polymerization, and so on have been developed to prepare hyperbranched polymers. Besides, self-condensing vinyl polymerization (SCVP) and self-condensing vinyl copolymerization (SCVCP; Chapter 5), convergent polymerization (Chapter 8); and proton-transfer polymerization to synthesize hyperbranched or dendritic polymers have been presented for the first time.

2. *Characterization: DB can be Determined Accurately and Controlled to Some Extent.*

   Direct and indirect methods have been set up to determine the degree of branching (DB) of hyperbranched polymers (Chapter 11). The direct methods include NMR measurements and degradation of polymer units. In the NMR measurements, both 1D and 2D techniques have been tried and model compounds are required sometimes in order to assign the signals of linear, dendritic, and terminal units correctly and calculate their integral accurately. For hyperbranched polymers that have neither well-resolved NMR spectra nor degradable linkages, the viscometry approach can be used to evaluate their DB since the relationship between viscosity and molecular weight of hyperbranched polymers is different from that of linear polymers.

   With respect to control of DB, several approaches have been developed (Chapters 7 and 12). The most general one is copolymerization by addition of another monomer, which can only develop into linear units or slightly branched structures. For some monomers, the DB of the polymer can be readily adjusted by either altering polymerization conditions such as temperature, concentration, monomer addition manner, feed ratio of monomer to catalyst or adding an extra substance that can influence the progress of polymerization and products such as complexing agents and core molecules to the reaction system. For the latent AB_x ($x \geq 2$) or asymmetric AB_x-type monomers, DB might be varied if the polymerization temperature is changed because the effect of the temperature on different reactions is different.[2] DB is normally increased by addition of multifunctional core molecules to the reaction system, and DB decreased if a substance that can form supramolecular complex, especially an inclusion complex, with the monomer or oligomer is added to the reaction system.[3] In addition, DB can be improved by postmodification of linear units of a hyperbranched polymer.

3. *Theory: Polymerization Kinetics has been Theorized and used to Calculate Molecular Parameters of Hyperbranched Polymers.*

   The kinetics theory of both SCVP and polycondensation of AB_x has been established, and can be used to calculate molecular parameters such as DB, molecular weight, and its distribution at any point of conversion accurately (Chapter 13).

4. *Hyperbranched Architecture: New Highly Branched Structures are Presented and Prepared.*

   Except the classic hyperbranched polymers with a globular architecture, several new highly branched structures have been reported: hypergrafts (or hyperbranched polymer-grafted linear polymers), core–shell suprabranched polymers, and segmented branched polymers (Figure 17.1). Hypergrafts can be regarded as linear hyperbranched polymers, which are analogs of dendronized polymers. Suprabranched polymers are highly branched macromolecules built with hyperbranched polymers.[4] So suprabranched polymers might be prototypes of the fifth-generation of polymer architecture, megamers.[5] Segmented branched polymers are constructed with linear macromolecular chains, showing certain mechanical strength due to chain entanglement (Chapter 3). These new structures greatly enrich the diversity of hyperbanched polymers.

5. *Surface Modification: Multifunctional Surfaces Ranging from Nanoforests to Polymer Brushes are Easily Accessible.*

   The combination of surface modification and hyperbranched polymers makes the multifunctional surfaces readily accessible due to the multifunctional groups of hyperbranched polymers. The "grafting to" and

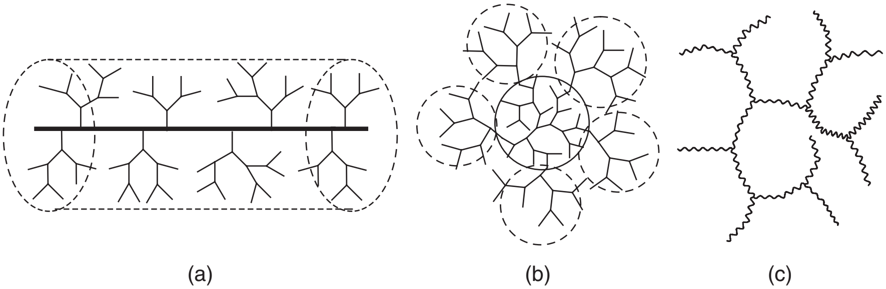


Figure 17.1 Schematic representation of (a) hypergraft, (b) core–shell suprabranched polymer, and (c) segmented branched polymer.

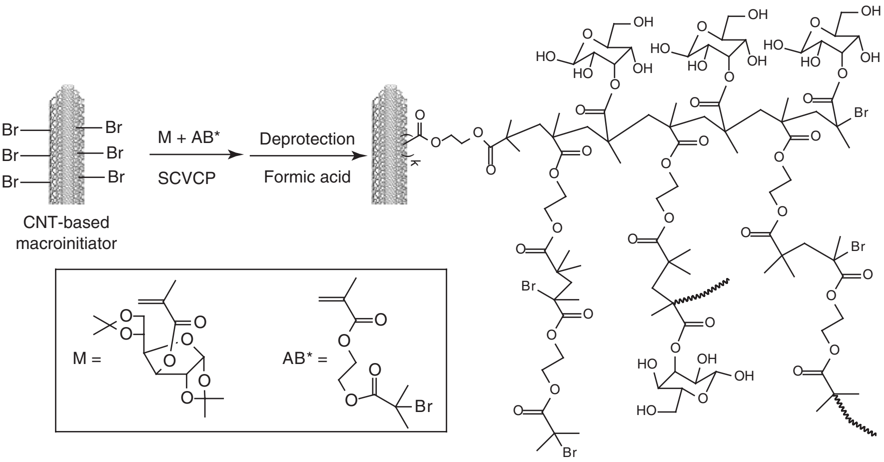


Figure 17.2 Grafting hyperbranched glycopolymer from surfaces of multiwalled carbon nanotubes (MWNTs) by SCVCP.[6]

"grafting from" approaches have been developed to functionalize surfaces with hyperbranched polymers (Chapter 14). The surfaces covered range from nanometer-scale fibers (e.g., carbon nanotubes) and particles (e.g., silica nanoparticles) to macroscopic substrates (e.g., silicon wafer). Figure 17.2 shows the reaction schemes of grafting hyperbranched glycopolymers from surfaces of multiwalled carbon nanotubes (MWNTs) by SCVCP.[6] The resulting hyperbranched nanoforests are well dispersible in polar solvents such as water and methanol. TEM observations showed that the hyperbranched polymer coated the tube surface uniformly. The biocompatible glycopolymer-functionalized CNTs might be useful in bionanotechnology.

6. *Nanotechnology: to be used as New Building Elements, Reactors, and Templates of Nanomaterials and Nanohybrids.*

   Similar to dendrimers, hyperbranched polymers can be used as molecular nanoboxes to encapsulate guest substances such as dyes and metal atoms, forming host–guest supramolecular nanohybrids. Significantly, both competing and synergistic encapsulation phenomena have been found for the hyperbranched poly(aminoamide) (PAMAM).[7] Besides, multifunctional hyperbranched polymers have also been employed as stabilizing agents and templates to fabricate functional polymers/nanocrystal nanohybrids. The nanocrystals normally used are quantum dots (QDs) such as CdXe and CdS.[8–10]

7. *Supramolecular Self-Assembly: Represents New Building Blocks, New Assembly Mechanisms, and New Assembly Objects.*

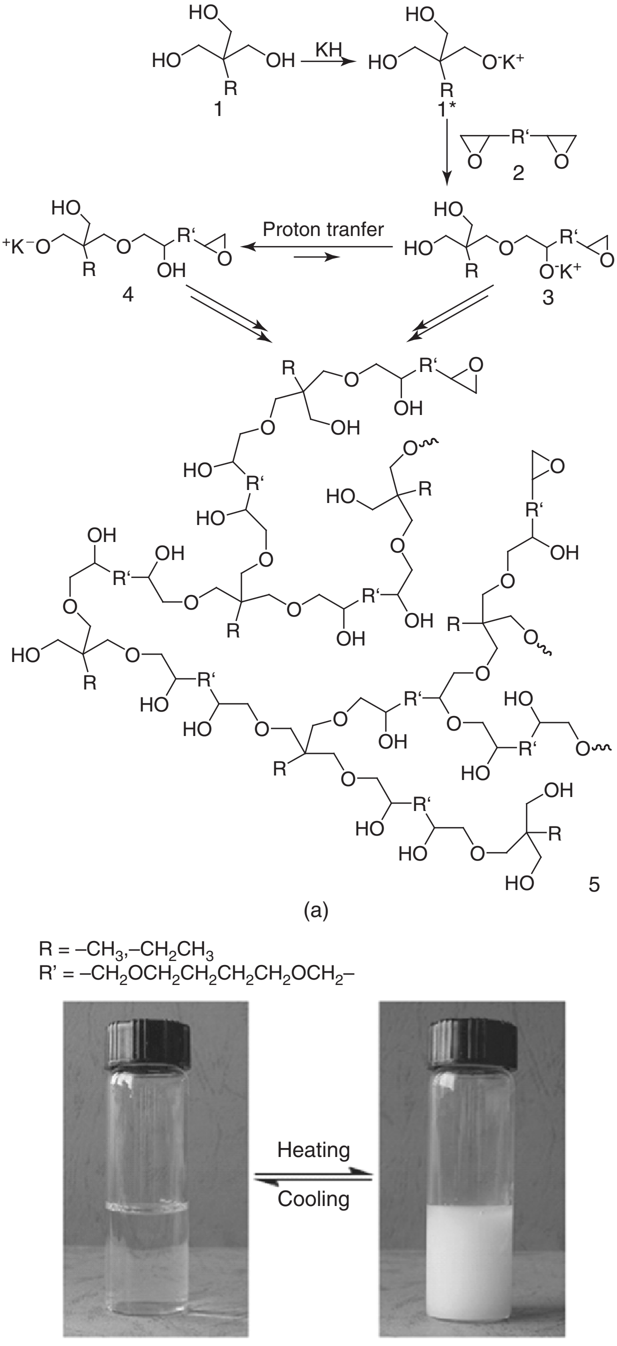
   Although much of the supramolecular self-assembly work has focused on linear polymers, the appearance of hyperbranched polymers significantly enlarges the structural diversity and makes the multifunctional self-assembly accessible due to their three-dimensional architecture and unique properties. It has been shown that hyperbranched polymers play a very important role in the self-assembly field, and indeed, greatly enrich the base of host materials and building blocks of supramolecular chemistry. Till date, nanofibers,[11] visible tubes,[12] and giant vesicles[13] have been obtained by self-assembly of amphiphilic hyperbranched polymers in a solvent. Recently, Gao *et al.*[14] fabricated honeycomb-patterned films by self-assembly of amphiphilic PAMAM on surfaces such as mica, quartz, and silicon wafer. Furthermore, the dye-loaded hyperbranched PAMAM can also assemble into honeycomb-patterned films, which can emit a variety of fluorescent lights by changing the loaded dye or the excitation wavelength. Therefore, fluorescent functional assembled films can be easily obtained.

As a new kind of building block, hyperbranched polymers will play a crucial role in the field of supramolecular chemistry. New assembly phenomena will be found, based on the new building blocks.

8. *Functional Materials: a Variety of Functional Materials Ranging from Stimuli-Responsive to Optical have been Obtained.*

A variety of functional hyperbranched polymers, including fluorescent, nonlinear optical, electric-conductive, ionic-conductive, magnetic, liquid crystalline, pH- or temperature-responsive, have been prepared. This promises more potential applications for hyperbranched polymers in the fields of functional materials and smart devices. Figure 17.3 shows the structure of a backbone-thermoresponsive hyperbranched polyether developed by Zhu and Yan.[15] The thermoresponsive behavior can be attributed to the integration of the hydrophilic groups (such as –OH and –O–) and hydrophobic groups (such as $-CH_3$, $-CH_2CH_3$, and $-C_4H_8-$) in the polymer backbone. At the temperature above the lower critical solution temperature (LCST), the interaction of the hydrophobic groups drives macromolecules to aggregate and then separate from water.

More recently, Huang and Yan made a thermoreversible physical gel from a hyperbranched polymer gelator.[16] The hyperbranched polymer was prepared by Michael addition of 1-(2-aminoethyl)piperazine (AEPZ) to methylene bisacrylamide (MBA) (Figure 17.4). The hyperbranched poly(AEPZ-MBA) is soluble in strong polar solvents such as DMF, DMAc, DMSO, NMP, and pyridine above a certain temperature, the sol–gel phase transition temperature (T_{gel}), whereas it forms immobile physical gels below T_{gel}. For the hyperbranched polymer with a 1:1 feed ratio of MBA to AEPZ, the T_{gel} values increase from about 41 to 61 °C with increasing polymer concentration in DMF. Cryogenic-transmission electron microscopy (cryo-TEM) measurements were performed to disclose the microstructure of the gels, as shown in Figure 17.4b. The dark stripes in the image (50–300 nm of width) represent the continuous open network of the polymer, and the light gray pools in the image denote



(a)

R = $-CH_3$,$-CH_2CH_3$
R’ = $-CH_2OCH_2CH_2CH_2CH_2OCH_2-$

(b)

Figure 17.3 Backbone-thermoresponsive hyperbranched polyether: (a) synthesis by proton-transfer copolymerization of 1,4-butanediol diglycidyl ether (BDE) and triols, and (b) photographs of the polymer in water.[15] The lower critical solution temperature (LCST) values can be readily adjusted from 19 to 40.3 °C by changing the hydrophilic/hydrophobic feed ratio of 1,4-butanediol diglycidyl ether (BDE) to triols.

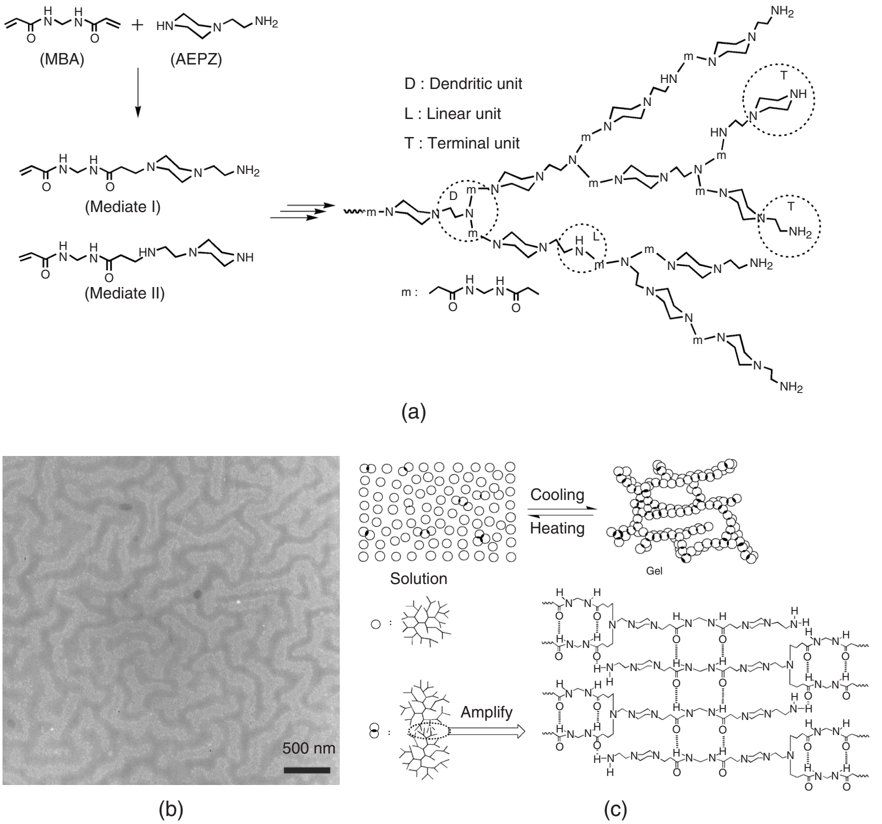


Figure 17.4 (a) Synthesis of hyperbranched poly(amido amine) by Michael addition of 1-(2-aminoethyl)piperazine (AEPZ) to methylene bisacrylamide (MBA), (b) the cryo-TEM image of hyperbranched polymer gel in DMF with a concentration of 10 mg/mL, and (c) the thermoreversible physical gelation mechanism of the hyperbranched polymer at the sol–gel transition temperature.[16]

the solvent molecules entrapped within the network. The gelation mechanism is also presented, as illustrated in Figure 17.4c. The intermolecular hydrogen bonds between amide and amine groups mainly contribute to the physical gelation.

9. *Coatings and Additives: Commercialization has been Launched.*

   Commercialized polyesters from Perstorp under the trade name "Boltorn,™" poly(ester-amide)s from DSM under the trade name "Hybrane,™" polyethyleneimines from BASF AG under the trade name "Lupasol,™" and polyurethanes from BASF AG are relatively widely studied typical examples for hyperbranched polymers that are specially suited for commercial coatings, additives, and resin applications (Chapter 16). Additional kinds of hyperbranched polymers will be commercialized in the near future, opening the avenue for their industry applications.

10. *Biomedical Application: a Promising Field has been Opened.*
    Several commercialized hyperbranched polymers such as poly (ethyleneimine), Boltorn (a hyperbranched aliphatic polyester), Hybrane (a hyperbranched polyesteramide), and polyglycerol, have been studied with respect to biomedical applications, especially as gene delivery carriers or drug delivery systems (Chapter 15). These explorations open up a promising field for the application of hyperbranched polymers and provide alternatives to linear polymers and inorganic materials.

17.1.2 Ten Noteworthy Problems and Topics

Despite the aforementioned progress in this field, the goal of large-scale production and wide application of hyperbranched polymers in a variety of industrial areas is still distant. From our point of view, the following ten problems or topics are noteworthy for the future.

1. *Easy Synthesis of Hyperbranched Polymers Composed of Heteroatoms.*
   Despite the efforts to synthesize hyperbranched polymers, easy synthesis of hyperbranched polymers composed of heteroatoms especially P, Ga, Se and Ge is still an unsolved problem.
2. *Synthesis of (Ultra)high Molecular Weight Hyperbranched Polymers.*
   Because of the cyclization effect, it is difficult to obtain high molecular weight hyperbranched polymers. Most of the reported hyperbranched polymers have M_n's of only 5000–50,000. Recently, Brooks *et al.* prepared hyperbranched polyglycerol with M_n up to 700,000 by ring-opening multibranching polymerization (ROMP) using dioxane as an emulsifying agent.[17] How to enhance the M_n of normal hyperbranched polymers to up to more than 100,000 while keeping a relatively narrow polydispersity index (PDI) remains a crucial question.
3. *Development of New Highly Branched Structures Built with Hyperbranched and Linear Polymers.*
   More highly branched structures are expected with hyperbranched and linear polymers as building blocks, including linear-block-linear, linear-block-hyperbranched, and hyperbranched-block-hyperbranched forms (Figure 17.5).
4. *Fabrication of Multifunctional Molecular Devices.*
   Integration of different functions into one hyperbranched polymer demonstrates a tendency to fabricate versatile materials and molecular devices.
5. *Molecular Weight Characterization.*
   To measure the true molecular weight of hyperbranched polymers is still a problem, baffling academic research and further application to some extent.

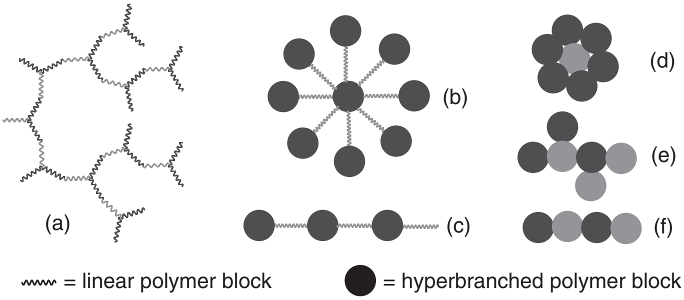


Figure 17.5 (a) Illustration of linear-*b*-linear, (b, c) linear-*b*-hyperbranched, and (d–f) hyperbranched-*b*-hyperbranched highly branched structures built with hyperbranched and linear polymers.

6. *Hyperbranched Supramolecular Polymers.*

   Supramolecular polymers are macromolecules constructed with repeating units, by noncovalent interactions. As far as we know, hyperbranched supramolecular polymers have rarely been reported.

7. *Building Elements of Nanotechnology.*

   Hyperbranched polymers occur in sizes of several nanometers, which could be used as building elements in nanotechnology to construct functional devices, surface patterns, and novel structures.

8. *Chemical Biology of Hyperbranched Polymers.*

   The relevant research mainly includes bionics, biomimic mineralization, toxicology, and biological and medical applications of hyperbranched polymers.

9. *Supramolecular Chemistry of Hyperbranched Polymers.*

   This is a relatively new area to be explored even though some important self-assembly results have been reported. Normally, only those well-defined polymers such as amphiphilic linear polymers and dendrimers can assemble into ordered structures. Hyperbranched polymers are ill-defined, but they can also organize into highly ordered structures. Hence, both the self-assembly process and the mechanism await further study.

10. *Application in Water-Phase Coatings.*

    Because of high solubility of hyperbranched polymers, their application in environment-friendly coatings such as high solid content coatings and water-phase coatings is quite favorable.

17.2 ROLE OF HYPERBRANCHED POLYMERS IN THE TWENTY-FIRST CENTURY

Polymers can be recognized as one of the greatest discoveries in the twentieth century. A host of polymer products had been developed and manufactured by the international chemical companies from the 1960s to the 1980s. Since the 1990s, however, rare new kinds of polymer products have been developed. Hyperbranched polymers, created to lead the next revolution of the polymer industry in the twenty-first century, were intentionally synthesized for the first time at the end of the 1980s. After around 20 years of development, research on hyperbranched polymers has mushroomed in many areas of chemistry. The role of hyperbranched polymers in the twenty-first century is illustrated in Figure 17.6. Taking root in almost every subclass of chemistry extending across polymer chemistry, organic chemistry, and material chemistry to physical chemistry, electrochemistry, and analytical chemistry, hyperbranched polymers have grown rapidly, and extended

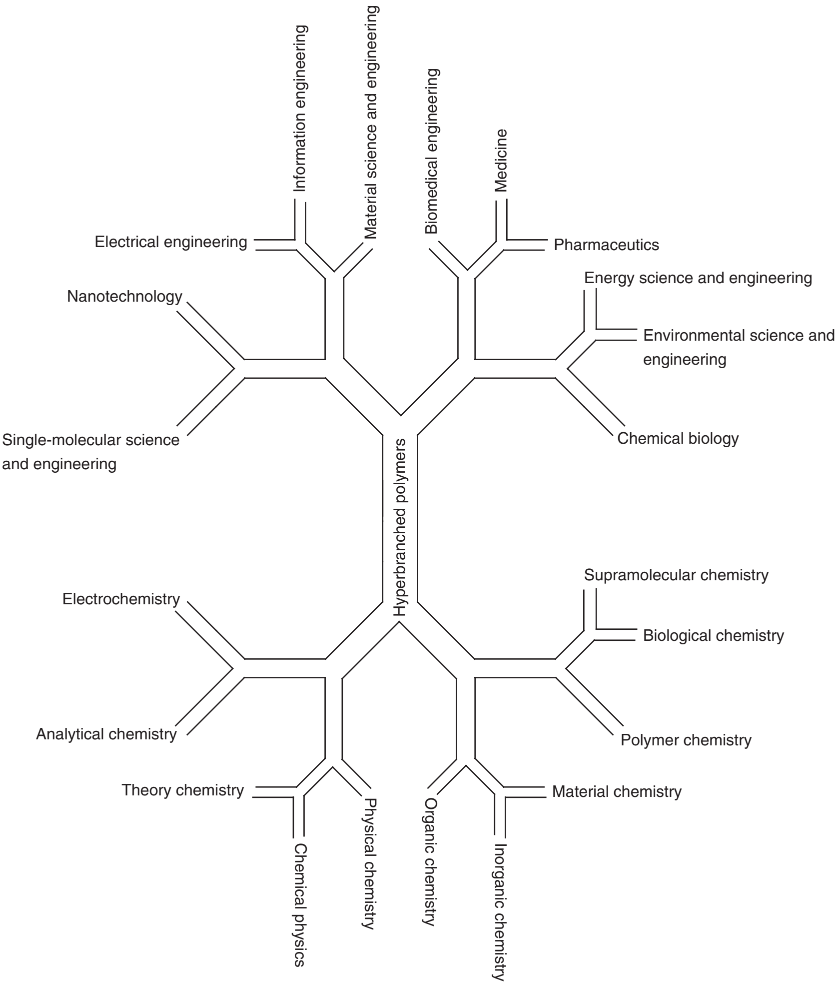


Figure 17.6 Role of hyperbranched polymers in the twenty-first century.

their branches into other areas. After 5–10 years of further R&D, hyperbranched polymers will bear fruit in both science and technology, including chemical biology; single-molecular science and technology; nanotechnology; material science and engineering; biomedical engineering; energy and environmental science and technology; and even electrical and information engineering. The last century has witnessed the great impact of linear polymers on human life, so will this century in the form of the impact of hyperbranched polymers.

17.3 HYPERBRANCHED/DENDRITIC STATE

As discussed above, it is expected that hyperbranched polymers will play a more and more important role in both science and technology in the twenty-first century. By expanding the concept of polymers to other substances, we can clearly see that almost every linear material can have a hyperbranched analog, ranging from nanometer-scale to macroscopy. From the commercialization potential point of view, hyperbranched/dendritic nanomaterials and biomaterials are of special interest since both *Biotechnology* and *Nanotechnology Ages* are emerging.[18] Indeed, hyperbranched nanomaterials and biomaterials are becoming the focus of corresponding fields succeeding to linear nanorods, nanofibers, nanowires, and nanotubes as well as linear proteins, DNA, and glycopolymers (Figure 17.7).[19–21] Therefore, the future of the *hyperbranched/dendritic state* is bright as this new major polymer class enters the twenty-first century, accompanied by the *hyperbranched* idea as it spreads through a variety of scientific fields and industrial areas.

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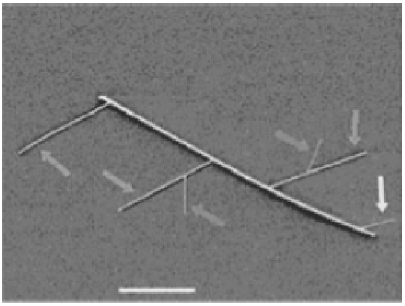

Figure 17.7 SEM image of a hyperbranched nanostructure reported by Lieber.[19] Scale bar is 1μm.

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