Macromolecules Containing Metal and Metal-Like Elements

Volume 1

Macromolecules Containing Metal and Metal-Like Elements

Volume 1

A Half-Century of Metal- and Metalloid-Containing Polymers

Alaa S. Abd-El-Aziz
Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba, Canada

Charles E. Carraher, Jr.
Department of Chemistry and Biochemistry, Florida Atlantic University, Boca Raton, Florida

Charles U. Pittman, Jr.
Department of Chemistry, Mississippi State University, Mississippi State, Mississippi

John E. Sheats
Department of Chemistry, Rider University, Lawrenceville, New Jersey

Martel Zeldin
Department of Chemistry, Hobart and William Smith Colleges, Geneva, New York

For general information on our other products and services please contact our Customer Care
Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print,
however, may not be available in electronic format.

Contents

**3. Polymers Containing 4-, 5-, and 6-Membered Rings
π-Coordinated to Metallic Moieties** **103**

**4. σ-Bonded Metals and Metal–Metal Bonds in
the Polymer Framework** **147**

5. Metal Coordination Polymers **171**

Preface

Most traditional macromolecules deal with less than 10 elements (mainly C, H, N, O, S, P, Cl, F), whereas metal and semi-metal-containing polymers allow properties that can be gained through the inclusion of nearly 100 additional elements. Macromolecules containing metal and metal-like elements are widespread in nature with metalloenzymes supplying a number of essential physiological functions including respiration, photosynthesis, energy transfer, and metal ion storage.

Polysiloxanes (silicones) are one of the most studied classes of polymers. They exhibit a variety of useful properties not common to non-metal-containing macromolecules. They are characterized by combinations of chemical, mechanical, electrical, and other properties that, when taken together, are not found in any other commercially available class of materials. The initial footprints on the moon were made by polysiloxanes. Polysiloxanes are currently sold as high-performance caulks, lubricants, antifoaming agents, window gaskets, O-rings, contact lens, and numerous and variable human biological implants and prosthetics, to mention just a few of their applications.

The variety of macromolecules containing metal and metal-like elements is extremely large, not only because of the larger number of metallic and metalloid elements, but also because of the diversity of available oxidation states, the use of combinations of different metals, the ability to include a plethora of organic moieties, and so on. The appearance of new macromolecules containing metal and metal-like elements has been enormous since the early 1950s, with the number increasing explosively since the early 1990s. These new macromolecules represent marriages among many disciplines, including chemistry, biochemistry, materials science, engineering, biomedical science, and physics. These materials also form bridges between ceramics, organic, inorganic, natural and synthetic, alloys, and metallic materials. As a result, new materials with specially designated properties have been made as composites, single- and multiple-site catalysts, biologically active/inert materials, smart materials, nanomaterials, and materials with superior conducting, nonlinear optical, tensile strength, flame retardant, chemical inertness, superior solvent resistance, thermal stability, solvent resistant, and other properties.

There also exist a variety of syntheses, stabilities, and characteristics, which are unique to each particular material. Further, macromolecules containing metal and metal-like elements can be produced in a variety of geometries, including linear, two-dimensional, three-dimensional, dendritic, and star arrays.

In this book series, macromolecules containing metal and metal-like elements will be defined as large structures where the metal and metalloid atoms are (largely) covalently bonded into the macromolecular network within or pendant to the polymer backbone. This includes various coordination polymers where combinations of ionic, sigma-, and pi-bonding interactions are present. Organometallic macromolecules are materials that contain both organic and metal components. For the purposes of this series, we will define metal-like elements to include both the metalloids as well as materials that are metal-like in at least one important physical characteristic such as electrical conductance. Thus the term includes macromolecules containing boron, silicon, germanium, arsenic, and antimony as well as materials such as poly(sulfur nitride), conducting carbon nanotubes, polyphosphazenes, and polyacetylenes.

The metal and metalloid-containing macromolecules that are covered in this series will be essential materials for the twenty-first century. The first volume is an overview of the discovery and development of these substances. Succeeding volumes will focus on thematic reviews of areas included within the scope of metallic and metalloid-containing macromolecules.

Alaa S. Abd-El-Aziz
Charles E. Carraher, Jr.
Charles U. Pittman, Jr.
John E. Sheats
Martel Zeldin

CHAPTER 1

Introduction

CONTENTS

I. HISTORICAL BACKGROUND

Metal-containing polymers form some of the basis of life as we know it. They are at the heart of respiration and photosynthesis and thus are integral to plant and animal life. It has also been established that metal-containing coordination polymers were formed in the ancient art of leather tanning, although it is unknown when

the first organometallic polymer was knowingly prepared and characterized. The field of metal-containing polymers has been known since the early 1950s and has rapidly grown in multiple directions simultaneously. Historically, polymers have only contained the elements C, H, N, O, S, Cl, Br, and P. The rapid rise of the polysiloxane industry in the 1960s expanded the elements found in polymers to include silicon. This was followed by antifouling marine coatings, which employed polymers containing tin, mostly in the form of $-OSnBu_3$ functions. Polymer chemists had overlooked the inclusion of metals into their systems mainly because the early chemistry of metals was largely based on coordination compounds. However, the number of metal elements exceeds 40, and many of these elements have several readily accessible oxidation states, a variety of bonding modes, and the ability to react with organic and inorganic moieties. It was recognized that the number of potential metal-containing polymers that might be imagined is astronomical and the possibilities for a wide array of applications are limited only by one's imagination. A series of books[1–11] and key review articles[12–26] have been devoted to the synthesis, properties, and applications of metal- and metalloid-containing polymers.

A. Polymers Containing Silicon

Silicon-containing polymers are one of the most widely studied classes of macromolecules. The synthesis and properties of silicon polymers have been extensively reviewed.[27–30] Polysiloxanes and polysilanes are the most important types of silicon-based polymers. Historically, the most important and extensively studied class of polysiloxanes are polydimethylsiloxanes (**1**). In the late 1800s, Ladenburg reported the synthesis of this polymer,[31,32] however, its structure was not identified until the early 1900s when Kipping established that silanediols condense intermolecularly to "silicones."[33–35] There was great interest in these compounds as intellectual curiosities as well as for their unusual physical properties, thermal stability and chemical inertness. These polymers were misnamed as silicones owing to the belief that the compounds were ketone-like in structure. However, it was determined that these materials do not contain a Si−O double bond. The name *silicone* has remained in common usage, however, the term *polysiloxane* is preferred.

$$\left[\begin{array}{c} Me \\ | \\ Si\!-\!O \\ | \\ Me \end{array} \right]_n$$

1
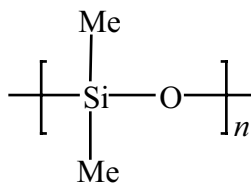
In 1942, Meyer produced the first treatise on polymers that included a section dealing with metal-containing polymers.[36] The work of Rochow in 1945 advanced the synthesis of monomer precursors to polysiloxanes,[37] and in 1947 he authored the first book dealing entirely with this important, commercial class of materials.[38] Polysiloxanes exhibited unique rheological and thermal properties that were unavailable to organic polymers. Pure polysiloxanes are rarely used in applications; however, on the addition of fillers, additives, curing agents and pigments, these materials have found an array of medical applications such as tubing, prostheses, and artificial organs.[39] A wide range of nonmedical applications also depend on the elastomeric nature of polysiloxanes. These include electrical insulators, membranes, coatings, adhesives, and high-performance elastomers. Historically, the development of polysiloxanes signaled a need to look beyond the 10 or so elements typically found in synthetic polymers.

Polysilanes, unlike the alternating silicon-oxygen chain structure of polysiloxanes, have only silicon atoms in the polymer backbone. Most early conventional wisdom considered that carbon was the only element that could form catenated polymer chains. While oligomeric phenylpolysilanes were reported by Kipping in the 1920s, the first article describing the synthesis of polymeric silanes was reported in 1949 by Burkhard.[40] In this study, polydimethylsilane (**2**) was synthesized by the reaction of metallic sodium with dimethyldichlorosilane. The resulting polymeric material contained both crystalline and amorphous regions and exhibited very poor solubility in organic solvents. Unlike polydimethylsiloxane, polysilanes showed poor oxidative stability but did exhibit excellent hydrolytic stability. The analogous diphenyltin product was formed by Krause and Becker in 1920 by the reaction of tin *tetra*-chloride with phenyl magnesium bromide.[41] The initial product was diphenyltin, which on standing formed polydiphenylstannane.
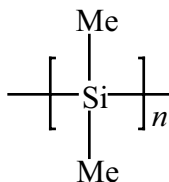
2

Despite the early work done on polysilanes, there were relatively few reports on their synthesis until the 1970s. Since that time, a number of different organic substituents have been introduced into these polymers resulting in interesting properties.[39] It was also found that polysilanes have intense UV absorption bands that shift to higher wavelength with increasing chain length. This behavior is very similar to that of polyenes, and suggests that the Si−Si bonds may be delocalized. It has been found that polysilanes exhibit σ-electron delocalization, while their carbon-based analogs (polyacetylenes) exhibit π-delocalization. Silicon–silcon bond cleavage

occurs when polysilanes are irradiated, allowing them to be used as photoinitiators. On exposure to oxygen plasmas they form SiO_2 layers, which has led to their use as photoresists. Another application of polysilanes is as a precursor to silicon carbide and other ceramics.

B. Metal Coordination Polymers

The history of coordination polymers is much harder to define clearly and dates back at least to the 1930s. Stone and Graham[18] reported some of the earliest examples of metal-coordination polymers. However, the insolubility of the products and their lack of molecular weight (MW) definition and characterization plagued early attempts to apply known coordination chemistry to polymer synthesis. One of the initial linear coordination polymers, silver cyanide (**3**), was reported in 1935 by West.[42]

3
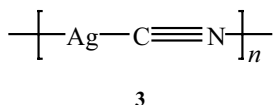
Another early coordination polymer was reported in 1944 by Jensen who proposed the linear product **4** from the chelation of nickel ions with rubeanate.[43]

4
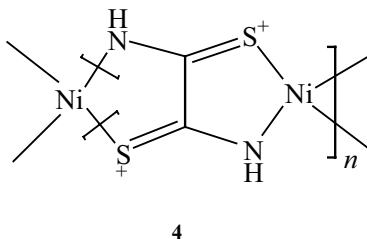
In the 1930s and 1940s a number of organic ligand-chelated metal compounds were synthesized. These materials exhibited good thermal stabilities to ~500°C. Since the monomeric chelated products were so stable, it was believed that polymeric analogs should be even more stable. During World War II, the U.S. Air Force sponsored a large research program to find thermally stable polymers (to ~600°C). Most of the work centered on chelation reactions. Unfortunately, the search did not yield useful materials. In most cases, the polymers were less stable than the monomeric chelated products. Moreover, the materials were intractable and only oligomeric in nature. At that time, definitive structural and molecular weight analyses of metal coordination polymers was rather primitive, and many such materials were never well characterized. The insolubility of many of these materials added to the problems.

The synthesis of copper phthalocyanine polymers was reported in the 1950s by Marvel and Rassweiler[44] and Drinkard and Bailar.[45] Bailar reported that the reaction of pyromellitic dianhydride, copper(II), and urea in the presence of a catalytic amount of ammonium molybdate resulted in the production of oligomeric copper phthalocyanines.[45] While it was postulated that the polymers had a linear structure (**5**), it is also possible that the polymer has a sheetlike structure (**6**). A number attempts were made to determine the molecular weights of these materials; however, accurate values were not obtained.

HOOC   COOH   HOOC   COOH

HOOC   COOH

HOOC   COOH

HOOC   COOH

HOOC   COOH

HOOC   COOH   HOOC   COOH

6
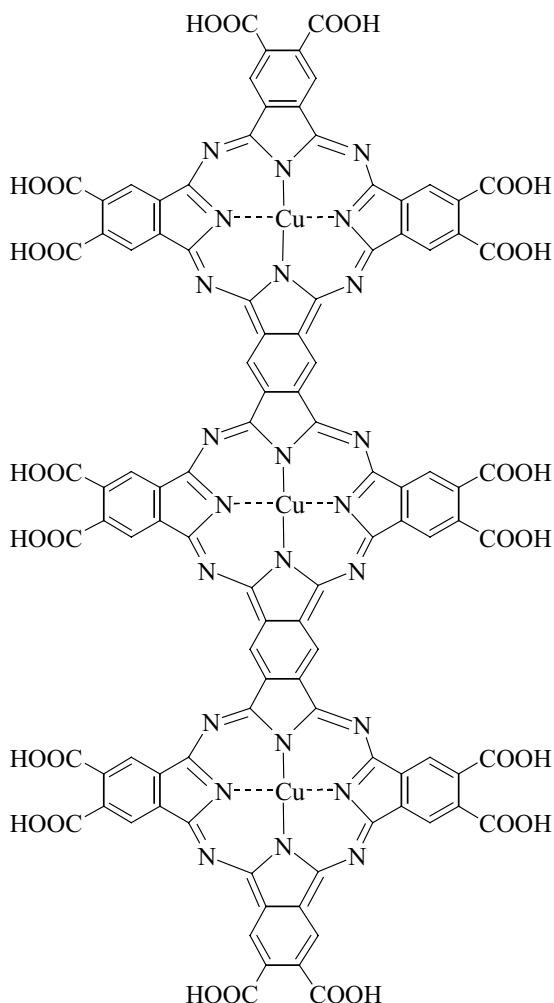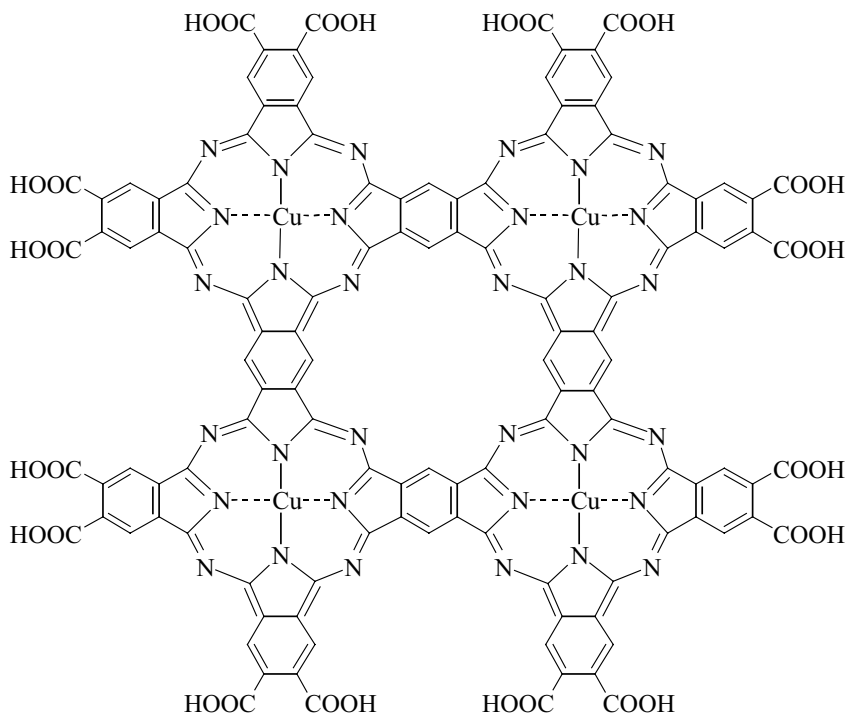
The most promising products were made by Martin and Judd, who synthesized derivatives of several thiopicolinamids, which were stable to 400°C.[46] From these studies, Bailar developed some guidelines that are still applicable, for instance (1) the least stable bonding, generally the organic bonding, limited the overall stability of the product and (2) the more rigid the structure, the less its inherent solubility.[47] All the reasons for carrying out this research are not fully known; however, in the end this work involved a quest for materials to be used in the construction of a heat shield for spacecraft. As we now know, the materials of choice are the honeycomb ceramic tiles.

Metal phosphinate polymers (**7–9**) having single-, double-, or triple-bridged structures were, however, successfully prepared with, in some cases, high MWs.[20,48] Unlike most earlier coordination polymers, soluble systems of these materials were obtained. The semimetals and metals used were Al, Be, Co, Cr, Ni, Ti, and Sn. The polymeric products were used commercially in films and were thermally stable to 450°C. Thus, chromium(III) polyphosphinates have been used as thickening agents for silicone greases to improve their high-pressure properties. Archer's book

provides a modern introduction to the classification and structures of coordination polymers as well as some historical information.[11]
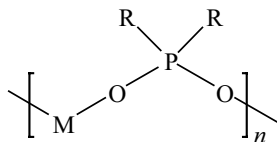
7
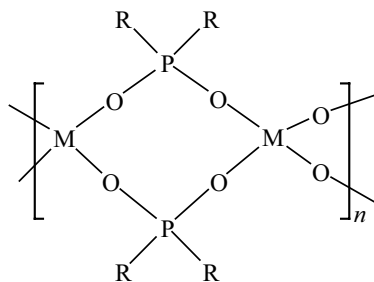
8
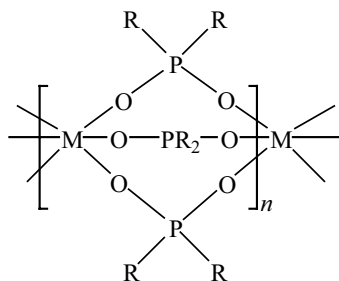
9

M = Al, Be, Co, Cr, Ni, Ti, Sn

A few examples of early coordination polymerizations are noted here to provide a flavor for this work. The reaction of Cu(II) with dithiooxamides, reported by Kanda in 1962, gives a three-dimensional (3D) insoluble material (**10**) that has the catana-μ -(*N,N″*-disubstituted dithiooxamido)copper structure.[49]

Rigid rod-shaped materials were synthesized from one-to-one complexes of 2,5-dihydroxy-*p*-benzoquinone with Cu(II), Ni(II), and Cd(II) (**11**).[50,51] Rods 1000–2000 Å long were claimed.

In analogy to the early work by Bailar, iron polymers with linear or two-dimensional sheet network structures such as **12** have been postulated to form when Fe^{2+} is reacted with 2,5-dihydroxybenzoquinone in basic media.[52,53] Each iron center is also coordinated to two water molecules.
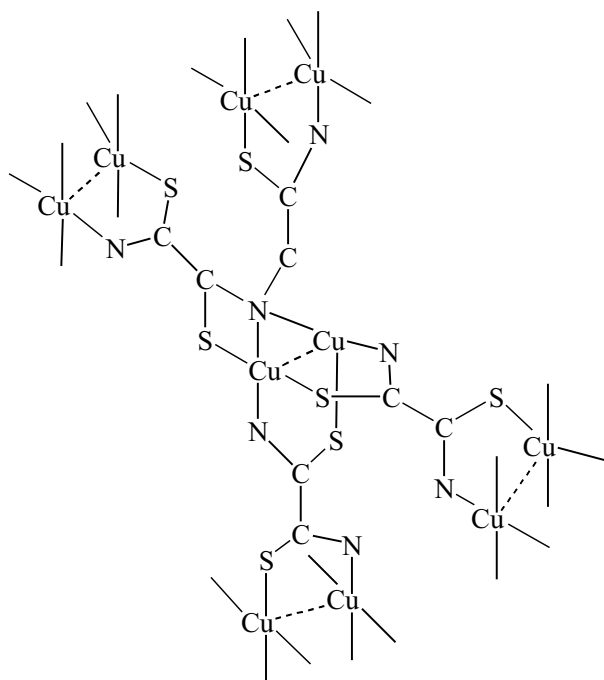
10
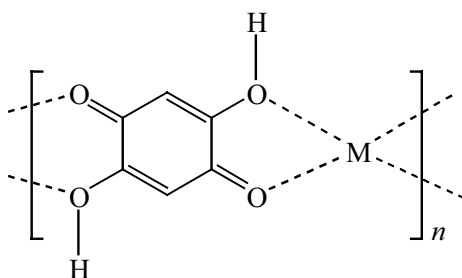
11 $M = Cu^{2+}, Ni^{2+}, Cd^{2+}$

The early coordination polymeric materials were very difficult to characterize because of their insolubility. It is worth noting that soluble, well-characterized systems have now been made. For example, linear cerium(IV) and zirconium(IV) Schiff base coordination polymers (**13**) have been synthesized and their MWs, solubilities and viscosity behavior have been investigated.[54]
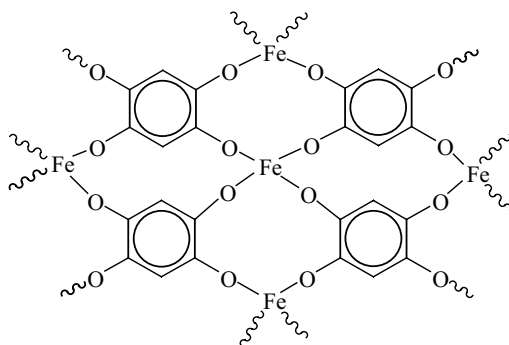
12
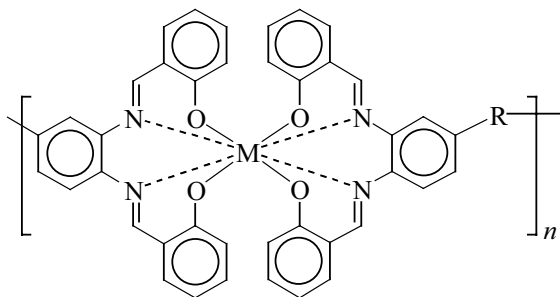
13   M = Ce(IV), Zr(IV)
R = CH$_2$, SO$_2$

C. Organometallic Polymers

The excitement of metal-containing polymers appeared to languish until the landmark report of the preparation of ferrocene by Kealy and Pauson[55] in 1951 and the elucidation of its structure and reactivity by Wilkinson and others in 1952.[56,57] These discoveries set the stage for the birth of organo-transition-metal polymer chemistry. Thus, in 1955, Arimoto and Haven at the Dupont Co. reported the radical-initiated homopolymerization of vinylferrocene (Scheme 1).[58] These reports did not appear to attract much attention until the work of Hayes and George[59–61] and Pittman and coworkers.[62] By the late 1960s and early 1970s Pittman, Carraher, Sheats, and others entered the arena.

Since metals exhibit different oxidation states, the polymerization behavior of vinylferrocene (**14**) was in question. Hayes and George found that the rate law for the radical-initiated homopolymerization of vinylferrocene was $r = k[M]^{1.1}[I]^{1.1}$ instead of the classic one-half order in initiator concentration exhibited in most

organic systems. This suggested that first-order chain termination occurred rather than bimolecular second-order termination. Their explanation was that an internal electron transfer from iron to the radical center occurred. Thus, an anion was created, which was quickly quenched to leave a ferricinium moiety at the terminus.
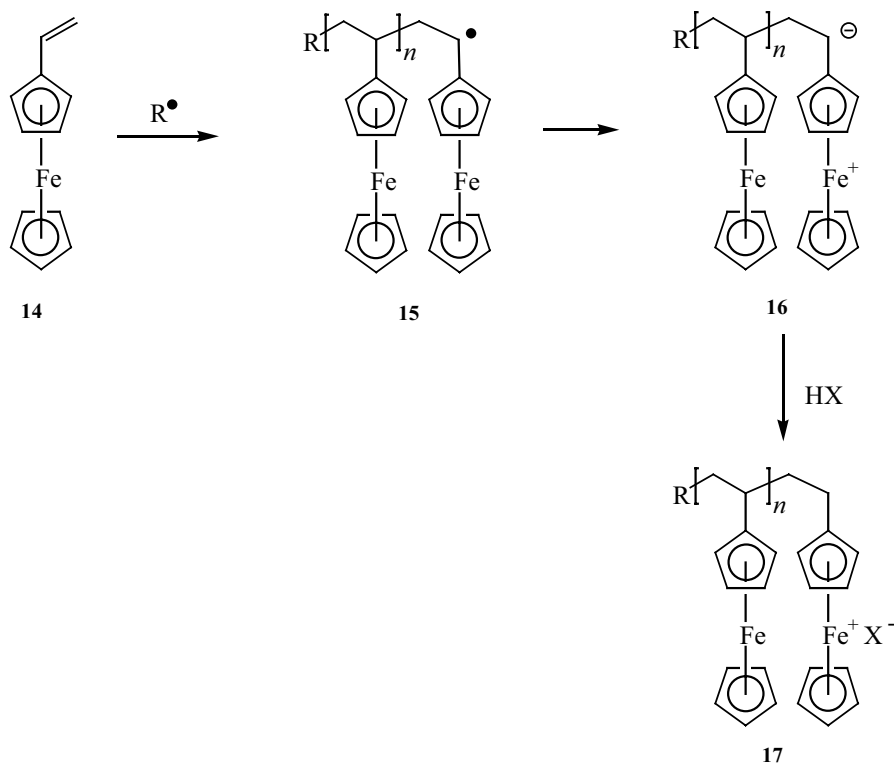
Scheme 1

Pittman et al. demonstrated that, unlike most vinyl monomers, the molecular weight of polyvinylferrocene does not increase with a decrease in initiator concentration.[62] This is a result that would be expected for an anomalously high chain-transfer constant for vinylferrocene ($C_m = 8 \times 10^{-3}$ vs. 6×10^{-5} for styrene at 60°C). Pittman's research also demonstrated that vinylferrocene could be copolymerized with a large number of monomers such as styrene, methyl methacrylate, N-vinylpyrrolidone, and acrylonitrile.[63–66] This provided an avenue to introduce a ferrocene moiety into a variety of organic polymers.

Pittman built on the premise that vinyl organometallic monomers might be styrene-like. Special metal-containing vinyl monomers were developed. Thus, acrylates and methacrylates of ferrocene were prepared and their homo- and copolymerizations

were studied including reactivity ratios.[67–70] Some of these polymers were oxidized with agents such as dichlorodicyanoquinone to form mixed-valence ferrocene–ferricenium systems, which were characterized by Mössbauer spectroscopy.[68,70] These observations raised the general question: Could vinyl organometallic monomers of a wide variety of other structures be polymerized? Consequently (η^5-vinylcyclopentadienyl)tricarbonyl-manganese (**18**) was made, homopolymerized, and copolymerized with several comonomers.[66,71] π-(Benzyl acrylate)chromiumtricarbonyl (**19**) was also prepared and both homo- and copolymerized.[72,73]
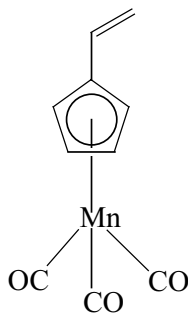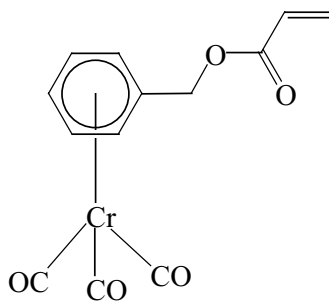
18   **19**

A rather large number of acrylic, styryl, and vinylcyclopentadienyl monomers were made and their polymerization behavior was established, thereby confirming the general ability to convert many metal-containing systems into polymers.[74–86] Furthermore, systematic copolymerizations were conducted to obtain reactivity ratios from which the Alfrey Price Q and e parameters were obtained. These results provided the first underlying physical-organic quantitative understanding of vinyl organometallic monomers.[85] The values of e established that several vinyl cyclopentadienyl metal monomers (**14**, **18**, **20**, **21**, **25**, **29**) were extraordinarily electron-rich ($e = -2.1$ to -1.98); each of these monomers were more electron-rich than 1,1-dianisylethylene. The large negative values of Q suggested that the radicals were strongly resonance stabilized. For comparison, consider the following values of e for common organic monomers (electron-deficient to electron-rich): maleic anhydride ($+2.25$), *p*-nitrostyrene ($+0.39$), styrene (-0.80), and 1,1-dianisylethylene (-1.96).

It became apparent that the presence of a metal center greatly influenced polymerization kinetic behavior. In several cases, the homopolymerization kinetics were unusual and did not follow the classic rate law ($r = k[M]^1[I]^{1/2}$) for radical chain polymerization. For example, (η^5-vinylcyclopentadienyl)tricarbonylmanganese, **18**, exhibited rate dependencies that were 1.5-order in monomer concentration and half-order in initiator concentration in benzene, benzonitrile, and acetone.[74] This rate

expression conforms to a very low initiator efficiency, and the initiation is proportional to [M]: $f = f'$ [M]. The rate equation requires that the degree of polymerization (DP) follow the expression

$$\text{DP} = \frac{R_p}{R_i} = \frac{k_p}{(2f'k_t k_d)^{0.5}} \left(\frac{[\text{M}]}{[\text{I}]} \right)^{0.5}$$

which was confirmed experimentally.[74] MW measurements confirmed that the degree of polymerization is proportional to $([\text{M}]/[\text{I}])^{0.5}$.[72,73]
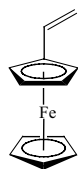
14[63–66]
$e = -2.1$
$Q = -1.03$
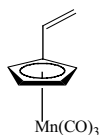
18[73–81]
$e = -1.99$
$Q = -1.1$
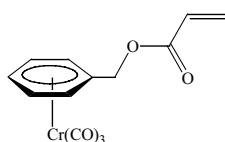
19[62]
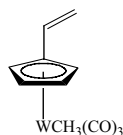
20[74,76,83]
$e = -1.98$
$Q = -1.66$

21[82]
$e = -1.98$
$Q = -3.1$

22[77]
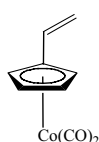
23[82]
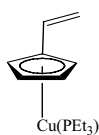
24
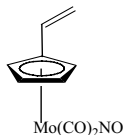
25[84]
$e = -1.98$
$Q = -3.1$

26[84]
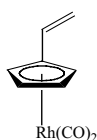
27[84]
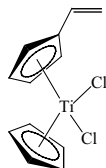
28[84]
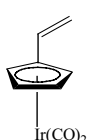
29[84]
$e = -2.08$
$Q = -4.1$
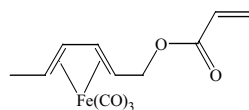
30[79]
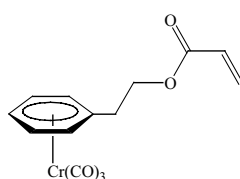
31[78]
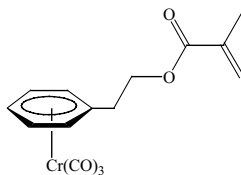
32[80]

The rate expression for the radical-initiated homopolymerization kinetic studies of (η^5-vinylcyclopentadienyl)methyltricarbonyltungsten (**20**) in benzene is as follows (see also Scheme 2):[75,76]

$$R_p = 1.13 \times 10^{-2}[M]^{0.8}[T]^{2.3}$$
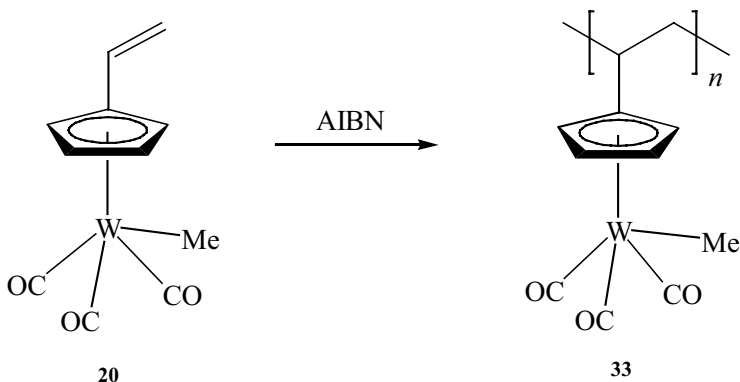
Scheme 2

Chain transfer and chain termination by hydrogen abstraction from the tungsten-bound methyl group, the cyclopentadienyl ring or the backbone alkyl groups were ruled out as the cause of the reaction sluggishness. All these results illustrated that the availability of additional oxidation states on the metal or related electronic effects could influence the addition polymerization mechanism.

While Pittman and others focused their efforts on equipping vinyl polymers with metals, Carraher and others focused efforts on incorporating metals into polymers by employing condensation reactions. The use of step-growth polymerization has been widely exploited to incorporate metal-containing moieties into polymers. In the mid 1970s, Carraher et al. were determining the thermal stability of some ferrocene-containing condensation polymers when a milligram-scale sample exploded almost destroying the thermal analyzer. They later learned that Russian scientists were studying these materials as rocket propellants.[87]

Polycondensation is a general method and Carraher's group extended this technique broadly to prepare a variety of new substances. By employing metal halides such as R_2ZrX_2, R_2HfX_2, R_2GeX_2, R_2PbX_2, R_3BiX_2, and R_2SnX_2 with diols, dithiols, diamines, hydrazines, dioximes, dithioamides, ureas, and other compounds, Carraher synthesized many new materials for physical property and processing studies. For example, the work was extended to the study of organometallic condensation polymer dyes such as **34**.
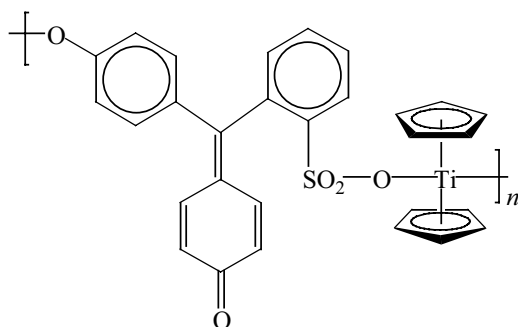
34

The application of step-growth polymerization at the metal itself was largely pioneered and developed by Carraher and coworkers in the 1970s.[88–96] In particular, the use of interfacial polycondensation was used to make a large variety of polymers with such metals as Zr, Hf, Ge, Sn, Pb, Sb, Bi, and Ti in the backbone. Carraher noticed that some organic and organometallic acid chlorides acted similarly to water and other Lewis bases. Thus, with the knowledge of how monofunctional organometallics acted, his and other groups designed systems that yielded oligomeric and polymeric materials. Polymers prepared using this methodology are shown in Scheme 3.

In addition to mixed-valence states and charge-transfer complex interactions, *d*-orbital interactions have been coupled with linear π-conjugated organic systems. The literature on the conductive properties of metal-containing polymers has been covered through 1996 in two excellent reviews.[97,98] A variety of structures involving *d-p* π interactions have been prepared, including Okamoto's arylethynyl copper coordination polymers **42**.[99–101] Doping with I_2 converts these insulating polymers (10^{-9} S/cm) to materials with metallic conductivity ($\sigma = 14$ S/cm), which originates from copper's partially filled *d* orbitals, enhanced interactions from Cu−Cu bonding, and cofacial Cu atom stacking.[102]

Metal-carbene-containing polymers are a more recent development in the area of organometallic polymers. Two reports have detailed the synthesis of polymers containing repeating metal-carbene units.[103,104] In 1988, Macomber and coworkers reported the synthesis of an unsaturated tungsten-carbene complex that polymerized to produce an insoluble polymer (**43**).[103] However, this polymer yielded a soluble copolymer (**44**) on standing in dimethyl sulfoxide for 4 days. Further reaction of this copolymer in DMSO (dimethyl sulfoxide) resulted in the isolation of the poly(methyl acrylate) devoid of metal. Masuda and coworkers have also described the synthesis of polymers with tungsten-carbene units attached to their backbones (**45**).[104] These polymers were air-stable; however, they were unstable in solutions containing air and exhibited poor thermal stability.

Scheme 3

42
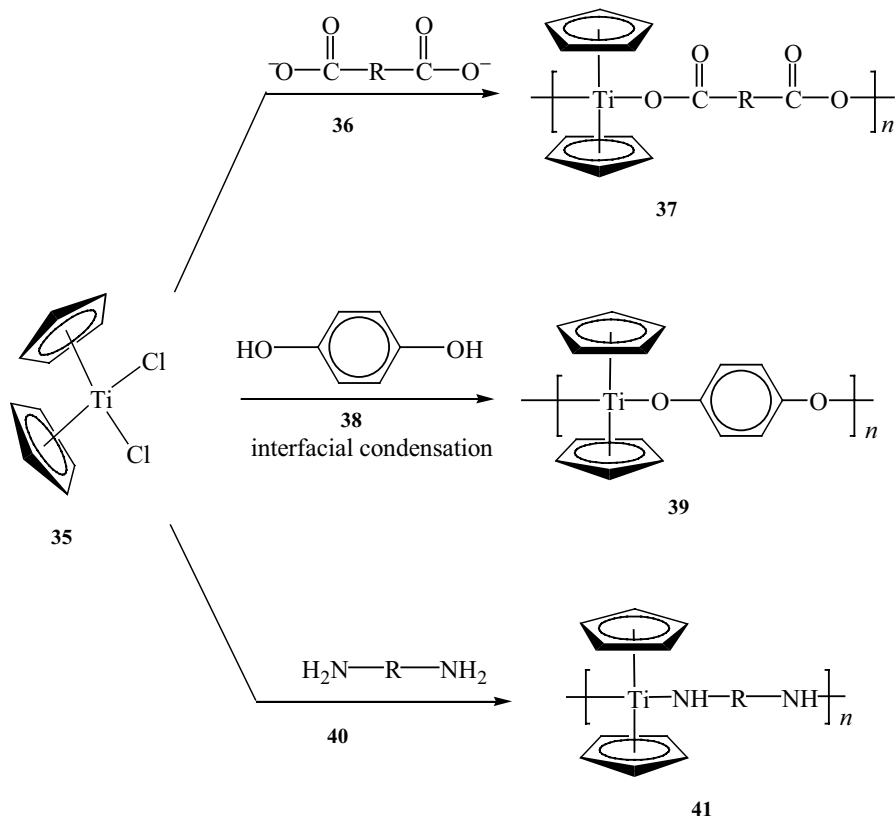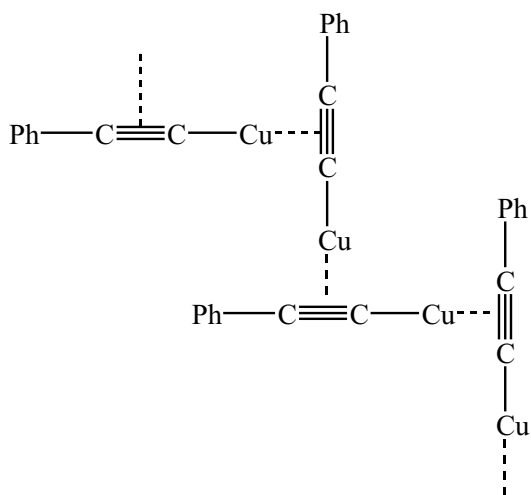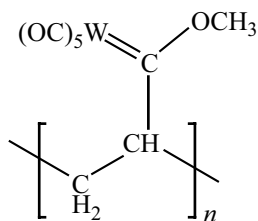
43
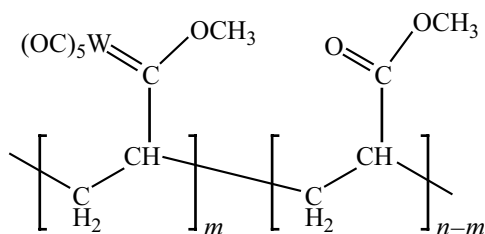
44
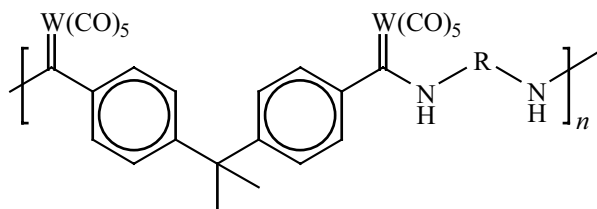
45

The study of metal- and metalloid-containing macromolecules has enriched the polymer field with materials possessing interesting properties. Depending on the structural makeup of the polymers and the types of metals that are incorporated into their structures, these materials can be varied to include catalytic, electrical, optical, magnetic, biological, and liquid crystalline properties. The following is a nonexhaustive list of potential and actual uses of metal-containing polymers: additives, electrical conductors, semi- and superconductors, piezoelectric devices, electrocatalysts, photoelectrocatalysts, photovoltaic cells, specialized electrodes, sensor devices, electrochromic materials, electroluminescent and multicolor displays, photoprotective agents, thickening agents, permanent coloring agents, and ceramic precursors. Because metals permit different oxidation states to exist, organometallic and other metal-containing polymers have attracted much attention as electrically conducting or semiconducting materials. This review will survey a diverse array of materials containing main group and transition metals and metalloids in or pendent to the polymer backbone.

II. STRUCTURES AND BONDING

The diversity of metal- and metalloid-containing polymers stems from the wide range of coordination numbers, oxidation states, and geometries that metals can possess. Interactions, including σ and π connections between two metals or metals and ligands, define the nature of bonding in these systems. The

classes of metal-containing polymers can be divided into three general groups: those with the metal in the polymer backbone, those with the metal coordinated to the polymer backbone, and those with the metal in the polymer sidechain. Highly branched, crosslinked, star-shaped, and dendritic polymers may or may not fit into these categories, and are, therefore, treated separately. Within these classes, there are many subclasses based on the types of metals, bonds, and ligands present.

A. Metals or Metalloids in the Backbone

Polymers incorporating metals or metalloids in their backbones possess a very large variety of structural features. For example, the polymer can contain metal- or metalloid–carbon σ bonds (**46, 47**) or π bonds (**48**) in their backbones.[105–107]
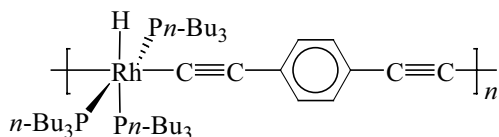
46
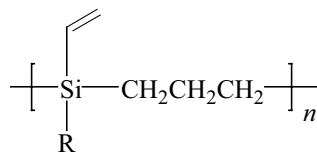
R = CHCH$_2$, CH$_3$, C$_6$H$_5$

47
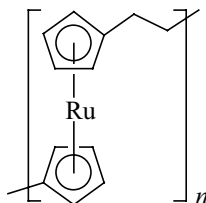
48

There are numerous examples of polymers that contain metals and metalloids coordinated to noncarbon elements. In these cases, the properties of the polymers are highly dependent on the ligands that are utilized. Polymer **49** is an example of a zinc porphyrin polymer.[108] It was found that incorporation of different substituents (electron acceptors or electron donors) on the aromatic rings in the polymer backbone altered the electronic properties of these materials.

Braid-shaped structures have been prepared as in the product of the phenyltetrazolate anion with metal ions.[109] The Ni(II) and Fe(II) adducts (**50**) give extremely viscous, aqueous solutions of polymers from which flexible sheets and threads have been made.

49

M = Ni, Fe

50
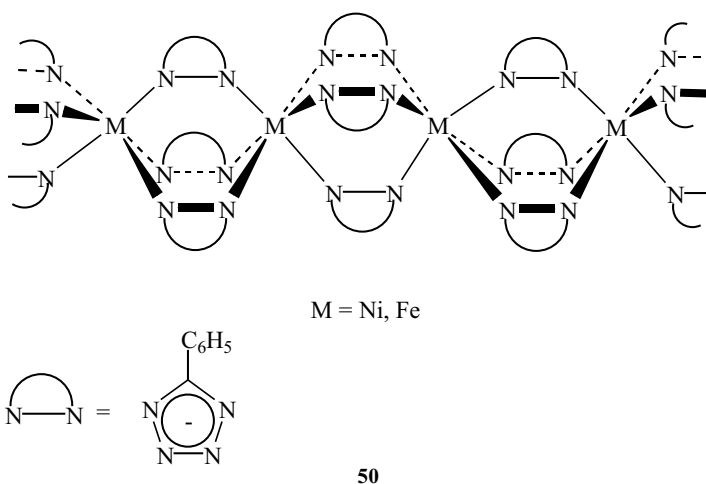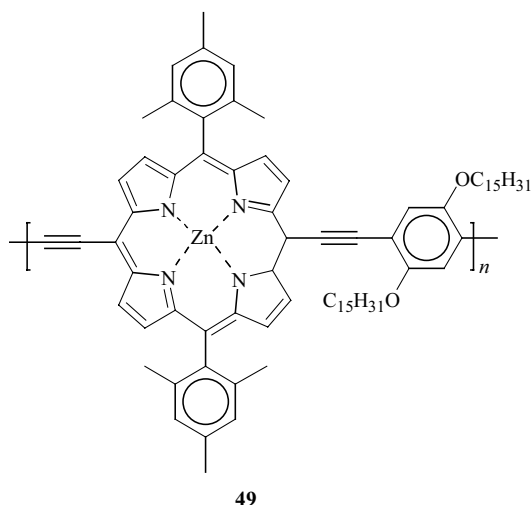
Metal-containing polymers exist in a plethora of wonderful shapes and structures including rods, sheets, and coils. There are a number of interesting structural classes of polymers known as "stacked" systems. These include both the shish-kebab type and the polydecker sandwich-type structures. A metal phthalocyanine structure with bridging pyrazine units (**51**) resembles a shish-kebab, in which the metal-pyrazine chain represents the skewer.[110]

Stacked phthalocyanine polymers (**52**) with oxygen bridges between the metal atoms have been prepared by dehydration of the phthalocyanine complexes of Si, Ge, and Sn to produce face-to-face stacking polymers.[111–113] When the oxygen-bridged systems are oxidatively doped, they become electrically conducting or semiconducting.
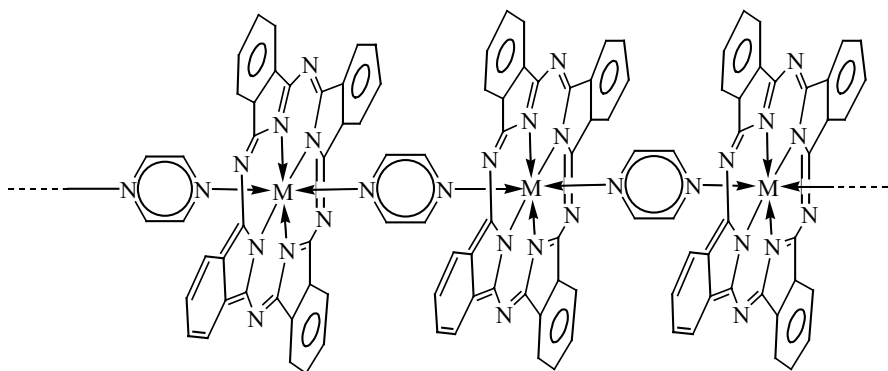
51
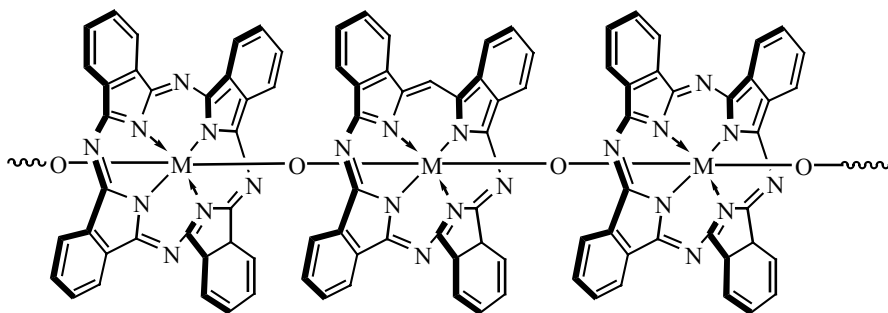
M = Si, Ge, Sn

52

The electrical, optical, and magnetic properties of stacked polymers are a delicate function of architectural and electronic control. For example, electrochemical oxidation in the presence of BF_4^- causes a change in structure from orthorhombic to tetragonal as the BF_4^- counterions move into the closely packed structure (Fig. 1).[113] Moreover, the electrical properties are tunable. This was the first case where the band filling of a molecular metal was broadly tunable.

There are also a number of reports that outline the synthesis of polymers containing metal–metal or metalloid–metalloid bonds in their backbones. These polymers may contain the metal σ-bonded or π-coordinated to organic ligands as shown for polymers **53** and **54**, respectively.

The other class of polymers containing M−M bonds includes the metals coordinated to elements such as nitrogen or oxygen. Polymer **55** is an example of a polymer with Rh−Rh single bonds,[116] while polymer **56** has Mo−Mo triple bonds in its structure.[117]

Figure 1

53

54

55
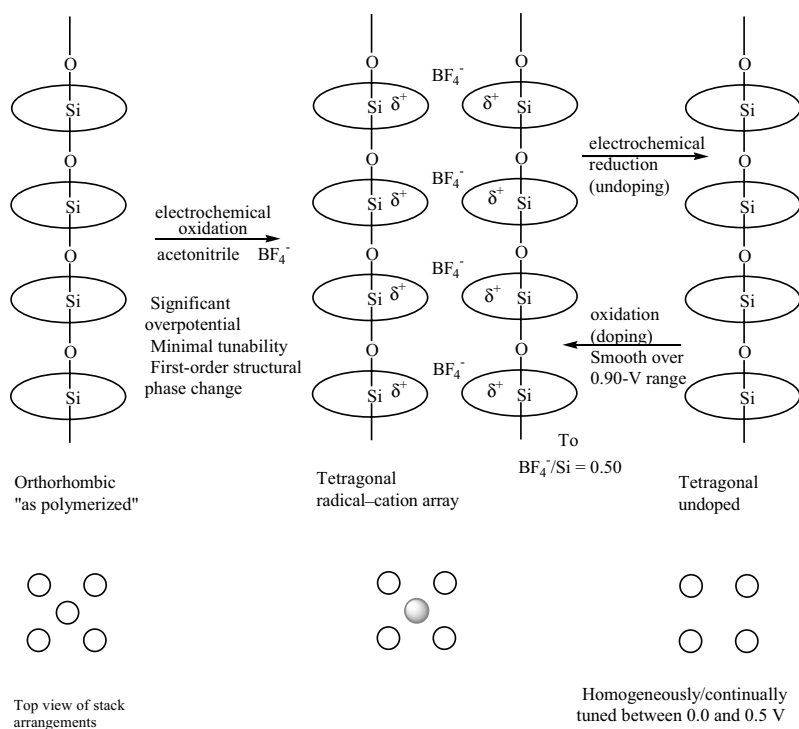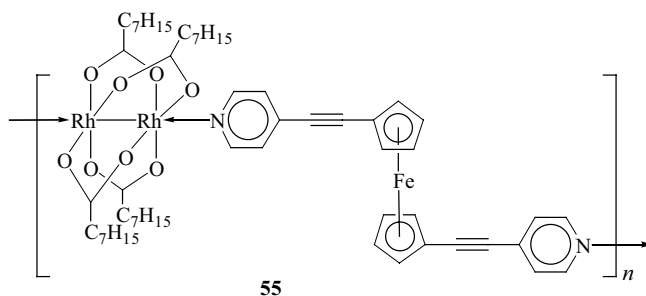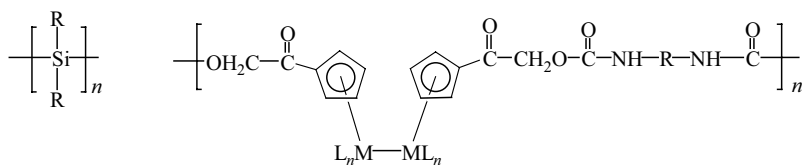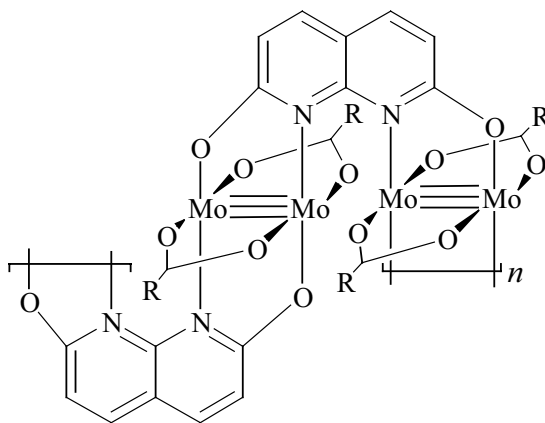
56

B. Metals or Metalloids in the Sidechain

There are numerous examples of polymers in which the metal or metalloid is present in the sidechain of the macromolecule. Polymer **57** is an organometallic polystyrene is which the chromium tricarbonyl moieties are π-coordinated to some of the benzene rings attached to polymer backbone.[77] The polynorbornene copolymer (**58**) incorporates polyhedral oligomeric silsesquioxane moieties into its sidechains.[118]
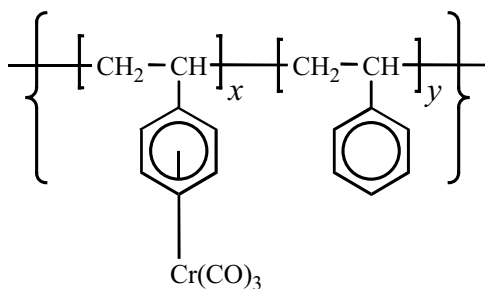
57

Polymer **59** is an example of a polystyrene substituted with sidechain zinc phthalocyanine moieties. These polymers formed aggregates in solution even with small degrees of phthalocyanine incorporation.[119] Aggregates result from phthalocyanine (cofacial) stacking interactions.

58

59
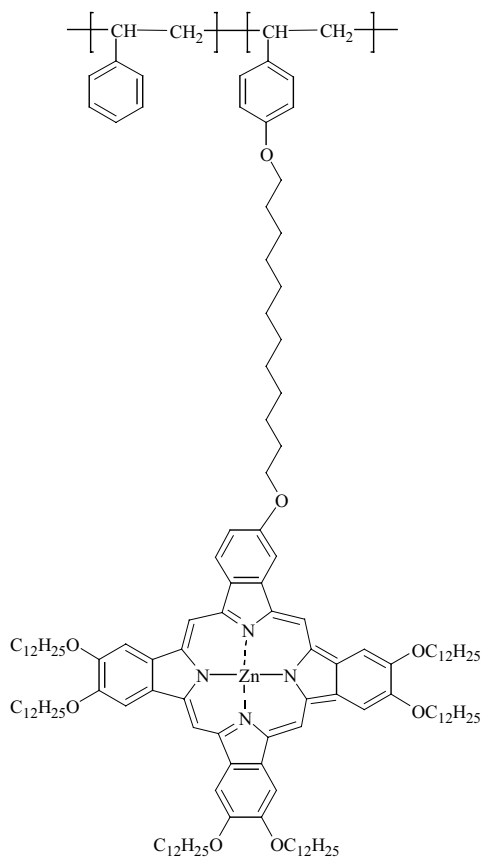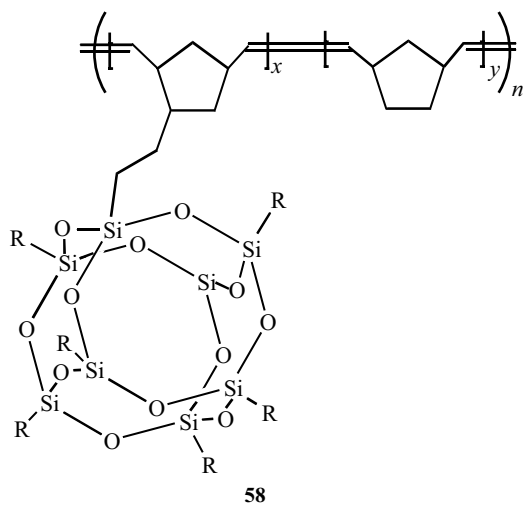
C. Transition Metals Coordinated to the Backbone

Another class of metal-containing polymer incorporates the metallic moieties coordinated to the polymer backbone. The metal can be bonded directly to the backbone as on polymers **60–62**.[120–122] Alternatively, the metallic moieties can be coordinated to the polymer backbones through pyridyl ligands (**63**).[123]

60

61

62

63
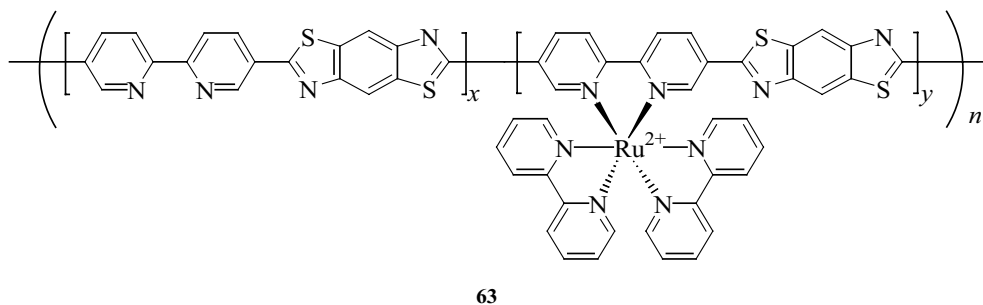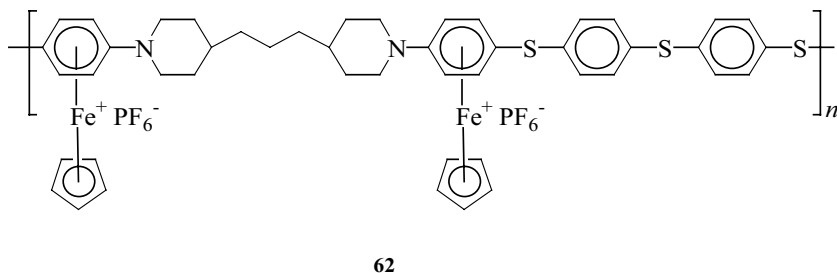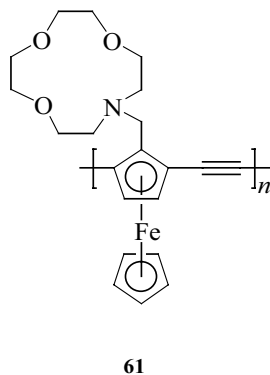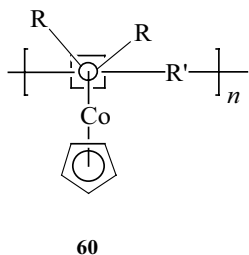
D. Branched Polymers

There are a number of examples of macromolecules with very complex structural features such as stars, dendrimers, hyperbranches, and crosslinks. Each of these classes of materials comes with its own advantages and disadvantages in terms of synthesis, processability, and properties. The crosslinked polymer **64** was prepared by the thermal copolymerization of ferrocenophanes.[124] The swelling properties of the crosslinked polymers allowed for determination of the solubility parameter of the analogous linear homopolymer. The crosslinked polymers were found to possess increased thermal stability relative to their linear analoges.

64
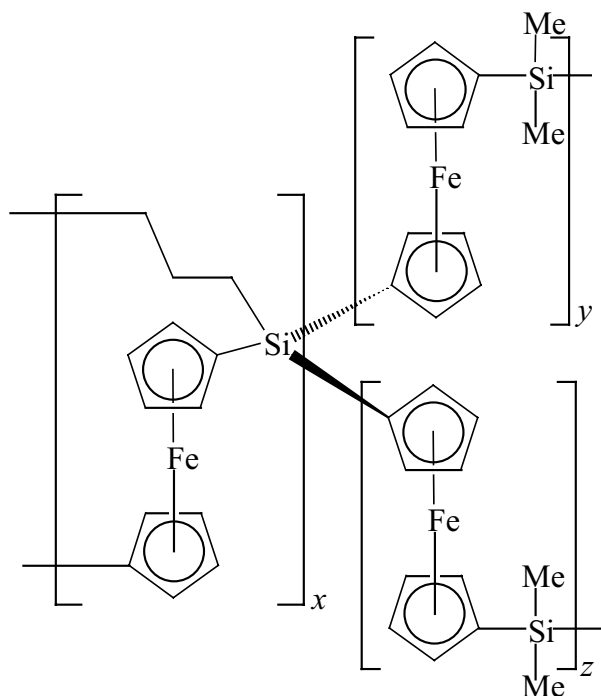
Dendrimers and star polymers have much higher architectural control than hyperbranched and crosslinked polymers. Polymers **65**[125,126] and **66**[127] are examples of branched polymers with organometallic or metal-coordinated complexes at the periphery.

M = Fe, Co$^+$ PF$_6^-$

65
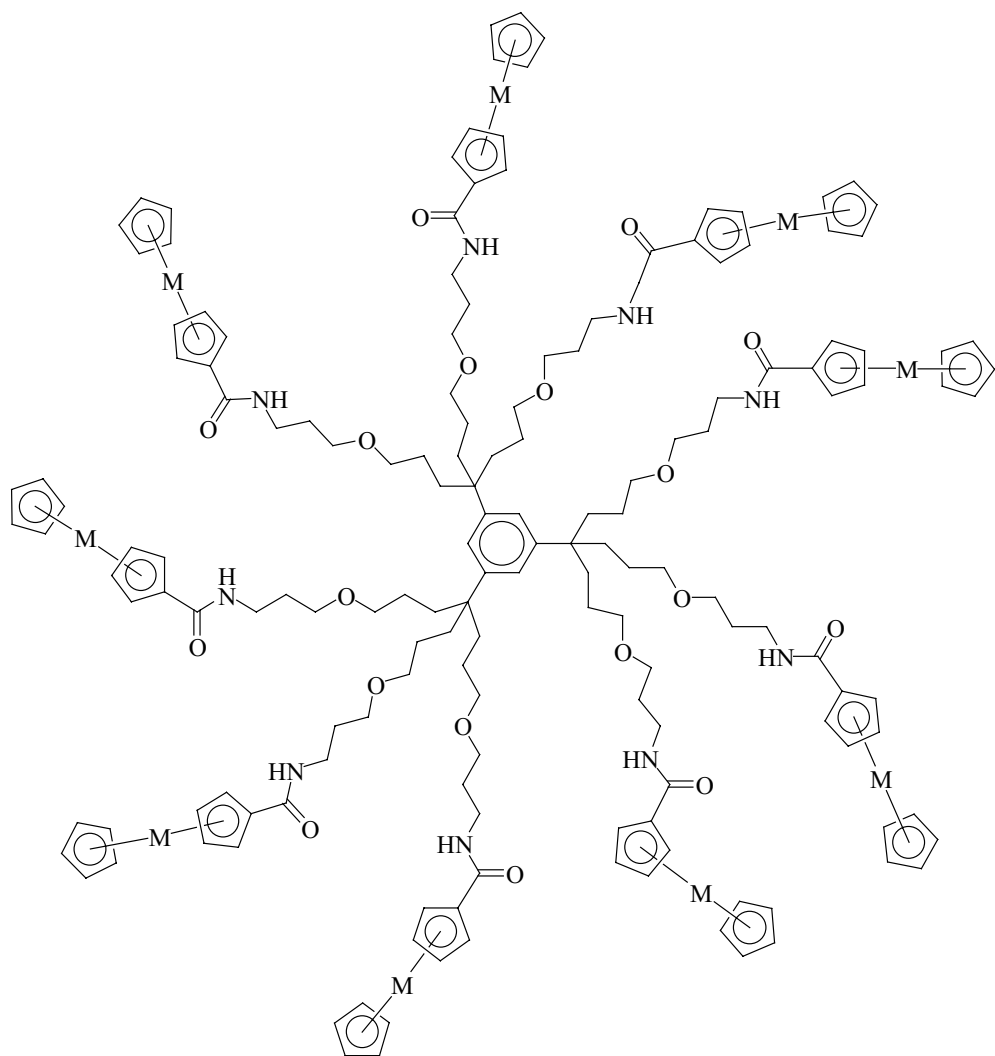
66
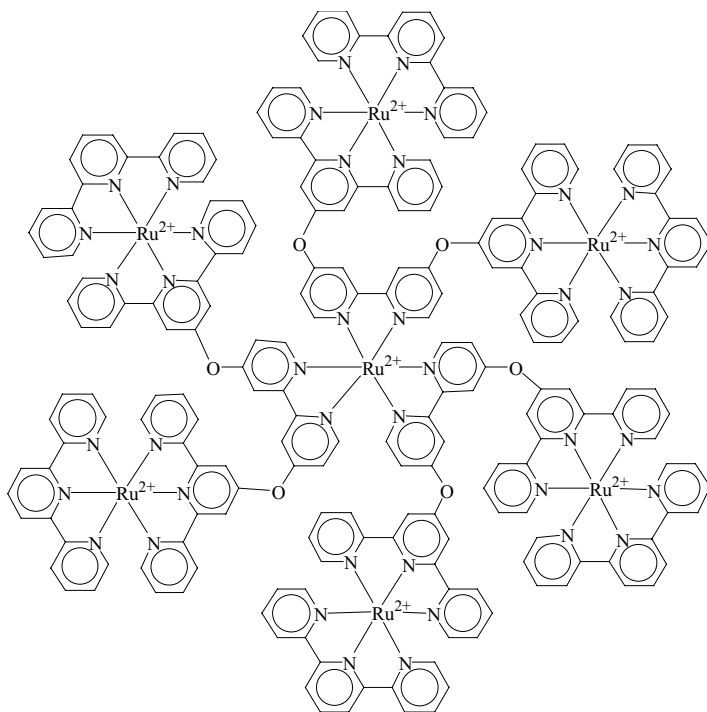
III. SYNTHETIC METHODOLOGIES

Few organometallic reaction mechanisms, other than the chain-growth examples cited earlier, have been studied using polymeric systems. Reaction mechanisms in polymer chemistry are generally ignored or inferred from the reaction mechanisms of similar small-product reactions. Here we discuss mainly organometallic reaction mechanisms employing examples of general concepts associated with small molecules. This is an area where much work is needed to determine reaction mechanisms for polymer-forming reactions. It is often assumed that small molecules will react in a similar fashion as macromolecules. It remains to be seen for many systems whether this assumption is valid. In general, the inference of mechanism similarity should hold for simple systems, but it is surely questionable for systems where inter- and intrachain effects can occur. Consider, for example, the reaction of ligand $^-XRX^-$ with a metal ion L_xM^{2+} to give a polymer $[-XRXM(L)_y-]_n$ as a coordination polymerization. This reaction must be considered in terms of the equilibria involved when RX^- reacts with L_xM^{2+}. Thus, consideration of the monomeric analogs could be essential for understanding the polymerization mechanism.

$$n RX^- + L_xM^{2+} \rightleftharpoons L_{x-1}MXR + L_x \rightleftharpoons L_{x-2}M(XR)_2 + L_x$$

Just as the variety of elements to work with are far greater when dealing with metal-containing polymers in comparison to classical polymers, so are the number and variety of reaction types. Most routes employed to synthesize metal-containing polymers follow the same strategies utilized to prepare organic polymers; specifically, condensation, coupling, substitution, addition and ring-opening polymerization (ROP). While some of these methods involve reactions at the metal centers, others include reactions with the organic ligands. Another route used in the synthesis of organometallic polymers proceeds via coordination of the metal to preformed organic polymers.

The following is a brief discussion of mechanistic and kinetic considerations based largely on small-molecule reactions since these are the reactions most studied.

Redox (reduction–oxidation) reactions, including atom and electron transfer, and substitution are just two of these reaction types. Several reaction types may occur simultaneously or in concert with one another. Even when the metal is somewhat removed physically from the reaction site, metal atom involvement may occur. Several research groups have found that many vinyl homo- and copolymerizations involving metal-containing vinyl units behave like classical non-metal vinyl reactions. However, in some cases charge transfer, redox, and other events may occur. For instance, Hayes and George found that the rate law for the homopolymerization of vinylferrocene did not follow the usual one-half order in initiator concentration. Rather, the rate was approximately first-order in both vinylferrocene and initiator due to an internal electron transfer from iron to the radical center, which generates an anion that is quenched thereby leaving a terminal ferricinium group at the growing end.[59–61]

The following sections highlight some of the most important methods that have been developed in the production of metal- and metalloid-containing polymers. A number of other techniques are outlined in Chapters 2–6.

A. Step-Growth Polymerization

A greater variety of substitution and condensation reactions are involved in the synthesis of metal-containing polymers than in classical nonmetal reactions. Despite extensive study, inorganic and organometallic mechanisms are less understood than organic reaction mechanisms. In this class of reaction, the ligand is typically a Lewis base that is the agent of either substitution or condensation. The reaction between *tetra*-chloroplatinate and diamines to form the anticancer and antiviral platinum(II) polyamines illustrates a substitution reaction. Chloride is the leaving group, while the amine is both the ligand and the substitution agent. The nitrogen retains its hydrogen atoms and has a net +1 formal charge. This reaction is the same as typical metal–ligand reactions except for a polymer results from the reaction (Scheme 4).

An example of organometallic polycondensation is illustrated by the reaction between dimethyltin dichloride and a diamine (Scheme 5). Again, the diamine acts as a Lewis base and the chloride and hydrogen are the leaving groups. Here, the nitrogen is covalently bonded after loss of the proton. This reaction is analogous to typical amide formation between diamines and diacid chlorides.

Scheme 4

Scheme 5
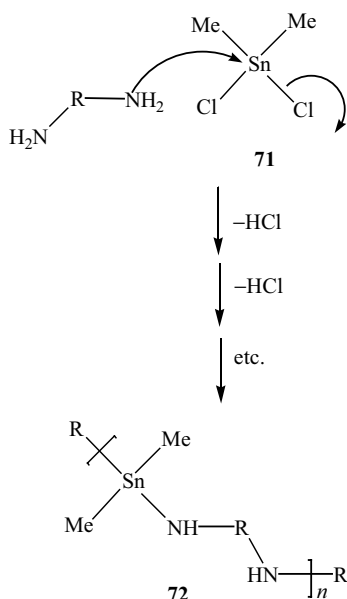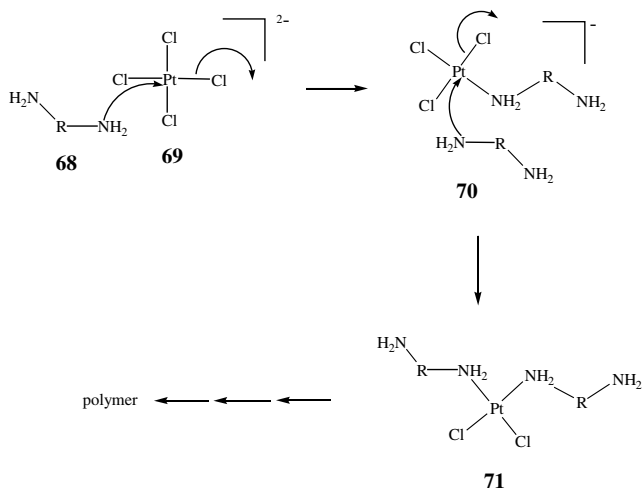
Step-growth polymerization of metal-containing monomers has been utilized in the synthesis of metal-containing polymers with the metallic moiety incorporated within or pendent to the backbone. Step-growth polymerization at the metal itself was largely pioneered and developed by Carraher and coworkers in the 1970s.[88–95] Step-growth polymerization of metal-containing monomers is commonplace where the reaction does not take place at the metal atom. Some early

examples of the formation of polymetallocenes that contain ester, amide, and siloxane linkages are shown below. The 1,1′-dicarboxylic acid of cobaltacenium PF_6^- and the 1,1′-diacid chloride of ferrocene were reacted with diols and diamines to generate **73** and **74**, respectively. 1,1′-*Bis*(*N*-dimethylaminodimethylsilyl)ferrocene was reacted with 4,4′-*bis*(dimethylhydroxysilyl)biphenyl to generate **75**. The latter had relatively high MW and was hydrolytically and thermally stable to $> 400°C$.[128]
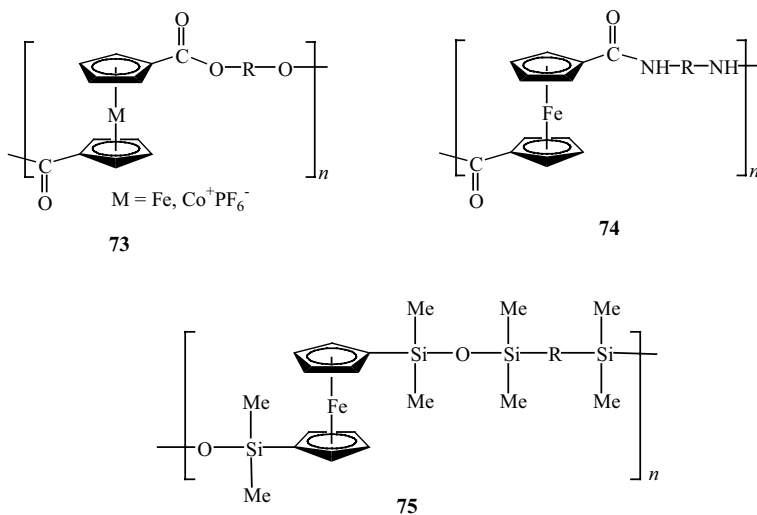
Scheme 6 shows the reaction of **76** with **77**, where the metal center is not at the reaction site.[129] The resulting organometallic polyimine (**78**) exhibited very low solubility in organic solvents. This polycondensation reaction proceeded with the formation of water.
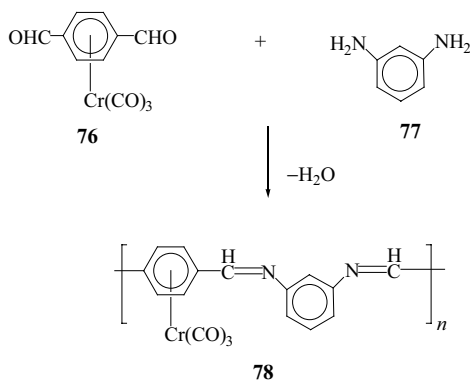
Scheme 6

Scheme 7 shows the polycondensation of the diethynyl monomer **79** with the dichloroplatinum complex **80**. In this example, the polymerization reaction occurs at the metal center to yield the platinum polyyne **81**.[130]
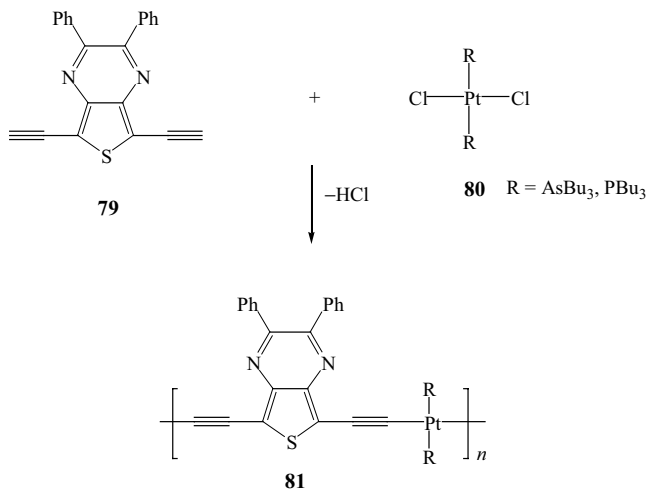
Scheme 7

B. Chain-Growth Polymerization

Chain-growth polymerization has been used to prepare a number of olefin-functionalized metal-containing monomers. For example, a number of articles have detailed the polymerization of organometallic olefinic monomers such as **82–84**.[131–133] Depending on the nature of the double bond and the metallic group, radical, cationic, and anionic initiators can be used to polymerize these monomers.

82

83

84
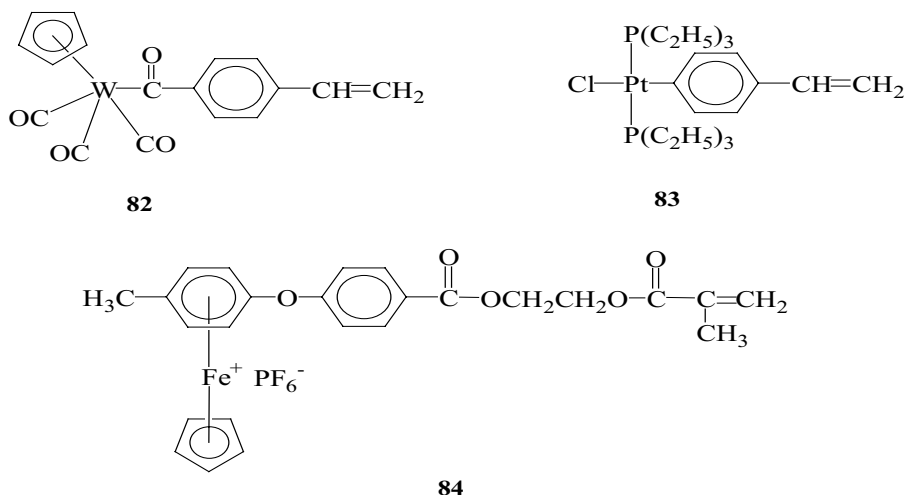
Scheme 8 shows the synthesis of polyacrylate **86** containing pendent ferrocenyl groups via the radical-initiated polymerization of the organoiron monomer **85**.[134]
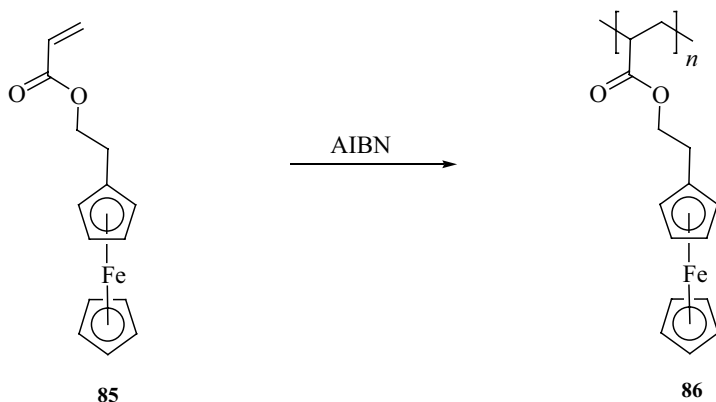
Scheme 8

C. Ring-Opening Polymerization

ROP reactions of cyclic metal-containing monomers have been utilized to prepare polymeric materials. This method has led to seminal advances in preparing high MW polymers with ferrocene in the mainchain. Ring-opening methods have led to enhanced control of polymer architecture. As with the other methods of polymerization, the metal can either be part of the cyclic structure or attached to an organic ligand bonded to the cyclic system.

Metallocenophanes are organometallic complexes in which a bridging atom is bonded to both of the cyclopentadienyl rings of a metallocene. This class of monomer can be polymerized thermally, anionically, cationically, and with transition metal catalysts.[135] The polymerization of the ferrocenophane with a dimethylsilyl bridge (**87**) is shown in Scheme 9.
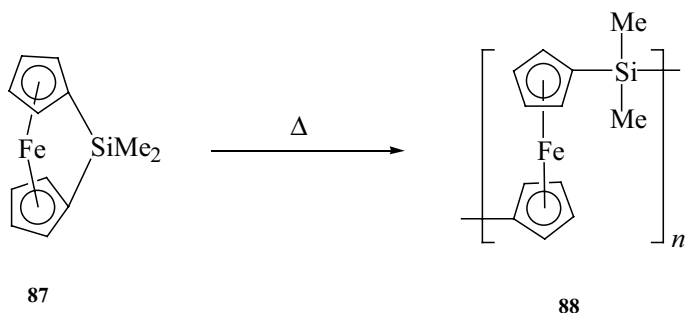
Scheme 9

Monomer **89** (Scheme 10) is a ferrocenyl-substituted cyclic phosphazene, which is ring-opened to give a polyphosphazene with ferrocenyl moieties attached as side-chains to two positions on the polymer backbone.[136] Attempted polymerization at 250°C resulted in no polymer formation; however, a catalytic amount of a perchlorinated cyclic phosphazene monomer under the same conditions resulted in the isolation of polymer **90**.
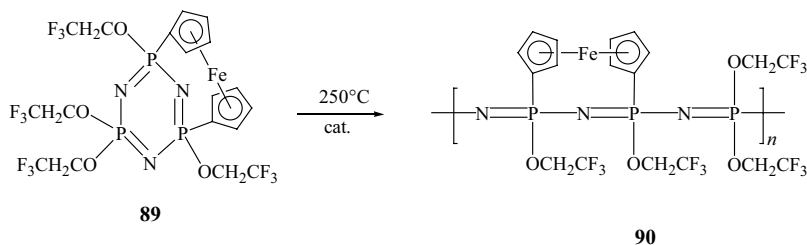
Scheme 10

Ring-opening metathesis polymerization (ROMP) of norbornene monomers (**91**) (Scheme 11) functionalized with cyclopentadienyliron cations has been accomplished using transition metal catalysts to yield the corresponding organoiron polymer (**92**).[137] The resulting polynorbornene has the metallic moieties present in the polymer sidechains.
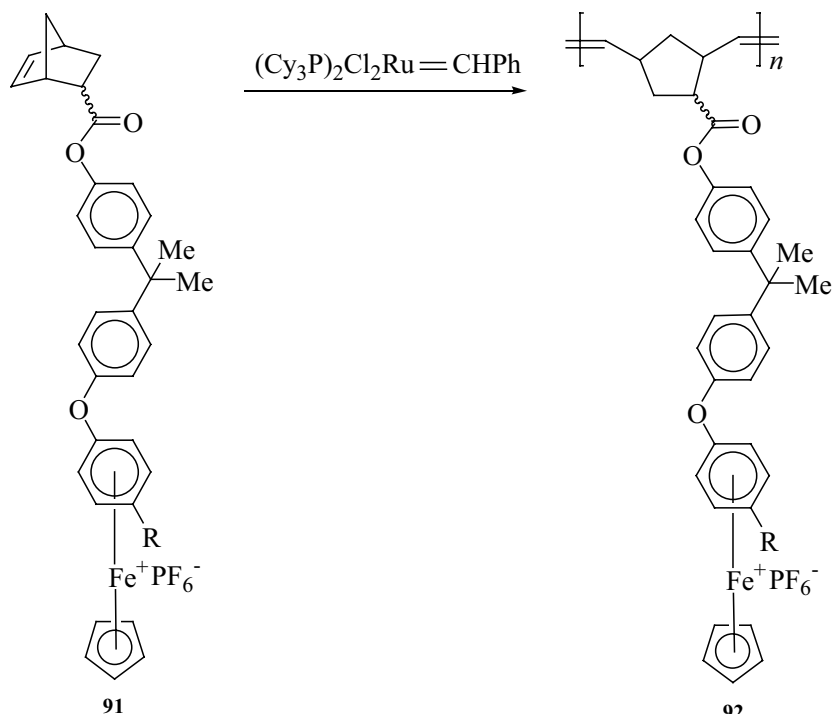
Scheme 11

D. Metal Coordination

There are two different ways in which metal coordination can yield a metal-containing polymer. The first methodology involves the coordination of metal complexes to preformed polymeric materials. This is illustrated in Scheme 12 by the coordination of a ruthenium complex (**94**) to the bipyridine ligands along the backbone of polymer **93**. This coordination reaction resulted in the formation of the corresponding ruthenium polymer **95**.[138]

93

Ru(Bpy)$_2$(OTf)$_2$(acetone)$_2$

94

95
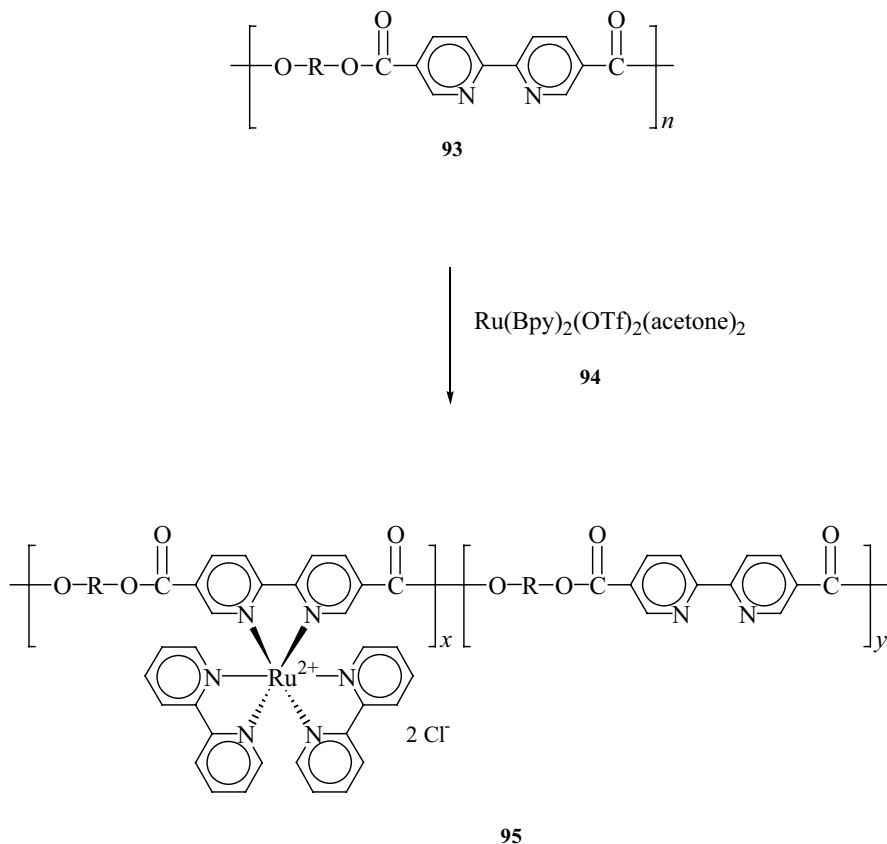
Scheme 12

Another strategy involving metal coordination reactions is shown in Scheme 13. In this case, the metal coordination reactions actually yield the metal-containing polymer (**98**). It can be seen that the reaction of a multidentate ligand (**96**) with a ruthenium complex (**97**) led to the formation of polymer **98** with the Ru atoms as an integral part of the polymer backbone.[139]
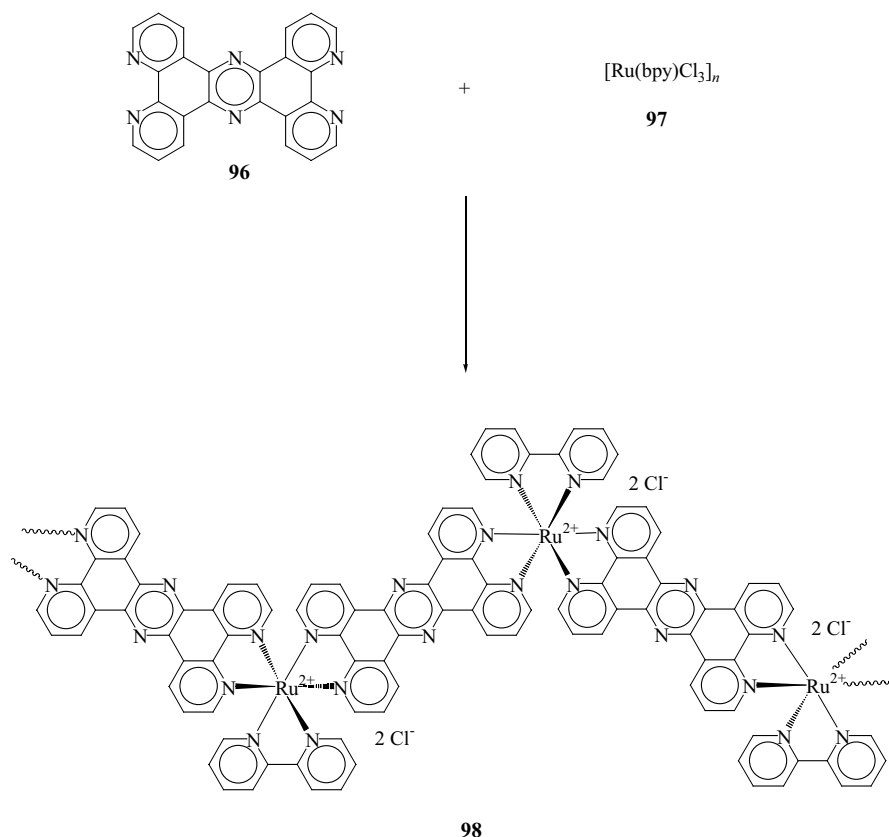
Scheme 13

IV. SUMMARY

Vast arrays of metal-containing polymers have been produced that offer a wide variety of properties. Key milestones in the history of this diverse topic and a sense of its growth and importance were discussed in this chapter. While initial efforts focused on polysiloxanes, today's efforts are quite diverse and include the production of multisite catalysts, variable oxidation state materials, and "smart" materials where the precise structure can be changed through the introduction of different counterions. These polymers have been produced by all of the well-established polymerization methodologies. The metal atoms reside as part of the macromolecular backbone, in sidechains, coordinated to the backbone, and as integral parts of dendrites, stars, and rods. Truly, many of tomorrow's critically important materials will have metal atoms as an integral part of the polymer framework, which will allow the materials to function as demanded.

V. REFERENCES

1. C. E. Carraher, Jr., J. E. Sheats, C. U. Pittman, Jr., eds., *Organometallic Polymers,* Academic Press, New York, 1978.

2. C. E. Carraher, Jr., J. E. Sheats, C. U. Pittman, Jr., eds., *Advances in Organometallic and Inorganic Polymers Science,* Marcel Dekker, New York, 1982.

3. J. E. Sheats, C. E. Carraher, Jr., C. U. Pittman, Jr., eds., *Metal-Containing Polymeric Systems,* Plenum Press, New York, 1985.

4. J. E. Sheats, C. E. Carraher, Jr., C. U. Pittman, Jr., M. Zeldin, B. Currell, eds., *Inorganic and Metal-Containing Polymeric Materials,* Plenum Press, New York, 1990.

5. C. U. Pittman, Jr., C. E. Carraher, Jr., M. Zeldin, J. E. Sheats, B. M. Culbertson, eds., *Metal-Containing Polymeric Materials,* Plenum Press, New York, 1996.

6. M. Zeldin, K. J. Wynne, H. R. Allcock, eds., *Inorganic and Organometallic Polymers,* ACS Symp. Series Vol. 360, ACS Publishers, Washington, DC, 1988.

7. M. Zeldin, "Inorganic and Organometallic Polymers," in *Encyclopedia of Physical Science and Technology,* 3rd ed., Vol. 12, J Wiley, New York, 2002, pp. 675–695.

8. K. A. Andrianov, *Metallorganic Polymers,* J Wiley, New York, 1965.

9. E. W. Neuse, H. Rosenburg, *Metallocene Polymers,* Marcel Dekker, New York, 1970.

10. A. D. Pomogailo, *Catalysis by Polymer Immobilized Metal Complexes,* Gordon and Breach Science Publishers, Amsterdam, 1998.

11. R. D. Archer, *Inorganic and Organometallic Polymers,* Wiley-VCH, New York, 2001.

12. A. S. Abd-El-Aziz, *Coord. Chem. Rev.* **233–234,** 177 (2002).

13. A. S. Abd-El-Aziz, "Metal-Containing Polymers," in *Encyclopedia of Polymer Science and Technology,* 3rd ed., J. I. Kroschwitz, ed., J Wiley, New York, 2002.

14. A. S. Abd-El-Aziz, E. K. Todd, *Polym. News* **5,** 26 (2001).

15. A. S. Abd-El-Aziz, *Macromol. Rapid Commun.* **23,** 995 (2002).

16. P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **99,** 1515 (1999).

17. I. Manners, *Angew. Chem. Int. Ed. Engl.* **35,** 1603 (1996).

18. F. G. A. Stone, W. A. G. Graham, *Inorganic Polymers,* Academic Press, New York, 1962.

19. C. E. Carraher, Jr., C. U. Pittman, Jr., *Inorganic Polymers,* in *Ullmann's Encyclopedia of Industrial Chemistry,* 5th ed., VCH Press, Vol. A14, 1989, pp. 241–262.

20. B. P. Block, *Inorganic Macromol. Rev.* **1**(2), 115 (1970).

21. M. D. Rausch, C. U. Pittman, Jr., et al., in *New Monomers and Polymers,* B. M. Culbertson, C. U. Pittman, Jr., eds., Plenum, New York, 1984, pp. 243–267.

22. C. U. Pittman, Jr., in *Organometallic Reactions,* E. I. Becker, M. Tsutsui, eds., Vol. 6, Marcel Dekker, New York 1977, pp. 1–62.

23. C. U. Pittman, Jr., C. E. Carraher, Jr., J. R. Reynolds, "Organometallic Polymers," in the *Encyclopedia of Polymer Science and Engineering,* H. Mark, N. Bikales, C. Overberger, J. Menges, eds., J Wiley, 1987, Vol. 10, pp. 541–594.

24. A. D. Pomogailo, V. S. Savostianov, *J. Macromol. Sci. Rev; Macromol. Sci. Chem. Phys.* **25**(3), 375–479 (1985).

25. C. U. Pittman, Jr. in *Comprehensive Organometallic Chemistry,* G. Wilkinson, F. G. A. Stone, E. W. Abel, eds., Pergamon Press, Oxford, UK, 1982, Vol. 8, pp. 553–608.

26. C. E. Carraher, Jr., *Inorg. Macromol. Rev.* **1,** 271 (1972).

27. R. G. Jones, W. Ando, J. Chojnowski, eds., *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications,* Kluwer Academic Publishers, Dordrecht/Boston/London, 2000.

28. J. M. Zeigler, F. G. Fearon, eds., "Silicon-Based Polymer Science: A Comprehensive Resource," in *Advances in Chemistry,* Vol. 224, American Chemical Society (ACS), Washington, DC 1990.

29. S. J. Clarson, J. J. Fitzgerald, M. J. Owen, S. D. Smith, eds., *Silicones and Silicone-Modified Materials,* ACS Symp. Series, Vol. 729, Washington, DC, 2000.

30. R. D. Miller, J. Michl, *Chem. Rev.* **89,** 1359 (1989).

31. A. Ladenburg, *Liebigs Ann. Chem.* **164,** 300 (1872).

32. A. Ladenburg, *Liebigs Ann. Chem.* **173,** 143 (1874).

33. F. S. Kipping, *J. Chem. Soc.* **101,** 2106 (1912).

34. F. S. Kipping, *J. Chem. Soc.* **130,** 104 (1927).

35. F. S. Kipping, *Proc. Royal Soc. A* **159,** 139 (1937).

36. K. H. Meyer, *Natural and Synthetic High Polymers,* Interscience, New York, 1942.

37. E. Rochow, *Chem. Eng. News,* **23,** 612 (1945).

38. E. G. Rochow, *An Introduction to the Chemistry of Silicones,* J Wiley, New York, 1947.

39. J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers,* Prentice Hall, Englewood Cliffs, NJ, 1992.

40. C. A. Burkhard, *J. Am. Chem. Soc.* **71,** 963 (1949).

41. E. Krause, R. Becker, *J. Am. Chem. Soc.* **52,** 4031 (1920).

42. C. D. West, *Z. Kristallogr.* **90,** 555 (1935).

43. K. A. Jensen, *Z. Anorg. Chem.* **252,** 227 (1944).

44. C. S. Marvel, J. H. Rassweiler, *J. Am. Chem. Soc.* **80,** 1197 (1958).

45. W. C. Drinkard, J. C. Bailar, Jr., *J. Am. Chem. Soc.* **81,** 4795 (1959).

46. K. V. Martin, M. L. Judd, Report on Contract AF 33(616) 3200 (Nov. 1956) to U.S. Air Force, Wright Air Development Center, Final Report on Contract AF 33(616) 3772 (Dec. 1957).

47. J. C. Bailar Jr., in Ref. 1, pp. 313–321.

48. B. P. Block, G. Dahl, U.S. Patent 3,415,781 (Dec. 10, 1968).

49. S. Kanda, *Nippon Kagaku Zasshi* **83,** 560 (1962).

50. S. Kanda, Y. Saito, *Bull. Chem. Soc. Jpn.* **30,** 192 (1957).

51. R. H. Bailes, M. Calvin, *J. Am. Chem. Soc.* **69,** 1886 (1947).

52. J. T. Wrobleski, D. B. Brown*, Inorg. Chem.* **18,** 498 (1979).

53. J. T. Wrobleski, D. B. Brown*, Inorg. Chem.* **18,** 2738 (1979).

54. R. D. Archer, H. Chen, J. A. Cronin, S. M. Palmer, in Ref. 5, pp. 81–91.

55. T. J. Kealy, P. L. Pauson, *Nature* **168,** 1039 (1951).

56. G. Wilkinson, M. Rosenblum, H. C. Whiting, R. B. Woodward, *J. Am. Chem. Soc.* **74,** 2125 (1952).

57. R. B. Woodward, M. Rosenblum, H. C. Whiting, *J. Am. Chem. Soc.* **74,** 3458 (1952).

58. F. S. Arimoto, A. C. Haven, Jr., *J. Am. Chem. Soc.* **77,** 6295 (1955).

59. M. George, G. Hayes, *J. Polym. Sci. Chem. Ed.* **13,** 1049 (1975).

60. M. George, G. Hayes, *J. Polym. Sci. Chem. Ed.* **14,** 475 (1976).

61. M. George, G. Hayes, *Polymer* **15,** 397 (1974).

62. Y. Sasaki, L. L. Walker, E. L. Hurst, C. U. Pittman Jr., *J. Polym. Sci., Polym. Chem. Ed.* **11,** 1213 (1973).

63. J. C. Lai, T. Rounsefell, C. U. Pittman, Jr., *J. Polym. Sci: A1* **9,** 651 (1971).

64. C. U. Pittman, Jr., R. L. Voges, J. Elder, *Polym. Lett.* **9,** 191 (1971).

65. C. U. Pittman, Jr., P. Grube, *J. Appl. Polym. Sci.* **18,** 2269 (1974).

66. C. U. Pittman, Jr., P. Grube, *J. Polym. Sci: A1* **9,** 3175 (1971).

67. C. U. Pittman, Jr., J. C. Lai, D. P Vanderpool, *Macromolecules* **3,** 105 (1970).

68. C. U. Pittman, Jr., J. C. Lai D. P Vanderpool, M. Good, R. Prado, *Macromolecules* **3,** 746 (1970).

69. J. C. Lai, T. D. Rounsefell, C. U. Pittman, Jr., *Macromolecules* **4,** 155 (1971).

70. C. U. Pittman, Jr., R. L. Voges, W. R. Jones, *Macromolecules* **4,** 291 (1971).

71. C. U. Pittman, Jr., G. V. Marlin, T. D. Rounsefell, *Macromolecules* **6,** 1 (1973).

72. C. U. Pittman, Jr., R. L. Voges, J. Elder, *Macromolecules* **4,** 302 (1971).

73. O. E. Ayers, S. P. McManus, C. U. Pittman, Jr., *J. Polym. Sci. Chem. Ed.* **11,** 1201 (1973).

74. C. U. Pittman, Jr., C. C. Lin, T. D. Rounsefell, *Macromolecules* **11,** 1022 (1978).

75. C. U. Pittman, Jr., T. V. Jayaraman, R. D. Priester, Jr., S. Spencer, M. D. Rausch, D. Macomber, *Macromolecules* **14,** 237 (1981).

76. C. U. Pittman, Jr., R. D. Priester, Jr., T. V. Jayaraman, *J. Polym. Chem. Ed.* **19,** 3351 (1981).

77. C. U. Pittman, Jr., P. L. Grube, O. E. Ayers, S. P. McManus, M. D. Rausch, G. A. Moser, *J. Polym. Sci. Part A1* **10,** 379 (1972).

78. C. U. Pittman, Jr., G. V. Marlin, *J. Polym. Sci; Polym. Chem. Ed.* **11,** 2753 (1973).

79. C. U. Pittman, Jr., O. E. Ayers, S. P. McManus, *J. Macromol. Sci. Chem.* **A7**(8), 1563 (1973).

80. C. U. Pittman, Jr., O. E. Ayers, S. P. McManus, *Macromolecules* **7,** 737 (1974).

81. C. U. Pittman, Jr., T. D. Rounsefell, *Macromolecules* **9,** 936 (1976).

82. C. U. Pittman, Jr., T. D. Rounsefell, E. A. Lewis, J. E. Sheats, B. H. Edwards, M. D. Rausch, E. A. Mintz, *Macromolecules* **11,** 560 (1978).

83. D. W. Macomber, M. D. Rausch, T. V. Jayaraman, R. D. Priester, C. U. Pittman, Jr., *J. Organomet. Chem.* **25,** 353 (1981).

84. D. W. Macomber, W. P. Hart, M. D. Rausch, *J. Am. Chem. Soc.* **104,** 884 (1982).

85. C. U. Pittman, Jr., M. D. Rausch, *Pure Appl. Chem.* **58**(4), 617 (1986).

86. M. D. Rausch, D. W. Macomber, K. Gonsalves, F. G. Fang, Z. -R. Lin, C. U. Pittman, Jr., in Ref. 3, pp. 43–57.

87. Private communication between Charles Carraher and Brian Currell, 1974.

88. C. E. Carraher, Jr., S. Bajah, *Polymer* **15,** 9 (1974).

89. C. E. Carraher, Jr., in *Interfacial Synthesis*, P. Millich, C. E. Carraher, Jr., eds., Marcel Dekker, New York, 1977, Vol. II, Chap. 20.

90. C. E. Carraher, Jr., R. J. Nordin, *J. Appl. Polym. Sci.* **18,** 53 (1974).

91. C. E. Carraher, Jr., S. T. Bajah, *Br. Polym. J.* **14,** 42 (1973).

92. C. E. Carraher, R. J. Nordin, *Makromol. Chem.* **164,** 87 (1973).

93. C. E. Carraher, Jr., J. Piersma, *Makromol. Chem.* **153,** 49 (1972).

94. C. E. Carraher, Jr., J. Reimer, *J. Polym. Sci.* A1 **10,** 3367 (1972).

95. C. E. Carraher, Jr., in Ref. 1, pp. 79–85.

96. C. E. Carraher, Jr., W. J. Scott, J. A. Schroeder, D. J. Giron, *J. Macromol. Sci. Chem. Part A,* **15**(4), 625 (1981).

97. H. Nishihara in H. S. Nalwa, eds., *Handbook of Organic Conductive Molecules and Polymers,* J Wiley, New York, 1997, Vol. 2, p. 799.

98. H. S. Nalwa, *Appl. Organomet. Chem.* **4,** 91 (1990).

99. Y. Okamoto, S. K. Kundu, *J. Phys. Chem.* **77,** 2677 (1973).

100. Y. Okamoto, M. Mincer, A. Golubovic, N. Dimond, *Nature* **229,** 157 (1971).

101. Y. Okamoto, M. C. Wang, *J. Polym. Sci. Polym. Lett.* **18,** 249 (1980).

102. K. Krikor, M. Rotti, P. Nagles, *Synth. Metals* **21,** 353 (1987).

103. D. W. Macomber, M. -H. Hung, M. Liang, A. G. Verma, P. Madhukar, *Macromolecules* **21,** 1189 (1988).

104. R. Nomura, K. Watanabe, T. Masuda, *Macromolecules* **33,** 1936 (2000).

105. H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor, T. B. Marder, *J. Chem. Soc., Chem. Commun.* 188 (1991).

106. C. X. Liao, W. P. Weber, *Macromolecules* **25,** 1639 (1992).

107. J. M. Nelson, A. J. Lough, I. Manners, *Angew. Chem. Int. Ed. Engl.* **33,** 989 (1994).

108. B. Jiang, S. -W. Yang, D. C. Barbini, W. E. Jones, Jr., *Chem. Commun.* 213 (1998).

109. L. Richards, I. Koufis, C. S. Chan, J. L. Richards, C. Cotter, *Inorg. Chem.* **105,** 121 (1985).

110. B. N. Diel, T. Inabe, N. K. Jaggi, J. W. Lyding, O. Schneider, M. Hanack, C. R. Kannewurf, T. J. Marks, L. H. Schwartz, *J. Am. Chem. Soc.* **106,** 3207 (1984).

111. J. L. Peterson, C. S. Schramm, D. R. Stojakovic, B. M. Hoffman, T. J. Marks, *J. Am. Chem. Soc.* **99,** 286 (1977).

112. T. J. Marks, *Science* **227,** 881 (1985).

113. J. G. Gaudiello, G. E. Kellogg, S. M. Tetrick, T. J. Marks, *J. Am. Chem. Soc.* **111,** 5259 (1989).

114. C. Aitken, J. F. Harrod, E. Samuel, *J. Am. Chem. Soc.* **108,** 4059 (1986).

115. D. R. Tyler, J. J. Wolcott, G. W. Nieckarz, S. C. Tenhaeff, in *Inorganic and Organometallic Polymers II,* P. Wisian-Neilson, H. R. Allcock, K. J. Wynne eds., ACS Symp. Series Vol. 572, American Chemical Society, Washington, DC, 1994; Chap. 36, pp. 481–496.

116. W. -M. Xue, F. E. Kuhn, E. Herdtweck, Q. Li, *Eur. J. Inorg. Chem.* 213 (2001).

117. M. H. Chisholm, *Acc. Chem. Res.* **33,** 53 (2000).

118. P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad, J. D. Lichtenhan, *Macromolecules* **32,** 1194 (1999).

119. S. Mahkseed, A. Cook, N. B. McKeown, *Chem. Commun.* 419 (1999).

120. Y. Sawada, I. Tomita, I. L. Rozhanskii, T. Endo, *J. Inorg. Organomet. Polym.* **10,** 221 (2000).

121. H. Plenio, J. Hermann, J. Leukel, *Eur. J. Inorg. Chem.* **12,** 2063 (1998).

122. A. S. Abd-El-Aziz, E. K. Todd, G. Z. Ma, *J. Poly. Sci., Part A, Poly. Chem.* **39,** 1216 (2001).

123. S. C. Yu, X. Gong, W. K. Chan, *Macromolecules* **31,** 5639 (1998).

124. K. Kulbaba, M. J. MacLachlan, C. E. B. Evans, I. Manners, *Macromol. Chem. Phys.* **202,** 1768 (2001).

125. C. Valerio, J. -L. Fillaut, J. Ruiz, J. Guittard, J. -C. Blais, D. Astruc, *J. Am. Chem. Soc.* **119,** 2588 (1997).

126. E. Alonso, C. Valerio, J. Ruiz, D. Astruc, *New J. Chem.* **21,** 1139 (1997).

127. E. C. Constable, *Chem. Commun.* 1073 (1997).

128. C. U. Pittman, Jr., W. J. Patterson, S. P. McManus, *J. Polym. Sci. Polym. Chem. Ed.* **14,** 1715 (1976).

129. M. E. Wright, C. K. Lowe-Ma, *Inorg. Chim. Acta* **232,** 223 (1995).

130. M. Younus, A. Kohler, S. Cron, N. Chawdhury, M. R. A. Al-Mandhary, M. S. Khan, J. Lewis, N. J. Long, R. H. Friend, P. R. Raithby, *Angew. Chem. Int. Ed.* **37,** 3036 (1998).

131. S. F. Mapolie, J. R. Moss, G. S. Smith, *J. Inorg. Organomet. Polym.* **7,** 233 (1997).

132. N. Fujita, K. Sonogashira, *J. Polym. Sci.* **12,** 2845 (1974).

133. A. S. Abd-El-Aziz, E. K. Todd, G. Z. Ma, J. DiMartino, *J. Inorg. Organomet. Polym.* **10,** 265 (2000).

134. Y. Yang, Z. Xie, C. Wu, *Macromolecules* **35,** 3426 (2002).

135. I. Manners, *Can. J. Chem.* **76,** 371 (1998).

136. I. Manners, G. H. Riding, J. A. Dodge, H. R. Allcock, *J. Am. Chem. Soc.* **111,** 3067 (1989).

137. A. S. Abd-El-Aziz, L. J. May, J. A., R. M. Okasha, *J. Polym. Sci. Part A, Polym. Chem.* **39,** 2716 (2001).

138. S. C. Yu, S. Hou, W. K. Chan, *Macromolecules* **33,** 3259 (2000).

139. R. Knapp, A. Schott, M. Rehahn, *Macromolecules* **29,** 478 (1996).

CHAPTER 2

Metallocene-Based Polymers

CONTENTS

I. INTRODUCTION

Metallocene-based polymers encompass one of the most important classes of organometallic polymers. There have been numerous studies that have examined the synthesis, properties, and applications of metallocene-based polymers.[1–10] The focus of this chapter will be on metallocene-based systems in which the polymer chain is attached to the metallocene through the cyclopentadienyl rings. Polymetallocenes in which the polymer backbone is σ-bonded to the metal atoms are described in Chapter 4. Metallocene-based polymers are described according to the placement of the metallocene into the macromolecule. The first polymer class is the sidechain polymetallocenes (**1**). These were the first types of organometallic polymers that were reported in the 1950s, and they continue to have a significant impact in polymer chemistry. Homoannular polymetallocenes (**2**) are polymers in which the polymer chain propagates from a disubstituted cyclopentadienyl ring. Currently, heteroannularly substituted polymetallocenes (**3**) are receiving tremendous interest. Although a great deal of research was directed at the synthesis of this class of polymer in the 1970s, high molecular weight polymetallocenes are now available by the ring-opening polymerization of strained ferrocenophanes. In addition to that strategy, this class of polymer can also be obtained from polycondensation reaction of 1,1′-disubstituted metallocene monomers as well as through other means. Multidecker or face-to-face polymetallocenes (**4**) are bound through coordination of the metals to the cyclopentadienyl rings. There are also metallocene-based polymers with more structurally complex features. For example, the synthesis of hyperbranched, crosslinked (**5**), star, and dendritic polymers have been examined. While the majority of the metallocene polymers described are based on the ferrocene molecule, other examples are also highlighted.

5
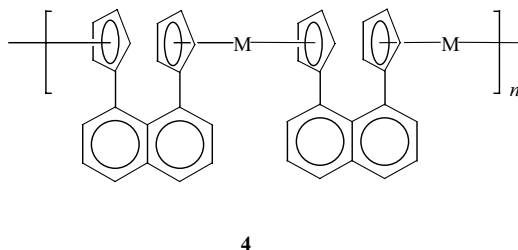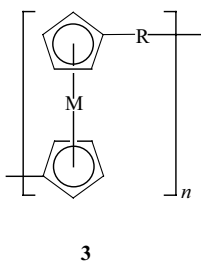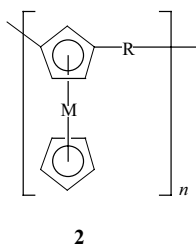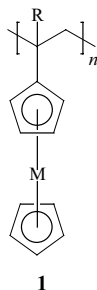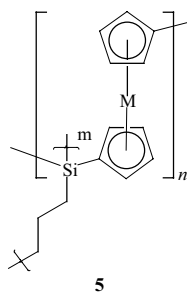
II. SIDECHAINS

A. Vinyl, Acrylate, and Acrylamide Polymers

The polymerization of ferrocene derivatives set the stage for a new era in polymer chemistry. After the 1955 report by Arimoto and Haven describing the synthesis of polyferrocenylethylene[11] (Scheme 1), a number of researchers pursued the synthesis and characterization of ferrocene-based polymers. In addition to the radical-initiated polymerization of monomer **6**, polymer **7** was also prepared using phosphoric acid or persulfate as catalysts. The copolymerization of vinylferrocene was examined with methyl methacrylate, styrene, and chloroprene.

6   **7**
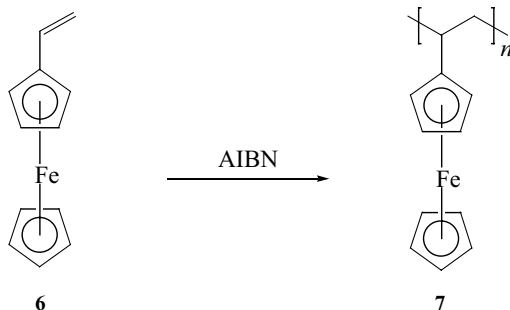
Scheme 1

Interest in this class of polymer continues to grow because of the interesting electrochemical and thermal properties that these materials exhibit. For example, in the 1970s, Pittman and coworkers reported the synthesis and conductivity of polymers prepared by the free-radical polymerization of vinylferrocene and 3-vinyl-*bis*-fulvalenediiron.[12–15] It was reported that high molecular weight polyvinylferrocene could be isolated by multiple additions of azo-*bis*-isobutyronitrile (AIBN) to the polymer solutions.[12] By decreasing the reaction temperature from 80 to 60°C in bulk polymerization reactions, higher-molecular-weight materials were isolated; however, the distribution was bimodal. The high molecular weight portions were found to be increasingly branched.[12] Frey and coworkers reported that styrene-vinylferrocene

random and block copolymers could be prepared by TEMPO (*tetra*-methylpiperadi-neoxyl)-mediated radical polymerization.[16]

Scheme 2 shows the homo- and copolymerization of 3-vinyl-*bis*-fulvalenedi-iron (**10**) using AIBN as the initiator.[14,15] On oxidation of poly(3-vinyl-*bis*-ful-valenediiron) (**11**) with TCNQ, the mixed-valence *bis*-fulvalenediiron cation forms, in which each iron atom shares the charge equally. The conductivity of this polymer steadily increased as the fraction of monomer units oxidized increased. At 71% oxi-dation, the conductivity was $6.9 \times 10^{-3} \ \Omega^{-1} \ cm^{-1}$.[14,15] On oxidation of the copoly-mer (**14**) prepared from 3-vinyl-*bis*-fulvalenediiron and styrene, this polymer (**15**) had a bulk conductivity of $2.5 \times 10^{-5} \ \Omega^{-1} \ cm^{-1}$.
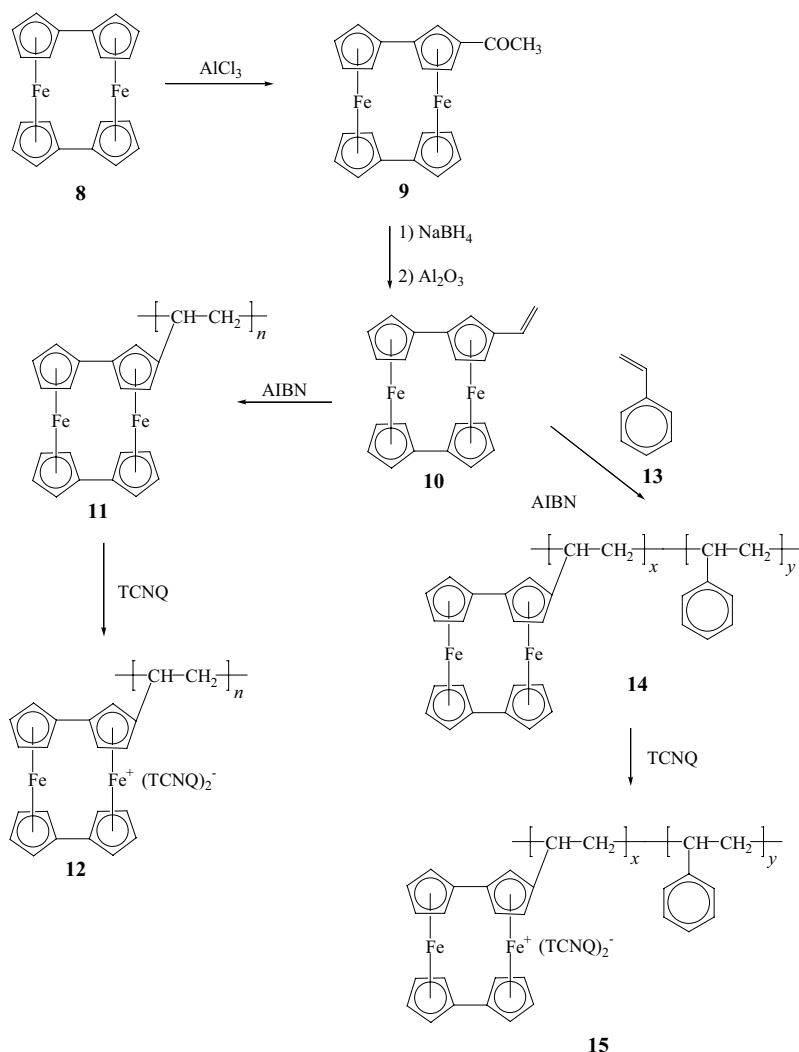
Scheme 2

The properties of a number of vinyl, acrylate, and methacrylate polymers that incorporate ferrocenyl groups in their sidechains were also examined.[17–21] The incorporation of ferrocene moieties into these classes of polymers resulted in materials with glass transition temperatures much higher than that of their organic analogs.[17] For example, radical polymerization of ferrocenyl methylacrylate (**16**) allowed for the isolation of polymer **17**, whose glass transition temperature (T_g) was 197–210°C versus only 3°C for poly(methyl acrylate) (**18**).
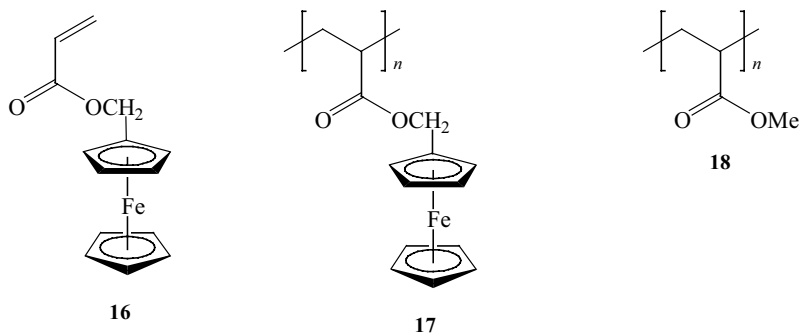
Oxidation of polymer **17** with *o*-chloranil resulted in the isolation of its ferrocenium salt.[17] Using Mössbauer spectroscopy, it was possible to determine the percentage of iron centers that were in the Fe(II) and Fe(III) oxidation states. This is due to the fact that ferrocenyl groups exhibit large quadropole splitting (2.4 mm/s), whereas the oxidized iron centers exhibit single peaks. Figure 1 shows the Mössbauer spectrum of oxidized polyferrocenylmethyl acrylate in which the outer peaks correspond to the unreacted ferrocene groups and the broad inner peak corresponds to the ferrocenium ions.[17]
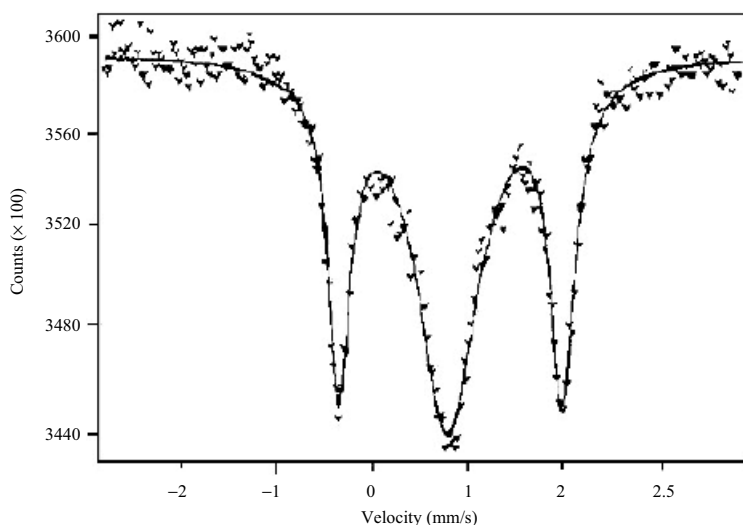
Figure 1. Mössbauer spectrum of polyferrocenylmethyl acrylate oxidized with *o*-chloranil (adapted from reference 17).

The homo- and copolymerization of 2-ferrocenylethyl acrylate and methacrylate was reported by Pittman and coworkers in the 1970s (Scheme 3).[20,21] It was found that both 2-ferrocenylethyl acrylate and 2-ferrocenylethyl methacrylate were more reactive than ferrocenylmethyl acrylate (16).[17–21]
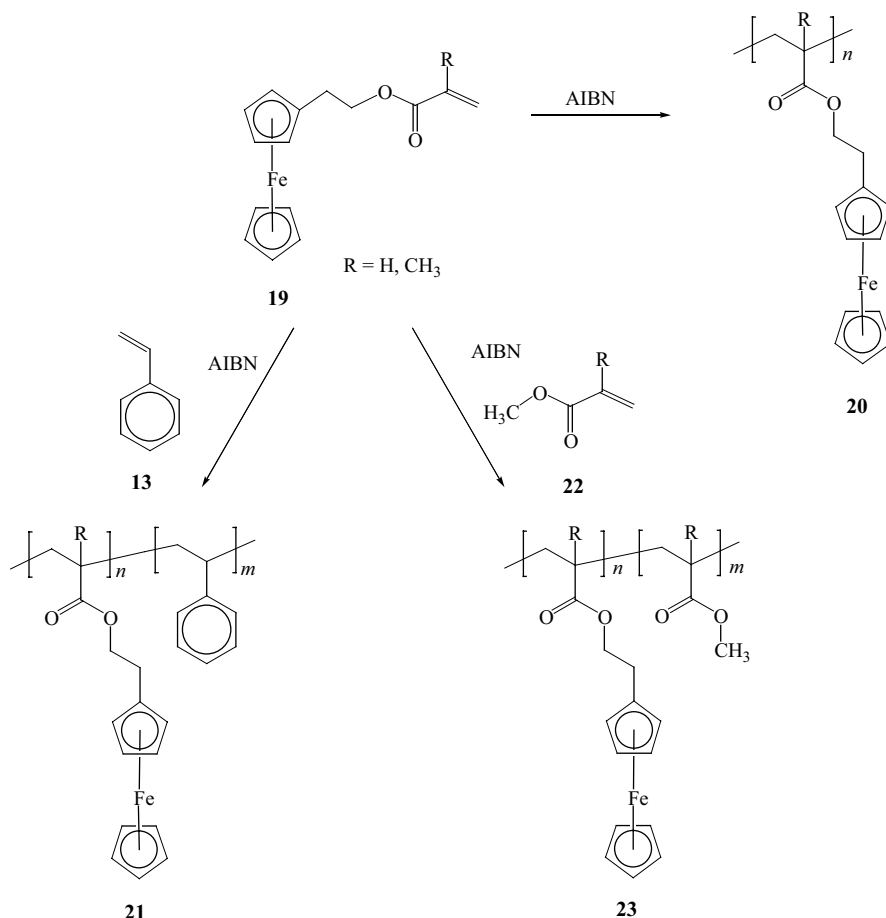
Scheme 3

The syntheses of 2-ferrocenylethyl methacrylate, acrylate, methacrylamide and acrylamide were reported by Yang et al. (Scheme 4).[22] Copolymerization of 2-ferrocenylethylacrylamide with isopropylacrylamide resulted in a water-soluble polymer (27) incorporating a small portion of the ferrocenyl moiety. The organometallic copolymer had low critical solution temperatures (LCST) of 26–29°C depending on the ratio of organoiron to organic units in the polymer. In comparison, poly(*N*-isopropylacrylamide) has a LCST values of ~32°C.
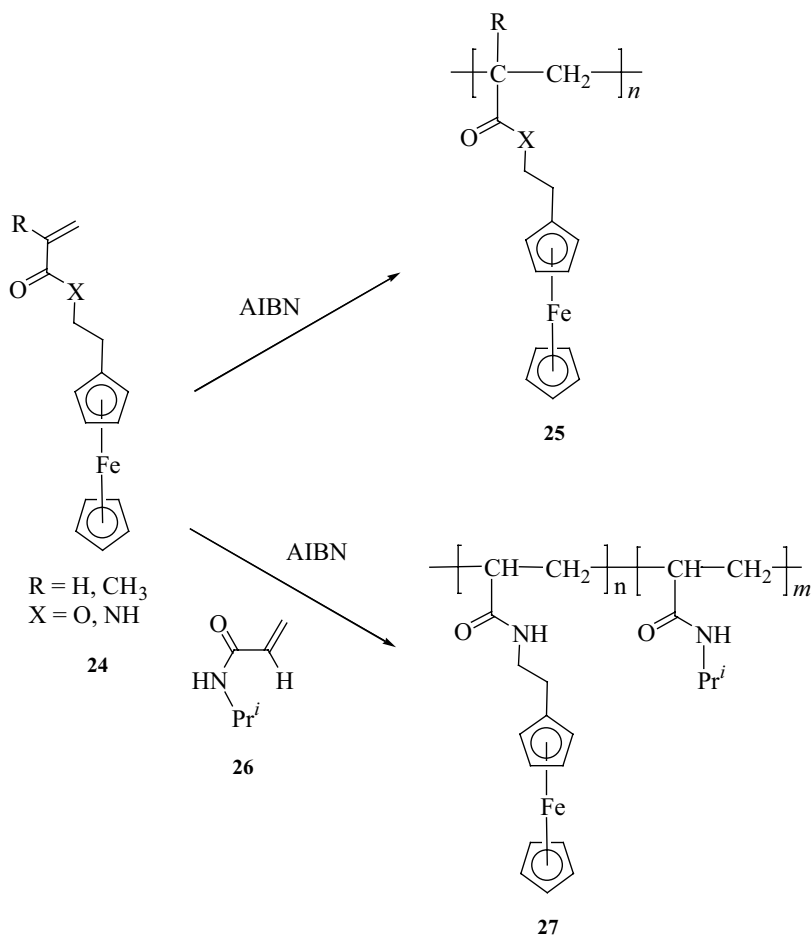
Scheme 4

Thermosensitive polymers have also been prepared from the AIBN-initiated copolymerization of *N*-ethyl- or *N,N*-diethyl-acrylamide with vinyl ferrocene.[23] Increasing the amount of organometallic comonomer resulted in decreased LCST values, while oxidation of these polymers resulted in increased LCST values. In all cases, there was less than 3% vinylferrocene incorporated into the polymers.

Sidechain ferrocene-based polymers possessing nonlinear optical properties have been described by Wright and coworkers as shown in Scheme 5.[24,25] The copolymerization of 5 mol% of the ferrocenyl functionalized monomer **28** with methyl methacrylate **29** resulted in an organometallic polymer (**30**) displaying second-harmonic-generation activity. The T_g and T_m values of this organometallic polymer were 120 and 225°C, respectively, which are similar to those of poly(methyl methacrylate).
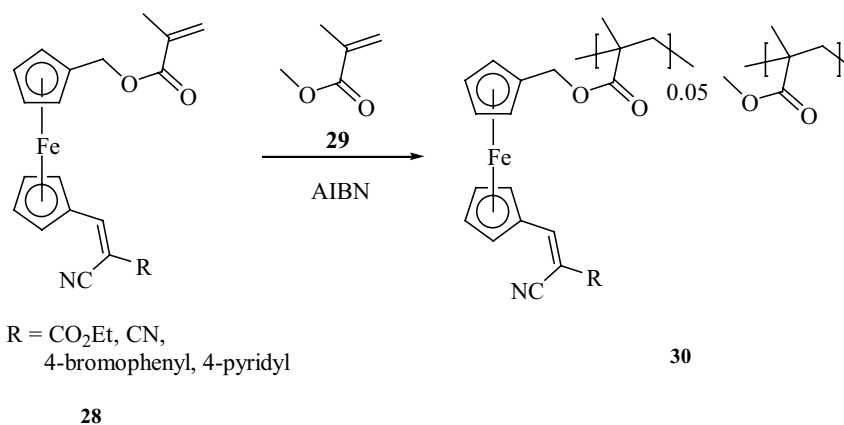
Scheme 5

Polymerization of organoiron monomers has also resulted in the production of liquid crystalline polymers containing ferrocene units in their sidechains.[26–31] Scheme 6 illustrates Deschenaux's free-radical synthesis of ferrocene functionalized thermotropic liquid crystalline polymethacrylates.[26] Monomer **31** and its corresponding polymer **32** exhibited enantiotropic smectic A and C phases.
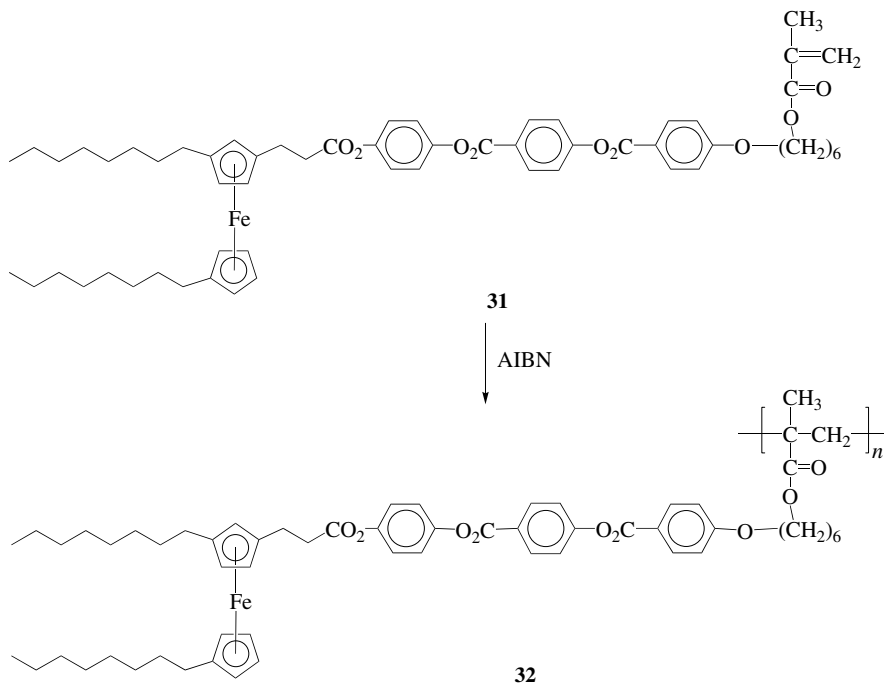
Scheme 6

The synthesis of liquid crystalline ferrocene-substituted polymers (**35**) from **33** and **34** have also been prepared according to the strategy shown in Scheme 7.[31] Oxidation of the ferrocenyl groups was achieved in the presence of copper(II) perchlorate or benzoquinone to produce the ionomers **36** and **37**, respectively. The presence of four alkyl substituents on the cyclopentadienyl rings increased the stability of the ferrocenium-based materials in relation to polymers containing only monoalkylated cyclopentadienyl rings. The perchlorate ionomer was unstable above 100°C, whereas the polymers with sulfate counterions were much more stable. Polymers containing up to 10 mol% of the ferrocene derivatives did not significantly lower the phase transition temperatures relative to the organic liquid crystalline polymers. On oxidation, the ferrocenium complexes were found to form clusters and segregate from the liquid crystalline phase.
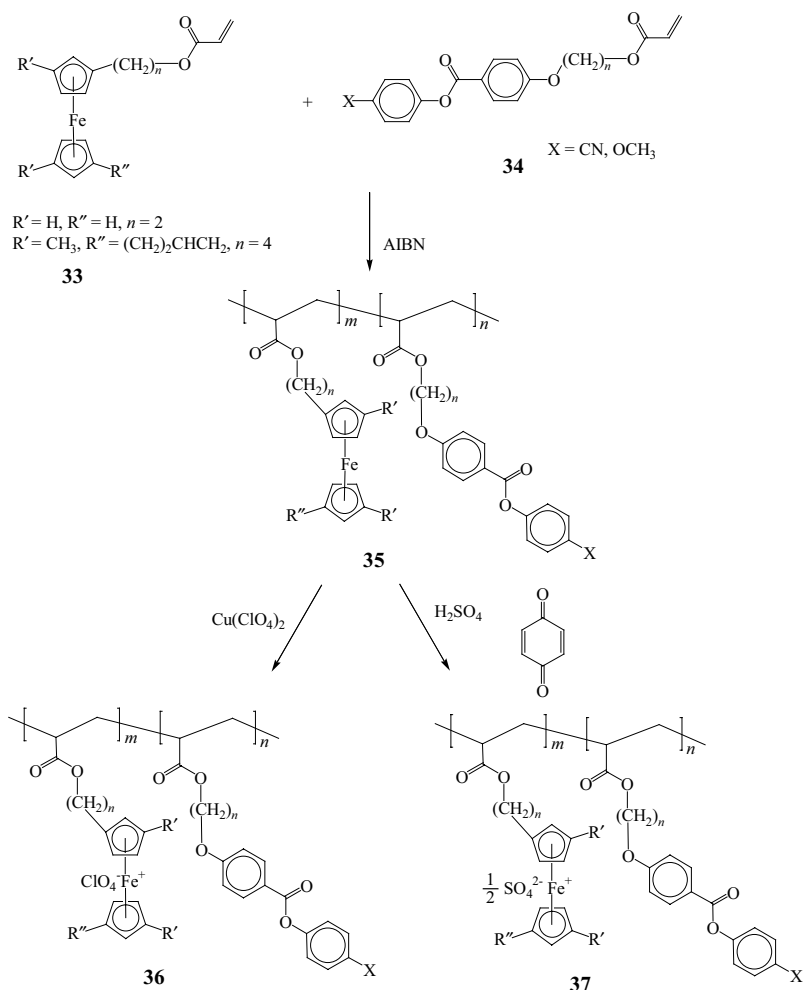
Scheme 7

B. Pyrrole and Thiophene Polymers

The electropolymerization of pyrrole and thiophene monomers functionalized with metallocenes has allowed for the production of the corresponding polymers.[32–35] Zotti and coworkers have reported the homo- and copolymerization of pyrrole monomers substituted through the 1 or 3 position with ferrocene groups.[34] The electrochemical copolymerization of monomer **38** with pyrrole (**39**) gave a polymer **40** with a conductivity of 1.5×10^{-2} S/cm (Scheme 8).
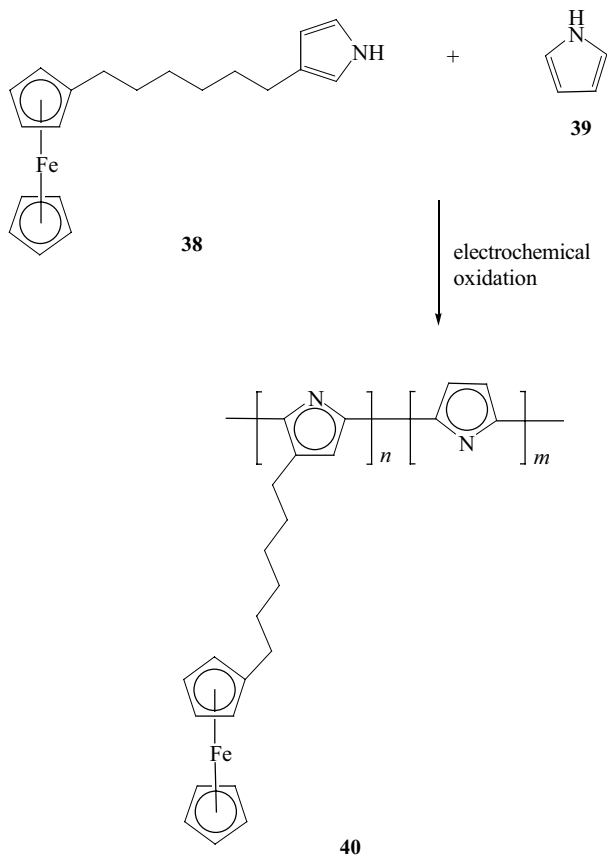
Scheme 8

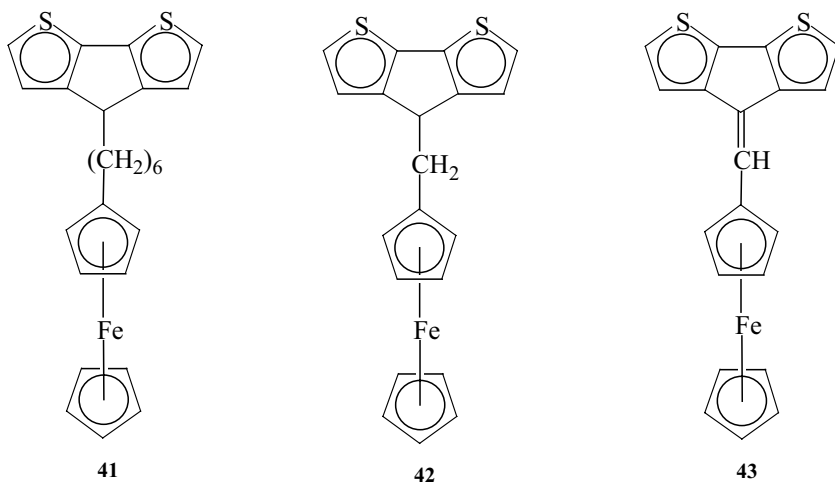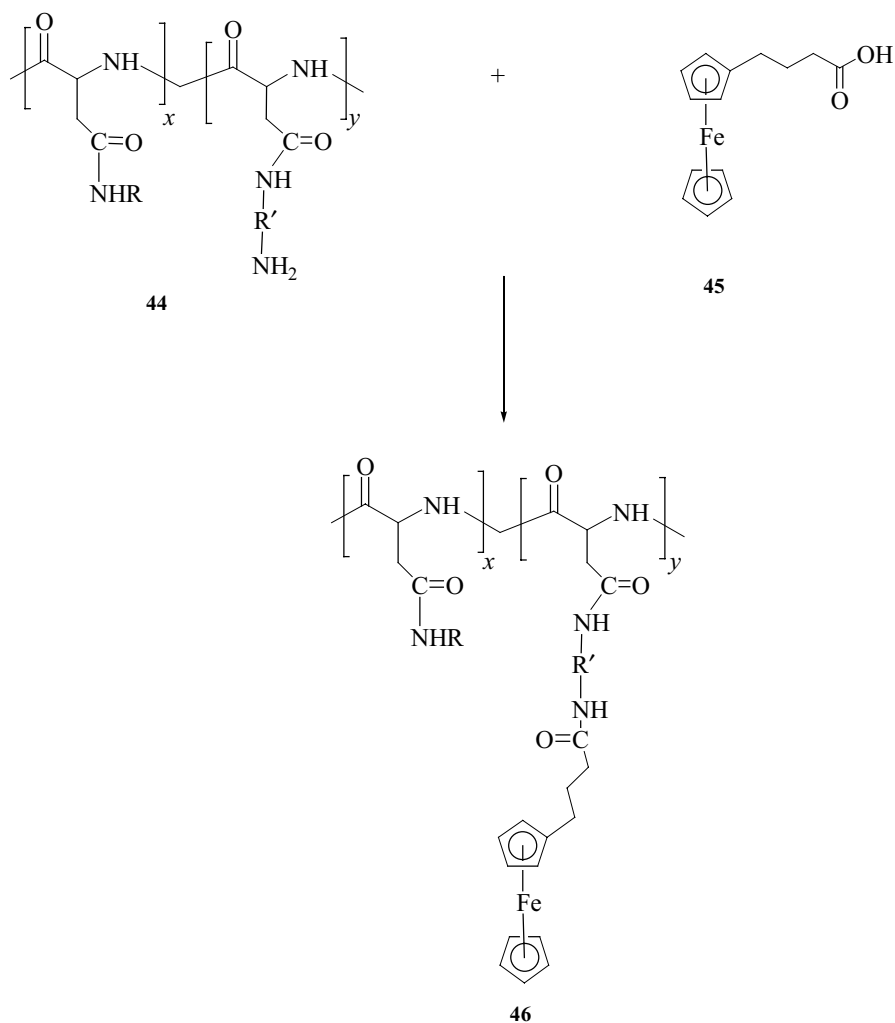The electrochemical polymerization of monomers **41–43** resulted in the isolation of polythiophenes with ferrocene groups pendent to the backbone.[34,35] It was noted that the redox potential of the polymer from the ferrocene-functionalized monomer **41** was the same as from *n*-hexylferrocene. However, increases of about

0.03 and 0.15 V were observed for the polymers derived from monomers **42** and **43** because of stronger interactions between the ferrocene moieties and the polymer backbone. As the spacer between the ferrocene groups and the polymer backbone increased from one to six methylene groups, there was a corresponding decrease in redox conductivity.[34,35] The redox conductivity of the polymer prepared from **41** was enhanced via copolymerization with 4-hexylcyclopentadithiophene and reached 1 S/cm. The in situ conductivity of the homopolymer prepared from electrochemical oxidation of **41** was 40 S/cm.

41   **42**   **43**

C. Polyaspartamide

Organometallic polymers may also play an important role in the healthcare industry. For example, the importance of platinum complexes as anticancer agents, particularly for testicular cancer, is well recognized. Polymers may also have advantages, and disadvantages, in terms of slow release, multidentate effects, and duration of retention in the patient. Neuse and coworkers have investigated the use of ferrocene-functionalized polymers in cancer research.[36–40] They have found that water-soluble polymers containing covalently bound ferrocene groups (**46**), made by coupling **44** and **45**, possess interesting antiproliferative properties (Scheme 9). An important structural feature of these polymers is the presence of a bond that can be broken to allow the release of the ferrocenyl groups. Ferricenium salts are able to trap free radicals, which apparently plays an important role in cancer progression.
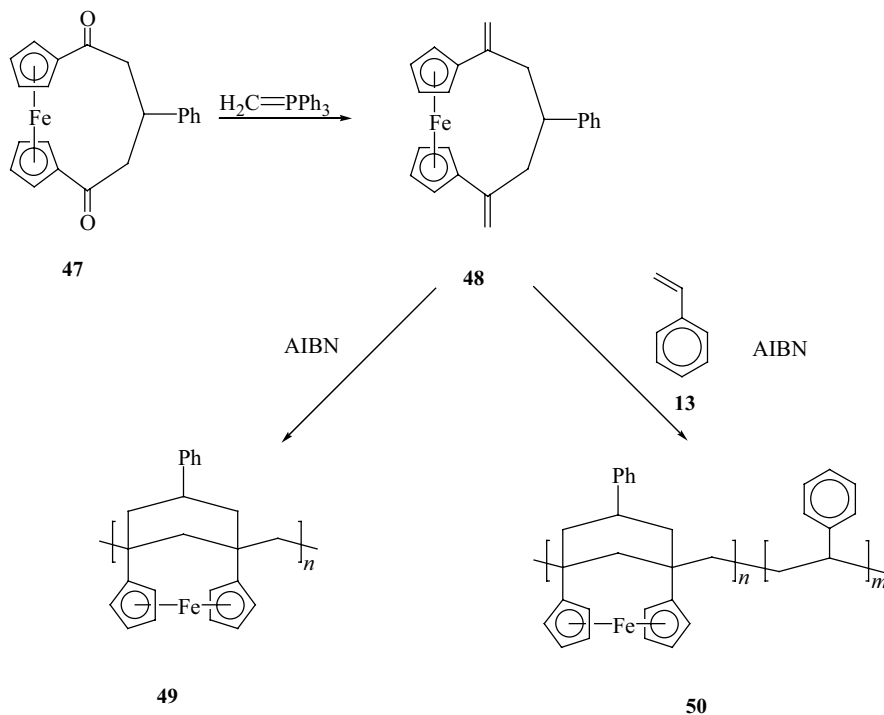
Scheme 9

D. Polyferrocenophanes

The synthesis of polyferrocenophanes has been achieved by the radical homo- and co-cyclopolymerization of monomer **48** as shown in Scheme 10.[41] The homopolymerization reaction was also investigated in the presence of cationic initiators; only AIBN-initiated reactions yielded high molecular weight polymers. Cyclic voltammetry of the homopolymer **49** showed two oxidation waves at -0.13 and $+0.05$ V in dichloromethane, while copolymer **50** showed only one oxidation wave at -0.03 V. The conductivity of these polymers was also examined. Doping of **49** and **50** with iodine under an argon atmosphere resulted in conductivities of 5.3×10^{-5} and 1.6×10^{-6} S/cm, respectively. However, under ambient condi-

tions, the conductivities of these iodine-doped polymers were 7.6×10^{-4} and 9.5×10^{-5} S/cm, respectively. Oxidation of **49** with quinone under vacuum resulted in conductivities from 10^{-10} to 10^{-9} S/cm on increasing the oxidation level from 8 to 56%; however, under ambient conditions, the conductivity was 10^{-6} S/cm.
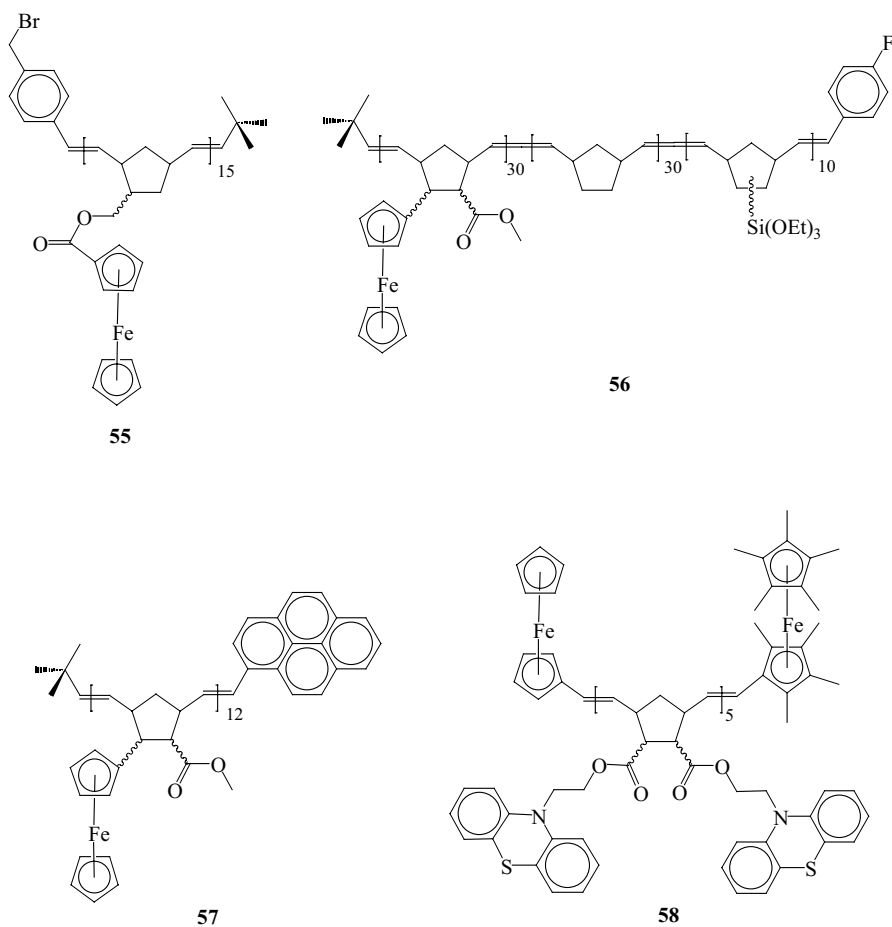

Scheme 10

E. Polyacetylenes

Scheme 11 shows the homopolymerization of ethynylferrocene **51a** or ethynylruthenocene **51b** to produce polymers **52a** and **52b** in which the metallocenyl unit is pendent to a conjugated polymer backbone.[42] Copolymerization of **51a** with **53** using the well-defined Schrock molybdenum metathesis catalyst [Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$] resulted in the production of polymer **54**. In their studies of these and related organometallic polyacetylenes, Buchmeiser and coworkers found that these polymers were soluble with up to 50 double bonds in their backbones and that the systems were "living."[42–45] The polymerization reactions were found to be and to produce head-to-tail polymers with the double bonds in *trans* configurations. Polyacetylene has also been surface grafted to a norbornene-functionalized silica support.[45] On oxidation of Fe(II) to Fe(III), this polymer was utilized to separate oligonucleotides through anion exchange chromatography.
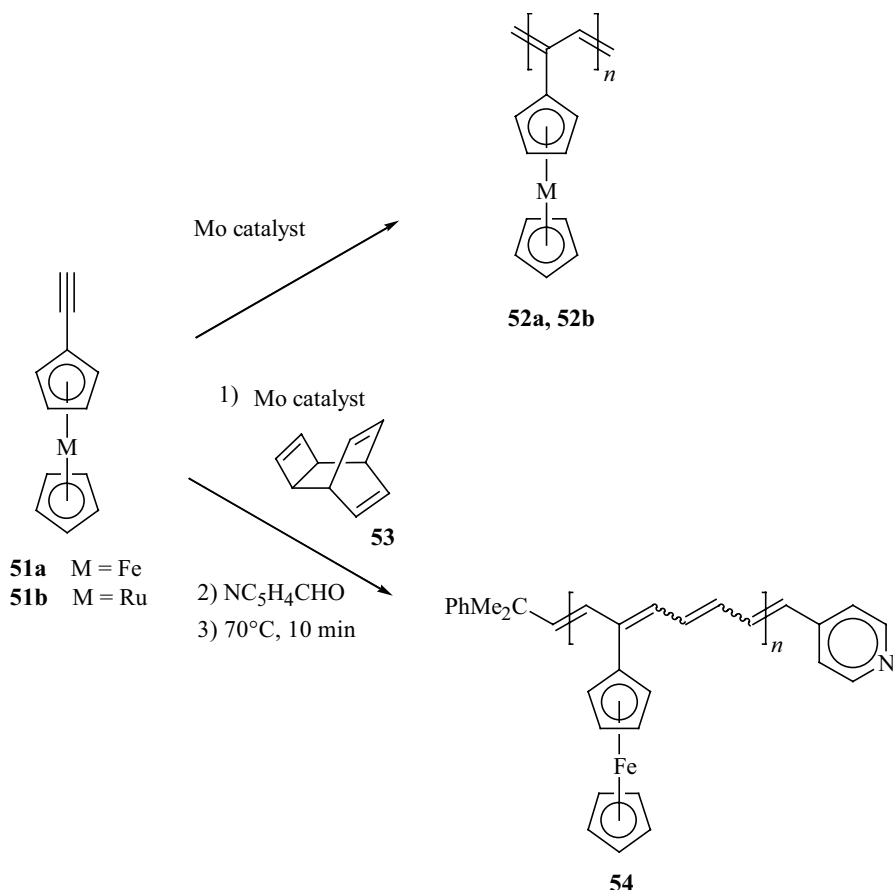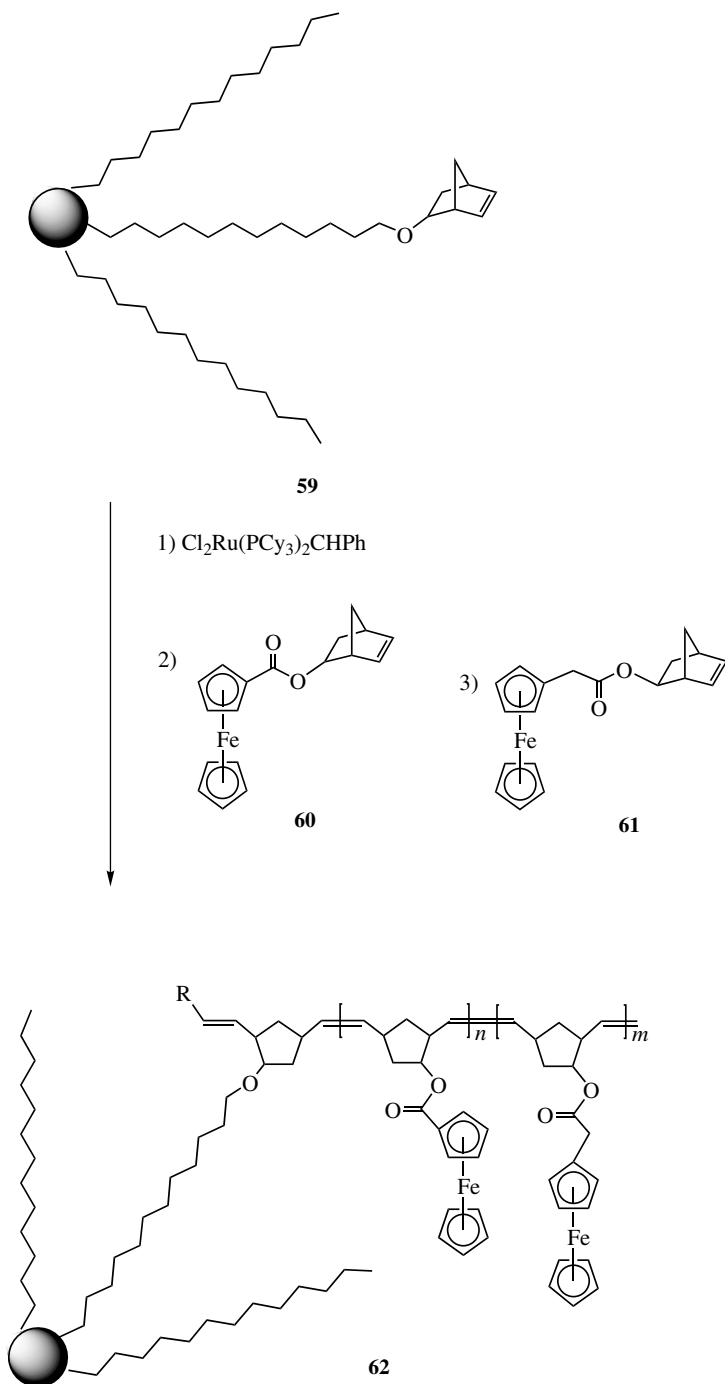
Scheme 11

F. Polynorbornenes

Schrock, Wrighton, and coworkers have reported that ring-opening metathesis polymerization (ROMP) of norbornene monomers functionalized with ferrocenyl groups allowed for the isolation of polymers such as **55–58**.[46,47] Alternatively, polynorbornenes capped with ferrocenyl units could be produced by using a molybdenum initiator functionalized with ferrocene. When this polymerization reaction was terminated through the addition of octamethyl-ferrocenecarboxaldehyde, low molecular weight polymers such as **58** were isolated.

55

56

57

58

Norbornene monomers functionalized with ferrocenyl moieties were copolymerized with gold nanoparticles substituted with a norbornene group through alkanethiol bonds.[48] Scheme 12 shows the synthesis of the ferrocene-based polymer (**62**) utilizing three monomers. The first step of this reaction is the metathesis of the norbornene rings on the gold nanoparticle using one equivalent of catalyst. Monomer **60** was subsequently added, and following 20 min, monomer **61** was added, resulting in the formation of **62**. This methodology could be used to prepare nanoparticles with varying layers of polynorbornenes.

59

1) Cl$_2$Ru(PCy$_3$)$_2$CHPh

2)   **60**

3)   **61**

62

Scheme 12

G. Polyphosphazenes

Allcock and coworkers have reported the ring-opening polymerization of trimeric cyclic phosphazenes functionalized with metallocenes.[49–53] Polymers with ferrocene and ruthenocene groups attached to their backbones, and a copolymer containing both of these organometallic groups was also synthesized.[49] The metallocenes were attached to the polymers through the phosphorous atoms to either one or both of the cyclopentadienyl rings as shown in Scheme 13.[50] Examples of the ring-opening polymerization of a cyclic 1,5-transannular tetramer were also described.
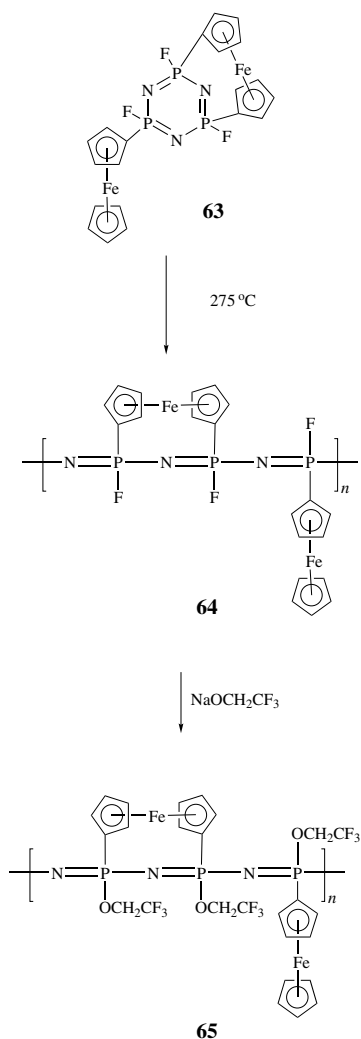
Scheme 13

The synthesis of polyphosphazenes derivatized with ferrocenyl units has also been achieved by functionalization of a preformed polyphosphazene.[54,55] Wisian-Neilson and Ford showed that when polymethylphenylphosphazene (**66**) was treated with *n*-BuLi, approximately half of the methyl substituents on the polymer deprotonated. These nucleophilic groups could subsequently be reacted with ferrocene derivatives as shown in Scheme 14. Polymer **68** had approximately 45% of its methyl groups converted to the organometallic groups, whereas substitution occurred at only 36% of the methyl groups in polymer **70**. The presence of the ferrocenyl groups resulted in increased glass transition temperatures for these polymers. For example, when 23% substitution occurred in **70**, the T_g was 65°C, whereas a 36% substitution level resulted in a T_g of 87°C.[55]
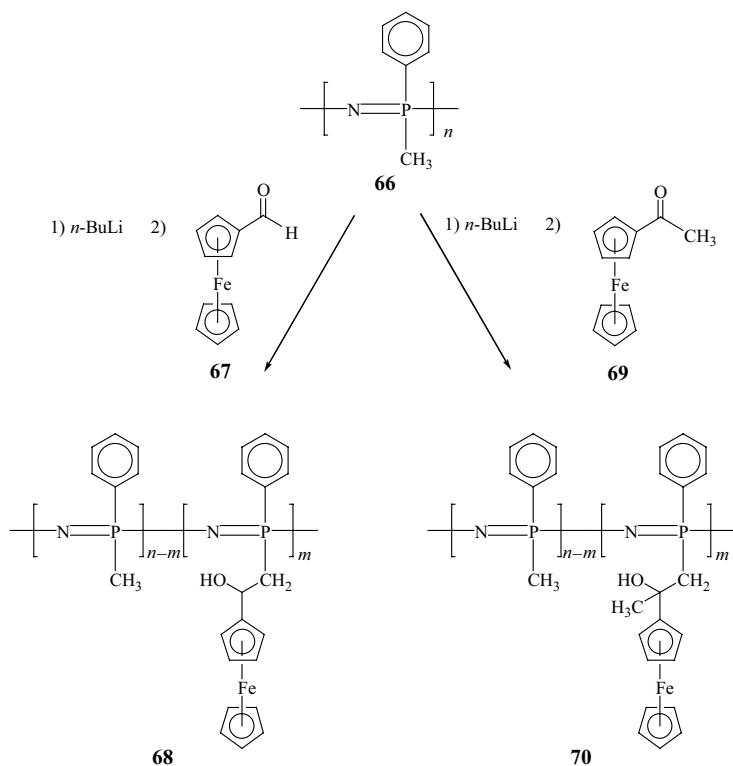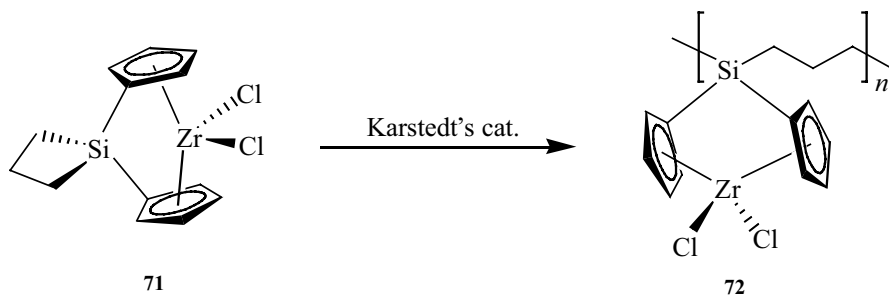

Scheme 14

H. Polysilanes

Ring-opening polymerization of the spirocyclic silacyclobutane-bridged monomer $(CH_2)_3Si(\eta^5-C_5H_4)_2ZrCl_2$ (**71**) with Karstedt's catalyst allowed for the production of the polycarbosilane $[(CH_2)_3Si(\eta^5-C_5H_4)_2ZrCl_2]_n$ (**72**) as shown in Scheme 15.[56] Although ring opening of the zirconocene ring was also attempted, polymerization did not occur under the conditions employed. The monomer and polymer demonstrated moderate activity as a catalyst for ethylene polymerization.
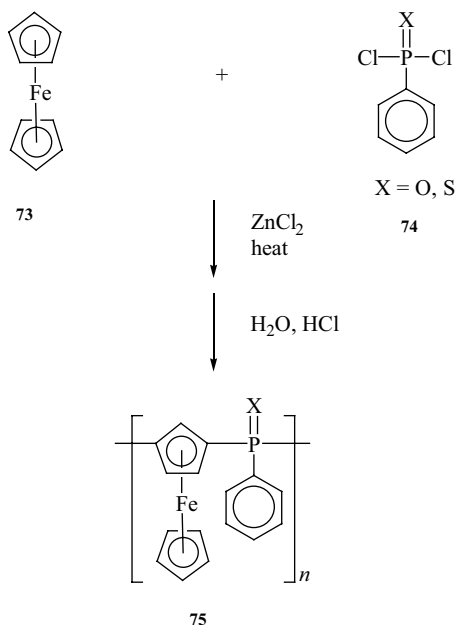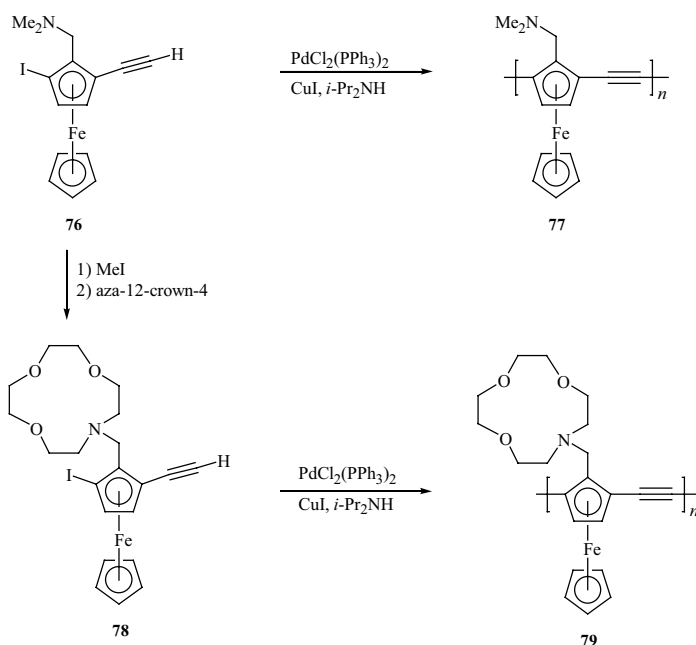
Scheme 15

III. HOMOANNULAR POLYMETALLOCENES

There are relatively few examples of polymers containing 1,3-disubstituted metallocene rings. In 1967, Pittman described the synthesis of ferrocene polymers (**75**) containing phosphine oxide or sulfide linkages using zinc chloride as a catalyst (Scheme 16).[57] The resulting low MW materials displayed good thermal stability; however, they were infusible solids. When the polymerization reactions were conducted above 140°C, cleavage of the cyclopentadienyl rings from iron, and cyclopentane-bridged polymers were produced. Heteroannular substitution patterns were also observed by increasing the reaction temperatures and time.
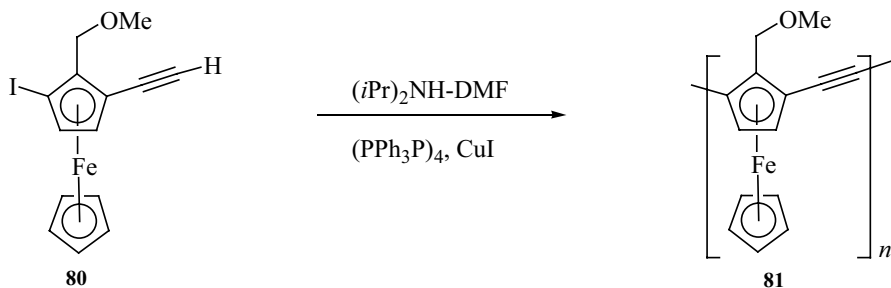

Scheme 16

Plenio et al. have described the synthesis of homoannular ferrocene polymers that contain conjugated spacers in their backbones.[58,59] Scheme 17 shows the reaction of a diastereomeric mixture of monomer **76** using Sonogashira coupling conditions to produce polymer **77**.[58] These soluble polymers were isolated in relatively low molecular weights as a bimodal fraction. Quaternization of the amine in monomer **76** using MeI allowed for its displacement by aza-12-crown-4. Polymerization of this monomer (**78**) using the same reaction conditions yielded a high molecular weight polymer (**79**). However, strong tailing in the gel permeation chromatography (GPC) traces indicated that the molecular weights might have been overestimated because of polymer aggregation.[59]

Scheme 17

More recently, the synthesis of an enantiomerically pure [enantiomeric excess (EE) > 98%] planar ferrocene complex (**80**) allowed for the production of polymer (**81**) as shown in Scheme 18.[59] Monomer **80** was prepared in a multistep synthesis starting from (*S*)-iodoferrocene-2-carbaldehyde. The palladium-catalyzed coupling reaction of **80** resulted in a polymer (**81**) with optical activity ($[\alpha]_D^{20} = -198.0$ per ferrocene unit) and a molecular weight estimated to be 10,000 by left-angle laser light scattering (GPS-LALLS).[59] An examination of oligomeric model complexes containing 1,1'- and 1,3-linked ferrocene units showed that the homoannularly substituted materials should possess better electronic communication. This was supported by longer bathochromic shifts in these materials.[58,59]

Scheme 18

## IV. HETEROANNULAR POLYMETALLOCENES

A. Polyferrocenylenes

Many efforts have been made to construct polyferrocenylenes (**82**), in which the ferrocene rings are directly bonded to one another along the polymer backbone. In the early 1960s, Korshak and Nesmeyanov reported the synthesis of ferrocene-based polymers by reacting ferrocene with *t*-butyl hydroperoxide.[60,61] Rosenberg and Neuse reported that these polymers consisted of homoannular and heteroannular aliphatic ether-substituted units with number-average molecular weights less than 7000.[62]
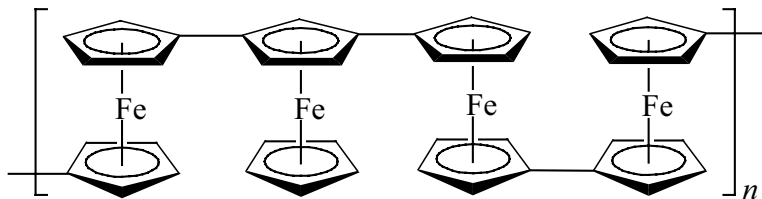

82

Reaction of ferrocenyllithium with cobaltous chloride was found to result in the formation of oligomeric ferrocene polymers.[63,64] Roling and Rausch reported that oligomeric 1,1′-polyferrocenylenes could be prepared by reaction of haloferrocenes with copper salts.[65] Polyferrocenylenes with MW of ≤10,000 were prepared by Neuse via reaction of 1,1′-dilithio- and 1,1′-diiodoferrocene with a catalytic amount of Cu(II) or Pd(II) salts.[66] Foucher and coworkers reported that higher-molecular-weight polyferrocenylenes containing methyl or trimethylsilyl groups on the cyclopentadienyl rings could be prepared using similar reaction conditions.[67] Scheme 19 shows the synthesis of these Me- and Me$_3$Si-functionalized polymers (**84**) that had weight-average molecular weights of 3430 and 8600, respectively.
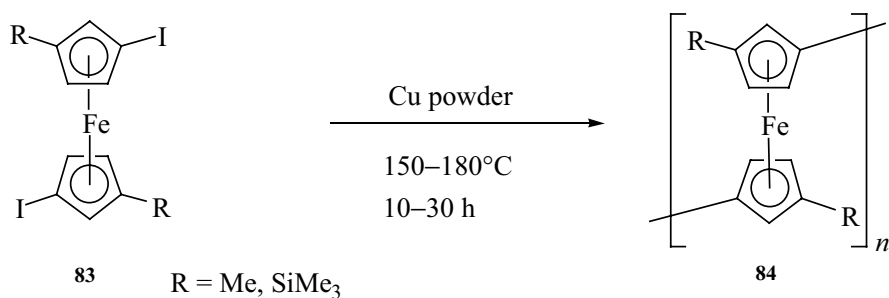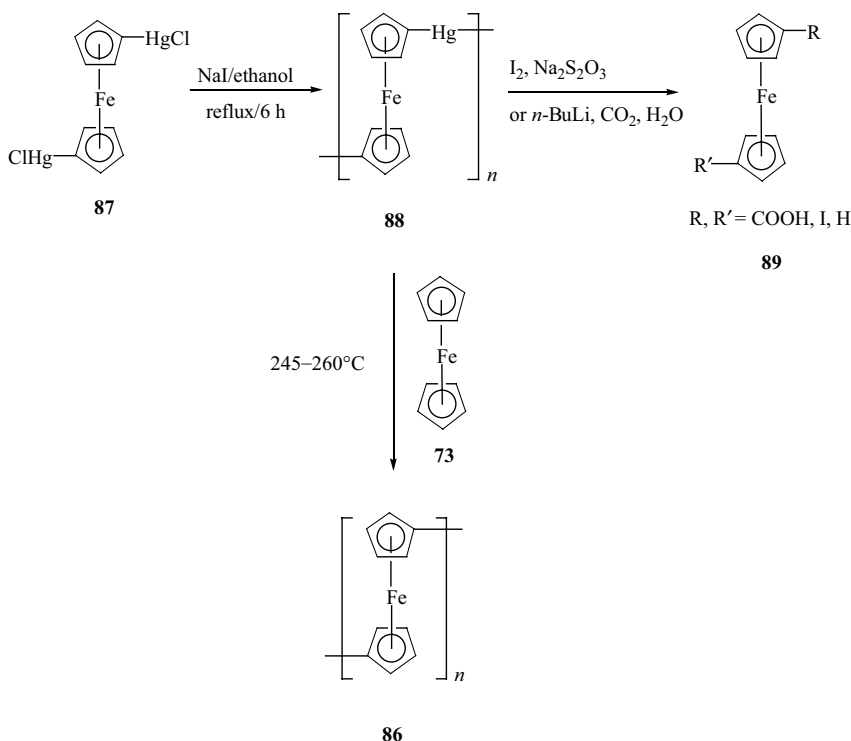
Scheme 19

Yamamoto and coworkers reported the synthesis of polyferrocenylenes with conductivities ranging from 10^{-2} to 10^{-4} S/cm via dehalogenation polymerization of dihaloferrocenes with magnesium as shown in Scheme 20.[68,69] The conductivity of this crystalline polymer was higher than that of the amorphous polyferrocenylene.
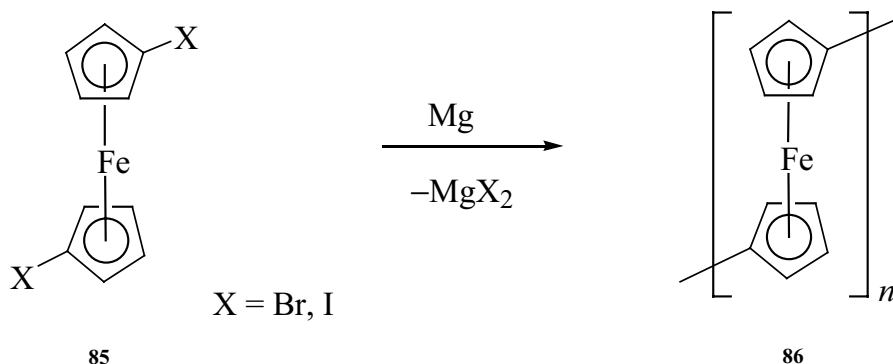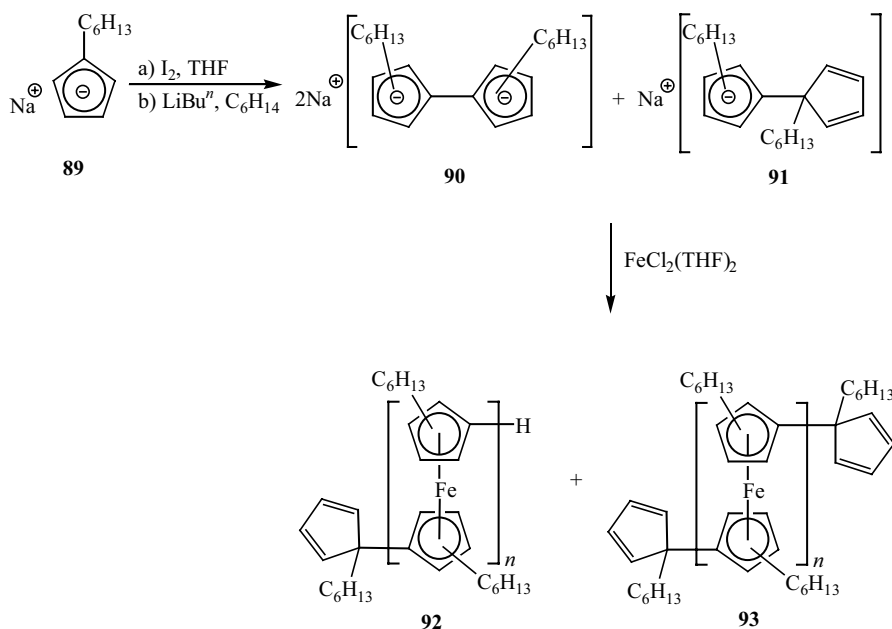

Scheme 20

In 1963, Rausch reported the synthesis of polymercuriferrocenylene (**88**) via reaction of 1,1-dichloromercuriferrocene (**87**) with either ethanolic sodium iodide or aqueous sodium thiosulfate.[70] This mercury-based polymer could be decomposed to give mono- and disubstituted ferrocenes in addition to ferrocene itself. Neuse and Crossland later reported that polymercuriferrocenylene could be converted to relatively low molecular weight polyferrocenylene (**86**) by reacting the mercury-containing polymer (**88**) with ferrocene (**73**) at 245–260°C as shown in Scheme 21.[71]

Scheme 21

In 1996, Nishihara and coworkers reported that soluble 1,1′-dihexylferrocene-based oligomers and polymers (**92**, **93**) could be synthesized by reaction of the dihexylfulvalene dianion with $[FeCl_2(THF)_2]$ as shown in Scheme 22.[72] The photoconductivity of the charge transfer complexes of this soluble polymer ($n > 10$) indicated that these materials are p-type semiconductors.

Pittman and coworkers reported the conductivities of polyferrocenylene and polyvinylferrocene in their neutral and oxidized states.[15,73] It was found that these polymers are insulators with conductivities of 1.2×10^{-14} and 8×10^{-15} Ω^{-1} cm^{-1}, respectively. On partial oxidation of these polymers, they became semiconducting, with highest conductivities between 35 and 65% of the iron centers in the Fe(III) oxidation states. Increasing the level of conjugation within the polymers did not have a significant influence on their conductivity. Figure 2 shows the effects of polymer structure, counterion, and degree of oxidation on the conductivity of these polymers. Curve **a** represents polyferrocenylene oxidized with iodine, curve **b** represents polyvinylferrocene oxidized with dichlorodicyanoquinone (DDQ), and curve **c** represents polyferrocenylene oxidized with DDQ. Oxidation of these polymers resulted in an approximate 10^6–10^8 increase in conductivity.[15,73]
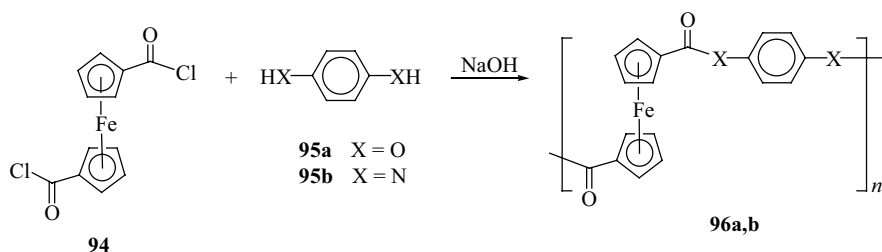
Scheme 22
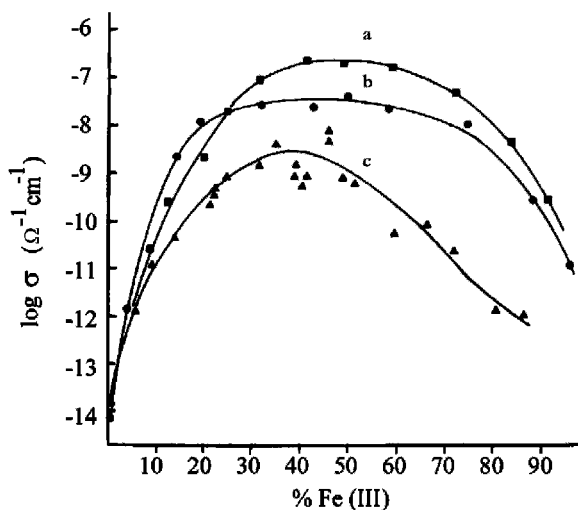
Figure 2. Conductivity of mixed-valence ferrocene-based polymers (adapted from Refs. 15 and 73).

B. Polyamides, Polyurethanes, Polyureas, Polyesters, and Polybenzimidazoles

A number of different classes of ferrocene-based polymers have also been prepared via reaction of ferrocenes functionalized with carboxylic acids, acid

chlorides, alcohols, amines, and thiols. These monomers were polymerized using condensation techniques to give organometallic polymers that contain ferrocenyl units in their backbones. The first report on this class of polymer was in 1961 by Knobloch and Rauscher.[74] These polymers (**96**) were prepared via interfacial polycondensation reactions of various diamines and diphenols with 1,1′-ferrocenedicarbonyl chloride (**94**) as shown in Scheme 23. When the nucleophiles were hydroquinone or phenylenediamine (**95a**, **95b**), the resulting polymers were insoluble.
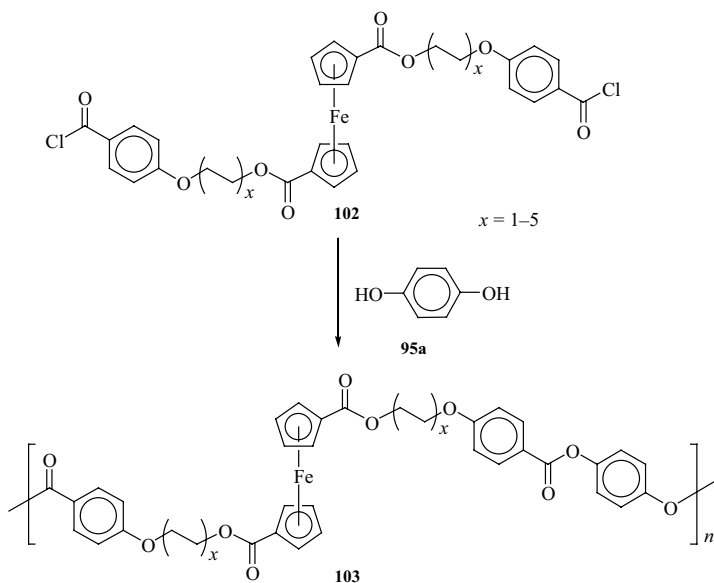

Scheme 23

Scheme 24 summarizes the preparation of polyamides (**99**) and polyureas (**101**) from the reaction of 1,1′-*bis*(β-aminoethyl)ferrocene (**97**) with diisocyanates (**98**) and diacid chlorides (**100**).[75–78] These polymers were prepared via solution or interfacial polycondensation reactions to yield polymers with intrinsic viscosities ranging from 0.1 to 1.5 dL/g.[75,76]
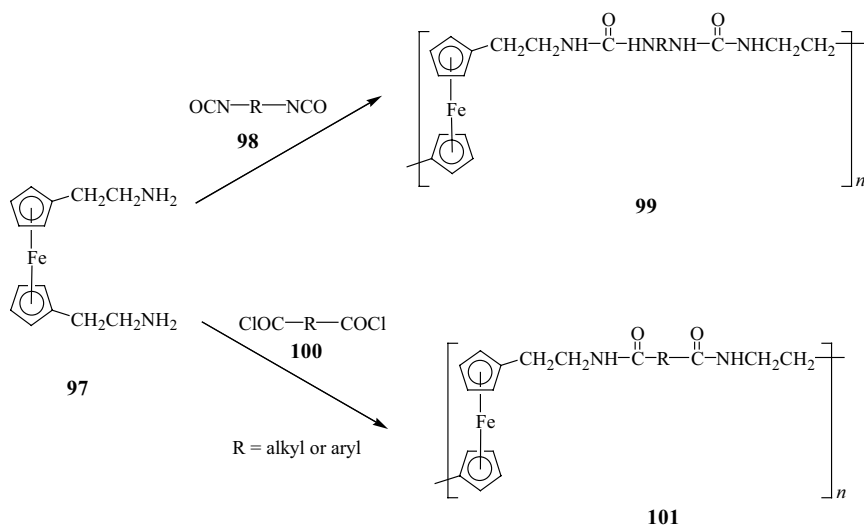
Scheme 24

Rausch also reported the synthesis of polyurethanes; however, these polymers exhibited low solubility and they precipitated from solution during the polymerization reactions.[75] Polyurethanes with polyether segments in their backbones have also been synthesized.[79,80] It has also been reported that polyurethanes with ferrocenyl units in their backbones exhibit enhanced thermal stability.[81] Polyesters containing ferrocenyl units in the mainchain have been the focus of numerous studies.[82–87] It has been reported that many of these organometallic polymers exhibit liquid crystalline properties.[84–87] Scheme 25 shows the synthesis of a liquid crystalline polyester (**103**) via polycondensation reactions.[85] Increasing the length of the alkyl chains decreased the thermal stability and glass transition temperatures of these polymers.
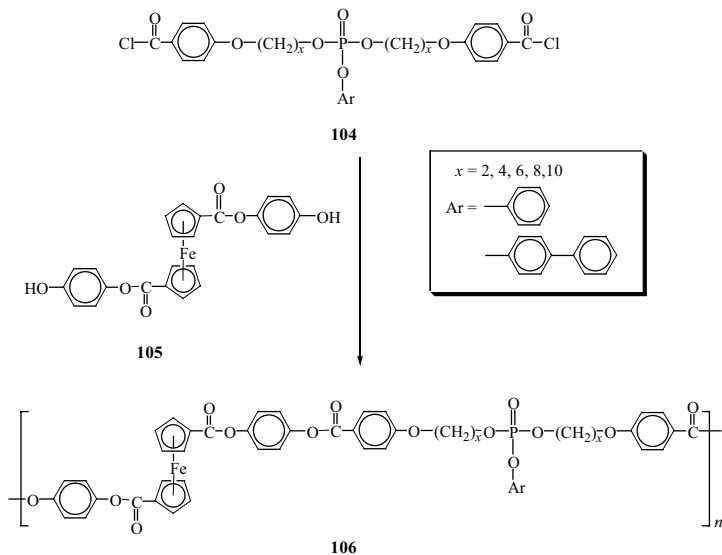

Scheme 25

Senthil and Kannan have also reported the synthesis of liquid crystalline ferrocene-based polymers containing phosphate groups in their backbones.[86,87] The molecular weights of these polymers were relatively low; however, they had very narrow polydispersities. Scheme 26 shows the synthesis of polymers **106** by the polycondensation of **104** with **105**.[87] The polymers with 8 and 10 methylene spacers in their backbones possessed clear nematic textures, while most of the other polymers with shorter aliphatic chains had a grainy texture. Only the polymer with ethylene spacers and a pendent phenyl group did not show anisotropic behavior.

In the 1960s, Marvel and coworkers reported the synthesis of polybenzimidazole and polybenzborimidazoline.[88,89] These polymers possessed low solubility in organic solvents. Polybenzimidazole containing ferrocenyl units in its backbone (**109**) (Scheme 27) was prepared by the 1:2 polycondensation of 1,1′-ferrocenedimethanol (**107**) with 3,3′,4,4′-biphenyl-*tetra*-amine (**108**) in the presence of [RuCl$_2$(PPh$_3$)$_3$].[90] Mössbauer spectroscopy showed that approximately 20% of the iron centers were

oxidized during the polymerization reaction. GPC showed that polymer **109** had a weight average molecular weight of 45,000. These polymers underwent irreversible electrochemical oxidation.
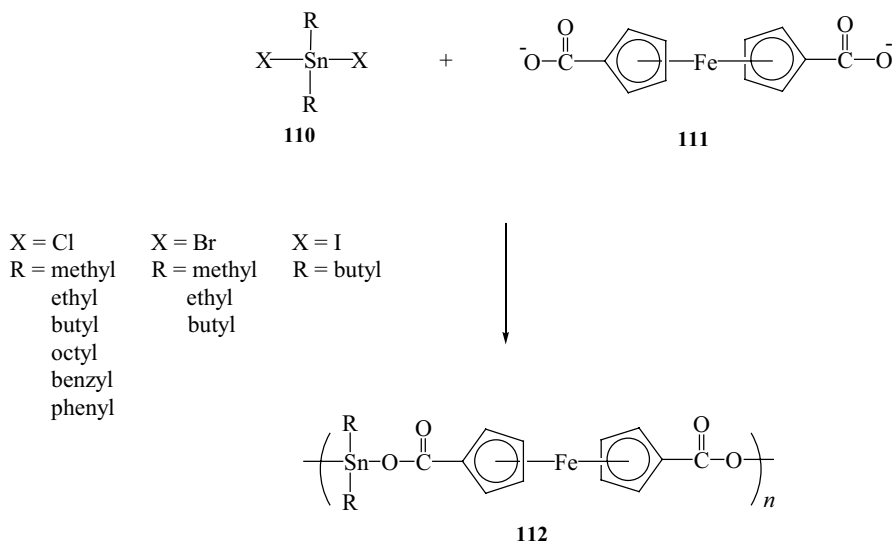

Scheme 26
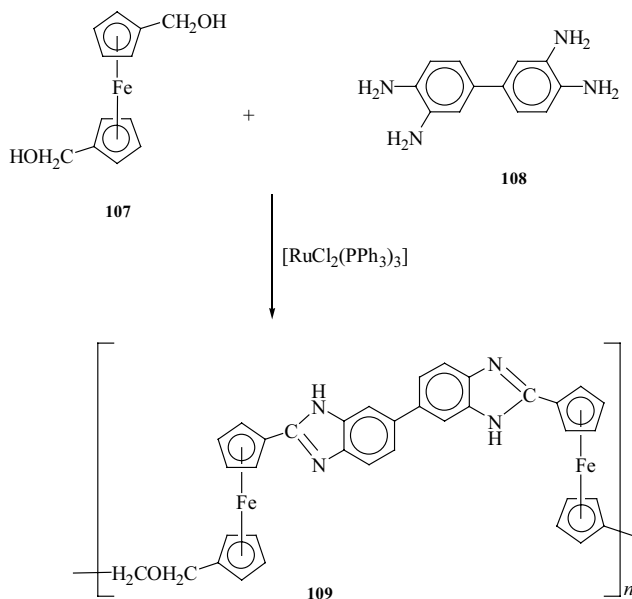
Scheme 27

C. Metal or Metalloid Spacers

A number of ferrocene-based polymers containing other metals or metalloids in their structures have been examined. Carraher and Lessek reported that tin-containing polyesters of ferrocene (**112**) could be prepared by reaction of the organotin dihalides (**110**) with disodium ferrocene dicarboxylate (**111**) as shown in Scheme 28.[91,92] The polymerization reactions proceeded rapidly, with yields reaching maximum values between 30 s and 2 min.[91] Polymer yields increased with smaller alkyl substituents and with the phenyl substituent, and yields also increased by changing the leaving group from Cl to Br to I. All of these polymers were found to be insoluble in the solvents tested.


| X = Cl	X = Br	X = I
R = methyl	R = methyl	R = butyl
ethyl	ethyl	
butyl	butyl	
octyl		
benzyl		
phenyl		

Scheme 28

Pittman and coworkers utilized two different strategies to prepare siloxane-bridging polyferrocenes.[93,94] Scheme 29 shows the polycondensation of *bis*-dimethylaminodimethylsilylferrocene (**113**) with disilanol **114** to produce polymer **115**.[93] Polymers prepared using this methodology had molecular weights exceeding 10^5 when melt polymerizations were conducted at 100°C and with pressures of ~1 torr. Reactions followed second-order kinetics and followed an S_Ni-Si-type mechanism. The second strategy involved the reaction of *bis*-dimethylaminosilanes with 1,1′-*bis*-hydroxymethylferrocene.[94] Both methods produced film-forming polymers and weak fibers that could be drawn from melts. Low-temperature mixing favored polymer formation, while higher temperatures produced more cyclic byproducts.

A siloxane-diacetylene ferrocene polymer with carborane groups in its backbone (**116**) was heated to 350°C under an inert atmosphere, resulting in the formation of an elastomeric thermoset.[95] Crosslinking of the butadiyne groups was confirmed

from IR analysis. Further heating of this polymer to 1000°C yielded a hard ceramic that displayed magnetic properties. This ceramic material exhibited excellent oxidative stability due to the presence of the boron. Low molecular weight diacetylene-organosilyl ferrocene-based polymers have also been synthesized.[96]
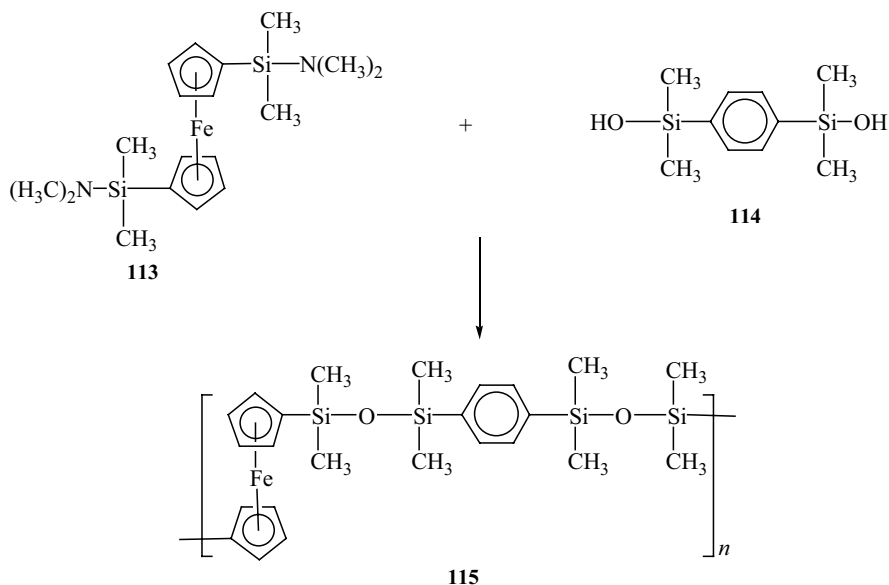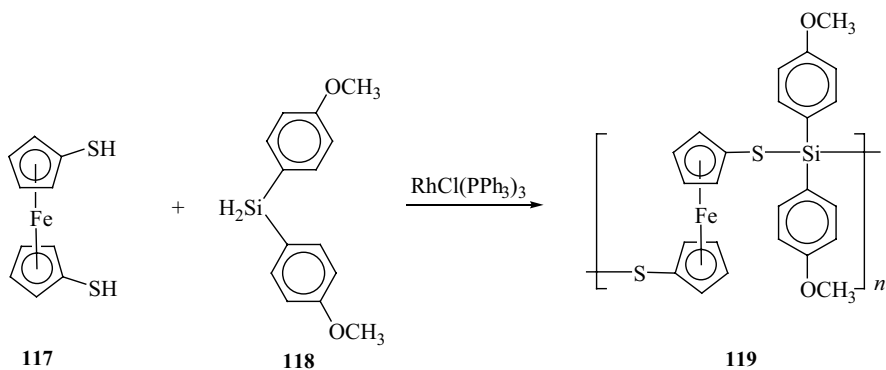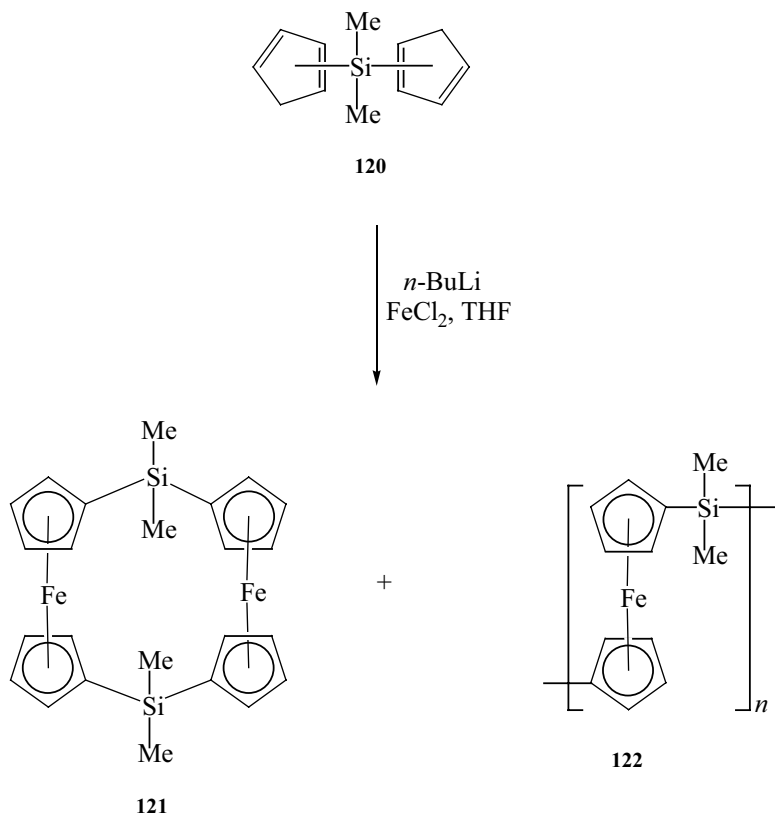

Scheme 29
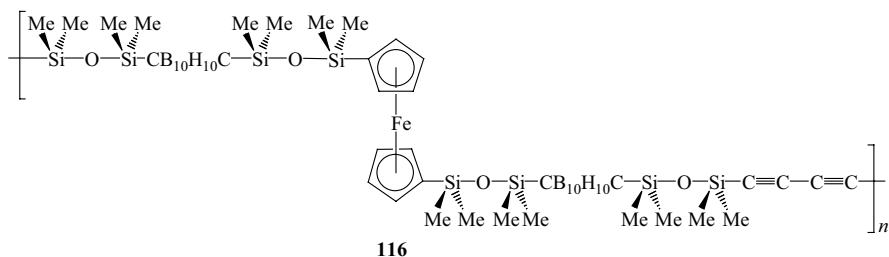
Osakada and coworkers have reported that 1,1′-dimercaptoferrocene (**117**) reacts with diarylsilanes to produce polymers and ferrocenophanes.[97] Scheme 30 shows the synthesis of a low molecular weight polymer (**119**) prepared using this methodology.

An isomeric mixture of dicyclopentadienyldimethylsilanes (**120**) was reacted with BuLi and ferrous chloride as shown in Scheme 31 to produce the cyclic [1.1]ferrocenophane (**121**) and the polyferrocenylsilane (**122**).[98] The molecular weight of **122** was determined to be M_w=4900 and M_n=4100 by GPC. Cyclic

voltammetry of **121** showed two reversible oxidation peaks at −0.02 and 0.21 V, indicating that there is significant interaction between the iron centers.
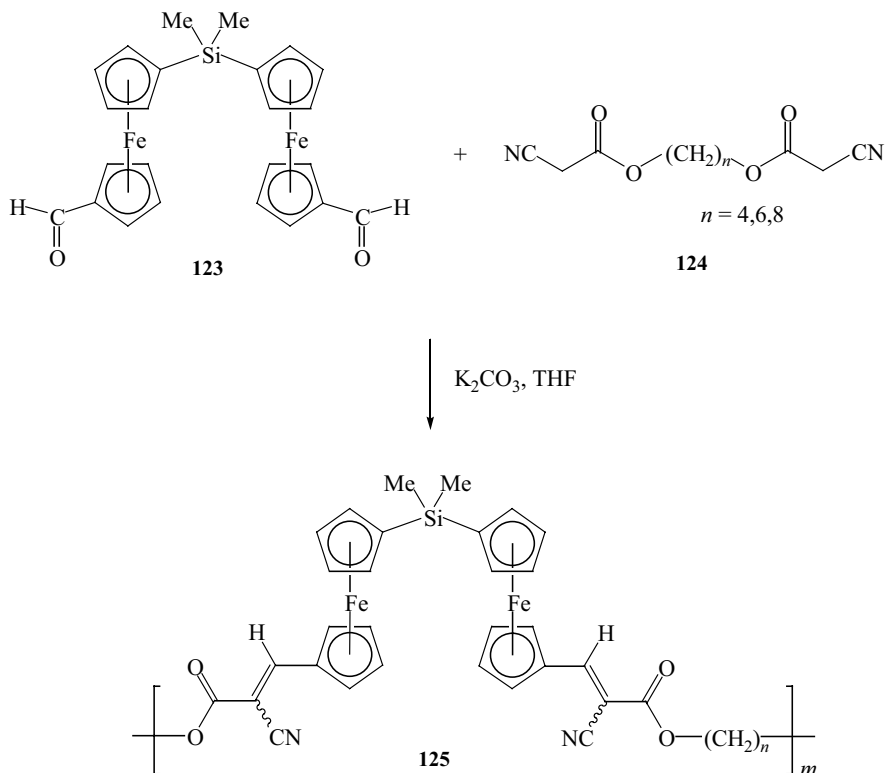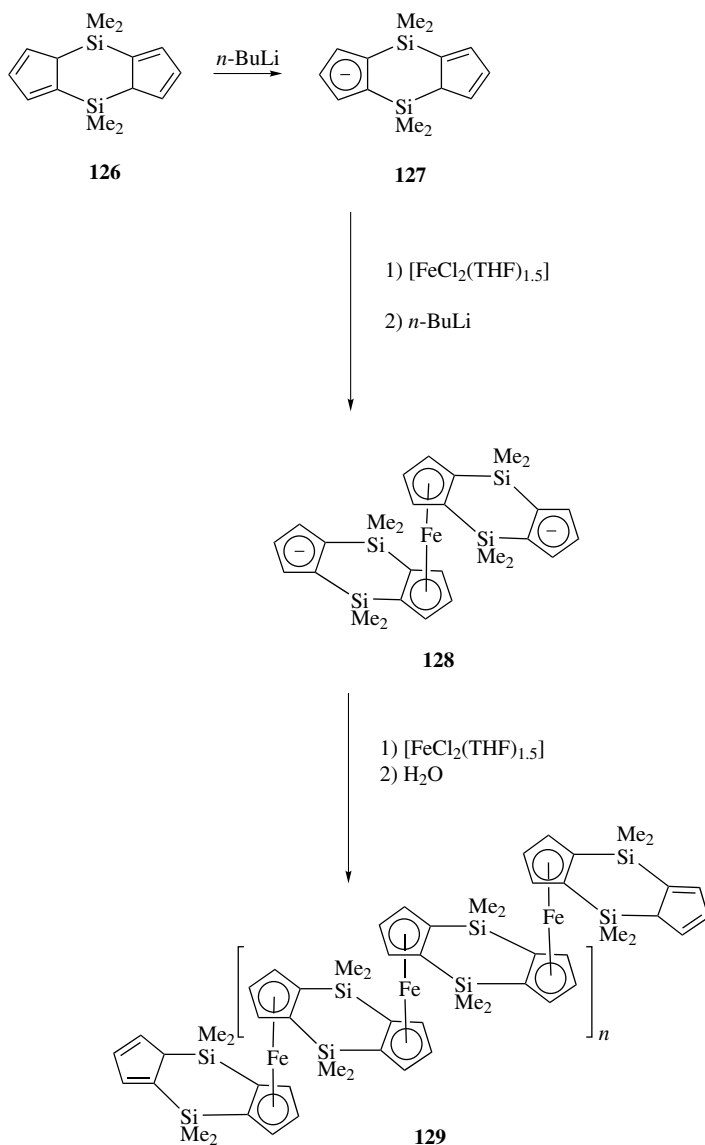

Scheme 30

Scheme 31

Ferrocene polymers with nonlinear optical properties were also prepared via Knoevenagel polycondensation reactions.[99–101] Scheme 32 shows the reaction of monomer **123** with **124** to give the accordion polymer **125** with M_n values ranging from 9100 to 26,600.[100] A mixture of *E* and *Z* isomers was initially obtained; however, an isomerically enriched polymer (98% *E* isomer) could be isolated through selective precipitation.
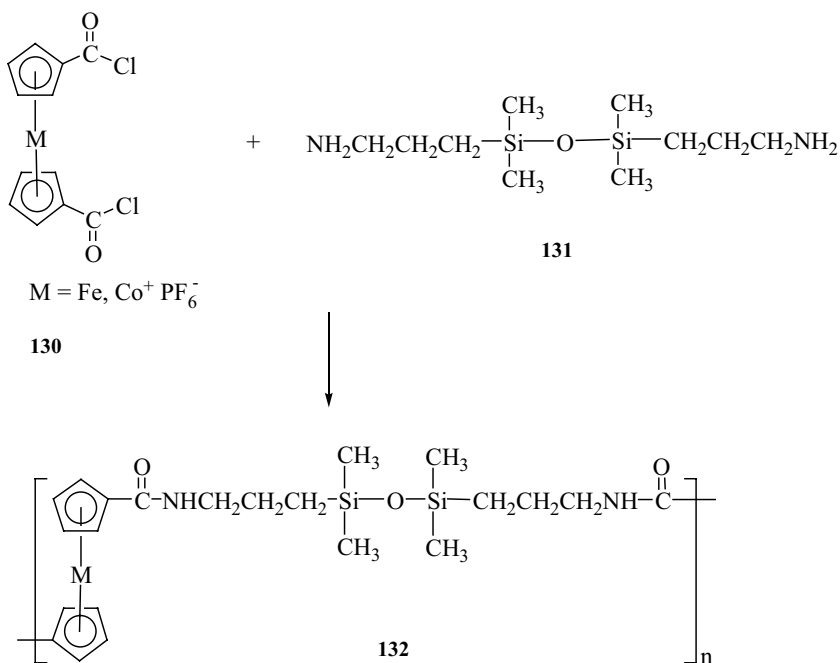

Scheme 32

The synthesis of cyclic and linear polymers containing cyclopentadienyl rings bridged by dimethylsilyl groups was achieved according to the methodology shown in Scheme 33.[102] Up to 17 ferrocenyl units were identified in the polymer (**129**) chains. The chains were found to contain only odd numbers of ferrocene units in their backbones. The size of the cyclic units was dependent on the reaction temperature utilized. For example, at 25°C, the mean ring size was 8.1, whereas at −20°C, the mean ring size increased to 10.8. As the reaction temperature was lowered to −78°C, the chain sizes began to decrease because of a decreased reaction rate.
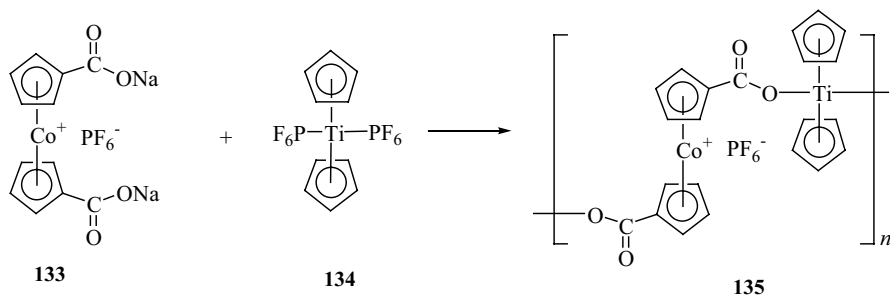
Scheme 33

Cobaltocene polymers have been prepared using methodologies similar to those employed in the design of ferrocene-based polymers, although these cationic polymers have received less attention.[103–109] Cuadrado et al. prepared polyamides (**132**) that contain siloxane bridges via condensation of 1,1′-*bis*-chlorocarbonylcobaltocenium *hexa*fluorophosphate or 1,1′-*bis*-chlorocarbonylferrocene with a siloxane-based diamine (Scheme 34).[32,103] While the organoiron polymer had an M_n value of 10,600,[103] the organocobalt polymer displayed very limited solubility in polar organic solvents.[32]

Scheme 34

In the 1970s, Carraher reported the synthesis of a number of cobaltocenium based polymers.[104–107] Titanium, zirconium, and hafnium polyesters were synthesized via reaction of the dicyclopentadienylmetal dichloride complexes with disodium dicarboxylates of cobaltocenium in either aqueous or organic solvents.[104] For example, the synthesis of a polymer (**135**) that contains cobaltocene and titanocene units in the backbone is shown in Scheme 35.[105]
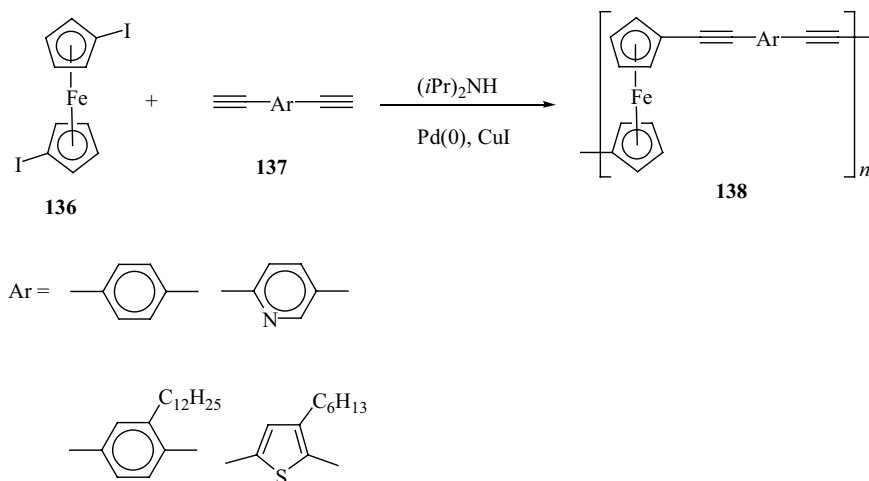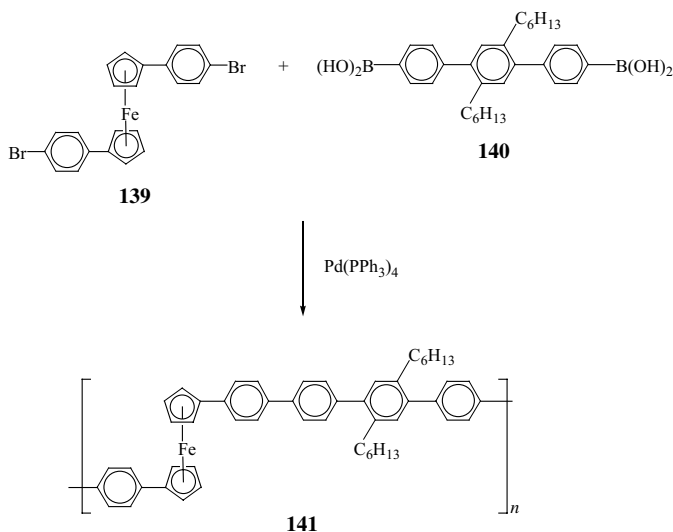

Scheme 35

D. Conjugated Systems

Conjugated polymetallocenes are an important class of organometallic polymers.[110–118] Scheme 36 shows the synthesis of polyaryleneethynylenes with ferrocene units in their backbones (**138**) via a palladium-catalyzed coupling reaction of

1,1′-diiodoferrocene (**136**) with diethynyl aromatic spacers (**137**).[110,111] These polymers became semiconducting (10^{-7} to 10^{-4} S/cm) on addition of iodine and had relatively low M_w (~ 6900 by GPC).
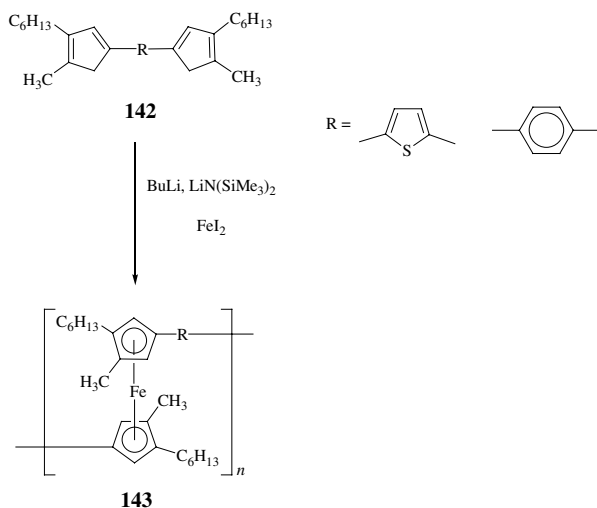

Scheme 36

The synthesis of polymer **141** was reported by Rehahn and coworkers via the palladium-catalyzed polycondensation reaction of monomers **139** and **140**.[114] This methodology shown in Scheme 37 allowed for the synthesis of soluble poly(1,1′-ferrocenylene-*alt-p*-oligophenylenes) that were isolated with high molecular weights.
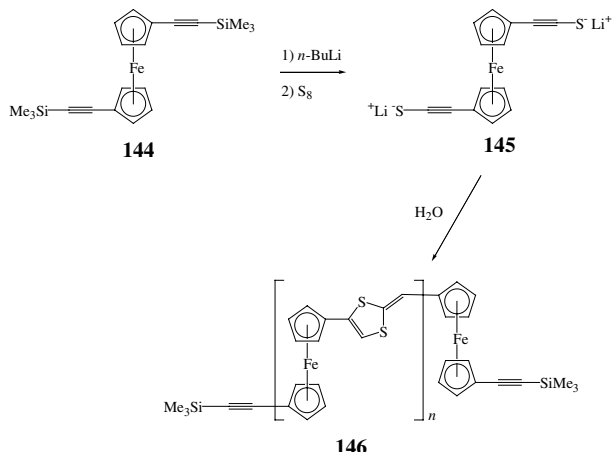

Scheme 37

Conjugated polymers (**143**) have also been prepared via coordination of iron(II) to dilithio *bis*(3-hexyl-4-methylcyclopentadienide)arylenes (**142**) (Scheme 38).[115–117] The weight average MW of these polymers were between 42,000 and 52,600 with polydispersity index (PDI) values ranging from 10.5 to 14.6. Oxidation of these polymers resulted in electrical conductivities ranging from 10^{-10} to 10^{-7} S/cm.
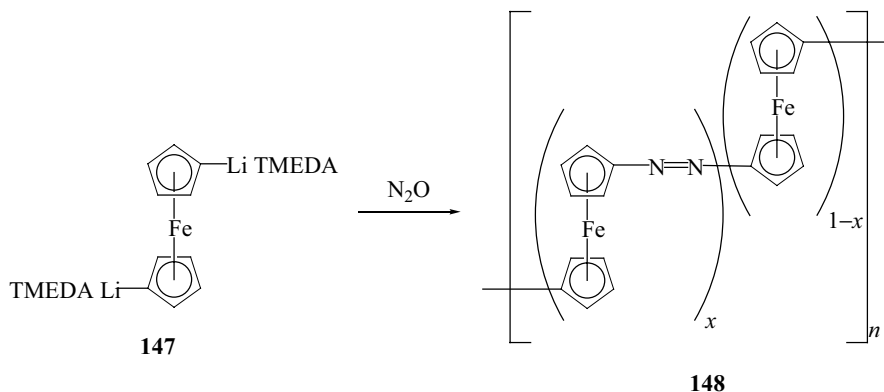

Scheme 38

A low molecular weight polymer with alternating ferrocene and dithiafulvene moieties in the backbone was prepared by cycloaddition polymerization using monomer **145** as shown in Scheme 39.[118] This polymer formed a soluble charge transfer complex with TCNQ, and on doping with iodine polymer **146** had an electrical conductivity of 3.6×10^{-3} S/cm.
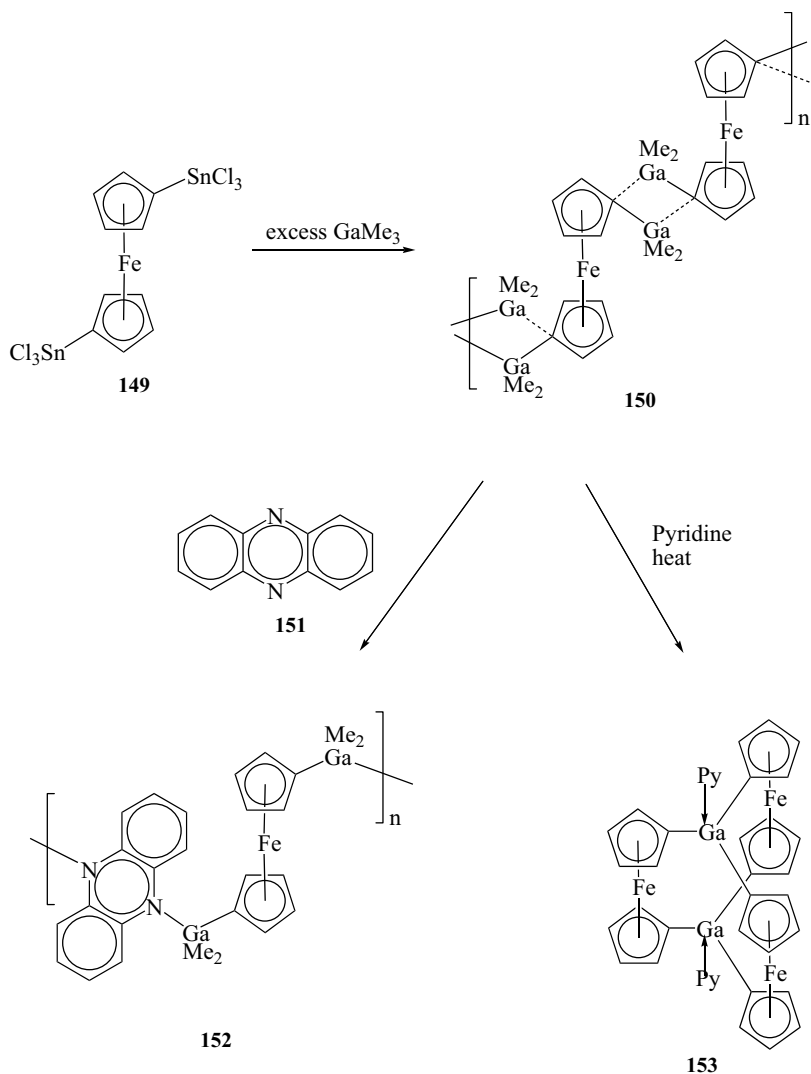

Scheme 39

Azo-substituted polyferrocenes (**148**) have been reported by Nishihara and coworkers by reaction of the dilithioferrocene complex **147** with N_2O using high pressure (Scheme 40).[119] Polymer **148** was composed of 60% azo-bridged units and 40% ferrocenylene units. The soluble portion of the polymer had a M_w of 87,000 and a M_n of 13,000.
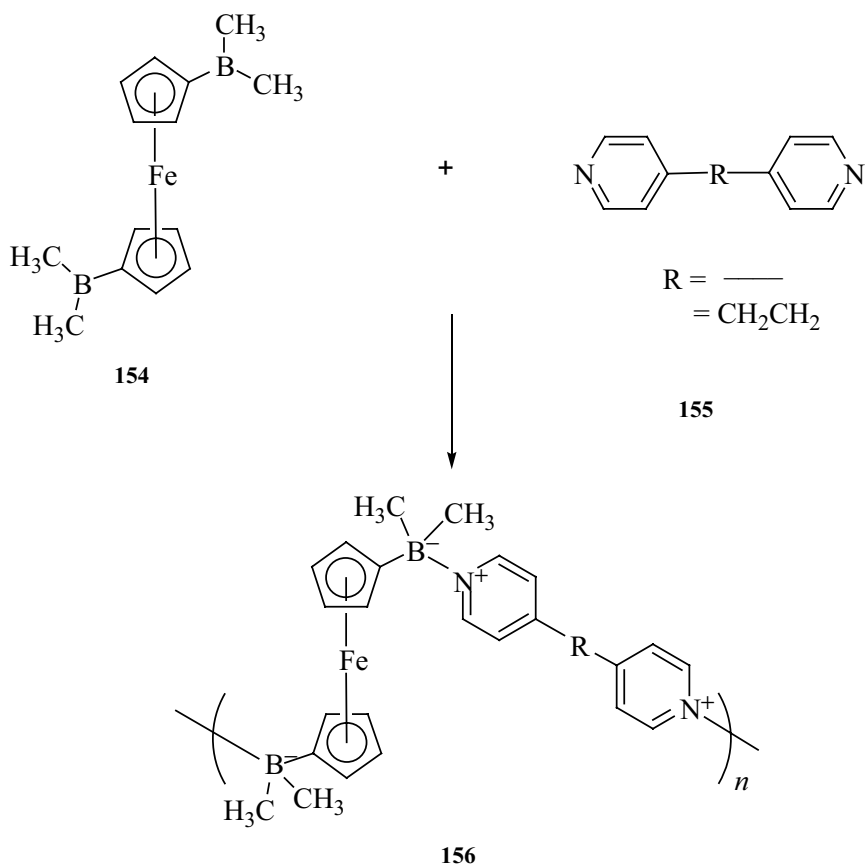

Scheme 40

E. Coordination Polymers

There are a number of examples of polymers that incorporate metallocenes and main-group element coordination complexes. These polymers represent an interesting class of materials that often involve reversible coordination to pyridine-based ligands. Reaction of 1,1′-*bis*-trichlorostannylferrocene with an excess of trimethylgallium resulted in the production of 1,1′-*bis*-dimethylgallylfer-rocene.[120,121] Crystals grown from toluene/trimethylgallium indicated that this product had the polymeric structure (**149**) shown in Scheme 41. Polymer **150** is thought to be composed of $[Fe(C_5H_4)\mu_2\text{-}GaMe_2)_2(C_5H_4)]_n$ units with $GaMe_2$ bridging units. The molecular 1,1′-*bis*-dimethylgallylferrocene units were oriented in a *trans* configuration allowing for parallel alignment of the polymeric strands. Reaction of **150** in pyridine resulted in the carousel-shaped complex **153**. Alternatively, reaction of **150** with phenazine (**151**) produced the coordination polymer (**152**).
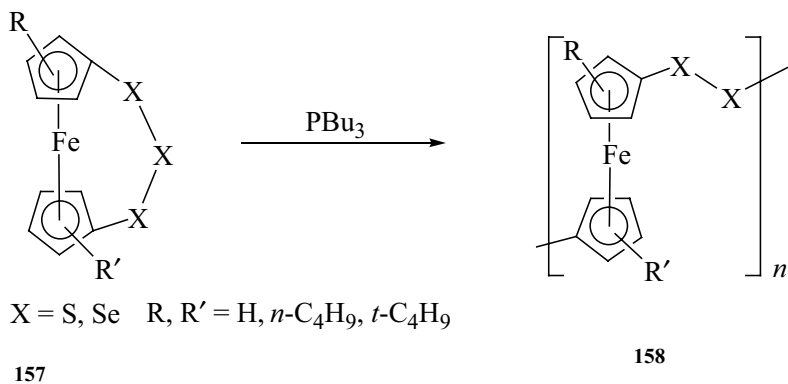
Scheme 41

Another class of coordination-type polymer containing ferrocene units in the backbone is shown in Scheme 42.[122] Reaction of monomer **154** with the bipyridine-based monomer **155** resulted in the isolation of polymer **156**. In the solid state, polymer **156** is thermally stable up to 240°C; however, depolymerization occurs at about 85°C in toluene.
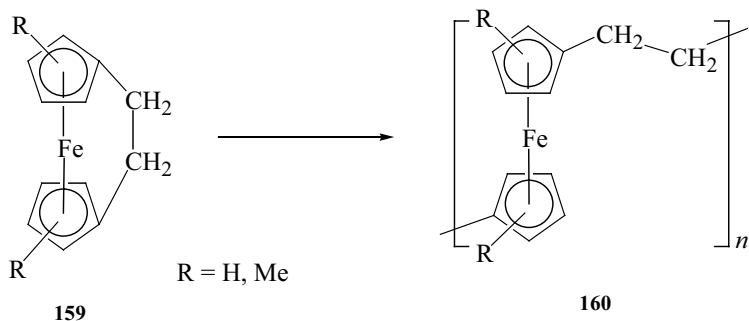
Scheme 42

F. Ferrocenophane-Based Polymers

In 1992, Brandt and Rauchfuss reported the synthesis of polyferrocenylene persulfides via ROP of and desulfurization of [3]-trithiaferrocenes.[123–126] High MW linear and network poly(ferrocene persulfide)s were produced by reaction of the trithiaferrocenes with PBu_3.[123–125] These disulfide-linked ferrocene polymers could be decomposed on addition of a reducing agent such as $LiBHEt_3$, and the polymer could be regenerated on addition of an oxidizing agent such as iodine. Ring opening and deselenization of an analogous selenium monomer of ferrocene formed the corresponding polyferrocene with Se–Se bonds.[126] Scheme 43 shows the ring-opening polymerization reaction of monomers **157**, resulting in the isolation of **158**. Incorporating butyl groups on the cyclopentadienyl rings enhanced the solubilities of polymers **158**. When the polymerizations were performed using THF or DMF as solvents, insoluble polymers were isolated; however, a mixed-solvent system consisting of dichloromethane and THF produced soluble high MW polymers.

X = S, Se   R, R′ = H, n-C$_4$H$_9$, t-C$_4$H$_9$

157

158

Scheme 43

Manners and coworkers have described the thermal and anionic ROP of [1]thia- and [1]selena-ferrocenophanes in the presence of anionic initiators.[127] Cyclic voltammetric analysis of the poly(ferrocenyl sulfide)s revealed two reversible oxidation processes, which indicated that these polymers possessed strong Fe−Fe interactions. Thermal or cationic ROP of [2]carbathioferrocenophane afforded ferrocene-based polymers containing sulfide linkages.[128,129] [2]Metallocenophanes (M=Fe, Ru) that contain hydrocarbon bridges have been polymerized thermally to give polymers (**160**) with insulating bridges between the cyclopentadienyl ligands as shown in Scheme 44.[130–132] Functionalization of the cyclopentadienyl rings with methyl groups gave soluble high MW polyferrocenylethylenes, and polyruthenocenylethylenes. Cyclic voltammetry of the ruthenium-based polymers indicated irreversible oxidation, while the iron-based polymers underwent reversible oxidation.[131] Oxidation of polyferrocenylethylenes with *tetra*-cyanoethylene (TCNE) resulted in materials displaying antiferromagnetic interactions.[132]


R = H, Me

159

160

Scheme 44

A number of conjugated ferrocene-based polymers have been synthesized via ROMP of ferrocenophanes that possess bridging olefinic units.[133–135] Buretea and Tilley reported the homopolymerization of *ansa*-vinyleneferrocene and its copolymerization with norbornene.[133] While the homopolymers were insoluble materials that had a conductivity of 10^{-3} Ω^{-1} cm^{-1}, the copolymer had M_w and M_n values of 21,000 and

11,000, respectively. Grubbs and Lee have found that the solubility of this class of polymer could be enhanced by incorporating substituents onto the bridging carbon chains.[134,135] Scheme 45 shows the ROMP of monomer **161** using W(=NPh)-(=CHPh(2-OMe))(OC(CF$_3$)$_2$(CH$_3$))$_2$)[tetrahydrofuran (THF)] as the catalyst. In this case, the weight-average molecular weight of polymer **162** was greater than 300,000.[135]
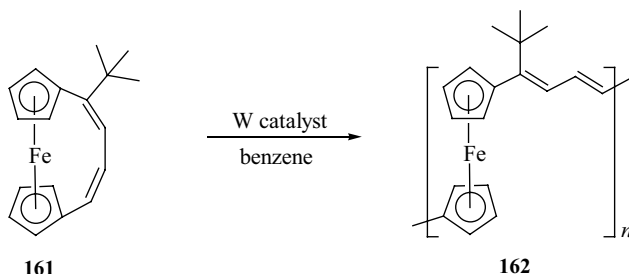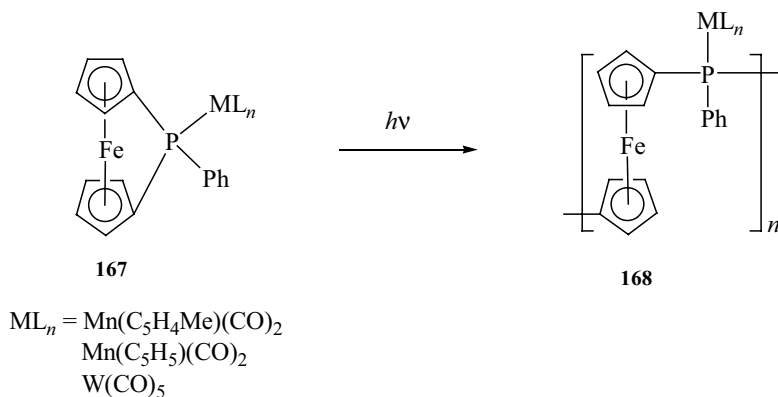

Scheme 45

Seyferth and coworkers reported in 1982 that phosphorus-bridged ferrocenophanes undergo anionic ring-opening to give polymers with molecular weights ranging from 8900 to 161,000.[136] Manners subsequently reported that thermal ROP of phosphorus-bridged [1]ferrocenophanes (**163**) resulted in the isolation of high MW polymers (**165**).[137] These polymers could be reacted with sulfur to give the corresponding poly(ferrocenylphosphine sulfide)s. Living anionic ROP of phosphorus-bridged [1]ferrocenophanes has also been shown to produce homo and block copolymers.[138] Borane adducts of polyferrocenylphosphines (**166**) have been isolated via thermal ROP of a borane-functionalized monomer, or by addition of BX$_3$ (X=H, Cl) to the polyferrocenylphosphines (**165**) (Scheme 46).[139]
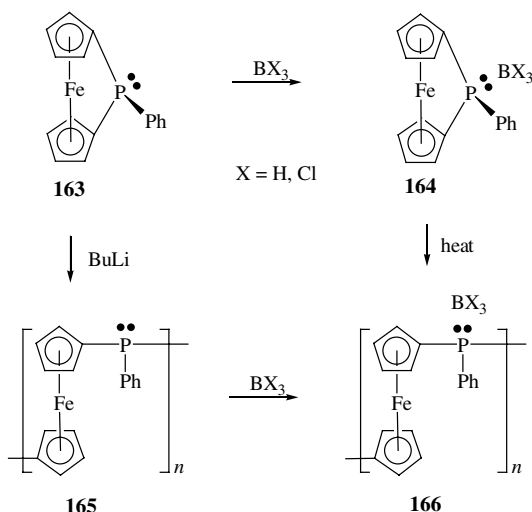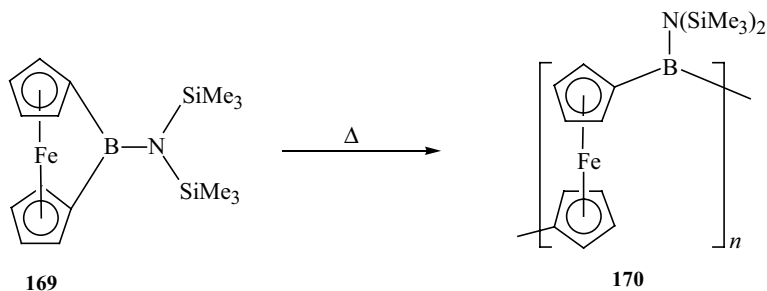

Scheme 46

Miyoshi et al. reported the ROP of ferrocenophanes bearing organometallic moieties on the bridging phosphorus ligand (Scheme 47).[140] On irradiation of monomer **167** for 10 min with UV–visible light, high MW polymers (**168**) were isolated. It was also determined that polymerization of (1,1′-ferrocenediyl)phenylphosphine underwent the same ROP reaction to give their corresponding polymeric materials.


$$ML_n = Mn(C_5H_4Me)(CO)_2$$
$$Mn(C_5H_5)(CO)_2$$
$$W(CO)_5$$

Scheme 47

The ring-opening polymerization of [1]ferrocenophanes bearing boron bridges has also been examined.[141–143] Scheme 48 shows the synthesis of the first polyferrocenylboranes via thermal ROP of a highly strained boron-bridged [1]ferrocenophane.[141] The hydrolytic instability of the boron-functionalized polymers precluded accurate molecular weight analysis; however, dynamic light scattering indicated low values.

Scheme 48

The thermal ROP of [1]germaferrocenophanes (**171**) has resulted in the production of a number of high molecular weight ($M_w = 10^6$) poly(ferrocenyl germanes).[144–148] The transition-metal-catalyzed homo- and copolymerization of germanium-bridged ferrocenophanes using platinum and palladium catalysts.[145,146] It was also reported that polyferrocenylenesilylene(germylene) copolymers went from insulators to conductors on doping with iodine.[148] Scheme 49 shows some of the poly(ferrocenyl germanes) (**172**) that have been synthesized.[144–148]

171   **172**
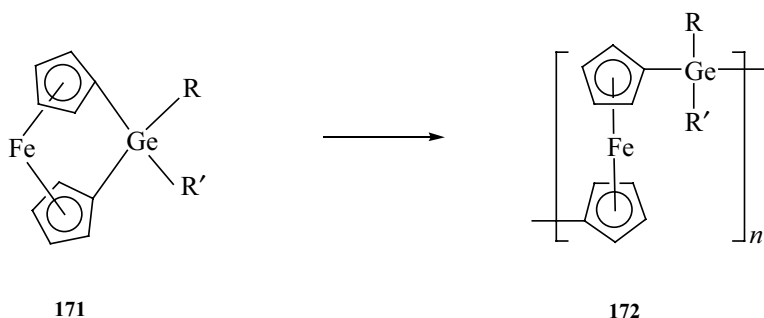
R = R′ = Me, Et, *n*-Bu, Ph
R = Me, R′ = *n*-Bu
R = Et, R′ = *n*-Bu

Scheme 49

The ROP of ferrocenophanes with tin bridges produces high molecular weight polymers by thermal ROP.[149–152] It has also been reported that the room temperature ring opening of tin-bridged [1]ferrocenophanes in solution occurs and that this process is accelerated by the addition of amines as shown in Scheme 50.[151–153] The same reaction was found to occur on the addition of base to ferrocenophanes containing silicon and germanium bridges. While the tin and germanium monomers displayed good reactivity, the silicon-containing monomers were much less reactive.[151] It was also reported that tin-bridged ferrocenophanes undergo cationic ring-opening polymerization in the presence of small quantities of Lewis acids.[153]

173   **174**
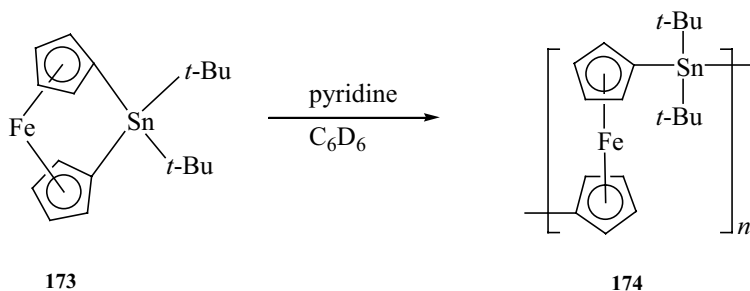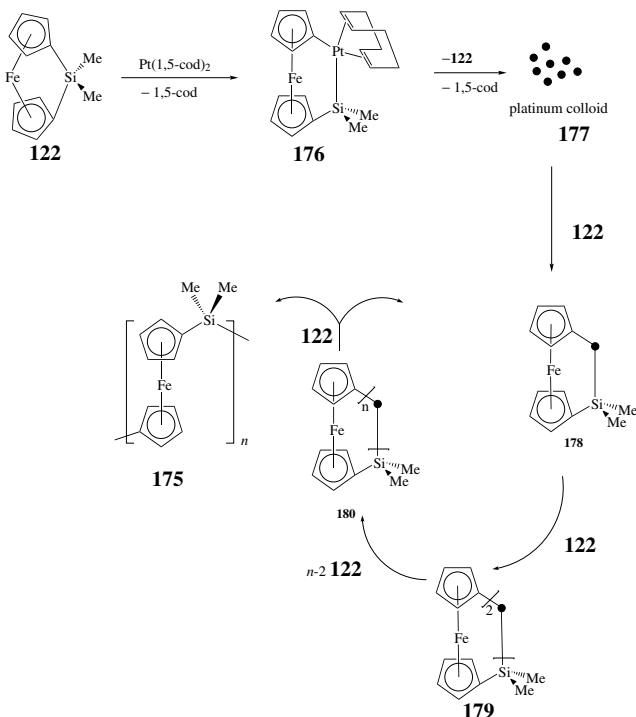
Scheme 50

The synthesis and properties of polyferrocenylsilanes have been studied by a number of research groups. The major contributions in this area came from the Manners laboratory at the University of Toronto.[154–156] Scheme 51 shows three well-developed methodologies that have been established for the ROP of monomer **175** resulting in the formation of high MW polyferrocenyldimethylsilane (**122**); specifically, by thermal, anionic, and transition metal catalysis.[157–159] It has also been reported that solid-state polymerization of Fe(η-C_5H_4)$_2$SiMePh using a ^{60}C γ-ray source resulted in the formation of a high MW stereoregular polymer.[160,161]
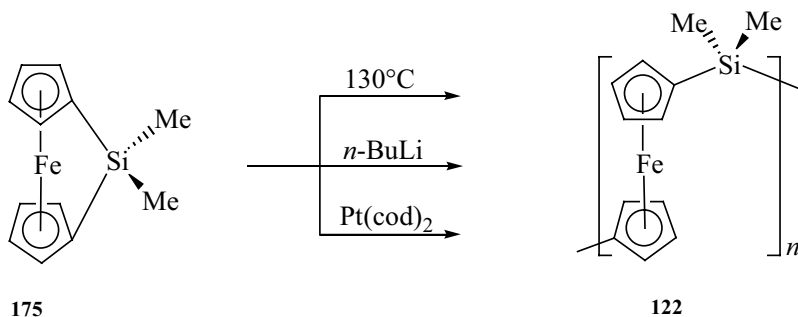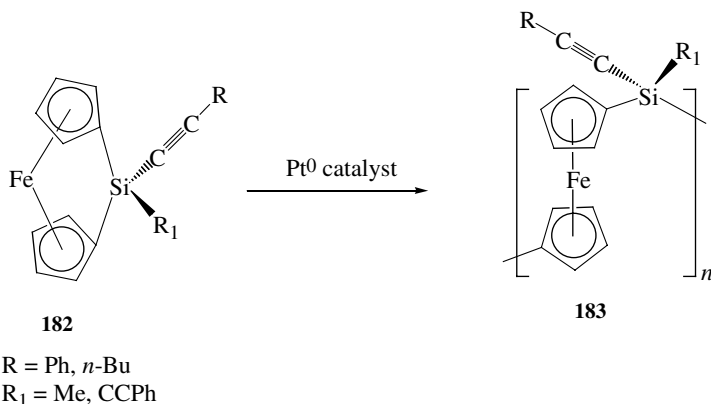
Scheme 51

It was initially proposed that the transition-metal catalyzed polymerization proceeded via a homogenous mechanism.[162] However, Manners proposed that the ROP of [1]silaferrocenophanes followed a heterogeneous catalytic cycle.[163] Scheme 52 shows the proposed mechanism in which $Pt(1,5\text{-}cod)_2$ is thought to initially form a [2]platinasilaferrocenophane (**176**) via oxidative addition of the zero-valence Pt complex with elimination of a 1,5-cod ligand. Elimination of a second 1,5-cod ligand then leads to the production of platinum colloids, which are believed to be the active catalyst. Subsequent oxidative addition and reductive elimination (or σ-bond metathesis) at the colloid surface forms the polymeric material (**175**).
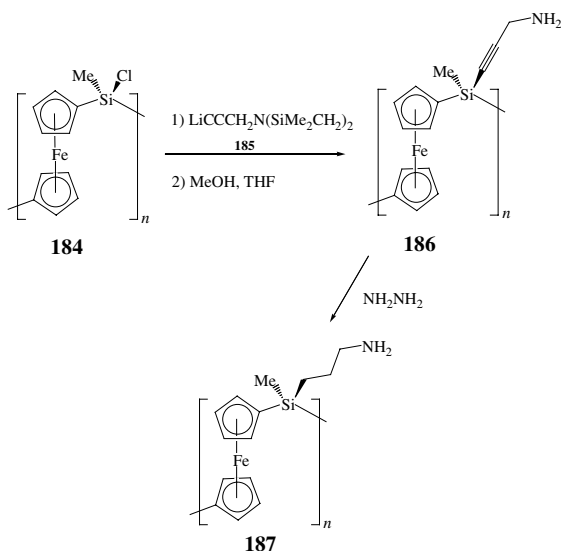

Scheme 52

A number of studies have focused on the synthesis of polymers with functionalized sidechains. For example, long-chain alkyl, chloroalkyl, chloro, and alkoxy substitutes polyferrocenylsilanes have been reported.[164–167] Polymers with acetylenic substituents have also been synthesized via transition-metal-catalyzed ROP (Scheme 53).[168] The resulting high MW polymers (**183**) were pyrolyzed to produce magnetic ceramics in high yields.


R = Ph, *n*-Bu
R$_1$ = Me, CCPh

Scheme 53

Reaction of chloro-substituted polymers with alcohols or amines resulted in the isolation of new classes of organometallic polymers containing interesting properties.[169–171] Scheme 54 shows the reaction of polymer **184** with the acetylide monomer (**185**) to produce polymer **186**. Reaction of this polymer with hydrazine resulted in the isolation of polymer **187**.[170,171]
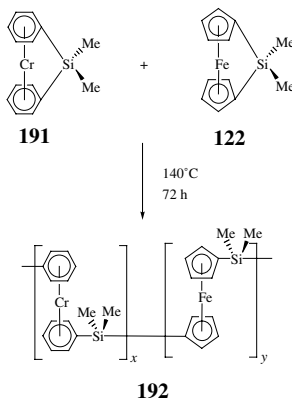

Scheme 54

Considerable attention has been directed toward the synthesis of water-soluble ferrocene-based polymers and polyelectrolytes.[169–176] Vancso and coworkers reported the synthesis and self-assembly of anionic and cationic polyelectrolytes.[172,173] Scheme 55 shows the strategy that was applied by Manners and coworkers in the design of polyanionic (**189**) and polycationic (**190**) water-soluble ferrocene-based electrolytes.[171]
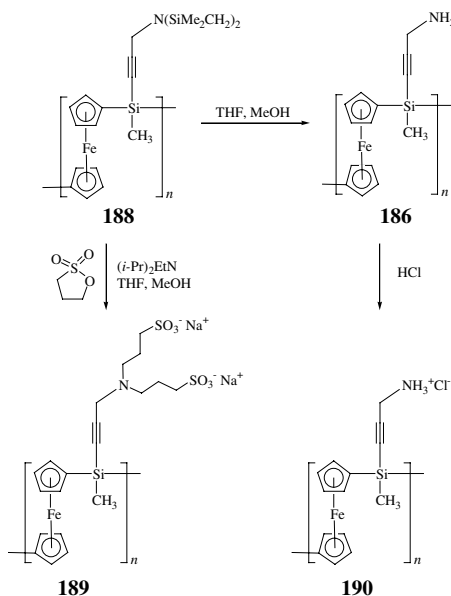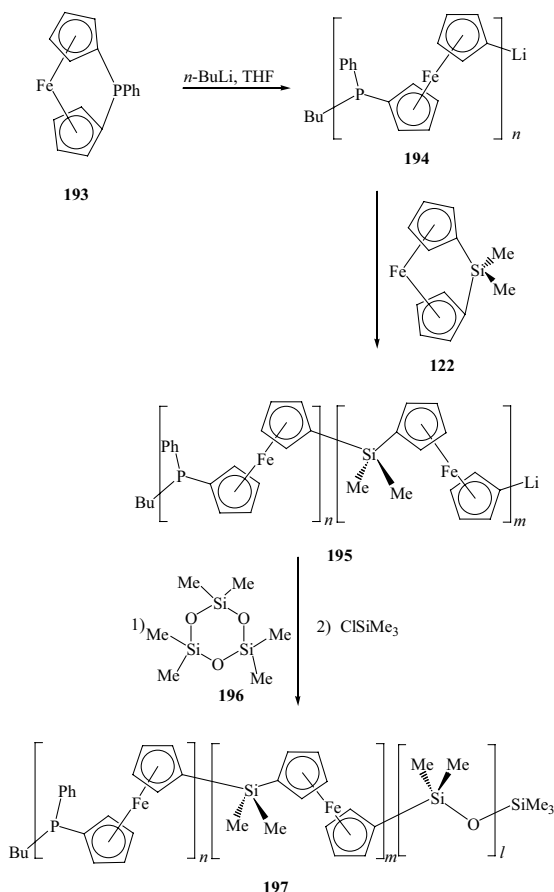

Scheme 55

Copolymerization reactions of ferrocenophanes have allowed for the preparation of a number of interesting organometallic polymers. Thermal copolymerization of a [1]chromarenophane (**191**) (Scheme 56) with a [1]ferrocenophane (**122**) resulted in the formation of a copolymer (**192**) containing both chromium and iron units in the polymer backbone.[177] Because of the low reactivity of the chromium monomer, its homopolymerization was not possible.


192
Scheme 56

Anionic polymerization of [1]ferrocenophanes has led to living polymers, which could then be copolymerized with a number of different monomers to produce block copolymers.[178–191] Scheme 57 shows the synthesis of the ABC triblock copolymer of the type **197** possessing narrow polydispersities.[191] When the polyferrocenylphenylphosphine blocks were small, self-assembly of the polymer yielded cyclindrical micelles with the organometallic blocks at the core and the polydimethylsiloxane blocks at the corona. When the degree of polymerization for the polyferrocenylphenylphosphine block was 11, spherical micelles were formed.

Scheme 57

Transition-metal-catalyzed ring-opening polymerization of ferrocenophanes has also resulted in polymers with interesting properties.[192–195] For example, the water-soluble block copolymer (**199**) shown in Scheme 58 formed micelles in THF/water solutions in which the hydrophobic ferrocenylsilane block occupied the core surrounded by the hydrophilic polyethyleneoxide block.[195]
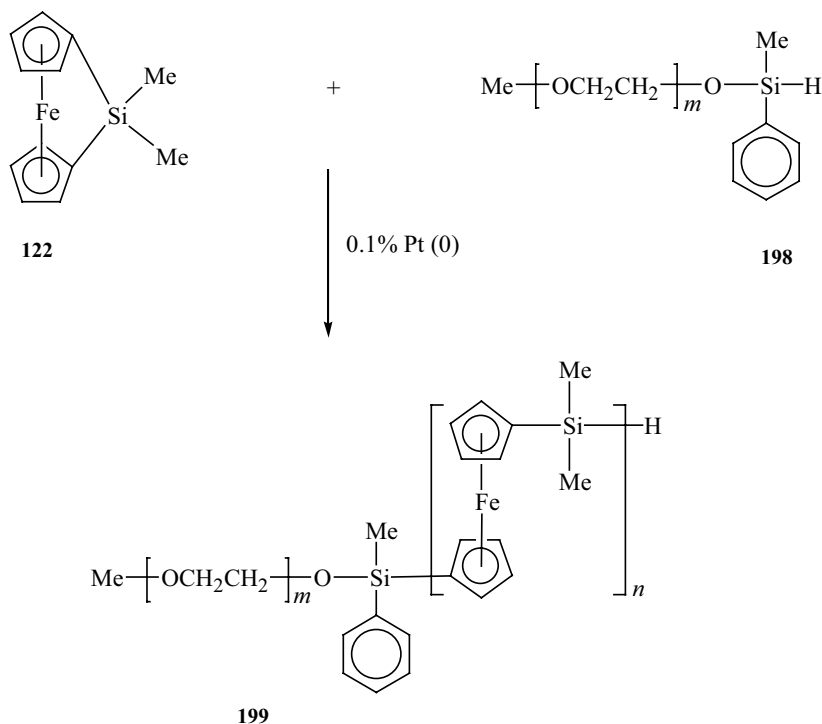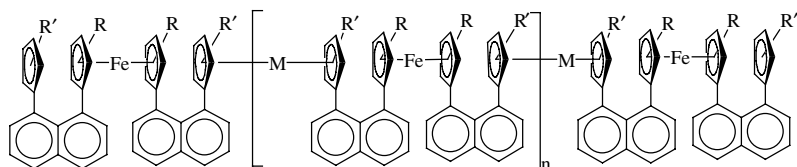
Scheme 58

Homo- and copolymers formed from ROP of [1]ferrocenophanes have been tested for a number of applications. These classes of ferrocene-based polymers have been examined by Vancso et al. as nanolithographic and plasma etch resistant materials.[196,197] Pannell et al. have described ferrocenylsilylene polymer coatings as tapered optical-fiber sensors in the detection of ammonia and carbon dioxide.[198]

V. MULTIDECKER POLYMERS

Rosenblum and coworkers have described a number of routes to face-to-face polymetallocenes.[199–201] Ruthenium- and iron-based materials were synthesized via palladium-catalyzed cross-coupling reaction of 1,8-diiodonaphthalene with metallocenylzinc chloride (M=Fe, Ru).[200] The MW of the face-to-face polyferrocenes with R=H, R′ = 2-octyl was in the range of 18,000, while that of **200** when R=R′=2-octyl, was 139,000. The conductivity of polymer **200** (M=Fe, R=H, R′=2-octyl) on doping with I_2 was 6.7×10^{-3} S/cm. The incorporation of nickelocene and cobaltocene units into the face-to-face polyferrocenes resulted in materials with magnetic susceptibilities of 3.51 and 5.2 μ_B for the Ni\Fe and Co\Fe oligomers, respectively.[200]

M = Fe, Ni, Co
R, R′ = H, alkyl,aryl group

200

Polydecker oligomers **202** (Scheme 59) and **203** were prepared by Siebert and coworkers.[202–204] Heating of **201** in vacuo gave **202** as a black film, which splinters into shiny metallic platelets when cooled. Electron micrographs show an isotropic distribution of fibrils. The conductivity of **202** was 10^{-2} S/cm, but **203** was an insulator at room temperature (10^{-10} S/cm). The insolubility of these materials prevented molecular weight determinations. These giant Dagwood sandwich-type structures further illustrate the plethora of shapes available with organometallic polymers.


**201**

Δ, vaccum

202
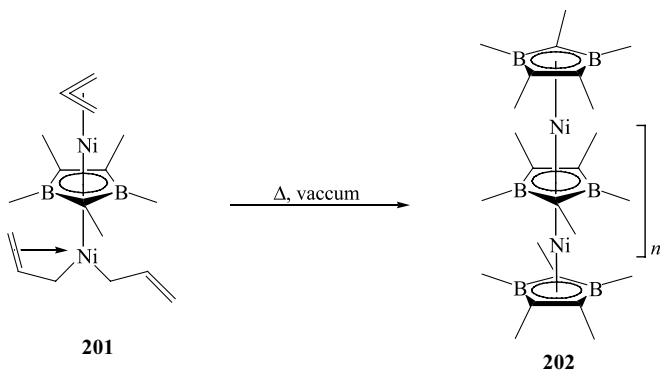
Scheme 59
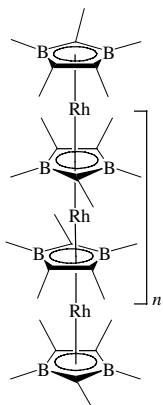
203

Polymetallacarborane staircase oligomers (**204**) containing cobalt and nickel have been reported by Grimes et al.[205,206] Electrochemical analysis of oligomers with up to 17 metal atoms indicated that there was very little electronic communication between the metal centers.[205] Optically active cobalt-based multi decker polymers have also been prepared by Katz and coworkers.[207]


M = Co, Ni

204
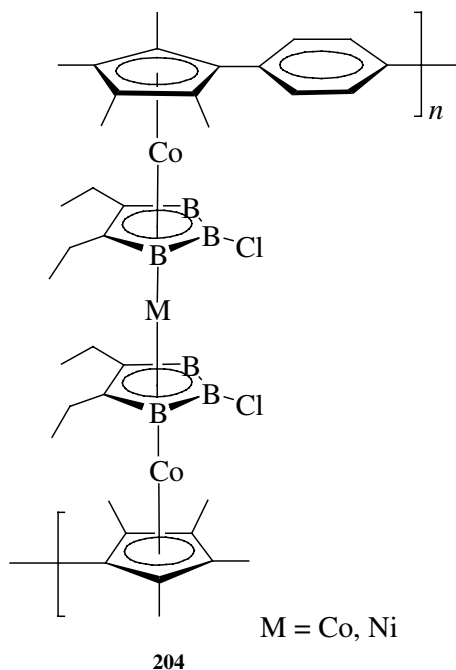
VI. HYPERBRANCHED AND CROSSLINKED POLYMERS

Tang and coworkers have synthesized and pyrolyzed a hyperbranched polymer (**205**) to produce magnetic ceramics. This polymer was prepared by reaction of 1,1′-dilithioferrocene with methyltrichlorosilane and had a weight-average molecular weight of 6300 with a polydispersity of 3.8. Polymer **205** had a glass transition temperature at $-54.5°C$ and at $306°C$ had experienced a 5% weight loss. Ceramics were prepared by heating the sample up to $1000°C$ under a nitrogen atmosphere or $1200°C$ under an argon atmosphere, and the sample was then calcinated or sintered at this temperature for one hour. The ceramic yields of these materials were found to be greater than those of their linear polymeric analogs.[208] The ceramic formed under a stream of argon had a high saturation magnetization with a M_s of approximately 49 emu/g and a near-zero coercivity and remanence, indicating that it is an excellent soft ferromagnetic material.

Fc = 1,1′-ferrocenylene
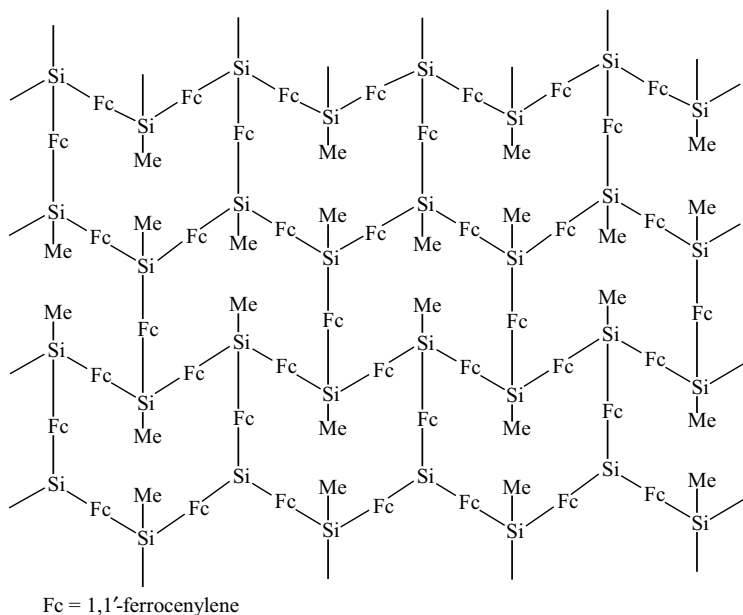
205

Cuadrado et al. have reported the synthesis of ferrocene-containing crosslinked polymers.[103] Polymers **206a** and **206b** are examples of these types of polymers that incorporated varying degrees of organoiron groups in their structures. Polymer **206a**, containing 34% organoiron units, displayed very limited solubility in organic solvents and swelled, whereas the polysiloxane with only 3% ferrocene-substituted groups was a viscous solution displaying good solubility in polar organic solvents.

206a $n = 0.34$, $m = 0.66$
**206b** $n = 0.03$, $m = 0.97$
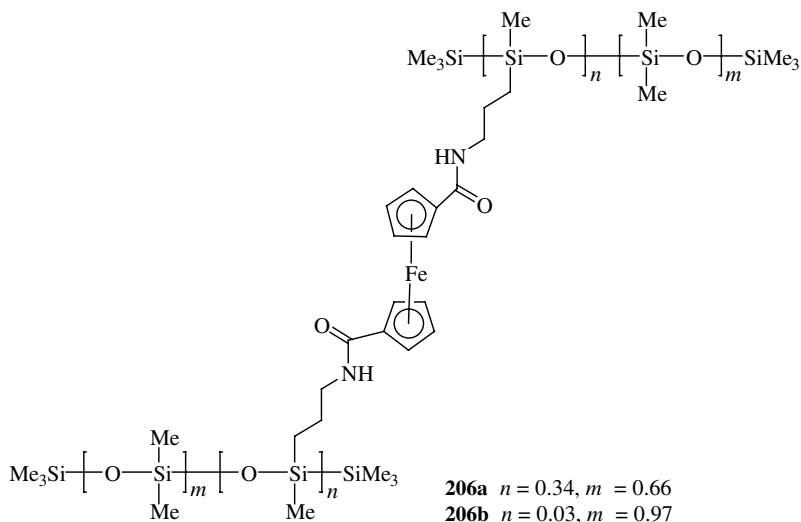
A [1]silaferrocenophane containing a 4-membered spirocyclic ring at the bridging silicon atom was subjected to thermal ROP to give a crosslinked polymer (**209**) due to ring opening of both the ferrocenophane and the spirocyclic group.[209,210] Scheme 60 shows the strategy utilized to incorporate varying degrees of crosslinker (**208, 210**) into polyferrocenylsilanes.[211–214] The cross-linked polymers possesses higher thermal stability than do their linear analogs. The pyrolysis of these crosslinked polyferrocenylsilanes has resulted in the production of ceramics that possess magnetic properties.[209–214]
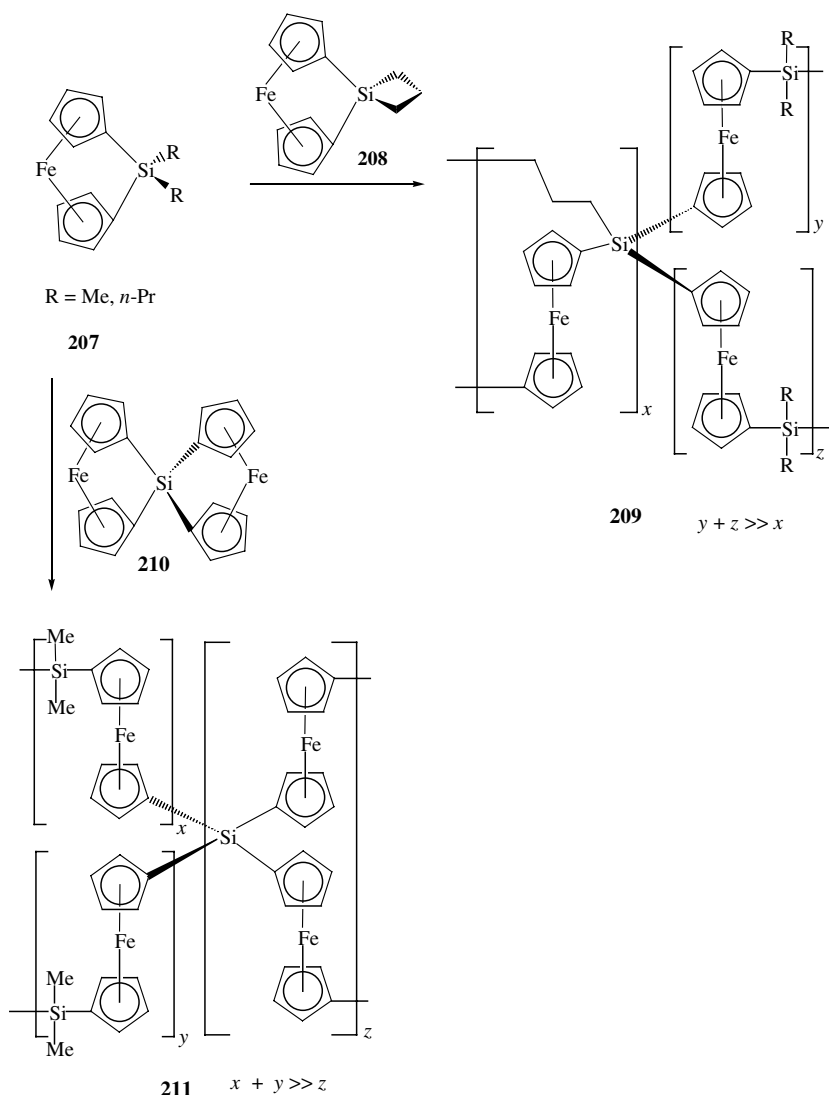

Scheme 60

VII. STARS AND DENDRIMERS

There has been a great deal of attention focused on the synthesis of dendrimers and star polymers functionalized with ferrocenyl groups.[215–226] Astruc et al. have explored the synthesis and properties of different classes of ferrocene-based star polymers and dendrimers.[215–217] A dendrimer containing 54 ferrocene units at its periphery was synthesized and reversible oxidation of all 54 iron centers was observed.[215] Chemical oxidation of the neutral iron centers to cationic species could also be accomplished using $NOPF_6$. Dendrimers containing nine peripheral organoiron[216] or organocobalt[217] groups (**212**) were synthesized by the reaction of amine-functionalized dendrimers with the acid chlorides of ferrocene or cobaltocenium. Astruc used the ferrocene-functionalized polymers as supramolecular redox sensors for the recognition of small inorganic anions.[216]

212

$ML_n = FeC_5H_5$
$CoC_5H_5PF_6$
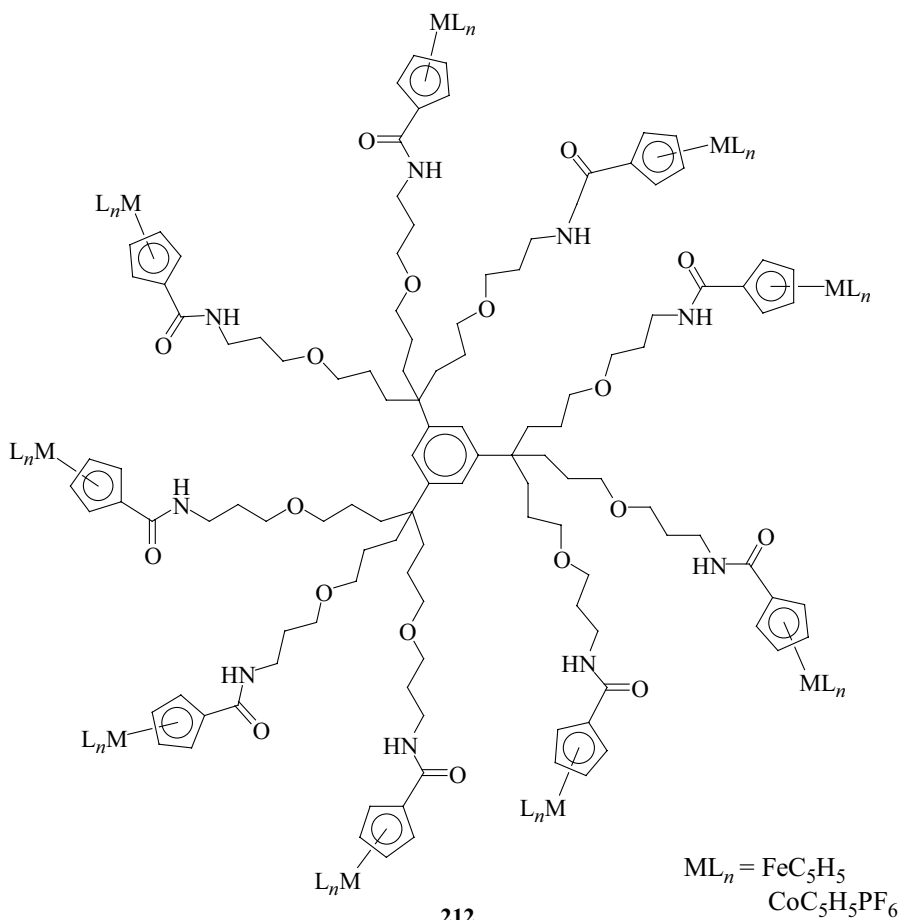
Finally, a dendrimer containing 243 ferrocenyl units at the periphery was synthesized by ferrocenylsilation of an allyl terminated dendrimer. This macromolecule could be oxidized to the corresponding stable ferrocenium dendrimer and reversibly reduced back to the neutral complex.[218] Cuadrado and coworkers have also been active in the synthesis of dendrimers containing ferrocene and cobaltocene moieties.[219–222] The synthesis of propylenimine based dendrimers with up to five generations and 64 peripheral ferrocenyl moieties underwent reversible oxidation at $E_{1/2}=0.59$ V.[220] Polymer **213** is an example of a dendrimer with 32 ferrocenyl units at the periphery.
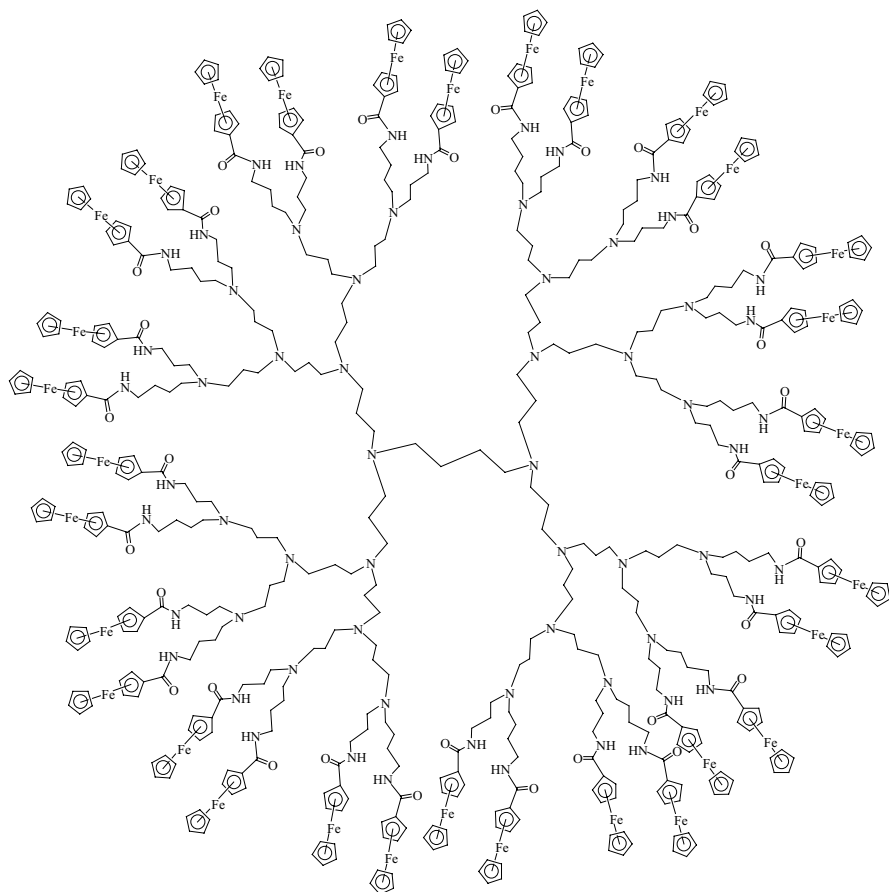

213

The guest–host relationships of some low-generation dendrimers with cyclodextrins were examined.[220] While dendrimers with 4 and 8 peripheral

ferrocene moieties appeared to complex completely to β-cyclodextrin, a higher MW dendrimer containing 16 peripheral ferrocene groups (**216**) displayed incomplete complexation, possibly due to steric congestion. The complexation resulted in higher solubility of the organometallic dendrimers in aqueous solution; however, reversible binding of the cyclodextrins could be achieved through addition of 2-naphthalenesulfonate, which resulted in precipitation of the dendrimers from solution. Silicon-based ferrocenyl dendrimers possessing electro-chemical communication between the iron centers were also synthesized (Scheme 61).[221] Dendrimers containing ferrocene and cobaltocenium units at their periphery were also examined.[222]
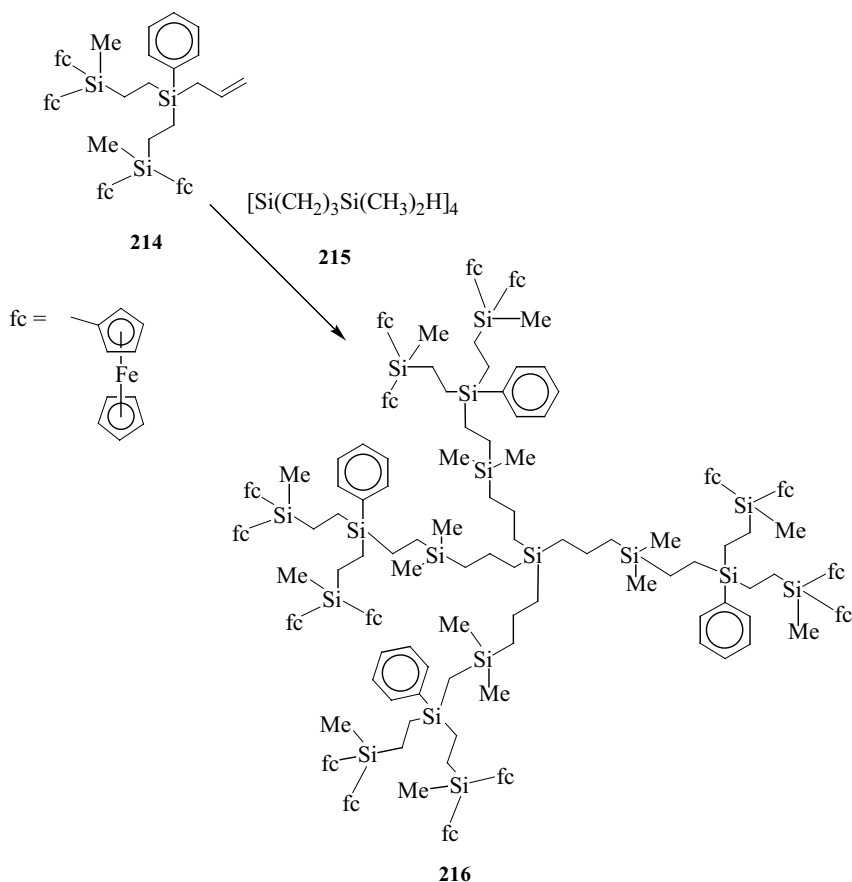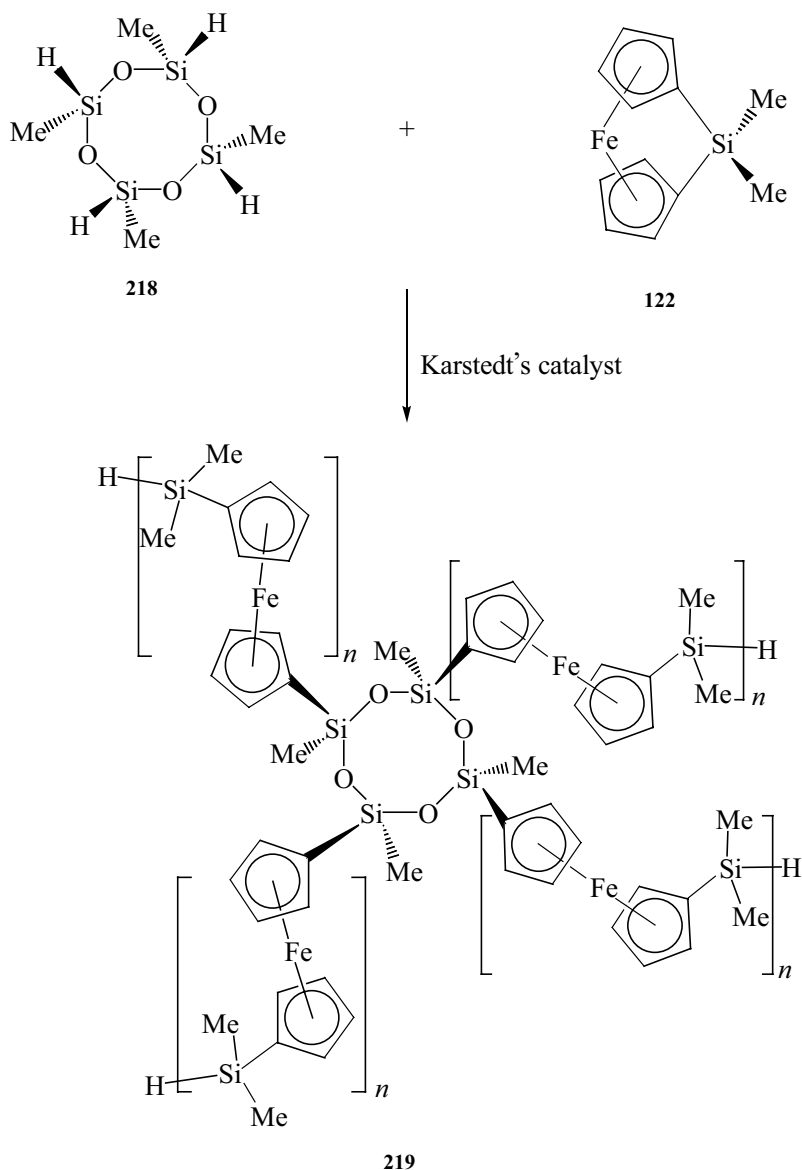

Scheme 61

Deschenaux et al. have investigated the synthesis of ferrocenyl-based polymers (**217**) with liquid crystalline properties.[223,224]
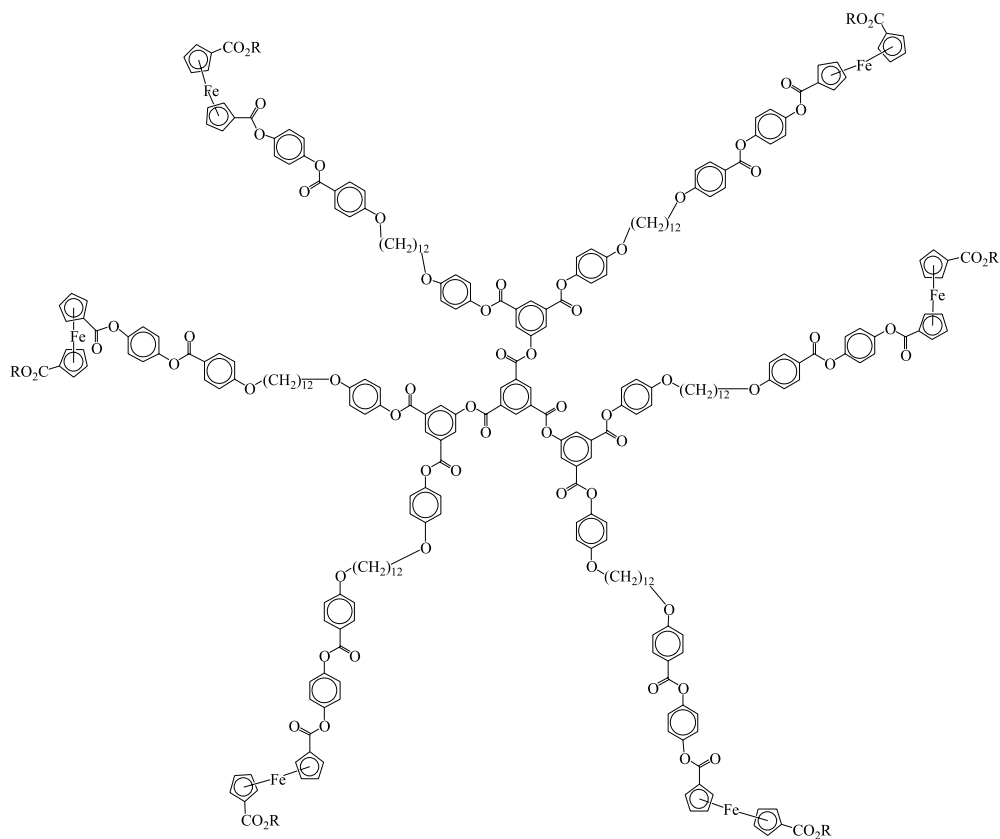
217

Star-shaped polymers (**219**) have been synthesized by platinum-catalyzed ROP of **122** in the presence of hydromethylcyclo-*tetra*-siloxane (**218**) as shown in Scheme 62.[226]

Scheme 62

VIII. SUMMARY

While ferrocene-derived polymers continue to be the best studied of the metallocene-based polymers, there exists a wide variety of other (symmetric) metallocenes. The metallocene portion of the polymer can be bound through the metallocene ring, through adjacent metallocene rings, or through the metal itself. Metallocenes may exist

as part of the backbone, sidechain, or as part of more complex structures such as hyper-branches, stars, sheets, rods, and dendrites. Some of these polymers have been shown to exhibit good electrical conductivity, show nonlinear optical behavior, be charge transfer complexes, have relatively high glass transition temperatures, and exist in multiple oxidation states. Other metallocene-containing polymers are involved in self-assembly scenarios and can be used as optical fiber sensors, nanolithographic and plasma etch resistant materials, and in liquid crystal systems.

IX. REFERENCES

1. I. Manners, *J. Polym. Sci. Part A, Polym. Chem.* **40,** 179 (2002).

2. A. S. Abd-El-Aziz, *Macromol. Rapid Commun.* **23,** 995 (2002).

3. A. S. Abd-El-Aziz, "Metal-Containing Polymers" in *Encyclopedia of Polymer Science and Technology,* 3rd ed.*,* J. I. Kroschwitz, ed., Wiley, New York, 2002.

4. R. D. A. Hudson, *J. Organomet. Chem.* **637-639,** 47 (2001).

5. P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **99,** 1515 (1999).

6. A. Togni, ed., *Metallocenes*, VCH, New York, 1998.

7. I. Manners, *Angew. Chem. Int. Ed. Engl.* **35,** 1603 (1996).

8. A. Togni, T. Hayashi, eds., *Ferrocenes*, VCH, New York, 1995.

9. C. U. Pittman, Jr., C. E. Carraher, Jr., J. R. Reynolds, "Organometallic Polymers," in the *Encyclopedia of Polymer Science and Engineering*, H. Mark, N. Bikales, C. Overberger, J. Menges, eds., Wiley, 1987, Vol. 10, pp. 541–594.

10. E. W. Neuse, H. Rosenburg, *Metallocene Polymers,* Marcel Dekker, New York, 1970.

11. F. S. Arimoto, A. C. Haven, Jr., *J. Am. Chem. Soc.* **77,** 6295 (1955).

12. Y. Sasaki, L. L. Walker, E. L. Hurst, C. U. Pittman Jr., *J. Polym. Sci., Polym. Chem. Ed.* **11,** 1213 (1973).

13. D. O. Cowan, J. Park, C. U. Pittman Jr., Y. Sasaki, T. K. Mukherjee, N. A. Diamond, *J. Am. Chem. Soc.* **94,** 5110 (1972).

14. C. U. Pittman Jr., B. Surynarayanan, *J. Am. Chem. Soc.* **96,** 7916 (1974).

15. C. U. Pittman Jr., B. Surynarayanan, Y. Sasaki, in *Inorganic Compounds with Unusual Properties*, Advances in Chemistry Series, Vol. 150, R. B. King, ed., ACS (American Chemical Society, Washington, DC), 1976.

16. M. Baumert, J. Frohlich, M. Stieger, H. Frey, R. Mulhaupt, H. Plenio, *Macromol. Rapid Commun.* **20,** 203 (1999).

17. C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, R. Prado, *Macromolecules* **3,** 746 (1970).

18. C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, *Macromolecules* **3,** 105 (1970).

19. J. C. Lai, T. D. Rounsefell, C. U. Pittman, Jr., *Macromolecules* **4,** 155 (1971).

20. C. U. Pittman, Jr., R. L. Voges, W. R. Jones, *Macromolecules* **4,** 291 (1971).

21. C. U. Pittman Jr., R. L. Voges, W. R. Jones, *Macromolecules* **4,** 298 (1971).

22. Y. Yang, Z. Xie, C. Wu, *Macromolecules* **35,** 3426 (2002).

23. N. Kuramoto, Y. Shishido, K. Nagai, *J. Polym. Sci., Part A, Polym. Chem.* **35,** 1967 (1997).

24. M. E. Wright, E. G. Toplikar, R. F. Kubin, M. D. Seltzer, *Macromolecules* **25,** 1838 (1992).

25. M. E. Wright, B. B. Cochran, E. G. Toplikar, H. S. Lackritz, J. T. Kerney, in *Inorganic and Organometallic Polymers II,* P. Wisian-Neilson, H. R. Allcock, K. J. Wynne, eds., ACS Symp. Series 572, American Chemical Society, Washington, DC, 1994.

26. R. Deschenaux, F. Turpin, D. Guillon, *Macromolecules* **30,** 3759 (1997).

27. R. Deschenaux, I. Jauslin, U. Scholten, F. Turpin, D. Guillon, B. Heinrich, *Macromolecules* **31,** 5647 (1998).

28. A. Wiesemann, R. Zentel, T. Pakula, *Polymer* **33,** 5315 (1992).

29. G. Wilbert, R. Zentel, *Macromol. Chem. Phys.* **197,** 3259 (1996).

30. G. Wilbert, S. Traud, R. Zentel, *Macromol. Chem. Phys.* **198,** 3769 (1997).

31. A. Wiesemann, R. Zentel, G. Lieser, *Acta Polym.* **46,** 25 (1995).

32. I. Cuadrado, C. M. Casado, F. Lobete, B. Alonso, B. Gonzalez, J. Losada, U. Amador, *Organometallics* **18,** 4960 (1999).

33. N. C. Foulds, C. R. Lowe, *Anal. Chem.* **60,** 2473 (1988).

34. G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani, A. Canavesi, *Chem. Mater.* **7,** 2309 (1995).

35. G. Zotti, G. Schiavon, S. Zecchin, A. Berlin, G. Pagani, A. Canavesi, *Synth. Met.* **76,** 255 (1996).

36. E. W. Neuse, M. G. Meirim, D. D. N"Da, G. Caldwell, *J. Inorg. Organomet. Polym.* **9,** 221 (1999).

37. B. Schechter, G. Caldwell, E. W. Neuse, *J. Inorg. Organomet. Polym.* **10,** 177 (2000).

38. E. W. Neuse, *Macromol. Symp.* **172,** 127 (2001).

39. M. G. Meirim, E. W. Neuse, G. Caldwell, *J. Appl. Polym. Sci.* **73,** 2143 (1999).

40. G. Caldwell, M. G. Meirim, E. W. Neuse, K. Beloussow, W.-C. Shen, *J. Inorg. Organomet. Polym.* **10,** 93 (2000).

41. C. J. Neef, D. T. Glatzhofer, K. M. Nicholas, *J. Polym. Sci.: Part A, Polym. Chem.* **35,** 3365 (1997).

42. M. Buchmeiser, R. R. Schrock, *Macromolecules* **28,** 6642 (1995).

43. M. R. Buchmeiser, *Macromolecules* **30,** 2274 (1997).

44. M. R. Buchmeiser, N. Schuler, G. Kaltenhauser, K.-H. Ongania, I. Lagola, K. Wurst, H. Scottenberger, *Macromolecules* **31,** 3175 (1998).

45. K. Eder, E. Reichel, H. Scottenberger, C. G. Huber, M. R. Buchmeiser, *Macromolecules* **34,** 4334 (2001).

46. D. Albagli, G. Bazan, M. S. Wrighton, R. R. Schrock, *J. Am. Chem. Soc.* **114,** 4150 (1992).

47. D. Albagli, G. Bazan, R. R. Schrock, M. S. Wrighton, *J. Am. Chem. Soc.* **115,** 7328 (1993).

48. K. J. Watson, J. Zhu, S. T. Nguyen, C. A. Mirkin, *J. Am. Chem. Soc.* **121,** 462 (1999).

49. H. R. Allcock, K. D. Lavin, G. H. Riding, *Macromolecules* **18,** 1340 (1985).

50. H. R. Allcock, G. H. Riding, K. D. Lavin, *Macromolecules* **20,** 6 (1987).

51. R. A. Saraceno, G. H. Riding, H. R. Allcock, A. G. Ewing, *J. Am. Chem. Soc.* **110,** 7254 (1988).

52. I. Manners, G. H. Riding, J. A. Dodge, H. R. Allcock, *J. Am. Chem. Soc.* **111,** 3067 (1989).

53. H. R. Allcock, J. A. Dodge, I. Manners, G. H. Riding, *J. Am. Chem. Soc.* **113,** 9596 (1991).

54. P. Wisian-Neilson, R. R. Ford, *Organometallics* **6,** 2258 (1987).

55. P. Wisian-Neilson, R. R. Ford, *Macromolecules* **22,** 72 (1989).

56. T. Peckham, P. Nguyen, S. C. Bourke, Q. Wang, D. G. Harrison, P. Zoricak, C. Russell, L. M. Liable-Sands, A. L. Rheingold, A. J. Lough, I. Manners, *Organometallics* **20,** 3035 (2001).

57. C. U. Pittman Jr., *J. Poly. Sci. Part A1* **5,** 2927 (1967).

58. H. Plenio, J. Hermann, J. Leukel, *Eur. J. Inorg. Chem.* **12,** 2063 (1998).

59. H. Plenio, J. Hermann, A. Sehring, *Chem. Eur. J.* **6,** 1820 (2000).

60. V. V. Korshak, S. L. Sosin, V. P. Alekseeva, *Dokl. Akad. Nauk SSSR* **132,** 360 (1960).

61. A. N. Nesmeyanov, V. V. Korshak, N. S. Voevodskii, S. L. Kochetkova, S. L. Sosin, R. B. Materikova, T. N. Bolotnikova, V. M. Chibrikin, N. M. Bazhin, *Dokl. Akad. Nauk SSSR* **137,** 1370 (1961).

62. H. Rosenberg, E. W. Neuse, *J. Organomet. Chem.* **6,** 76 (1966).

63. H. Watanabe, I. Motoyama, K. Hata, *Bull. Chem. Soc. Jpn.* **39,** 790 (1966).

64. I. J. Spilners, J. P. Pellegrini, Jr., *J. Org. Chem.* **30,** 3800 (1965).

65. P. V. Roling, M. D. Rausch, *J. Org. Chem.* **37,** 729 (1972).

66. E. W. Neuse, L. Bednarik, *Macromolecules* **12,** 187 (1979).

67. P. Park, A. J. Lough, D. A. Foucher, *Macromolecules* **35,** 3810 (2002).

68. K. Sanechika, T. Yamamoto, A. Yamamoto, *Polym. J.* **13,** 255 (1981).

69. T. Yamamoto, K. Sanechika, A. Yamamoto, M. Katada, I. Motoyama, H. Sano, *Inorg. Chim. Acta* **73,** 75 (1983).

70. M. D. Rausch, *J. Org. Chem.* **28,** 3337 (1963).

71. E. W. Neuse, R. K. Crossland, *J. Organomet. Chem.* **7,** 344 (1967).

72. T. Hirao, M. Kurashina, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.* 2929 (1996).

73. C. U. Pittman, Jr., Y. Sasaki, *Chem. Lett.* 383 (1975).

74. F. W. Knobloch, W. H. Rauscher, *J. Polym. Sci.* **54,** 651 (1961).

75. C. U. Pittman, Jr., M. D. Rausch, *Pure Appl. Chem.* **58,** 617 (1986).

76. K. Gonslaves, M. D. Rausch, in *Inorganic and Organometallic Polymers*, M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, American Chemical Society, Washington, DC, 1988, p. 437.

77. K. Gonslaves, L. Zhan-ru, M. D. Rausch, *J. Am. Chem. Soc.* **106,** 3862 (1984).

78. K. E. Gonsalves, M. D. Rausch, *J. Polym. Sci.: Part A: Polym. Chem.* **26,** 2769 (1988).

79. K. E. Gonsalves, M. D. Rausch, *J. Polym. Sci.: Part A: Polym. Chem.* **24,** 1599 (1986).

80. Q.-D. Shen, S.-L. Ni, H.-S. Xu, C.-Z. Yang, *J. Appl. Polym. Sci.* **74,** 2674 (1999).

81. N. Najafi-Mohajeri, G. L. Nelson, R. Benrashid, *J. Appl. Polym. Sci.* **76,** 1847 (2000).

82. M. M. Abd-Alla, M. F. El-Zohry, K. I. Aly, M.M.M. Abd-El-Wahab, *J. Appl. Polym. Sci.* **47,** 323 (1993).

83. P. Singh, M. D. Rausch, R. W. Lenz, *Polym. Bull.* **22,** 247 (1989).

84. G. Wilbert, A. Wiesemann, R. Zentel, *Macromol. Chem. Phys.* **196,** 3771 (1995).

85. P. Kannan, S. Senthil, R. Vijayakumar, R. Marimuthu, *J. Appl. Polym. Sci.* **86,** 3494 (2002).

86. S. Senthil, P. Kannan, *J. Polym. Sci., Part A, Polym. Chem.* **39,** 2396 (2001).

87. S. Senthil, P. Kannan, *J. Appl. Polym. Sci.* **85,** 831 (2002).

88. L. Plummer, C. S. Marvel, *J. Polym. Sci., Part A* **2,** 2559 (1964).

89. J. E. Mulvaney, J. J. Bloomfield, C. S. Marvel, *J. Polym. Sci.* **62,** 59 (1962).

90. I. Yamaguchi, K. Osakada, T. Yamamoto, M. Katada, *Bull. Chem. Soc. Jpn.* **72,** 2557 (1999).

91. C. E. Carraher, Jr., P. J. Lessek, *Angew. Makromol. Chem.* **38,** 57 (1974).

92. C. E. Carraher, Jr., S. Jorgensen, P. J. Lessek, *J. Appl. Polym. Sci.* **20,** 2255 (1976).

93. W. J. Patterson, S. P. McManus, C. U. Pittman Jr., *J. Polym. Sci., Poly. Chem.* **12,** 837 (1974).

94. C. U. Pittman Jr., W. J. Patterson, S. P. McManus, *J. Polym. Sci., Part A1* **9,** 3187 (1971).

95. E. J. Houser, T. M. Keller, *Macromolecules* **31,** 4038 (1998).

96. R. J. P. Corriu, N. Devylder, C. Guerin, B. Henner, A. Jean, *Organometallics* **13,** 3194 (1994).

97. I. Yamaguchi, H. Ishii, T. Sakano, K. Osakada, T. Yamamoto, *Appl. Organomet. Chem.* **15,** 197 (2001).

98. J. Park, Y. Seo, S. Cho, D. Whang, K. Kim, T. Chang, *J. Organomet. Chem.* **489,** 23 (1995).

99. M. E. Wright, E. G. Toplikar, *Macromolecules* **25,** 6050 (1992).

100. M. E. Wright, M. S. Sigman, *Macromolecules* **25,** 6055 (1992).

101. M. E. Wright, E. G. Toplikar, H. S. Lackrita, J. Y. Kerney, *Macromolecules* **27,** 3016 (1994).

102. F. H. Kohler, A. Schell, B. Weber, *Chem. Eur. J.* **8,** 5219 (2002).

103. C. M. Casado, M. Moran, J. Losada, I. Cuadrado, *Inorg. Chem.* **34,** 1668 (1995).

104. C. E. Carraher, Jr., *Makromol. Chem.* **166,** 31 (1973).

105. C. E. Carraher, Jr., J. E. Sheats, *Makromol. Chem.* **166,** 23 (1973).

106. J. E. Sheats in C. E. Carraher, Jr., J. E. Sheats, C. U. Pittman, Jr., eds., *Organometallic Polymers,* Academic Press, New York, 1978, p. 87.

107. C. E. Carraher, Jr., G. F. Peterson, J. E. Sheats, T. Kirsch, *Makromol. Chem.* **175,** 3089 (1974).

108. C. U. Pittman, Jr., O. E. Ayers, S. P. McManus, J. E. Sheats, C. E. Whitten, *Macromolecules* **4,** 360 (1971).

109. C. U. Pittman, Jr., O. E. Ayers, B. Suryanarayanan, S. P. McManus, J. E. Sheats, *Makromol. Chem.* **175,** 1427 (1974).

110. T. Yamamoto, T. Morikita, T. Maruyama, K. Kubota, M. Katada, *Macromolecules* **30,** 5390 (1997).

111. T. Morikita, T. Mauyama, T. Yamamoto, K. Kubota, M. Katada, *Inorg. Chim. Acta* **269,** 310 (1998).

112. S. L. Ingham, M. S. Khan, J. Lewis, N. J. Long, P. R. Raithby, *J. Organomet. Chem.* **470,** 153 (1994).

113. M. Bochmann, J. Lu, R. D. Cannon, *J. Organomet. Chem.* **518,** 97 (1996).

114. R. Knapp, U. Velten, M. Rehahn, *Polymer* **39,** 5827 (1998).

115. G. E. Southard, M. D. Curtis, *Organometallics* **16,** 5618 (1997).

116. G. E. Southard, M. D. Curtis, *Organometallics* **20,** 508 (2001).

117. G. E. Southard, M. D. Curtis, *Synthesis* **9,** 1177 (2002).

118. K. Naka, T. Uemura, Y. Chujo, *Macromolecules* **33,** 6965 (2000).

119. M. Kurosawa, T. Nankawa, T. Matsuda, K. Kubo, M. Kurihara, H. Nishihara, *Inorg. Chem.* **38,** 5113 (1999).

120. P. Jutzi, N. Lenze, B. Neumann, H.-G. Stammler, *Angew. Chem. Int. Ed.* **40,** 1424 (2001).

121. A. Althoff, P. Jutzi, N. Lenze, B. Neumann, A. Stammler, H.-G. Stammler, *Organometallics* **21,** 3018 (2002).

122. M. Fontani, F. Peters, W. Scherer, W. Wachter, M. Wagner, P. Zanello, *Eur. J. Inorg. Chem.* 1453 (1998).

123. P. F. Brandt, T. B. Rauchfuss, *J. Am. Chem. Soc.* **114,** 1926 (1992).

124. C. P. Galloway, T. B. Rauchfuss, *Angew. Chem. Int. Ed. Eng.* **32,** 1319 (1993).

125. D. L. Compton, T. B. Rauchfuss, *Organometallics* **13,** 4367 (1994).

126. D. L. Compton, P. F. Brandt, T. B. Rauchfuss, D. F. Rosenbaum, C. F. Zukoski, *Chem. Mater.* **7,** 2342 (1995).

127. R. Rulkens, D. P. Gates, D. Balaishis, J. K. Pudelski, D. F. McIntosh, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **119,** 10976 (1997).

128. R. Resendes, P. Nguyen, A. J. Lough, I. Manners, *Chem. Commun.* 1001 (1998).

129. R. Resendes, J. M. Nelson, A. Fischer, F. Jakle, A. Bartole, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **123,** 2116 (2001).

130. J. M. Nelson, H. Rengel, I. Manners, *J. Am. Chem. Soc.* **115,** 7035 (1993).

131. J. M. Nelson, A. J. Lough, I. Manners, *Angew. Chem. Int. Ed. Engl.* **33,** 989 (1994).

132. J. M. Nelson, P. Nguyen, R. Petersen, H. Rengel, P. M. Macdonald, A. J. Lough, I. Manners, N. P. Raju, J. E. Greedan, S. Barlow, D. O'Hare, *Chem. Eur. J.* **3,** 573 (1997).

133. M. A. Buretea, T. D. Tilley, *Organometallics* **16,** 1507 (1997).

134. C. E. Stanton, T. R. Lee, H. R. Grubbs, N. S. Lewis, J. K. Pudelski, M. R. Callstrom, M. S. Erickson, M. L. McLaughlin, *Macromolecules* **28,** 8713 (1995).

135. R. W. Heo, F. B. Somoza, T. R. Lee, *J. Am. Chem. Soc.* **120,** 1621 (1998).

136. H. P. Withers, Jr., D. Seyferth, J. D. Fellmann, P. E. Garrou, S. Martin, *Organometallics* **1,** 1283 (1982).

137. C. H. Honeyman, D. A. Foucher, F. Y. Dahmen, R. Rulkens, A. J. Lough, I. Manners, *Organometallics* **14,** 5503 (1995).

138. C.E.B. Evans, A. J. Lough, H. Grondey, I. Manners, *New J. Chem.* **24,** 447 (2000).

139. T. J. Peckham, J. A. Massey, C. H. Honeyman, I. Manners, *Macromolecules* **32,** 2830 (1999).

140. T. Mizuta, M. Onishi, K. Miyoshi, *Organometallics* **19,** 5005 (2000).

141. H. Braunschweig, R. Dirk, M. Muller, P. Nguyen, R. Resendes, D. P. Gates, I. Manners, *Angew. Chem. Int. Ed. Engl.* **36,** 2338 (1997).

142. A. Berenbaum, H. Braunschweig, R. Dirk, U. Englert, J. C. Green, F. Jakle, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **122,** 5765 (2000).

143. F. Jakle, A. Berenbaum, A. J. Lough, I. Manners, *Chem. Eur. J.* **6,** 2762 (2000).

144. D. A. Foucher, M. Edwards, R. A. Burrow, A. J. Lough, I. Manners, *Organometallics* **13,** 4959 (1994).

145. N. P. Reddy, H. Yamashita, M. Tanaka, *J. Chem. Soc., Chem. Commun.* 2263 (1995).

146. T. J. Peckham, J. A. Massey, M. Edwards, I. Manners, D. A. Foucher, *Macromolecules* **29,** 2396 (1996).

147. R. N. Kapoor, G. M. Crawford, J. Mahmoud, V. V. Dementiev, M. T. Nguyen, A. F. Diaz, K. H. Pannell, *Organometallics* **14,** 4944 (1995).

148. L. Espada, K. H. Pannell, V. Papkov, L. Leites, S. Bukalov, I. Suzdalev, M. Tanaka, T. Hayashi, *Organometallics* **21,** 3758 (2002).

149. F. Jakle, R. Rulkens, G. Zech, J. A. Massey, I. Manners, *J. Am. Chem. Soc.* **122,** 4231 (2000).

150. H. K. Sharma, F. Cervantes-Lee, J. S. Mahmoud, K. H. Pannell, *Organometallics* **18,** 399 (1999).

151. R. Rulkens, A. J. Lough, I. Manners, *Angew. Chem. Int. Ed. Engl.* **35,** 1805 (1996).

152. F. Jakle, R. Rulkens, G. Zech, D. A. Foucher, A. J. Lough, I. Manners, *Chem. Eur. J.* **4,** 2117 (1998).

153. T. Baumgartner, F. Jakle, R. Rulkens, G. Zech, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **124,** 10062 (2002).

154. I. Manners, *Can. J. Chem.* **76,** 371 (1998).

155. I. Manners, *Chem. Commun.* 857 (1999).

156. K. Kulbaba, I. Manners, *Macromol. Rapid. Commun.* **22,** 711 (2001).

157. D. A. Foucher, B. Z. Tang, I. Manners, *J. Am. Chem. Soc.* **114,** 6246 (1992).

158. R. Rulkens, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **116,** 797 (1994).

159. Y. Ni, R. Rulkens, J. K. Pudelski, I. Manners, *Makromol. Chem. Rapid Commun.* **16,** 637 (1995).

160. J. Rasburn, D. A. Foucher, W. F. Reynolds, I. Manners, G. J. Vancso, *Chem. Commun.* 843 (1998).

161. J. Rasburn, R. Petersen, T. Jahr, R. Rulkens, I. Manners, G. J. Vancso, *Chem. Mater.* **7,** 871 (1995).

162. I. Manners, *Polyhedron* **15,** 4311 (1996).

163. K. Temple, F. Jakle, J. B. Sheridan, I. Manners, *J. Am. Chem. Soc.* **123,** 1355 (2001).

164. H. Yim, M. D. Foster, D. Balaishis, I. Manners, *Langmuir* **14,** 3921 (1998).

165. K. N. Power-Billard, T. J. Peckham, A. Butt, F. Jakle, I. Manners, *J. Inorg. Organomet. Polym.* **10,** 159 (2000).

166. D. L. Zechel, K. C. Hultzsch, R. Rulkens, D. Balaishis, Y. Ni, J. K. Pudelski, A.J. Lough, I. Manners, *Organometallics* **15,** 1972 (1996).

167. P. Nguyen, G. Stojcevic, K. Kulbaba, M. J. MacLachlan, X.-H. Liu, A. J. Lough, I. Manners, *Macromolecules* **31,** 5977 (1998).

168. A. Berenbaum, A. Lough, I. Manners, *Organometallics* **21,** 4415 (2002).

169. K. N. Power-Billard, I. Manners, *Macromolecules* **33,** 26 (2000).

170. F. Jakle, Z. Wang, I. Manners, *Macromol. Rapid. Commun.* **21,** 1291 (2000).

171. Z. Wang, A. Lough, I. Manners, *Macromolecules* **35,** 7669 (2002).

172. M. A. Hempenius, G. J. Vancso, *Macromolecules* **35,** 2445 (2002).

173. M. A. Hempenius, M. Peter, N. S. Robins, E. S. Kooij, G. J. Vancso, *Langmuir* **18,** 7629 (2002).

174. M. A. Hempenius, N. S. Robins, R.G.H. Lammertink, G. J. Vancso, *Macromol. Rapid Commun.* **22,** 30 (2001).

175. K. Power-Billard, I. Manners, *Macromol. Rapid Commun.* **23,** 607 (2002).

176. J. Halfyard, J. Galloro, M. Ginzburg, Z. Wang, N. Coombs, I. Manners, G. A. Ozin, *Chem. Commun.* 1746 (2002).

177. K. C. Hultzsch, J. M. Nelson, A. J. Lough, I. Manners, *Organometallics* **14,** 5496 (1995).

178. R. Rulkens, Y. Ni, I. Manners, *J. Am. Chem. Soc.* **116,** 12121 (1994).

179. L. Cao, I. Manners, M. A. Winnik, *Macromolecules* **34,** 3353 (2001).

180. L. Cao, I. Manners, M. A. Winnik, *Macromolecules* **35,** 8258 (2002).

181. J. Raez, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **124,** 10381 (2002).

182. J. Raez, I. Manners, M. A. Winnik, *Langmuir* **18,** 7229 (2002).

183. J. A. Massey, K. Temple, L. Cao, Y. Rharbi, J. Raez, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **122,** 11577 (2000).

184. X. S. Wang, M. A. Winnik, I. Manners, *Macromol. Rapid. Commun.* **23,** 210 (2002).

185. H. B. Eitouni, N. P. Balsara, H. Hahn, J. A. Pople, M. A. Hempenius, *Macromolecules* **35,** 7665 (2002).

186. R.G.H. Lammertink, M. A. Hempenius, G. J. Vancso, *Langmuir* **16,** 6245 (2000).

187. R.G.H. Lammertink, M. A. Hempenius, G. J. Vancso, K. Shin, M. H. Rafailovich, J. Sokolov, *Macromolecules* **34,** 942 (2001).

188. J. Massey, K. N. Power, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **120,** 9533 (1998).

189. J. A. Massey, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **123,** 3147 (2001).

190. Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **118,** 4102 (1996).

191. X. S. Wang, M. A. Winnik, I. Manners, *Macromolecules* **35,** 9146 (2002).

192. K. Temple, S. Dziadek, I. Manners, *Organometallics* **21,** 4377 (2002).

193. R. Resendes, J. Massey, H. Dorn, K. N. Power, M. A. Winnik, I. Manners, *Angew. Chem. Int. Ed. Engl.* **38,** 2570 (1999).

194. R. Resendes, J. A. Massey, K. Temple, L. Cao, K. N. Power-Billard, M. A. Winnik, I. Manners, *Chem. Eur. J.* **7,** 2414 (2001).

195. R. Resendes, J. Massey, H. Dorn, M. A. Winnik, I. Manners, *Macromolecules* **33,** 8 (2000).

196. R.G.H. Lammertink, M. A. Hempenius, V.Z.-H. Chan, E. L. Thomas, G. J. Vancso, *Chem. Mater.* **13,** 429 (2001).

197. R.G.H. Lammertink, M. A. Hempenius, J. E. van den Enk, V.Z.-H. Chan, E. L. Thomas, G. J. Vancso, *Adv. Mater.* **12,** 98 (2000)

198. L. I. Espada, M. Shadaram, J. Robillard, K. Pannell, *J. Inorg. Organomet. Polym.* **10,** 169 (2000).

199. H. M. Nugent, M. Rosenblum, P. Klemarczky, *J. Am. Chem. Soc.* **115,** 3848 (1993).

200. M. Rosenblum, H. M. Nugent, K.-S. Jang, M. M. Labes, W. Cahalane, P. Klemarczyk, W. M. Reiff, *Macromolecules* **28,** 6330 (1995).

201. R.D.A. Hudson, B. M. Foxman, M. Rosenblum, *Organometallics* **18,** 4098 (1999).

202. T. Kuhlmann, S. Roth, J. Roziére, W. Siebert, *Angew. Chem. Int. Ed. Engl.* **25,** 105 (1986).

203. T. Kuhlmann, S. Roth, J. Roziére, W. Siebert, U. Zenneck, *Synth. Met.* **19,** 757 (1987).

204. W. Siebert, *Pure Appl. Chem.* **60,** 1345 (1988).

205. X. Meng, M. Sabat, R. N. Grimes, *J. Am. Chem. Soc.* **115,** 6143 (1993).

206. X. Wang, M. Sabat, R. N. Grimes, *J. Am. Chem. Soc.* **117,** 12227 (1995).

207. T. J. Katz, A. Sudhakar, M. F. Teasley, A. M. Gilbert, W. E. Geiger, M. P. Robben, M. Wuensch, M. D. Ward, *J. Am. Chem. Soc.* **115,** 3182 (1993).

208. Q. Sun, J.W.Y. Lam, K. Xu, H. Xu, J.A.K. Cha, P.C.L. Wong, G. Wen, X. Zhang, X. Jing, F. Wang, B. Z. Tang, *Chem. Mater.* **12,** 2617 (2000).

209. M. J. MacLachlan, I. Manners, G. A. Ozin, *Adv. Mater.* **12,** 675 (2000).

210. J. Galloro, M. Ginzburg, H. Miguez, S. M. Yang, N. Coombs, A. Safa-Sefat, J. E. Greedan, I. Manners, G. A. Ozin, *Adv. Funct. Mater.* **12,** 382 (2002).

211. M. J. MacLachlan, A. J. Lough, I. Manners, *Macromolecules* **29,** 8562 (1996).

212. K. Kulbaba, M. J. MacLachlan, C. E. B. Evans, I. Manners, *Macromol. Chem. Phys.* **202,** 1768 (2001).

213. K. Kulbaba, R. Resendes, A. Cheng, A. Bartole, A. Safa-Sefat, N. Coombs, H.D.D. Stover, J. E. Greedan, G. A. Ozin, I. Manners, *Chem. Mater.* **13,** 732 (2001).

214. K. Kulbaba, A. Cheng, A. Bartole, A. Breenberg, R. Resendes, N. Coombs, A. Safa-Sefat, J. E. Greedan, H.D.H. Stover, G. A. Ozin, I. Manners, *J. Am. Chem. Soc.* **124,** 12522 (2002).

215. S. Nlate, J. Ruiz, J.-C. Blais, D. Astruc, *Chem. Commun.* 417 (2000).

216. C. Valerio, J.-L. Fillaut, J. Ruiz, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **119,** 2588 (1997).

217. E. Alonso, C. Valerio, J. Ruiz, D. Astruc, *New J. Chem.* **21,** 1139 (1997).

218. S. Nlate, J. Ruiz, V. Sartor, R. Navarro, J.-C. Blais, D. Astruc, *Chem. Eur. J.* **6,** 2544 (2000).

219. I. Cuadrado, M. Moran, C. M. Casado, B. Alonso, F. Lobete, B. Garcia, M. Ibisate, J. Losada, *Organometallics* **15,** 5278 (1996).

220. R. Castro, I. Cuadrado, B. Alonso, C. M. Casado, M. Moran, A. E. Kaifer, *J. Am. Chem. Soc.* **119,** 5760 (1997).

221. I. Cuadrado, C. M. Casado, B. Alonso, M. Moran, J. Losada, V. Belsky, *J. Am. Chem. Soc.* **119,** 7613 (1997).

222. C. M. Casado, B. Gonzalez, I. Cuadrado, B. Alonso, M. Moran, J. Losada. *Angew. Chem., Int. Ed.* **39,** 2135 (2000).

223. R. Deschenaux, E. Serrano, A.-M. Levelut, *Chem. Commun.* 1577 (1997).

224. B. Dardel, R. Deschenaux, M. Even, E. Serrano, *Macromolecules* **32,** 5193 (1999).

225. C.-F. Shu, H.-M. Shen, *J. Mater. Chem.* **7,** 47 (1997).

226. P. Gomez-Elipe, R. Resendes, P. F. Macdonald, I. Manners, *J. Am. Chem. Soc.* **120,** 8348 (1998).

CHAPTER 3

Polymers Containing 4-, 5-, and 6-Membered Rings π-Coordinated to Metallic Moieties

CONTENTS

I. INTRODUCTION

Polymers containing 4-, 5-, and 6-membered rings coordinated to metallic moieties have been the focus of numerous studies in light of their interesting properties and applications. The π coordination of organometallic moieties to arenes activated these complexes toward nucleophilic substitution reactions. Linear organometallic polymers containing arene complexes in their backbones were prepared via substitution reactions of dihaloarene complexes with dinucleophilic reagents (**1**). Polycondensation reactions were also implemented in the production of linear polymeric materials (**2**). While these two routes provide organometallic polymers with arene complexes as integral parts of their backbones, polymers with sidechain-coordinated arene complexes were also prepared (**3**). These classes of polymers were produced via the polymerization of their corresponding organometallic monomers; however, organometallic polymers containing arene complexes could also be prepared via the coordination of metallic moieties to preexisting polymeric materials (**4**).
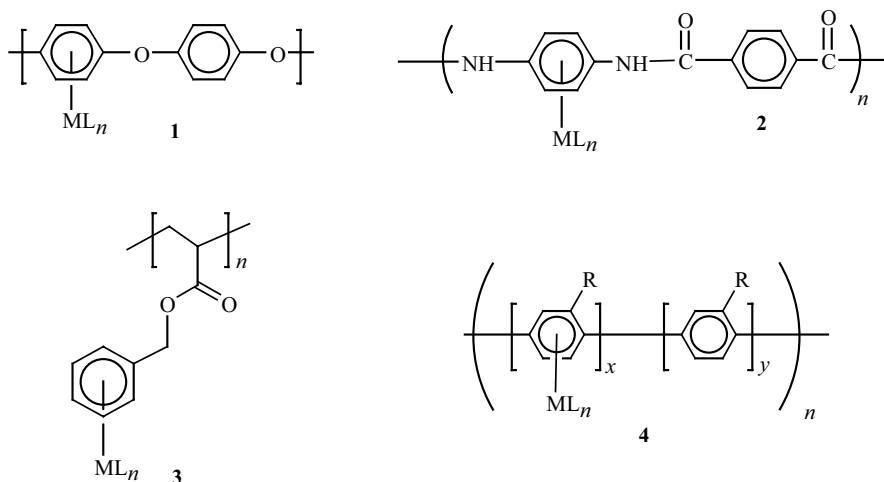
In Chapter 2, the chemistry of metallocene-based polymers was reviewed. Herein, other classes of polymers containing cyclopentadienyl rings coordinated to transition metal moieties are described (**5**). The chemistry of polymers containing 4-membered rings coordinated to transition metal moieties has been investigated; however, there are fewer reports on the synthesis and characterization of this type of polymer (**6**). Within each of these classes of polymers, the synthesis of dendrimeric and/or star-shaped polymers will also be highlighted.
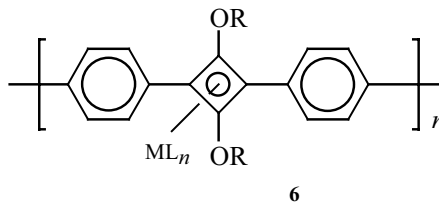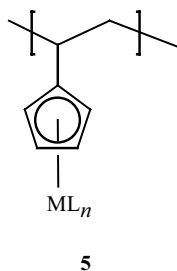
II. POLYMERS CONTAINING ARENE COMPLEXES

A. Pendent to the Backbone

Eyring and coworkers have reported the synthesis of organometallic poly (*p*-phenylenes) (PPPs) via reaction of the organic polymer (**7**) with $M(CO)_3(CH_3CN)_3$ or $M(CO)_6$ (M=Cr, Mo).[1,2] Molybdenum tricarbonyl was complexed to about 25% of the aromatic rings in the polymer (**9**). The structures of these polymers are similar to those shown in Scheme 1. Photoacoustic infrared spectroscopy showed that the C–O stretching frequencies shifted on complexation to 1890 and 1965 cm^{-1} from ~2000 cm^{-1} in $Mo(CO)_3$, which is indicative of donation of electron density to the molybdenum from the polymer backbone. This in turn weakened the metal–carbonyl bonds through donation to the carbonyl π^* orbitals. There were also peaks in the spectra of the metallated polymers that were consistent with poly(*p*-phenylene) and conducting poly(*p*-phenylene) doped with potassium. The conductivity of the $Mo(CO)_3$-coordinated polymer was ~10^{-4} S/cm, and was much higher than that observed for undoped PPP (~10^{-8} S/cm).[2]

Nishihara and coworkers subjected poly(*n*-hexylphenylene) (PHP) to ligand exchange reactions to give molybdenum tricarbonyl and cyclopentadienyliron coordinated polymers as shown in Scheme 1.[3–6] These hexyl-substituted polymers displayed better solubility than metallated PPP in organic solvents as a result of the flexible alkyl chains on its backbone. Elemental analysis of the $Mo(CO)_3$-functionalized polymer showed that 1 in every 4.8 aromatic rings was coordinated to a metallic moiety.[3,4] A $Cr(CO)_3$-coordinated poly(*n*-butylphenylene) (PBP) was also synthesized. This ligand exchange reaction was less efficient when $Mo(CO)_3$ was used.[3] In the case of the organoiron polymer, one in every 1.6 aromatic rings of the complexed PHP was coordinated to a cyclopentadienyliron moiety.[5] Spectroelectrochemical measurements of this organoiron polymer indicated the formation of a network between aromatic rings of neighboring polymer chains after reduction of the cationic iron centers to neutral radicals. Electrochemical and spectroscopic analysis of the organic and organometallic polymers showed that their conductivity increased on metal coordination.
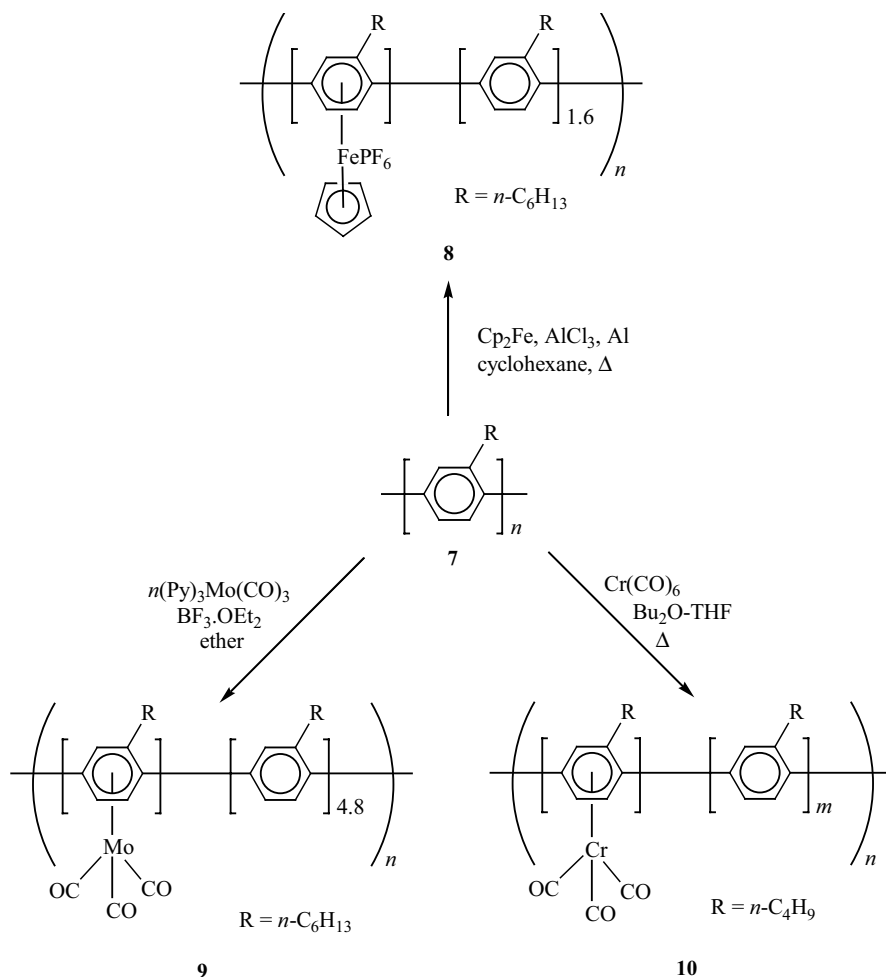
Scheme 1

Jin and Kim reported the synthesis of polyamides coordinated to chromium tricarbonyl moieties (**11**) by condensation of (η^6-phenylenediamine)Cr(CO)$_3$ (**12**) with various diacid chlorides (**13**) (Scheme 2).[7] It was noted that this polymer exhibited enhanced solubility due to incorporation of pendent chromium tricarbonyl moieties along its backbone. The viscosities of these polymers were determined in concentrated sulfuric acid or *N,N*-dimethylacetamide containing 5% LiCl. The inherent viscosities of these metallated polymers ranged from 0.72 to 1.53 dL/g, and were found to be higher than those of their organic analogs.

Dembek and coworkers have reported that high MW polyamides coordinated to Cr(CO)$_3$, such as **16** (shown in Scheme 3) display nematic liquid crystalline texture. This indicated that the rigid-rod nature of the 1,4-phenylene bridged polymer was retained on metal coordination even though its solubility was enhanced significantly.[8] The intrinsic

viscosities of these polymers were in the range of 4.5 dL/g, and GPC using a viscosity detector gave an absolute weight average molecular weight of 78,000. It was also demonstrated that the copolymer (**18**) exhibited enhanced solubility and liquid crystallinity.
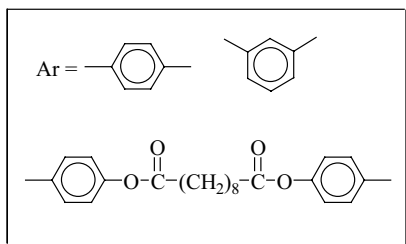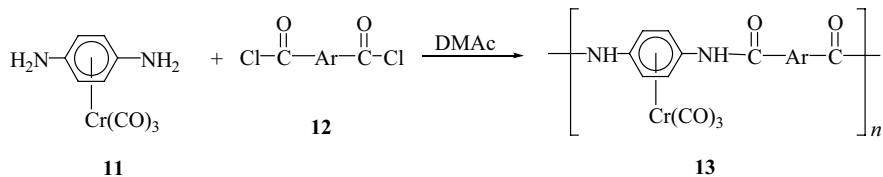
Scheme 2
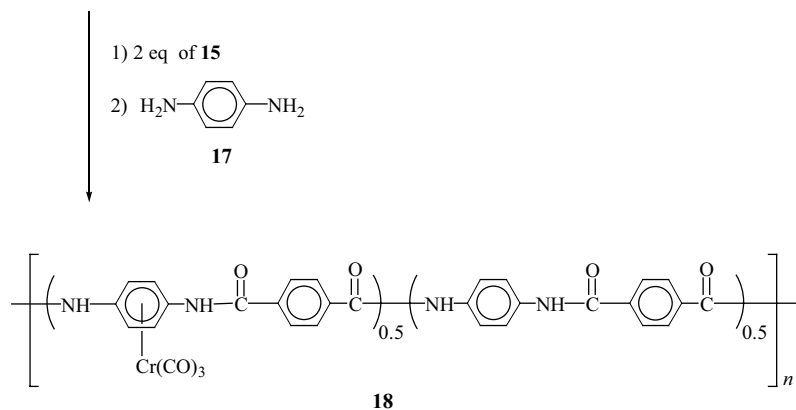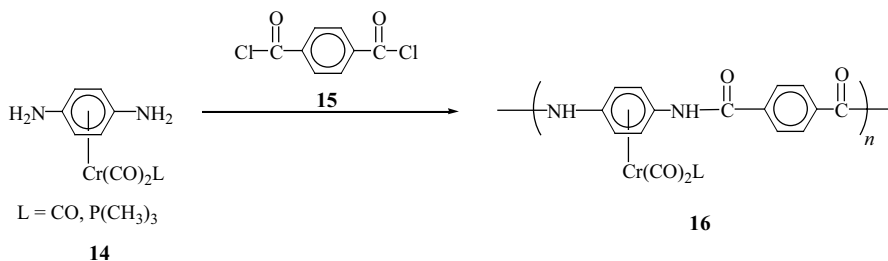
Scheme 3

Wright examined the synthesis of different classes of chromium tricarbonyl-coordinated polymers. Poly(phenyl ethynyl)s coordinated to chromium tricarbonyl moieties (**21, 23**) were synthesized by palladium catalyzed cross-coupling of (η^6-1,4-dichloroarene)tricarbonyl chromium complexes with organostannane reagents (Scheme 4).[9,10] Combustion analysis of these polymers indicated that their degree of polymerization was ~18, which corresponds to a MW of ~7800. Combustion and IR analysis of polymers that were heated above 200°C indicated that crosslinking reactions occurred followed by loss of carbon monoxide from the Cr(CO)$_3$ moieties.
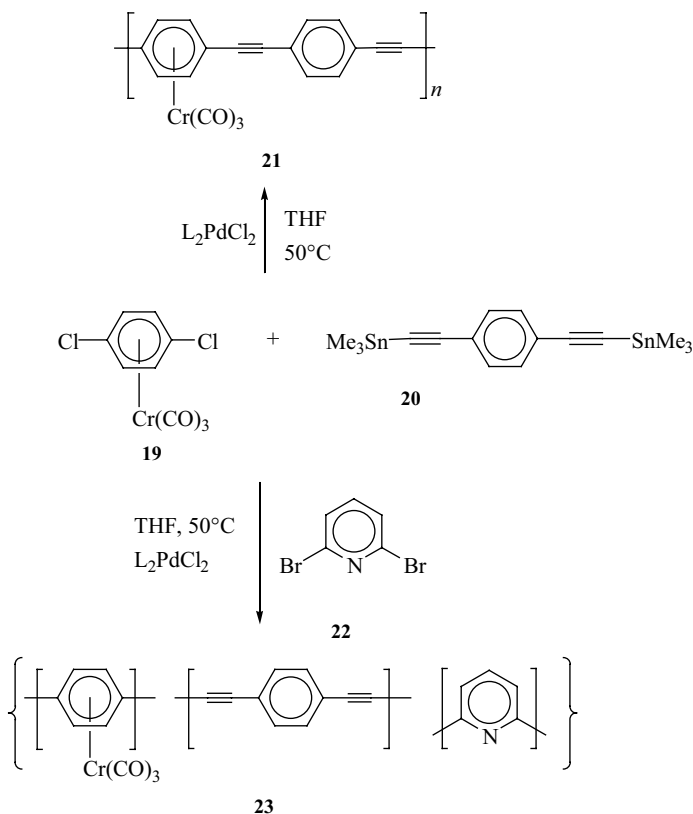
Scheme 4

In the 1970s, Pittman showed that linear organic polymers containing (η^6-aryl) Cr(CO)$_3$ and (η^4-diene)Fe(CO)$_3$ functions decomposed photochemically or thermally to produce small metal oxide particles (Cr$_2$O$_5$ or Fe$_2$O$_3$) dispersed in polymer matrices that had been crosslinked.[11,12] This represented one of the first ways to "synthesize" tiny metal oxide particles within polymers in contrast with grinding metal oxides and then mixing them into monomers and polymers.

Chujo and coworkers described the synthesis of chromium tricarbonyl coordinated polymers (**27**) via reaction of the 1,4-diethynylbenzene complex (**24**) with various 3-alkyl-2,5-dibromothiophenes (**25**) as shown in Scheme 5.[13] These polymers had fairly broad polydispersities (3.2-3.6) and weight-average molecular weights from 13,500 to 24,400. Thermogravimetric analysis in air showed two weight loss steps corresponding to dissociation of the chromium tricarbonyl and decomposition of the polymer backbones. The UV spectra of these polymers showed that they absorbed between 375 and 386 nm, and on excitation at 370 nm, these materials had weak emissions at 450 nm. Cyclic voltammetry showed one irreversible oxidation step at about 1.5 V for the dodecyl substituted polymer and its electrical conductivity was 8.1×10^{-6} S/cm.[13]
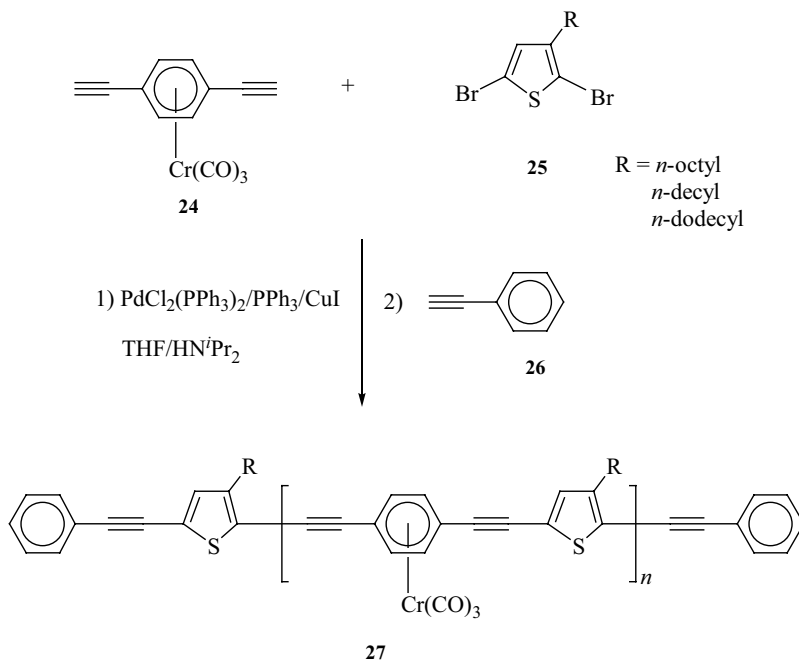
Scheme 5

A polyimine containing chromium tricarbonyl moieties pendent to aromatic rings in the backbone was prepared by the reaction of η^6-terephthaldialdehyde-$Cr(CO)_3$ with 1,3-phenylenediamine.[14] The resulting conjugated polyimine was insoluble in common organic solvents because of the rigidity of its backbone. The synthesis of polyether/imines coordinated to cyclopentadienyliron moieties has also been reported.[15] These polymers were prepared by reaction of a dialdehyde complex of cyclopentadienyliron with a number of aliphatic and aromatic diamines as shown in Scheme 6. The resulting polyimines exhibited good solubility in polar aprotic solvents such as DMF and DMSO (dimethylformamide and dimethylsulfoxide).

Thermogravimetric analysis indicated the presence of two distinct weight loss steps corresponding to loss of the organoiron groups and degradation of the polymer backbones. It was interesting to note that the cyclopentadienyliron moieties were cleaved at approximately 350°C for the polymers with long aliphatic spacers (4–12 CH_2 groups) in their backbones, and at about 250°C for the more rigid polymers.[15,16]
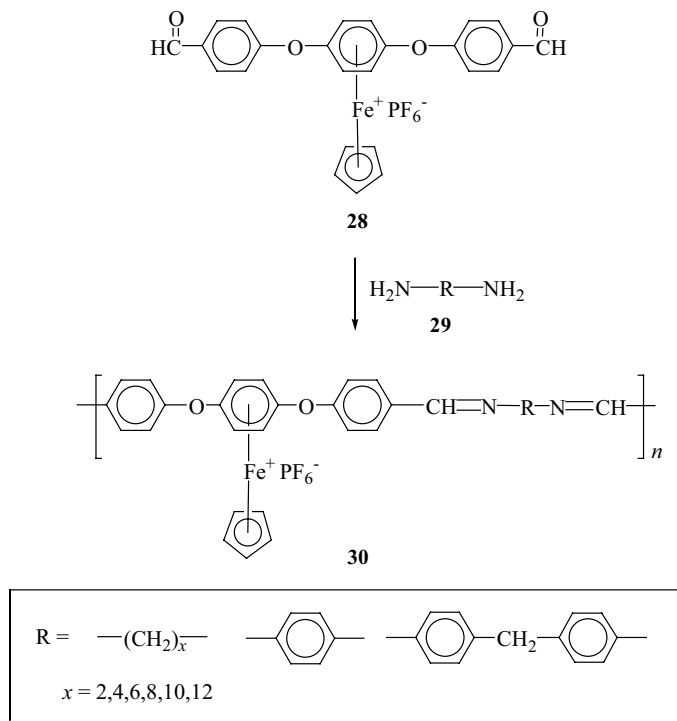
Scheme 6

Polymers with pendent chromium tricarbonyl moieties and rhodium complexes in their backbone were prepared via coordination of phosphine complexes (**31**) to a Rh-containing complex (**32**) as shown in Scheme 7.[17] The resulting polymers (**33**) precipitated from solution over time and their molecular weights were not obtained due to their thermal decomposition and air sensitivity.
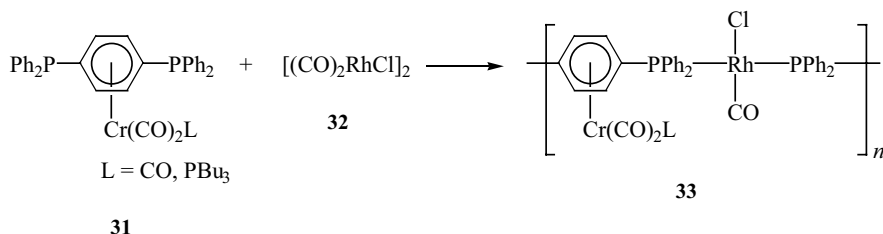
Scheme 7

It is well established that the π coordination of transition metal moieties to chloroarenes activates these materials toward nucleophilic substitution and addition reactions.[18,19] The π-coordinated metal moiety can stabilize negative charge buildup caused by an incoming nucleophile that is attacking the aryl ring, converting it into a metal-coordinated cyclo-*hexa*-dienyl anion. This lowers the activation energy for nucleophilic aromatic substitution, enhancing the reaction rate and making polymerization reactions via this route feasible. The synthesis of aromatic ether complexes of cyclopentadienyliron has been achieved in a stepwise manner to produce polymers with up to 35 metallic moieties pendent to their backbones.[20] The strategy used to prepare this class of polymer is shown in Scheme 8. Each mol of complex containing two chloro substituents was reacted with 0.5 mol of hydroquinone (**35**) in the presence of potassium carbonate to eventually yield the high molecular weight polymers. The organometallic polymer (**38**) had a calculated molecular weight of 15,800, which was consistent with its elemental analysis.
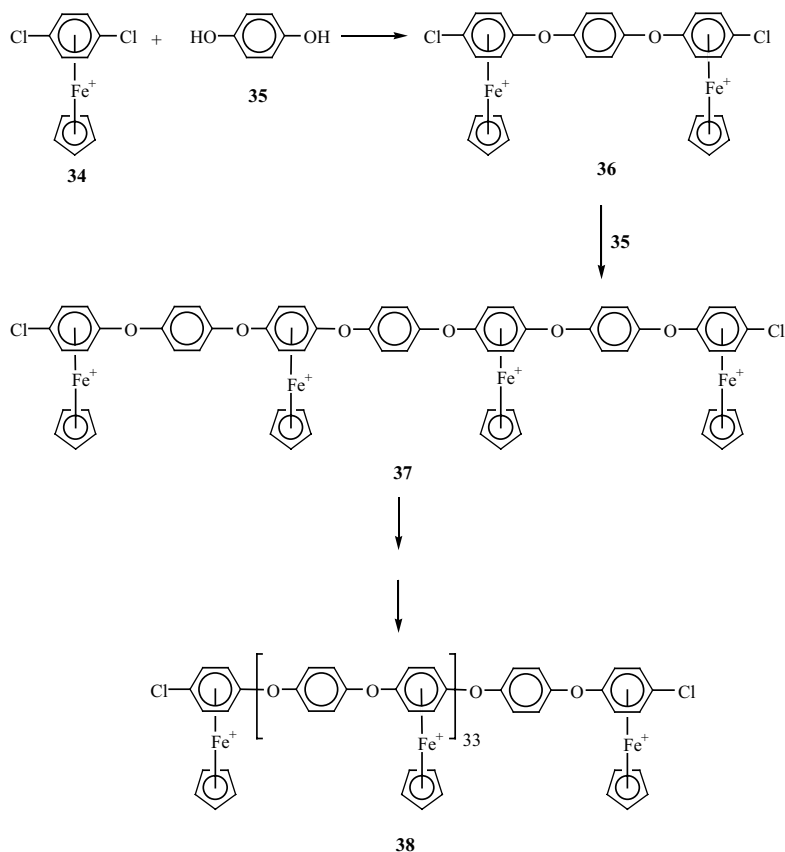
Scheme 8

The cyclopentadienyliron-coordinated polyethers shown (**39**) in Scheme 9 were reacted with sodium cyanide, resulting in the isolation of one isomer of adduct (**40**).[21] These neutral adducts were subsequently demetallated by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to yield the nitrile functionalized polyaromatic ethers (**41**).
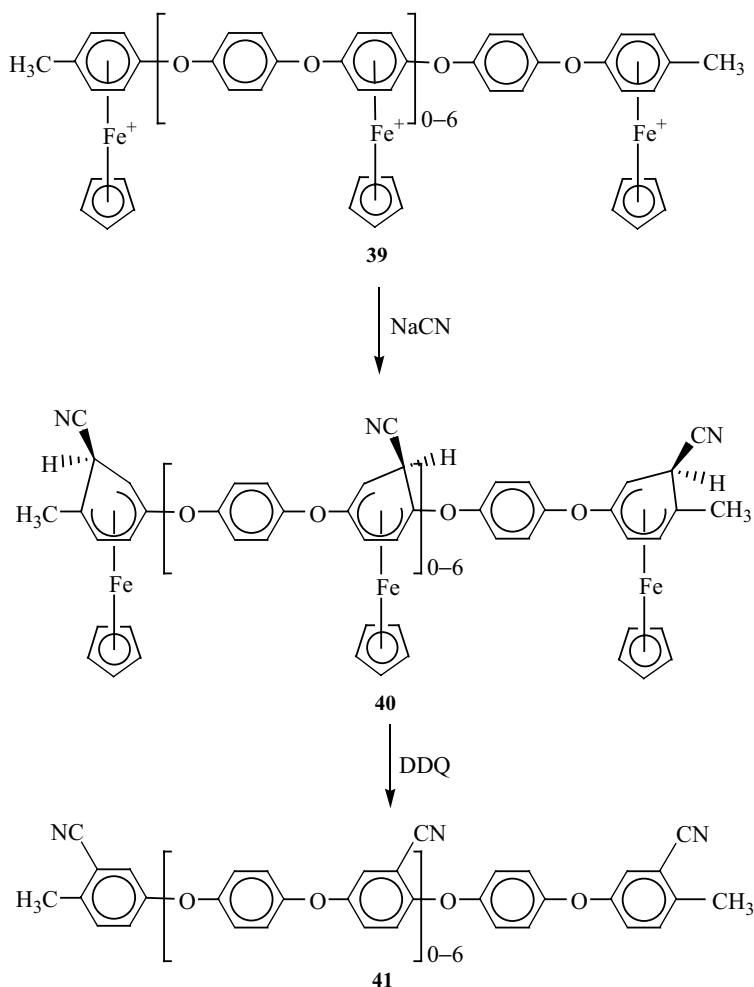
Scheme 9

Soluble polyaromatic ethers coordinated to cyclopentadienylruthenium cations (**44**) were first reported by Segal.[22] These polymers were synthesized by nucleophilic aromatic substitution of dichloroareneruthenium complexes with diphenolic compounds as shown in Scheme 10.
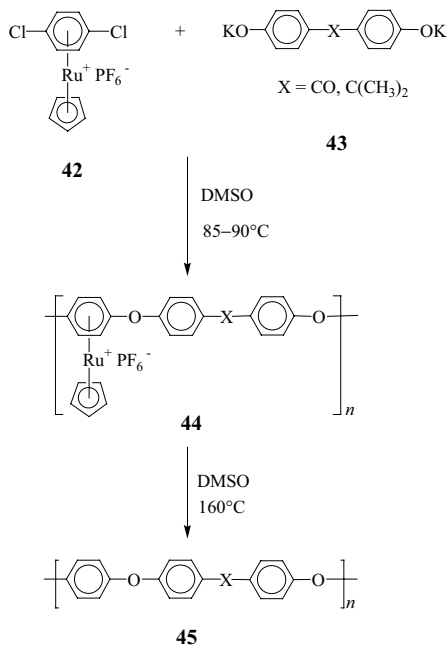
Scheme 10

Dembek et al. later prepared polyaromatic ethers and thioethers coordinated to pentamethylcyclopentadienylruthenium moieties (Scheme 11).[23,24] The inherent viscosities of the polymer solutions (0.5%) were measured in DMF to be between 0.52 and 1.49 dL/g. Lithium chloride was added to these ruthenium-based polymers (**48**) in order to suppress polyelectrolyte effects.
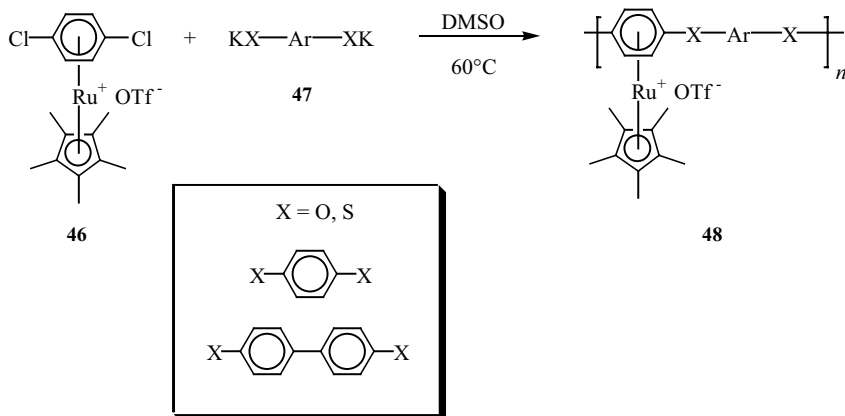
Scheme 11

The synthesis of soluble polyaromatic ethers, thioethers, and amines by S_NAr reactions of dichloroarene complexes of cyclopentadienyliron with oxygen-, sulfur-, and nitrogen-based dinucleophiles has also been examined by Abd-El-Aziz and coworkers.[25–27] Scheme 12 shows the synthesis of cyclopentadienyliron-coordinated polymers via reaction of the dichloroarene complex **34** with dinucleophiles **49** in the presence of potassium carbonate.[27] It was found that all cyclopentadienyliron-coordinated polymers (**50**) displayed good solubility in polar organic solvents. Photolytic demetallation of the polymers was achieved in acetonitrile solutions by irradiating the polymers with a light source. Irradiation of the complexes results in its excitation to the triplet state, resulting in ring slippage from η^6 to η^4. Coordination of this unstable complex to the solvent eventually results in the formation of $[CpFe(NCCH_3)_3]^+$, which then decomposes to produce ferrocene and various iron salts. Following photolysis, only some of the organic analogs (**51**) were soluble in common organic solvents. Solubility was enhanced in the polymers that had aliphatic groups in their backbones, and the soluble portions of these organic polymers had weight-average molecular weights ranging from 7300 to 21,400. Enhanced solubility was also achieved by utilizing 1,2- and 1,3-dichlorobenzene complexes in the polymerization reactions.[27]

Electrochemical analysis of the organoiron polymers showed that these materials underwent reversible reduction steps.[28] Figure 1 shows the cyclic voltammogram of one of the cyclopentadienyliron-coordinated polyaromatic thioethers obtained at $-30°C$ with a scan rate of 2 V/s. The half-wave potential of this polymer in propylene carbonate was -0.85 V.

The effects of various aromatic and aliphatic spacers on the thermal stability and glass transition temperature of these materials were examined.[27] These polymers displayed excellent thermal stability after the loss of the metallic moieties. Figure 2 shows the thermograms of a metallated and demetallated polyphenylene sulfide. The organometallic polymer underwent an initial weight loss starting at 245°C, corresponding to decomposition of the cyclopentadienyliron moieties from the polymer backbones and a second weight loss beginning at 511°C, corresponding to degradation of the polymer backbone. The organic analog of this polymer only shows one weight loss step beginning at 512°C. Differential scanning calorimetry showed that the polymers with oxygen spacers had the highest glass transition temperatures, while those with aliphatic thioether spacers possessed the lowest T_g values.

The synthesis of polymers containing alternating ether–thioether or amine–thioether bridges was also reported.[27] All of these organoiron polymers displayed good solubility in organic solvents; however, if the cyclopentadienyliron moieties were cleaved from the polymer backbones, polymer **53** became insoluble while polymer **55** still displayed good solubility (Scheme 13). The polymer isolated following photolytic removal of the iron complexes from **55** had a weight-average molecular weight of 21,700 and a polydispersity of 2.4.
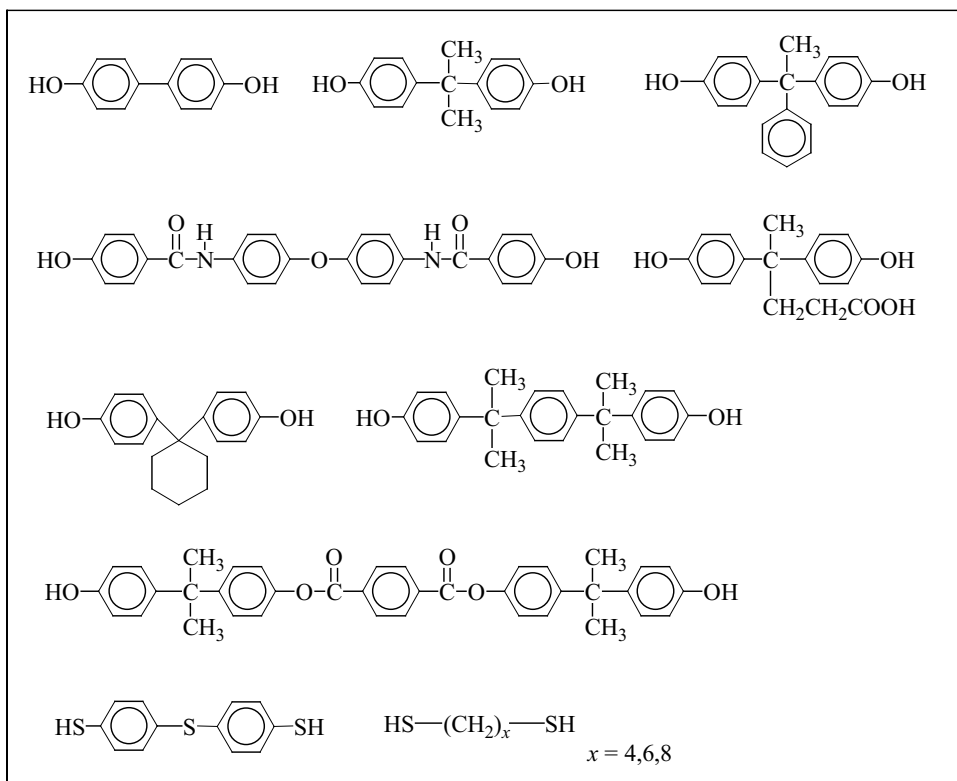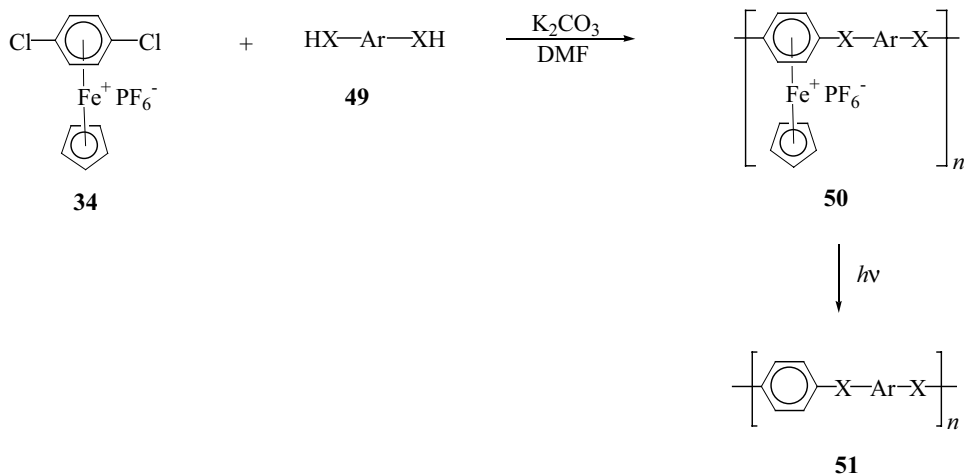
Scheme 12
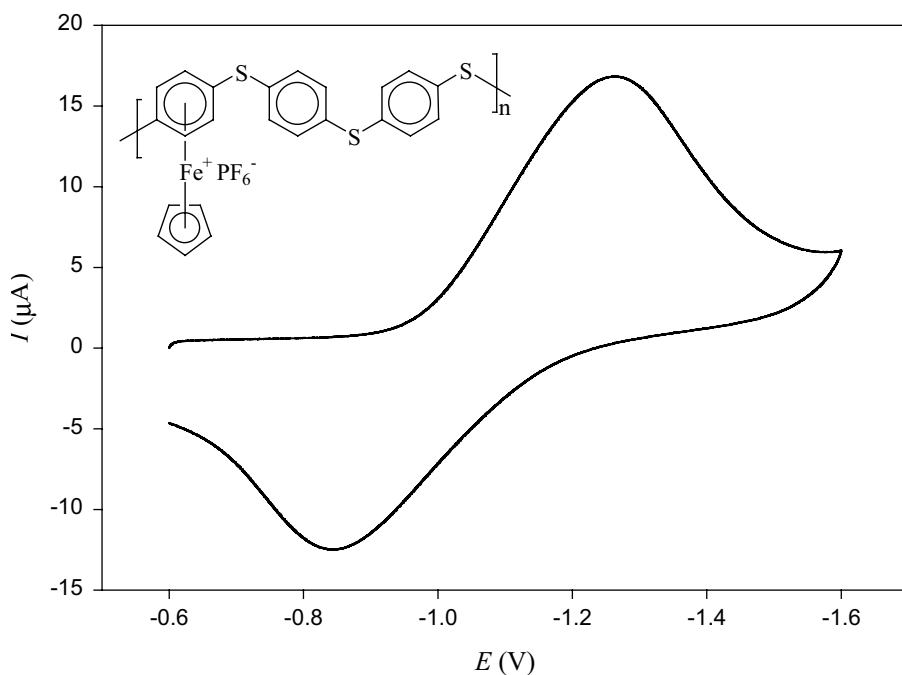
Figure 1. Cyclic voltammogram of organoiron polyphenylene sulfide obtained at −30°C in propylene carbonate with a scan rate of 2 V/s.
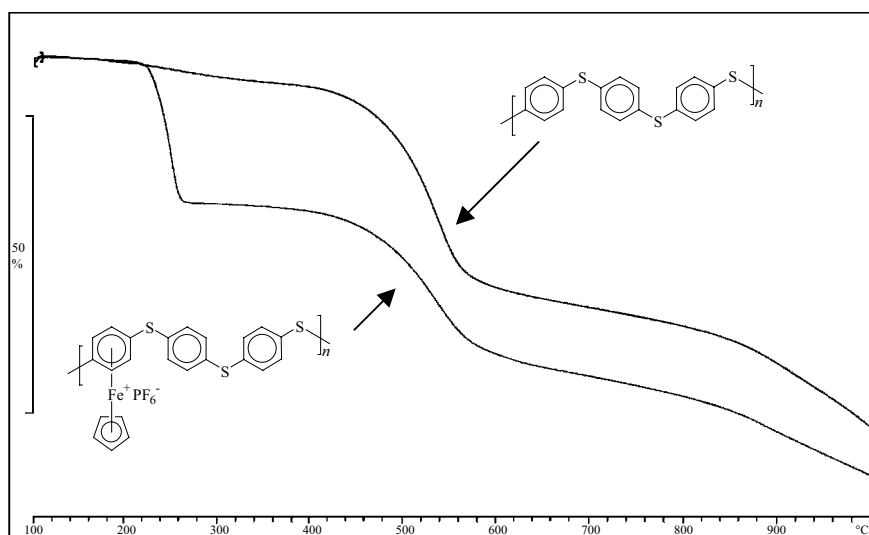
Figure 2. TGA thermograms of cyclopentadienyliron-coordinated polyphenylene sulfide and its organic analogue.

53

$HS(C_6H_4)S(C_6H_4)SH$

52

36

$HS(CH_2)_8SH$

54

55
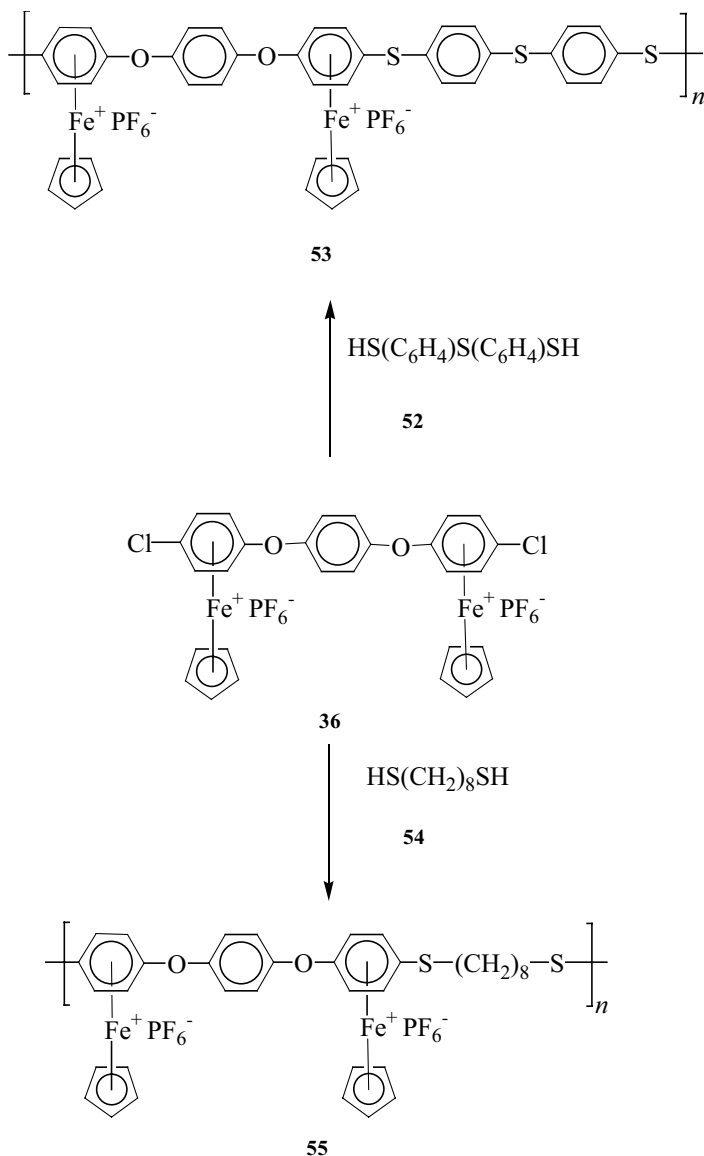
Scheme 13

Abd-El-Aziz and coworkers have also reported the preparation of organoiron polymers containing azobenzene chromophores in their sidechains.[29] Scheme 14 shows the synthesis of orange and red-colored cationic polymers (**58**) that absorbed between 417 and 489 nm. Polymers **58** were subsequently demetallated to produce their corresponding organic analogs (**59**). Photolysis of polymers **59** in the presence of hydrogen peroxide resulted in the decoloration of these polymers.
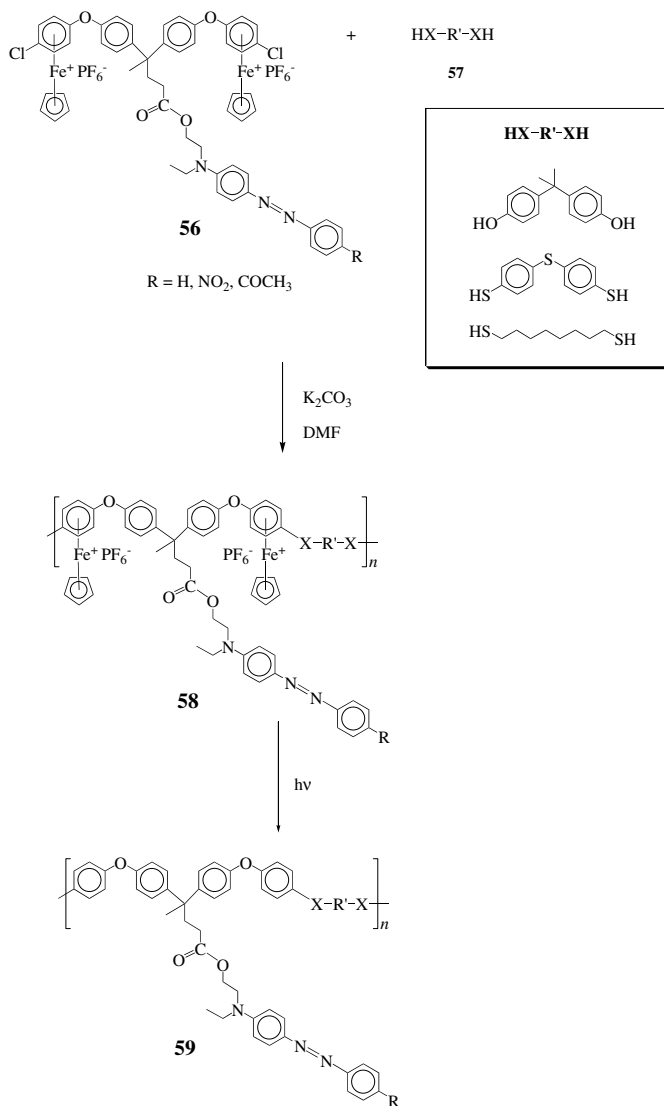
Scheme 14

The synthesis of polymers such as **60** (Scheme 15), which contain backbone arenes coordinated to both CpFe$^+$ and Cp*Ru$^+$, has also been reported.[30,31] A number of oligomers and polymers were synthesized by reaction of dichloroarene complexes of iron and ruthenium with oxygen, sulfur, and nitrogen nucleophiles. Following photolytic demetallation of **61**, the aromatic ether-bridged organic polymer had a weight-average molecular weight of 12,600 (PDI=1.9), which corresponds to a molecular weight of ~19,000 for its metallated analog.
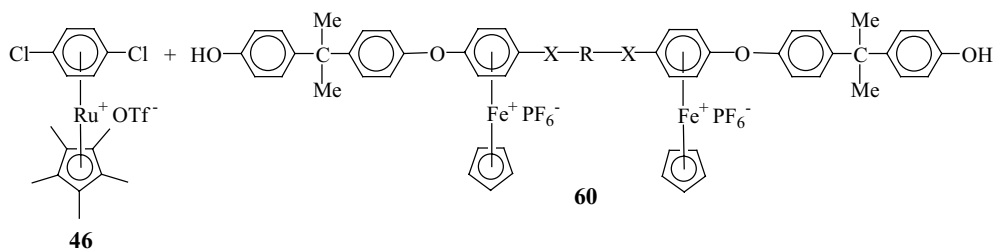
Scheme 15

The synthesis of polymers containing both pendent cyclopentadienyliron moieties and mainchain ferrocenyl groups has also been reported.[32] It was found that polymers such as **64** (Scheme 16) had glass transition temperatures between 65 and 161°C. After removal of the cyclopentadienyliron cations pendent to the polymer backbones, their ferrocene-based materials (**65**) had T_g values between 10 and 92°C. The M_w values for **64** were calculated to range from 11,000–20,600 with polydispersities from 1.13 to 2.19 based on the molecular weights measured for **65**.
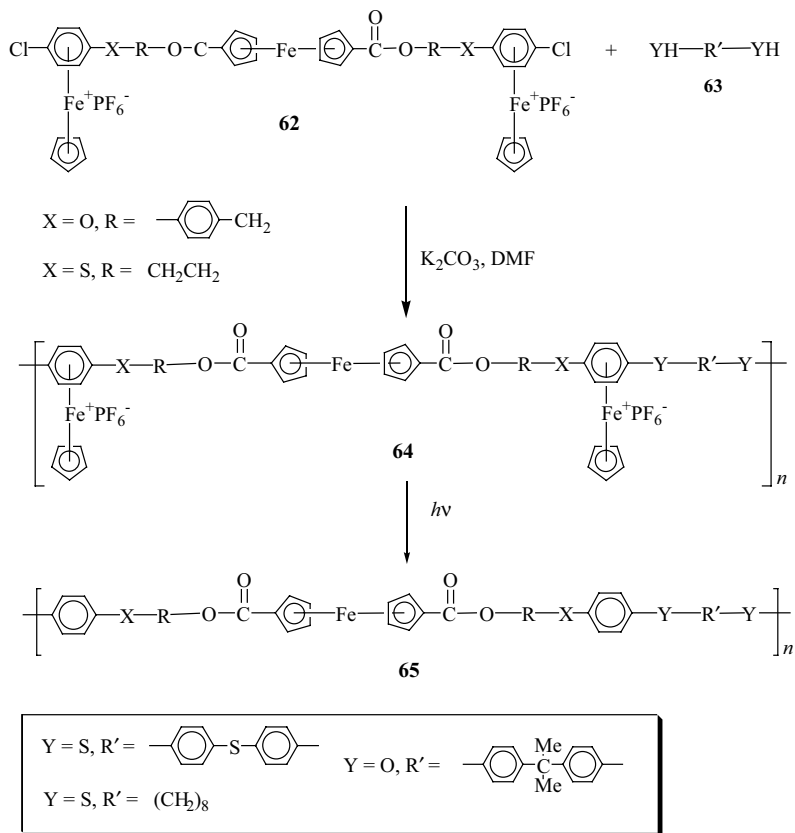
Scheme 16

B. Sidechain

In the early 1970s, Pittman and coworkers examined the polymerization behavior of a number of olefinic monomers functionalized with chromium tricarbonyl-coordinated arenes.[33–36] The first monomer containing an arene complex to be polymerized was π-(benzyl acrylate)chromium tricarbonyl (**66**).[33] Homopolymers (**67**) with M_n values as high as 60,000 were synthesized as shown in Scheme 17 via the radical polymerization of **66** with AIBN. Monomer **66** was also copolymerized with styrene, methyl acrylate, and 2-ferrocenylethyl acrylate (**68**) to give copolymers such as **69**. The thermal and photochemical decompositions of homo- and copolymers prepared from η^6-(2-phenylethyl acrylate) chromium tricarbonyl were also examined.[35] Irradiation caused some crosslinking to occur, and the materials isolated from decomposition by sunlight in air showed the formation of tiny Cr_2O_3 particles. Thermal decomposition was achieved at 150°C in the absence of light, resulting in crosslinked polymers containing mixed oxides embedded in their structures.
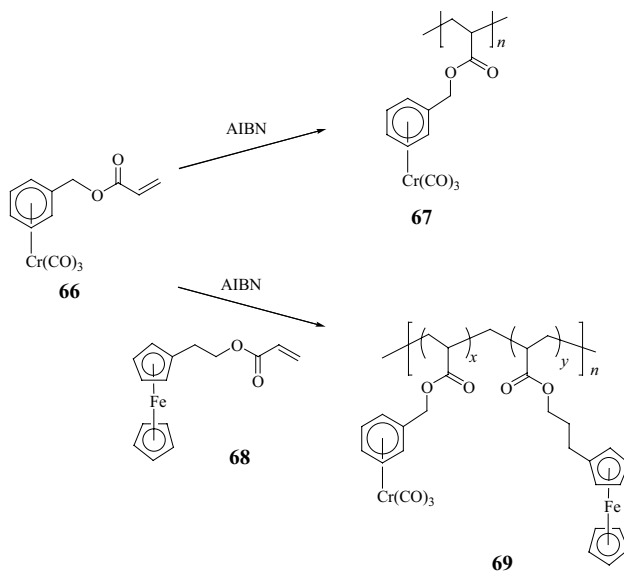
Scheme 17

η^6-Styrenetricarbonylchromium (**70**) has been copolymerized with styrene (**71**) to give the corresponding organometallic polymer (**73**) as shown in Scheme 18.[36] Alternatively, polystyrene could be reacted with chromium hexacarbonyl to generate copolymers such as **73**. The advantage to the second strategy is that polystyrene with narrow molecular weight distributions can be utilized. It was determined that 32.2% of the phenyl rings became coordinated to the chromium complexes. The number-average molecular weight (M_n) of **72** was 20,200, and following reaction with $Cr(CO)_6$, the molecular weight of **73** was 32,400.
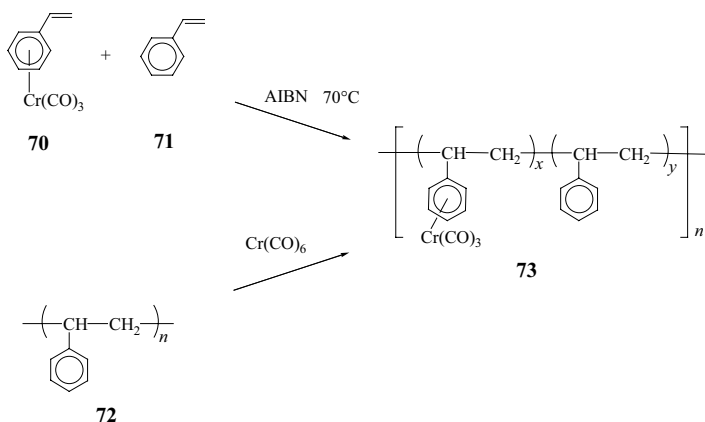
Scheme 18

Polymethacrylates and polystyrenes with cationic cyclopentadienyliron moieties coordinated to their sidechains were prepared by radical polymerization of their corresponding organoiron monomers as shown in Scheme 19.[37,38] Electrochemical analysis showed that the cyclopentadienyliron coordinated monomers (**74**) and polymers (**75**) underwent reversible reduction processes. Photolytic demetallation of the cyclopentadienyliron-coordinated polymethacrylates resulted in the corresponding organic analogs with $M_w = 48,000-68,000$.
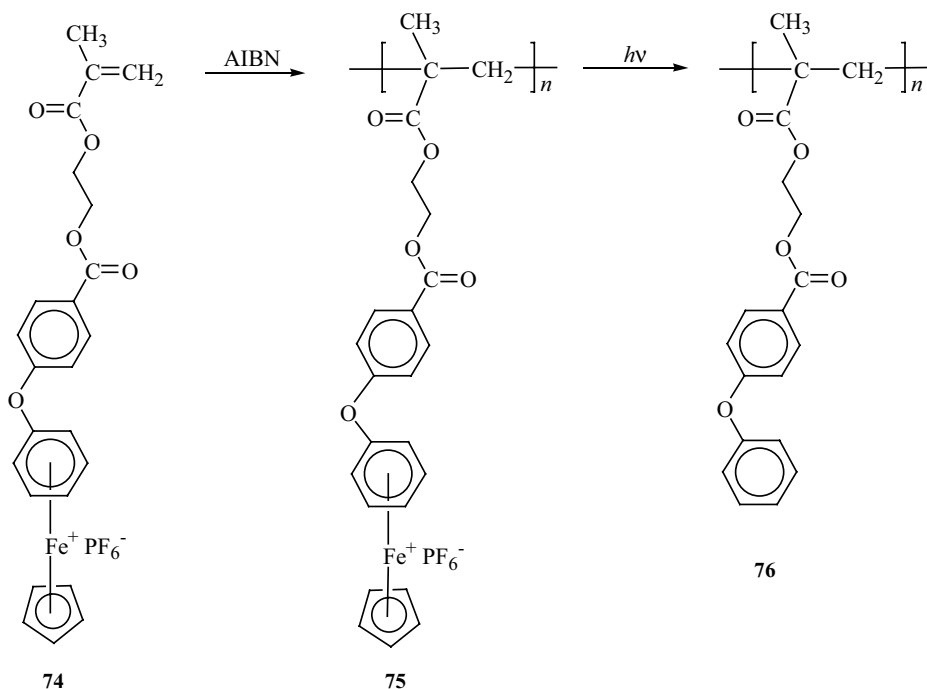
Scheme 19

The synthesis of polynorbornenes functionalized with cationic cyclopentadienyliron-coordinated aryl ethers were also reported by Abd-El-Aziz and coworkers.[39,40] Scheme 20 shows the ring-opening metathesis polymerization of monomers containing pendent cyclopentadienyliron cations (**77**) using Grubbs' ruthenium benzylidene catalyst.[40] The resulting organometallic polymers (**78**) were demetallated using photolytic means to produce the corresponding organic polymers (**79**), which had M_w values ranging from 10,600 to 18,600 with PDI values ranging from 1.3 to 1.6. Electrochemical analysis of these metallated polymers indicated that the cationic iron centers were reduced between -1.2 and -1.4 V.
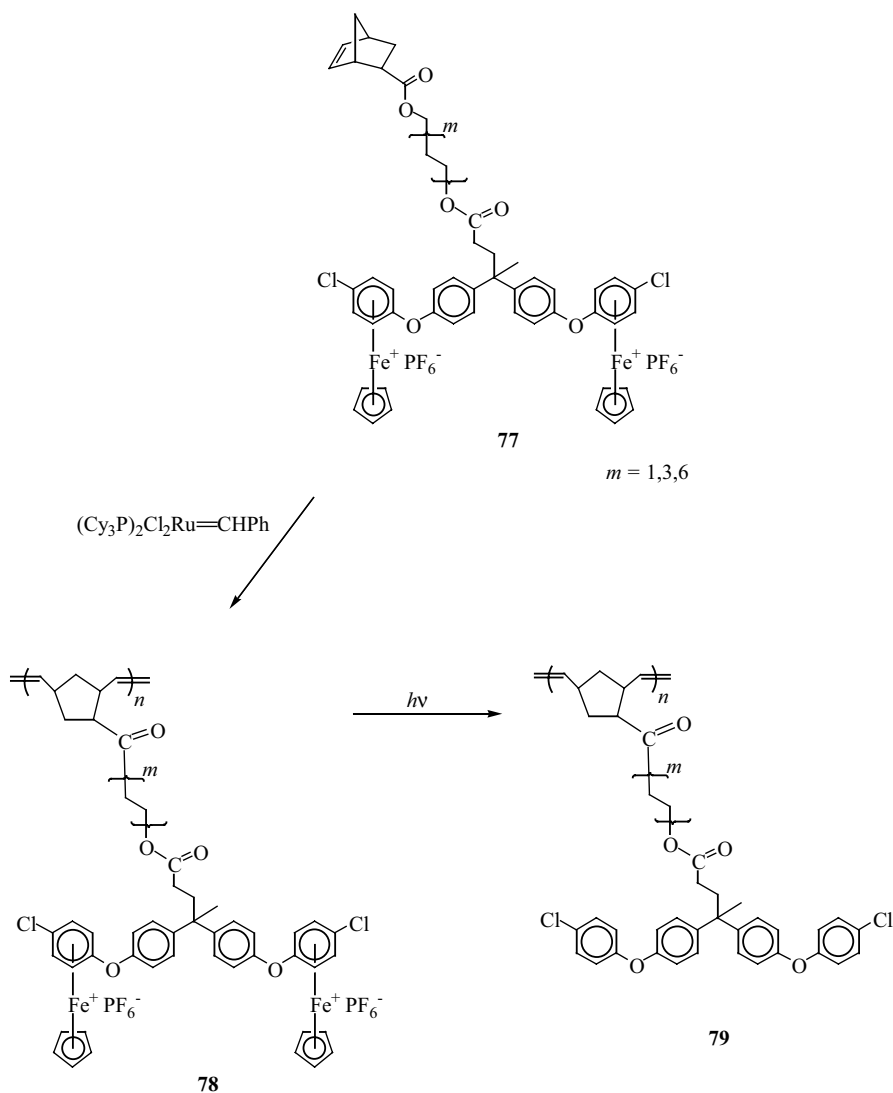
Scheme 20

Scheme 21 shows the synthesis of polystyrenes functionalized with cationic ruthenium complexes.[41] These polymers (**81**) were prepared via coordination of Ru^+Cp^*, $Ru^+C_8H_{11}$, or $Ru^+H(PCy_3)_2$ to the aromatic rings of polystyrene. Depending on the bulkiness of the ligand attached to ruthenium, 25–90% of the aromatic rings in the polymers became complexed to the ruthenium. There have not yet been any reports on the polymerization of analogous styrene monomers.

80

81

$$L = C_5Me_5$$
$$C_8H_{11}$$
$$H(PCy_3)_2$$
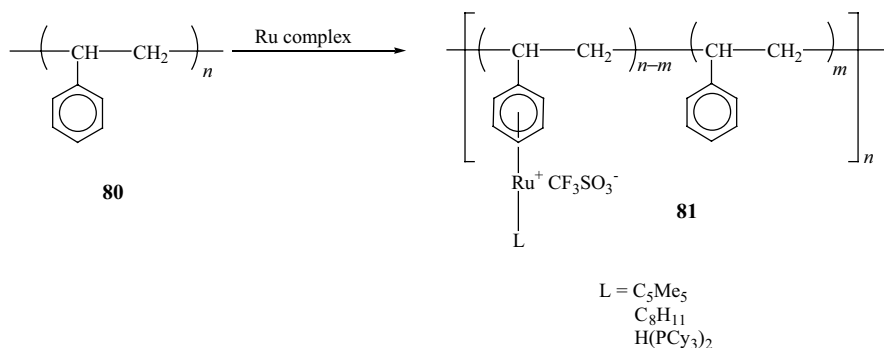
Scheme 21

Allcock and coworkers have reported the isolation of polyphosphazenes containing chromium tricarbonyl units in their sidechains (**84**) as shown in Scheme 22.[42] These polymers were synthesized by the ROP of a chloro-substituted cyclic phosphazene and subsequent functionalization of the resulting polymer (**82**) with a chromium tricarbonyl-functionalized complex (**83**). The glass transition temperatures of the $Cr(CO)_3$-functionalized polymers were higher than their inorganic analogs by about 50°C. It was not possible to accomplish the ring-opening polymerization on a chromium tricarbonyl substituted cyclic phosphazene. Another strategy that was attempted was the reaction of an aryl-functionalized polyphosphazene with chromium hexacarbonyl. However, this methodology was less successful.

82   **83**

84
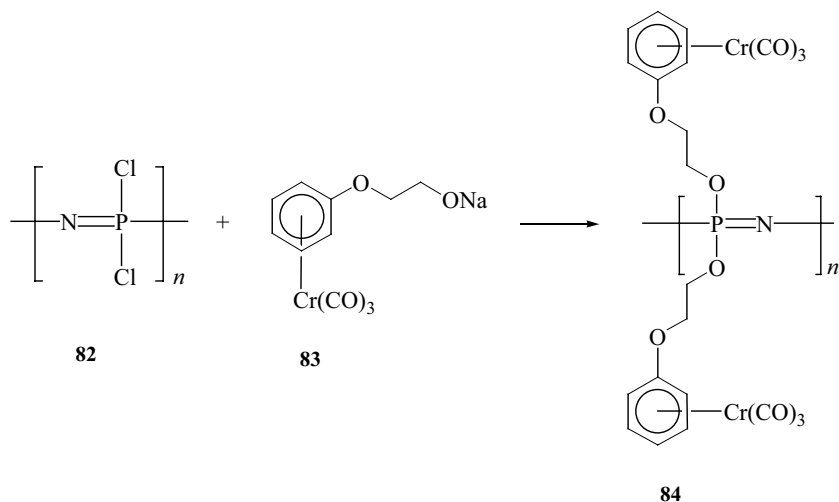
Scheme 22

The synthesis of polysiloxanes containing arenes coordinated to chromium tricarbonyl moieties was reported by Pittman and coworkers.[43] Scheme 23 shows the strategy used to isolate polymer **86** from the reaction of polysiloxane **85** with $Cr(CO)_6$. The influence of time on the complexation reactions was studied by determining the mole percent Cr by atomic absorption and by analysis of the polymers' molecular weights and viscosities after reaction times of 1 to 48 h. The molecular weight of polysiloxane **85** was determined to be 385,200. After one hour, it was found that the molecular weight had decreased to 368,000 and that 3% of the phenyl rings were coordinated to chromium. After 16 h, the molecular weight had decreased to 89,400, and 15% of the phenyl rings were coordinated to $Cr(CO)_3$ moieties. Another polysiloxane containing sidechain phenyl groups was also subjected to the same complexation reactions. It was found that between 3 and 4 h was the best compromise between polymer degradation and chromium incorporation.
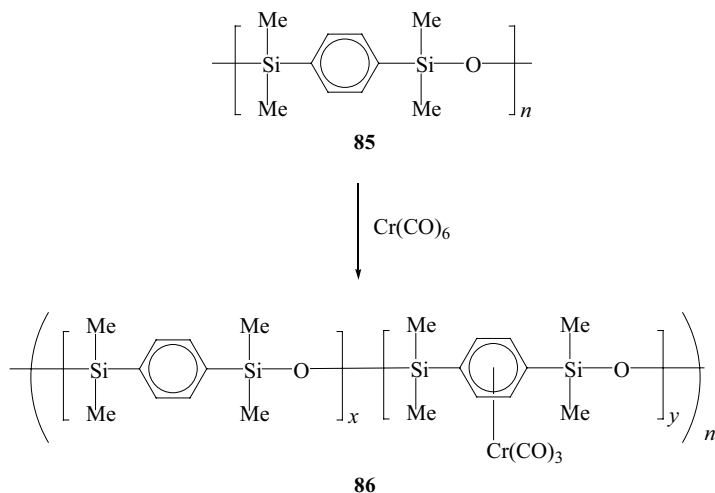
Scheme 23

C. Supramolecular Assemblies

Since 1998, a new class of supramolecular polymers containing arene complexes has emerged.[44–47] Brammer and coworkers have reported the use of arene chromium tricarbonyl complexes as building blocks in supramolecular assemblies.[44,45] Carboxylate-functionalized arenes coordinated to chromium tricarbonyl moieties assembled via hydrogen bonds on the arene carboxylic acid substituents. Complexes containing one carboxylic acid group formed discrete dimers; however, di- and tri-functionalized complexes formed extended supramolecular assemblies. In addition to hydrogen bonding via the carboxylic acid groups on the arenes, the three carbonyl oxygen atoms in the ligands on chromium also acted as hydrogen bond acceptors to C−H donors in the 2 and 5 positions on the arene rings. The C−H group in the 3 position of the arene also formed C−H− − −O hydrogen bonds to neighboring hydroxy oxygen atoms.

Sweigart and coworkers recently reported the self-assembly of deprotonated hydroquinone manganese tricarbonyl complexes to produce a novel class of organometallic supramolecular polymers (**87**).[46,47] The η^6-hydroquinone manganese complex readily deprotonated because of the enhanced acidity of the arene caused by the electron-withdrawing manganese tricarbonyl group. On formation of the polymers, the complexed arenes shifted from η^6 to η^4 (**87**) or η^5 (**88**) structures. The oxygen atoms in the η^4-quinone complex were found form σ bonds with divalent metal ions either in the presence of light or a basic solution of the metal ion.[46]
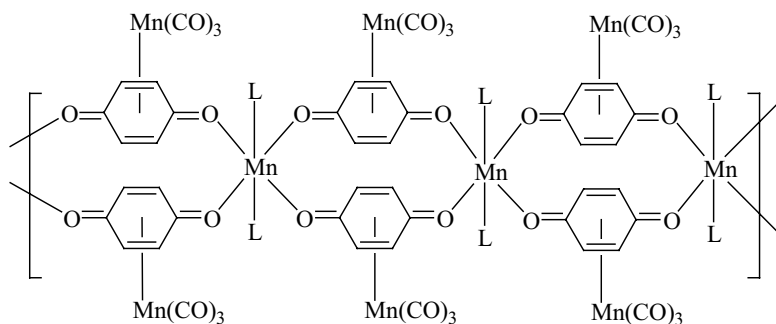
87
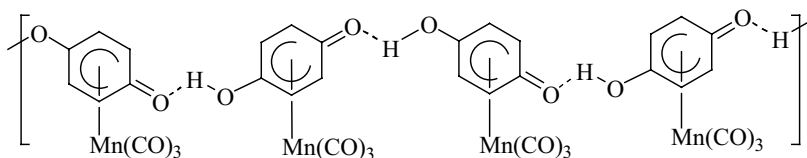
88

D. Dendrimers and Stars

Astruc and coworkers have reported the synthesis of highly branched polymers coordinated to cyclopentadienyliron and pentamethylcyclopentadienyl-ruthenium cations.[48–58] The catalytic and sensing ability of star polymers and dendrimers has also been reviewed.[59,60] Multifunctional core molecules suitable for the synthesis of star and dendritic materials were synthesized by peralkylation or allylation of methyl-substituted arene complexes of cyclopentadienyliron.[48–58] The benzylic protons on these complexed arenes are acidic, which permits their facile alkylation. These branched polymers contained cationic cyclopentadienyliron moieties at the core and/or the periphery. The synthesis of a water-soluble metallodendrimers

containing six cationic cyclopentadienyliron moieties (**89**) was reported by the same group.[53] The *hexa*-metallic complex was examined as a redox catalyst for the cathodic reduction of nitrates and nitrites to ammonia.

89
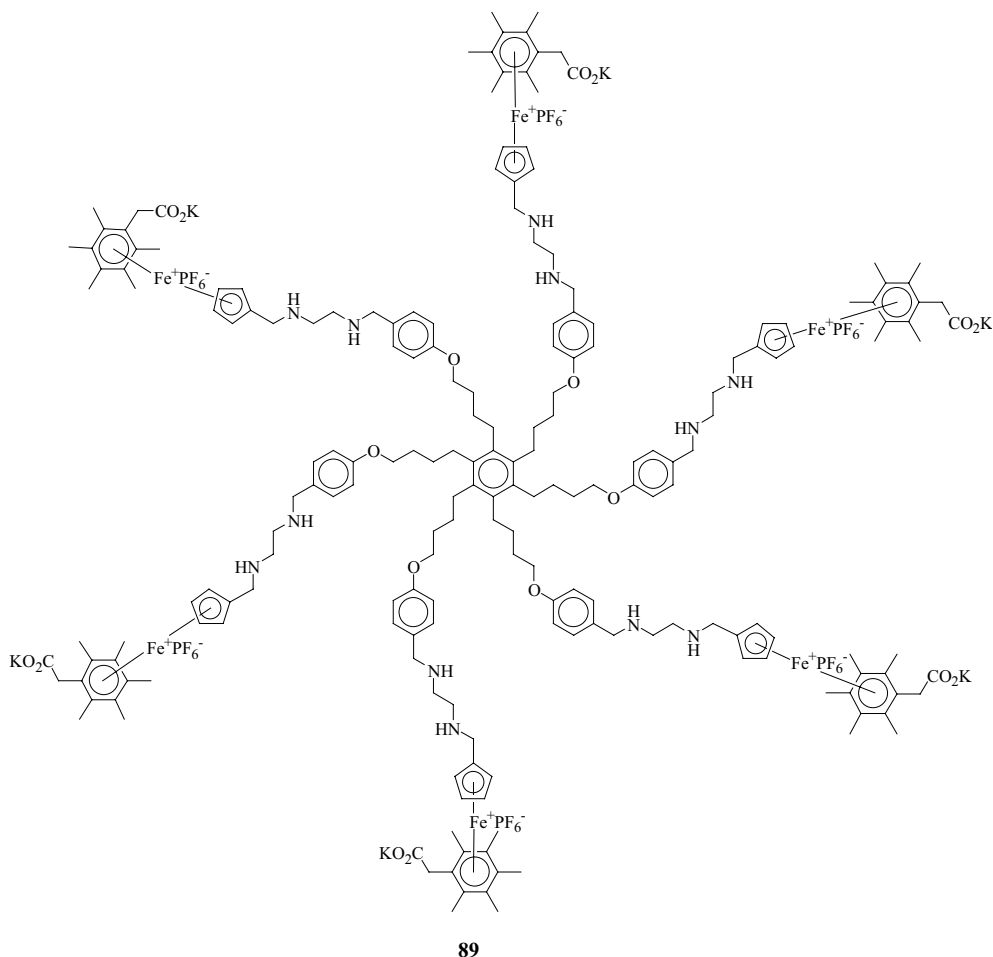
Star-shaped polyaromatic ethers complexed with cyclopentadienyliron cations (**92**) have been prepared, in which the metallic moieties are evenly spaced throughout the length of the macromolecular branches (Scheme 24).[61] By altering the nature of the aromatic spacers between the complexed arenes, it was possible to alter the properties of these materials. Electrochemical analysis of these polymers demonstrated that the iron centers underwent reversible reduction processes. For the *hexa*-metallic stars (*n*=1), two distinct redox couples were observed at $E_{1/2}=-1.20$ and -1.30 V.
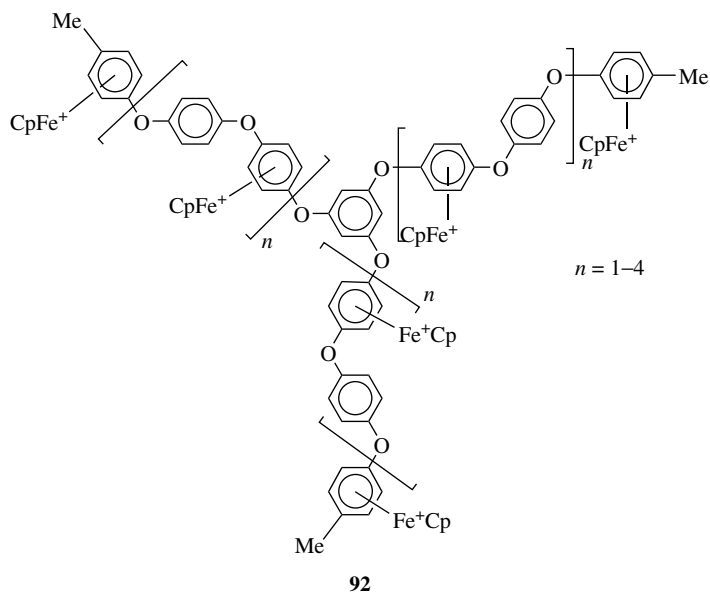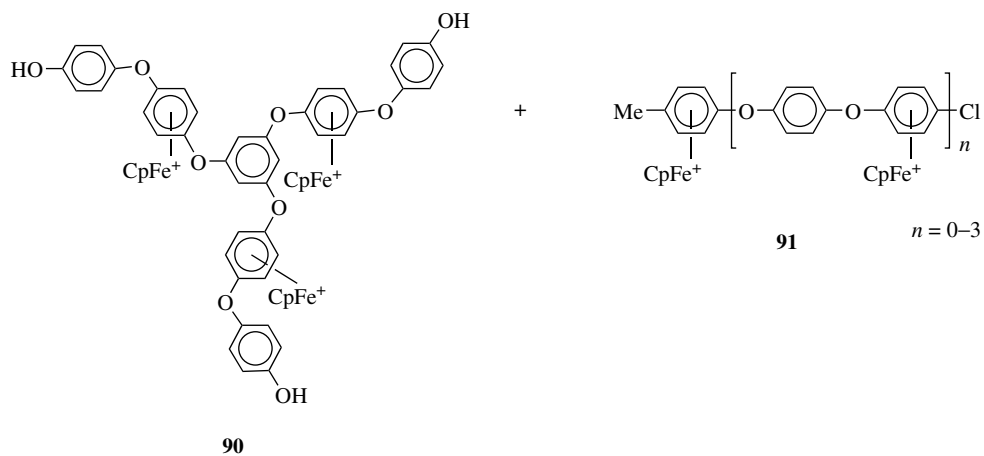
Scheme 24

Astruc has also reported the use of arene complexes of iron and ruthenium in the design of star-shaped complexes.[57] The cyclopentadienyliron moiety in **93** (Scheme 25) was utilized to activate the complexed arene toward bromobenzylation to produce **95**. Following photolytic demetallation, **96** was reacted with **97** to yield the *hexa*-metallic complex **98**. These complexed arenes were then subjected to nucleophilic aromatic substitution reactions with **99** allowing for the isolation of **100**.
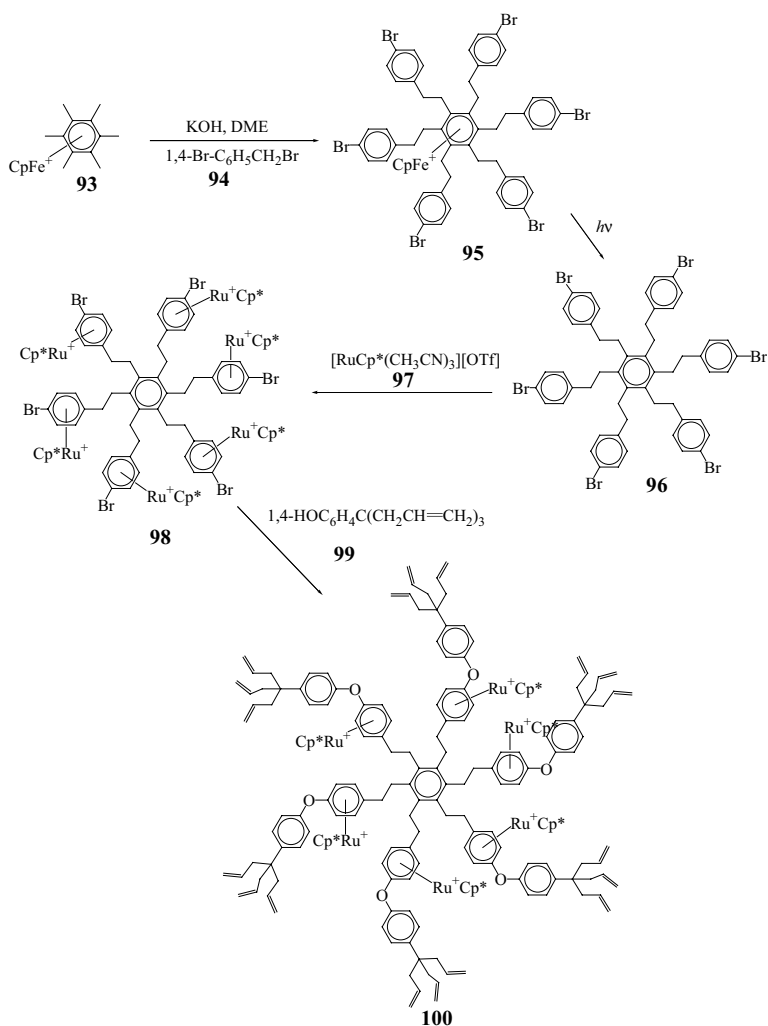
Scheme 25

Organosilicon dendrimers containing chromium tricarbonyl moieties pendent to peripheral aromatic rings (**101**) have been synthesized by Cuadrado.[62] These organometallic dendrimers were isolated following reaction of a precursor silane dendrimer with chromium hexacarbonyl. It was not possible to effect complexation of every aromatic ring due to steric hindrance. Cyclic voltammetry of these materials indicated that oxidation of the chromium atoms occurred reversibly in the absence of nucleophilic species and that the chromium tricarbonyl units behaved as isolated redox centers.
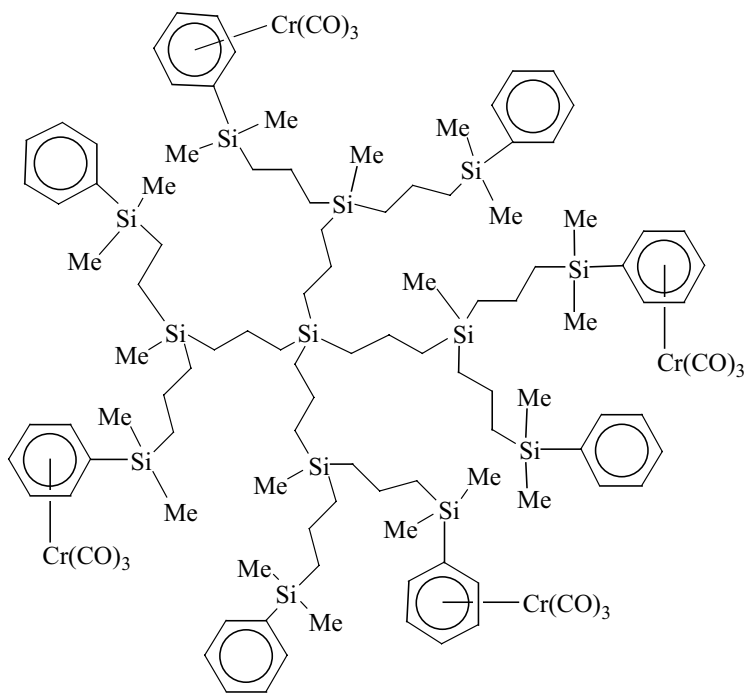
101

The synthesis of organosilane dendrimers with peripheral Cp*Ru$^+$ moieties has been reported by Tilley and coworkers.[63] Using the strategy shown in Scheme 26, dendritic complexes containing 12, 24, 36, and 72 metallic moieties were isolated. Mass spectrometry revealed that in the case with 72 ruthenium complexes (**104**), although the desired complex was present in the sample, complete coordination of all the aromatic rings was limited by steric crowding. A first generation dendrimer with 12 pentamethylcyclopentadienyl-ruthenium moieties pendent to its aryl groups was characterized by single-crystal X-ray diffraction.
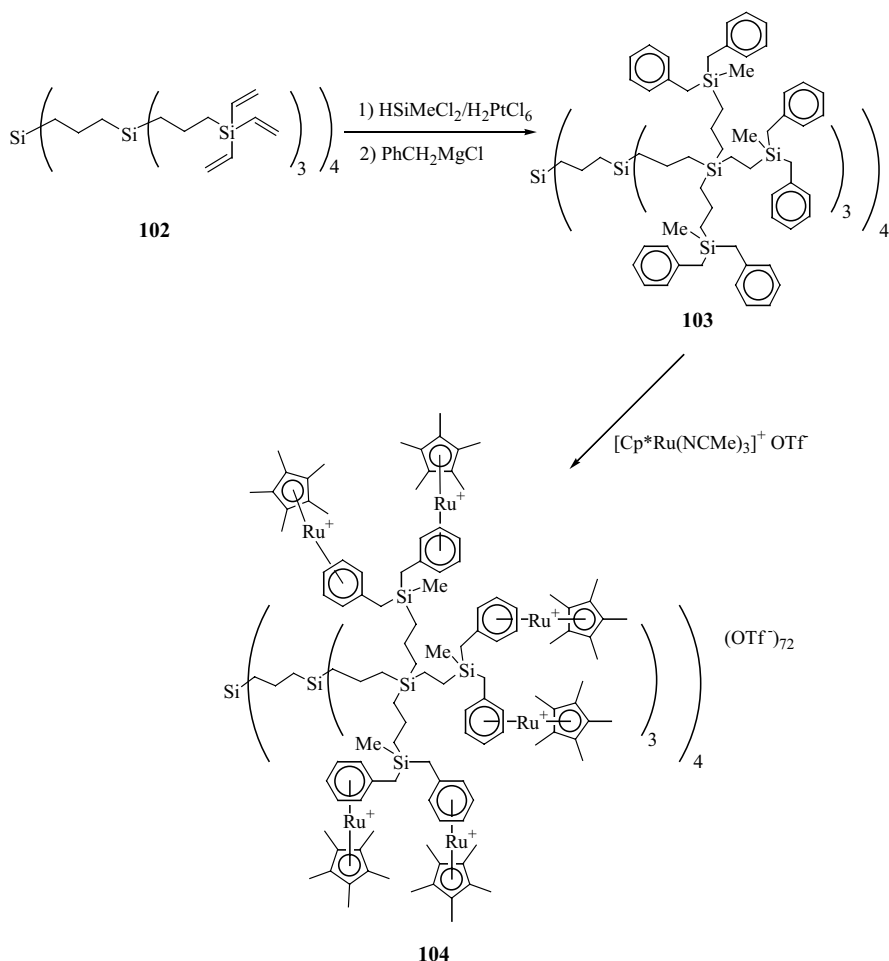
Scheme 26

III. POLYMERS CONTAINING COMPLEXED 5-MEMBERED RINGS

A. Cyclopentadienylmetal Carbonyl Complexes

Vinylcyclopentadienylmanganese tricarbonyl (**105**) was copolymerized via radical addition reactions with acrylonitrile, methyl acrylate, vinyl acetate, styrene, and vinylferrocene (**106**).[64] Scheme 27 shows a number of the interesting copolymers (**107**) that were synthesized by Pittman and coworkers. The weight average molecular weights of these polymers were found to range from 13,800 to 85,500. Films of these polymers exhibited fungus resistance properties and were electrical insulators. It was also reported that monomer **105** could be chemically incorporated into linseed oil films through crosslinking reactions.[65]
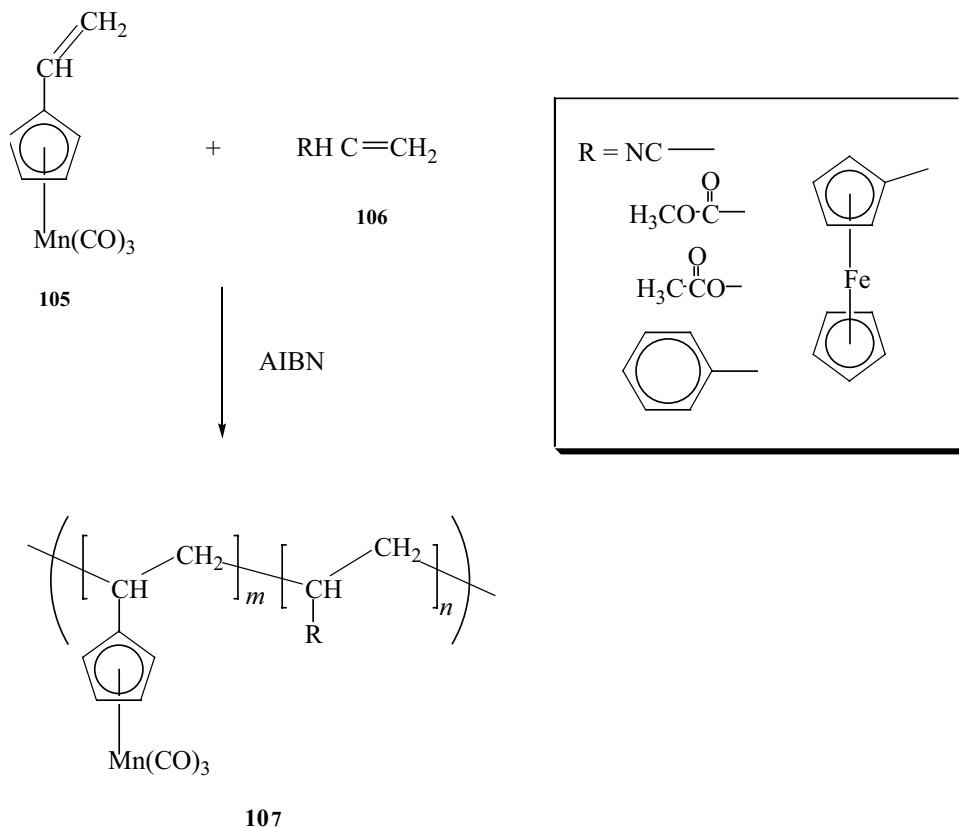
Scheme 27

(η^5-Vinylcyclopentadienyl)dicarbonylnitrosyl complexes of chromium[66] and molybdenum[67] (**108**) have been homo- and copolymerized with a number of organic and organometallic monomers to produce the polymers (**109**, **110**, **112**, **113**, **115**, **116**) shown in Scheme 28.

Rausch, Pittman, and coworkers also reported that a vinylcyclopentadi-enyldicarbonyl iridium complex could be homo- or copolymerized with styrene to produce the corresponding organometallic polymers.[67] The homopolymer was reduced with NaBHBEt$_3$ and was utilized to catalyze the hydrogenation of 1,5-cyclooctadiene. The polymerizations of (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten (**117**) were also investigated using radical, cationic, and anionic initiators; however, only rad-ical initiation produced significant amounts of polymer.[68] The yields of the polymer-ization reactions could be increased by multiple initiations. The reactivity ratios for the copolymerization reaction of monomer **117** (Scheme 29) with styrene were found to be 0.16 and 1.55, and the Alfrey–Price parameters, e and Q were determined to be -1.98 and $+1.66$, respectively, indicating that **117** is a very electron-rich monomer.[68]
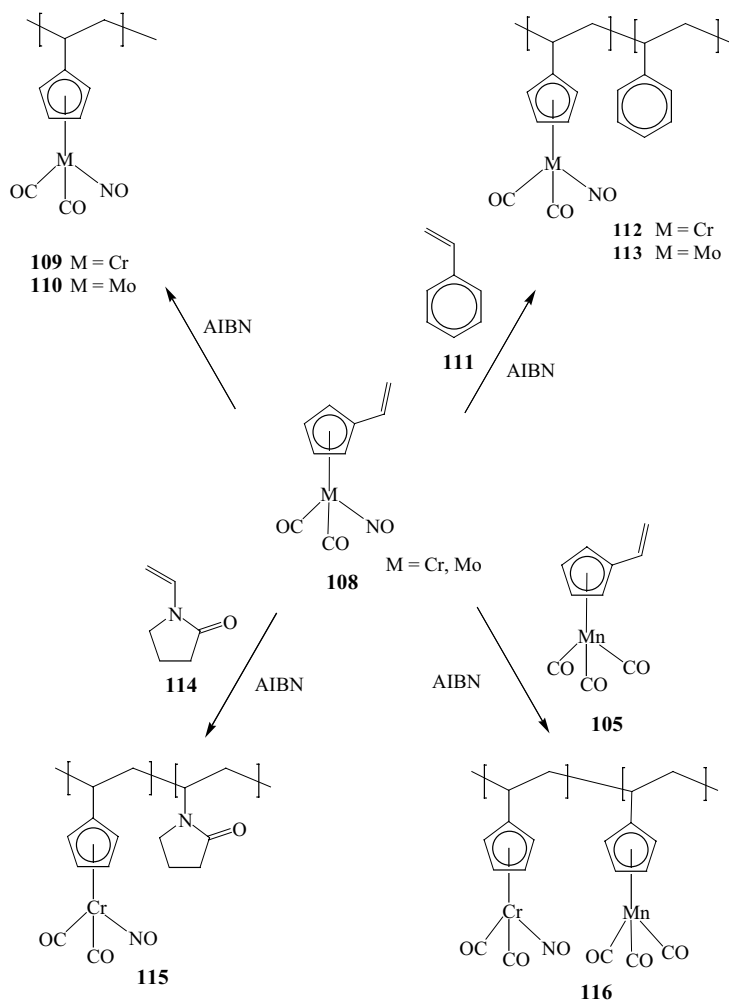
Scheme 28
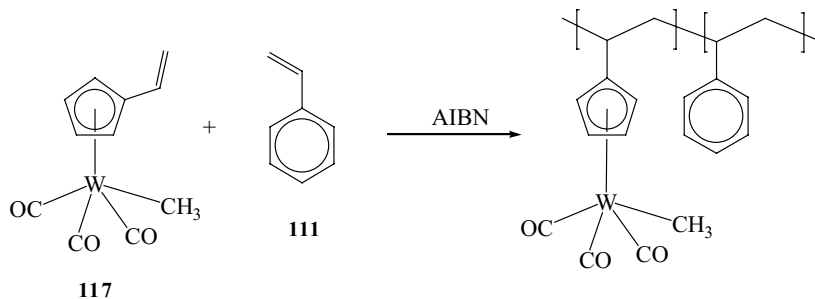
Scheme 29

The synthesis of polymers (**120**) containing cyclopentadienyl-coordinated metal complexes in their sidechains has also been examined by Mapolie and coworkers.[69,70] Vinyl monomers containing iron or tungsten complexes in their structures were homo- or copolymerized with styrene to produce the corresponding organometallic polymers.[69] It was reported that rhenium and iron complexes could be incorporated into the sidechains of low molecular weight polyesters as shown in Scheme 30.[70] With increasing reaction time, there was an increasing amount of insoluble materials recovered. The infrared spectra of the toluene-soluble and -insoluble fractions were both consistent with polymer formation.
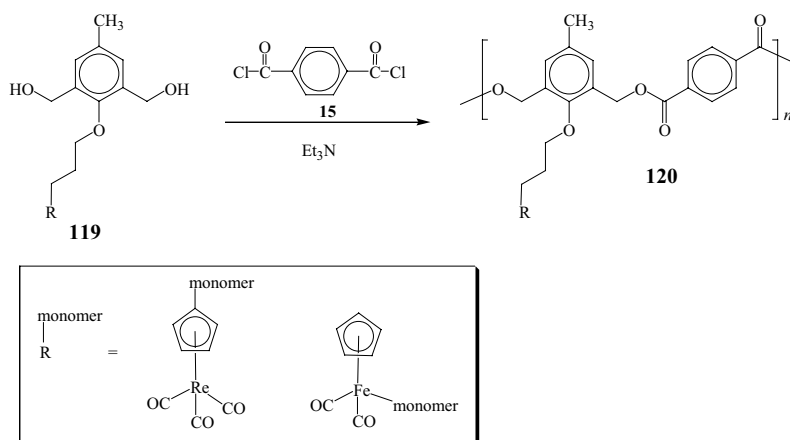
Scheme 30

Nishihara and coworkers have also examined the coordination of tricarbonylmanganese and pentamethylcyclopentadienylcobalt to poly(9-hexylfluorene) as shown in Scheme 31.[71] This polymer has both 6- and 5-membered rings that could react with these transition metal complexes; however, it was determined that coordination to the 5-membered rings occurred preferentially under the conditions employed in these experiments. Reaction of poly(9-hexylfluorene) (**121**) with $MnBr(CO)_5$ resulted in a 1:1.5 ratio of complexed to uncomplexed units in polymer **122**. Reaction of **121** with BuLi, followed by $(C_5Me_5)Co(acac)$ and then oxidation of this solution with HCl resulted in the isolation of polymer **123**. This polymer was isolated as a mixture of products that was determined to consist of cobalt-coordinated η^5-fluorenyl and η^4-fluorene rings. Electrical conductivity measurements showed that the manganese-complexed polymer had a higher conductivity than did organic poly(9-hexylfluorene), while the conductivity of the cobalt-complexed polymer was slightly lower than that of poly(9-hexylfluorene).

122

Mn(CO)$_5$Br, AlCl$_3$

121

1) BuLi
2) (C$_5$Me$_5$)Co(acac)
3) HCl, O$_2$

123
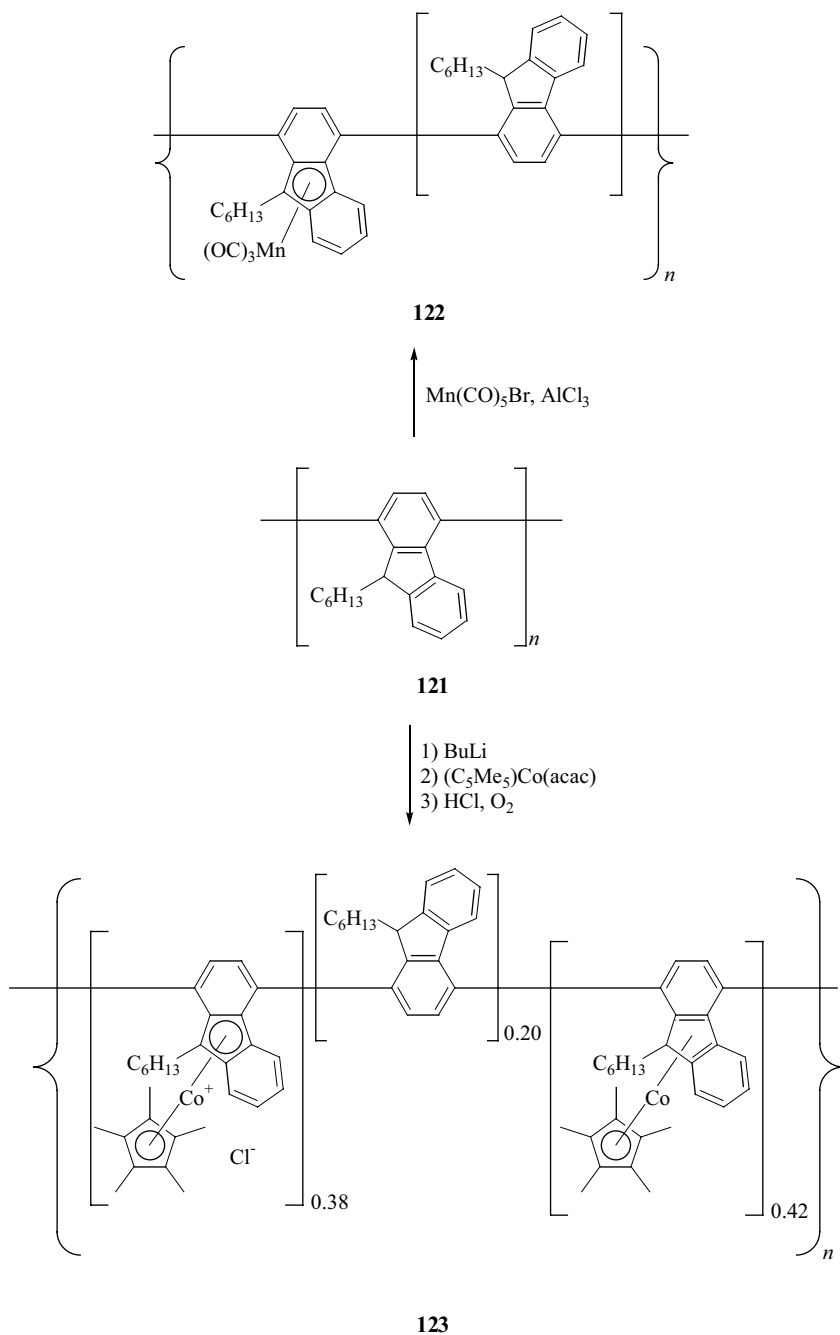
Scheme 31

The synthesis of polymers containing manganese tricarbonyl units pendent to the polymer backbones were reported by Bunz and coworkers using Hay[72] or Suzuki[73] coupling reactions. Scheme 32 shows the reaction of a diiodocyclo-pentadienyl complex (**124**) with diboronic acid monomers (**125**) to produce high molecular weight rigid-rod organometallic polymers (M_n=1.1–1.2 $\times$ 10^4) with broad (6–6.4) polydispersities.
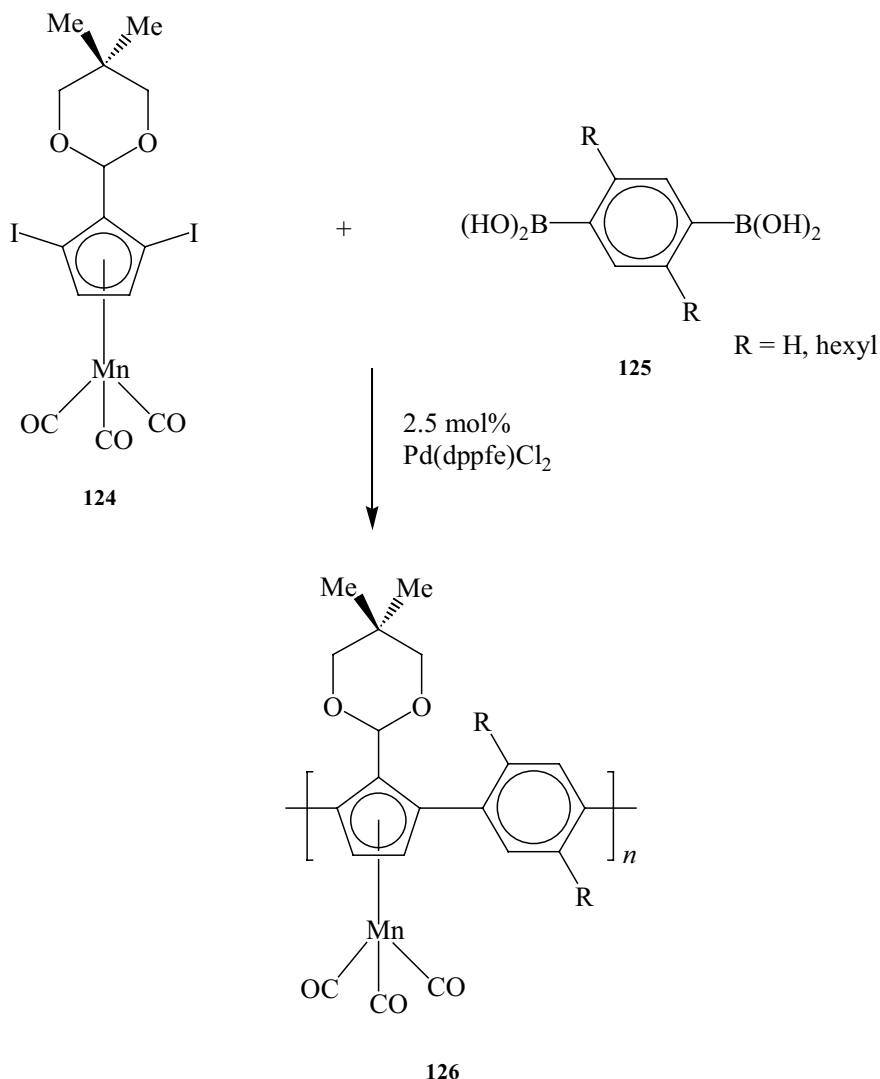
Scheme 32

B. Complexation of Silole Rings

Scheme 33 shows the reaction of polymer **127** with an excess of iron pentacarbonyl under UV irradiation to produce the iron tricarbonyl-coordinated polymer **128**.[74] NMR spectroscopy was used to determine that the ratio of coordinated to non-coordinated silole rings was 2:1. Conductivity measurements were performed on polymers **127** and **128** doped with $FeCl_3$. It was found that doped **127** had a conductivity of 10^{-8} S/cm, while the conductivity of doped **128** had a conductivity of 10^{-5} S/cm. X-ray crystallography studies of model compounds indicated that $Fe(CO)_3$-coordinated silole rings have enhanced π conjugation.

127

128
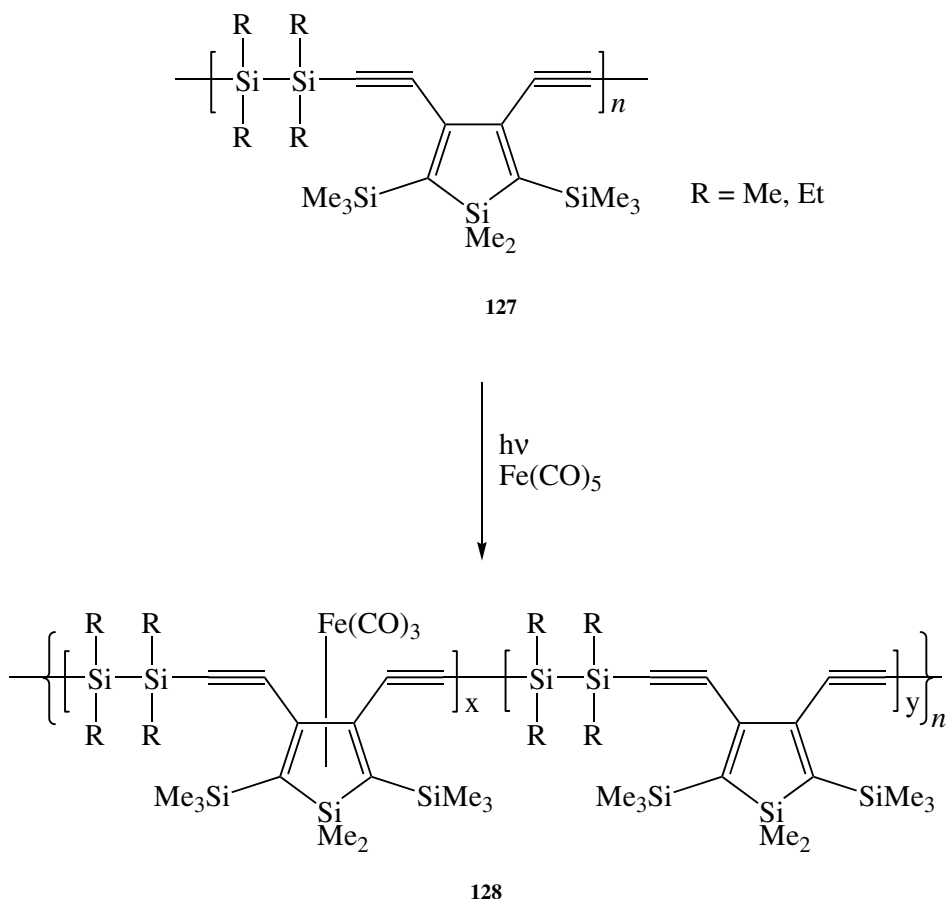
Scheme 33

C. Dendrimers

Hurley and Mohler have functionalized of polyamine dendrimers with 2, 4, 8, and 16 (**129**) terminal amine groups with the activated ester of tricarbonylcyclopentadienylmethyl-tungsten (**130**) shown in Scheme 34.[75] The resulting organometallic dendrimers (**131**) were photolyzed, and the resulting radical complexes with two and four tungsten moieties were found to cleave plasmid DNA in a double-stranded manner. While these low-generation materials were effective at DNA scission, the higher generation dendrimers precipitated from solution and formed aggregates.

129

130

131
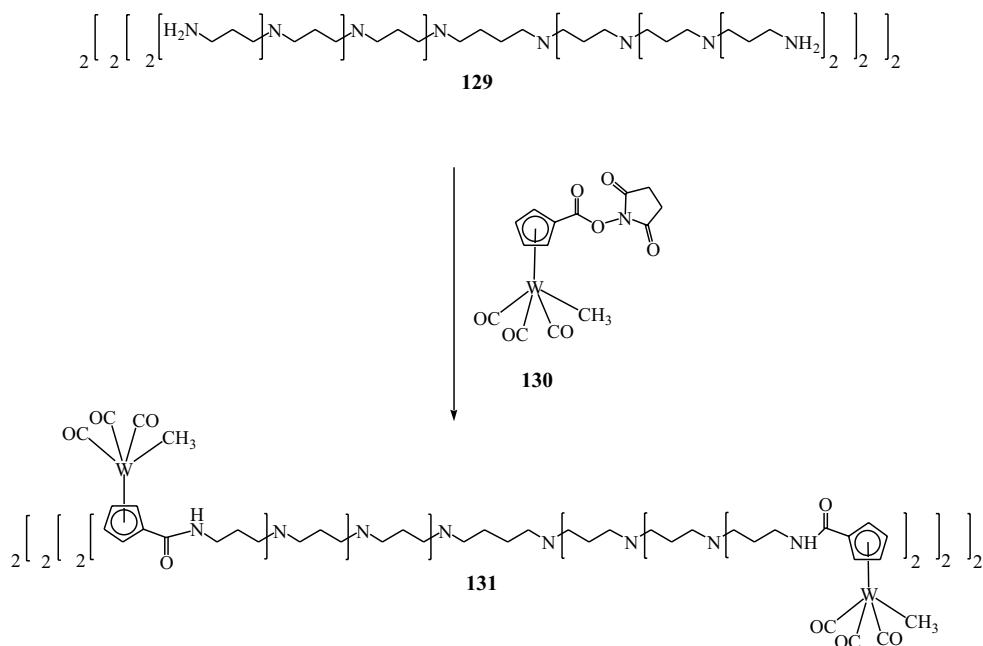
Scheme 34

The synthesis of poly(benzyl phenyl ether) dendrimers containing up to 48 ruthenium dicarbonyl moieties coordinated to terminal cyclopentadienyl rings has been described by Liao and Moss.[76,77] Scheme 35 shows the synthesis of a low-generation dendrimer (**134**) via reaction of the organometallic monomer **132** with the trifunctional core molecule **133**. The glass transition temperatures of the organometallic dendrimers increased with increasing generation up to a maximum of 47°C.

134
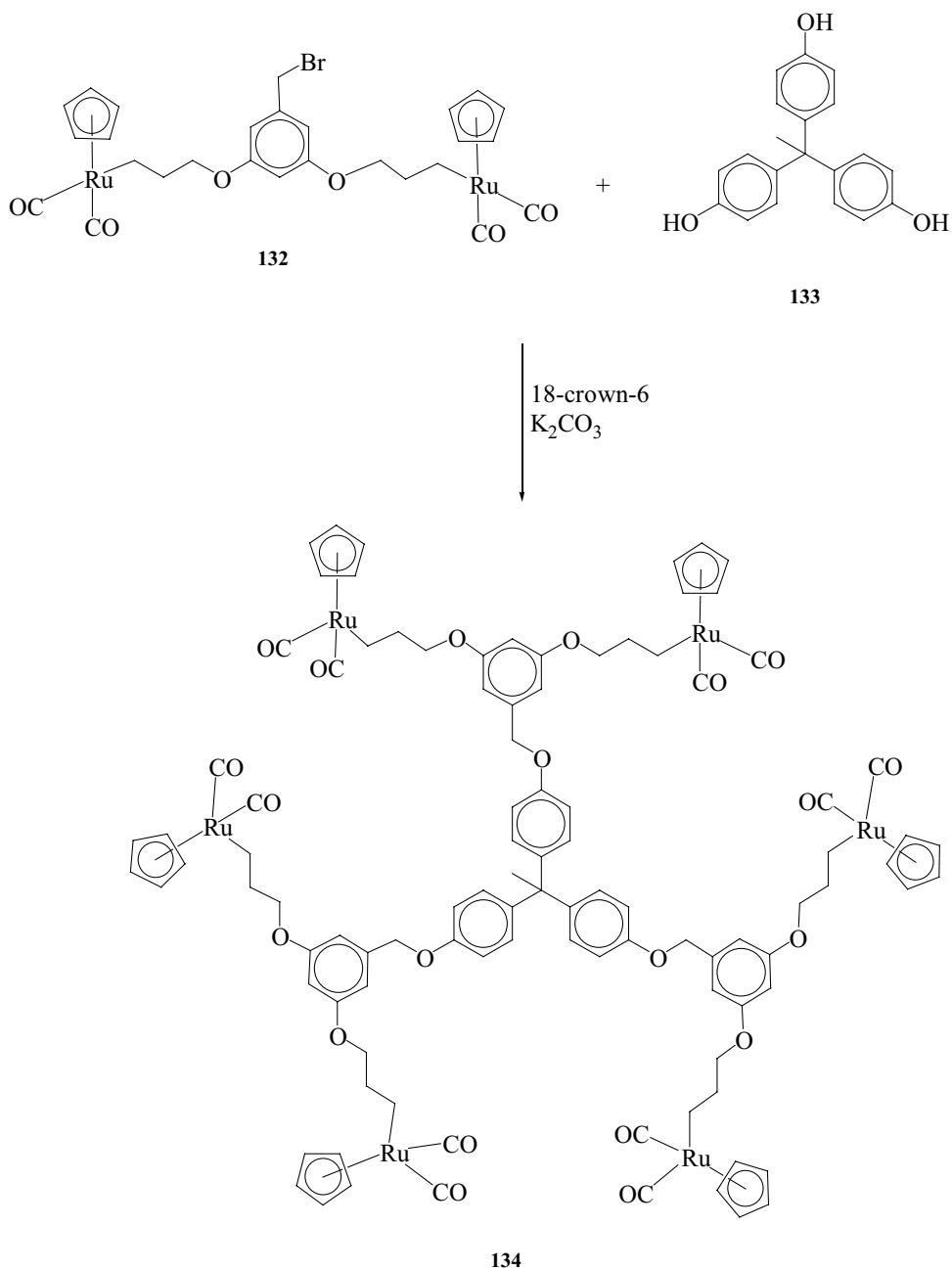
Scheme 35

IV. POLYMERS CONTAINING CYCLOBUTADIENE COMPLEXES

Polymers containing cyclobutadiene rings coordinated to cyclopentadienyl-cobalt moieties have been the focus of a number of investigations in light of their interesting properties and reactivities.[78–88] These polymers have been synthesized by direct reaction of monomers containing cyclopentadienylcobalt moieties coordinated to cyclobutadiene rings,[78–83] or by rearrangement of cobaltacyclopenta-diene units present in polymeric materials.[84–88] Bunz has reported the synthesis of organocobalt polymers (**137**) that possess thermotropic and nematic lyotropic liquid crystallinity using the palladium catalyzed coupling reaction shown in Scheme 36.[78,79] The circular dichroism spectrum of polymer **137** containing the chiral substituent, (*S*)-2,7-dimethyloctyl, was attempted, however, it could not be obtained. It was thought that the bulky organocobalt moieties acted as a stereochemical insulator.[79] Bunz has also reported that the incorporation of cyclopentadienylcobalt moieties pendent to polyaryleneethynylenes quenches their fluorescent properties.[80]
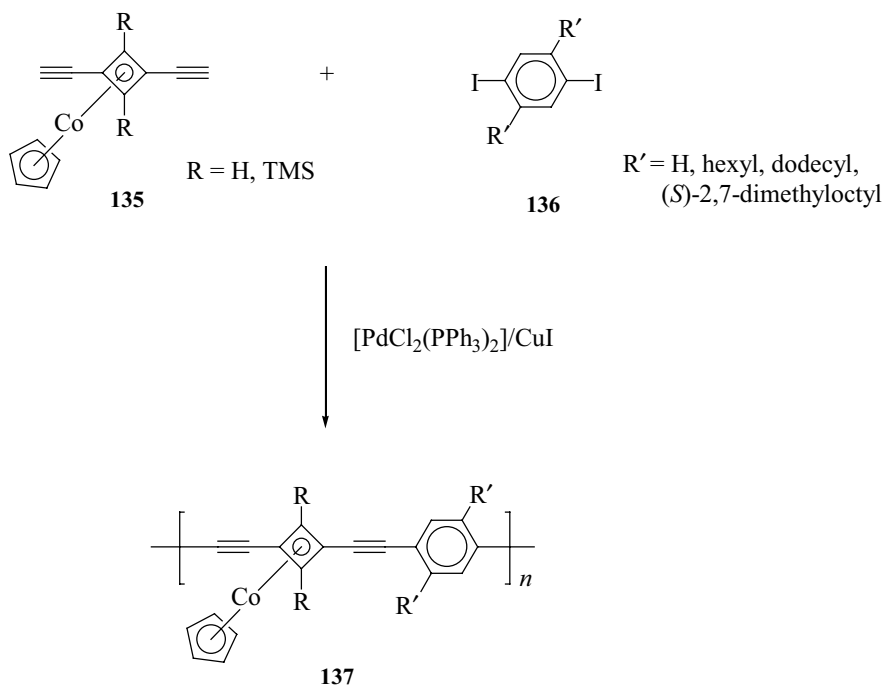
Scheme 36

Tomita, Endo, and coworkers have reported the synthesis of thermotropic liquid crystalline polymers containing cyclopentadienylcobalt moieties coordinated to cyclobutadiene rings.[82,83] Scheme 37 shows the polymerization of monomers **138**

using the Heck reaction to produce the corresponding organocobalt polymers **139**, containing long aliphatic chains pendent to their backbones. These polymers were partially soluble in THF, dichloromethane and chloroform, and had degrees of polymerization of 15–17.[83]

R = $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$

138

139
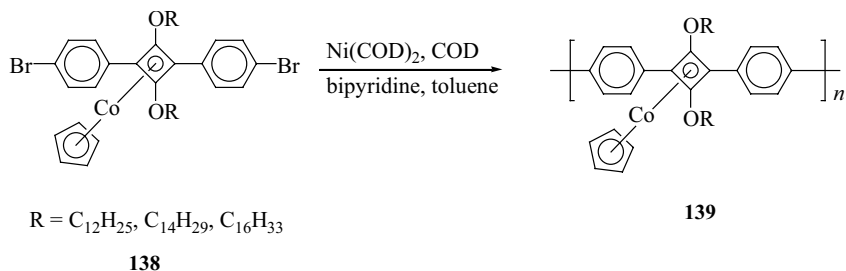
Scheme 37

Metallacycling polymerization of CpCo(PPh$_3$)$_2$ with diacetylenes has been reported to produce polymers with cobaltacyclopentadienyl rings in their back-bones.[84–89] This class of polymer undergoes rearrangement reactions to yield the corresponding polymers with cyclopentadienylcobalt moieties pendent to cyclobutadiene rings in the mainchain.[84–88] Scheme 38 shows the reaction of an excess of (η^5-cyclopentadienyl)*bis*(triphenylphosphine)cobalt (**140**) with *p-bis*ferrocenylethynyl benzene (**141**) to yield polymer **143**.[84] Polymer **143** underwent two chemically reversible redox steps at 0.143 and 0.219 V, corresponding to oxidation of the ferrocenyl moieties.

140

141

142

143
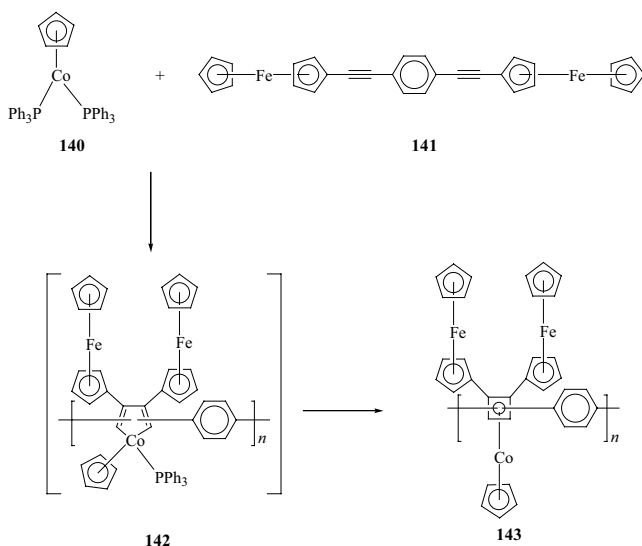
Scheme 38

The metallacyclization of CpCo(PPh$_3$)$_2$ (**140**) with the diacetylene (**144**) resulted in the isolation of polymer (**145**), which was thermally rearranged to produce **146**.[88] It was established that the first step of the rearrangement was the loss of the triphenylphosphine ligands from cobalt. In the presence of isocyanate, the cobaltacyclopentadiene rings were converted to 2-pyridone rings as shown in Scheme 39.
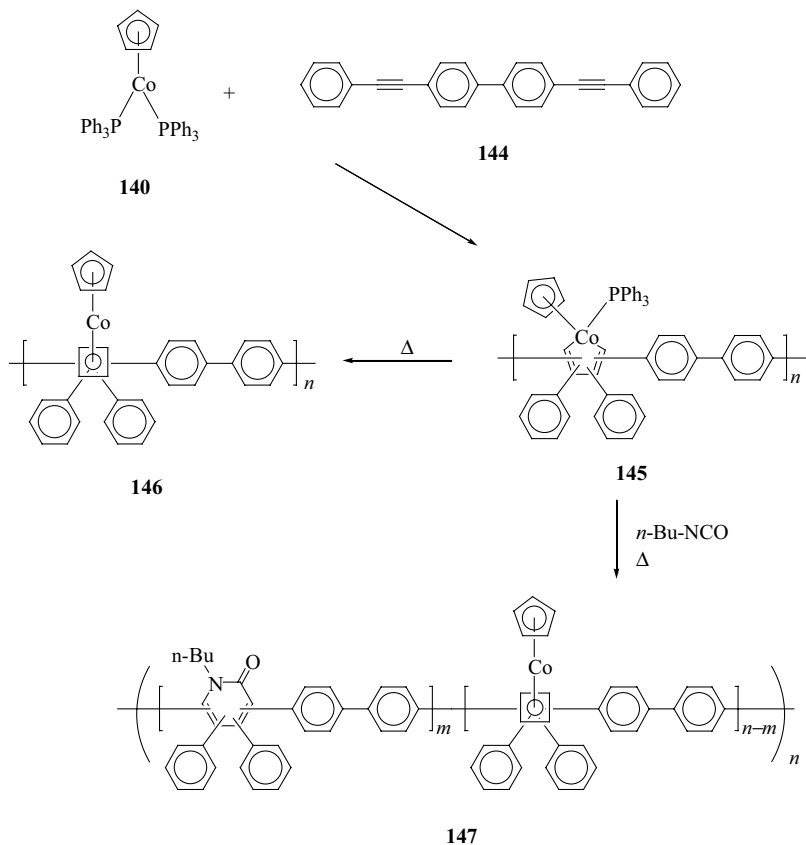
Scheme 39

Polyphenylene dendrimers containing a central cyclobutadiene core coordinated to cyclopentadienylcobalt moieties have been synthesized by metal-mediated dimerization reactions of di- and *tetra*-ethynyltolanes as shown in Scheme 40.[90] Oxidation of the cobalt complexes was examined using scanning pulse voltammetry. The oxidation potential increased from 0.80 V for **151** to 0.83 V as the steric crowding around the cobalt complexes increased.

1) CpCo(CO)$_2$

2) Bu$_4$NF

148

149

150

151
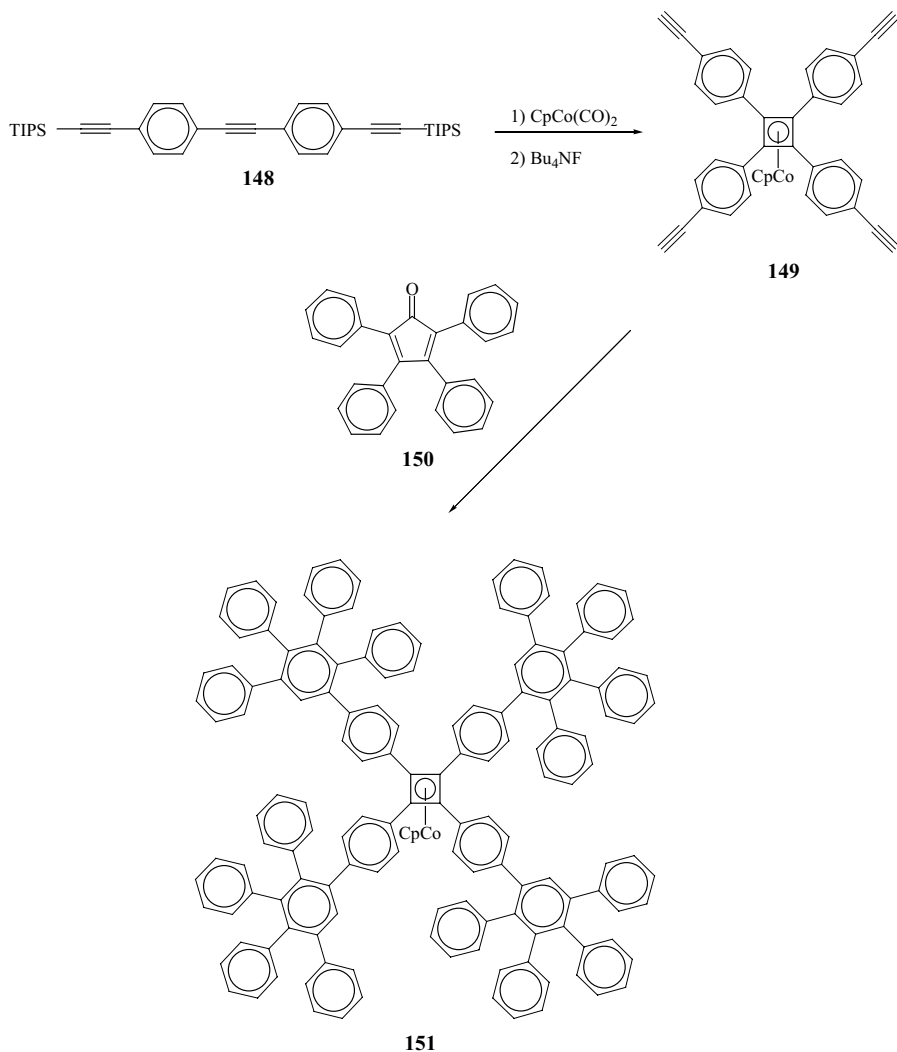
Scheme 40

V. SUMMARY

Chapter 2 dealt with so-called symmetric sandwiched metallocenes. In addition to these more traditional symmetric metallocenes, a wide variety of metal-containing macromolecules exist where the metal is bonded to a lone ring system or to an asymmetric sandwich-like system. As in the case of the symmetric metallocenes, attachment of the metal is via π or π-type bonding. Here, the metal is

normally not part of the backbone but rather resides directly adjacent (pendent) to the backbone or is further removed form the backbone within sidechains. The metal can be uncharged or present as a cation. Introduction of the metal-containing moiety has been achieved using all the traditional synthetic routes. Metal carbonyls are often chosen as the metal-containing moiety for single-ring systems. Generally, the metal-containing moiety is introduced in the polymer-forming step, but there are ample examples of the metal being introduced to already formed polymer systems. Some polymers have been produced using supramolecular assembly. Some appear as part of star, sheet, and dendrite structures.

VI. REFERENCES

1. S. I. Yaniger, D. J. Rose, W. P. McKenna, E. M. Eyring, *Appl. Spectrosc.* **38,** 7 (1984).

2. S. I. Yaniger, D. J. Rose, W. P. McKenna, E. M. Eyring, *Macromolecules* **17,** 2579 (1984).

3. H. Nishihara, H. Funaki, T. Shimura, K. Aramaki, *Synth. Met.* **55–57,** 942 (1993).

4. H. Funaki, K. Aramaki, H. Nishihara, *Chem. Lett.* 2065 (1992).

5. H. Funaki, K. Aramaki, H. Nishihara, *Synth. Met.* **74,** 59 (1995).

6. H. Nishihara, in H. S. Nalwa, ed., *Handbook of Organic Conductive Molecules and Polymers,* J Wiley, New York, 1997, Vol. 2, p. 799.

7. J.-I. Jin, R. Kim, *Polym. J.* **19,** 977 (1987).

8. A. A. Dembek, R. R. Burch, A. E. Feiring, *J. Am. Chem. Soc.* **115,** 2087 (1993).

9. M. E. Wright, *Macromolecules* **22,** 3256 (1989).

10. M. E. Wright, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **29,** 294 (1988).

11. C. U. Pittman, Jr., P. L. Grube, R. M. Hanes, *J. Paint Technol.* **46**(597), 35 (1974).

12. C. U. Pittman, Jr., O. E. Ayers, S. P. McManus, *J. Macromol. Sci. Chem.* **A7**(8), 1563 (1973).

13. Y. Morisaki, H. Chen, Y. Chujo, *Polym. Bull.* **48,** 243 (2002).

14. M. E. Wright, C. K. Lowe-Ma, *Inorg. Chim. Acta* **232,** 223 (1995).

15. A. S. Abd-El-Aziz, T. H. Afifi, E. K. Todd, G. Z. Ma, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **42**(2), 450 (2001).

16. A. S. Abd-El-Aziz, T. C. Corkery, E. K. Todd, T. H. Afifi, G. Z. Ma, *J. Inorg. Organomet. Polym.* **13**(3), in press.

17. M. E. Wright, L. Lawson, R. T. Baker, D. C. Roe, *Polyhedron* **11,** 323 (1992).

18. R. D. Pike, D. A. Sweigart, *Coord. Chem. Rev.* **187,** 183 (1999).

19. A. S. Abd-El-Aziz, S. Bernardin, *Coord. Chem. Rev.* **203,** 219 (2000).

20. A. S. Abd-El-Aziz, C. R. de Denus, M. J. Zaworotko, L. R. MacGillivray, *J. Chem. Soc. Dalton Trans.* 3375, (1995).

21. A. S. Abd-El-Aziz, D. A. Armstrong, S. Bernardin, H. M. Hutton, *Can. J. Chem.* **74,** 2073 (1996).

22. J. A. Segal, *J. Chem. Soc. Chem. Commun.* 1338 (1985).

23. A. A. Dembek, P. J. Fagan, M. Marsi, *Macromolecules* **26,** 2292 (1993).

24. A. A. Dembek, P. J. Fagan, M. Marsi, *Polym. Mater. Sci. Eng.* **71,** 158 (1994).

25. A. S. Abd-El-Aziz, E. K. Todd, K. M. Epp, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **39**(1), 300 (1998).

26. A. S. Abd-El-Aziz, E. K. Todd, K. M. Epp, *J. Inorg. Organomet. Polym.* **8,** 127 (1998).

27. A. S. Abd-El-Aziz, E. K. Todd, G. Z. Ma, *J. Poly. Sci. Part A: Poly. Chem.* **39,** 1216 (2001).

28. A. S. Abd-El-Aziz, E. K. Todd, R. M. Okasha, unpublished results.

29. A. S. Abd-El-Aziz, T. Afifi, W. Budakowski, K. Friesen, E. K. Todd, *Macromolecules* **35,** 8929 (2002).

30. A. S. Abd-El-Aziz, E. K. Todd, C. R. de Denus, A. A. Dembek, P. J. Fagan, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **40**(2), 926 (1999).

31. C. R. de Denus, L. M. Hoffa, E. K. Todd, A. S. Abd-El-Aziz, *J. Inorg. Organomet. Polym.* **10,** 189 (2000).

32. A. S. Abd-El-Aziz, E. K. Todd, R. M. Okasha, T. E. Wood, *Macromol. Rapid Commun.* **23,** 743 (2002).

33. C. U. Pittman, Jr., O. E. Ayers, S. P. McManus, *Macromolecules* **7,** 737 (1974).

34. C. U. Pittman, Jr., R. L. Voges, J. Elder, *Macromolecules* **4,** 302 (1971).

35. C. U. Pittman, Jr., G. V. Marlin, *J. Polym. Sci.: Polym. Chem. Ed.* **11,** 2753 (1973).

36. C. U. Pittman, Jr., P. L. Grube, O. E. Ayers, S. P. McManus, M. D. Rausch, G. A. Moser, *J. Polym. Sci., Part A1* **10,** 379 (1972).

37. A. S. Abd-El-Aziz, E. K. Todd, G. Z. Ma, J. DiMartino, *J. Inorg. Organomet. Polym.* **10,** 265 (2000).

38. A. S. Abd-El-Aziz, E. K. Todd, *Polym. Mater. Sci. Eng.* **86,** 104 (2002).

39. A. S. Abd-El-Aziz, L. J. May, J. A., R. M. Okasha, *J. Polym. Sci., Part A, Polym. Chem.* **39,** 2716 (2001).

40. A. S. Abd-El-Aziz, R. M. Okasha, J. Hurd, E. K. Todd, *Polym. Mater. Sci. Eng.* **86,** 91 (2002).

41. B. Chaudret, G. Chung, Y.-S. Huang, *J. Chem. Soc., Chem. Commun.* 749 (1990).

42. H. R. Allcock, A. A. Dembek, E. H. Klingenberg, *Macromolecules* **24,** 5208 (1991).

43. C. U. Pittman, Jr., W. J. Patterson, S. P. McManus, *J. Polym. Sci.: Polym. Chem. Ed.* **13,** 39 (1975).

44. R. Atencio, L. Brammer, S. Fang, F. C. Pigge, *New J. Chem.* **23,** 461 (1999).

45. L. Brammer, J. C. Mareque Rivas, R. Atencio, S. Fang, F. C. Pigge, *J. Chem. Soc., Dalton Trans.* 3855 (2000).

46. M. Oh, G. B. Carpenter, D. A. Sweigart, *Angew. Chem. Int. Ed.* **40,** 3191 (2001).

47. M. Oh, G. B. Carpenter, D. A. Sweigart, *Organometallics* **21,** 1290 (2002).

48. F. Moulines, D. Astruc, *J. Chem. Soc., Chem. Commun.* 614 (1989).

49. F. Moulines, L. Djakovitch, R. Boese, B. Gloaguen, W. Thiel, J.-L. Fillaut, M.-H. Delville, D. Astruc, *Angew. Chem. Int. Ed. Engl.* **32,** 1075 (1993).

50. J.-L. Fillaut, D. Astruc, *New J. Chem.* **20,** 945 (1996).

51. C. Valerio, B. Gloaguen, J.-L. Fillaut, D. Astruc, *Bull. Soc. Chim. Fr.* **133,** 101 (1996).

52. E. Alonso, C. Valerio, J. Ruiz, D. Astruc, *New J. Chem.* **21,** 1139 (1997).

53. S. Rigaut, M.-H. Delville, D. Astruc, *J. Am. Chem. Soc.* **119,** 11132 (1997).

54. C. Valerio, E. Alonso, J. Ruiz, J.-C. Blais, D. Astruc, *Angew. Chem. Int. Ed.* **38,** 1747 (1999).

55. C. Valerio, F. Moulines, J. Ruiz, J.-C. Blais, D. Astruc, *J. Org. Chem.* **65,** 1996 (2000).

56. J. Ruiz, C. Pradet, F. Varret, D. Astruc, *Chem. Commun.* 1108 (2002).

57. B. Alonso, J.-C. Blais, D. Astruc, *Organometallics* **21,** 1001 (2002).

58. S. Nlate, Y. Nieto, J.-C. Blais, J. Ruiz, D. Astruc, *Chem. Eur. J.* **8,** 171 (2002).

59. C. Valerio, S. Rigaut, J. Ruiz, J.-L. Fillaut, M.-H. Delville, D. Astruc, *Bull. Pol. Acad. Sci.* **46,** 309 (1998).

60. D. Astruc, F. Chardac, *Chem. Rev.* **101,** 2991 (2001).

61. A. S. Abd-El-Aziz, E. K. Todd, T. H. Afifi, *Macromol. Rapid Commun.* **23,** 113 (2002).

62. F. Lobete, I. Cuadrado, C. M. Casado, B. Alonso, M. Moran, J. Losada, *J. Organomet. Chem.* **509,** 109 (1996).

63. J. W. Kriesel, S. Konig, M. A. Freitas, A. G. Marshall, J. A. Leary, T. D. Tilley, *J. Am. Chem. Soc.* **120,** 12207 (1998).

64. C. U. Pittman, Jr., G. V. Marlin, T. D. Rounsefell, *Macromolecules* **6,** 1 (1973).

65. C. U. Pittman, Jr., R. M. Hanes, *J. Paint. Technol.* **45,** 78 (1973).

66. C. U. Pittman, Jr., T. D. Rounsefell, E. A. Lewis, J. E. Sheats, B. H. Edwards, M. D. Rausch, E. A. Mintz, *Macromolecules* **11,** 560 (1978).

67. D. W. Macomber, W. P. Hart, M. D. Rausch, R. D. Priestner, C. U. Pittman, Jr., *J. Am. Chem. Soc.* **104,** 884 (1982).

68. C. U. Pittman, Jr., T. V. Jayaraman, R. D. Priestner, Jr., S. Spencer, M. D. Rausch, D. Macomber, *Macromolecules* **14,** 237 (1981).

69. S. F. Mapolie, J. R. Moss, G. S. Smith, *J. Inorg. Organomet. Chem.* **7,** 233 (1997).

70. S. F. Mapolie, I. J. Mavunkal, J. R. Moss, G. S. Smith, *Appl. Organomet. Chem.* **16,** 307 (2002).

71. J. Matsuda, K. Aramaki, H. Nishihara, *J. Chem. Soc. Faraday Trans.* **91,** 1477 (1995).

72. U. H. F. Bunz, V. Enkelmann, F. Beer, *Organometallics* **14,** 2490 (1995).

73. S. Setayesh, U. H. F. Bunz, *Organometallics* **15,** 5470 (1996).

74. J. Ohsita, T. Hamaguchi, E. Toyoda, A. Kunai, K. Komaguchi, M. Shiotani, M. Ishikawa, A. Naka, *Organometallics* **18,** 1717 (1999).

75. A. A. Hurley, D. L. Mohler, *Org. Lett.* **2,** 2745 (2000).

76. Y.-H. Liao, J. R. Moss, *Organometallics* **14,** 2130 (1995).

77. Y.-H. Liao, J. R. Moss, *Organometallics* **15,** 4307 (1996).

78. M. Altmann, U. H. F. Bunz, *Angew. Chem. Int. Ed. Engl.* **34,** 569 (1995).

79. W. Steffen, B. Kohler, M. Altmann, U. Scherf, K. Stitzer, H.-C. zur Loye, U. H. F. Bunz, *Chem. Eur. J.* **7,** 117 (2001).

80. W. Steffen, U. H. F. Bunz, *Macromolecules* **33,** 9518 (2000).

81. M. Altmann, V. Enkelmann, F. Beer, U. H. F. Bunz, *Organometallics* **15,** 394 (1996).

82. Y. Sawada, I. Tomita, T. Endo, *Polym. Bull.* **43,** 165 (1999).

83. Y. Sawada, I. Tomita, I. L. Rozhanskii, T. Endo, *J. Inorg. Organomet. Polym.* **10,** 221 (2000).

84. M. Murata, T. Hoshi, I. Matsuoka, T. Nankawa, M. Kurihara, H. Nishihara, *J. Inorg. Organomet. Polym.* **10,** 209 (2000).

85. J.-C. Lee, A. Nishio, I. Tomita, T. Endo, *Macromolecules* **30,** 5205 (1997).

86. I. Matsuoka, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.* 147 (1998).

87. T. Shimura, A. Ohkubo, K. Aramaki, H. Uekusa, T. Fujita, S. Ohba, H. Nishihara, *Inorg. Chim. Acta* **230,** 215 (1995).

88. I. Tomita, A. Nishio, T. Endo, *Macromolecules* **28,** 3042 (1995).

89. T. Shimura, A. Ohkubo, N. Matsuda, I. Matsuoka, K. Aramaki, H. Nishihara, *Chem. Mater.* **8,** 1307 (1996).

90. S. M. Waybright, K. McAlpine, M. Laskoski, M. D. Smith, U. H. F. Bunz, *J. Am. Chem. Soc.* **124,** 8661 (2002).

σ-Bonded Metals and Metal–Metal Bonds in the Polymer Framework

CONTENTS

I. INTRODUCTION

There are many examples of polymers that contain metal-element σ bonds in their backbones. Early research in this area, pioneered by Carraher and his research group, dealt with the synthesis of group IVB metallocenes containing metal–oxygen (**1**), metal–sulfur, and metal–nitrogen bonds. Many classes of polymers containing metal–carbon σ-bonds in their backbones (**2**) have also emerged. These types of polymers include those with backbone metal–aryl bonds (**2a**), polymers with mainchain metallacyclopentadiene rings (**2b**), and metal-acetylide-containing polymers (**2c**). Polymers with metal–metal single (**3**) and multiple (**4**) bonds in their backbones are

also described. These polymers often have very different properties and methods of synthesis than other classes of metal-containing polymers. The last area covered will be star and dendritic polymers with metal–carbon σ bonds.
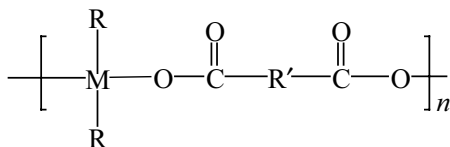
1

2a

2b

2c

3

4
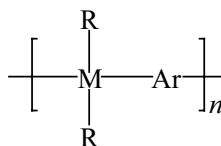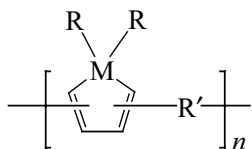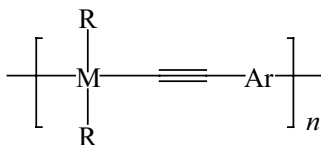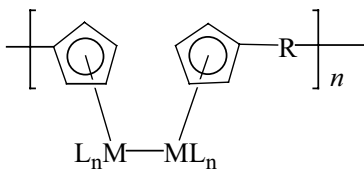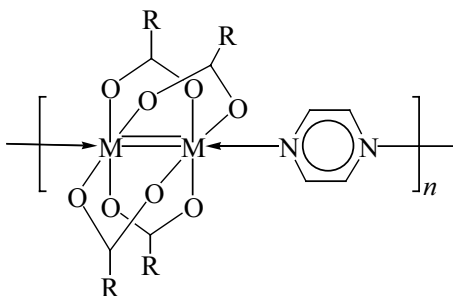
II. METAL σ BONDS

A. Metal–Oxygen, Metal–Sulfur, and Metal–Nitrogen Bonds

In the early 1970s, Carraher and coworkers developed a number of different organometallic polymers containing metal–oxygen, metal–sulfur, and metal–nitrogen bonds in the polymer backbone. For example, a number of polyethers,[1–5] thioethers,[6–9] amines,[10,11] esters,[12–15] and oximes[16–22] of titanium, zirconium, and hafnium were prepared. Scheme 1 shows the synthesis of hafnium, zirconium, and

titanium polyesters (**7a–c**) synthesized by reaction of the dicyclopentadienylmetal dichloride complexes **5a–c** with the sodium salt of terephthalic acid (**6**).[1] These polymers were prepared using either interfacial or solution polymerization techniques in water. In aqueous solution, the dicyclopentadienylmetal dichloride complexes ionize to their corresponding dicationic species and were subsequently reacted with various dicarboxylates.[12–15]

M = Ti, Zr, Hf

5a–c

6

7a–c
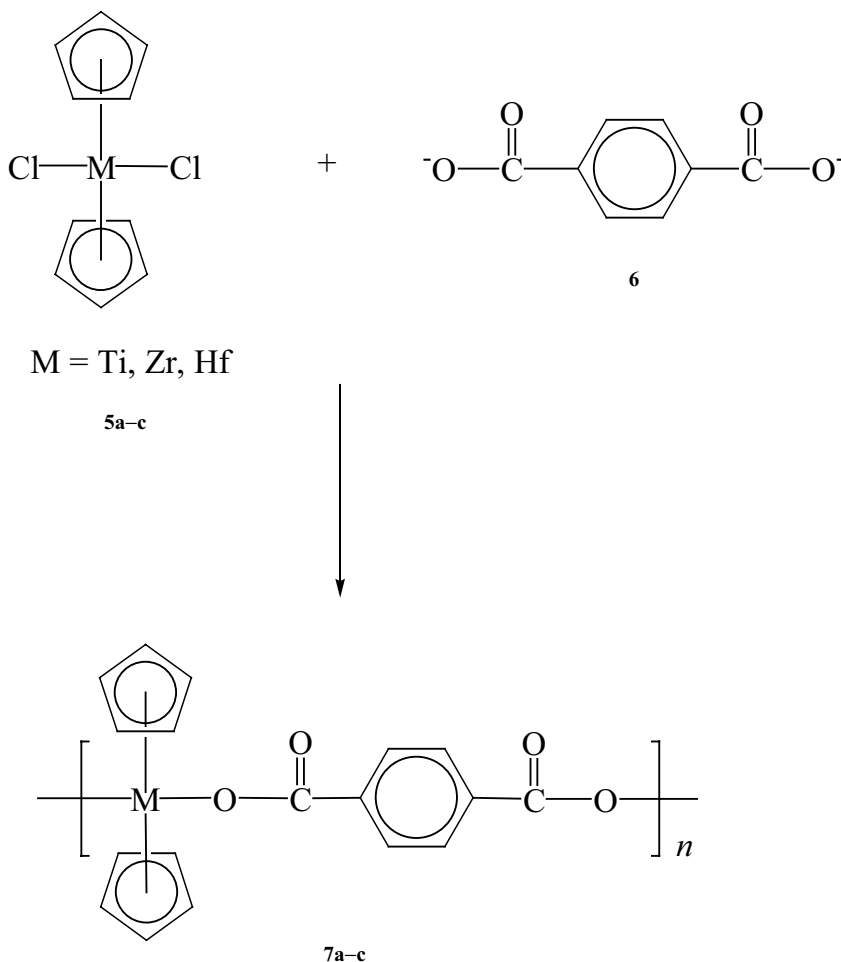
Scheme 1

The electrical properties of polyoximes of the group IVB metallocenes were also examined.[16–22] These polymers (**9**) were semiconductors.[16] By using a larger molar ratio of the metallocene, crosslinked polymers such as **10** (Scheme 2) could also be produced.[17]
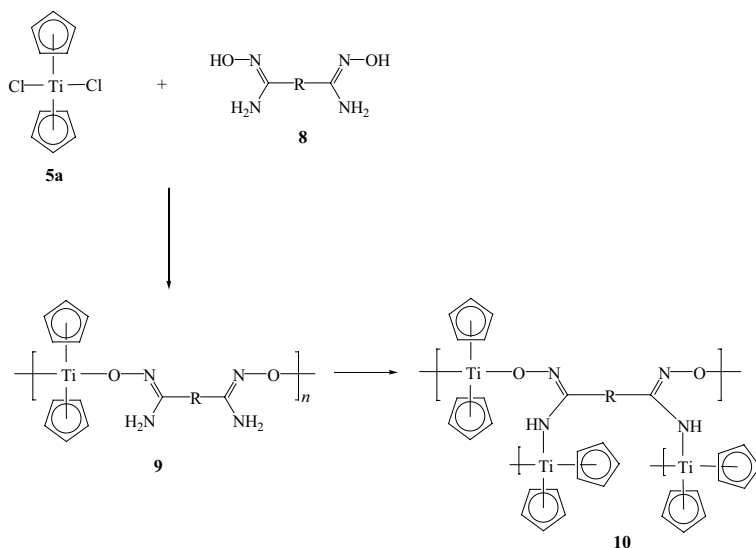
Scheme 2

B. Metal–Aryl Bonds

Organometallic polymers containing M–C σ bonds in their structures have been the focus of many investigations because of their electrical and optical properties. Rodlike organonickel polymers (**13**) (Scheme 3) have been synthesized by reaction of dibrominated nickel complexes such as **12** with dilithiated aromatic compounds such as **11**.[23,24] These polymers displayed air and moisture stability up to 220°C. The weight-average molecular weights of these polymers ranged from 1.8 to 11.1×10^4 by GPC using a universal calibration.[24]
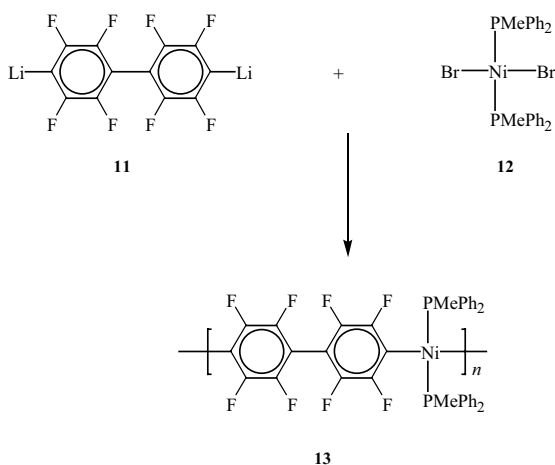
Scheme 3

C. Metallacyclopentadienes

Tilley and coworkers synthesized polymers containing zirconacyclopentadiene rings (**15**) in their backbones (Scheme 4).[25–29] Polymer **15** had a weight-average molecular weight of 13,000 and a number-average molecular weight of 4600.[25] It was found that when the polymerization reaction was conducted at high temperatures or if the polymer was refluxed in THF, depolymerization occurred and a low molecular weight trimeric macrocycle (**16**) was produced quantitatively. Hydrolysis of the macrocycle with HCl resulted in the conversion of the metallacycle rings to *trans*-dienyl units (**17**).[25–27]
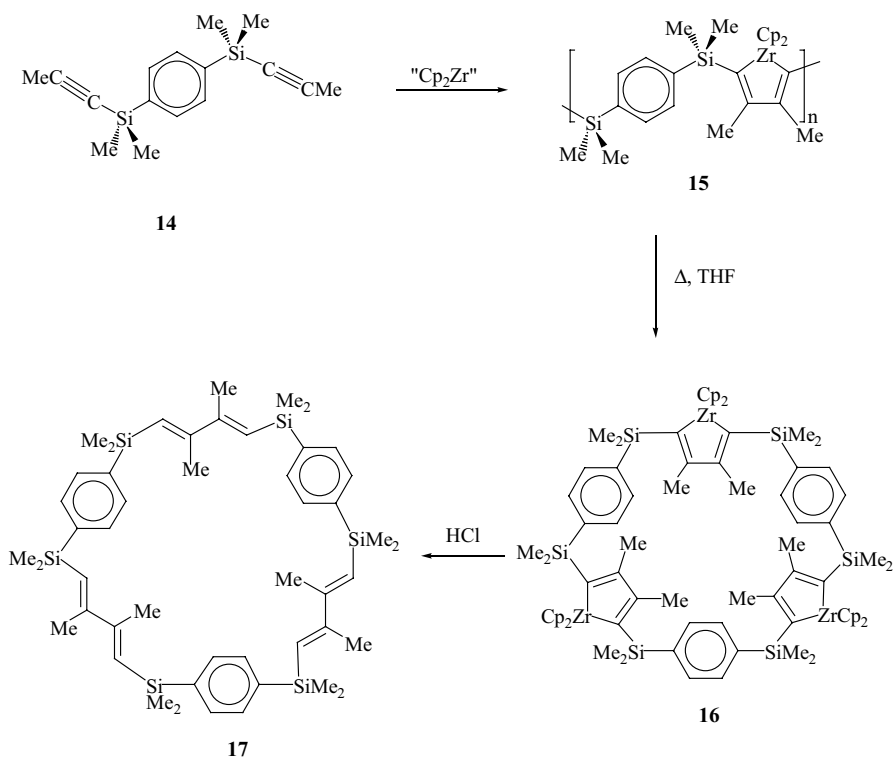
Scheme 4

The zirconacyclopentadiene units in this class of polymer could also be converted into various functionalities while maintaining the integrity of the polymers (Scheme 5).[28,29] For example, reaction of polymer **20** with dimethylaceteylene dicarboxylate (**21**) in the presence of CuCl/LiCl produced the phenylene-based polymer **22**. Polymer **20** could also be reacted with acid or iodine to produce polymers with dienyl units in their backbones. Alternatively, polymers with thiophene and phosphole units in the backbone (**23**) were also synthesized.
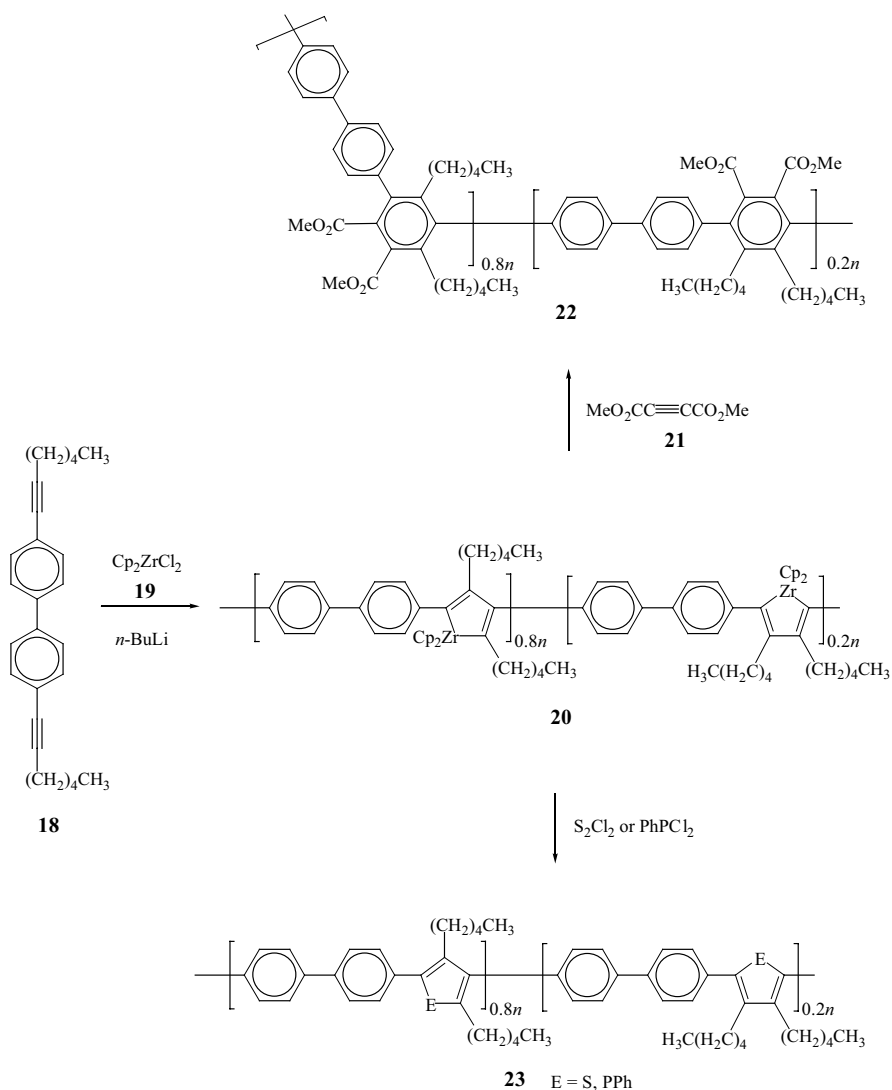
Scheme 5

The synthetic methodology used by Tilley is similar to that used by Nishihara and Endo to prepare polymers with cobaltacyclopentadiene groups in the backbone.[30–35] For example, Scheme 6 shows the reaction of **24** with **25** to produce the cobaltacyclopentadiene-containing polymer (**26**).[35] Reaction of polymer **26** with an isocyanate (**27**) resulted in the formation of a 2-pyridone ring (**28**).
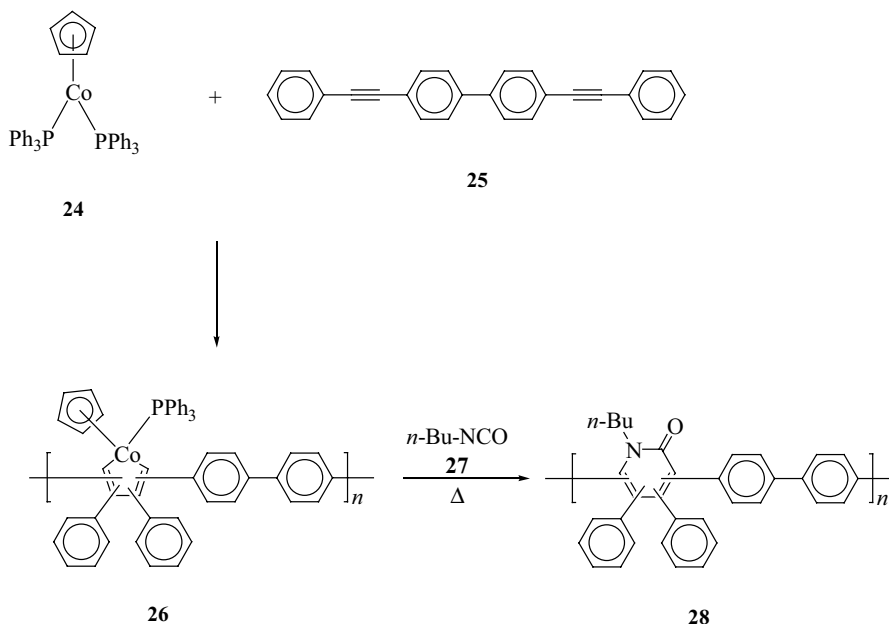
Scheme 6

D. Metal Acetylides

An interesting group of rigid-rod, organometallic polymers emerged in the late 1970s and early 1980s from Takahashi et al. in which transition metals were bonded to alkyne carbon atoms.[36–43] For example, *bis*-phosphine *bis*-alkynyl platinum complexes (**29**) reacted with *bis*-phosphinedichloroplatinum (**30**) in the presence of CuI and Et$_2$NH to generate the conjugated rigid-rod polymer (**31**, Scheme 7). The linear structure of these polymers was required by the *trans* geometry of the monomers. The incorporation of transition metals into polymers containing triple bonds enhanced metal $d\pi$-$p\pi$* backbonding, which contributes to π-electron delocalization.[44] All of these polymers formed nematic liquid crystals in trichloroethylene. Some exhibited mainchain alignment perpendicular to an applied magnetic field while others aligned parallel to the field.[37,38] The nature of the transition metal controlled the magnetic properties. Large values of the Mark–Houwink exponent ($\alpha = 1.7$ for **31**) and the lack of an intrinsic viscosity dependence on solvent confirmed the rodlike nature of the polymers.

Scheme 8 describes the synthesis of polymeric acetylides (**34**) containing both platinum and palladium moieties in their backbones.[43]

$$HC{\equiv}C{-}C{\equiv}C{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}{-}C{\equiv}C{-}C{\equiv}CH \qquad + \qquad Cl{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}{-}Cl$$

29   **30**

$$\Big\downarrow \begin{array}{l} CuI \\ (C_2H_5)_2NH \end{array}$$

$$\Big[\!\!-C{\equiv}C{-}C{\equiv}C{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{Pt}}{-}C{\equiv}C{-}C{\equiv}C{-}\!\!\Big]_n$$

31

Scheme 7

$$HC{\equiv}C{-}C{\equiv}C{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{M}}{-}C{\equiv}C{-}C{\equiv}CH \qquad + \qquad Cl{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{M'}}{-}Cl$$

M = Pt, M′ = Pd
M = Pd, M′ = Pt   **33**

32

$$\Big[\!\!-C{\equiv}C{-}C{\equiv}C{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{M}}{-}C{\equiv}C{-}C{\equiv}C{-}\overset{\displaystyle PBu_3}{\underset{\displaystyle PBu_3}{M'}}{-}\!\!\Big]_n$$

34
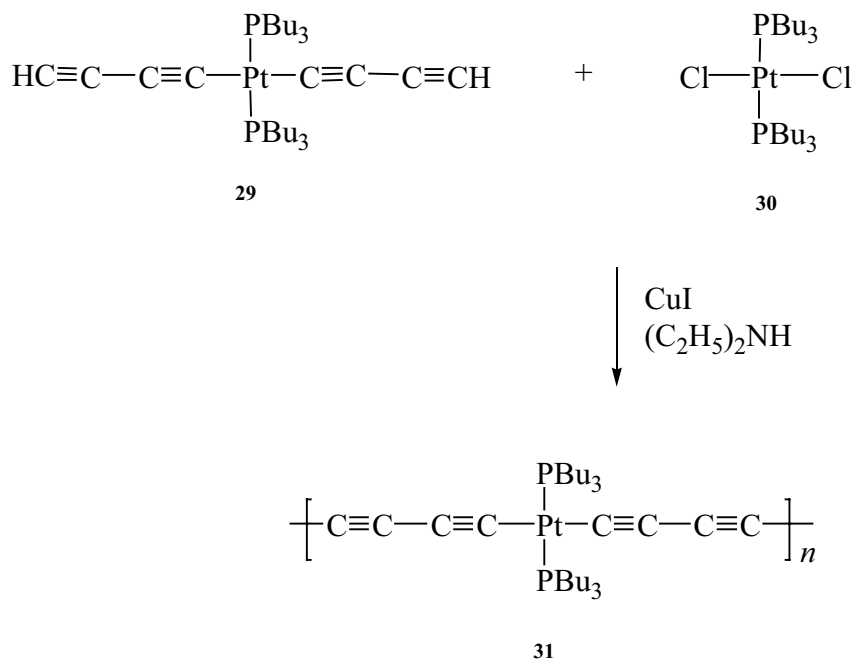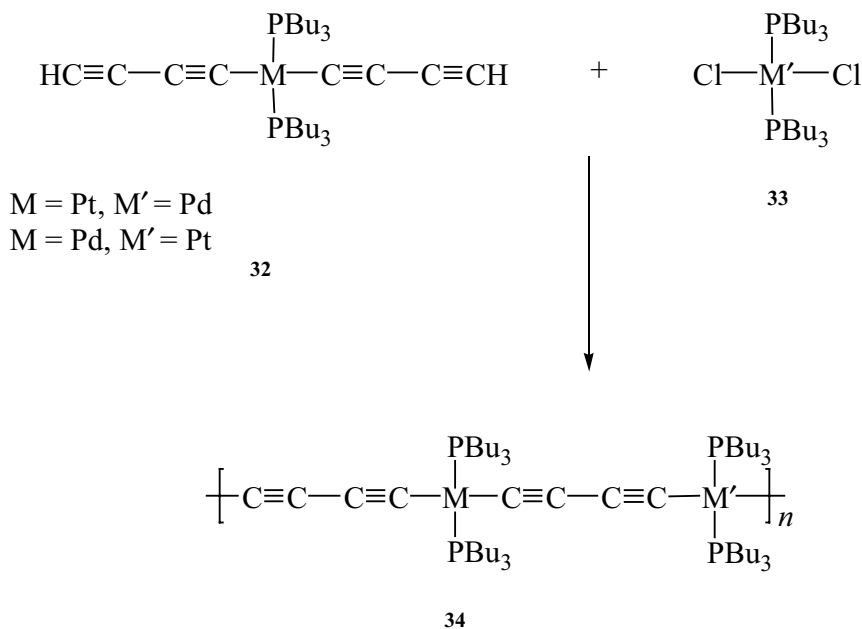
Scheme 8

The 1990s gave rise to new classes of organometallic polymers when Lewis et al. developed an innovative route to rigid-rod metal-containing polyynes by reaction of *bis*-trimethylstannylacetylide, $Me_3SnC\equiv C-R-C\equiv CSnMe_3$, with $(PBu_3)_2MCl_2$ to give polymers having molecular weights in the range of 1×10^5.[45–56] Using trialkyne-substituted tin derivatives (**35**) gave crosslinked polymers that had structures **37** and **39** (Scheme 9).[53] It is noteworthy that platinum polyynes of this type exhibited third-order optical nonlinearity.[57–60]
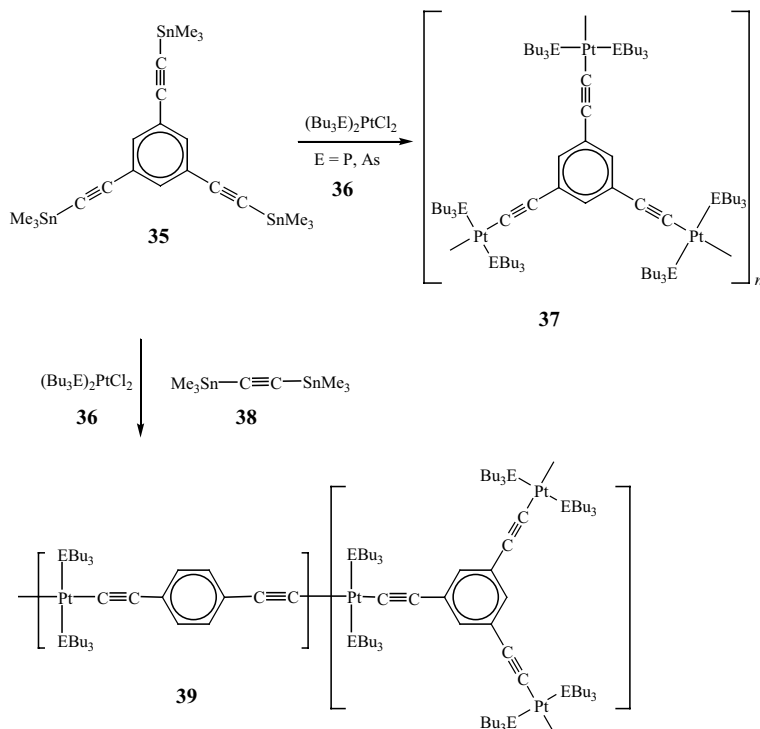
Scheme 9

High MW, rigid-rod, conjugated transition metal acetylide polymers (**42**, Scheme 10) were synthesized by reaction of the dichloro iron or ruthenium chelated diphosphine complexes (**40**) with a *bis*-trimethylstannylacetylide monomer (**41**).[55,56]

Reaction of the rhodium complex **43** with an equimolar amount of compound **44** gave a rigid-rod acetylide organometallic polymer **45** (Scheme 11).[61] This rhodium-containing polymer was soluble in THF.

Low solubility of products is a major difficulty associated with the synthesis of conjugated transition metal acetylide polymers. Puddephatt and coworkers found that the solubility of gold acetylide polymers could be controlled by altering the phosphine ligands on Au.[62–65] Scheme 12 shows the synthesis of low-solubility polymers (**48**) that had molecular weights estimated to range from 13,700 to 27,000.[62]

Et$_2$P   PEt$_2$

Cl—M—Cl   +   Me$_3$Sn—C≡C—Ar—C≡C—SnMe$_3$

Et$_2$P   PEt$_2$

41

40

M = Fe, Ru

CuI

Et$_2$P   PEt$_2$

$\left[\vphantom{\begin{array}{c}a\\a\end{array}}\right.$ M—C≡C—Ar—C≡C $\left.\vphantom{\begin{array}{c}a\\a\end{array}}\right]_n$

Et$_2$P   PEt$_2$

42

Scheme 10

[Rh(P^{n}Bu$_3$)$_4$]BPh$_4$ +   H—C≡C—⟨◯⟩—C≡C—H

43   **44**

MeLi

H   P^{n}Bu$_3$

$\left[\vphantom{\begin{array}{c}a\\a\end{array}}\right.$ Rh—C≡C—⟨◯⟩—C≡C $\left.\vphantom{\begin{array}{c}a\\a\end{array}}\right]_n$

^{n}Bu$_3$P   P^{n}Bu$_3$

45
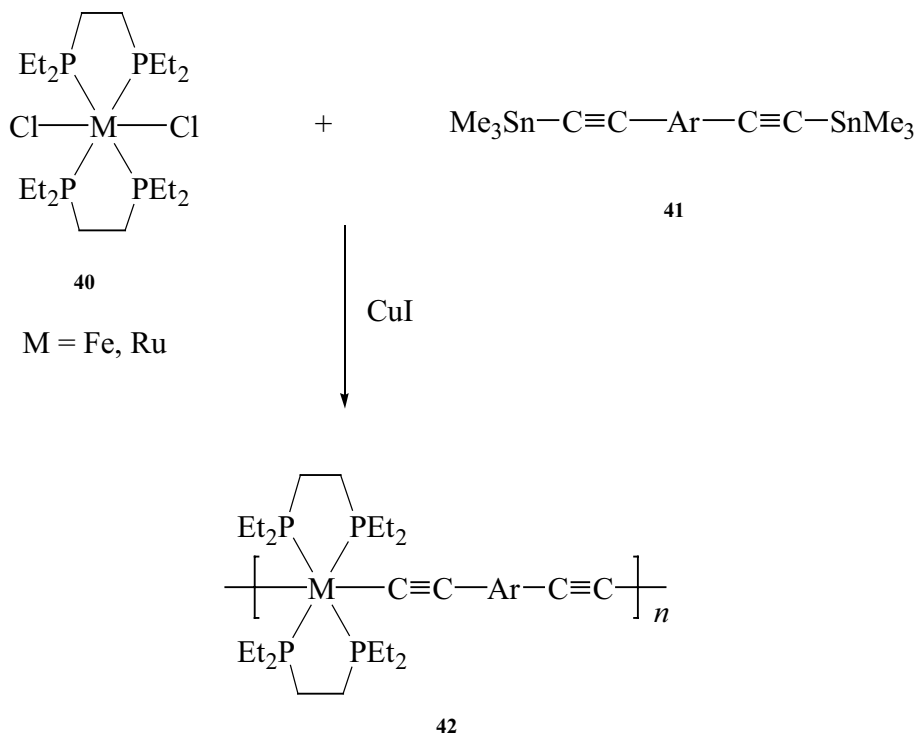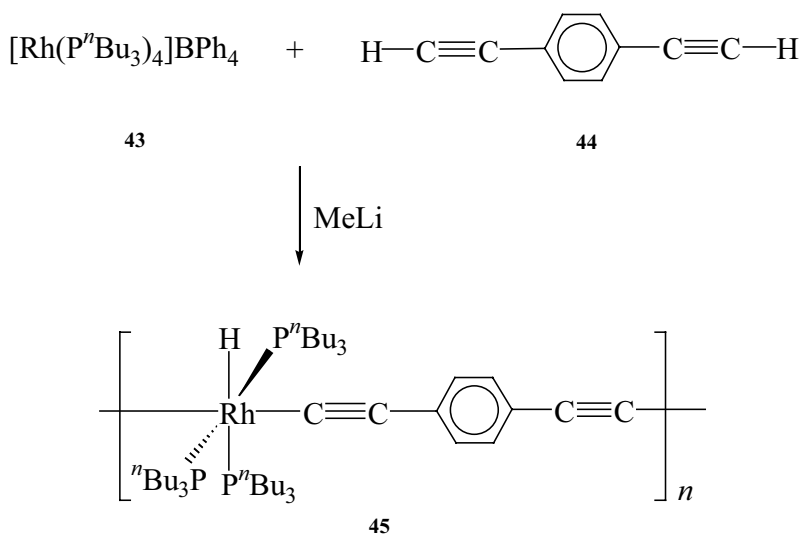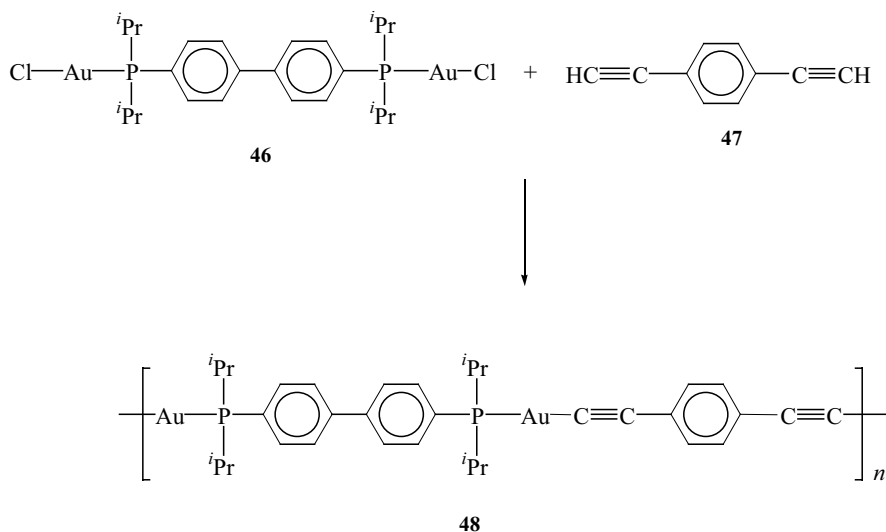
Scheme 11

Scheme 12

Similarly conjugated zirconocene acetylene polymers (**51**) were prepared by reaction of *bis*-pentamethylcyclopentadienyl zirconium(IV) dichloride (**49**) with dilithioacetylene or dilithiodiacetylene (**50**) (Scheme 13).[66] These relatively high MW polymers (M_w=55,000–68,000) displayed limited solubility in organic solvents other than *n*-hexane.
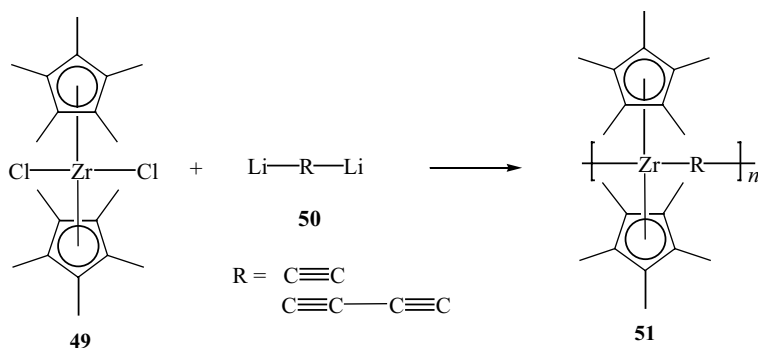
Scheme 13

One of the current trends in transition metal acetylide-containing polymers is the incorporation of heterocyclic rings into their backbones in order to alter their electronic and optical properties.[67–74] Scheme 14 shows the reaction of monomers **52** and **54** with the platinum complex **30** to produce polymers **54** and **55**, respectively.[67] The optical gap and intersystem crossing from the singlet to triplet states decreased with increasing conjugation in the polymers.
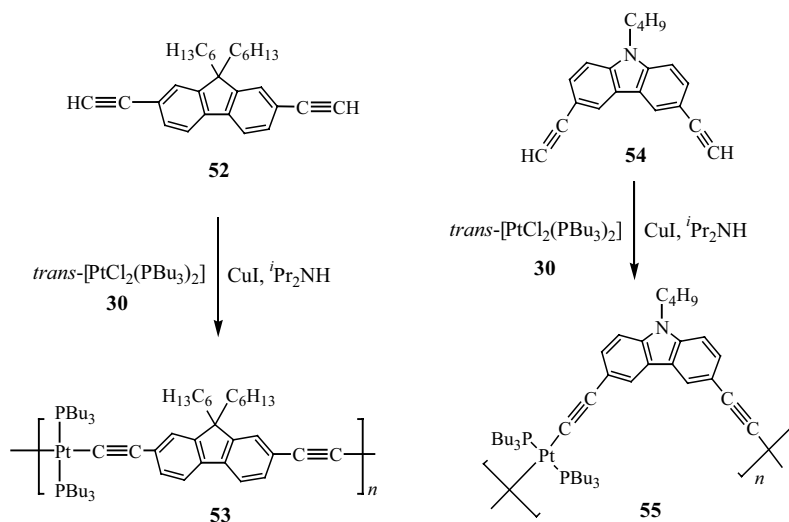
Scheme 14

Wong and coworkers have reported the synthesis of a soluble platinum polyyne containing bithiazole units in the backbone.[68] Monomer **56** was chosen because of its electron-donating and electron-withdrawing substituents. Scheme 15 shows the synthesis of polymer **57** by the reaction of **30** with **56** where dehydrohalogenation occurs. Polymer **57** had a M_w of 47,500 and a M_n of 40,390, corresponding to a degree of polymerization of 44. Excitation of polymer **57** at 425 nm resulted in a luminescence peak at 539 nm. This polymer is also photoresponsive and its photocurrent increased with increasing bias voltage.
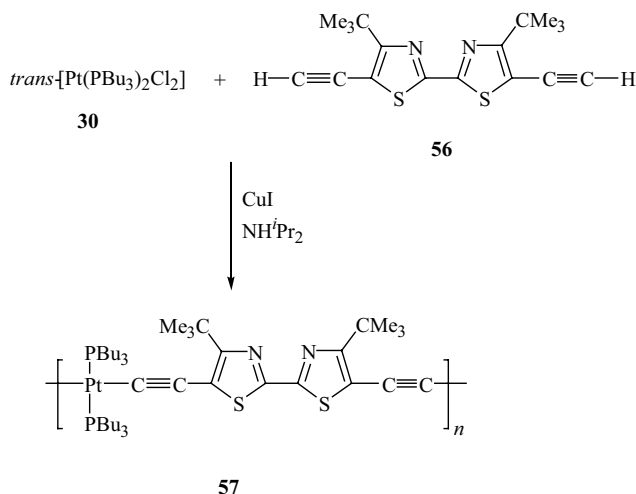
Scheme 15

Scheme 16 shows the synthesis of platinum and palladium acetylides that contain cyclodiborazane units in the backbone.[75] Reaction of monomers **58**, functionalized with cyano groups, with tripylborane (**59**) resulted in the production of polymer **60** via hydroboration polymerization. The platinum- and palladium-containing polymers (**60**) displayed good solubility in organic solvents and had weight-average molecular weights of 9700 and 10,400, respectively. The fluorescence spectra of these polymers were obtained on excitation at 400 nm. The platinum-based polymer showed a weak emission at 460 nm, while the palladium-based polymer showed a stronger emission at 460 nm. In addition, the palladium-containing polymer also fluoresced at 530 nm when it was excited at 450 nm.[75]
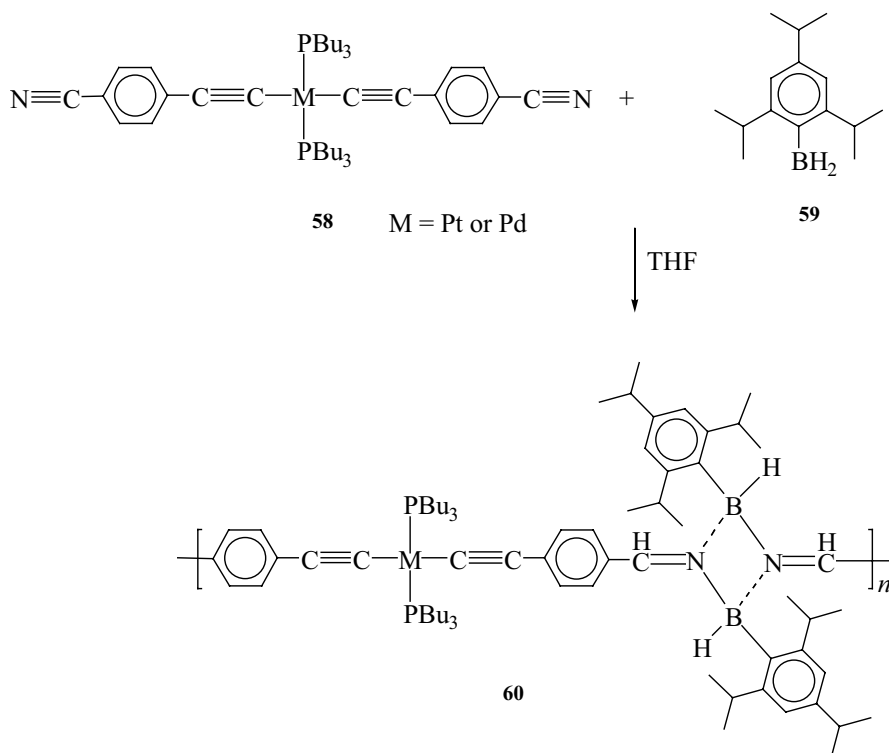
Scheme 16

III. METAL–METAL BONDS

Polymers containing metal–metal bonds are of interest due to the electrical properties that these materials may possess. Because of the synthetic difficulties that are frequently encountered in the production of these materials, it was not until the mid-1980s that reports on this class of polymer emerged. One of the most bizarre of all metal-containing polymer structures was reported by Magnus and Becker.[76] They allowed the dimeric monomer **61** (Scheme 17) to stand in methanol solutions. A

black insoluble polymer precipitated from solution and was assigned structure **62**. Microanalytical analysis provided evidence that the material was a polyacetylene of approximately 30 units in which each triple bond was capped with a $Co_2(CO)_6$ unit.
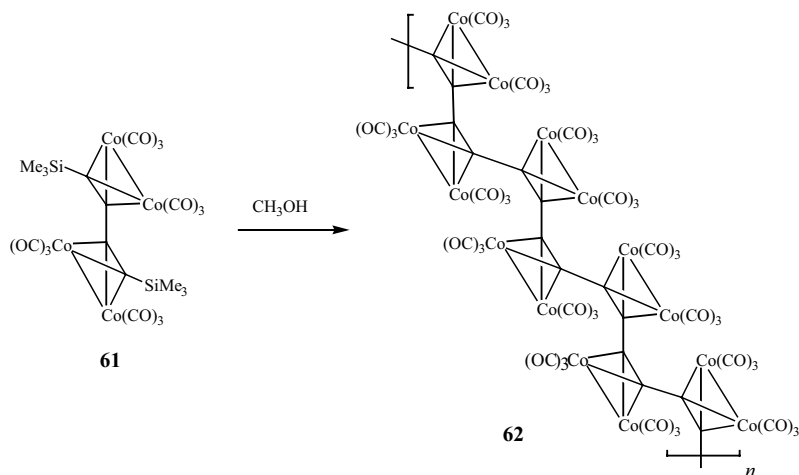
Scheme 17

Brook and coworkers reported the formation of an organocobalt polymer (**65**, Scheme 18) from the reaction of $Co_2(CO)_8$ (**64**) with a polysiloxane that contained acetylenic units in the backbone (**63**).[77] Mixed-metal systems were also described in which arenes complexes coordinated to chromium tricarbonyl were reacted with $Mo_2Cp_2(CO)_6$ or $Co_2(CO)_8$.

Scheme 18

Cuadrado et al. prepared a polymer with Fe−Fe bonds (**68**) by the reaction of a cyclopentadiene-substituted polysiloxane (**66**) with $Fe(CO)_5$ (Scheme 19).[78] The insolubility of the polymer indicated that crosslinking between polysiloxane chains also occurred. Polymers with more controlled structures were prepared by polycondensation of monomers already containing Fe−Fe bonds with disilanols.[78]

Scheme 19

Tyler and coworkers have developed photochemically reactive polymers (**69**) by condensation of organic monomers with complexes that incorporated Fe−Fe or Mo−Mo bonds in their structures.[79–83] On photolysis, the resulting polymers could be depolymerized via cleavage of the metal–metal bonds to produce species such as **70**. A polymer with a metal–metal triple bond could also be isolated to give Mo- and W-based polymeric materials (**71**, Scheme 20).[79,80]

Scheme 20

A polymer with molybdenum–molybdenum σ bonds in the backbone has also been synthesized by Royo and coworkers according to the methodology shown in Scheme 21.[84] A dinuclear complex containing *trans*-Mo(CO)$_3$Cl moieties pendent to cyclopentadienyl rings (**72**) was reacted with MeMgCl, resulting in the formation of polymer **73** containing Mo−Mo bonds. Polymer **73** was insoluble in all common organic solvents.
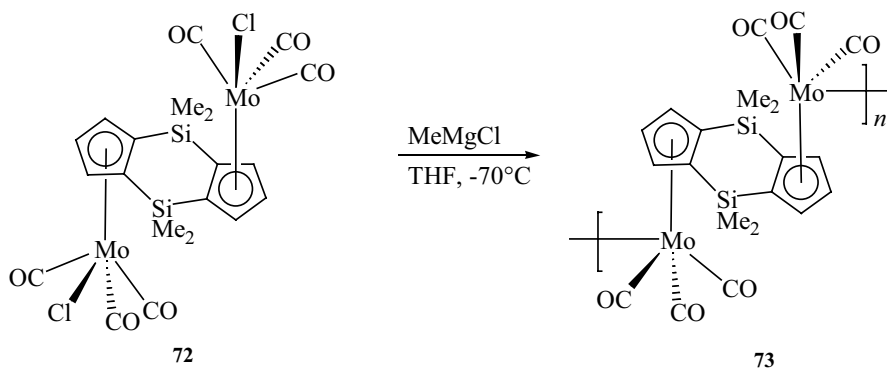
Scheme 21

Polymeric materials containing Pt−Pt bonds in their backbones have been examined by Puddephatt.[85] The formation of low molecular weight platinum oligomers (**76**) (Scheme 22) was achieved by reaction of complex **74** with diacetylides, diphosphines, or diisocyanides (**75**). These materials exhibited very poor solubilities in organic solvents.

X = HC≡C, C≡N, PR$_2$ Y = C≡C, $n = 0$
                              C≡N, PR$_2$, $n = 2$
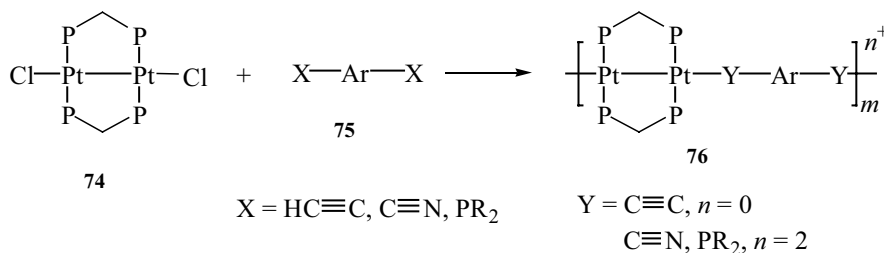
Scheme 22

Electrochemical reduction of ruthenium and osmium complexes containing *trans*-chloride ligands leads to metal-containing polymers in which metal–metal bonds make up the entire polymer backbone.[86,87] Hence, reduction of [M^{II}(*trans*-Cl$_2$)(bipy)(CO)$_2$] (M=Ru, Os) (**77**) to M^0 complexes generated a polymeric film (**78**) after loss of the chloride ligands (Scheme 23). Both the ruthenium- and osmium-based coordination polymers were selective for the reduction of carbon dioxide to carbon monoxide and formate.
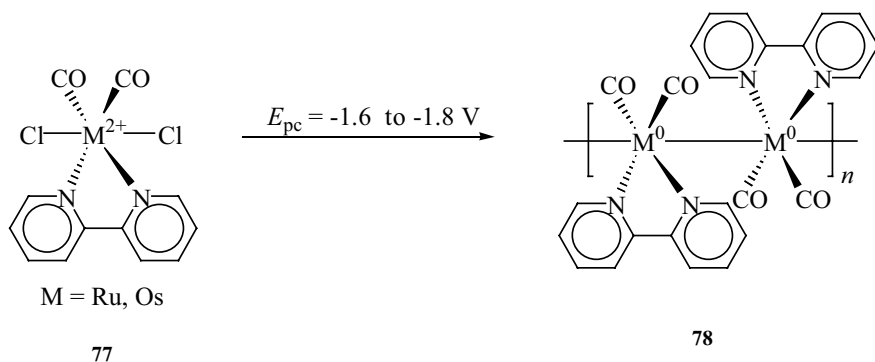
Scheme 23

A number of examples of oligomers and polymers containing metal–metal multiple bonds also have been reported.[88–93] Chisolm has synthesized polymers with metal–metal single and multiple bonds from bimetallic carboxylates and coordinating ligands.[88–90] Scheme 24 illustrates the synthesis of a ruthenium coordination polymer that contains Ru−Ru double bonds. Polymer **81** was prepared from reaction of the ruthenium carboxylate monomer (**79**) with pyrazine (**80**).[88] The polymer dissociated in coordinating solvents such as THF, and the MW was dependent on its concentration in noncoordinating solvents such as benzene. The polymer was thermally stable only to ≈140°C, at which point pyrazine was evolved.
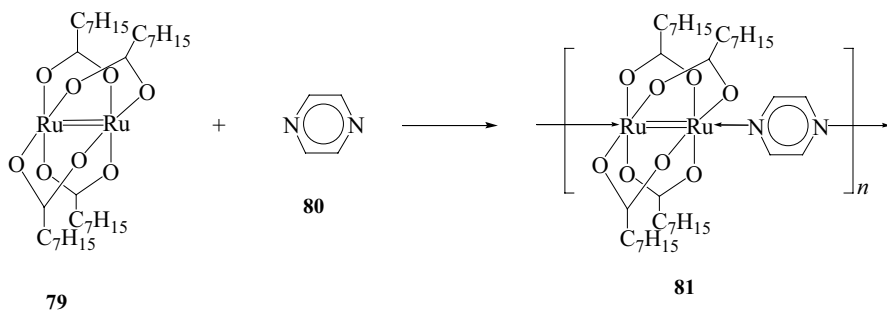
Scheme 24

IV. STARS AND DENDRIMERS

Moss et al. have synthesized dendrimers containing Ru−C bonds using a convergent approach.[94] A fourth-generation dendrimer containing 48 organometallic moieties was prepared. Polymer **82** is an example of a low-generation dendrimer containing six ruthenium complexes at its periphery.
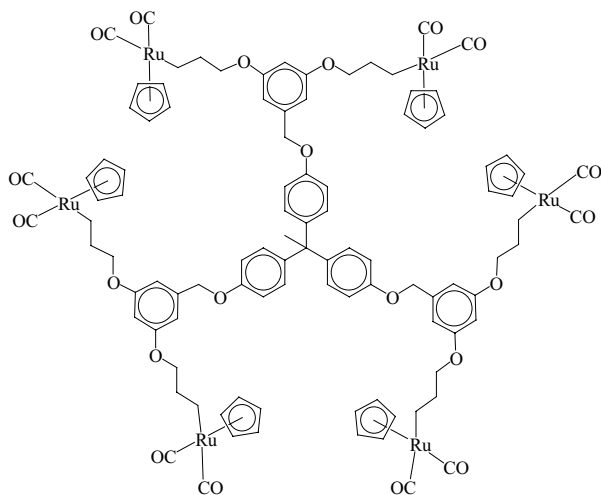
82

Platinum and palladium complexes containing metal–carbon σ bonds and metal–bipyridine coordination bonds have been incorporated into dendrimeric materials.[95–99] Polymers with both platinum and palladium coordinated to bipyridine ligands (**83**) have been synthesized by Puddephatt and coworkers.[97] These dendrimers were prepared by oxidative addition of a C−Br bond to a platinum complex to give the core molecule. Further reaction with the metal complex resulted in homo- or heterometallic materials.
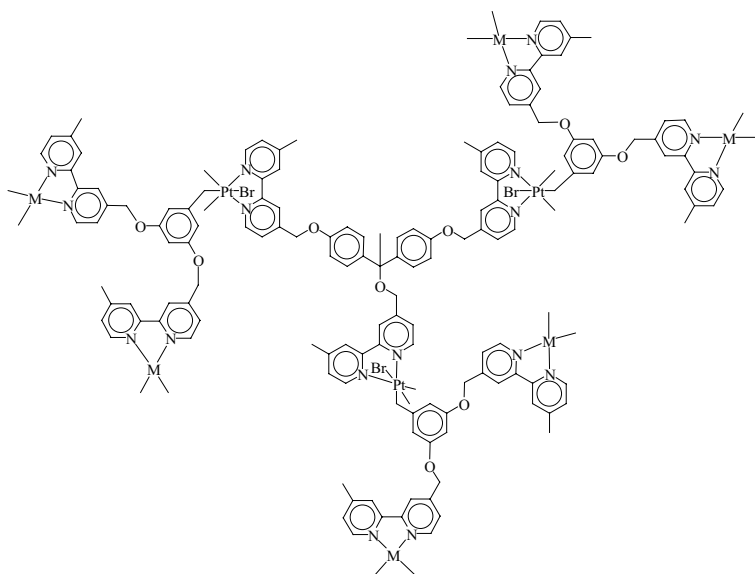
83   M = Pt, Pd

Carbosilanes containing palladium complexes at their peripheries have been synthesized by van Koten and coworkers by insertion of palladium(0) into carbon–iodine bonds.[99,100] Dendrimer **84** is an example of a first-generation dendrimer containing 12 palladium complexes in its structure.[100]
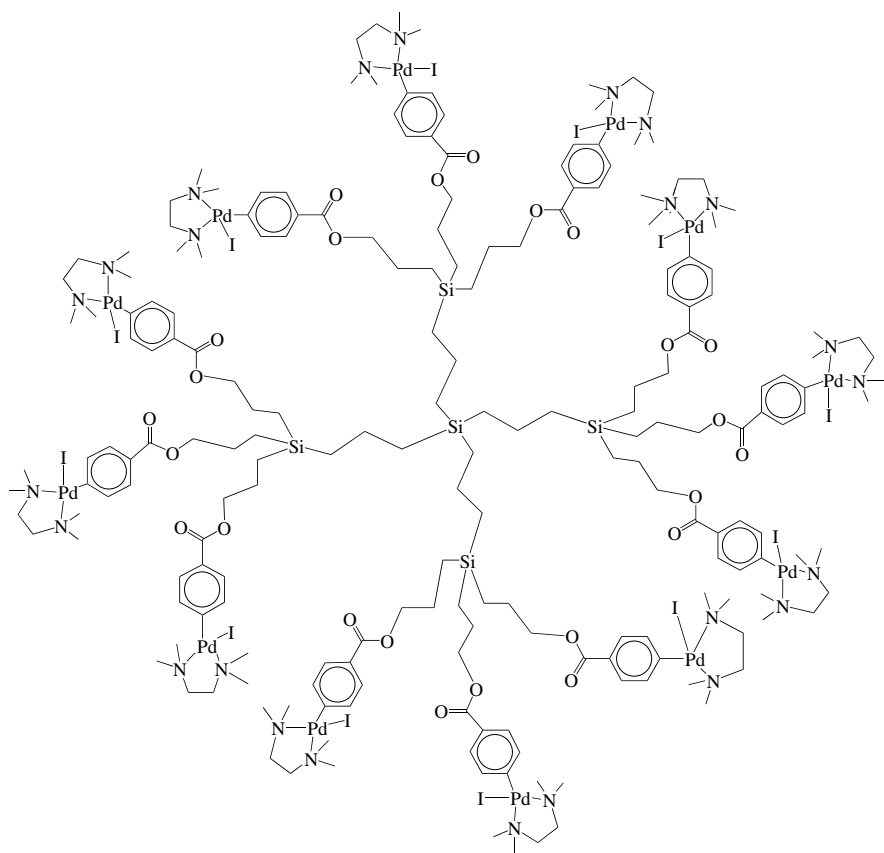
84

A number of metal acetylide-containing dendrimers and stars have also been prepared.[101–105] Scheme 25 shows the synthesis of a first-generation platinum acetylide dendrimer (**87**) containing 9 platinum complexes in its structure. Dendrimer **87** was made by the reaction of a chloro-substituted platinum complex (**85**) with an ethynyl functionalized dendron (**86**) in the presence of CuI.[101] Dendrimers with up to 45 platinum units were synthesized using this methodology.
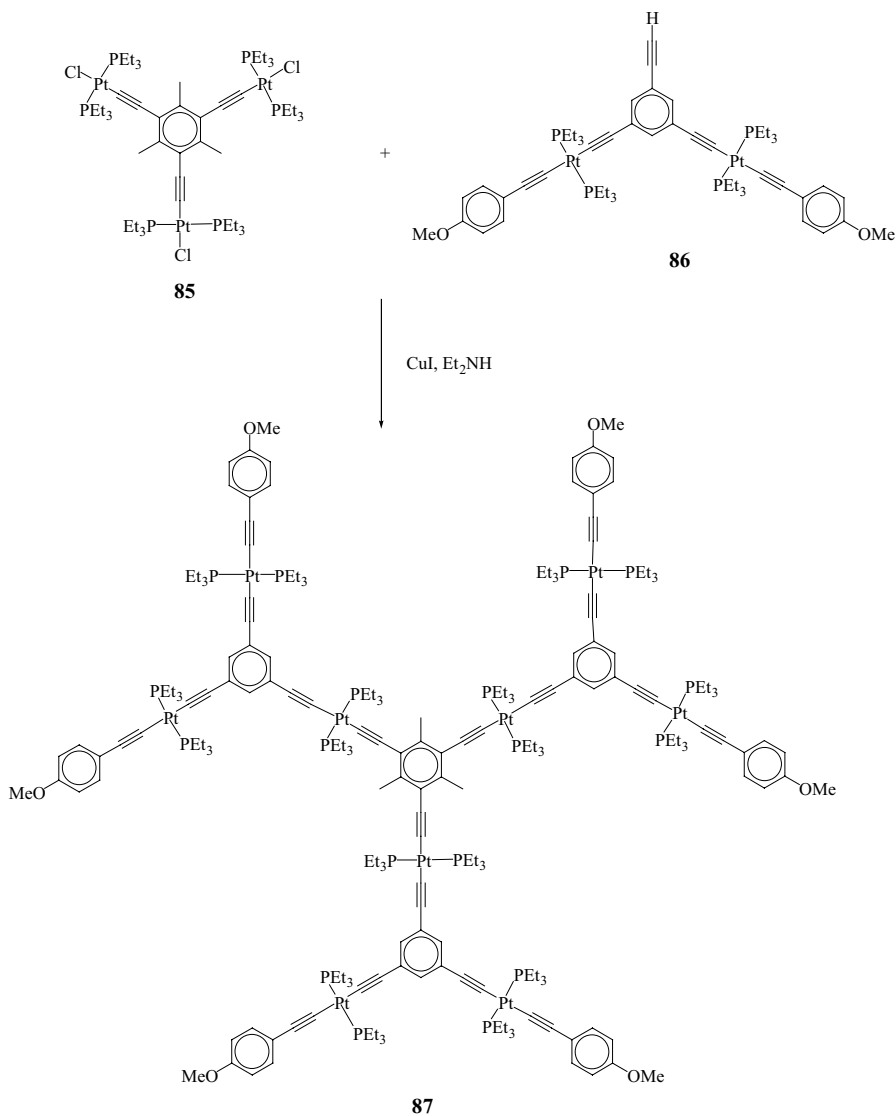
Scheme 25

V. SUMMARY

Metal atoms have been incorporated into macromolecular structures utilizing sigma bonding. While the "primary" bonding occurs via sigma bonding, π bonding is also often present. The metal may be attached to the macromolecular structure via sigma bonding to (most commonly) carbon, oxygen, nitrogen, and sulfur as well as

metal to metal bonding. Again, the formation of σ-bond linkages has been accomplished through a wide range of reactions including addition and condensation. Many of these materials show nonlinear optical, electrical, conducting and semiconducting, and liquid crystal properties. As with many of the other metal-containing polymers, there is an emphasis in the creation of star and dendrimer structures generally because such structures may allow the metal–atom sites to function somewhat independently for various purposes such as catalytic and sensing.

VI. REFERENCES

1. C. E. Carraher, Jr., S. T. Bajah, *Polymer* **15,** 9 (1974).
2. C. E. Carraher, Jr., G. F. Burrish, *J. Macromol. Sci.-Chem.* **A10**(8), 1457 (1976).
3. C. E. Carraher, Jr., L. M. Jambaya, *Angew. Makromol. Chem.* **39,** 69 (1974).
4. C. E. Carraher, Jr., L. M. Jambaya, *J. Macromol. Sci.-Chem.* **A8**(7), 1249 (1974).
5. C. E. Carraher, Jr., L. M. Jambaya, *Angew. Makromol. Chem.* **52,** 111 (1976).
6. C. E. Carraher, Jr., R. J. Nordin, *Makromol. Chem.* **164,** 87 (1973).
7. C. E. Carraher, Jr., R. J. Nordin, *J. Polym. Sci., Part A1* **10,** 521 (1972).
8. C. E. Carraher, Jr., R. J. Nordin, *J. Appl. Polym. Sci.* **18,** 53 (1974).
9. C. E. Carraher, Jr., *Polymer* **17,** 231 (1976).
10. C. Carraher, P. Lessek, *Eur. Polym. J.* **8,** 1339 (1972).
11. C. E. Carraher, Jr., R. Pfeiffer, P. Fullenkamp, *J. Macromol. Sci.-Chem.* **A10**(7), 1221 (1976).
12. C. E. Carraher, Jr., J. E. Sheats, *Makromol. Chem.* **166,** 23 (1973).
13. C. E. Carraher, Jr., *Eur. Polym. J.* **8,** 215 (1972).
14. C. E. Carraher, Jr., J. T. Reimer, *Polymer* **13,** 153 (1972).
15. C. E. Carraher, Jr., *Angew. Makromol. Chem.* **28,** 145 (1973).
16. C. Carraher, Jr., R. J. Linville, T. A. Manek, H. S. Blaxall, J. R. Taylor, L. R. Torre, in *Conductive Polymers,* R. B. Seymour, ed., Plenum Press, New York, **1981,** pp. 77–84.
17. C. E. Carraher, Jr., R. Frary, *Br. Polym. J.* **6,** 255 (1974).
18. C. E. Carraher, Jr., R. Frary, *Makromol. Chem.* **175,** 2307 (1974).
19. C. E. Carraher, Jr., M. J. Christensen, *Angew. Makromol. Chem.* **69,** 61 (1978).
20. C. E. Carraher, Jr., M. J. Christensen, J. A. Schroeder, *J. Macromol. Sci.-Chem.* **A11**(11), 2021 (1977).
21. C. E. Carraher, Jr., L. P. Torre, H. M. Molloy, *J. Macromol. Sci.-Chem.* **A15**(5), 757 (1981).
22. C. E. Carraher, Jr., R. A. Frary, *J. Polym. Sci., Polym. Chem. Ed.* **12,** 799 (1974).
23. K. G. Sturge, A. D. Hunter, R. McDonald, B. D. Santarsiero, *Organometallics* **11,** 3056 (1992).
24. X. A. Guo, K. G. Sturge, A. D. Hunter, M. C. Williams, *Macromolecules* **27,** 7825 (1994).
25. S. S. H. Mao, T. D. Tilley, *J. Am. Chem. Soc.* **117,** 5365 (1995).
26. S. S. H. Mao, T. D. Tilley, *Macromolecules* **29,** 6362 (1996).
27. S. S. H. Mao, F.-Q. Liu, T. D. Tilley, *J. Am. Chem. Soc.* **120,** 1193 (1998).
28. S. S. H. Mao, T. D. Tilley, *Macromolecules* **30,** 5566 (1997).
29. B. L. Lucht, S.S.H. Mao, T. D. Tilley, *J. Am. Chem. Soc.* **120,** 4354 (1998).
30. M. Murata, T. Hoshi, I. Matsuoka, T. Nankawa, M. Kurihara, H. Nishihara, *J. Inorg. Organomet. Polym.* **10,** 209 (2000).
31. J.-C. Lee, A. Nishio, I. Tomita, T. Endo, *Macromolecules* **30,** 5205 (1997).

32. I. Matsuoka, K. Aramaki, H. Nishihara, *J. Chem. Soc., Dalton Trans.* 147 (1998).

33. T. Shimura, A. Ohkubo, K. Aramaki, H. Uekusa, T. Fujita, S. Ohba, H. Nishihara, *Inorg. Chim. Acta* **230,** 215 (1995).

34. T. Shimura, A. Ohkubo, N. Matsuda, I. Matsuoka, K. Aramaki, H. Nishihara, *Chem. Mater.* **8,** 1307 (1996).

35. I. Tomita, A. Nishio, T. Endo, *Macromolecules* **28,** 3042 (1995).

36. S. Takahashi, H. Morimoto, E. Murata, S. Kataoka, K. Sonogashira, N. Hagihara, *J. Polym. Sci. Polym. Chem. Ed.* **20,** 565 (1982)

37. S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, *J. Chem. Soc. Chem. Commun.* 3 (1984)

38. S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, N. Hagihara, *Mol. Cryst. Liq. Cryst.* **82,** 139 (1982)

39. K. Sonogashira, S. Takahashi, N. Hagihara, *Macromolecules* **10,** 879 (1977)

40. K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, N. Hagihara, *J. Organomet. Chem.* **145,** 101 (1978)

41. S. Takahashi, M. Kariya, T. Yatake, K. Sonogashira, N. Hagihara, *Macromolecules* **11,** 1063 (1978)

42. S. Takahashi, K. Sonogashira, *Kobunshi* **29**(5), 395 (1980); *Chem. Abs.* **93,** 8542u (1980)

43. K. Sonogashira, S. Kataoka, S. Takahashi, N. Hagihara, *J. Organomet. Chem.* **160,** 319 (1978).

44. M. H. Chisolm, *Angew. Chem. Int. Ed. Engl.* **30,** 673 (1991).

45. S. J. Davies, B.F.G. Johnson, M. S. Khan, J. Lewis, *J. Chem. Soc., Chem. Commun.* 187, (1991).

46. M. S. Khan, S. J. Davies, A. K. Kakkar, D. Schwartz, B. Lin, B.F.G. Johnson, J. Lewis, *J. Organomet. Chem.* **424,** 87 (1992).

47. J. Lewis, M. S. Khan, A. K. Kakkar, B.F.G. Johnson, T. B. Marder, H. B. Fyfe, F. Wittmann, R. H. Friend, A. E. Dray, *J. Organomet. Chem.* **425,** 165 (1992).

48. N. Chawdhury, A. Kohler, R. R. Friend, M. Younus, N. J. Long, P. R. Raithby, J. Lewis, *Macromolecules* **31,** 722 (1998).

49. R. D. Markwell, I. S. Butler, A. K. Kakkar, M. S. Khan, Z. H. Al-Zakwani, J. Lewis, *Organometallics* **15,** 2331 (1996).

50. M. Younus, A. Kohler, S. Cron, N. Chawdhury, M. R. A. Al-Mandhary, M. S. Khan, J. Lewis, N. J. Long, R. H. Friend, P. R. Raithby, *Angew. Chem. Int. Ed.* **37,** 3036 (1998).

51. A. E. Dray, R. Rachel, W. O. Saxton, J. Lewis, M. S. Khan, A. M. Donald, R. H. Friend, *Macromolecules* **25,** 3473 (1992).

52. M. S. Khan, A. K. Kakkar, N. L. Long, J. Lewis, P. Raithby, P. Nguyen, T. B. Marder, F. Wittmann, R. L. Friend, *J. Mater, Chem.* **4,** 1227 (1994)

53. M. S. Khan, D. J. Schwartz, N. A. Pasha, A. K. Kakkar, B. Lin, P. R. Raithby, J. Lewis, *Z. Anorg. Allg. Chem.* **616,** 121 (1992)

54. S. J. Davies, B.F.G. Johnson, J. Lewis, P. R. Raithby, *J. Organomet. Chem.* **414,** C51 (1991).

55. B. F .G. Johnson, A. K. Kakkar, M. S. Khan, J. Lewis, *J. Organomet. Chem.* **409,** C12 (1991).

56. Z. Atherton, C. W. Faulkner, S. L. Ingham, A. K. Kakkar, M. S. Khan, J. Lewis, N. J. Long, P. R. Raithby, *J. Organomet. Chem.* **462,** 265 (1993).

57. C. C. Frazier, S. Guha, W. P. Chen, M. P. Cockerham, P. L. Porter, E. A. Chauchard, C. H. Lee, *Polymer* **28,** 553 (1987)

58. S. Guha, C. C. Frazier, P. L. Porter, K. Kang, S. E. Finberg, *Opt. Lett.* **14,** 952 (1989)

59. H. B. Fyfe, M. Mlekuz, G. Stringer, N. J. Taylor, T. B. Marder, in *Inorganic and Organometallic Polymers with Special Properties,* R. M. Laine, ed., NATO ASI Series, Series E, Applied Sciences, Kluwer Academic, Dordecht, 1992, Vol. 206, pp. 331–344.

60. M. Yang, L. Zhang, Z. Lei, P. Ye, J. Si, Q. Yang, Y. Wang, *J. Appl. Polym. Sci.* **70,** 1165 (1998).

61. H. B. Fyfe, M. Mlekuz, D. Zargarian, N. J. Taylor, T. B. Marder, *J. Chem. Soc., Chem. Commun.* 188 (1991).

62. G. Jia, R. J. Puddephatt, J. D. Scott, J. J. Vittal, *Organometallics* **12,** 3565 (1993).

63. G. Jia, N. C. Payne, J. J. Vittal, R. J. Puddephatt, *Organometallics* **12,** 4771 (1993).

64. R. J. Puddephatt, *Chem. Commun.* 1055 (1998).

65. M. J. Irwin, L. Manojlovic-Muir, K. W. Muir, R. J. Puddephatt, D. S. Yufit, *Chem. Commun.* 219 (1997).

66. P. K. Sahoo, S. K. Swain, *J. Polym. Sci., Part A Polym. Chem.* **37,** 3899 (1999).

67. W.-Y. Wong, G.-L. Lu, K.-H. Choi, J.-X. Shi, *Macromolecules* **35,** 3506 (2002).

68. W.-Y. Wong, S.-M. Chan, K.-H. Choi, K.-W. Cheah, W.-K. Chan, *Macromol. Rapid Commun.* **21,** 453 (2000).

69. M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, A. K. Hisahm, P. R. Raithby, B. Ahrens, M. F. Mahon, L. Male, E. A. Marseglia, E. Tedesco, R. H. Friend, A. Kohler, N. Feeder, S. J. Teat, *J. Chem. Soc., Dalton Trans.* 1358 (2002).

70. M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, N. Feeder, S. Nahar, A. Kohler, R. H. Friend, P. J. Wilson, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* 2441 (2002).

71. J. S. Wilson, N. Chawdhury, M. R. A. Al-Mandhary, M. Younus, M. S. Khan, P. R. Raithby, A. Kohler, R. H. Friend, *J. Am. Chem. Soc.* **123,** 9412 (2001).

72. G. Polzonetti, G. Lucci, P. Altamura, A. Ferri, G. Paolucci, A. Goldoni, P. Parent, C. Laffon, M. V. Russo, *Surf. Interface Anal.* **34,** 588 (2002).

73. P. Altamura, G. Giardina, C. Lo Sterzo, M. V. Russo, *Organometallics* **20,** 4360 (2001).

74. A. Buttinelli, E. Viola, E. Antonelli, C. Lo Sterzo, *Organometallics* **17,** 2574 (1998).

75. F. Matsumoto, N. Matsumi, Y. Chujo, *Polym. Bull.* **48,** 119 (2002).

76. P. Magnus, D. P. Becker, *J. Chem. Soc. Chem. Commun.* 640 (1985).

77. T. Kuhnen, M. Stradiotto, R. Ruffolo, D. Ulbrich, M. J. McGlinchey, M. A. Brook, *Organometallics* **16,** 5048 (1997).

78. M. Moran, M. C. Pascual, I. Cuadrado, J. Losada, *Organometallics* **12,** 811 (1993).

79. D. R. Tyler, J. J. Wolcott, G. W. Nieckarz, S. C. Tenhaeff, in *Inorganic and Organometallic Polymers II,* P. Wisian-Neilson, H. R. Allcock, K. J. Wynne, eds., ACS Symp. Series Vol. 572, American Chemical Society, Washington, DC, 1994, Chap. 36, pp. 481–496.

80. S. C. Tenhaeff, D. R. Tyler, *Organometallics* **10,** 1116 (1991).

81. S. C. Tenhaeff, D. R. Tyler, *Organometallics* **10,** 473 (1991).

82. S. C. Tenhaeff, D. R. Tyler, *Organometallics* **11,** 1466 (1992).

83. J. L. Male, M. Yoon, A. G. Glenn, T. J. R. Weakley, D. R. Tyler, *Macromolecules* **32,** 3898 (1999).

84. F. Amor, E. de Jesus, A. I. Perez, P. Royo, A. V. de Miguel, *Organometallics* **15,** 365 (1996).

85. M. J. Irwin, G. Jia, J. J. Vittal, R. J. Puddephatt, *Organometallics* **15,** 5321 (1996).

86. S. Chardon-Noblat, A. Deronzier, D. Zsoldos, R. Ziessel, M. Haukka, T. Pakkanen, T. Venalainen, *J. Chem. Soc., Dalton Trans.* 2581 (1996).

87. S. Chardon-Noblat, A. Deronzier, F. Hartl, J. van Slageren, T. Mahabiersing, *Eur. J. Inorg. Chem.* 613 (2001).

88. J. L. Wesemann, M. H. Chisolm, *Inorg. Chem.* **36,** 3258 (1997).

89. M. H. Chisholm, *Acc. Chem. Res.* **33,** 53 (2000).

90. R. H. Cayton, M. H. Chisolm, J. C. Huffman, E. B. Lobkovsky, *J. Am. Chem. Soc.* **113,** 8709 (1991).

91. W.-M. Xue, F. E. Kuhn, E. Herdtweck, Q. Li, *Eur. J. Inorg. Chem.* 213 (2001).

92. W.-M. Xue, F. E. Kuhn, *Eur. J. Inorg. Chem.* 2041 (2001).

93. M. C. Kerby, B. W. Eichhorn, J. A. Creighton, K.P.C. Vollhardt, *Inorg. Chem.* **29,** 1319 (1990).

94. Y.-H. Liao, J. R. Moss, *Organometallics* **15,** 4307 (1996).

95. S. Achar, R. J. Puddephatt, *Angew. Chem. Int. Ed. Engl.* **33,** 847 (1994).

96. S. Achar, J. J. Vittal, R. J. Puddephatt, *Organometallics* **15,** 43 (1996).

97. G.-X. Liu, R. J. Puddephatt, *Organometallics* **15,** 5257 (1996).

98. S. Achar, C. E. Immoos, M. G. Hill, V. J. Catalano, *Inorg. Chem.* **36,** 2314 (1997).

99. N. J. Hovestad, J. L. Hoare, J. T.B.H. Jastrzebski, A. J. Canty, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **18,** 2970 (1999).

100. J. L. Hoare, K. Lorenz, N. J. Hovestad, W. J. J. Smeets, A. L. Spek, A. J. Canty, H. Frey, G. van Koten, *Organometallics* **16,** 4167 (1997).

101. K. Onitsuka, A. Iuchi, M. Fujimoto, S. Takahashi, *Chem. Commun.* 741 (2001).

102. S. Leininger, P. J. Stang, S. Huang, *Organometallics* **17,** 3981 (1998).

103. K. Onitsuka, M. Fujimoto, N. Ohshiro, S. Takahashi, *Angew. Chem. Int. Ed.* **38,** 689 (1999).

104. A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, *Organometallics* **18,** 5195 (1999).

105. S. K. Hurst, M. P. Cifuentes, M. G. Humphrey, *Organometallics* **21,** 2353 (2002).

CHAPTER 5

Metal Coordination Polymers

CONTENTS

I. INTRODUCTION

Coordination polymers are one of the earliest developed classes of metal-containing polymers. They continue to attract a great deal of attention because of their widespread applications. Coordination complexes of platinum, for example, were prepared as potential biologically active agents by the reaction of K_2PtCl_4 with pyrimidines, purines, hydrazines, and diamines.[1] Polymer **1**, for example, represses the replication of poliovirus I and L-RNA virus at a 10–20-μg/mL level.

Carraher and coworkers have reported that the removal of toxic metal ions from water can be achieved by polychelation of dicarboxylic acids (**2**) to uranyl ions, (**3**) resulting in the production of coordination polymers such as **4** (Scheme 1).[2] This

method was found to be effective for removing all except 10^{-5} molar of the water-soluble uranyl ion from solution.

1

2   +   **3**

4
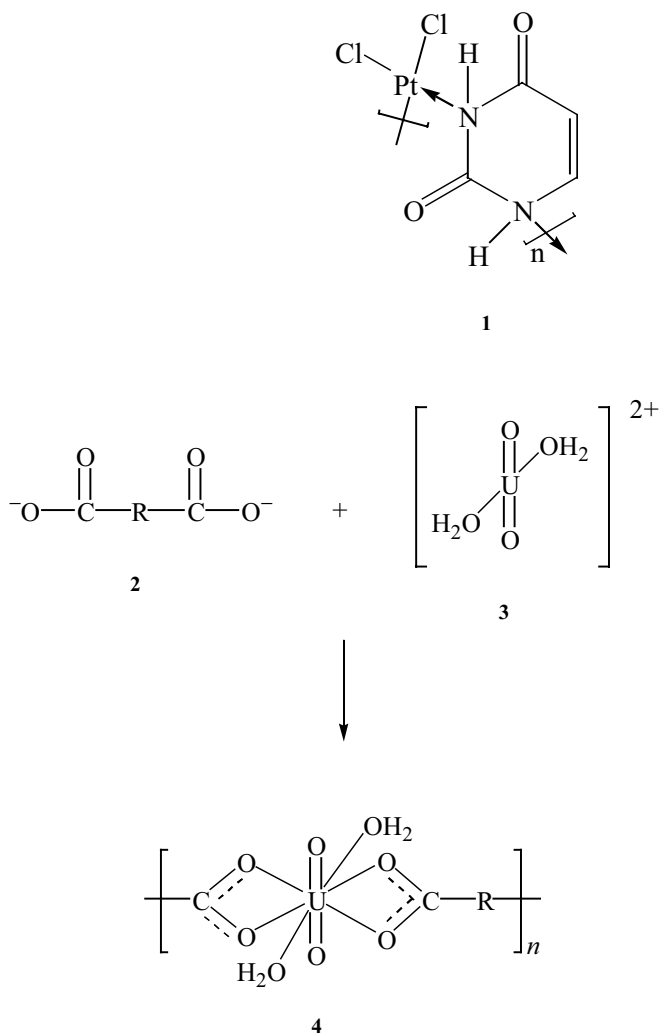
Scheme 1

This chapter describes the synthesis and properties of a number of classes of polymers containing metal coordination complexes in their structures. These polymers are prepared by polymerization reactions of metal-containing monomers and through metal coordination reactions. Schiff base–containing polymers (**5**) were one of the earliest classes of coordination polymers examined. Polymers incorporating macrocyclic porphyrins (**6**) and phthalocyanines (**7**) in their backbones and sidechains are known to exhibit interesting optical and electrical properties. The best-studied classes of metal-containing polymers contain bipyridyl and other related units coordinated to metal ions (**8**).
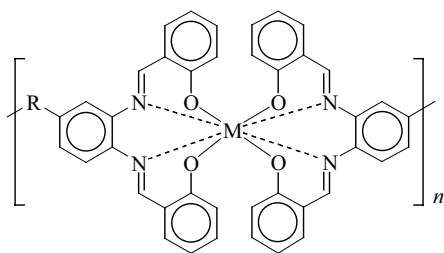
5
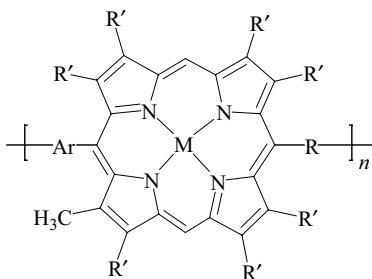
6
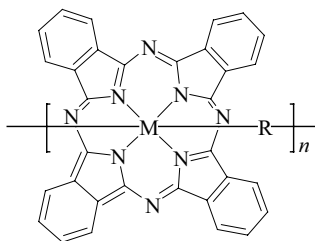
7
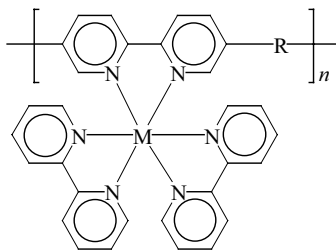
8

II. SCHIFF BASE POLYMERS

Schiff base ligands have been used in the design of metal-containing polymers by the coordination reaction of metal ions to these organic ligands. In 1961, Goodwin and Bailar used this strategy to prepare Schiff base polymers (**10**) coordinated to Cu, Ni, and Co ions (Scheme 2).[3] Unfortunately, these materials exhibited low solubility in organic solvents.

Archer et al. overcame many of these early barriers and obtained characterizable coordination polymers.[4–7] Thus, they prepared and studied the luminescent properties of lanthanide-coordinated Schiff base polymers.[4–6] The influence of different spacer groups and counterions of the metal complexes on the solubilities of these polymers has been examined. Unlike the strategy described by Goodwin and Bailar, which involved the coordination of metal ions to preexisting polymers, Archer and coworkers reacted organic ligands with metal ions to produce the polymers through coordination reactions. Scheme 3 shows the synthesis of polymer **13** by reaction of ligands containing imine and phenolic groups (**11**) with europium and yttrium ions (**12**).[4,5] It was estimated by NMR end-group analysis that these polymers had molecular weights of 21,600 and 18,500, respectively. Analogous polymers with lanthanum, gadolinium, ytterbium, and cerium ions coordinated to *bis-tetra*-dentate Schiff base ligands were also described.[4–6] Zirconium-coordinated Schiff base polymers were found to adhere to glass and metal surfaces.[7]

9

X = SO$_2$, CH$_2$

M^{2+}

10

Scheme 2

11

+

M(NO$_3$)$_3$ •3 DMSO

M = Y, Eu

12

Na$^+$

13
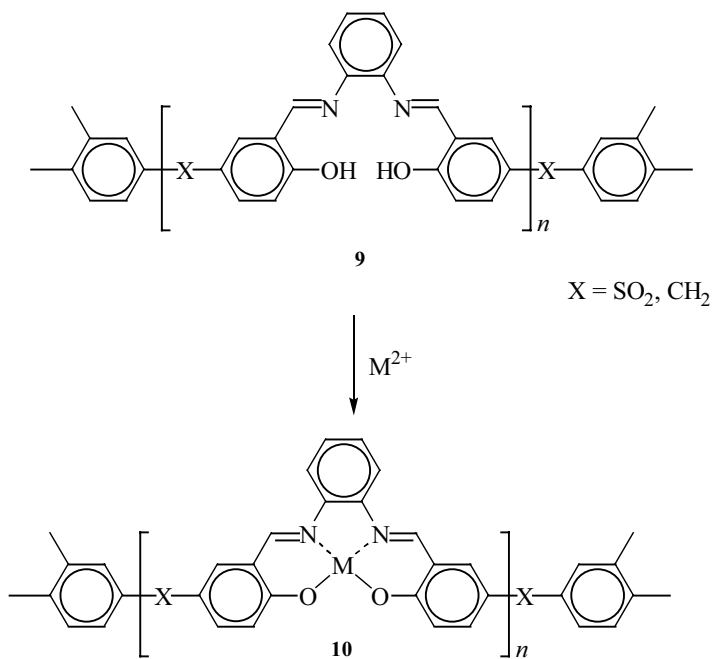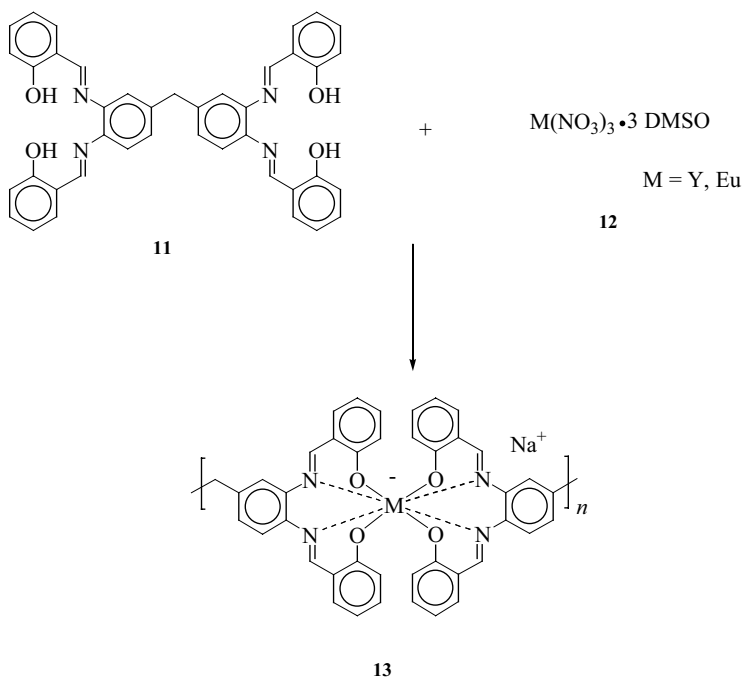
Scheme 3

Reddinger and Reynolds have conducted the electropolymerization of Schiff base metal-coordinated monomers.[8,9] When monomer **14** (R, R′=H) was electrochemically oxidized, polymerization occurred through the phenylene linkages, placing the copper complexes in the polymer backbone (**15**) (Scheme 4). However, when methyl groups blocked the polymerization site on the phenylene rings, polymerization occurred through the thiophene rings, thereby leaving the copper Schiff base complex pendent to the mainchain as shown in polymer **16**.
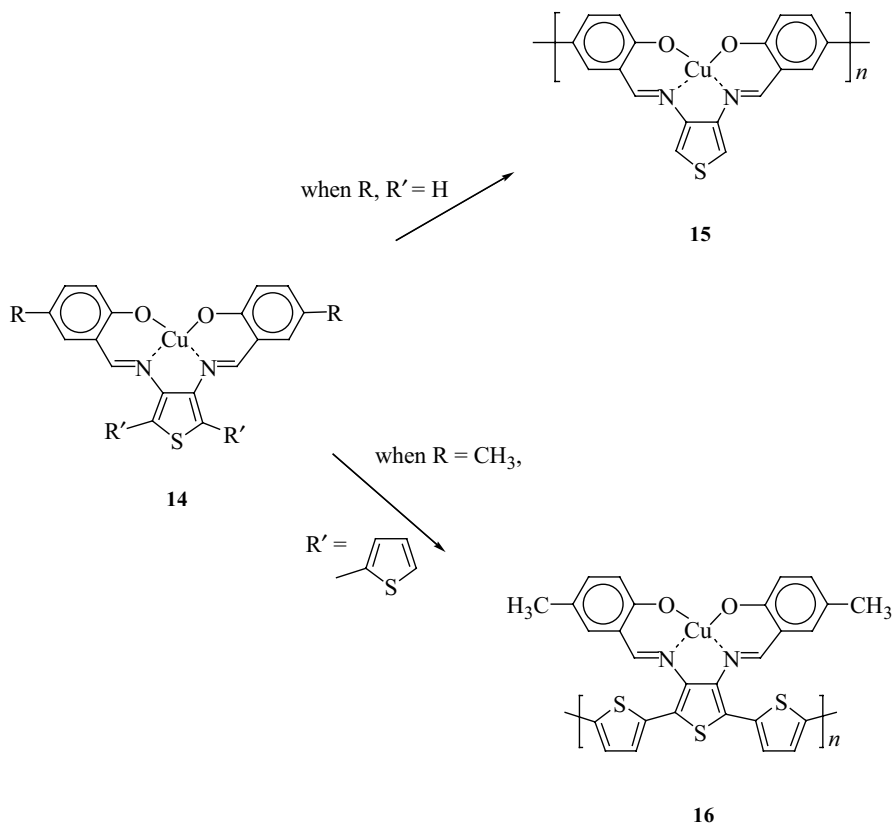
Scheme 4

The polymerization of diacrylate monomers functionalized with Schiff base complexes of Cu(II), Pd(II), and Zn(II) has been investigated.[10] Thermal polymerizations of monomer **17** (M=Pd and Zn) were successful; however, polymers were not obtained when the copper analog was subjected to the same conditions. Photopolymerization of these monomers in the presence of a titanium initiator and their copolymerization with monoacrylate organic monomers were also examined. In all cases, the copper complexes inhibited the polymerization reaction. The palladium-containing polymers exhibited liquid crystalline properties.[10]
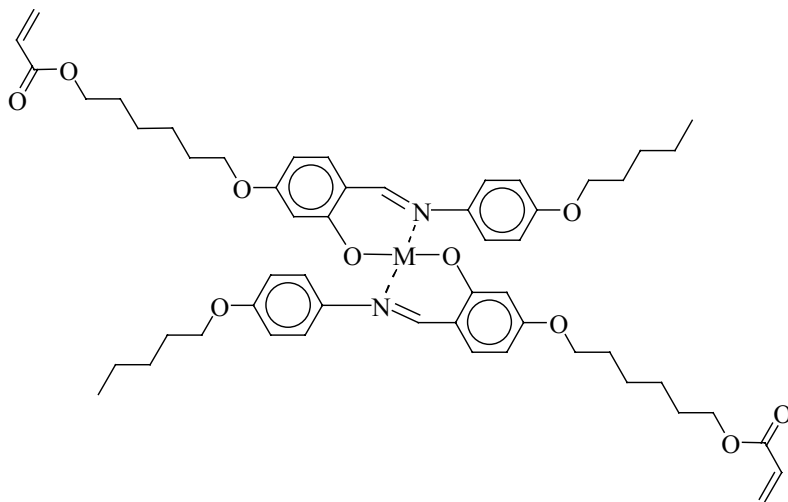
17

Scheme 5 shows the proposed crosslinking mechanism of monomer **23** with an excess of the diglycidyl ether of *bis*-phenol A (**22**) using t*etra*-butylammonium hydroxide as the initiator to produce the copolymer **24**.[11] The first step is the thermally initiated formation of the *tetra*-dentate complex (**19**) from the hexadentate complex **18**. When the polymerization reactions were conducted at 110°C, the crosslinking reaction required 4 h to reach completion; however, at 130°C, the crosslinking reaction was complete in 1 h. Addition of a large excess of *tetra*-butylammonium hydroxide to the solution reduced the amount of crosslinking observed. Direct reaction of monomer **18** with **22** resulted in the isolation of hexadentate Schiff base metal-containing epoxy polymers.[11] The generation of Schiff base coordination polymers, crosslinked via noncovalent π–π interactions, has also been reported.[12] A homochiral silver Schiff base polymer has been described by Wild and coworkers.[13]

III. PORPHYRINS

Conjugated polymers containing metal porphyrins within their structures have potential use in optical and electronic devices, in solar energy conversion, and as enzyme mimics.[14–23] Metalloporphyrin polymers have also been used to sense dissolved oxygen by taking advantage of their luminescent properties.[20] Pomogailo and coworkers have described the incorporation of metalloporphyrins into the side-chains of polymers.[15] For example, the copper and zinc complexes of monomers **25** and **26** were copolymerized with styrene to produce high molecular weight polymers.[15] The incorporation of these metal complexes reduced the molecular weights of these materials. High MW polymetalloporphyrins are often difficult to isolate because of their poor solubility.[14–17] It has also been reported that the bulkiness of metalloporphyrins can inhibit the formation of extended π-conjugated systems.
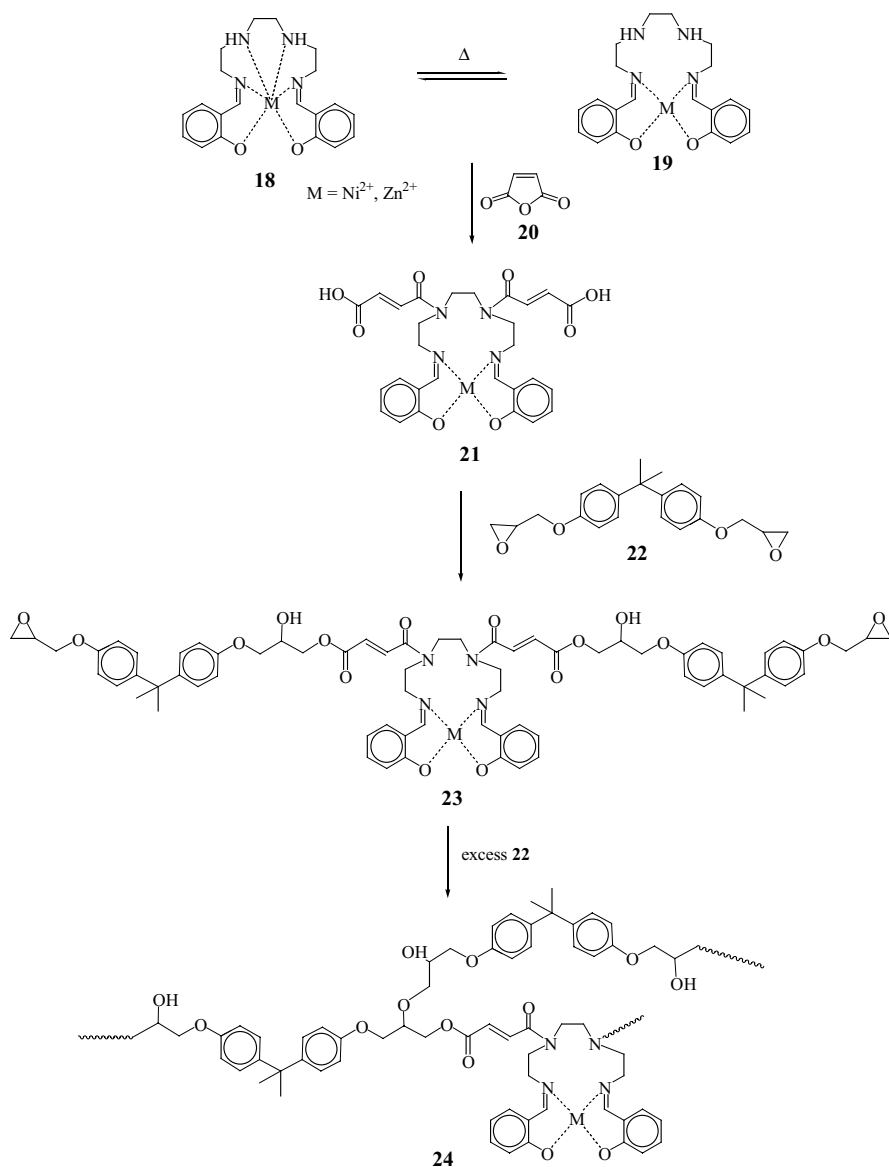
Scheme 5

Metalloporphyrin functions, when properly aligned, are of interest for inducing nonlinear optical properties.[16,17] Anderson and coworkers have found that the microscopic polarizabilities of porphyrins within polymers are three orders of magnitude greater than those of monomeric porphyrins.[17] This report described the largest one-photon, off-resonance, third-order optical susceptibility for an organic substance, which is indicative of interporphyrin conjugation. Soluble zinc polymers

were synthesized by including bulky groups in the *meso* positions of the porphyrin rings (Scheme 6).[16] Polymer **28** exhibited good solubility in the presence of a small amount of a coordinating ligand such as pyridine.

25

26

27

28
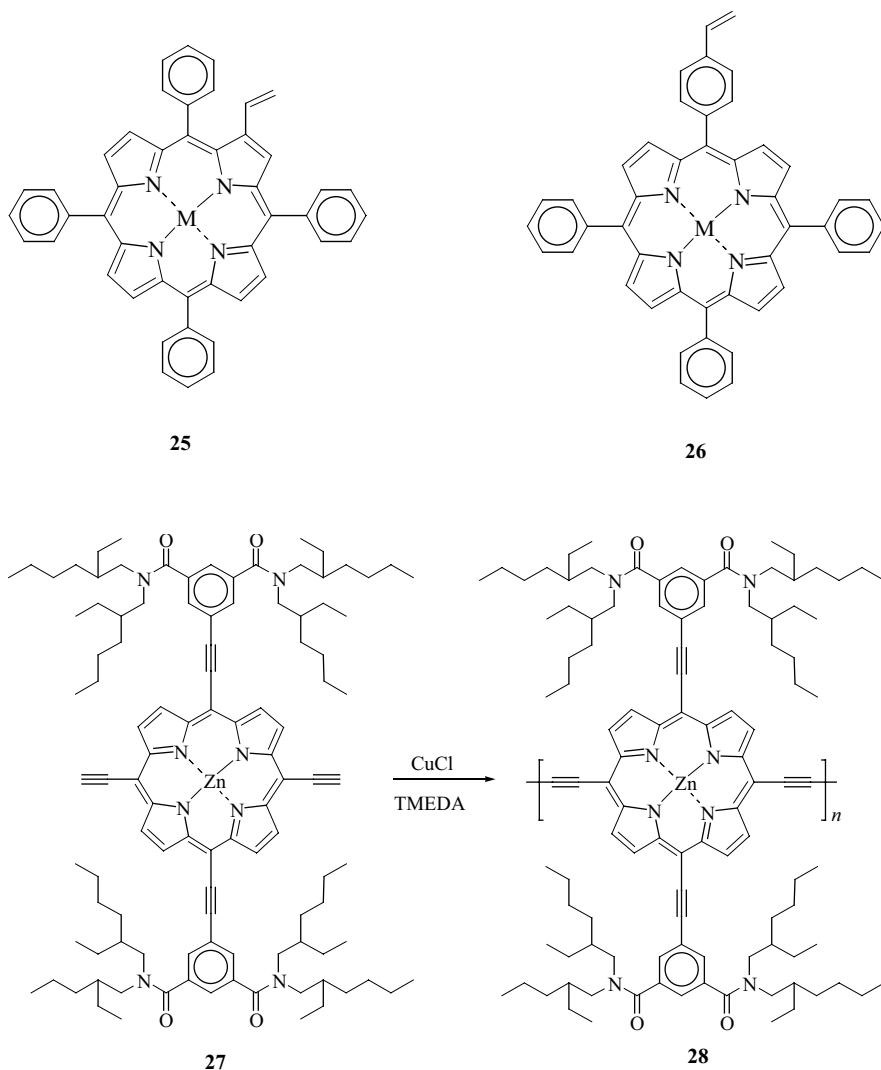
Scheme 6

The paramagnetic copper porphyrin polymer (**32**), shown in Scheme 7, was formed by the Heck coupling of monomers **29, 30,** and **31**.[23] This polymer had a very low metal content (0.01%) incorporated into its structure. Polymer **32** had a number-average molecular weight of 18,000 and a glass transition temperature of 16°C.
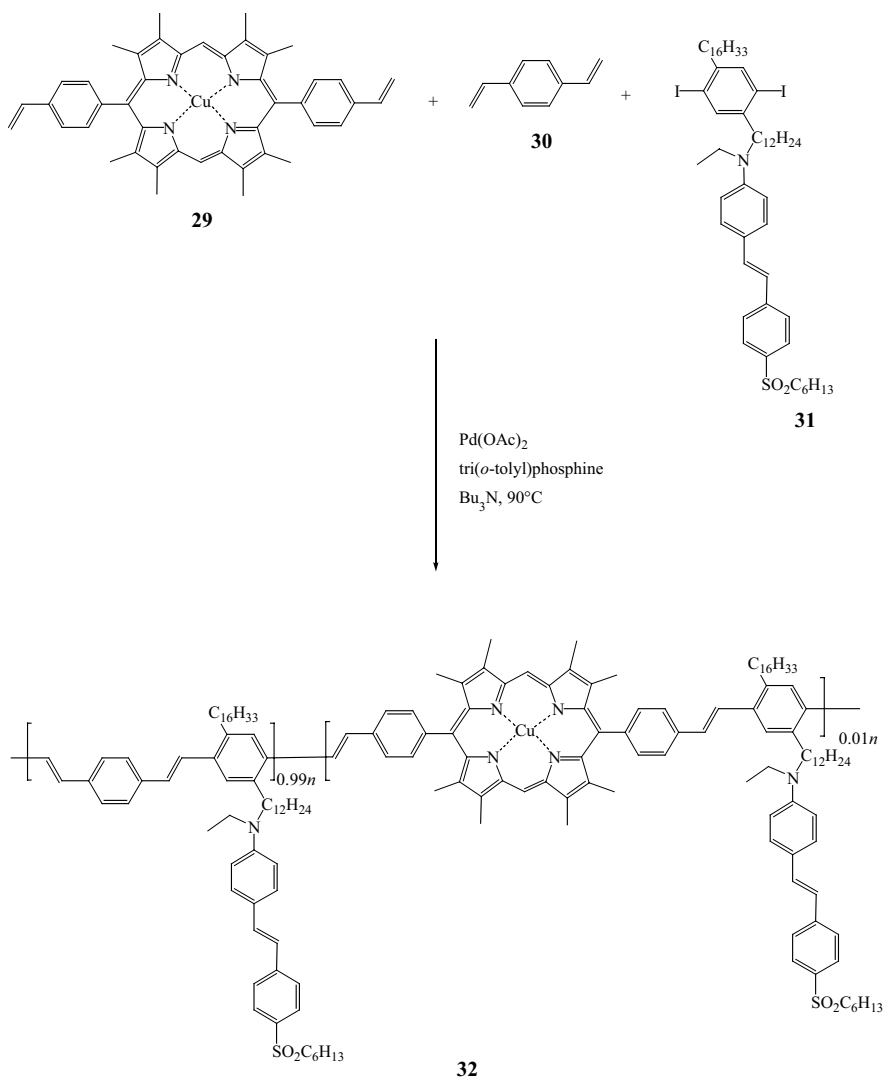
Scheme 7

IV. PHTHALOCYANINES

Polymetallophthalocyanines are structurally similar to polymetalloporphyrins; however, the presence of an additional four arenes and four nitrogen atoms in their structures has a strong influence on their UV–visible spectra.[24–26] In 1958, Marvel and Rassweiler reported the synthesis of copper-coordinated phthalocyanine polymers, where polymerization occurred through the aromatic rings.[27] Polymer **33** is an

example of a polymer that was prepared by the reaction of pyromellitic acid, phathalic anhydride, and urea. These copper phthalocyanine polymers were blue-green to green-black in color, and the intensity of their colors deepened with increasing solution viscosities. Polymeric copper phthalocyanines with functional groups on all four of the aromatic rings were also synthesized.[28]
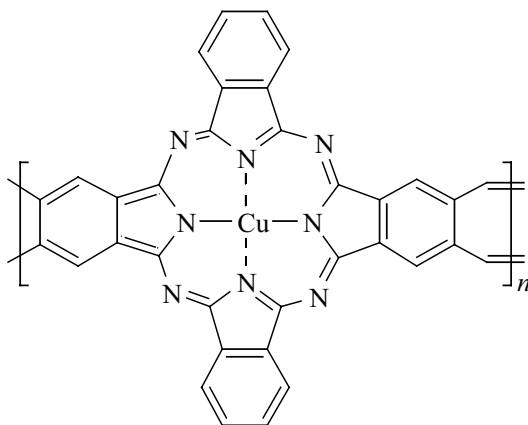
33

A report by Kimura and coworkers described the synthesis of linear and network copper and zinc polyphthalocyanines via olefin metathesis polymerization of the corresponding monomers.[29] For example, Scheme 8 shows the synthesis of the copper phthalocyanine monomer **36** and its subsequent polymerization, catalyzed by $(PCy_3)_2Cl_2Ru(=CHC_6H_5)$, to produce the linear polymer **37**. X-ray diffraction and transmission electron micrographs of polymer **37** indicate that the phthalocyanine units stack in an ordered fashion.[29]

Phthalocyanine complexes of copper and zinc have also been incorporated into copolymers of polyethers and polystyrene.[30,31] Polymer **38** is an example of a polystyrene prepared by free-radical polymerization of a zinc porphyrin complex and styrene.[31] This high molecular weight metallopolymer formed aggregates in solution.

Cofacial phthalocyanine polymers are materials in which the macrocyclic rings are stacked in a "shish-kebab" manner with the metals as part of the polymeric chain.[24–26,32] These polymers often display excellent thermal and chemical stability and are electrically conducting, sometimes even in the absence of a doping agent. Scheme 9 shows the synthesis of polymer **41** by reaction of the ferrous phthalocyanine complex (**39**) with pyrazine (**40**).[32]

Scheme 8

38

39

40

41
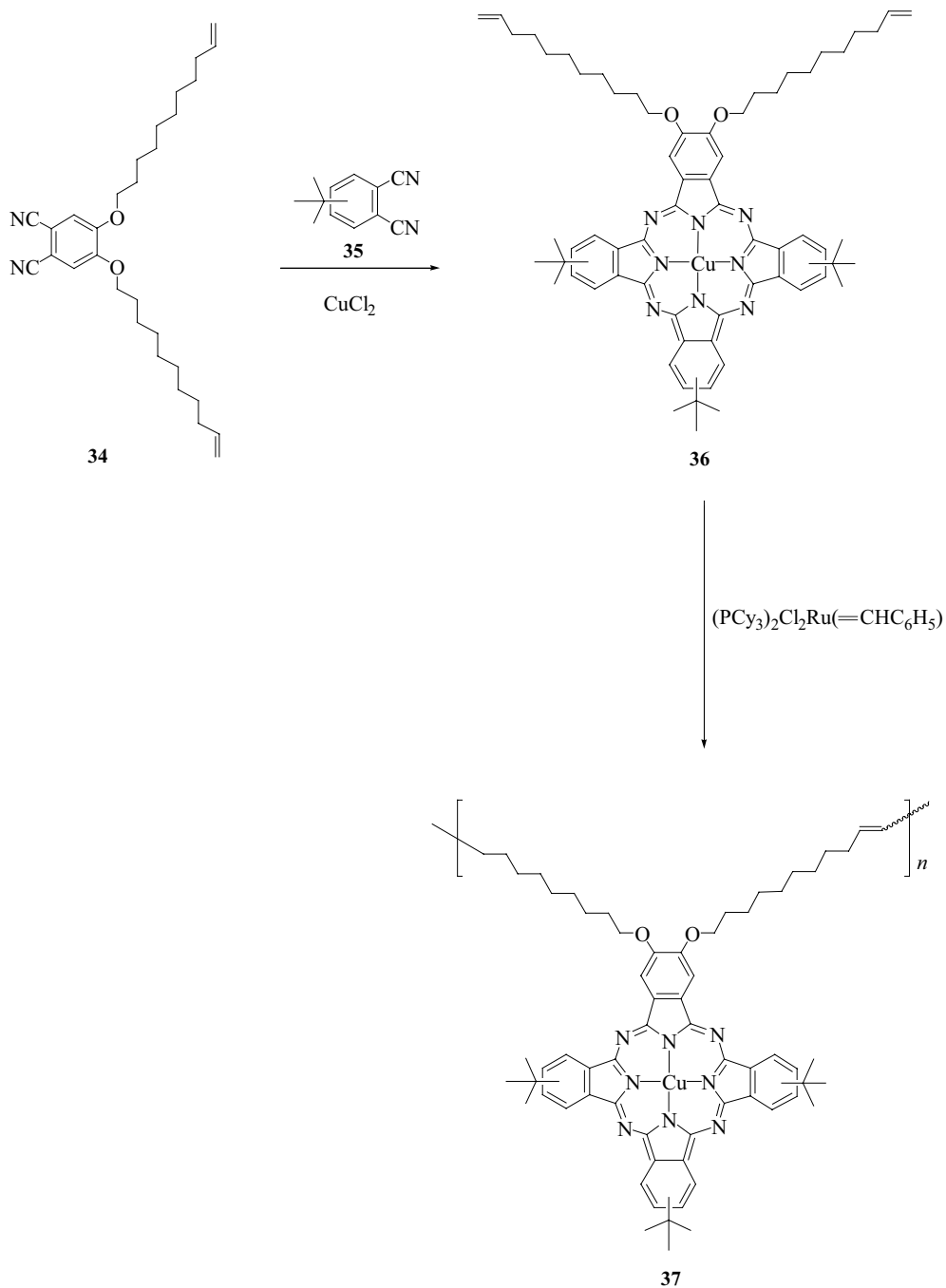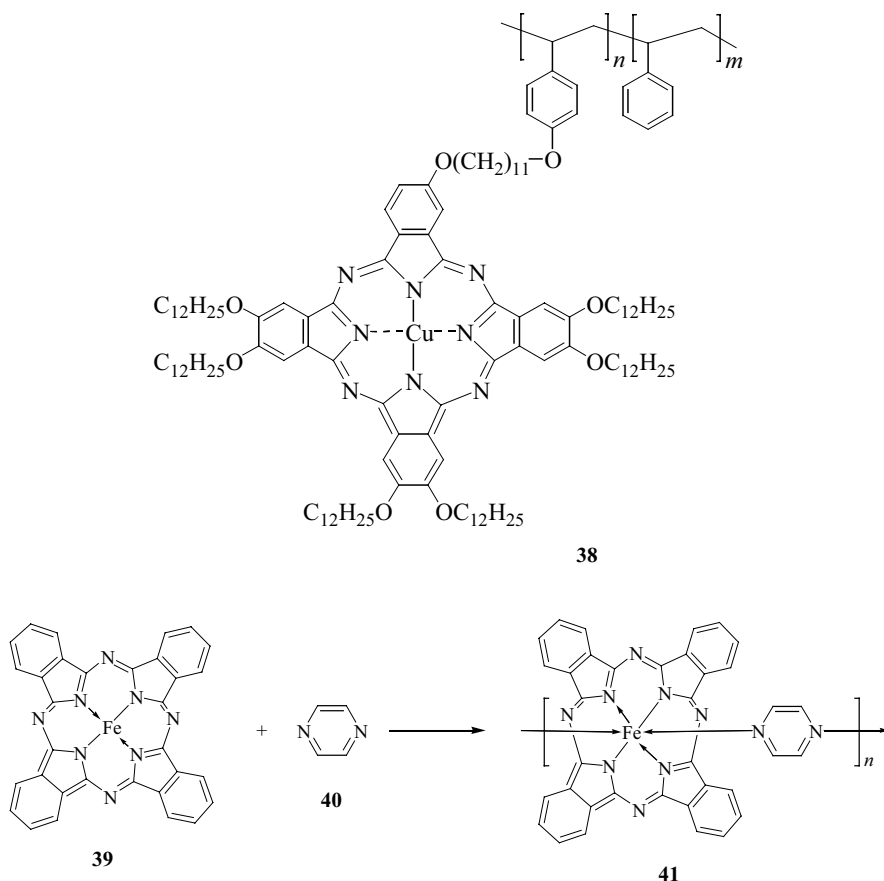
Scheme 9

V. PYRIDINE AND RELATED SYSTEMS

A. Bi- and Terpyridine-Based Materials

Polymers containing transition metals coordinated to pyridine-based ligands have been the focus of many investigations because of the ease with which these materials can be prepared and the properties they exhibit, in particular their luminescent properties. There are three general classes of polymers incorporating metal–pyridine complexes into their structures. These include the metal complex in the mainchain, pendent to the mainchain and pendent to the polymer sidechains. Schubert and coworkers reported the synthesis of micelles containing a ruthenium terpyridine complex in its structure.[33] Scheme 10 shows the synthesis of block copolymer (**46**), containing polyethylene oxide and polystyrene blocks joined at the *bis*-terpyridine ruthenium complex, by coordinating (**45**) to (**44**).
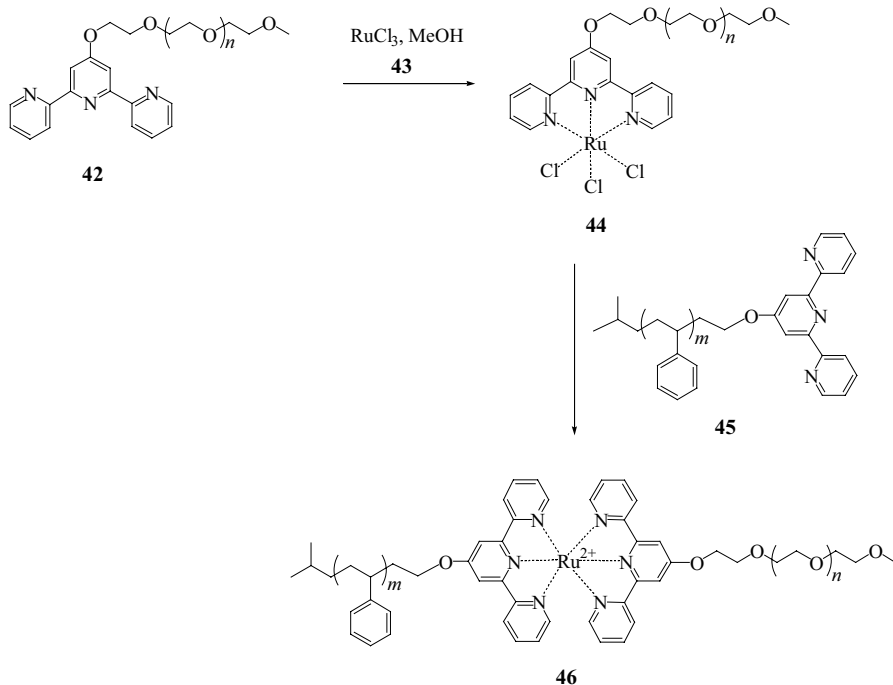
Scheme 10

Petzold and Harruna have synthesized three-dimensional high-performance coordination polymers.[34,35] A number of these thermally stable, soluble ruthenium-coordinated polymers (**47**) were examined by optical spectroscopy. Solutions of rigid polyamides exhibited birefringence and the 3D polymers emitted at a λ_{max} of 620 nm.

47
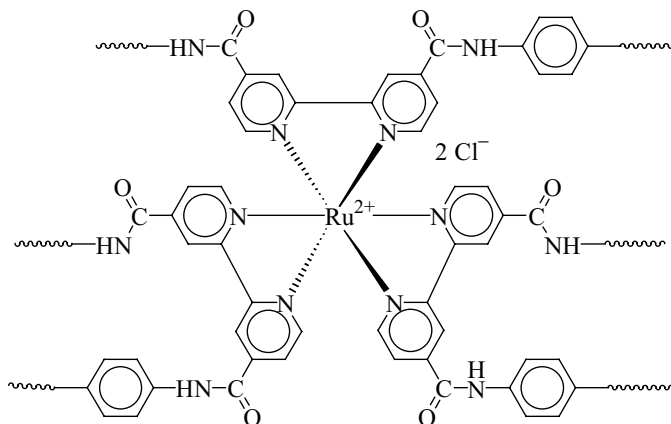
Rehahn et al. have synthesized ruthenium(II) coordination polymers that could be solubilized in organic or aqueous solutions depending on the counterion employed.[36–39] This class of polymer could be prepared either by complexation of terpyridine ligands to ruthenium or by polycondensation of organometallic monomers.[36] For example, Scheme 11 shows the reaction of monomer **48** with ruthenium chloride, which resulted in the production of the high molecular weight polymer **49**. The palladium catalyzed Suzuki coupling reaction between monomers **50** and **51** resulted in the formation of oligomeric materials. Polymer **49**, and related polymers, exhibited typical polyelectrolyte effects, and the ruthenium centers behave as electronically isolated centers.[36] The synthesis of Fe(II) coordination polymers using chiral ligands has been reported by Kimura and coworkers.[40] The monomers self-assembled into helical high molecular weight polymers. Ruthenium *tris*-bipyridyl polymers have also been utilized with TiO_2 nanoparticles and graphite oxide sheets in the production of self-assembled diode junctions.[41]
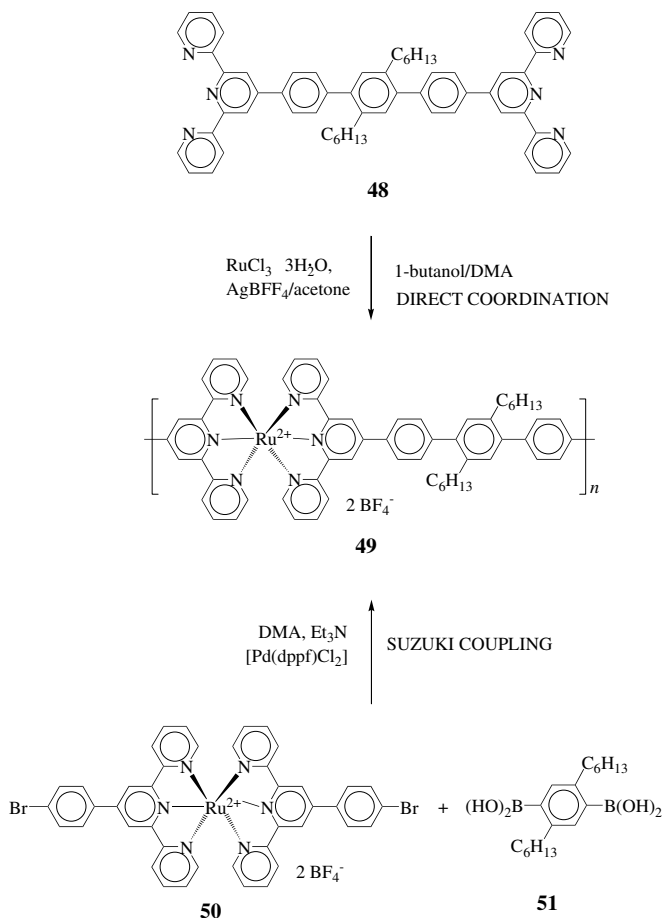
Scheme 11

The second type of pyridyl-based coordination polymers incorporates the metal complex pendent to the polymer backbone. Yu and coworkers have reported the synthesis of conjugated polymers containing metal coordination complexes using the Heck reaction.[42,43] For example, the ruthenium- or osmium-containing monomer (**52**) and **54** are terpolymerized with divinylbenzene (**53**) to generate the conjugated polymer **55** (Scheme 12).[43] These polymers incorporate nonlinear optical chromophores in their backbones, and showed large net optical gains at a zero external electric field.
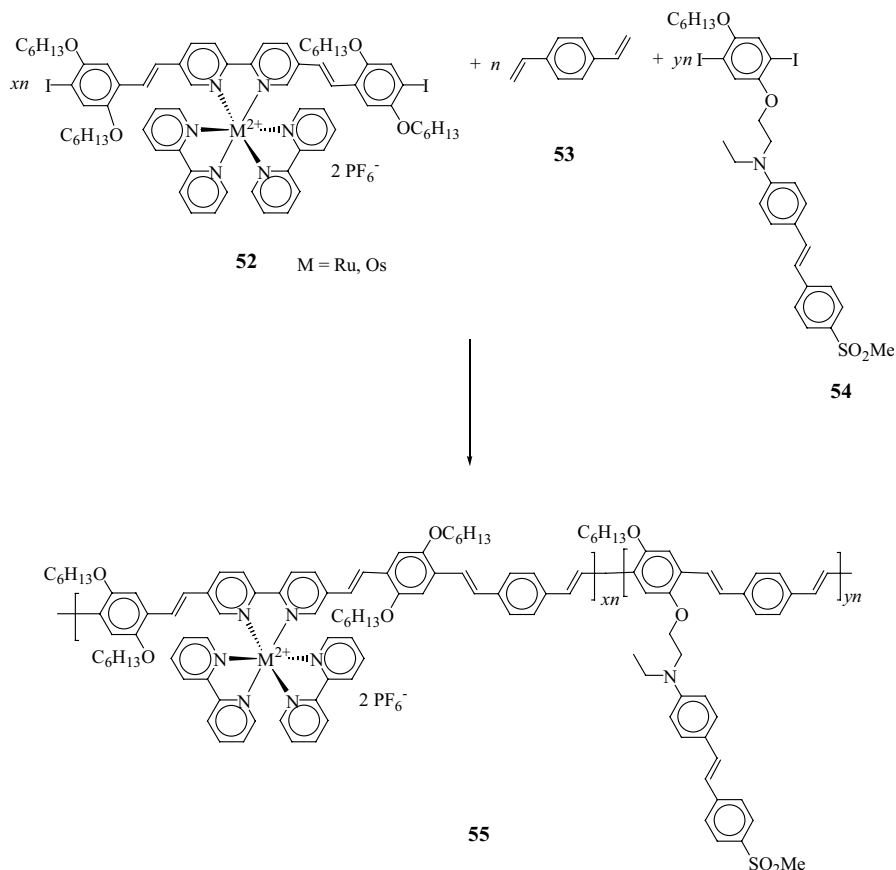
Scheme 12

Scheme 13 illustrates an alternative route to this class of conjugated metallopolymer. Using the strategy shown below, the ruthenium complex was reacted with the preformed polymer (**59**), resulting in the isolation of polymer **60**.[42]
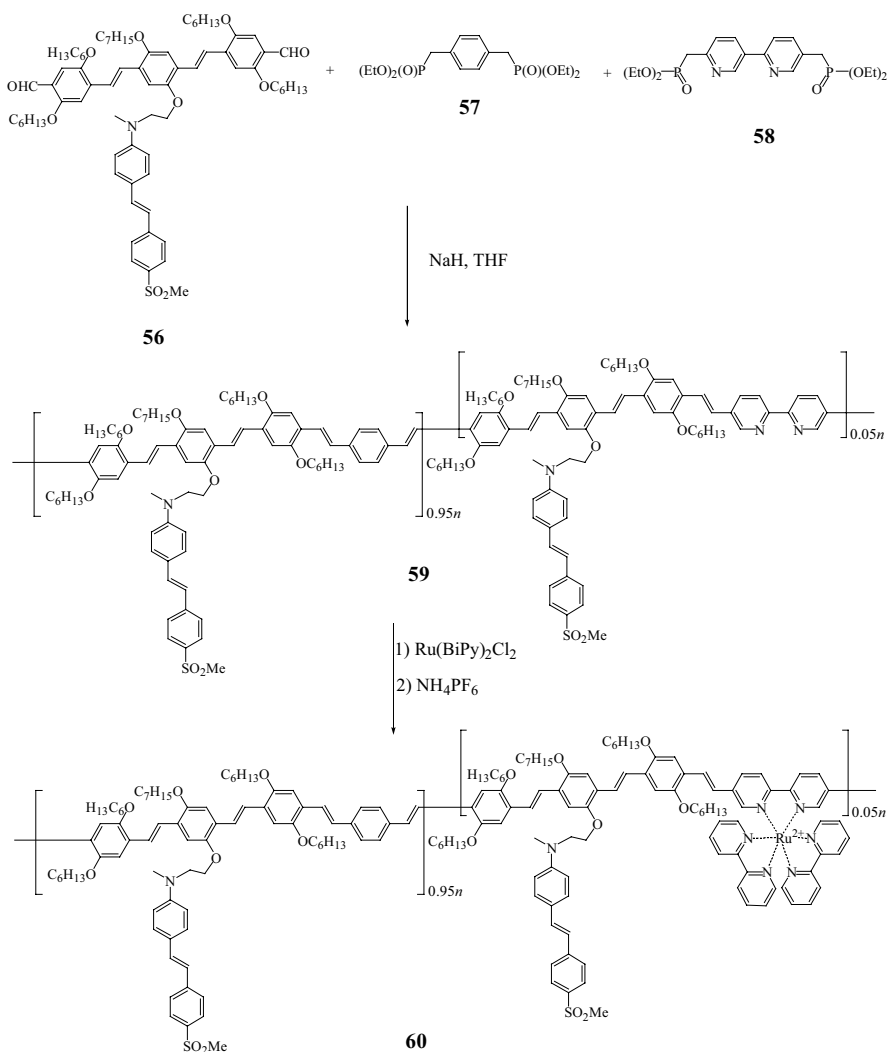
Scheme 13

Polyamides and polyesters containing ruthenium bipyridine complexes in their structures have been synthesized by Chan and coworkers.[44] Scheme 14 depicts the synthesis of polymer **64** by reaction of the metal-containing dicarboxylic acid complex **61** and the organic dicarboxylic acid (**62**) with an aromatic or aliphatic diamine (**63**). These polymers were thermally stable to temperatures between 320 and 500°C. Many of the polymers exhibited liquid crystalline characteristics. The photoconductivity of this class of polymer increased with increasing metal content.[44] Chan also reported that polybenzo-*bis*-oxazoles and polybenzo-*bis*-thiazoles that contain ruthenium complexes coordinated to 2,2′-bipyridyl units in the backbone

have charge carrier mobilities two orders of magnitude greater than did their non-metallated analogs.[45] Guillerez and coworkers provided evidence that conjugated polymers with thiophene units in the backbone exhibit electronic interactions between the organic portions of the polymer and the metal complex.[46] The synthesis and properties of conjugated polymers that contain $Re(CO)_3Cl$ units coordinated to bipyridine in the polymer backbone have also been examined.[47]
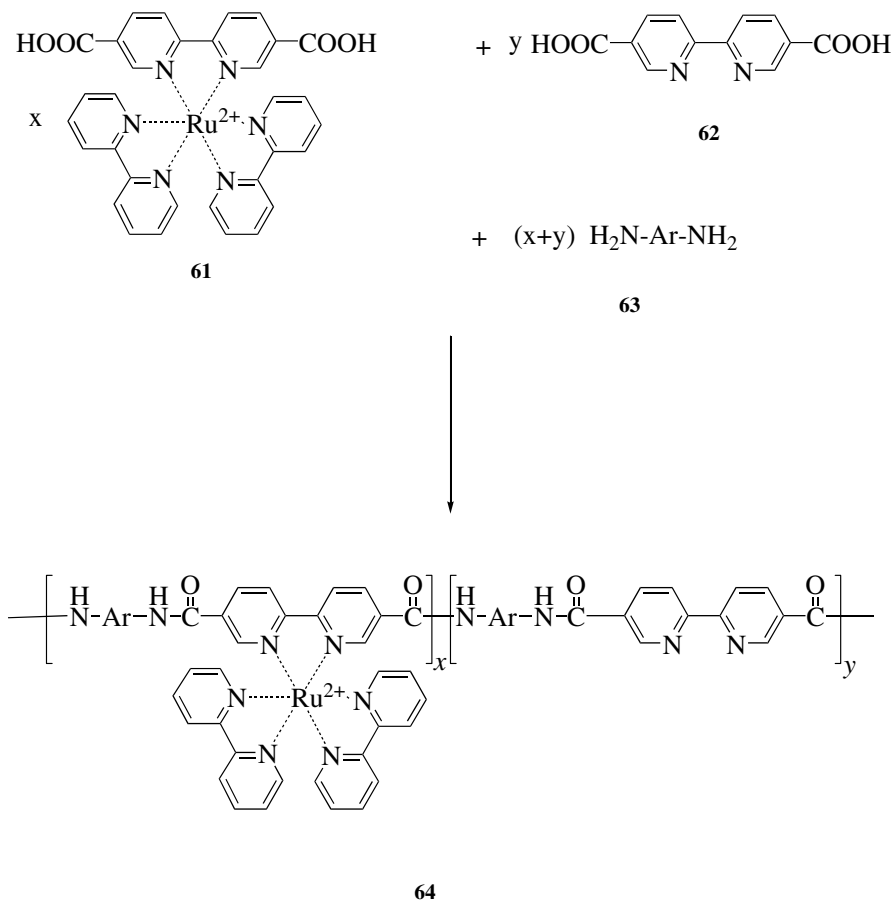
Scheme 14

The incorporation of bipyridine molecules coordinated to transition metals into the sidechains of polymers has also been utilized to tune the electronic and optical properties of polymers.[48–51] Frechet and coworkers synthesized polymers incorporating coumarin dyes and $Ru(BpyMe_2)_3{}^{2+}$ complexes into their structures using two strategies.[50] The first strategy, shown in Scheme 15, involves the coordination of the metal complex (**68**) to the preexisting polymer (**67**) to yield the metallopolymer **69**. This polymer exhibited limited solubility in organic solvents.
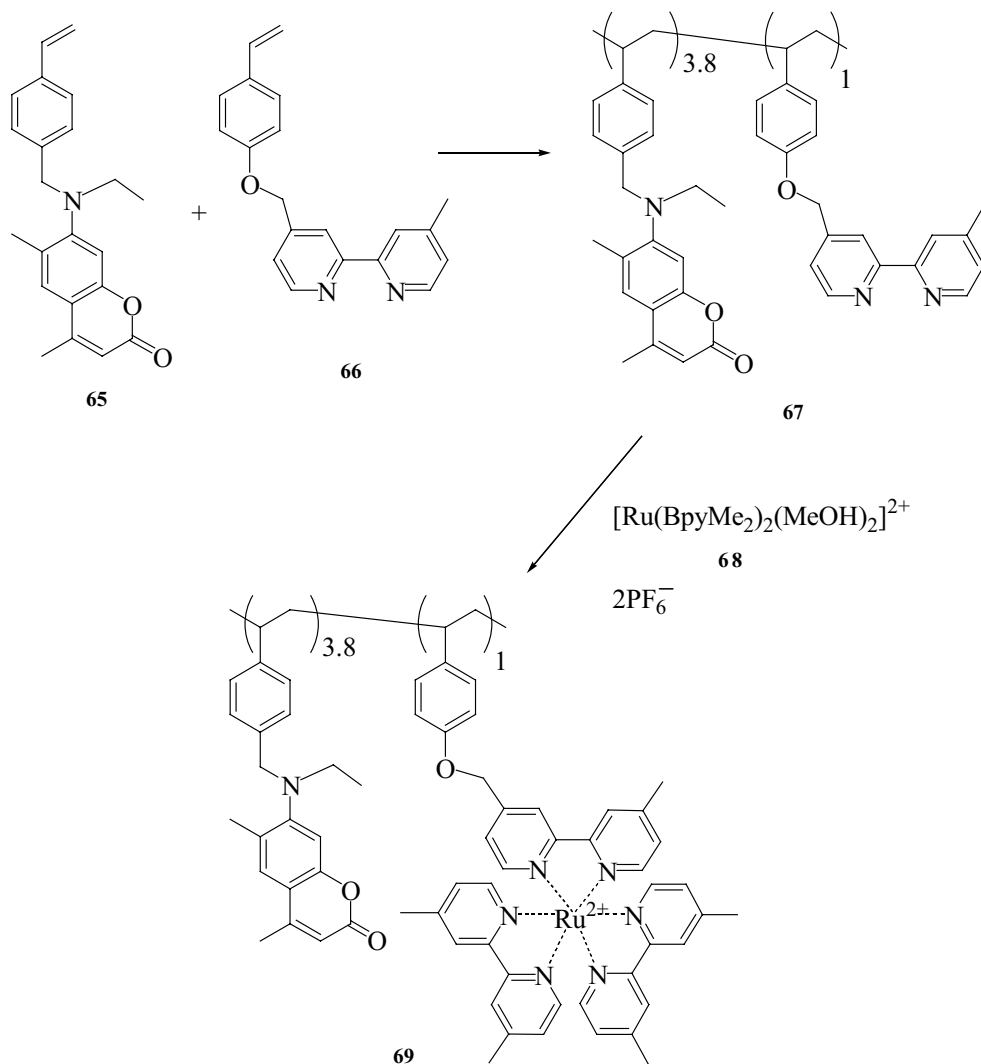
Scheme 15

Scheme 16 shows the second strategy utilized to prepare this class of polymer.[50] In this example, a ruthenium-containing monomer (**71**) was reacted with **65** and **70** to produce polymer **72**. Polymers prepared using the derivatized styrene monomers were much more soluble than polymers prepared by the grafting approach. The absorption and luminescent properties of polymers **69** and **72** were greater than those of their corresponding monomeric metallated analogues due to efficient energy transfer between the dyes and the complexes.[50]

72
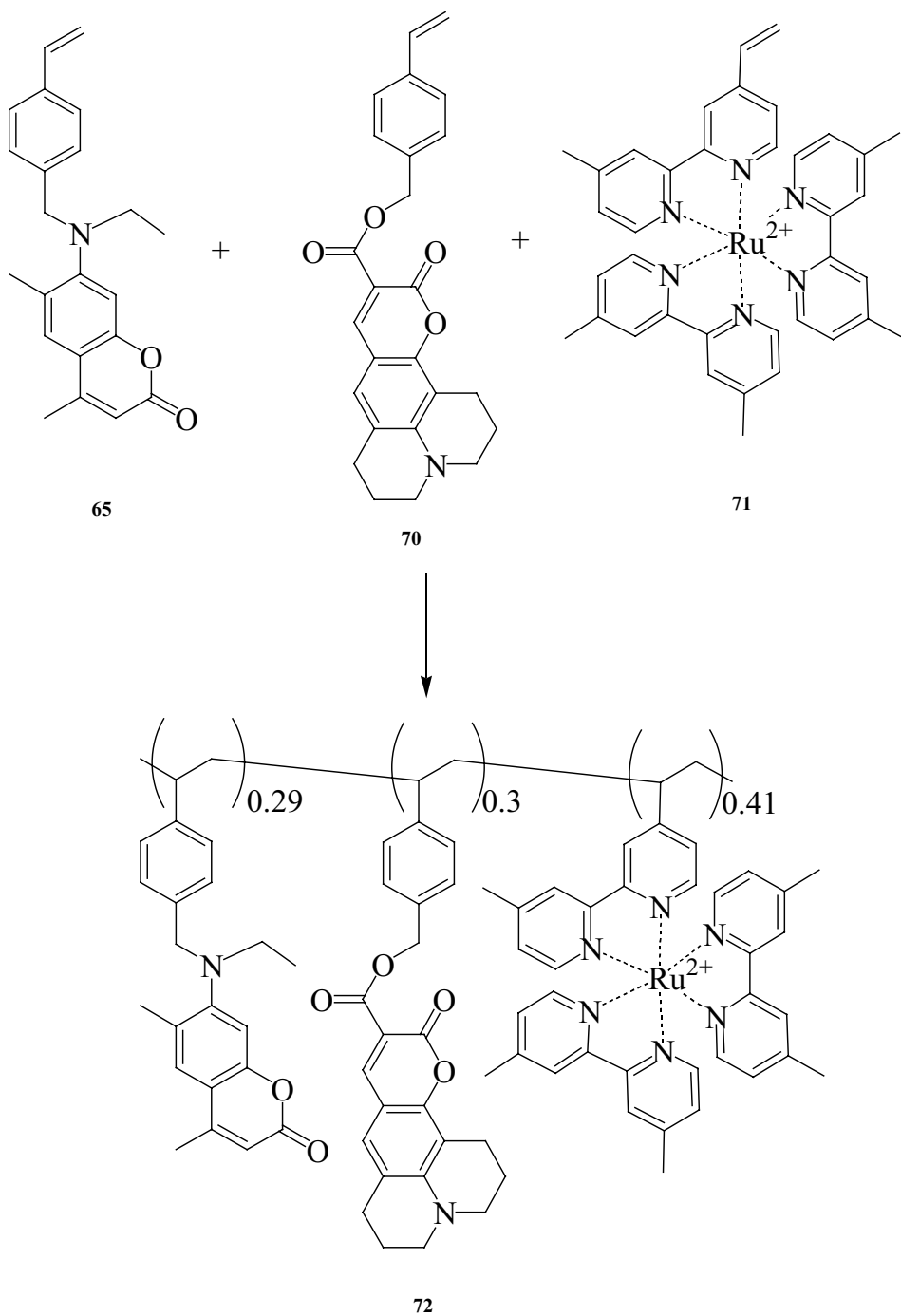
Scheme 16

The synthesis of polydiacetylenes with bipyridine metal complexes in their sidechains has been achieved by Lindsell and coworkers (Scheme 17).[51] Complexes of nickel, copper, ruthenium, and molybdenum were synthesized and the nonlinear optical properties of the resulting polymers examined.
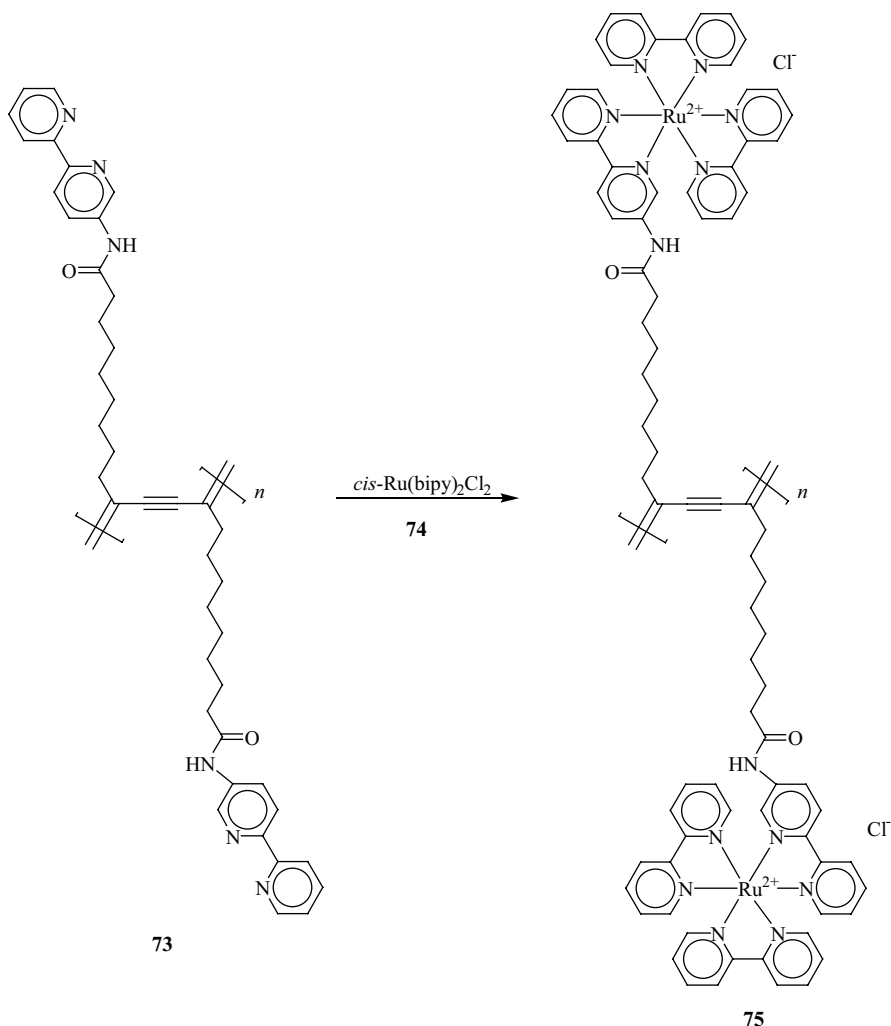
Scheme 17

B. Catenanes, Rotaxanes, and Calixarenes

Polymeric systems that contain interlocking rings (catenanes) and threaded rings (rotaxanes) with metals coordinated to their structures have been studied

because of their electro- and photoactivity.[52–54] A high MW polymer that contained copper ions coordinated to pyridine-based ligands within its structure was synthesized via polycondensation of a dicarboxylic acid with a dialcohol-derivatized copper(I) catenate.[52] Swager and coworkers have reported the synthesis of conducting polymetallorotaxanes that are coordinated to zinc and copper ions.[53,54] Thus, reaction of bithionyl-substituted bipyridine (**77**) with the macrocyclic phenanthroline molecule (**76**) gave a metallorotaxane (**78**), which was electropolymerized to give the polymetallorotaxane (**79**) (Scheme 18). A tungsten-capped calixarene functionalized with ethylenedioxythiophene groups was also recently electropolymerized to produce the corresponding polymer.[55]
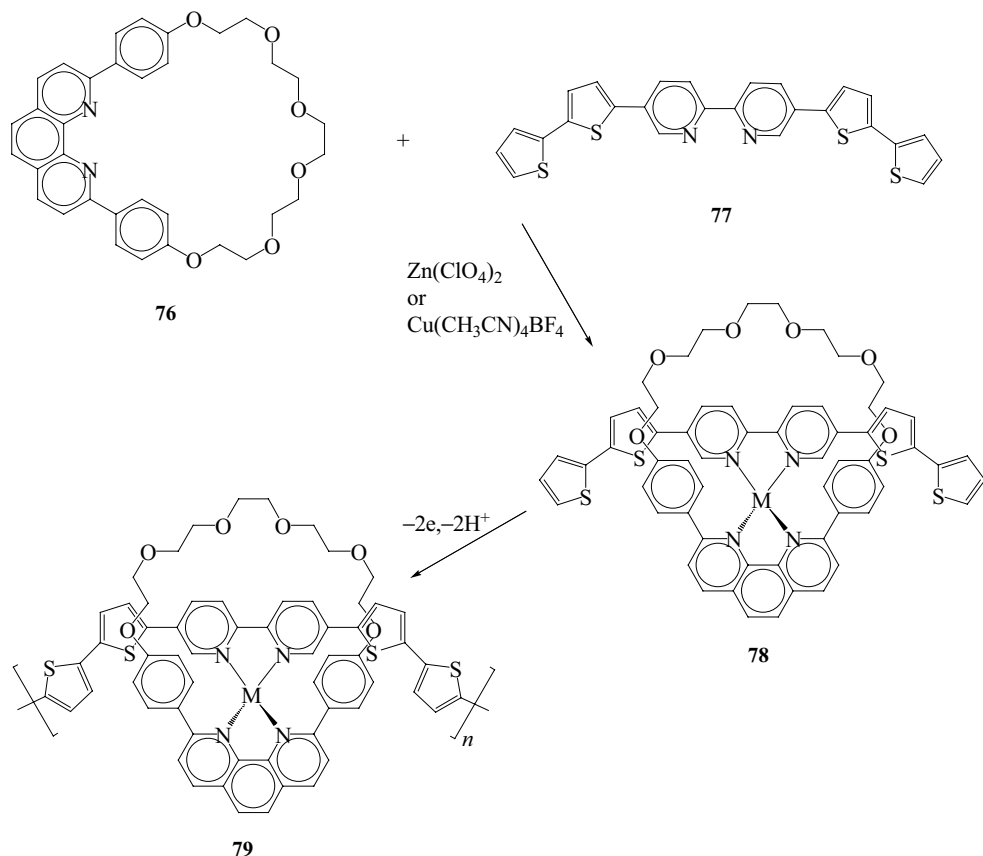
Scheme 18

C. Benzimidazoles

Polymers containing benzimidazole units in their backbones have been used in the synthesis of coordination metallopolymers that exhibit electronic communication between the metal centers.[56–60] The synthesis of osmium and ruthenium polymers, where the metal was coordinated with bipyridine ligands, has been accomplished by Cameron and Pickup.[56–59] Scheme 19 shows the reaction of polymer **80**, containing benzimidazole units in the backbone, with the osmium complex **81** to produce polymer **82**.[57] These polymers possess metal–metal interactions through their conjugated backbones. The osmium-coordinated polymer (**82**) showed two reduction waves separated by 0.32 V, which is indicative of strong communication between the Os centers.[57] Communication between the ruthenium centers of the analogous polymer is increased by deprotonating the imidazole rings.[58]
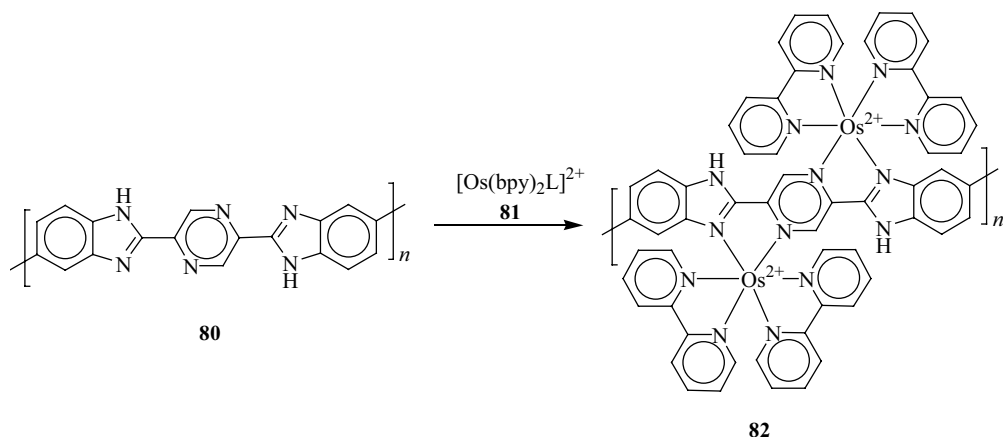
Scheme 19

A conjugated polymer that contains a tridentate 2,6-*bis*(benzimidazol-2-yl)pyridine ligand coordinated to ruthenium has also been synthesized by Chan et al. (Scheme 20).[60] Reaction of polymer **83** with 2,6-*bis*(benzimidazol-2-yl)pyridine ruthenium trichloride formed polymer **84.** The complexation reactions were greater than 90% successful according to elemental analyses. While polymer **83** was luminescent, its ruthenium complexed form (**84**) was not luminescent because of photodissociation of the terminal benzimidazole rings.[60]
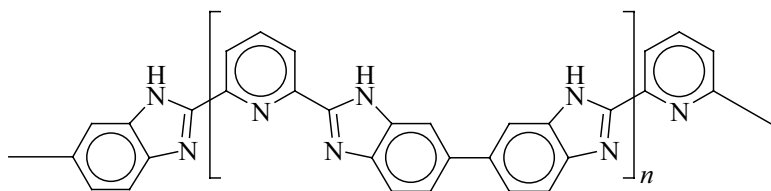
83

Ru complex
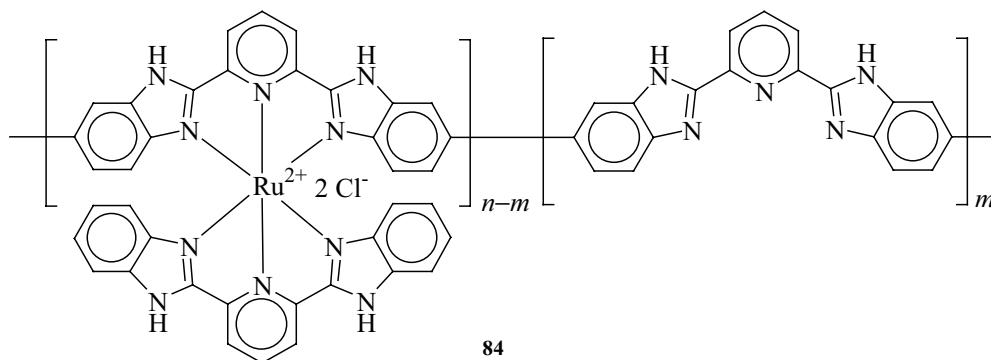
84

Scheme 20

D. Dendrimers and Stars

There are numerous examples of dendrimers and star polymers that contain metal coordination complexes based on pyridine ligands.[61–71] There is also interest in the incorporation of more than one type of metal complex into these materials.[65,66] Constable and coworkers have reported the synthesis of heptametallic complexes containing six peripheral ruthenium coordination complexes and a central iron or cobalt complex.[65] Scheme 21 illustrates the reaction of **89** with either iron or cobalt complexes to produce the heptametallic dendrimer **90**.[65] A heptametallic star-shaped complex with a CpFe$^+$-coordinated arene as the core and ruthenium *hexa*-pyridine complexes at the periphery has also been reported by Astruc.[66]
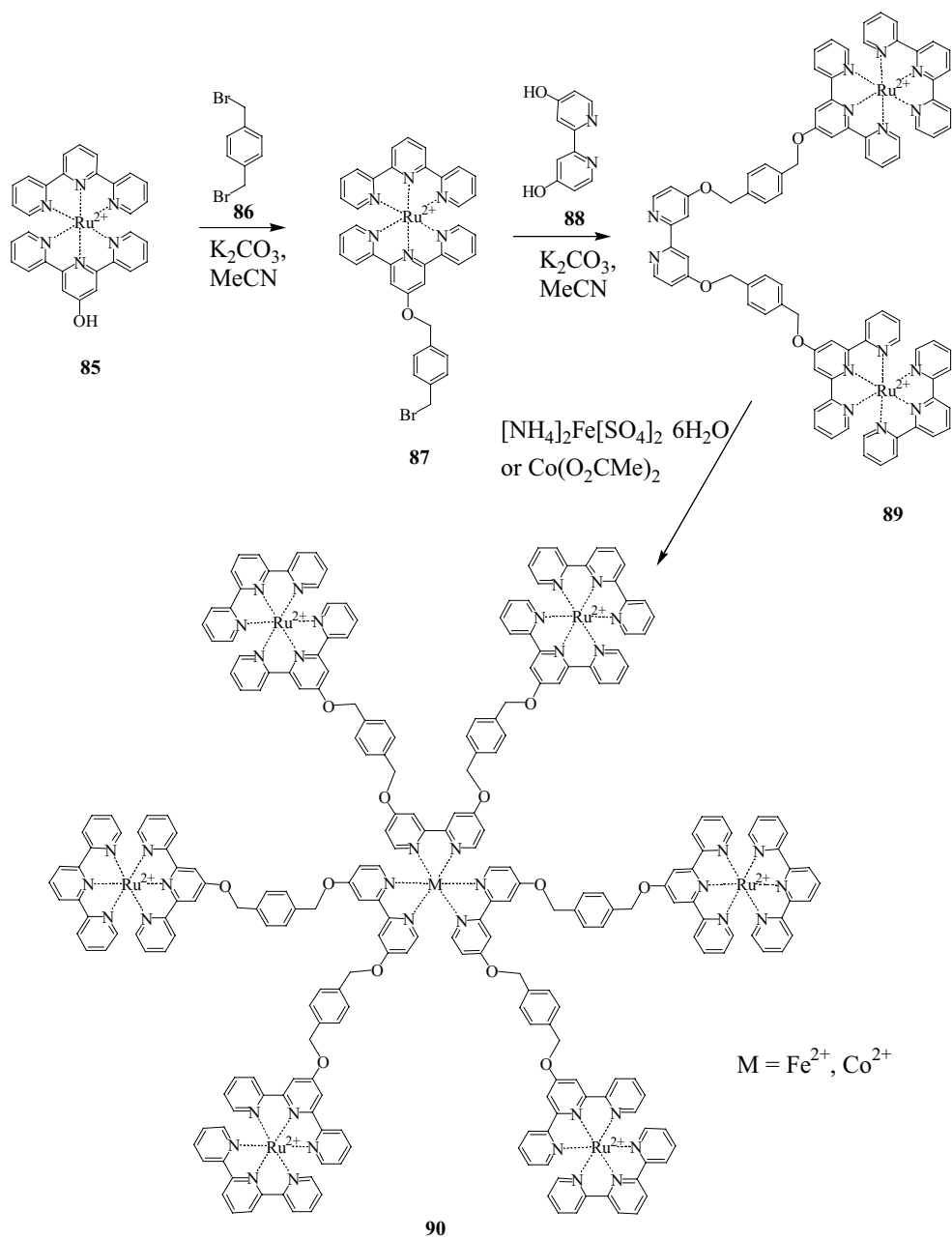
Scheme 21

Newcome and coworkers have reported the synthesis of a tetraarm complex containing two ruthenium coordination complexes in each branch.[68] Polymer **91** was prepared by reaction of a core molecule containing four terpyridine units with 4 eq of a bimetallic complex containing a reactive ruthenium trichloride moiety.
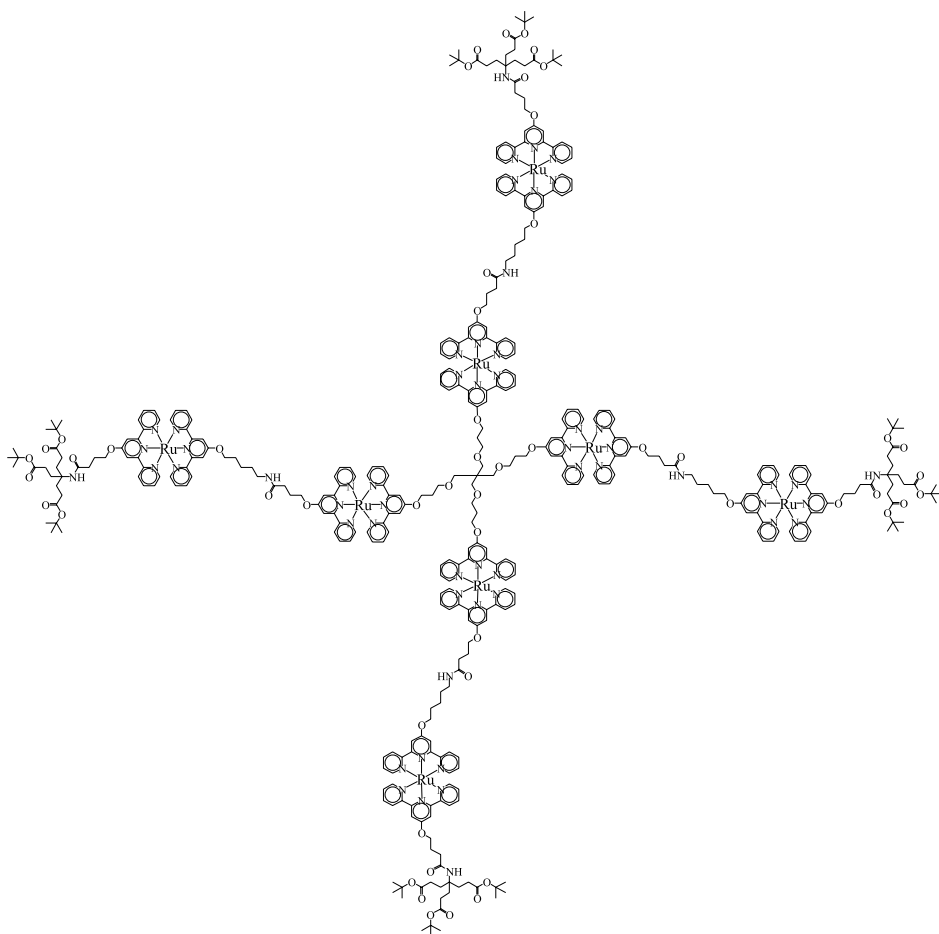
91

Polypyridine ruthenium complexes prepared by palladium-catalyzed grafting reactions have shown properties indicating their potential for use as light-harvesting devices.[70] Fraser and coworkers have utilized ruthenium *tris*-bipyridine complexes as the core molecule in the preparation of star polymers.[71,72]

VI. SUMMARY

Coordination macromolecules of the metalloenzyme class are responsible for life through their role in photosynthesis and respiration. There exists a wide variety of coordination polymers utilizing nitrogen, oxygen, and sulfur as the "chelating" atoms. These macromolecules are generally made by introducing the metal-containing unit during the formal polymer-forming sequence. In such cases the polymer is formed through chelation with the metal, through inclusion of the metal-containing unit in the polymer forming step where the connective sequence is removed from the metal, or through introduction of the metal to already formed macromolecular structures.

Coordinating groups include porphyrins (as present in hemoglobin), Schiff bases, phthalocyanines, and pyridine-related systems, but any appropriate Lewis base can be utilized as the chelating agent. The metal atoms are included in macromolecular systems, typically through sigma bonding, but metals can also be attached through other bonding avenues. The metal-containing unit may be neutral or it may contain a net charge and thus exist as a salt.

As with other metal-containing systems, the polymer architecture can be linear, two- or three-dimensional, star, dendritic or "shish-kebab." The metal-containing unit may be oriented along the mainchain or as an appendage, or in some combination of placements. In general, such products exhibit fairly high glass and melting points and poor solubilities. The structures are also generally not as stable in solution as some other metal-containing systems, such as those described in Chapter 4, due to the ready reversibility of the metal–chelate atom bond. Some of the materials exhibit optical nonlinearity, electrical conductivity, charge-carrier ability, photoactivity, and luminescence.

VII. REFERENCES

1. C. E. Carraher, Jr., W. J. Scott, J. A. Schroeder, D. J. Giron, *J. Macromol. Sci. Chem., Part A,* **15,** 625 (1981).

2. C. E. Carraher, Jr., in *Seymour/Carraher's Polymer Chemistry,* 5th ed., Marcel Dekker, New York, 2000.

3. H. A. Goodwin, J. C. Bailar, Jr., *J. Am. Chem. Soc.* **83,** 2467 (1961).

4. H. Chen, R. D. Archer, *Macromolecules* **28,** 1609 (1995).

5. H. Chen, R. D. Archer, *Macromolecules* **29,** 1957 (1996).

6. H. Chen, J. A. Cronin, R. D. Archer, *Inorg. Chem.* **34,** 2306 (1995).

7. B. Wang, R. D. Archer, *Chem. Mater.* **5,** 317 (1993).

8. J. L. Reddinger, J. R. Reynolds, *Synth. Met.* **84,** 225 (1997).

9. J. L. Reddinger, J. R. Reynolds, *Chem. Mater.* **10,** 1236 (1998).

10. M. Cano, L. Oriol, M. Pinol, J. L. Serrano, *Chem. Mater.* **11,** 94 (1999).

11. N. Chantarasiri, N. Sutivisedsak, C. Pouyuan, *Eur. Polym. J.* **37,** 2031 (2001).

12. Y. -B. Dong, M. D. Smith, H. -C. zur Loye, *Inorg. Chem.* **39,** 4927 (2000).

13. P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis, S. B. Wild, *Chem. Commun.* 1153 (1998).

14. H. L. Anderson, *Chem. Commun.* 2323 (1999).

15. A. D. Pomogailo, N. M. Bravaya, V. F. Razumov, I. S. Voloshanovskii, N. A. Kitsenko, V. V. Berezovskii, A. I. Kuzaev, A. G. Ivanchenko, *Russ. Chem. Bull.* **45,** 2773 (1996).

16. T. E. O. Screen, K. B. Lawton, G. S. Wilson, N. Dolney, R. Ispasoiu, T. Goodson III, S. J. Martin, D. D. C. Bradley, H. L. Anderson, *J. Mater. Chem.* **11,** 312 (2001).

17. S. M. Kuebler, R. G. Denning, H. L. Anderson, *J. Am. Chem. Soc.* **122,** 339 (2000).

18. T. Yamamoto, N. Fukushima, H. Nakajima, T. Maruyama, I. Yamaguchi, *Macromolecules* **33,** 5988 (2000).

19. B. Jiang, S. -W. Yang, D. C. Barbini, W. E. Jones, Jr., *Chem. Commun.* 213 (1998).

20. A. S. Holmes-Smith, A. Hamill, M. Campbell, M. Uttamlal, *Analyst* **124,** 1463 (1999).

21. K. Susumu, H. Maruyama, H. Kobayashi, K. Tanaka, *J. Mater. Chem.* **11,** 2262 (2001).

22. W. You, L. Wang, Q. Wang, L. Yu, *Macromolecules* **35,** 4636 (2002).

23. Q. Wang, L. Wang, L. Yu, *J. Am. Chem. Soc.* **120,** 12860 (1998).

24. N. B. McKeown, *J. Mater. Chem.* **10,** 1979 (2000).

25. S. Venkatachalam, in H. S. Nalwa, ed., *Handbook of Organic Conductive Molecules and Polymers,* J Wiley, New York, 1997, Vol. 2, p. 741.

26. M. Hanack, in P. Wisian-Neilson, H. R. Allcock, K. J. Wynne, eds., *Inorganic and Organometallic Polymers II,* ACS Symp. Series Vol. 572, American Chemical Society: Washington, DC, 1994, Chap. 35, p. 472.

27. C. S. Marvel, J. H. Rassweiler, *J. Am. Chem. Soc.* **80,** 1197 (1958).

28. W. C. Drinkard, C. S. Marvel, *J. Am. Chem. Soc.* **81,** 4795 (1959).

29. M. Kimura, K. Wada, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *Macromolecules* **34,** 4706 (2001).

30. Y. Meng, I. A. Abu-Yousef, A. R. Hlil, A. S. Hay, *Macromolecules* **33,** 9185 (2000).

31. S. Makhseed, A. Cook, N. B. McKeown, *Chem. Commun.* 419 (1999).

32. B. N. Diel, T. Inabe, N. K. Jaggi, J. W. Lyding, O. Schneider, M. Hanack, C. R. Kannewurf, T. J. Marks, L. H. Schwartz, *J. Am. Chem. Soc.* **106,** 3207 (1984).

33. J.-F. Gohy, B. G. G. Lohmeijer, U. S. Schubert, *Macromolecules* **35,** 4560 (2002).

34. O. N. Petzold, I. I. Harruna, *J. Inorg. Organomet. Polym.* **10,** 231 (2000).

35. O. N. Petzold, I. I. Harruna, *J. Inorg. Organomet. Polym.* **10,** 249 (2000).

36. S. Kelch, M. Rehahn, *Macromolecules* **32,** 5818 (1999).

37. S. Kelch, M. Rehahn, *Macromolecules* **30,** 6185 (1997).

38. S. Kelch, M. Rehahn, *Macromolecules* **31,** 4102 (1998).

39. R. Knapp, A. Schott, M. Rehahn, *Macromolecules* **29,** 478 (1996).

40. M. Kimura, M. Sano, T. Muto, K. Hanabusa, H. Shirai, N. Kobayashi, *Macromolecules* **32,** 7951 (1999).

41. T. Cassagneau, J. H. Fendler, S. A. Johnson, T. E. Mallouk, *Adv. Mater.* **12,** 1363 (2000).

42. Z. Peng, L. Yu, *J. Am. Chem. Soc.* **118,** 3777 (1996).

43. Z. Peng, A. R. Gharavi, L. Yu, *J. Am. Chem. Soc.* **119,** 4622 (1997).

44. S. C. Yu, S. Hou, W. K. Chan, *Macromolecules* **33,** 3259 (2000).

45. S. C. Yu, Z. Gong, W. K. Chan, *Macromolecules* **31,** 5639 (1998).

46. L. Trouillet, A. De Nicola, S. Guillerez, *Chem. Mater.* **12,** 1611 (2000).

47. K. D. Ley, C. E. Whittle, M. D. Bartberger, K. S. Schanze, *J. Am. Chem. Soc.* **119,** 3423 (1997).

48. L. A. Worl, W. E. Jones, Jr., G. F. Strouse, J. N. Younathan, E. Danielson, K. A. Maxwell, M. Sykora, T. J. Meyer, *Inorg. Chem.* **38,** 2705 (1999).

49. C. N. Fleming, K. A. Maxwell, J. M. DeSimone, T. J. Meyer, J. M. Papanikolas, *J. Am. Chem. Soc.* **123,** 10336 (2001).

50. J. Serin, X. Schultz, A. Adronov, J. M. J. Frechet, *Macromolecules* **35,** 5396 (2002).

51. M. A. Camacho, A. K. Kar, W. E. Lindsell, C. Murray, P. N. Preston, B. S. Wherrett, *J. Mater. Chem.* **9,** 1251 (1999).

52. J. -L. Weidmann, J. -M. Kern, J. -P. Sauvage, D. Muscat, K. Mullen, *Chem. Commun.* 1243 (1996).

53. S. S. Zhu, P. J. Carroll, T. M. Swager, *J. Am. Chem. Soc.* **118,** 8713 (1996).

54. S. S. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **119,** 12568 (1997).

55. A. Vigalok, Z. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **123,** 7917 (2001).

56. P. G. Pickup, *J. Mater. Chem.* **9,** 1641 (1999).

57. C. G. Cameron, P. G. Pickup, *J. Am. Chem. Soc.* **121,** 7710 (1999).

58. C. G. Cameron, P. G. Pickup, *Chem. Commun.* 303 (1997).

59. C. G. Cameron, P. G. Pickup, *J. Am. Chem. Soc.* **121,** 11773 (1999).

60. S. C. Yu, S. Hou, W. K. Chan, *Macromolecules* **32,** 5251 (1999).

61. E. C. Constable, *Chem. Commun.* 1073 (1997).

62. V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **31,** 26 (1998).

63. S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano, V. Balzani, *Angew. Chem. Int. Ed. Engl.* **31,** 1493 (1992).

64. E. C. Constable, P. Haverson, *Chem. Commun.* 33 (1996).

65. E. C. Constable, P. Haverson, M. Oberholzer, *Chem. Commun.* 1821 (1996).

66. V. Marvaud, D. Astruc, *Chem. Commun.* 773 (1997).

67. D. Armspach, M. Cattalini, E. C. Constable, C. E. Housecroft, D. Phillips, *Chem. Commun.* 1823 (1996).

68. G. R. Newkome, E. He, *J. Mater. Chem.* **7,** 1237 (1997).

69. G. R. Newkome, E. He, L. A. Godinez, *Macromolecules* **31,** 4382 (1998).

70. M. Osawa, M. Hoshino, S. Horiuchi, Y. Wakatsuki, *Organometallics* **18,** 112 (1999).

71. X. Wu, C. L. Fraser, *Macromolecules* **3,** 4053 (2000).

72. A. P. Smith, C. L. Fraser, *Macromolecules* **35,** 594 (2002).

CHAPTER 6

Silicon-, Germanium-, Tin-, and Lead-Containing Polymers

CONTENTS

I. INTRODUCTION

Group IVA starts with carbon, which is a nonmetal, followed by silicon and germanium, which are metalloids (semimetals), and tin and lead, which are metals. All of the group IVA elements have the ability to catenate; however, as you move down the group, this ability decreases. Some of the more important inorganic polymers are polysilanes, in which there are repeat Si−Si units in the polymer backbone. However, the bond energy of Si−Si bonds is 222 kJ/mol, while the

C−C bond energy is 346 kJ/mol.[1] In contrast, Si−O bonds are more stable (452 kJ/mol), and have properties that lend themselves well to practical applications. For this reason, polysiloxanes are the best-studied class of silicon-containing polymer.

The chemistry of germanium developed more slowly than did that of the other group IVA elements because of its relative rarity and high cost. It wasn't until 1864 that Newlands first suspected that germanium was a missing element between silicon and tin.[2] Seven years later, Mendeleev recognized that germanium was a missing element in the periodic table, and predicted its general properties on the basis of similiarities to silicon and tin. It was also believed that the chemistry of germanium would be very similar to that of silicon and tin. All group IVA elements form compounds with oxidation states of +4, which involves covalent bonding. Tin and lead also form stable ionic compounds with oxidation states of +2, whereas the +4 oxidation state is more thermodynamically stable for carbon and germanium. Carbon, silicon and germanium can also have oxidation states of −4 when they are bonded to more electropositive elements.

There are examples of polymers containing each of the group IVA semimetal and metals; however, polymers containing silicon are the most prevalent. Much of the interest in polysilanes, polygermanes, and polystannanes involves their σ delocalization and their σ–π delocalization when coupled with arenes or acetylenes. In exhibiting electrical conductivity germanium and tin show more typical "metallic" bonding. Some polystannanes have been referred to as "molecular metals."[3] Conductivity is increased by doping,[4] illumination,[5] and application of an electric field.

II. SILICON

A. Polysilylenes (Polysilanes)

Polysilylenes are chains, rings and 3D network polymers of silicon that contain the Si−Si bond in the polymer backbone. The tetravalency of silicon is generally completed with hydrogen or organic (aliphatic or aromatic) moieties. The basic structural unit of a polysilylene has formula **1**.

R, R′ = H, organic

1
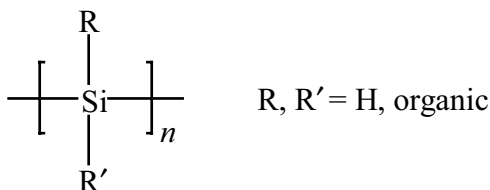
Polydiphenylsilanes were first reported by Kipping in the early 1920s, however, the oligomeric and/or polymeric products were not characterized.[6,7] It wasn't until 1949 that Burkhard[8] and subsequently Wesson and Williams[9] described the preparation and isolation of polydimethylsilane by the condensation of a dimethyldichlorosilane with an alkali metal dispersed in an inert solvent (i.e., Wurtz-type reaction). The products were reported as insoluble, infusible, and intractable substances and, therefore, could be only partially characterized. Thus, further investigation was discouraged and this class of materials was neglected for several decades until the issuance of patents by Clark[10] and publications by Kumada and Tamao[11] on linear polydimethylsilanes and the pioneering work of West et al.[12–14] and Trujillo,[15] who reported soluble linear polymethylphenylsilanes. The incentives for continued investigations of these and related materials (e.g., polycarbosilanes and polysilazanes) were based on their interesting and potentially important applications as precursors for thermally stable ceramics, photoresist materials in microlithography, photoreceptors in electrophotography, piezoelectric and piezochromic properties, and solid-state phase transition behavior, as well as promise as semiconductors, photoconductors, photocatalysts in polymerization reactions, and devices requiring nonlinear optical materials.

The synthesis of polysilylenes has been extensively reviewed.[16–23] A number of effective methods are currently being used to prepare polysilylenes. They include (1) reductive (Wurtz-type) coupling of halosilanes, (2) dehydrogenative coupling of hydrosilanes, (3) ring-opening polymerization of cyclic oligosilanes, (4) anionic polymerization of "masked" of disilylenes, (5) photochemical vapor deposition (PCVD) of small cyclic oligosilanes, and (6) electrochemical polymerization of chlorosilanes. A brief discussion of each is given below.

Wurtz-type reductive coupling of halosilanes (Scheme 1) is widely used in the synthesis of silane homo- and copolymers. This is a heterogeneous reaction that uses dispersed molten alkali metals (Li, Na, K) and alloys such as Na/K in relatively high-boiling organic solvents.[7–15] Thus, metal/alloy slurries can be reacted with R_2SiX_2 (X=halogen) (**2** or **4**) where the R groups are alkyl, aryl, and/or organosilyl substituents that are inert to strongly reducing media. The types of products formed [i.e., cyclic and/or linear homopolymers (**3**) or copolymers (**5**)], and their molecular weight and polydispersity depend on the reaction conditions (i.e., monomers used, reaction time, temperature, polarity of the solvent, stirring speed, and metal or alloy used). Under suitable reaction conditions and at low product conversion, reasonably high molecular weight polymers (i.e., 1×10^6) may be obtained. As the reaction proceeds, however, cyclic oligomers (mainly Si_6 and Si_8) are formed to give an overall broad and polymodal distribution of chain and ring products.[24–26] The mechanism of polymerization appears to include a slow initiation step to produce the ion pair, $R_2SiCl^- M^+$, which is followed by fast rate-determining propagation steps involving (1) reaction of the monomer with the ion pair to give a chlorine end-functional dimer and the metal halide and (2) reduction of the dimer by the metal to give a new ion pair. If a trifunctional silane (e.g., $RSiCl_3$) is the monomer, a network polysilylene is formed. Furthermore, West et al.[27] have shown that if mixtures of monomers are used, random copolymers (**5**) are obtained.

$n\mathrm{R_2SiX_2}$ $\xrightarrow[\substack{2n\ \mathrm{M,}\\ \text{where M = Li, Na, Na/K}}]{\text{high-boiling solvent}}$

X = Cl, Br
R = H, organic

2

$$\left[\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{Si} \\ | \\ \mathrm{R} \end{array}\right]_n$$

3

$\Big\downarrow$ $m\mathrm{R'_2SiX_2}$

4

$$\left[\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{Si} \\ | \\ \mathrm{R} \end{array}\right]_n \left[\begin{array}{c} \mathrm{R'} \\ | \\ \mathrm{Si} \\ | \\ \mathrm{R'} \end{array}\right]_m$$

5
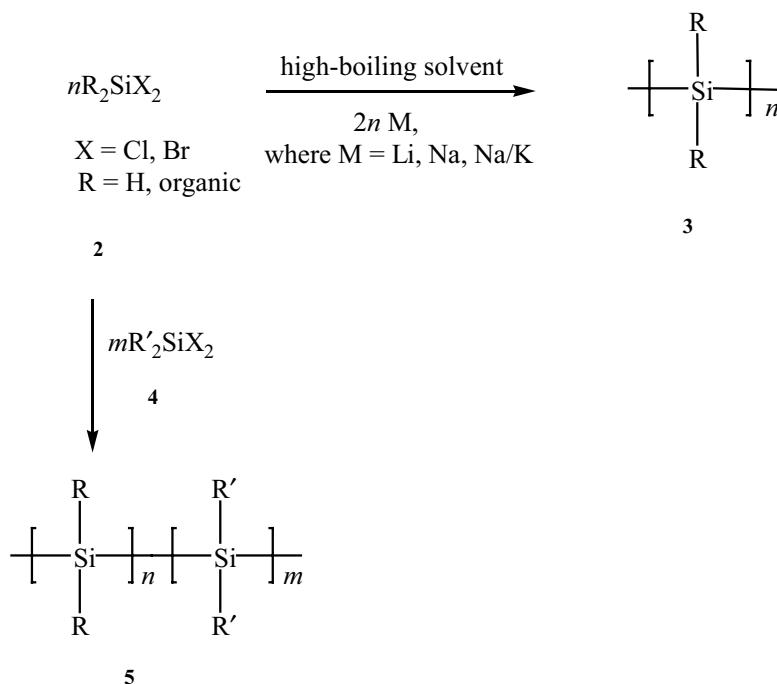
Scheme 1

Shizuka et al.[28,29] and Wildeman et al.[30] have reported that the Wurtz-type reaction may also be used to prepare alternating copolymers as in the coupling of diorganolithium compounds (**6**) with dihalosilanes (**7**) (Scheme 2). The product (**8**) of the reaction in this case forms a liquid crystalline, mesophase material that exhibits σ–π conjugation.

Aitken et al. have shown that catalytic dehydrogenative coupling of primary alkylsilanes ($\mathrm{RSiH_3}$, **9**) using titanocene, zirconocene, organolanthanum (e.g., $[\mathrm{C_5(CH_3)_5}]_2\mathrm{LaH}$) or organoplatinum compounds as a catalyst affords reasonably good yields of soluble polysilylenes (Scheme 3).[31,32] The reaction product (**10**) had a modest molecular weight ($M_n \leq 20{,}000$) and a fairly broad degree of polymerization ($n = 10$–20) depending on the monomer and catalyst used and the reaction conditions employed.

Diorganosilanes ($\mathrm{R_2SiH_2}$) under the same reaction conditions gave only dimers: $\mathrm{H(R_2Si)_2H}$. Generally, to obtain reasonably high molecular weights, reactions are carried out with a minimum quantity or no solvent. Furthermore, as shown by Tilley et al. and others, the reaction is assisted by removal of $\mathrm{H_2}$ gas, say, under vacuum.[33–42] Arylsilanes, for example, couple more rapidly than do alkylsilanes, which suggests that steric factors play an important role in the reaction mechanism. Moreover, the reaction can tolerate the presence of some reactive groups (e.g., halogens) on the aryl moiety thereby providing a route to substituent functionalization.
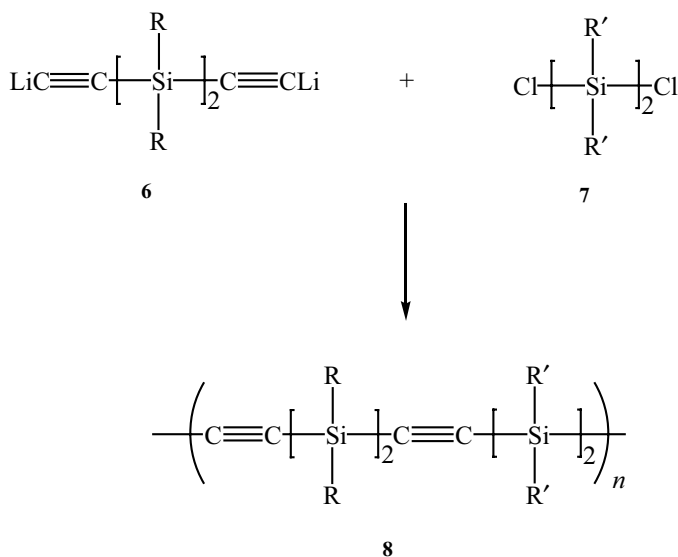
Scheme 2
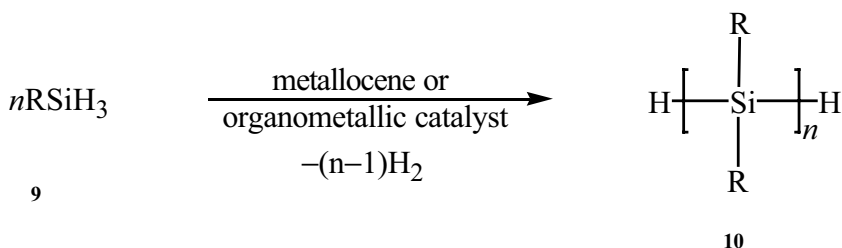
Scheme 3

In an extension of this reaction, Chauhan et al. used $Pt(cod)_2$ to dehydrogenate and couple 5- and 6-membered silacycloalkanes to obtain heteropolymers of intermediate molecular weight; specifically, 4-membered rings underwent both dehydrogenation and ring-opening polymerization.[43] In addition, cross-dehydrogenative coupling reactions were reported by Li and Kawakami.[44,45] Thus polymers with the formula **11**, where X is −O−, −NH−, −ORO− (R=alkyl, aryl), were prepared by the reaction of the corresponding silane with H−X−H. The mechanism of this reaction is not fully understood and may involve a H-bridged intermediate, such as **12** or species **13**.[31] Alternatively, Woo and Tilley suggested that the reaction may proceed to the polymer through a series of σ-bond metathesis steps involving a four-centered transition state (**14**).[33]

Dendrimeric products can also be formed through dehydrogenative coupling.[46–48] These materials exhibit multidirectional σ conjugation and show good electrical conductivity. These materials have also been used as negative-type photoresists because their exposure to air or light yields insoluble products.
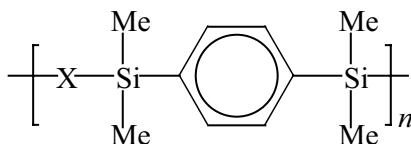
11
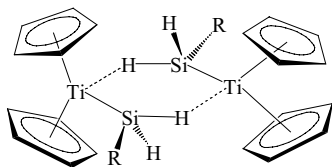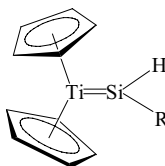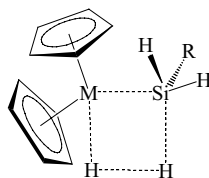
12   **13**   **14**

Most cyclic silanes are thermodynamically stable relative to their linear analogs. Therefore, ring-opening polymerization of cyclic oligosilanes requires kinetic control of the ring scission reaction through, for example, structural control in the form of strained cyclosilanes (Scheme 4) to obtain linear polysilylenes. Consequently, Matyjaszewski et al.[19,49] and Sakurai et al.[50] prepared strained ring silanes (**16**) from 1,2-dichloro-1,1,2,2-*tetra*-organodisilanes (**15**) by Wurtz coupling. Using the appropriate R substituents on silicon, a ring-opening polymerization reaction was initiated with an anionic catalyst (e.g., R^-Li^+ or $R_3Si^-K^+$) to obtain the linear polysilylene (**17**). The reaction involved an initial ring-opening nucleophilic attack of the anion on an electrophilic silicon atom in the strained ring monomer. The resulting silyl anion propagates by further monomer addition to form a linear polysilylene (enthalpic control) or it undergoes an intramolecular "backbiting" reaction to produce a cyclic oligomer with reduced stain (entropic control). Which process prevails depends on the nature of R, the monomer isomer used, reaction time, polarity of the solvent, monomer-to-catalyst concentration, temperature, and catalyst counterion. This method is most effective if the rings are small (e.g., Si_4) and the substituents are not excessively bulky (e.g., H, CH_3, C_6H_5). Under optimum conditions polysilylenes with molecular weights greater than 1×10^5 have been prepared. Moreover, the use of mixtures of monomers affords copolymers.[51]

Polysilylenes have also been prepared by anionic polymerization of "masked" disilylenes. For example, Sakurai et al. have shown that when disilabicyclooctadiene (**18**) is treated with *n*-BuLi, a polysilylene (**19**) with $M \approx 50,000$ is obtained with biphenyl (**20**) as a byproduct (Scheme 5).[46,52] This synthetic method may be used to prepare highly ordered and stereoregular polysilylenes. The reaction is also useful

since addition of unsaturated organic monomers such as methyl methacrylate to the masked organodisilylene gives block copolymers, such as poly(methyl methacrylate-co-polysilylene).
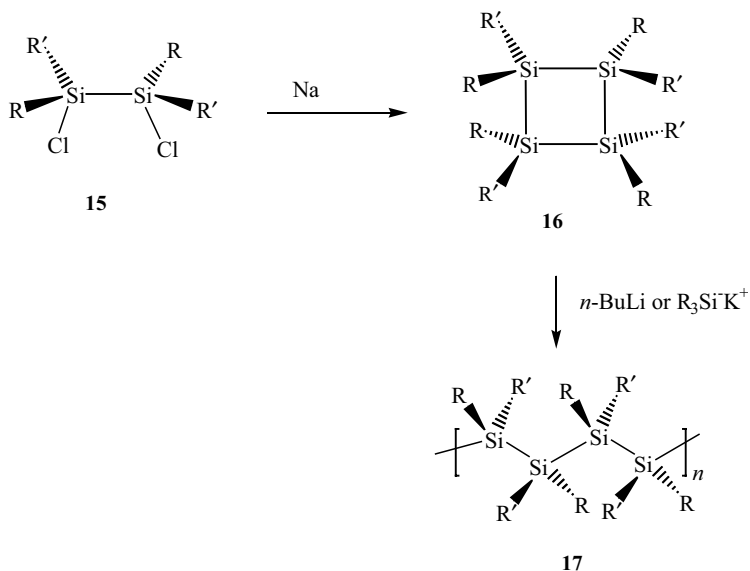
Scheme 4
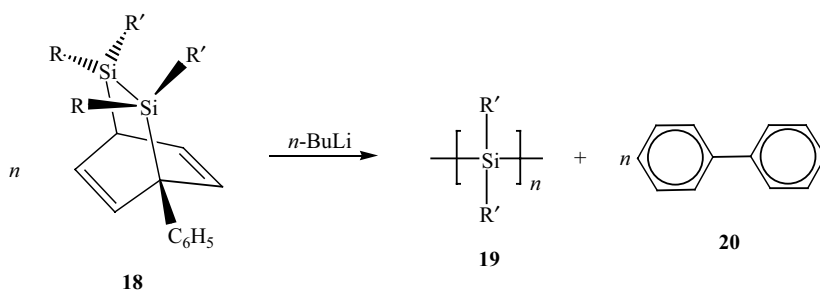
Scheme 5

Linear polysilylenes, which are bonded to a silica surface, can be prepared by photolysis coupled with chemical vapor deposition (photoCVD) of small cyclic oligosilanes (Scheme 6). For example, Obata and coworkers have shown that octapropylcyclo-*tetra*-silane (**21**) can be vaporized under vacuum at 270°C.[53] Photolysis of the vapor at 254 nm presumably gives the transient species, [Pr$_2$Si:] (**22**), which can be deposited on a pretreated quartz surface (**24**→**25**) to form a poly-silylene film (**26**). The presence of polysilylene on the quartz surface is confirmed

by absorption and emission spectroscopy. This novel synthetic method offers the promise of forming various substituted polysilylenes as coatings on glass and metal surfaces.
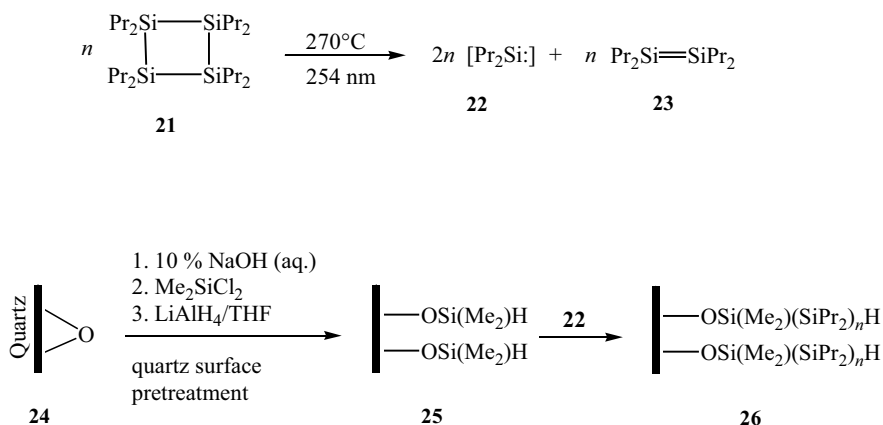
Scheme 6

Several research groups have developed electrochemical polymerization of chlorosilanes as an innovative, practical, and convenient route to a range of catenated silanes (e.g., di-, tri-, pentasilanes) as well as relatively high molecular weight polysilylenes (Scheme 7, where r.t.=room temperature).[54–63] The molecular weights and polydispersities of polymers formed by this method depend on the reaction conditions: concentration of the monomer, concentration of the electrolyte, sacrificed metal electrode used, and current density. For example, electroreduction of methylphenyldichlorosilane (**27**) with a magnesium cathode (sacrificed electrode) and anode in a one-compartment electrolysis cell gave the corresponding chlorine end-functional polysilylene (**28**) with $M_n \approx 30,000$ and $M_w/M_n \approx 1.8$. Polygermylenes, silane-germane copolymers (**30**) with $M_n \approx 20,000$, poly[p-(disilanylene) phenylene] (**32**) with $M_n \approx 10,000$ and $M_w/M_n \approx 1.9$, and polystannanes were also prepared in this manner.

The physical properties of polysilylenes (R_2Si) depend on the organic substituents R attached to the silicon. Polymers with relatively small and identical organic groups (e.g., R=Me, Et, Ph) bonded to Si are highly crystalline and generally insoluble and infusible solids. The crystallinity of the polymer decreases and the solubility increases with an increase in the length of the alkyl group, branching of the alkyl group and the presence of two different substituents on silicon.[64] Thus, polysilylenes of formula [CH_3RSi]$_n$, where R=n-butyl to n-dodecyl, are soluble elastomers, and [$CH_3Si(n$-hexyl)]$_n$ is a soluble, meltable polymer with a glass transition temperature near $-75°C$. If R is C_6H_5, the polymer is a high-melting resinous solid and is soluble in organic solvents.[65] It is interesting to note that copolymers [e.g., $(R_2Si)_x(R'_2Si)_y$; R=Me, R'=Ph] have a lower crystallinity and are more soluble in organic solvents than the corresponding homopolymers.
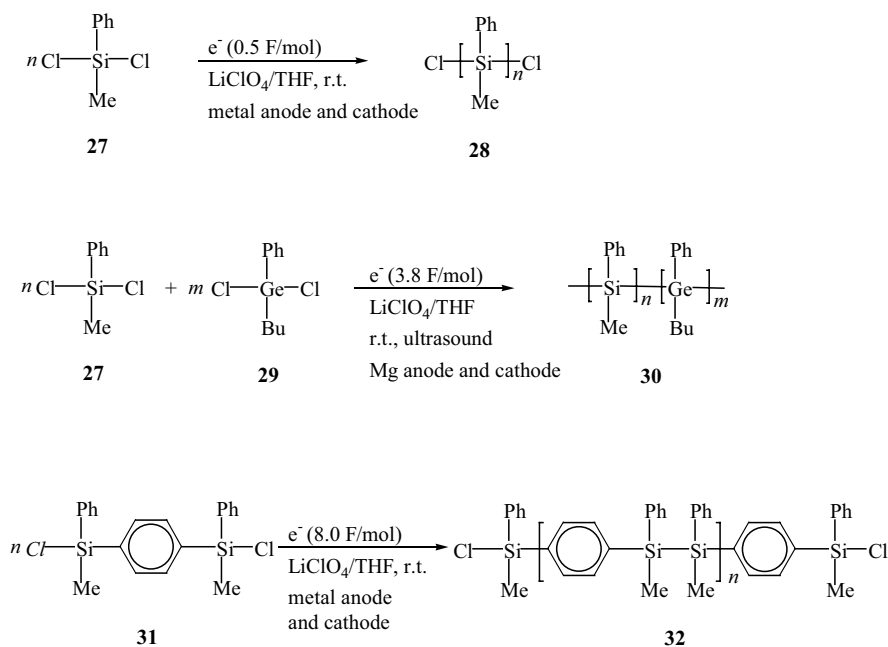
Scheme 7

The molecular weights of polysilylenes (see Table 1) depend on the method of synthesis and the substituents on silicon. Although size-exclusion chromatography (SEC) may be used to estimate molecular weight and polydispersity, more accurate values of M_w, M_w/M_n, and radius of gyration (RG) are obtained from light-scattering experiments.[66] The data indicate that polysilylenes assume a random coil configuration in solution.

Table 1 Molecular Weight Data for Polysilylenes[66]

Polymer	Solvent	$M_w^{\mathrm{LS}\,a}$	$M_w^{\mathrm{GPC}\,b}$	$M_w/M_n{}^c$	RG^d (nm)
$(n\text{-PrSiMe})_n$	THF	210,000	180,000	3.2	31
$(c\text{-HexSiMe})_n$	c-Hexane	2,540,000	500,000	2.7	76
$(n\text{-Hex}_2\text{Si})_n$	n-Hexane	6,100,000	1,900,000	2.3	108
$(n\text{-Hex}_2\text{Si})_n$	THF	6,300,000	1,900,000	2.3	92
$(n\text{-Oct}_2\text{Si})_n$	THF	320,000	2,600,000	2.4	100
$(\text{PhSiMe})_n$	THF	46,000	19,000	4.2	21
$[n\text{-BuC}_6\text{H}_4^p)_2\text{Si}]_n$	THF	450,000	500,000	—	60

$^a M_w^{\mathrm{LS}}$-weight average molecular weight from light scattering.
$^b M_w^{\mathrm{GPC}}$-weight average molecular weight from gel permeation chromatography.
$^c M_w/M_n$-polydispersity.
^{d}RG-radius of gyration.

The structure of polysilylenes has also been explored with ^{1}H, ^{13}C, and ^{29}Si NMR methods.[27,67–70] The studies indicate that polysilylene chain configurations in solution are varied and quite complex for a wide range of asymmetrically substituted homopolymers and copolymers. Thus, at high field (500 MHz) the alkyl protons in poly(methyl-*n*-hexylsilylene) are well resolved and assigned using 2D spectra. The ^{13}C spectra provide information about the microstructure and the ^{29}Si spectra appear sensitive to stereochemical configuration at least to the pentad level.

Perhaps the most interesting property of polysilylenes is related to the nature of the bonding in the catenated chains, namely, the effect of sigma-electron delocalization resulting from relatively loosely held electrons in relatively low-lying σ-bonding and σ*-antibonding orbitals that are associated with the (Si)$_n$ backbone.[16,71–77] These unusual molecular orbitals coupled with the polymer backbone conformation are responsible for strong electronic absorptions, electro- and photoconductivity, thermochromism, and photosensitivity. Consequently, polysilylenes absorb in the ultraviolet region of the spectrum with λ_{max} values between 300 and 400 nm by excitation of electrons from the σ valence band to the σ* conduction band. λ_{max} depends on chain length, chain conformation, and the substituent(s) present. For example, λ_{max} (1) increases with an increase in polymer chain length to a limit of ∼30 Si atoms (λ_{max} [Me$_6$Si$_2$]=190 nm, λ_{max} [Me$_{22}$Si$_{10}$]=312 nm); (2) increases with an increase in the branching of the alkyl substituent (λ_{max} [*n*-hexylSiMe]$_n$=315 nm, λ_{max} [cyclohexylSiMe]$_n$=325 nm); (3) increases with an increase in the number of aryl groups (λ_{max} [PhSiMe]$_n$ ≈ 326 nm, λ_{max} [Ph$_2$Si]$_n$ ≈ 400 nm); and (4) increases with the number of *trans–anti* (e.g., staggered) conformations along the silicon chain backbones. In some instances, absorption is reversible with temperature (*thermochromism*), which may be a result of equilibria between conformational orientations. These allowed transitions also give rise to intense spectra with extinction coefficients as large as 10,000 per Si−Si bond! Furthermore, for well-oriented films, this band is polarized and exhibits a large dichroism along the chain axis.[78] As a result of their anisotropic electrooptical properties, polysilylenes have found applications, for example, as photoresist materials in microlithography and free-radical photoinitiators in polymerization of unsaturated hydrocarbons.[16,79–80] The unusual electronic and photochemical properties have lead to additional applications as semiconducting polymers, photoreceptors in electrophotography and devices requiring nonlinear optical materials.[81–89]

B. Polycarbosilanes

Polycarbosilanes are polymers in which organosilicon moieties as silanes, disilanes, and trisilanes and carbon as aliphatic or aromatic units lie in the polymer backbone. The general formula for this class of material may be represented by structure **33**. Polycarbosilanes may be linear, cyclic, polycyclic, extended networks, or any combination thereof. R and R′ are the usual substituents found in organosilanes, and (C) represents difunctional aliphatic (saturated or unsaturated) or aromatic groups that can serve as bridges between the silicon moieties. Consequently, a

large number of polycarbosilane structures are conceivable and have been prepared. The present discussion will be limited, for the most part, to materials with silicon–carbon bonds in the oligomer/polymer backbone. These materials have attracted considerable attention owing to their applications, particularly in the fields of ceramics and metallurgy, and more recently for their potential as photoresists in lithography, photoinitiators in polymerization reactions and nonlinear optical materials. Currently, polycarbosilanes are supplied commercially by several companies (e.g., Nippon Carbon Company and Starfire Systems) as preceramic oligomers to high purity, high temperature stability silicon carbide fibers.

$$\left[\left(\underset{R'}{\overset{R}{Si}}\right)_x (C)\right]_n \qquad \begin{array}{l} R, R' = H, \text{ organic group} \\ (C) = \text{organic spacer} \\ x \geq 1 \end{array}$$
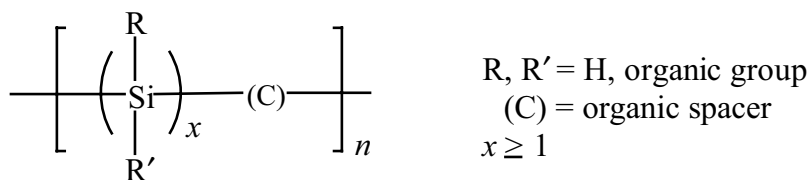
33

There are a number of excellent reviews on the subject of polycarbosilane synthesis.[90–96] A brief overview is given here. The methods of polycarbosilane synthesis include (1) coupling of multifunctional halosilanes using active metals or organometallic reagents, (2) ring-opening polymerization of cyclic carbosilanes, (3) catalytic hydrosilylation of silanes that contain unsaturated organic substituents, and (4) electrochemical polymerization of chlorosilanes.

Low molecular weight polycarbosilanes were first prepared in the late 1940s and early 1950s using organometallic routes. Specifically, difunctional halogenated organosilanes such as **34** (Scheme 8) react with alkaline metals (e.g., Na, Na/Li) or organometallics (RLi) to give linear oligomers (**35**) and 1,3-disilacyclobutane (**36**).[97–102] More complex branched and crosslinked structures were obtained by Interrante et al.[103] and Tessier et al.[104] from silanes that contain multifunctional groups, such as X−RSiX$_2$ or X−RSiX$_3$. Coupling reactions have also been reported by Jung et al. using metallic copper.[105] The yield of products (linear and/or cyclic carbosilanes) depends on reaction conditions, specifically, metal, solvent, and temperature. The molecular weight of the "linear" polymers, however, was relatively low (<1000) and **35** was the principal byproduct. Since small ring compounds were recognized as important precursors to high molecular weight polycarbosilanes via catalytic ring-opening polymerization, considerable effort was expended in controlling this reaction and improving the yield. Thus, Kriner[106] and Nametkin et al.[107] using magnesium metal were able to obtain the cyclic derivatives with yields as high as 60%. The byproducts were larger rings (viz., cyclic hexamer and octamer) and low molecular weight linear compounds.
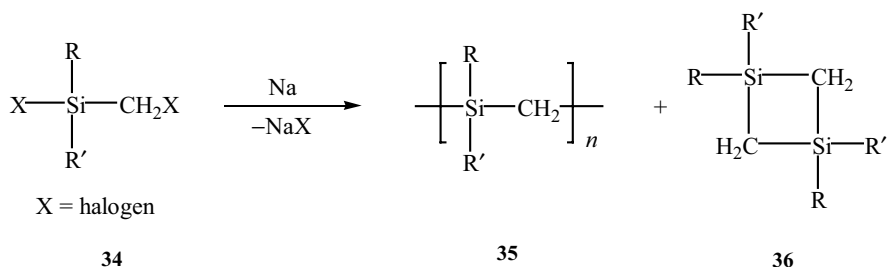
Scheme 8

Polycarbosilanes (**38**) have been obtained by the ring-opening polymerization of cyclic carbosilanes (**37**) either thermally or catalytically (Scheme 9). Regarding the latter, Nametkin et al. found that polymerization of a disilacyclobutane could be initiated with anionic catalysts such as KOH and metal silanolates, although organolithium compounds in THF solution were not found to be catalytically effective.[108] Several research groups have since shown that transition metal catalysts (i.e., complexes of Pt, Au, Pd, Ir, Cu, and Cr), are considerably more operative in ring opening and, in some cases, result in polymers with molecular weights as high as 100,000.[109–113]
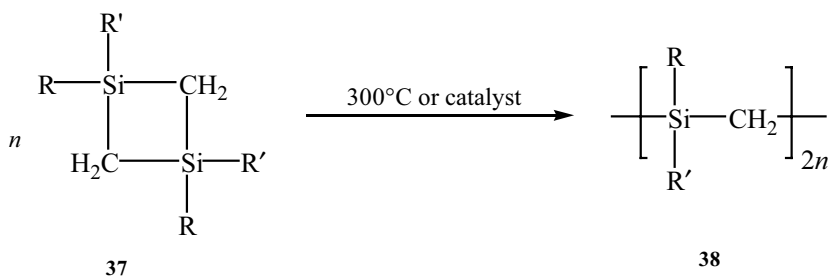
Scheme 9

Weber and his group took a different approach. Thus, Liao and Weber reported that vinyl-substituted silacyclobutanes such as **39** undergo anionic ring-opening polymerization using *n*-BuLi in a THF/HMPA solvent medium (Scheme 10).[114] The products (**40**) were soluble in organic solvents and had molecular weights (M_n) in the range of 6000–11,000 and polydispersities from 1.4 to 3.0 depending on R. Moreover, the polymers were stable to 450°C and gave char yields of 45% above 1000°C. Importantly, the reactive vinyl group in **40** provided ready access to polycarbosilanes that contained other pendent substituents.

R = Me, Ph, vinyl
R′ = vinyl
R″ = H

39

40
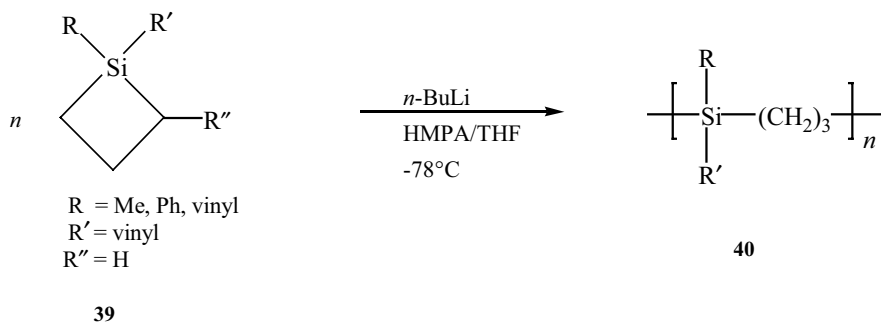
Scheme 10

More recently, Kawakami et al. have shown that when the R, R″, and R″ substituents of **39** are methyl groups, this molecule undergoes regiospecific (head-to-tail) ring-opening polymerization of silacyclobutanes in bulk using a platinum 1,3-divinyl-1,1,3,3-*tetra*-methyldisiloxane catalyst at 80°C or an alkyllithium catalyst in THF at −40°C. Although M_n values were relatively low (~3000), the molecular weight distributions were narrow and conversions were quantitative.[115] If an optically active carbosilane (**41**) is used, an optically active head-to-tail polycarbosilane (**42**) is obtained with $M_n > 10^6$ and a molecular weight distribution of 1.7–2.4 (Scheme 11).[115–117]

41

42
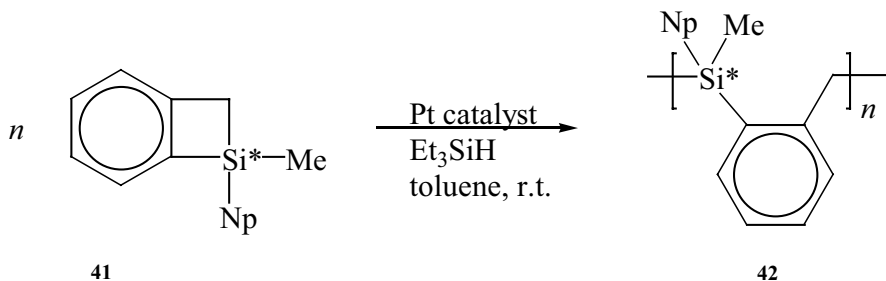
Scheme 11

In the early 1990s, Wu and Interrante found that platinum catalysts (e.g., chloroplatinic acid or Pt-divinyl-*tetra*-methyldisiloxane complex) effected ring-opening polymerization of 1,1,3,3-*tetra*-chloro-1,3-disilacyclobutane (**43**) to poly-dichlorosilamethane (**44**) (Scheme 12).[118,119] Remarkably, the Si−Cl bonds remained intact. The molecular weight (M_n) of **44** was 12,300 and M_w/M_n ~ 3. The Si−Cl bonds in **44** could be hydrogenated with LiAlH$_4$ to give the linear polymer **45**. The chlorinated polymer **44**, however, could not be completely alkoxylated with either NaOEt or EtOH/Et$_3$N mixture.
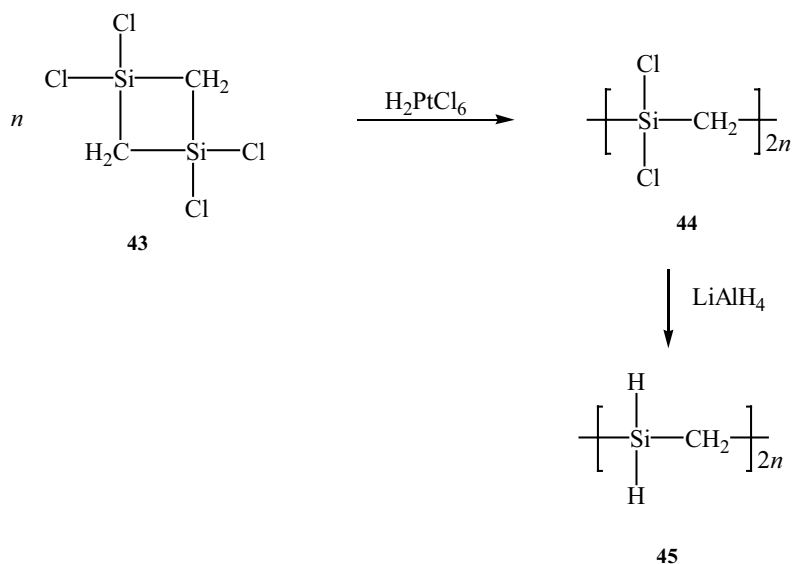
Scheme 12

Alkoxylated polymers are accessible by Pt-catalyzed ring-opening polymerization of the alkoxyl-substituted disilylcyclobutanes (**46**) (Scheme 13).[120] The products (**47**) of this reaction have lower molecular weights and higher polydispersity than does **45**.
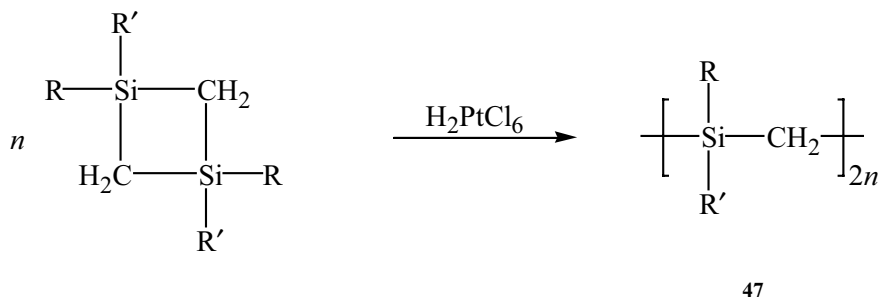
46a R, R′ = OC_2H_5, OCH_2CF_3
46b R = Me, R′ = OC_2H_5, OCH_2CF_3

Scheme 13

Corriu et al. achieved polycarbosilane synthesis by catalytic hydrosilylation of vinylsilanes.[121–123] For example, polydichlorosilaethane (**49**) was prepared from vinyldichlorosilane (**48**) using a platinum-on-carbon catalyst (Scheme 14). The product **49** was hydrolytically sensitive. However, owing to the reactivity of the Si−Cl bonds, **49** could be chemically modified to a variety of products containing either Si−H (**50**), Si−R [R=Me (**51**), naphthyl, vinyl], or Si-alkoxy substituents and Si−F (**52**).
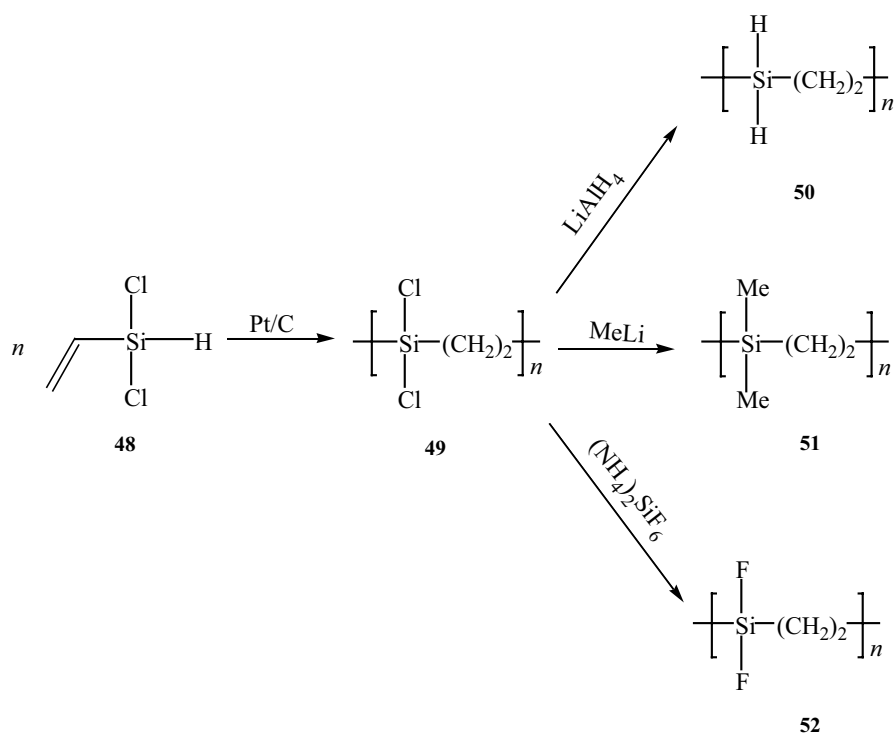
Scheme 14

Lach and Frey have shown that silanes containing multiple vinyl groups such as **53**, yield hyperbranched polycarbosilanes (**55**) in the presence of a Pt catalyst (Scheme 15).[124] A derivative of this product was characterized by the ^{29}Si NMR spectra and had an M_w of ~1800 with a degree of dendritic branching (DB) of ~0.5.
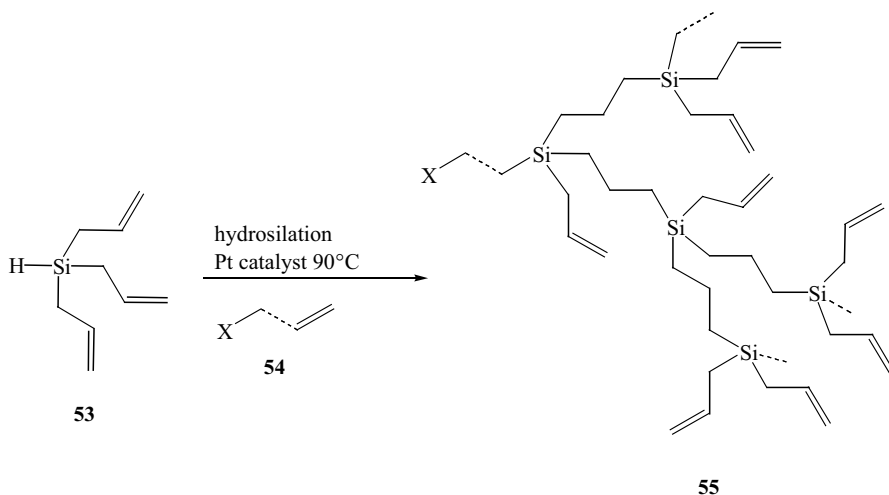
Scheme 15

In a similar reaction, Xiao et al. reported that the hydrosilylation of a diethynylsilane (**56**) produced an unusual dendrimer that contained $-C=C-$ units bridging silicon atoms with terminal $C\equiv C$ bonds (**57**) as deduced from the ^{1}H NMR spectrum (Scheme 16).[125] The molecular weight of **57** was ~3000, and the DB was ~0.56. These polymers were thermally stable to 1200°C and gave a ceramic yield of 87% in N_2 and 62% in air.
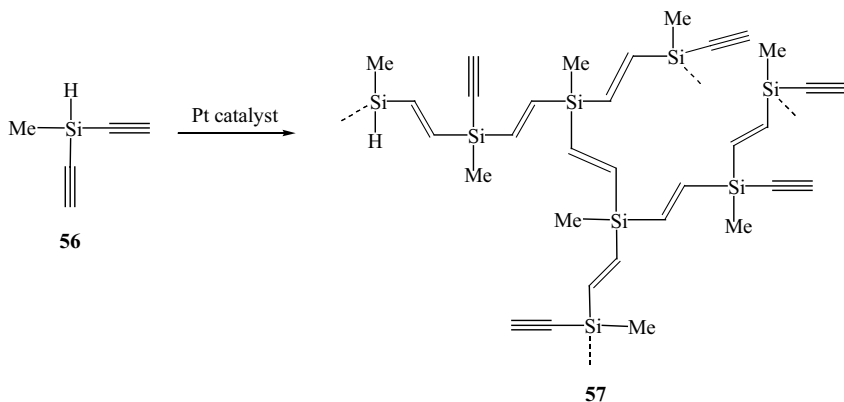
Scheme 16

Polycarbosilanes may also be prepared using difunctional hydrosilanes (**58**) and difunctional unsaturated organic hydrocarbons [i.e., dienes (**59**) or diynes]. For example, Zhou and Weber found that if $R=-(CH_2)_4-$ and $R'=-(CH_2)_8-$, careful control of reaction stoichiometry gives the polymer, $[Me_2Si(CH_2)_8]_n$ (**60**) with M_n ~30,000 (Scheme 17).[126] Similar reactions have been carried out by Tsumura et al. for $R=R'=-C_6H_4-$.[127]

60
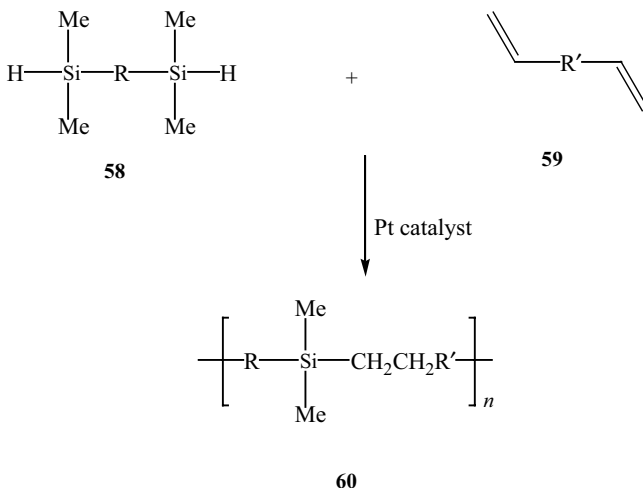
Scheme 17

It was mentioned earlier that polysilanes could be prepared by electrochemical polymerization of chlorosilanes. In a similar manner, chloromethyldimethylchlorosilane gives reasonable quantities ($\approx$40% yield) of relatively low molecular weight polycarbosilanes using aluminum as a sacrificial electrode and a current density of 2.2 F/mol in a THF/DMF solution with Et_4NBF_4 as a supporting electrolyte.[57]

One important application of polycarbosilanes is their use as precursors in the preparation of high-temperature, high-strength silicon carbide fibers. It was advantageous, therefore, to seek polysilylenes as a source of polycarbosilanes. High molecular weight polydimethylsilylene is thermally stable in an inert atmosphere to ~450°C. Bamford et al. found that when heated to ~1000°C, polydimethylsilylene undergoes a chain scission and depolymerization rather than crosslinking and rearrangement to preceramic materials.[128] In the early 1980s, however, Yajima et al. pioneered the development of an effective rearrangement of polysilylenes to polycarbosilanes, the latter of which could be pyrolyzed to give high-ceramic residues (Scheme 18).[129,130] The Yajima process is based on the thermal rearrangement of $[(CH_3)_2SiCH_2]_n$ (**62**) at 450°C to a complex polymer **63** that contains Si−CH$_3$, Si−H, and Si−CH$_2$ bonds as well as cyclic structures. Further pyrolysis of **63** above 1000°C in a stepwise fashion gave a β-SiC (**64**), which can be melt-spun into filaments and pyrolyzed into commercial SiC (e.g., Nicalon) fibers.[131]
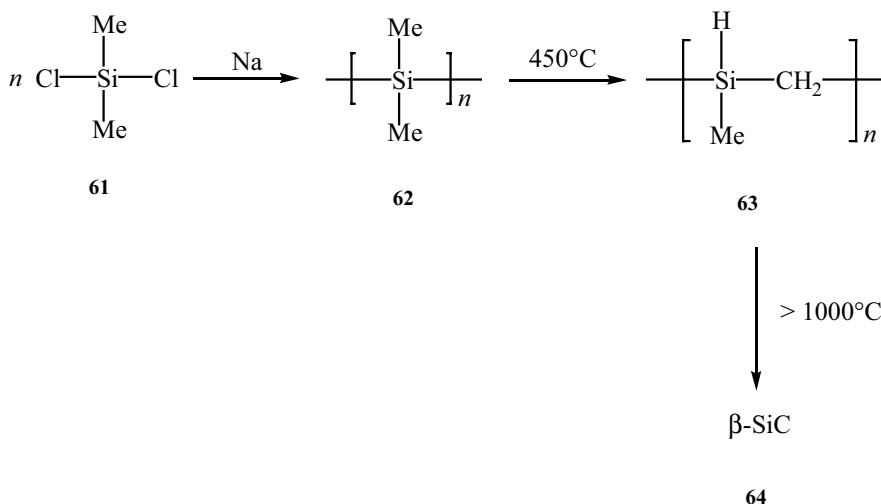
Scheme 18

C. Polysilazanes

Polysilazanes represent another important class of ceramic materials that contain N−Si−N and C−Si−N units, sometimes with or without oxygen. The structural forms of polysilazanes may be chains, rings, crosslinked networks, or, more recently, dendrimers. Generally, the prepolymers contain silicon bonded to nitrogen in the backbone and organic groups or hydrogen as substituents on Si and N (**65**).

R   R″
| |
—Si—N—
|
R′   n
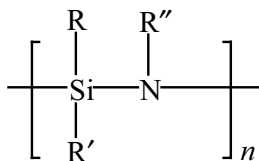
65

Ceramic materials such as silicon nitride, which are derived from the thermolysis of silazane prepolymers, possess high thermal stability, high tensile strength, and chemical resistance even under the most severely corrosive conditions. Silicon nitride can be obtained directly by the reaction of (1) elemental silicon with N_2, (2) silica with N_2, H_2 and carbon, or (3) $SiCl_4$ with NH_3 at high temperatures. The products from these reactions are insoluble, infusible, refractory substances (i.e., Si_3N_4) that are difficult to fabricate or to incorporate into composites with other materials. The highly desirable thermal and mechanical properties as well as chemical inertness of silicon nitride has prompted considerable effort to develop synthetic sources of soluble, meltable, and/or processable oligomers and polymers that contain the Si–N bond.

There are a number of published reviews on the synthesis of polysilazanes.[96,132–141] The present discussion is limited to a brief history and development of oligo- and polysilazane synthesis. The methods of synthesizing polysilazanes include (1) polymerization by aminolysis (or ammonolysis) of chlorosilanes, (2) ring-opening polymerization of oligomeric cyclosilazanes, (3) deamination and condensation of *bis*- and *tris*-aminosilanes, (4) redistribution polymerization of chlorosilanes and aminosilanes, and (5) catalyzed dehydrocoupling of diamines and organosilanes.

Aminolysis of difunctional chlorosilanes (Scheme 19) generally leads to low molecular weight oligosilazanes (**68**), particularly if sterically small substituents (H or Me) are present on silicon. Larger substituents generally yield ring compounds. Thus, Seyferth found that if R=R′=H and R″=Me, the principal product is a mixture of oligomers with an average degree of polymerization of <10, in addition to the cyclic tetramer **69**.[142,143] The oligomers, however, are believed to have a nonlinear, complex structure that may contain oligosilazane rings bridged by disilazane units.
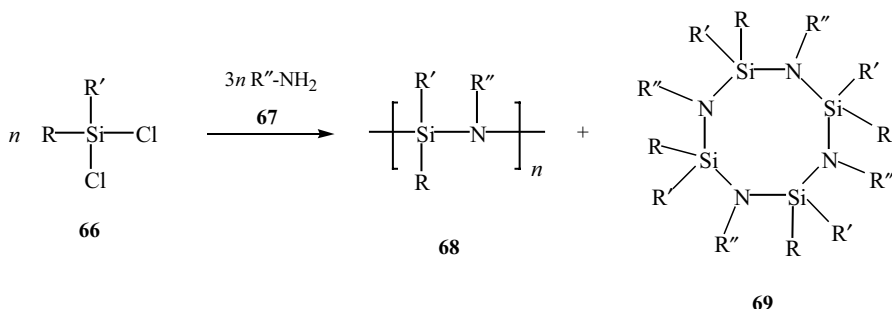
Scheme 19

In a related reaction, Arai et al. reported that ammonolysis of RHSiCl$_2$·2py (**70**), where R=H or Me (Scheme 20) gave a viscous material (**72**) that could be pyrolyzed at 1300°C to silicon nitride with a ceramic yield of 80%.[144]

$$n \text{ RHSiCl}_2 \cdot 2\text{py} \quad + \quad n \text{ NH}_3 \xrightarrow{-\text{pyHCl/NH}_4\text{Cl}}$$

70   **71**

72
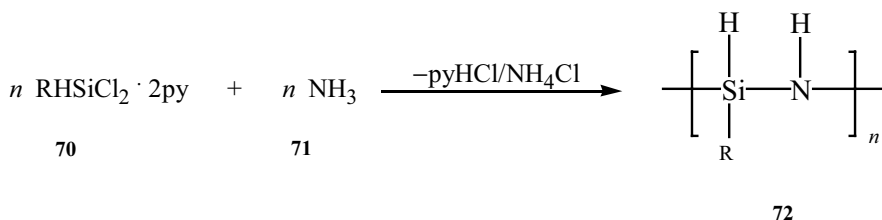
Scheme 20

Ring-opening polymerization of cyclosilazanes to give tractable materials was first reported by Rochow et al.[145–147] Thus, heating [R$_2$SiNH]$_3$ or [R$_2$SiNH]$_4$ (R=Me) at 160°C with ammonium chloride as a catalyst gave a viscous, waxy mixture of linear and cyclic products. Only low molecular weight oligomers were obtained in this manner, and pyrolysis of the oligomers gave low ceramic yields (<30%). Seyferth et al. examined the anionic ring-opening polymerization of the cyclic tetramers (e.g., [Me$_2$SiNMe]$_4$, [MeHSiNH]$_4$) using alkyllithium (RLi or RLi/Me$_3$CONa) catalysts.[148,149] They obtained low molecular weight materials with Me−Si, H−Si, H−N and Me−N bonds and postulated sheetlike polymeric structures were formed in which the silazane ring frameworks were bridged by cyclodisilazane units (**73**).
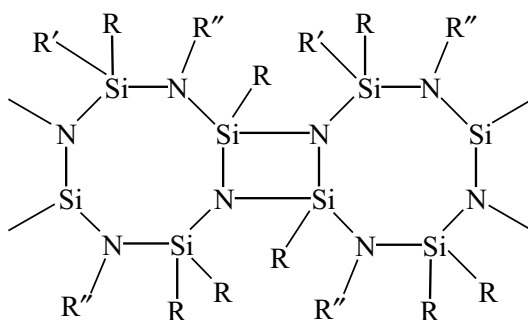
73

Laine et al. have shown that ring-opening oligomerization of the cyclic tetramer (**74**) can also be catalyzed by transition metal complexes such as Ru$_3$(CO)$_{12}$ (Scheme 21).[150,151] In the presence of an end-blocking agent such as (Me$_3$Si)$_2$NH, only low molecular weight oligomers (**76**) are obtained. Without the end-blocker, more complex oligomers with condensed rings are isolated.
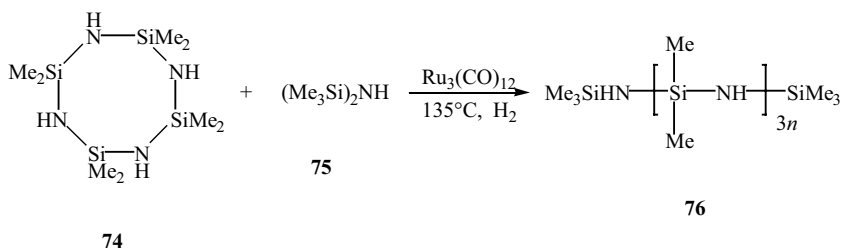
Scheme 21

In the early 1990s, Soum et al. opened highly strained cyclodisilazanes under specifically controlled conditions with anionic or cationic catalysts to give reasonably high molecular weight polymers. Consequently, the cyclic tetramer (**77**), which contained a vinyl group on each silicon, could be ring-opened with anionic initiators such as benzyllithium or sodium naphthalenide in THF at −40°C to give the linear polymer (**78**) (Scheme 22).[152] Polymer 78 had an $M_n \sim 93{,}000$ and a polydispersity of 1.3. The reaction appears to involve a "living" polymerization process and, therefore, generates polymers with controlled architecture. Although cationic catalysts (e.g., $BF_3{:}Et_2O$, $MeOBF_4$, triflic acid) also open the cyclic tetramer, the products are a mixture of linear and larger cyclic oligomers.[153]
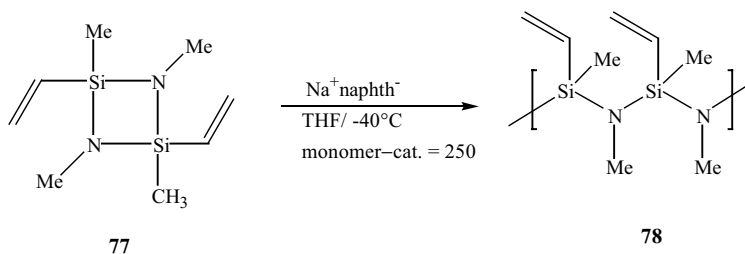
Scheme 22

Soum et al. also examined anionic copolymerization reactions involving mixtures of different cyclodisilazanes. Reactivity ratios suggest that "block-like" copolymers are obtained.[153–155] When the cyclodisilazane is copolymerized with $(Me_2SiO)_3$, mixed cyclic oligomers (**79, 80**) are obtained in addition to the block copolymer.
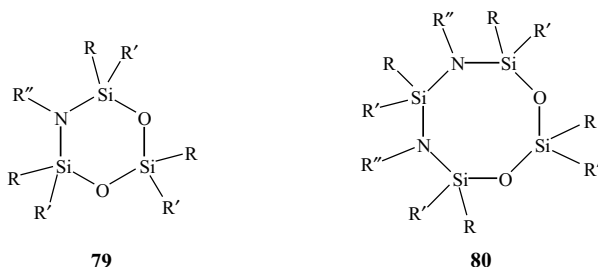
Bis- and tri-saminosilanes, $R_2Si(NHMe)_2$ and $RSi(NHMe)_3$, can be deaminated to give preceramic polysilazanes (**84**) and cyclic oligomers, such as **83**, at elevated temperatures (Scheme 23).[156,157] The efficiency of this commercial process was improved by recycling the volatile products to give better yields of the resinous material, which could be spun and then pyrolyzed into silicon nitride fibers. Little is known about the structure of these prepolymers, although there have been suggestions that they are comparable to **73** with a variety of ring sizes and chain crosslinks present.[158]
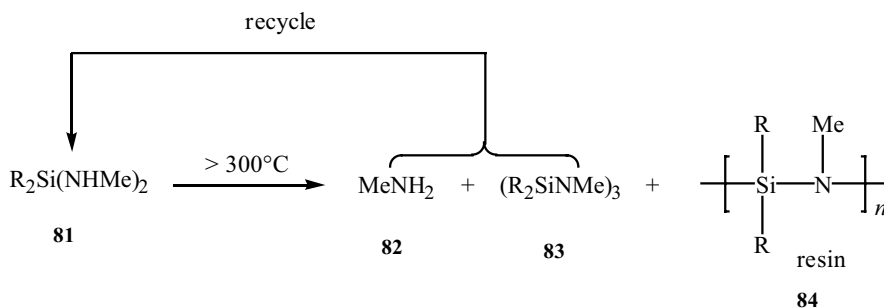
Scheme 23

Dow Corning Corporation scientists have explored SiCl/SiN redistribution reactions as a source of silazane prepolymers for silicon-containing ceramic materials. For example, a commercial process was developed in which $(Me_3Si)_2NH$ and $HSiCl_3$ were redistributed to give a silazane oligomer (**88**) with $M_n \sim 3500$ (Scheme 24).[159] This prepolymer could be spun into filaments that were subsequently pyrolyzed at $\geqslant 750°C$ in an inert atmosphere or under vacuum into low carbon-containing Si_3N_4 fibers (**89**) with ceramic yields of $\sim 50\%$.[160,161]
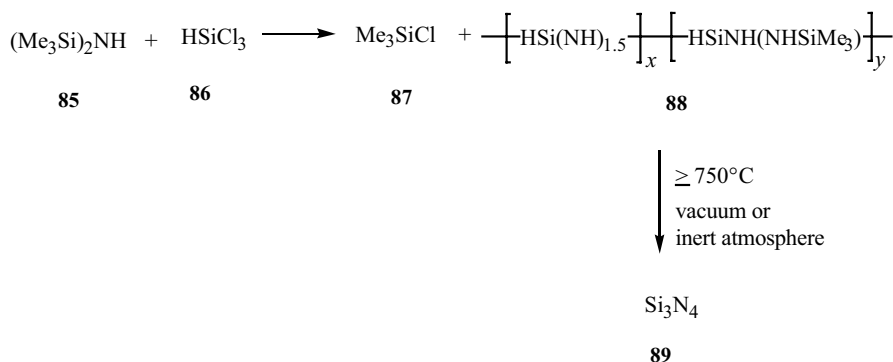
Scheme 24

Si$_3$N$_4$ ceramics were also prepared from (R$_3$Si)$_2$NH, where R=vinyl, Ph, or alkyl, by first treating the polymer with a reactive metal halide; [e.g., MX$_n$ (M=Si, B, P; X=Cl, Br)]. For example, if the prepolymer from (Me$_3$Si)$_2$NH was treated with SiCl$_4$ and subsequently pyrolyzed at 1600°C under N$_2$, the resulting ceramic material contained mainly low carbon (<4%) Si$_3$N$_4$. Catalyzed dehydrocoupling of amines (or diamines) with organosilanes was first reported by Fink[162] and Andrianov et al.[163] The reaction was later explored by Seyferth et al. for the catalytic synthesis of oligosilazanes.[142,164] Laine et al. then showed that the dehydrocoupling of a *bis*-silazane (**90**) is a facile method for obtaining a variety of preceramic oligomeric silazanes (**92**) (Scheme 25).[165] His group studied the reaction mechanism and concluded that the rate law had a complex dependence on catalyst and amine concentration. Moreover, the products that were formed depended on reaction conditions. Thus, they were able to optimize the reaction to produce a tractable, processable species (e.g., R=H, R′=Me) of modest molecular weight ($M_n \sim 1600$) that could be transformed at elevated temperatures into gels and then into ceramic coating, fibers, and molded composites (ceramic yield $\sim$ 70%).
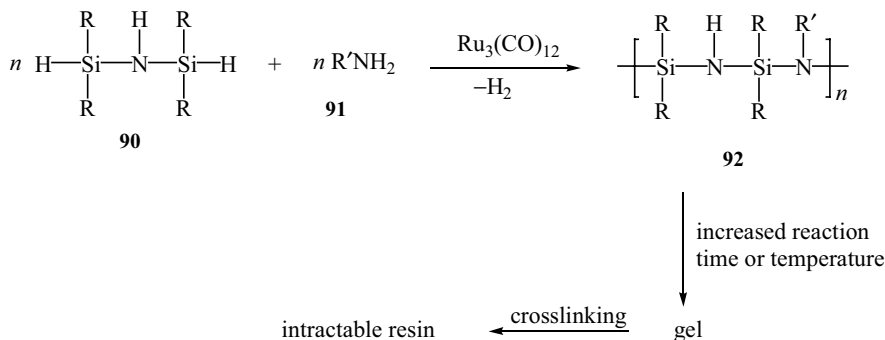
Scheme 25

D. Polysiloxanes

A comprehensive review of polysiloxanes is beyond the scope of this review of organometallic polymers. The reader should, nevertheless, be aware of the many more recently published reviews.[166–176] We will (1) review briefly the development of polysiloxanes as the most commercially important class of commodity organometallic polymer, (2) summarize the general methods of synthesis, and (3) briefly discuss the properties of these materials that translate into versatile, industrial, and consumer applications.

It is well known that the useful properties of siloxanes stem from the nature of the siloxane bond (**93**), the structural characteristics of the polymer, the synthetic control over molecular weight and polydispersity, and the character of the framing groups (R). Polysiloxanes are presently available commercially as linear chains (**93**), rings, ladders, and three-dimensional networks (e.g., polyhedral oligomeric

silsesquioxanes) that contain siloxane bonds in the polymer framework. The tetravalency of silicon is generally completed with hydrogen, organic or organometallic moieties, or silyl groups, although other substituents on silicon have been included. The low rotational barriers about the Si−O bonds give low T_g (glass transition) values and high chain flexibility.

93
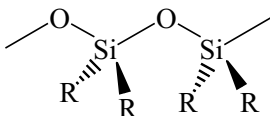
Historically, the most important and extensively studied class of polysiloxanes is polydimethylsiloxanes (PDMS), which are linear chains composed of difunctional siloxyl units. Although PDMS was first reported, but not recognized as such, in the late 1800s by Ladenburg,[177,178] it wasn't until the early 1900s that Kipping[179,180] established that silanediols condense intermolecularly to a new class of species, which were named "silicones" owing to the initial belief that they were silicon analogs to ketones. There was great interest in these compounds as intellectual curiosities as well as for their unusual physical properties, thermal stability, and chemical inertness. However, polysiloxanes did not become commercially practical until the 1940s, when Rochow discovered a direct and efficient method, the "direct process," of preparing the monomer precursor, dimethyldichlorosilane (**96**, $n=2$), from inexpensive silica (**94**) and methyl chloride (Scheme 26).[181] The process could be optimized to maximize the yield of dimethyldichlorosilane and thus provide a ready and inexpensive source of the monomer.

Scheme 26
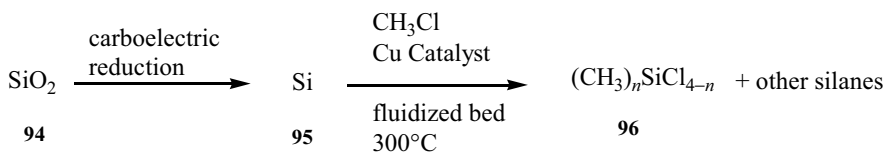
The period between the discovery of the direct process and the mid-1960s was a renaissance for the development of commercial methods for the synthesis of PDMS and related materials.[182–186] The preparative approach that was used was the controlled hydrolysis of $(CH_3)_2SiCl_2$ (Scheme 27). The isolated products of this reaction are a mixture of small cyclic dimethylsiloxanes, mainly the cyclic trimer and tetramer (**99**), in addition to linear hydroxyl end-functional oligomers (**100**). The formation of rings and linear species occurs presumably through hydrolytic polycondensation of the silanediol intermediate (**98**). The linear compounds that are prepared by this method are relatively short-chain oligomers. However, higher molecular weight

polymers can be obtained from **100** by removing water from the reaction mixture and/or by catalytic polycondensation. Importantly, **100** can undergo thermal or catalytic redistribution– depolymerization to increase the yield of cyclic materials, which in a separate reaction, can be polymerized by ring-opening polymerization (ROP) methods. Industrially, chain–ring interconversion reactions have been sufficiently refined so that there currently exists excellent control over the linear or cyclic species that are obtained.[187] Which species prevails depends on the kinetics of the competition between intra- or intermolecular condensation. Thus, the concentration of the intermediates can be used to direct the reaction in water or other protonic solvents.
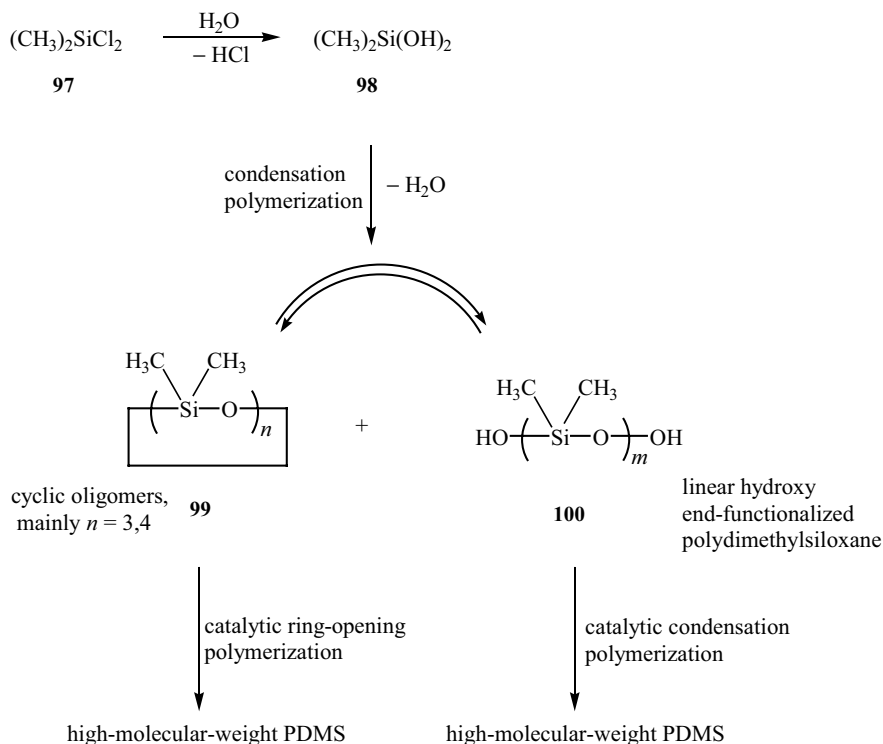
Scheme 27

The kinetics and mechanism of oligosilanol polycondensation are further complicated by redistribution–disproportionation, and depend on the monomers, catalyst (e.g., acids, bases, metal salts, chlorinated PN oligomers), solvent, whether catalysis is homogeneous or heterogeneous, the length of the reacting chains, the concentration of reacting oligomers, and the presence of surfactants.[188] For example, Chojnowski et al. have shown that cyclic products are preferred in dilute solutions.[189] On the other hand, if polycondensation is carried out in an aqueous emulsion containing a

sulfonic acid surfactant, linear polymers with molecular weights as high as 1×10^6 can be obtained.[190]

Catalytic ring-opening polymerization (CROP) is the synthetic method of choice to obtain high molecular weight linear polysiloxanes. Control of polydispersity, framing group functionality, degree of crosslinking, and other important characteristics lead to commercially useful products. Much of the published work on CROP involves studies of the cyclic trimer and tetramer (**99**, $n=3,4$).[191,192] They are usually used as a mixture in the commercial preparation of siloxane polymers.

Regardless of initiator or monomer used, the CROP reaction may be carried out to equilibrium (thermodynamic control) if a high yield of polymer is sought. Both rings and linear materials are formed. The process is almost enthalphically neutral and thus independent of temperature. The driving force of the reaction, therefore, is attributed to the large increase in entropy that results from the higher degree of conformational flexibility of the open-chain polysiloxanes relative to the rings.[193] Furthermore, the presence bulky or polar substituents on the cyclic monomer decreases the entropy change on ring scission and leads to lower yields of linear polymers. For example, when taken to equilibrium, the CROP of $[(CH_3)_2SiO]_3$ gives ~82% by weight of linear polymers (i.e., ~12% cyclics) whereas $[(CF_3CH_2CH_2)(CH_3)SiO]_3$ gives only 18% linears (82% cyclics, mainly of $n=3$–6). $[Ph_2SiO]_3$ gives essentially no linear materials.[194]

The molecular weight of the linear polymers can be controlled to some extent in equilibration polymerization in two ways: (1) by adjusting the quantity of initiator used in the reaction and (2) by adding an end-blocking agent such as *hexa*-methyldisiloxane, which places nonreacting trimethylsilyl groups at the chain terminals. In addition to the pervasive presence of cyclics in the products, other drawbacks to equilibration polymerization are the large polydispersity of the polymer (≥ 2) and the lack of chain microstructure control when the monomer contains several different framing groups. In order to minimize the ring closure reaction and an equilibrium distribution of products, the polymerization reaction can be prematurely quenched by deactivating the catalytically active terminus.[188]

Kinetic control and early quenching of the ring-opening reaction avoid many of the problems associated with the equilibrium polymerization process, where (1) advantage is taken by the relatively high reactivity of strained cyclic oligomers, (2) the rate of chain extension exceeds the rate of ring closure and depropagation, and (3) redistribution is kept to a minimum, thereby reducing the polydispersity of the final product. Kinetic control is achieved with anionic or cationic catalysts. For example, anionic CROP may be represented, in its simplest form, by the following initiation and aggregation steps (Scheme 28). In this reaction, catalyst **102** is an alkaline metal or other positively charged inorganic or organometallic ion and X^- is a basic anion (OH^-, silanolate ion, etc.).[195] The reaction may be accelerated by the addition of a strong nucleophile.
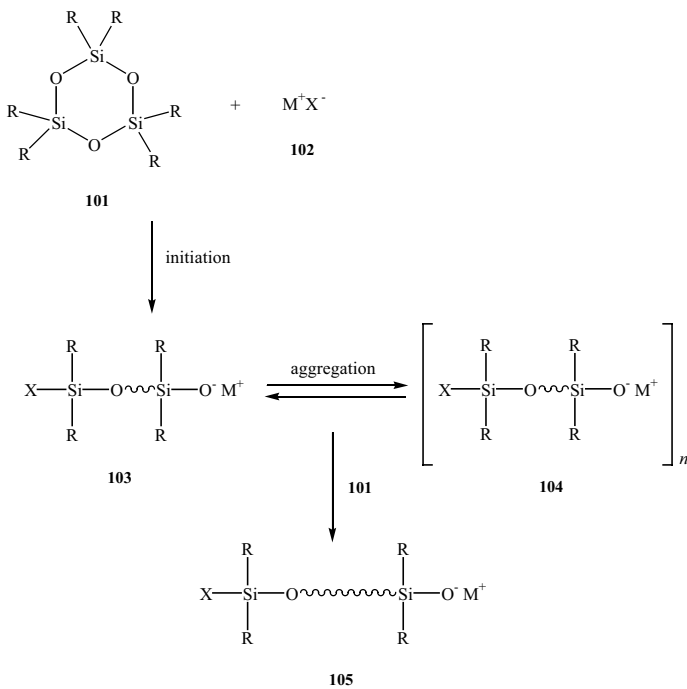
Scheme 28

Kinetic investigations of model reactions indicate that the propagation process is quite complex and involves ion–oligomer (**103**) and intermolecular oligomer–oligomer (**104a**) and/or associative–intramolecular (**104b**) aggregate interactions.[191,196,197] In addition, the presence of even small quantities of protonic solvents such as water or alcohols leads to polymers with broad and bimodal molecular weight distributions.[198]
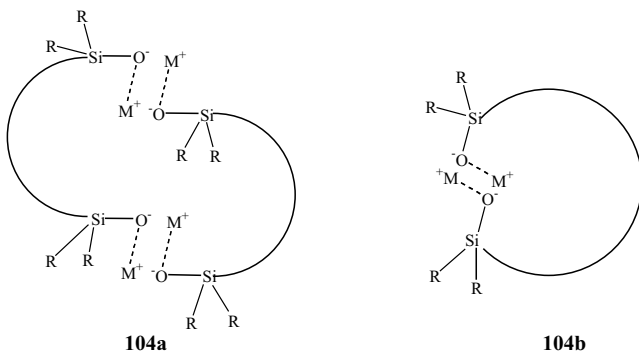
It is widely recognized that the properties of random, alternating, and block polysiloxane copolymers differ. These properties depend on the sequencing of the substituents on silicon; i.e., regularity of the polymer microstructure. As a result,

there has been substantial interest in understanding those factors that control stereo- and regioselectivity in the ROP of cyclic oligomers. To date (2003), it has been extremely difficult to isolate highly stereoregular (e.g., isotactic) polysiloxanes even if stereospecific monomers are used.[199] For example, Mazurek et al. found that equilibration polymerization of 1,1-diphenyl-3,3,5,5-*tetra*-methycyclotrisiloxane (**106**) gives the same random distribution of siloxyl units as does the copolymerization of equivalent amounts of the perphenylated and permethylated cyclic tetramers.[200] Some regiospecificity is obtained by quenching a cationic-ROP of oligomer **106** using triflic acid as a catalyst. The product in this case is mainly a symmetric arrangement of triad units ($\sim$68% $-$O$-$SiMe$_2$$-O-$SiPh$_2$$-O-$SiMe$_2$$-$) that result mainly from ring opening at the oxygen, which bridges the Me$_2$Si groups (**106**, *a)*. The reaction leads to a lesser quantity of the unsymmetrical triad units ($\sim$32%$-$O$-$SiMe$_2$$-O-$SiMe$_2$$-O-$SiPh$_2$$\sim$), which result from unsymmetric scissions (**106**, *b*).[201]

106
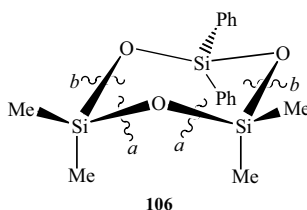
Weber and Cai, on the other hand, have reported that anionic ROP of a cyclic trimer containing a divinylsilyl moiety (**107**, Scheme 29) proceeds through the intermediate **109** using dilithiodiphenylsilanediolate as a catalyst. This gives the regiospecific polysiloxane (**111**).[202] However, if a cationic catalyst such as triflic acid is used, monomer **107** undergoes a chemoselective ROP to give a complex mixture of dimethylsiloxane-divinylsiloxane copolymers with four divinyl-centered and seven dimethylsiloxyl-centered pentads.
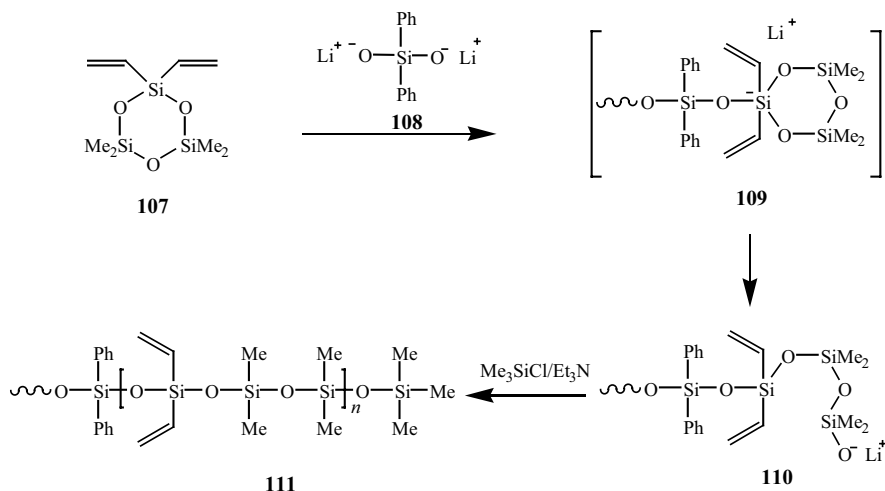
Scheme 29

There has been considerable attention to developing materials that take advantage of the unique properties of the siloxane chain (e.g., low glass transition temperature, low surface energy, high gas permeability, high thermal and oxidative stability, high resistance to electromagnetic radiation, and chemical inertness) and to coupling these features with the properties of organic polymers.[203–206] The ability to include a wide variety of reactive substituents either along the chain or at the termini of a polysiloxane provides a convenient synthetic route to hybrid polymers. In this manner, an array of block, graft, and network organic siloxane copolymers has been prepared. For example, Chaumont et al. have shown that hydrosilylation of a difunctional α,ω-divinyl-terminated organic polymers (**112**) with a difunctional α,ω-SiH-terminated oligo- or polysiloxane (**113**) produces block copolymers with hydrolytically stable Si−C linkages between the siloxane and the organic units (**114**, Scheme 30).[207] The same type of reaction can give graft copolymers if Si−H functional groups are along the polysiloxane chain.[203]

Scheme 30

A series of hybrid organic PDMS block copolymers linked by a Si−Y−C bridge (Y=O, N, etc.) have also been prepared.[208–212] One of earliest reports in this area was by Vaughn,[213] who synthesized copolymers of bisphenol A polycarbonate and PDMS by polymer–monomer polycondensation of chlorine-terminated PDMS (**115**) with excess bisphenol A (**116**) and phosgene (Scheme 31). The composition of the product (**117**) depends on the relative quantities of reagents used in the synthesis. The microstructure and morphology of these random alternating copolymers were later elucidated by Lind.[214] Similar methods have been used to prepare polyester-PDMS,[215] polyamide-PDMS,[216] polyurea-PDMS,[208,217] polyisoprene-PDMS,[218] and polyurethane-PDMS copolymers.[219] Extension of this method involving polymer–polymer polycondensation was used to obtain other regularly alternating PDMS-organic (e.g., polyethylene,[220] polystyrene,[221] polyketone,[222] and polysulfone[223]) hybrids.

Scheme 31

An interesting approach to the synthesis of "perfect" hybrid organic PDMS multiblock copolymers was reported by Nair and Clouet.[224] The combined thermal initiator-chain transfer-chain terminator (*iniferter*) properties of alkylthiuram disulfides were applied to initiate the polymerization.[225] PDMS copolymers (**121**) with methylmethacrylate, styrene, and acrylamide were made using this strategy (Scheme 32). PDMS segments with molecular weight from 400 and 3000 were used. The average number of A-B copolymer blocks ranged from 2 to 11 and the molecular weight of the vinyl block was as high as 10^5.
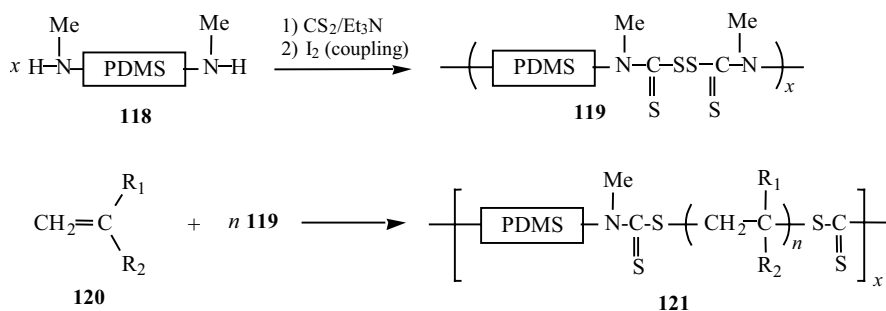
Scheme 32

Side-group modification of polysiloxanes was used to obtain copolymers with organic grafts (**124**, **127**, **130**, **132**). Thus, polysiloxanes containing Si−X and Si−C−X groups, where −X is a reactive group on silicon (e.g., X=H, C=C, OH, SH, OR, CN, NH_2), and −C−X has an organic functional substituent, have been prepared. Several examples of graft polymer formation are given in Scheme 33. These include catalytic hydrolsilylation,[226] hydrophosphination,[227,228] and thiol-ene addition.[229]

Polycondensation reactions have also led to some interesting and unusual liquid crystalline and conducting polysiloxanes. For example, one-dimensional disk-shaped (shish-kebab) polysiloxanes (**133**) with a degree of polymerization of ~15 have been prepared by polycondensation of dihydroxysilicon phthalocyanines.[230,231] The product is uniformly hydrophobic, rotationally symmetric, and highly ordered, and has multilayered chains. These materials also have favorable dynamic and mechanical properties that are comparable to polyamides such as Kevlar. Furthermore, if doped with iodine, the materials have useful magnetic, electric, and optical properties.

E. Polysilsesquioxanes

In 1946, Scott reported the first the example of oligomeric organosilsesquioxanes $[CH_3SiO_{1.5}]_n$.[232] This compound was isolated from the thermal rearrangement of the cohydrolysis product of dimethyldichlorosilane and methyltrichlorosilane. Reviews by Pittman et al. and Baney et al. showed the increasing interest in the chemistry of silsesquioxanes since the early 1950s.[233,234] Polyhedral oligomeric silsesquioxanes (POSS) are inorganic–organic hybrid materials with an inner inorganic framework of silicone and oxygen. The organic substituents on the outer surface of POSS permit the incorporation of these compounds into polymeric materials.

Polyhedral oligomeric silsesquioxanes have been divided into categories according to their architectural makeup. These include ladder (**134**) random (**135**), partial cage (**136**) and cage (**137–139**) structures. The cage structures **137–139** have T_8, T_{10}, and T_{12} geometries, respectively.
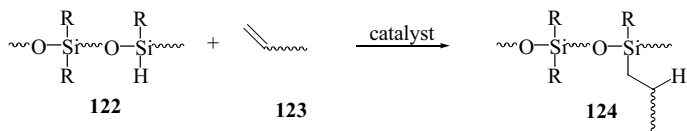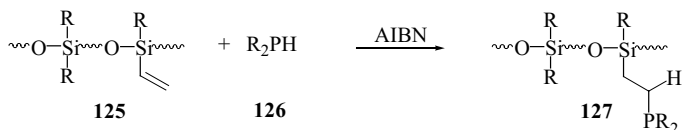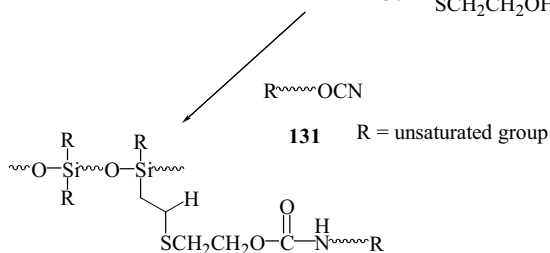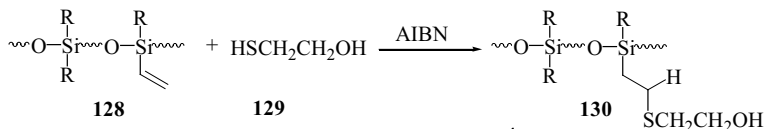
Scheme 33

133
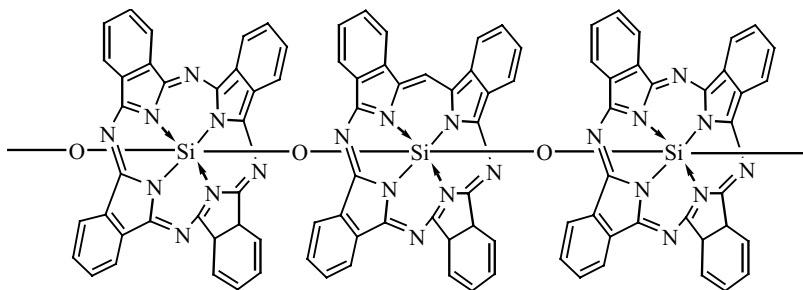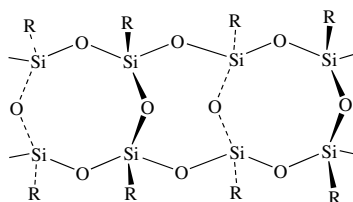
ladder
134
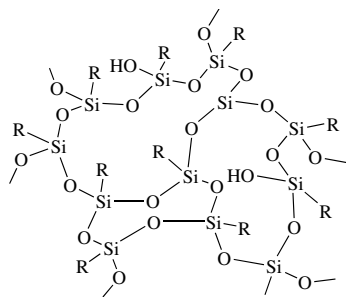
random
135
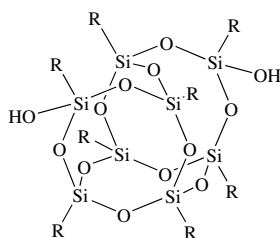
partial cage
136
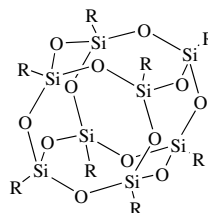
T$_8$
137
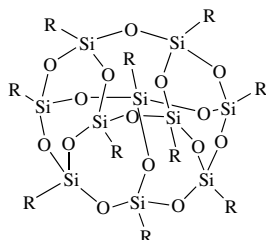
T$_{10}$
138
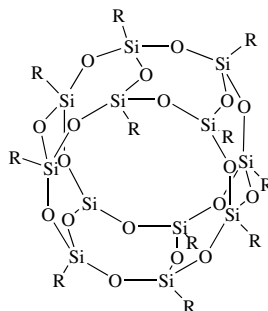
T$_{12}$
139

The synthesis and polymerization of a styryl-substituted POSS, R$_7$(Si$_8$O$_{12}$) (CH$_2$CH$_2$C$_6$H$_4$CH=CH$_2$) (**142**) (Scheme 34), was accomplished by Haddad and Lichtenhan.[235] Reaction of trisilanols (**140**) with a 3:1 mixture of the *para* and *meta* isomers of (styrylethyl)trichlrosilane (**141**) resulted in the isolation of **142**. Homo-polymerization of **142** initiated by AIBN led to the formation of the styryl-POSS polymer (**143**). The copolymerization of **142** with 4-methylstyrene generated copolymer (**144**). The polymers with cyclohexyl substituents on the POSS cage exhibited much higher solubility than the cyclopentyl derivatives.[235] Using a similar strategy, norbornenes with pendent POSS groups were also synthesized and poly-merized using ring-opening metathesis polymerization.[236]
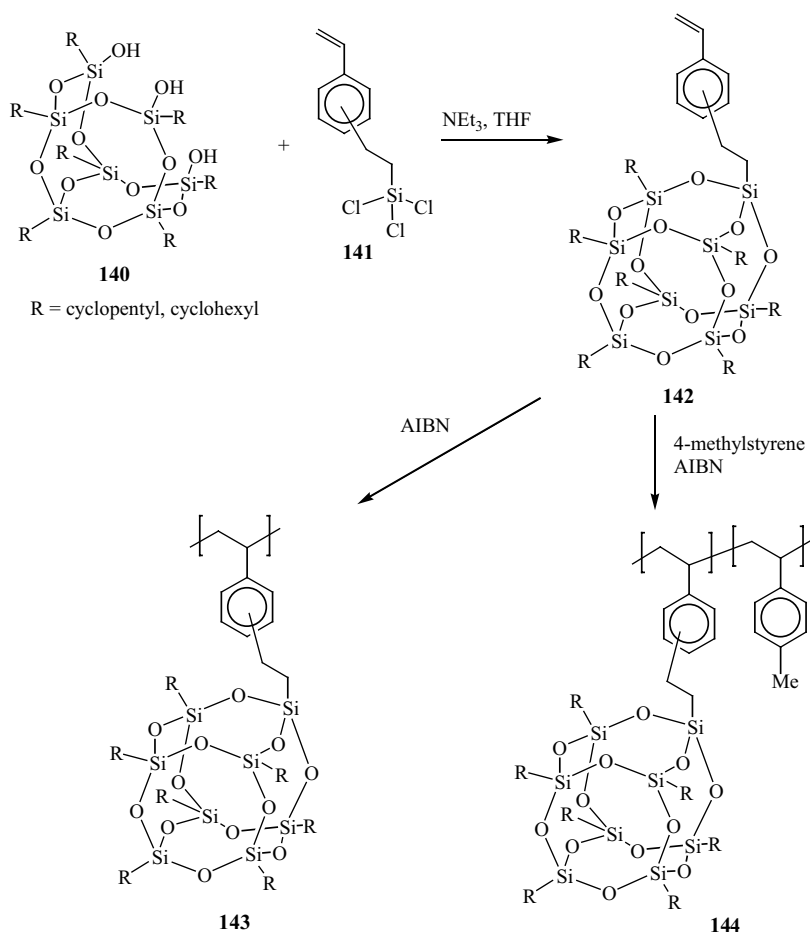
Scheme 34

Pittman and coworkers have reported the synthesis of epoxy copolymerized composites incorporating either a multifunctional polyhedral oligomeric silsesquioxane (**145**) or polyphenylsilsesquioxane (**146**) in their structures through thermal curing reactions.[237] The incorporation of these silsesquioxane units into the epoxy resin increased its flexular modulus; however, their flexular strengths are lower than that of the neat epoxy. The units of monomer **145** appeared to be molecularly dispersed throughout the epoxy matrix when observed by TEM at a magnification of 8×10^5. Pittman's group also copolymerized commercial vinyl esters with **145** using a MEP peroxide/cobalt salt catalyst system.[238] Some of monomer **145** was molecularly dispersed and silicon-rich domains as large as 80 nm were also present as a result of phase separation. These phase-separated regions were polymerized and could not be extracted or dissolved. A number of other crosslinked polymers have been isolated from the reaction of multifunctional epoxy and methacrylate POSS monomers.[239–242]
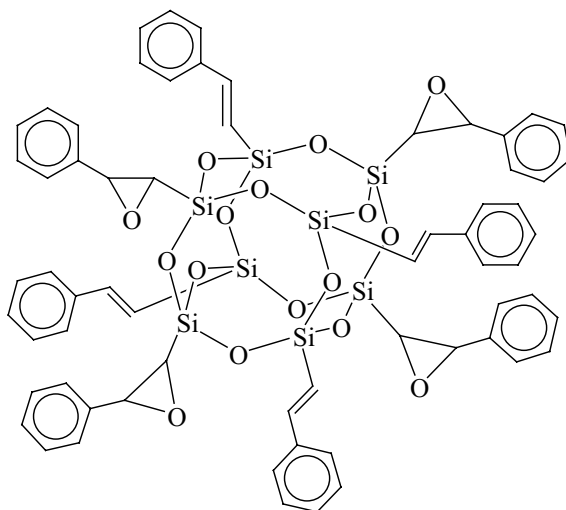
145
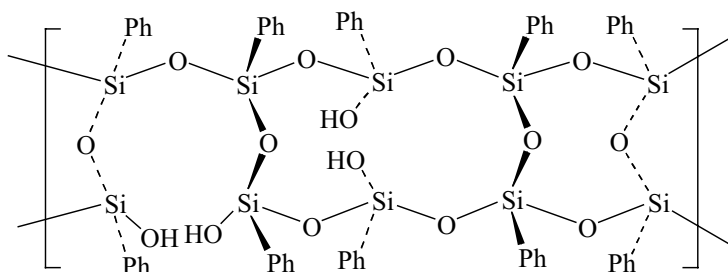
146

Laine and coworkers have reported the hydrosilation copolymerization of octahydridooctasilsesquioxane (**147**) with the octavinylsilsesquioxane (**148**) (Scheme 35) using platinum divinyl-*tetra*-methyldisiloxane as the catalyst.[243] The resulting polymer (**149**) formed a gel within 9 h and had a degree of condensation of 43%. Lengthening the spacers between the cubes resulted in a greater degree of reaction, and gelation occurred more rapidly.

The synthesis of polyhedral oligomeric silsesquioxane-siloxane copolymers has been achieved by Lichtenhan and coworkers.[244,245] Reaction of the hydroxyl groups on monomer **150** with *bis*-dimethylaminosilanes and siloxanes (**151**) resulted in the formation of polymers such as **152** using the methodology described in Scheme 36.[244] This polymer had a glass transition at 23°C and a melting transition at 114°C. On the basis of GPC measurements, this polymer had a degree of polymerization of 21.

147

148

Pt(dvs)
toluene

149
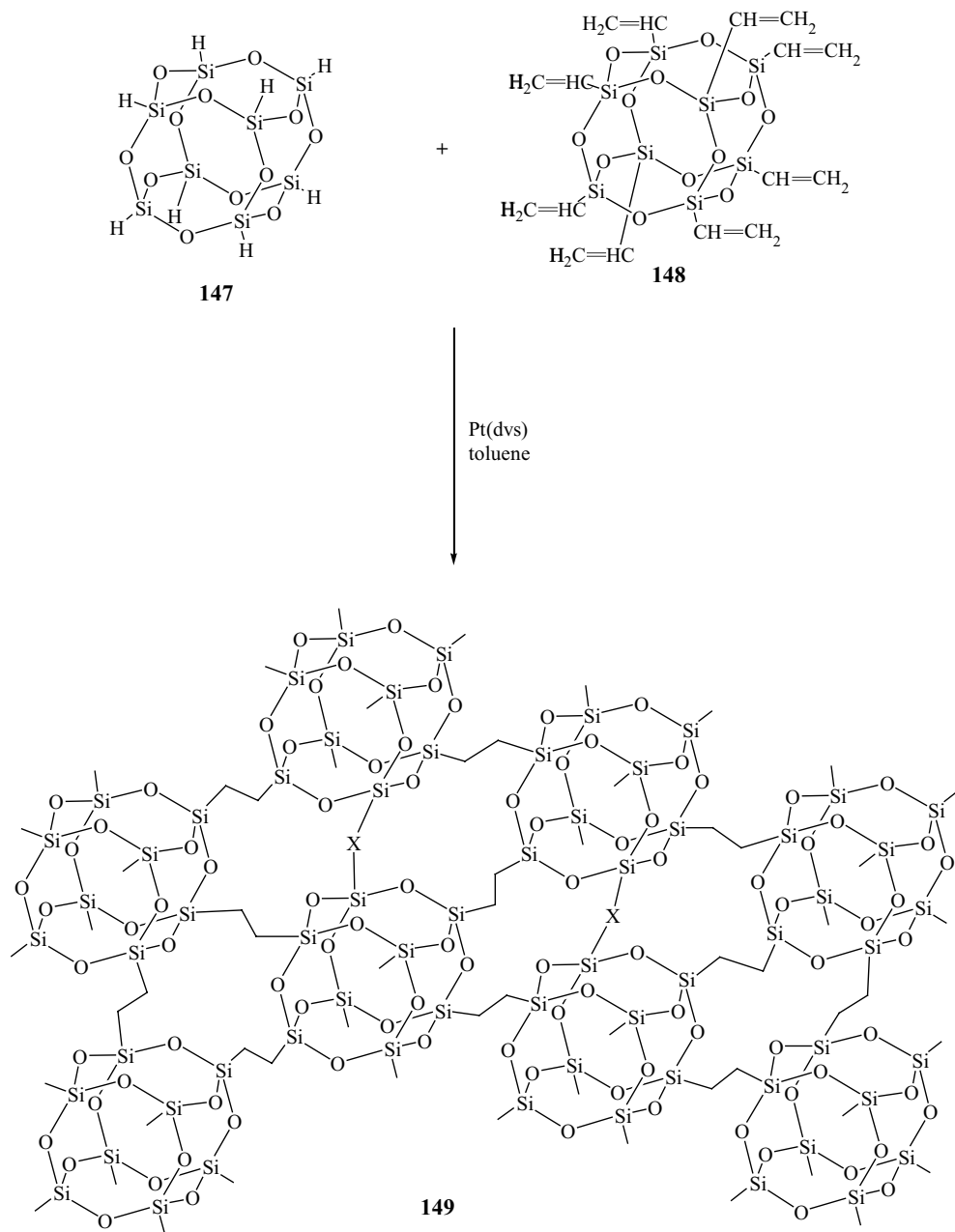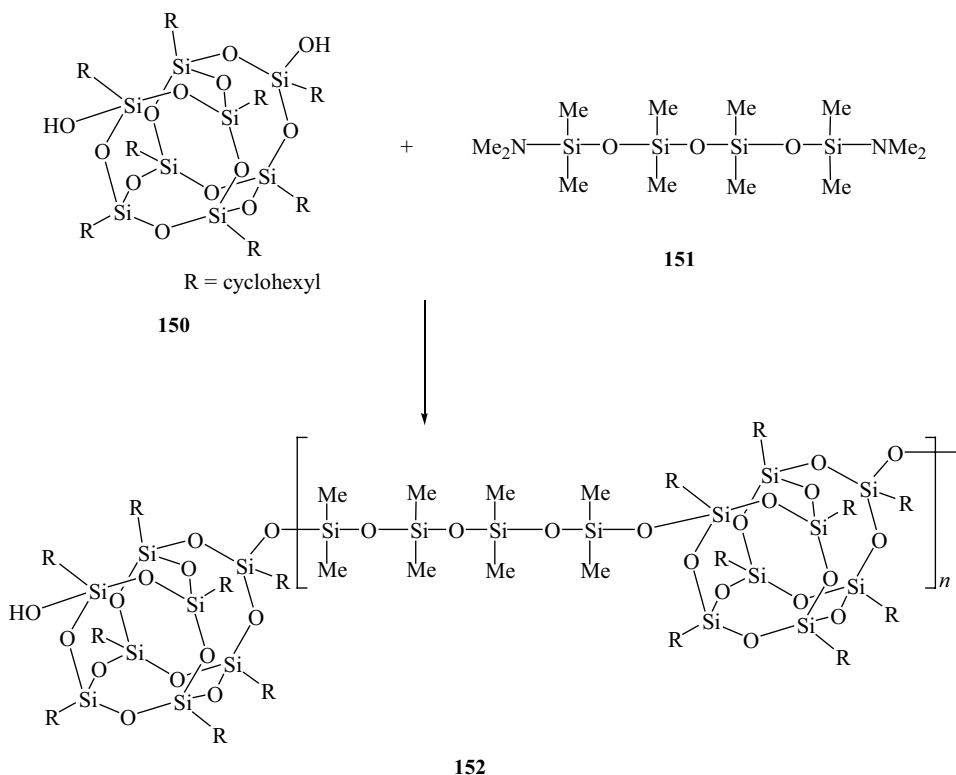
Scheme 35

Scheme 36

III. GERMANIUM

The successful preparation of high molecular weight polysilanes suggested that catenated germanium analogs might also be accessible. Like silicon, germanium derivatives form cyclic and acyclic catenates. Soluble, high MW, substituted germanium homopolymers (**154**) and silicon-germanium copolymers (**156**) have been made by the Wurtz-type reaction of dichlorogermanium precursors (**153**) with sodium dispersions (Scheme 37).[246,247] As frequently found in polysilane synthesis, polygermanes (**154**) seem to exhibit binodal molecular weight distributions. The charge transfer spectra of the TCNE adducts of permethylated polygermane have been described by Mochida and coworkers.[248] The spectra of the charge transfer complexes were red-shifted with increasing polymer chain length. The polygermanes inserted into TCNE to produce 1–1 adducts at 50°C.
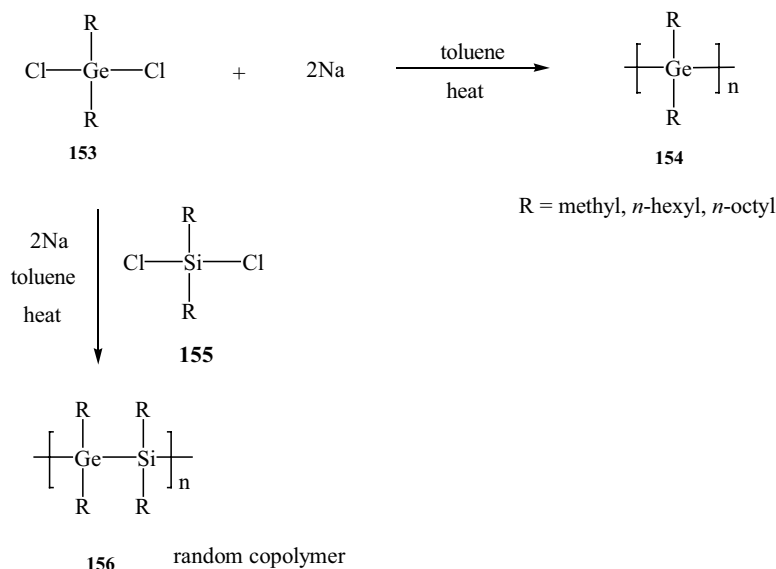
Scheme 37

Highly branched polygermanes have also been isolated in high yields by the demethanative coupling of $HGeMe_3$ using a catalytic amount of $Ru(PMe_3)_4(GeMe_3)_2$ (Scheme 38).[249] The molecular weights of the polymers prepared using this methodology were on the order of 10^4 to 10^5. High molecular weight polygermanes have also been prepared by reaction of a germanium dichloride complex of 1,4-dioxane (**157**) with alkyl lithium compounds.[250,251] This methodology gave better yields than did the traditional Wurtz-type coupling reactions typically used to prepare polygermanes. The polymers (**159**) displayed high UV absorption as a result of the conjugation within the polymer backbone and were photosensitive.[251]
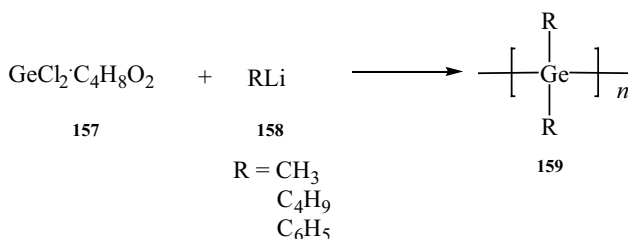
Scheme 38

Since the early 1990s, there has been an increased interest in the design of new polymeric materials containing germanium. A monomeric system developed by Sakurai and coworkers permitted the formation of a silane-germole copolymer, in which the silane portion of the polymer is electron-donating.[252] As shown in Scheme 39,

monomer **161** reacted with a catalytic amount of butyllithium to undergo a highly regioselective anionic polymerization to give polymer **162**. This polymer had a M_n of 11,000 and a polydispersity index of 1.8.
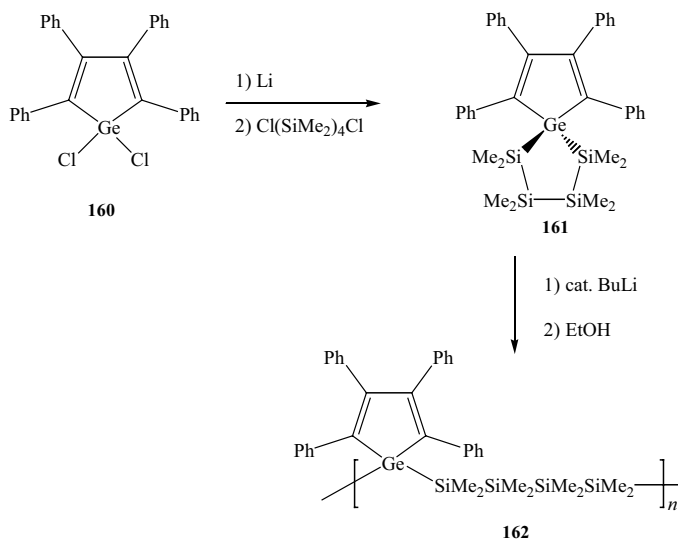
Scheme 39

Tilley and coworkers have also described the incorporation of a germole ring into polymers to investigate the novel charge-transporting properties that these materials may display.[253] These conjugated polymers were prepared by Ni-catalyzed coupling reactions of chloro- and bromo-substituted monomers (**165**). The M_n of polymer **166** was 20,000 with a polydispersity of ~2.9 when the bromo-substituted monomer was polymerized (Scheme 40). The optical properties of the polymers were examined. The λ_{max} values for the absorption and emission of polymer **166** were 442 and 500 nm, respectively, and were red-shifted relative to monomer **165**, which showed λ_{max} values at 376 and 464 nm, respectively. In comparison to other conjugated polymers such as poly(*p*-phenylene), the germole-containing polymers had a greater degree of delocalization. The higher level of conjugation may be a result of the low-lying LUMO (lowest unoccupied molecular orbital) of the germole ring. Higher-molecular-weight polymers possessed higher quantum yields. For example, a polymer with M_n=4700 had a quantum yield of 0.52, while a polymer with M_n=20,000 had a quantum yield of 0.79. The cyclic voltammogram (CV) of the monomer showed an irreversible reduction at -3.02 V versus Fc/Fc$^+$, while the CV of the polymer showed a quasi-reversible reduction at -2.66 V. The difference between monomer and polymer redox potentials and their reversibility is consistent with the expected drop in the HOMO–LUMO (highest occupied–lowest unoccupied molecular orbital) gap accompanying an increase in conjugation on polymer formation. Both the monomers and polymers oxidized at approximately 0.6 V.[253]
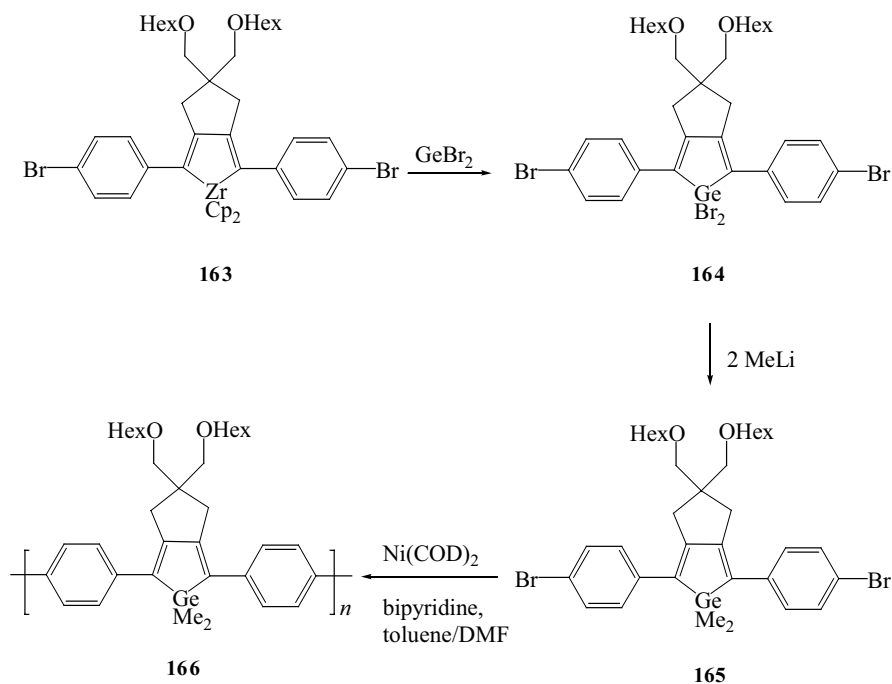
Scheme 40

Wagener and Gomez reported the synthesis of organogermanium polymers, such as **171** (Scheme 41) via acyclic diene metathesis polymerization (ADMET).[254] These ADMET polymerizations were catalyzed using Grubbs' or Schrock's catalysts to give 71–84% *trans*-polymers as determined by ^{13}C NMR. The M_n values were in the range of 5000–18,000, with polydispersities ranging from 1.4 to 1.8. These polymers were 100% amorphous with T_g values ranging from -89 to $-98°C$.
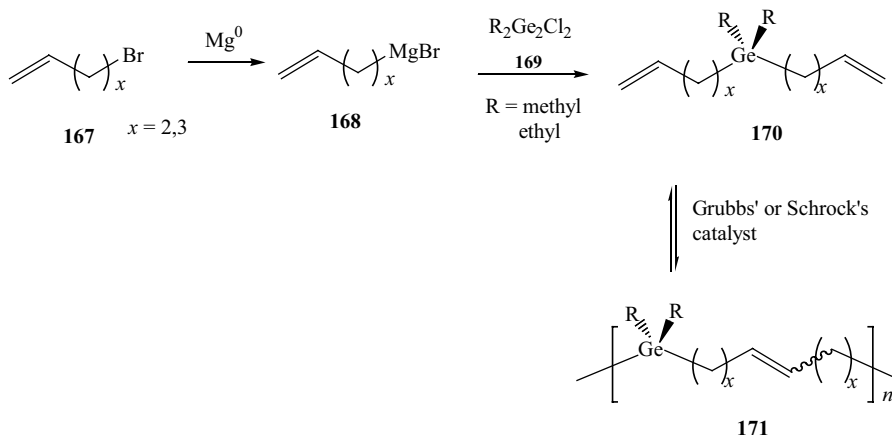
Scheme 41

The synthesis of polyesters and polyamides containing germane units in the polymer backbone were reported Tagle and coworkers.[255,256] Scheme 42 shows the phase-transfer-catalyzed polymerization of phosgene (**172**) with **173** to produce the germanium-containing polycarbonate (**174**). Although the polymer yields were not high, the inherent viscosities of the solutions increased somewhat. The authors attempted the reaction in the absence of catalyst and found that no reaction occurred.
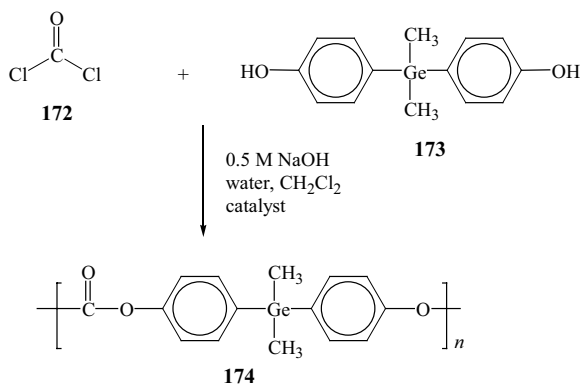
Scheme 42

Organogermanium polymers were prepared by Kobayashi and coworkers via the reaction of a germylene (**175**) with acetylene monomers (**176**) in the presence of a rhodium catalyst (Scheme 43).[257] Copolymer **177** incorporated a larger ratio of polyacetylene units than germanium units in the backbone.
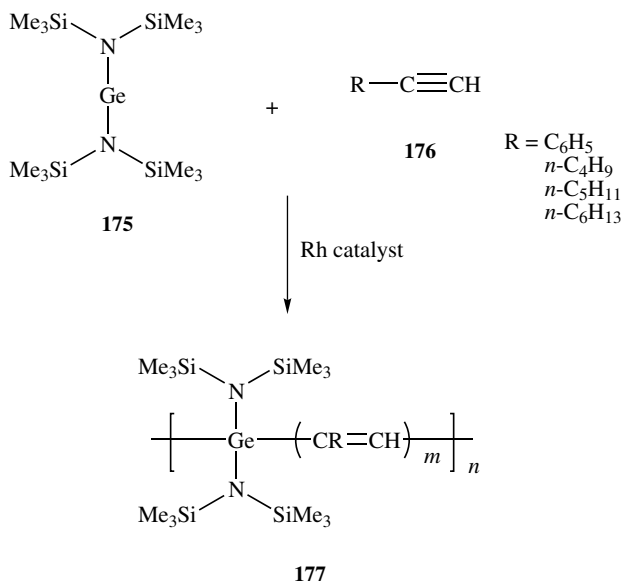
Scheme 43

Kobayashi's group also conducted the oxidation–reduction polymerization (Scheme 44), where the germylene (**178**) acts as a reductant and the *p*-benzoquinone (**179**) as an oxidant.[258,259] This polymerization occurs at −78°C to give high MW polymers ($>10^6$) within 1 h. These copolymers (**180**) were stable at room temperature and were resistant to moisture and air. The mechanism of this reaction was studied by ESR spectroscopy. It was found that the reaction proceeded via a biradical mechanism involving a germyl and a semiquinone radical.[259]

Ge[N(SiMe₃)₂]₂ has been described...

178   **179**   R = H, Ph, ^{t}Bu   **180**
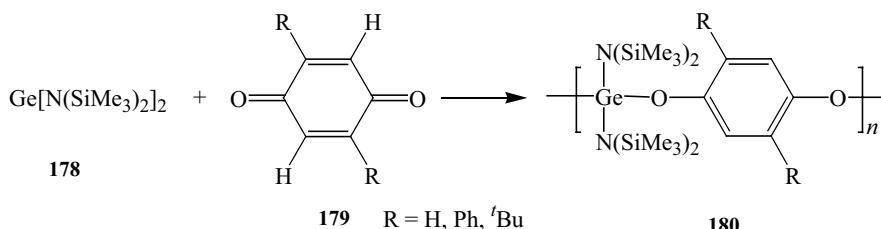
Scheme 44

Both 5- and 6-membered cyclic germylenes (e.g., **181**) have also been reacted with *p*-benzoquinones (**182**) in a 2:1 ratio to give the organogermanium polymers with metal-metal bonds in their backbones (**183**) (Scheme 45).[250,260] The MWs of these materials were approximately 10^5, with polymer yields around 90%. The polymers had lower thermal stabilities than did their linear analogs because of the instability of the Ge−Ge bonds. The decomposition temperatures were around 150°C, while the melting temperatures of the polymers with acyclic germylenes were about 235°C.[260]

181   **182**   **183**
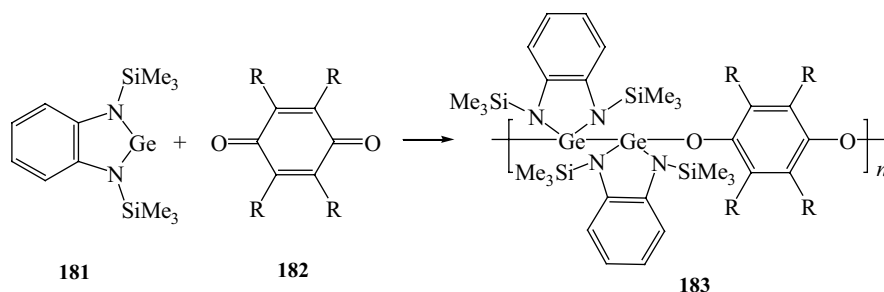
Scheme 45

Poly(germanium enolate) (**186**) has been synthesized as shown in Scheme 46.[250,261] In order to form a polymeric material, α,β-unsaturated carbonyl compound was required to react with a germylene in the presence of a lithium catalyst such as LiCl or LiR. It was believed that initial formation of a germyl anion species was achieved by coordination of the Li catalyst to the germylene compound.

Nucleophilic attack of the germyl anion toward the β carbon of the cyclic ketone formed a lithium enolate that coordinated to the germylene regenerating a germyl anion. The organogermanium polymer was stable in aqueous solution and had a $M_w > 10^5$, $T_g=40°C$, and $T_m=221°C$.
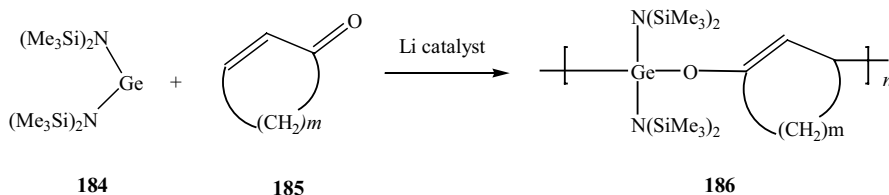
Scheme 46

Poly(germyl ether)s (**189**) were synthesized by Nishikubo and coworkers by reaction of dimethyldiphenoxygermane (**187**) with *bis*-epoxides (**188**) (Scheme 47).[262] The reactions were carried out with *tetra*-butylphosphonium chloride as the catalyst to give the organogermanium polymers in good yields and moderate molecular weights. The analogous poly(silyl ether)s had much higher molecular weights and were not as sensitive to water and wet solvents. Germanium polyesters were also reported by Carraher and Dammeier in 1971.[263]
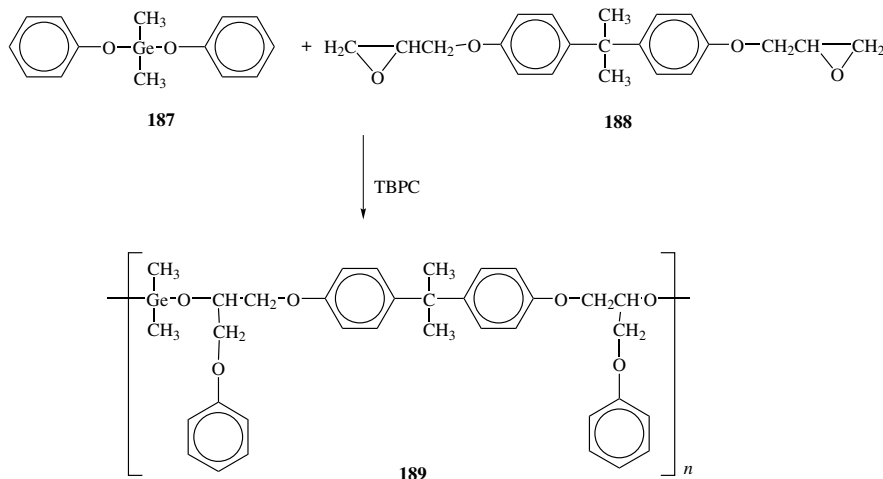
Scheme 47

Reaction of $CaGe_2$ with HCl led to the formation of crystalline, layered polygermyne $(GeH)_n$ (Scheme 48).[264] The crystallinity of the polygermyne could be increased by lowering the reaction temperature. The crystalline polygermyne (**191**) prepared in this study was reddish in color and displayed intense photoluminescence

at 920 nm. The polymer also displayed semiconducting properties with an activation energy of ~460 nm (i.e., half of the energy of the photoluminescence maximum).[264] Amorphous polygermynes $(GeR)_n$ formed by Wurtz coupling of organotrichlorogermanes are light brown and display weak photoluminescence at 560 nm.[265] Branched oligogermanes with alkyl or aryl substituents have also found applications in micropatterning as a result of their UV light sensitivity.[266]

$$n\ CaGe_2\ +\ 2n\ HCl\ \longrightarrow\ (GeH)_{2n}\ +\ n\ CaCl_2$$

190   **191**

<div align="center">
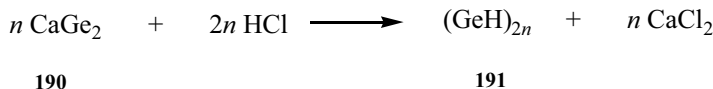
Scheme 48

</div>

IV. TIN

In 1849, Sir Edward Frankland reported the first example of an organotin compound.[267] It was over 100 years later that Adrova et al. reported the synthesis of polyolefins with tin ester side chains (**192**).[268] Crosslinked polymers incorporating organotin moieties in the structures (**193**) were also synthesized by Leebrick.[269]

192   **193**
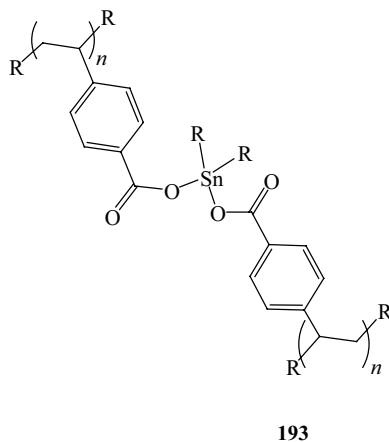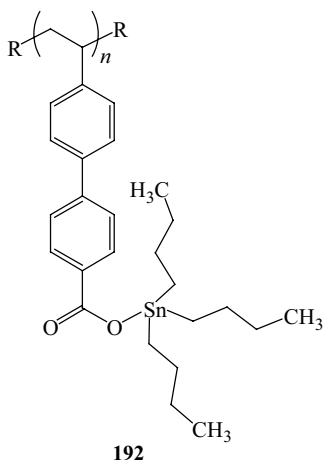
Developments in this field then became rapid due to those polymers' bioactivity, and in the 1960s organotin polymers were reviewed.[270–272] Adrova et al. also described the incorporation of organotin moieties into the backbones of polymers using the strategy shown in Scheme 49.[273] The reaction of monomer **194** with organotin hydrides such as **195** led to the isolation of polymer **196**. This polymer had a degree of polymerization of approximately 25.
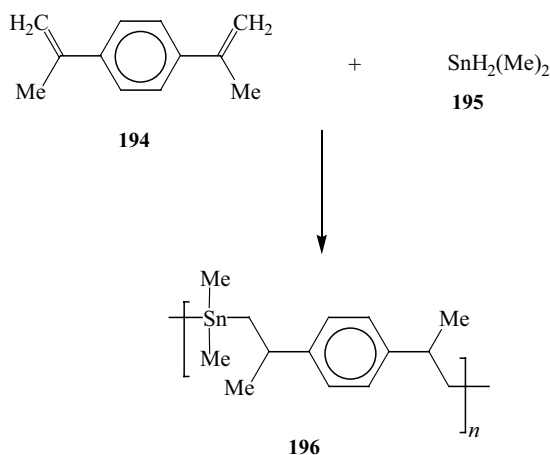
Scheme 49

Polymers with organotin side chains are also important because of their applications in lithography. Trimethylstannyl groups are sensitive to electron-beam radiation, and they resist oxygen- and fluorocarbon-based plasma degradation.[274] For example, polymethacrylates containing trimethylstannyl groups in their sidechains were prepared by the AIBN-initiated polymerization of the organotin methacrylate monomers as shown in Scheme 50. Copolymerization reactions with methyl methacrylate were also performed and reactivity ratios showed that these reactions formed perfectly random copolymers. The influence of the trimethyltin groups on the glass transition temperatures of these polymers were compared to that of poly(methyl methacrylate) (PMMA) prepared using the same reaction conditions. PMMA had a T_g of 115°C, while the T_g values of the tin-containing polymers were dependent on the R group. When R=H, the T_g was 40°C, however, the incorporation of dimethyl groups into the polymer side chains resulted in a T_g at 145°C.
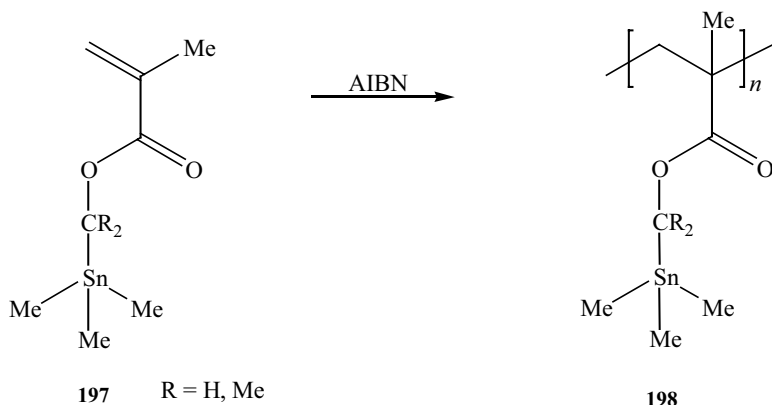
Scheme 50

High molecular weight linear and branched polystannanes have been synthesized by dehydropolymerization of secondary organostannanes.[275–277] Polystannane homopolymers such as **200** (Scheme 51) have been prepared via dehydropolymerization of $Bu^n_2SnH_2$ (**199**), $Hex^n_2SnH_2$, and $Oct^n_2SnH_2$ using zirconocene catalysts. While some cyclic species were obtained, the predominant product was a polymer with an average degree of polymerization of ~51.[275] These polymers had λ_{max} values between 380 and 400 nm, which were assigned to σ to σ* transitions. Thin films of the dialkyl substituted polystannanes doped with SbF_5 had conductivities as high as 0.3 S/cm.[275] Polystannanes are readily oxidized and are sometimes spontaneously flammable.

$$Bu^n_2SnH_2 \quad \xrightarrow{[Zr(C_5H_5)(C_5Me_5)\{Si(SiMe_3)_3\}Me]} \quad$$

199

200
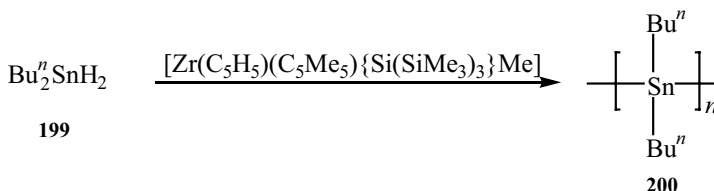
Scheme 51

Tin-containing polymers are also known to possess biological properties. Organotin groups in the form of tributyltin functions (Bu_3Sn-) have proven to have powerful antimicrobial properties and are generally biocidal. For example, they were widely used in marine antifouling coatings for ship bottoms, for paints, and in wood preservatives both in low molecular weight compounds and as polymers.[278] The antiviral agent acyclovir (**201**) has also been incorporated into a polymer containing a tin moiety (**203**) (Scheme 52).[279]

201

+

202

203
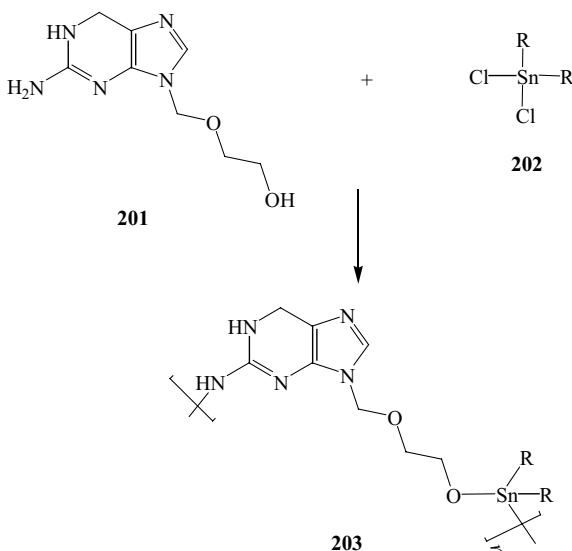
Scheme 52

In the mid 1970s, monomers that were derivatives of triphenyl- or tributyltin were found to be much more effective than cuprous oxide paints in controlling fouling. Organotin compounds formulated into paints slowly leached, so the coatings were excellent at first, but lost their antifouling ability with time. Thus polymers of tin were prepared where the tin could leach from the polymer only via a chemical hydrolysis of covalently bonded tin functions. This produced a low and steady leach rate and created hydrophilic sites on the binder resin. This layer of resin then washed away, exposing a new layer of polymer-bound organotin. Zeldin and Lin prepared isotactic, syndiotactic, and heterotactic poly(tributyltin methacrylate) and copolymers with styrene and have shown that tin release depends on polymer microstructure.[280,281] These coatings are known as *controlled-release*, *self-polishing*, or *ablative coatings.* The tin-containing polymers lasted about 5 years when applied at a dry-film thickness of 375 μm. Typical representative structures are **204** and **205**. Since organotin compounds kill many organisms and affect the growth and reproduction of others, many nations now restrict organotin coatings to vessels with aluminum hulls greater than 25 mm long.[282,283]
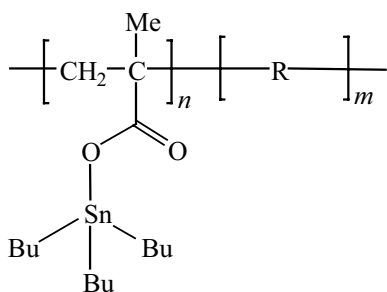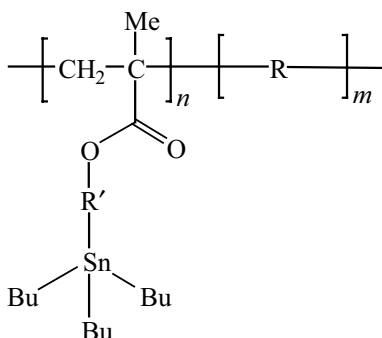
204   **205**

A series of organotin polyesters, polyethers, polyamines, polythioethers, polyaminoesters, and polyetheresters (**207–212**) have also been prepared by reacting dialkyl (or *bis*-alkoxycarbonylalkyl) dichlorides with (1) organic dicarboxylic acids, (2) diols or diphenols, (3) diamines, (4) dithiols, (5) amino acids, and (6) hydroxy acids as shown in Scheme 53.[284]

A number of polymers containing tin and silicon have also been synthesized.[285–287] The poly(organostanno-organosiloxane)s (**215**, **217**) shown in Scheme 54 were found to have improved thermal stability and lubricating properties over polysiloxane lubricating oils.[287]

Tin–oxygen polymers derived from alkanestannoic acids [RSn(O)OH] are reported to be hydrolytically stable, insoluble in most organic solvents but soluble in alcohols (MeOH, EtOH, PrOH) via formation of some tin esters. Evaporation of alcohol and heating gives transparent "plastics," which Noltes has described as having complicated crosslinked structures (**218**).[288] Another contributor to this area, Zhivukhin et al., characterized the structure of the product from 1-butanestannoic

acid after heating as having cyclic units in a sometimes crosslinked structure (**219**).[289] The polymerization of distannoic acids in alkali media gives tin–oxygen–carbon-bonded polymers. These are stable on heating to 360°C and are generally stable to alkali.[290]

$$R' = \text{aromatic and/or aliphatic}$$
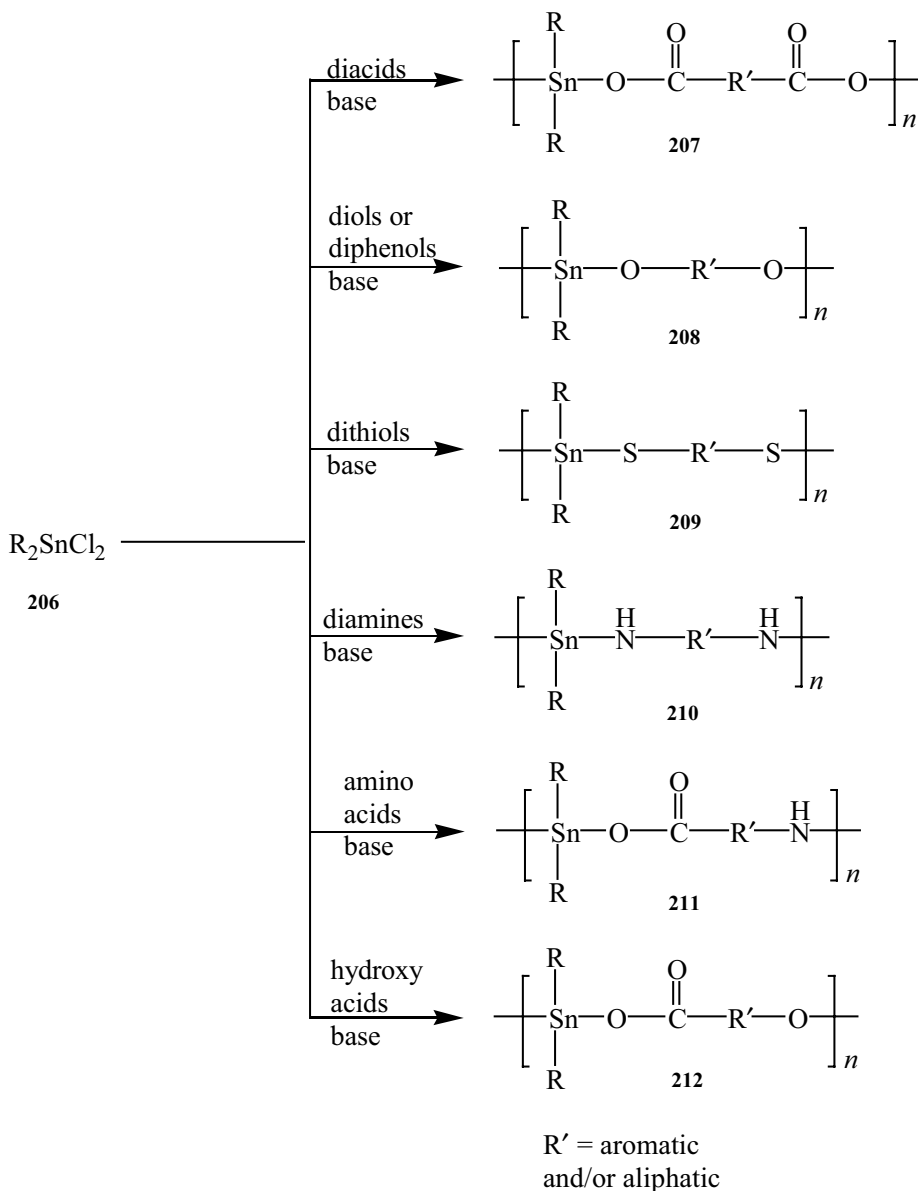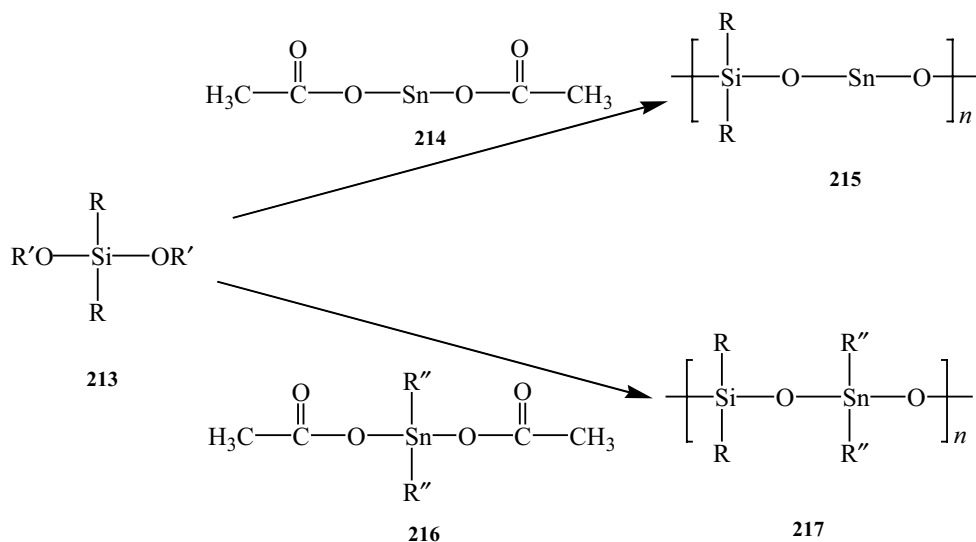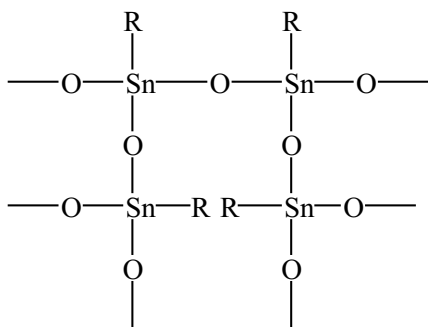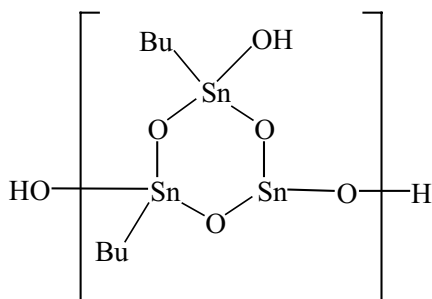
Scheme 53

Scheme 54

The synthesis of one- and two-dimensional polymers has been achieved by Wang et al. via the self-assembly of dicarboxylic acids with trimethyltin chloride.[291] Scheme 55 shows the synthesis of a two-dimensional sheet polymer (**223**) consisting of dimeric dicarboxylato-*tetra*-organodistannoxane secondary building blocks via reaction of diphenic acid (**220**) with trimethyltin chloride (**221**) under hydrothermal conditions. The synthesis of a rhombohedral grid polymer with *tetra*-organodistannoxane units has also been synthesized by reaction of 4-hydroxy-3-methoxybenzoic acid with trimethyltin chloride.[292]
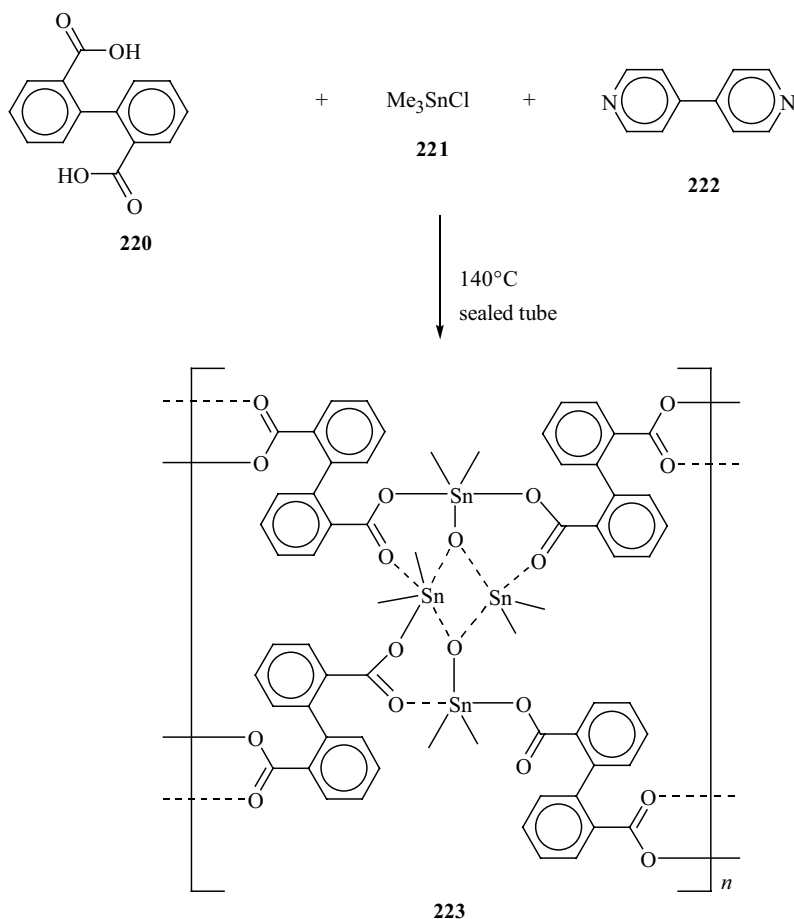
Scheme 55

V. LEAD

There are a limited number of examples of lead-containing polymers. This is attributed partially to the insolubility of suitable organolead monomers. In the 1970s, Carraher and Deremo Reese reported the synthesis and thermal properties of lead(IV) polyesters.[293–295] Reaction of dialkyllead dichloride (**224**) (Scheme 56) in DMSO with dicarboxylic acids (**225**) in 50% DMSO-H$_2$O led to the isolation of the lead containing polymers (**226**) (Scheme 56).

Thermal analysis showed that initial degradation steps occurred between 200 and 300°C. At higher temperatures, PbO$_2$ was determined to be the residue formed. Table 2 shows the percent yields and percent lead measured for the polymerization of different monomers.[293–295]

224 R = Et, Bu, Ph

225

226
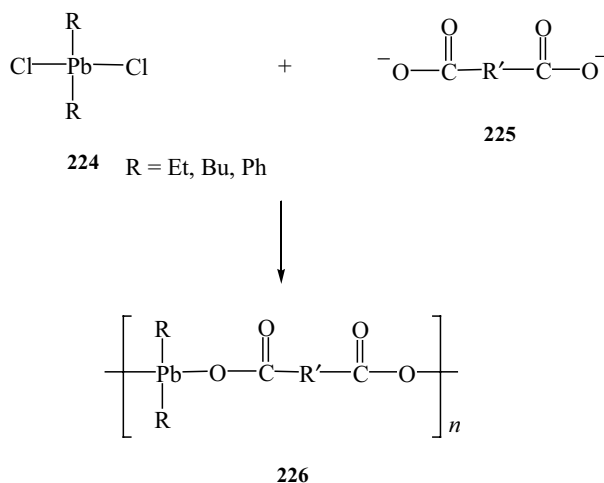
Scheme 56

Table 2 Yields for Lead-Containing Polymers

	Et$_2$PbCl$_2$		Ph$_2$PbCl$_2$	
Diacid	% Yield	% Lead	% Yield	% Lead
2,5-Dichloroterephthalic	30	44.8	12	35.4
Terephthalic	67	48.3	24	41.0
2,5-Dimethylterephthalic	75	47.8	27	34.6
Nitroterephthalic	32	46.3	—	—
Bromoterephthalic	44	44.5	—	—

The synthesis of organolead polymers has been reported by Fischer and coworkers by combining aqueous solutions of Me$_3$PbCl and K$_4$[M(CN)$_6$] (M=Fe, Ru), assemble to give supramolecular assemblies.[296] Edelmann and coworkers have also reported the supramolecular assembly of triphenyllead(IV) dimethylphosphino-dithioate to produce a linear polymer with the structure **227**.[297] It was noted that the phosphinodithioate ligands were bridging with nearly linear S−Pb−S segments.
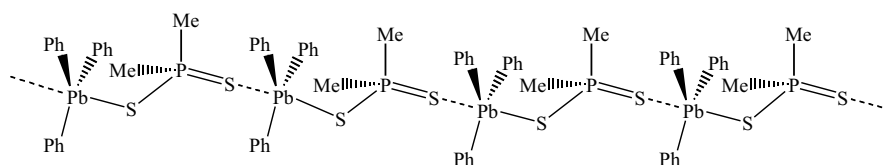
227

VI. SUMMARY

With the exception of carbon, which is a nonmetal, a wide variety of macromolecular structures containing Group IVA main group elements have been discussed in this chapter. Most of the work has been done with silicon-containing structures because of the industrial importance of polysiloxanes, polysilanes, polycarbosilanes, polysilazanes, and oligomeric silsesquioxanes. Tin-containing macromolecules have also received a great deal of attention, much of it driven by the biological activities of the organotin compounds. The variety of germanium-containing products is greatly reduced compared to tin and silicon mainly because of its expense and the lack of suitable commercially available starting materials. The least well studied of the group IVA–containing macromolecules are those of lead, possibly because of their generally poor solubility and toxicity.

VII. REFERENCES

1. G. Rayner-Canham, *Descriptive Inorganic Chemistry* 2nd ed., Freeman, New York, 2000.
2. F. Glockling, *The Chemistry of Germanium,* Academic Press, New York, 1969.
3. S. Adams, J. Drager, *Angew. Chem. Int. Ed. Engl.* **26,** 1255 (1987).
4. J. Mark, H. Allcock, R. West, *Inorganic Polymers,* Prentice-Hall, Englewood Cliffs, NJ, 1992.
5. H. Suzuki, H. Meyer, J. Simmerer, J. Yang, D. Naarer, *Adv. Mater.* **5,** 743 (1993).
6. F. Kipping, *J. Chem. Soc.* **19,** 830 (1921).
7. F. Kipping, *J. Chem. Soc.* **125,** 2291 (1924).
8. C. A. Burkhard, *J. Am. Chem. Soc.* **71,** 963 (1949).
9. J. P. Wesson, T. C. Williams, *J. Polym. Sci. Chem. Ed.* **19,** 65 (1981).
10. H. A. Clark U.S. Patent 2,563,005 (Aug. 5, 1951); U.S. Patent 2,606,879 (Aug. 12, 1953).
11. M. Kumada, K. Tamao*, Adv. Organomet. Chem.* **6,** 19 (1968).
12. R. West, L. D. David, P. I. Djurovich, K. S. Stearly, K. S. V. Srinivasan, H. Yu, *J. Am. Chem. Soc.* **103,** 7352 (1981).
13. R. West, E. Carberry, *Science* **189,** 179 (1975).
14. R. West, *Pure Appl. Chem.* **54,** 1041 (1982).
15. R. E. Trujillo, *J. Organomet. Chem.* **198,** C7 (1980).
16. R. D. Miller, J. Michl, *Chem. Rev.* **89,** 1359 (1989).
17. J. M. Zeigler, F. G. Fearon, eds., *Silicon-Based Polymer Science: A Comprehensive Resource,* Advances in Chemistry Series Vol. 224*,* American Chemical Society, Washington, DC, 1990.
18. K. Matyjaszewski, *J. Inorg. Organomet. Polym.* **1,** 463 (1991).
19. K. Matyjaszewski, *J. Inorg. Organomet. Polym.* **2,** 5 (1992).
20. R. West, R. Menescal, T. Asuke, J. Eveland, *J. Inorg. Organomet. Polym.* **2,** 29 (1992).
21. E. F. Hengge, *J. Inorg. Organomet. Polym.* **3,** 287 (1993).
22. P. Wisian-Neilson, H. R. Allcock, K. J. Wynne, eds., *Inorganic and Organometallic Polymers II. Advanced Materials and Intermediates,* ACS Symp. Series Vol. 572, American Chemical Society, Washington, DC, 1994.
23. R. G. Jones, W. Ando, J. Chojnowski, eds., *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications,* Kluwer Academic Publishers, Dordrecht/Boston/London, 2000.

24. F. C. Schilling, F. A. Bovey, D. D. Davis, A. J. Lovinger, R. B. Macgregor, Jr., C. Walsh, J. M. Zeigler, *Macromolecules* **22,** 4645 (1989).

25. J. F. Rabolt, K. Song, H. Kuzmany, R. Sooriyakumaran, G. Fickes, R. D. Miller, *Macromolecules* **23,** 3870 (1990).

26. S. Gauthier, D. J. Worsfold, *Macromolecules* **22,** 2213 (1989).

27. A. Wolff, I. Nozue, J. Maxka, R. West, *J. Polym. Sci. Polym. Chem. Ed.* **24,** 701 (1988).

28. H. Shizuka, Y. Sato, Y. Ueki, M. Ishikawa, M. Kumada, *J. Chem. Soc., Faraday Trans.* **80,** 341 (1984).

29. H. Shizuka, H. Obuchi, M. Ishikawa, M. Kumada, *J. Chem. Soc., Faraday Trans.* **80,** 383 (1984).

30. J. Wildeman, J. K. Herrema, G. Hadziioannou, E. Shomaker, *J. Inorg. Organomet. Polym.* **1,** 567 (1991).

31. C. Aitken, J. F. Harrod, E. Samuel, *J. Organomet. Chem.* **279,** C11 (1985).

32. C. Aitken, J. F. Harrod, E. Samuel, *J. Am. Chem. Soc.* **108,** 4059 (1986).

33. H. Woo, T. Tilley, *J. Am. Chem. Soc.* **111,** 3757 (1989).

34. R. West, S. Hayase, T. Iwahara, *J. Inorg. Organomet. Polym.* **1,** 545 (1991).

35. J. Wilderman, J. Herrema, G. Hadziioannou, E. Schomaker, *J. Inorg. Organomet. Polym.* **1,** 567 (1991).

36. C. Forsyth, S. Nolan, T. Marks, *Organometallics* **10,** 2543 (1991).

37. J. Herrema, P. Hutten, R. Gill, J. Wildeman, R. Wieringa, G. Hadziioannou, *Macromolecules* **28,** 8102 (1995).

38. J. Banovetz, K. Stein, R. Waymouth, *Organometallics* **10,** 3430 (1991).

39. J. Corey, X. Zhu, T. Bedard, L. Lange, *Organometallics* **10,** 924 (1991).

40. H. Li, F. Gauvin, J. Harrod, *Organometallics* **12,** 575 (1993).

41. C. Van Wakreem, T. Cleiji, J. Zwikker, L. Jenneskens, *Macromolecules* **28,** 8696 (1995).

42. T. Imori, T. D. Tilley, *Polyhedron* **13,** 2231 (1994).

43. B. P. S. Chauhan, T. Shimizu, M. Tanaka, *Chem. Lett.* 785 (1997).

44. Y. Li, Y. Kawakami, *Macromolecules* **32,** 6871 (1999).

45. Y. Li, Y. Kawakami, *Macromolecules* **32,** 8768 (1990).

46. A. Sekignchi, M. Naugo, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **117,** 4195 (1995).

47. H. Suzuki, Y. Kimata, S. Satoh, A. Kuriyama, *Chem. Lett.* 293 (1995).

48. J. Lambert, J. Pfing, C. Stem, *Angew. Chem. Int. Ed. Engl.* **34,** 98 (1995).

49. M. Cypryk, Y. Gupta, K. Matyjaszewski, *J. Am. Chem. Soc.* **113,** 1046 (1992).

50. T. Sanji, T. Sakai, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **120,** 4552 (1998).

51. H. Frey, M. Moeller, K. Matyjaszewski, *Synth. Met.* **41,** 1571 (1991).

52. K. Sakamoto, K. Obata, H. Hirata, M. Nakajima, H. Sakurai, *J. Am. Chem. Soc.* **111,** 7641 (1989).

53. K. Obata, K. Sakamoto, M. Kira, *Macromolecules* **34,** 2739 (2001).

54. T. Shono, S. Kashimura, M. Ishifune, R. Nishida, *J. Chem. Soc. Chem. Commun.* 1160 (1990).

55. S. Kashimura, M. Ishifune, H.-B. Bu, M. Takebayashi, S. Kitajima, D. Yoshiwara, R. Nishida, S. Kawasaki, H. Murase, T. Shono, *Tetrahedron Lett.* **38,** 4607 (1997).

56. S. Kashimura, M. Ishifune, N. Yamashita, H.-B. Bu, M. Takebayashi, S. Kitajima, D. Yoshiwara, Y. Kataoka, R. Nishida, S. Kawasaki, H. Murase, T. Shono, *J. Org. Chem.* **64,** 6615 (1999).

57. C. Biran, M. Bordeau, P. Pons, M. P. Leger, J. Dunogues, *J. Organomet. Chem.* **382,** C17 (1990).

58. M. Bordeau, C. Biran, M. P. Leger-Lambert, F. Spirau, D. Deffieux, *Inorganic and Organometallic Polymers II. Advanced Materials and Intermediates,* P. Wisian-Neilson, H. R. Allcock, K. J. Wynne, eds., ACS Symp. Series Vol. 572, American Chemical Society, Washington, DC, 1994.

59. M. Okano, T. Toriumi, H. Hamano, *Electrochem. Acta* **44,** 659 (1998).

60. M. Okano, H. Fukai, M. Arakawa, *Electrochem. Commun.* **1,** 223 (1999).

61. M. Okano, T. Toriumi, H. Hamano, *Electrochemica Acta* **44,** 3475 (1999).

62. L. A. Vermeulen, K. Smith, J. Wang, *Electrochemica Acta* **45,** 1007 (1999).

63. L. A. Vermeulen, K. Huang, *Polymer* **41,** 441 (2000).

64. Z.-H. Zhang, R. West, *J. Polym. Sci., Polym. Lett. Ed.* **23,** 497 (1985).

65. R. D. Miller, R. Sooriyakumaran, *J. Polym. Sci., Polym. Lett. Ed.* **25,** 321 (1987).

66. P. M. Cotts, R. D. Miller, P. T. Trefonas III, R. West, G. Fickes, *Macromolecules* **20,** 1046 (1987).

67. R. West, L. D. David, P. I. Djurovich, H. Yu, R. Sinclair, *Am. Cer. Soc. Bull.* **62,** 825 (1983).

68. F. C. Schilling, F. A. Bovey, J. M. Zeigler, *Macromolecules* **19,** 2309 (1986).

69. F. C. Schilling, F. A. Bovey, A. J. Lovinger, J. M. Zeigler, in *Silicon-Based Polymer Science: A Comprehensive Resource,* J. M. Zeigler, F. G. Fearon, eds., Advances in Chemistry Series Vol. 224, American Chemical Society, Washington, DC, 1990.

70. H. Bock, W. Ensslin, *Angew. Chem. Int. Ed. Engl.* **10,** 404 (1971).

71. A. R. Wolff, J. Maxka, R. West, *J. Polym. Sci., Polym. Chem. Ed.* **26,** 713 (1988).

72. R. West, *Pure Appl. Chem.* **54,** 1041 (1982).

73. P. Trefonas III, R. West, R. D. Miller, D. Hofer, *J. Polym. Sci., Polym Lett. Ed.* **21,** 832 (1983).

74. P. Trefonas III, J. R. Damewood, R. West, R. D. Miller, *Organometallics* **4,** 1318 (1985).

75. L. H. Harrah, J. M. Zeigler, *J. Polym. Sci., Polym. Lett. Ed.* **23,** 209 (1985).

76. K. Takeda, H. Teramae, N. Matsumoto, *J. Am. Chem. Soc.* **108,** 8186 (1986).

77. H. Kuzmany, J. F. Rabolt, B. L. Farmer, R. D. Miller, *J. Chem. Phys.* **85,** 7413 (1986).

78. A. J. Klingensmith, J. Downing, R. Michl, R. D. Miller, *J. Am. Chem. Soc.* **108,** 7438 (1986).

79. M. Shimomura, H. Okumoto, A. Kaito, K. Ueno, J. Shen, K. Ito, *Macromolecules* **31,** 7483 (1998).

80. R. Srinivasan, *Science* **234,** 559 (1986).

81. R. D. Miller, C. G. Wilson, G. M. Wallraff, N. Clecak, R. Sooriyakumaran, R. Michl, J. Karatsu, A. J. McKinley, A. J. Klingensmith, J. Downing, *Polym. Eng. Sci.* **29,** 882 (1989).

82. R. West, A. R. Wolff, D. J. Peterson, *J. Radiat. Curing* **13,** 35 (1986).

83. A. R. Wolff, R. West, *Appl. Organomet. Chem.* **1,** 7 (1987).

84. R. G. Kepler, J. M. Zeigler, L. A. Harrah, S. R. Kurtz, *Phys. Rev. B* **35,** 2818 (1987).

85. M. Fujino, *Chem. Phys. Lett.* **136,** 451 (1987).

86. E. E. Marinero, *Chem. Phys. Lett.* **115,** 501 (1985).

87. F. Kajzar, J. Messier, C. Rosilio, *J. Appl. Phys.* **60,** 3040 (1986).

88. J. C. Baumert, G. C. Bjorklund, D. H. Jundt, M. C. Jurich, H. Looser, R. D. Miller, J. Rabolt, R. Soorijakumaran, J. D. Swalen, R. J. Twig, *J. Appl. Phys. Lett.* **53,** 1174 (1991).

89. N. Matsumoyo, *Kotai Butsuri* **22,** 907 (1987).

90. D. Seyferth, in *Inorganic and Organometallic Polymers,* M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, American Chemical Society, Washington, DC, 1988, Chap. 3.

91. G. Fritz, E. Matern, *Carbosilanes. Synthesis and Reactions,* Springer-Verlag, Berlin, 1986.

92. R. M. Laine, F. Babonneau, *Chem. Mater.* **5,** 260 (1993).

93. Y. Kawakami, in *Silicones and Silicone-Modified Materials,* S. J. Clarson, J. J. Fitzgerald, M. J. Owen, S. D. Smith, eds., ACS Symp. Series Vol. 729, American Chemical Society, Washington, DC, 2000, Chap. 32.

94. L. V. Interrante, Q. Shen, in *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*, R. G. Jones, W. Ando and J. Chojnowski, eds., Kluwer Academic Publishers, Dordrecht/Boston/London, 2000. Chapt. 10.

95. S. W. Krska, D. Y. Son, D. Seyferth, in *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*, R. G. Jones, W. Ando and J. Chojnowski, eds., Kluwer Academic Publishers, Dordrecht/Boston/London, 2000 Chapt. 23.

96. M. Birot, J. P. Pillot, J. Dunogues, *Chem. Rev.* **95,** 1443 (1995).

97. L. H. Sommer, G. M. Goldberg, J. Gold, F. C. Whitmore, *J. Am. Chem. Soc.* **69,** 980 (1947).

98. J. T. Goodwin Jr., W. E. Baldwin, R. R. McGregor, *J. Am. Chem. Soc.* **69,** 2247 (1947).

99. H. A. Clark, U.S. Patent 2,507,517 (1950); *Chem. Abs.* **45,** 2259 (1951).

100. H. A. Clark, U.S. Patent 2,507,521 (1950); *Chem. Abs.* **45,** 2265 (1951).

101. J. T. Goodwin, Jr., U.S. Patent 2,507,512 (1950); *Chem. Abs.* **45,** 3410 (1950).

102. J. T. Goodwin, Jr., U.S. Patent 2,544,079 (1951); *Chem. Abs.* **45,** 6654 (1951).

103. C. K. Whitmarsh, L. V. Interrante, *Organometallics* **10,** 1336 (1991).

104. G. Ouyang, R. Simmons, C. Tessier, in *Metal-Contaianing Polymers,* C. U. Pittman Jr., C. E. Carraher Jr., M. Zeldin, J. E. Sheats, B. M. Culbertson, eds., Plenum Press, New York, 1996, p. 189.

105. I. N. Jung, S. H. Yeon, J. S. Han, *Organometallics* **12,** 2360 (1993).

106. W. A. Kriner, *J. Org. Chem.* **29,** 1601 (1961).

107. N. S. Nametkin, V. M. Vdovin, V. I. Zav'yalov, P. L. Grinberg, *Izv. Akad. Nauk SSSR Ser. Khim.* 929 (1965).

108. N. S. Nametkin, V. M. Vdovin, V. I. Zav'yalov, *Izv. Akad. Nauk SSSR Ser. Khim.* 1153 (1974), and references cited therein.

109. N. S. Nametkin, V. M. Vdovin, P. L. Grinberg, *Izv. Akad. Nauk SSSR Ser. Khim.* 1123 (1964).

110. D. R. Weyenberg, L. E. Nelson, *J. Org. Chem.* **30,** 2618 (1965).

111. W. R. Bamford, J. C. Lovie, J. A. C. Watt, *J. Chem. Soc. C* 1137 (1966).

112. C. S. Cundy, C. Eaborn, M. F. Lappet, *J. Organomet. Chem.* **44,** 291 (1972).

113. V. A. Poletaev, V. M. Vdovin, N. S. Nametkin, *Dokl. Akad. Nauk SSSR Ser.* **208,** 1112 (1973).

114. C. X. Liao, W. P. Weber, *Macromolecules* **25,** 1639 (1992).

115. Y. Kawakami, in *Silicones and Silicne-Modified Materials,* S. J. Clarson, J. J. Fitzgerald, M. J. Owen, S. D. Smith, eds., ACS Symp. Series Vol. 729, American Chemical Society, Washington DC, 2000, Chap. 31.

116. Y. Kawakami, *Polym. Adv. Technol.* **12,** 658 (2001).

117. K. Uenishi, I. Imae, E. Shirakawa, Y. Kawakami, *Macromolecules* **35,** 2455 (2002).

118. H.-J. Wu, L. V. Interrante, *Macromolecules* **25,** 1840 (1992).

119. L. V. Interrante, H.-J. Wu, T. Apple, Q. Shen, B. Ziemann, D. Narsavage, *J. Am. Chem. Soc.* **116,** 12085 (1994).

120. I. L. Rushkin, L. V. Interrante, *J. Am. Chem. Soc.* **28,** 5160 (1995).

121. R. J.-P. Corriu, W. E. Douglas, E. Layher, R. Shankar, *J. Inorg. Organomet. Polym.* **3,** 129 (1993).

122. B. Boury, L. S. Carpenter, R. Corriu, H. Mutin, *Chem. Mater.* **3,** 487 (1991).

123. B. Boury, L. S. Carpenter, R. Corriu, *Angew. Chem. Int. Ed. Engl.* **29,** 785 (1990).

124. C. Lach, H. Frey, *Macromolecules* **31,** 2381 (1998).

125. Y. Xiao, R. A. Wong, D. Y. Son, *Macromolecules* **33,** 7232 (2000).

126. S. Q. Zhou, W. P. Weber, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **33,** 1103 (1992).

127. M. Tsumura, T. Iwahara, T. Hirose, *J. Polym. Sci., Part A, Polym Chem.* **34,** 3155 (1996).

128. W. R. Bamford, J. C. Lovie, J. A. C. Watt, *J. Chem. Soc. C* 1137 (1966).

129. S. Yajima, *Am. Ceram. Soc. Bull.* **62,** 893 (1983).

130. S. Yajima, J. Hayashi, M. Omori, K. Okamura, *Nature* **261,** 683 (1976).

131. Y. Hasegawa, K. Okamura, *J. Mater. Sci.* **21,** 321 (1986).

132. A. Soum, in *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications,* R. G. Jones, W. Ando, J. Chojnowski, eds., Kluwer Academic Publishers, Dordrecht/Boston/London, 2000, Chap. 11.

133. R. M. Laine, Y. D. Blum, D. Tse, R. Glaser, in Ref. 401, Chap. 10.

134. D. Seyferth, G. H. Wiseman, J. M. Schwark, Y.-F. Yu, C. A. Poutasse, in *Inorganic and Organometallic Polymers,* M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, American Chemical Society, Washington, DC, 1988, Chap. 11.

135. Lipowitz, J. A. Rabe, T. M. Carr, in *Inorganic and Organometallic Polymers,* M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, American Chemical Society, Washington, DC, 1988, Chap. 12.

136. Lasocki, B. Dejak, J. Kulpinski, E. Lesniak, S. Piechucki, M. Witwkowa, in *Inorganic and Organometallic Polymers,* M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, American Chemical Society, Washington, DC, 1988, Chap. 13.

137. R. Riedel, W. Dressler, *Ceramics Int.* **22,** 233 (1996).

138. M. Schwark, A. Lukacs III, in *Inorganic and Organometallic Polymers II,* P. Wisian-Neilson, H. R. Allcock, K. J. Wynne, eds., ACS Symp. Series Vol. 572, American Chemical Society, Washington, DC, 1994, Chap. 5.

139. L. M. Manocha, A. Patel, S. Manocha, *Metals, Mater. Proc.* **5,** 163 (1993).

140. J. Pola, *Chemicke Listy* **87,** 418 (1993).

141. D. Seyferth, in *Silicon-Based Polymer Science: A Comprehensive Resource,* J. M. Zeigler, F. G. Fearon, eds., Advances in Chemistry Series Vol. 224. American Chemical Society, Washington, DC, 1990, Chap. 31.

142. D. Seyferth, G. H. Wiseman, C. Prud'homme, *J. Am. Ceram. Soc.* **66,** C13 (1983).

143. D. Seyferth, G. H. Wiseman, *J. Am. Ceram. Soc.* **67,** C132 (1984).

144. M. Arai, S. Sakurada, T. Isoda, T. Tomizawa, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **28,** 407 (1987).

145. E. G. Rochow, *Monatsch. Chem.* **95,** 750 (1964).

146. C. R. Kruger, E. G. Rochow, *J. Polym. Sci. A* **2,** 3179 (1964).

147. G. Redl, E. G. Rochow, *Angew. Chem.* **76,** 650 (1964).

148. D. Seyferth, M. J. Schwark, M. R. Stewart, *Organometallics* **85,** 1980 (1989).

149. D. Seyferth, in *Silicon-Based Polymer Science: A Comprehensive Resource,* J. M. Zeigler, F. G. Fearon, eds., Advances in Chemistry Series Vol. 224, American Chemical Society, Washington, DC, 1990, p. 573.

150. T. M. Zoeckler, R. M. Laine, *J. Org. Chem.* **48,** 2539 (1983).

151. Y. D. Blum, R. M. Laine, *Organometallics* **5,** 2081 (1986).

152. E. Duguet, M. Schappacher, A. Soum, *Macromolecules* **25,** 4835 (1992).

153. S. Bruzaud, A. Soum, *Macromol. Chem. Phys.* **197,** 2379 (1996).

154. C. Cazalis, A. F. Mingotaud, A. Soum, *Macromol. Chem. Phys.* **198,** 3441 (1997).

155. M. Bouquey, C. Brochon, A. F. Mingotaud, M. Schappacher, A. Soum, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **39,** 444 (1998).

156. W. Verbeek, U.S. Patent 3,853,567 (Dec. 1974).

157. G. Winter, W. Verbeek, M. Mansmann, U.S. Patent 3,892,583 (July 1975).

158. K. J. Wynne, R. W. Rice, *Ann. Rev. Mater. Sci.* **14,** 297 (1984).

159. J. P. Cannady, U.S. Patent 4,543,344 (Sept. 1985).

160. G. E. Legrow, T. F. Lim, J. Lipowitz, R. S. Reaoch, *Mater. Res. Soc. Symp. Proc.* **73,** 553 (1986).

161. G. E. Legrow, T. F. Lim, J. Lipowitz, R. S. Reaoch, *J. Chim. Phys. Phys. Chim. Biol.* **83,** 869 (1986).

162. W. Fink, *Angew. Chem. Int. Ed. Eng.* **5,** 760 (1966).

163. K. A. Andrianov, M. I. Sholnik, Z. S. Syrtsova, K. I. Petrov, V. M. Kojylov, M. Zaitseva, E. Z. Koroleva, *Dokl. Nauk SSSR* **223,** 347 (1975).

164. G. H. Wiseman, D. R. Wheeler, D. Seyferth, *Organometallics* **5,** 146 (1986).

165. R. M. Laine, Y. D. Blum, D. Tse, R. Glaser, in *Inorganic and Organometallic Polymers,* M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, American Chemical Society, Washington, DC, 1988, Chap. 10.

166. S. J. Clarson, J. J. Fitzgerald, M. J. Owen, S. D. Smith, eds., *Silicones and Silicone-Modified Materials,* ACS Symp. Series Vol. 729, American Chemical Society, Washington, DC, 2000.

167. R. G. Jones, W. Ando, J. Chojnowski, eds., *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications,* Kluwer Academic Publishers, Dordrecht/Boston/London, 2000.

168. S. J. Clarson, J. A. Semlyen, eds., *Siloxane Polymers,* PTR Prentice-Hall, Englewood Cliffs, NJ, 1993.

169. J. M. Zeigler, F. G. Fearon, eds., *Silicon-Based Polymer Science: A Comprehensive Resource,* Advances in Chemistry Series Vol. 224, American Chemical Society, Washington, DC, 1990; Chap. 3–16.

170. L. J. Mathias, T. W. Carothers, *Adv. Dendritic Macromol.* **2,** 101 (1995).

171. J. C. Saam, *J. Inorg. Organomet. Polym.* **9,** 3, (1999).

172. H. Mayer, *Surf. Coat. Interface* **82,** 77 (1999).

173. J.-P. Majoral, A.-M. Caminade, *Chem. Rev.* **99,** 845 (1999).

174. I. Manners, *Ann. Rep. Progr. Chem. Sect. A, Inorg. Chem.* **93,** 129 (1997).

175. I. Manners, *Ann. Rep. Progr. Chem. Sect. A, Inorg. Chem.* **92,** 127 (1996).

176. J. Chojnowski, *Roy. Soc. Chem. Spec. Publ.* **166,** 59 (1995).

177. A. Ladenburg, *Liebig Ann. Chem.* **164,** 300 (1872).

178. A. Ladenburg, *Liebig Ann. Chem.* **173,** 143 (1874).

179. F. S. Kipping, *J. Chem. Soc.* **101,** 2106 (1912).

180. F. S. Kipping, *Proc. Roy. Soc. A* **159,** 139 (1937).

181. E. G. Rochow, *Chem. Eng. News* **23,** 612 (1945).

182. R. J. H. Voorhoeve, *Organohalosilanes: Precursors to Silicones,* Elsevier, New York, 1967.

183. E. G. Rochow, *Silicon to Silicones,* Springer-Verlag, Berlin, 1987.

184. W. Noll, *Chemistry and Technology of Silicones,* Academic Press, New York, 1968.

185. M. G. Voronkov, V. P. Mileshkevich, Y. A. Yuzhelevskii, *The Siloxane Bond,* Plenum Press, New York, 1978.

186. P. F. Bruins, *Silicone Technology,* J Wiley, New York, 1970.

187. K. Itoh, T. Shinohara, H. Kizaki, S. Tanaka, Y. Satou, K. Umemura, U.S. Patent 5,473,037 (1995).

188. J. Chojnowski, M. Cypryk, in *Silicon-Containg Polymers: The Science and Technology of Their Synthesis and Applications,* R. G. Jones, W. Ando, J. Chojnowski, eds., Kluwer Academic/Plenum Publishers, Boston, 2000, Chap. 1.

189. J. Chojmowski, S. Rubinsztajn, L. Wilczek, *Macromolecules* **20,** 2345 (1987).

190. J. C. Saam, D. J. Huebner, *J. Polym. Sci., Polym. Chem. Ed.* **20,** 3351 (1982).

191. P. V. Wright, M. S. Beevers, in *Cyclic Polymers,* J. A. Semlyen, ed., Elsevier, London, 1986.

192. M. Mazurek, M. Scibiorek, J. Chojnowski, B. G. Zavin, A. Zhdanov, *Eur. Polym. J.* **16,** 57 (1980).

193. L. Wilczek, J. P. Kennedy, *Polym. J.* **190,** 531 (1987).

194. L. Wilczek, S. Rubinsztajn, J. Fortuniak, J. Chojnowski, I. I. Tverdokhlebova, R. V. Volkova, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **37,** 91 (1989).

195. B. Suryanarayanan, B. W. Pearce, K. G. Mayhan, *J. Polym. Sci., Polym. Chem. Ed.* **12,** 1089 (1974).

196. E. Orthmanm, G. Wegner, *Angew. Chem. Int. Ed. Engl.* **25,** 1105 (1986).

197. C. Sirlin, L. Bosio, J. Simon, *Mol. Cryst. Liq. Cryst.* **155,** 231 (1988).

198. R. G. M. Crockett, A. J. Campbell, F. R. Ahmed, *Polymer* **31,** 602 (1990).

199. J. Chojnowski, *J. Inorg. Organomet. Polym.* **1,** 299 (1991).

200. M. Mazurek, J. Zietera, W. Sadowska, J. Chojnowski, *Makromol. Chem.* **181,** 777 (1980).

201. J. Chojnowski, M. Cypryk, K. Kazmeierski, *Macromolecules* **35,** 9904 (2002).

202. W. P. Weber, G. Cai, *Macromolecules* **34,** 4355 (2001).

203. I. Yilgor, J. E. McGrath, *Adv. Polym. Sci.* **86,** 1 (1988).

204. R. F. T. Septo in *Polymer Networks. Principles of Their Formation, Structure and Properties,* R. F. T. Septo, ed., Blackie Academic & Professional Publishers, London, 1998.

205. G. Belorgey, G. Sauvet, in *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications,* R. G. Jones, W. Ando, J. Chojnowski, eds., Kluwer Academic Publishers, Dordrecht/Boston/London, 2000, Chap. 2.

206. B. Boutevin, F. Guida-Pietrasanta, A. Ratsimihety, in *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications,* R. G. Jones, W. Ando, J. Chojnowski, eds., Kluwer Academic Publishers, Dordrecht/Boston/London, 2000, Chap. 3.

207. P. Chaumont, G. Beinert, J. Herz, P. Rempp, *Eur. Polym. J.* **15,** 459 (1979).

208. I. Yilgor, A. K. Sha'aban, W. P. Steckle Jr., D. Tyagi, G. L. Wilkes, J. E. McGrath, *Polymer* **25,** 1800 (1984).

209. D. Gagenbein, P. J. Madec, E. Marechal, *Eur. Polym. J.* **21,** 271 (1985).

210. D. Gagenbein, P. J. Madec, E. Marechal, *Eur. Polym. J.* **21,** 289 (1985).

211. D. Gagenbein, P. J. Madec, E. Marechal, *Eur. Polym. J.* **21,** 301 (1985).

212. B. C. Auman, V. Perec, H. D. Schneider, W. Jishan, H. J. Canton, *Polymer* **28,** 119 (1987).

213. H. A. Vaughn Jr., *J. Polym. Sci., Part B* **B7,** 569 (1969).

214. A. C. Lind, *Macromolecules* **17,** 300 (1984).

215. J. E. McGrath, L. F. Wang, J. B. Mecham, Q. Ji, *Polym. Preprints* **39**(1), 455 (1998).

216. I. Yilgor, B. Lee, W. P. Steckle Jr., J. S. Riffle, D. Tyagi, G. L. Wilkes, J. E. McGrath, *Polym. Preprints* **24**(2), 35 (1983).

217. M. Kajiyama, M. Kakimoto, Y. Imai, *Macromolecules* **23,** 1244 (1990).

218. A. D. Bowens, M. A. F. Robertson, J. S. Riffle, *Polym. Preprints* **39**(1), 569 (1998).

219. E. Yilgor, I. Yilgor, *Polym. Preprints,* **39**(1), 465 (1998).

220. W. K. Busfield, J. M. G. Cowie, *Polym. Bull.* **2,** 619 (1980).

221. A Noshay, M. Matzger, G. Karoly, G. B. Stampa, *J. Appl. Polym. Sci.* **17,** 619 (1973).

222. G. Lents, K. Lyon, S. Smith, M. Weber, D. Rodrigues, G. L. Wilkes, J. E. McGrath, *Polym. Preprints* **34**(1), 578 (1993).

223. V. Hamciuc, D. Giurgiu, E. Butuc, M. Marcu, C. Ionescu, L. Pricop, *Polym. Bull.* **37,** 329 (1996).

224. C. P. Reghunadhan Nair, G. Clouet, *Macromolecules* **23,** 1361 (1990).

225. C. P. Reghunadhan Nair, G. Clouet, P. Chaumont, *J. Polym. Sci., Polym. Chem. Ed.* **27,** 1795 (1989).

226. B. Marciniec, ed., *Comprehensive Handbook on Hydrosilylation,* Pergamon Press, Oxford, 1992.

227. W. Urbaniak, B. Marciniec, *Synth. React. Inorg. Met. Org. Chem.* **18,** 695 (1988).

228. J. Chojnowski, K. Rozga, *J. Inorg. Organomet. Polym.* **2,** 297 (1992).

229. L. Abdellah, B. Boutevin, B. Youssef, *Eur. Polym. J.* **27,** 821 (1991).

230. T. J. Marks, J. G. Gaudiello, G. E. Kellog, S. M. Tetrick, in *Inorganic and Organometallic Polymers,* M. Zeldin, K. J. Wynne, H. R. Allcock, eds., ACS Symp. Series Vol. 360, ACS Publishers, Washington, DC, 1988.

231. T. J. Marks, *Science* **227,** 881 (1985).

232. D. W. Scott, *J. Am. Chem. Soc.* **68,** 356 (1946).

233. G. Li, L. Wang, H. Ni, C. U. Pittman, Jr., *J. Inorg. Organomet. Polym.* **11,** 123 (2002).

234. R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **95,** 1409 (1995).

235. T. S. Haddad, J. D. Lichtenhan, *Macromolecules* **29,** 7302 (1996).

236. P. T. Mather, H. G. Jeon, A. Romo-Uribe, T. S. Haddad, J. D. Lichtenhan, *Macromolecules* **32,** 1194 (1999).

237. G. Z. Li, L. Wang, H. Toghiani, T. L. Daulton, K. Koyama, C. U. Pittman, Jr., *Macromolecules* **34,** 8686 (2001).

238. G. Z. Li, L. Wang, H. Toghiani, T. L. Daulton, C. U. Pittman, Jr., *Polymer* **43,** 4167 (2002).

239. D. P. Fasce, R.J.J. Williams, F. Mechin, J. P. Pascault, M. F. Llauro, R. Petiaud, *Macromolecules* **32,** 4757 (1999).

240. A. Sellinger, R. M. Laine, *Chem. Mater.* **8,** 1592 (1996).

241. A. Sellinger, R. M. Laine, *Macromolecules* **29,** 2327 (1996).

242. C. Zhang, R. M. Laine, *J. Am. Chem. Soc.* **122,** 6979 (2000).

243. C. Zhang, F. Babonneau, C. Bonhomme, R. M. Laine, C. L. Soles, H. A. Hristov, A. F. Yee, *J. Am. Chem. Soc.* **120,** 8380 (1998).

244. J. D. Lichtenhan, N. Q. Vu, J. A. Carter, J. W. Gilman, F. J. Feher, *Macromolecules* **26,** 2141 (1993).

245. R. A. Mantz, P. F. Jones, K. P. Chafee, J. D. Lichtenhan, J. W. Gilman, I.M.K. Ismail, M. J. Burmeister, *Chem. Mater.* **8,** 1250 (1996).

246. P. Trefonas, R. West, *J. Polym. Sci. Polym. Chem. Ed.* **23,** 2099 (1985).

247. R. D. Miller, R. Sooriyakumaran, *J. Polym. Sci. Polym. Chem. Ed. 25,* 111 (1987).

248. K. Mochida, C. Hodota, R. Hata, *Organometallics* **12,** 586 (1993).

249. J. Reichi, C. Popoff, L. Gallagher, E. Remsen, D. Berry, *J. Am. Chem. Soc.* **118,** 9430 (1996).

250. S. Kobayashi, S. Shoda, S. Iwata, M. Hiraishi, S. Cao, *Macromol. Symp.* **98,** 91 (1995).

251. S. Kobayashi, S. Cao, *Chem. Lett.* 1385 (1993).

252. T. Sanji, M. Funaya, H. Sakurai, *Chem. Lett.* 547 (1999).

253. B. L. Lucht, M. A. Buretea, T. D. Tilley, *Organometallics* **19,** 3469 (2000).

254. F. J. Gomez, K. B. Wagener, *J. Organomet. Chem.* **592,** 271 (1999).

255. L. H. Tagle, J. C. Vega, F. R. Diaz, D. Radic, L. Gargallo, P. Valenzuela, *J. Macromol. Sci., Part A, Pure Appl. Chem.* **37,** 997 (2000).

256. L. H. Tagle, F. R. Diaz, D. Radic, A. Opazo, J. M. Espinoza, *J. Inorg. Organomet. Polym.* **10,** 73 (2000).

257. S. Kobayashi, S. Cao, *Chem. Lett.* 25 (1993).

258. S. Kobayashi, S. Iwata, M. Abe, S. Shoda, *J. Am. Chem. Soc.* **112,** 1625 (1990).

259. S. Kobayashi, S. Iwata, M. Abe, S. Shoda, *J. Am. Chem. Soc.* **117,** 2187 (1995).

260. S. Kobayashi, S. Iwata, M. Hiraishi, *J. Am. Chem. Soc.* **116,** 6047 (1994).

261. S. Kobayashi, S. Iwata, K. Yajima, K. Yagi, S. Shoda, *J. Am. Chem. Soc.* **114,** 4929 (1992).

262. T. Nishikubo, A. Kameyama, Y. Kimura, T. Nakamura, *Macromolecules* **29,** 5529 (1996).

263. C. E. Carraher, Jr., R. L. Dammeier, *Makromol. Chem.* **141,** 245 (1971).

264. G. Vogg, M. S. Brandt, M. Stutzmann, *Adv. Mater.* **12,** 1278 (2000).

265. W. J. Szymanski, G. T. Visscher, P. A. Bianconi, *Macromolecules* **26,** 869 (1993).

266. K. Mochida, T. Ohkawa, H. Kawata, A. Watanabe, O. Ito, M. Matsuda, *Bull. Chem. Soc. Jpn.* **69,** 2993 (1996).

267. E. Frankland, *J. Chem. Soc.* **2,** 263 (1849).

268. N. A. Adrova, M. Koton, E. Moskvina, Izv. Akad. Nauk. SSSR Otdel. Khim. Nauk 1804 (1962).

269. J. Leebrick, U.S. Patent 3,167,532 (1965).

270. R. K. Ingham, S. D. Rosenberg, H. Gilman *Chem. Rev.* **60,** 459 (1960).

271. W. P. Neuman, *Angew. Chem. Int. Ed. Engl.* **2,** 165 (1963).

272. W. P. Neman, B. Schneider, *Angew. Chem. Int. Ed. Engl.* **3,** 751 (1964).

273. N. Adrova, M. Koton, V. Klages, *Vysokomol. Soden.* **3,** 1041 (1961).

274. J. W. Labadie, S. A. MacDonald, C. G. Wilson, *Macromolecules* **20,** 10 (1987).

275. T. Imori, T. Tilley, *J. Chem. Soc. Commun.* 1607 (1993).

276. N. Devylder, M. Hill, K. Molloy, C. Price, *Chem. Commun.* 711 (1996).

277. V. Lu, T. Tilley, *Macromolecules* **29,** 5763 (1996).

278. M. H. Gitlitz, C. B. Beiter, *Disinfection, Sterilization and Preservation,* 4th ed., S. S. Block, ed., Lea Febiger, Philadelphia, 1991, pp. 344–357.

279. R. Bleicher, C. Carraher, *Polym. Mater. Sci. Eng.* **86,** 289 (2002).

280. M. Zeldin, J. J. Lin, *J. Polym. Sci., Polym. Chem. Ed.* **23,** 2333 (1985).

281. J. J. Lin, Ph.D. dissertation, Polytechnic Univ. 1983.

282. D. Atherton, J. Verborgt, M. A. Winkler, *J. Coating, Technol.* **51,** 657 (1979).

283. R. Abel, N. J. King, J. L. Vosser, T. G. Wilkinson, *Proc. Oceans'86,* M. A. Champ, ed., Marine Techonology Society, Washington, DC, 1986, p. 1314.

284. W. Rongbao, Y. Liang, J. Wu, Q. Xue, "Organotin Polymers," in *Concise Polymeric Materials Encyclopedia,* J. C. Salamone, ed., CRC Press, New York, 1999, pp. 981–982. [see also W. Rongbao et al., *Acta Polym. Sinica* **4,** 403 (1992), *Tianjin Technol.* **1,** 1 (1989), *Tianjin Technol.* **2,** 1 (1989) and *Chin. React. Polym.* **2,** 23 (1993)].

285. R. D. Crain, P. E. Koenig, F. A. Henglein, *WADC Tech. Rep.* **69-429,** 15 (1960).

286. R. Lang, L. Schmack, *Macromol. Chem.* **22,** 103 (1957).

287. K. A. Andrianov, *Metalorganic Polymers,* (Engl. transl.), Interscience, New York, 1965, Chap. IV.

288. J. G. Noltes, *WADC Tech. Rep.* **59-427,** 217 (1960).

289. S. M. Zhivukhin, E. D. Dudikova, N. B. Pshiyalkovaskaya, *Zh. Obshch. Khim.* **33,** 2958 (1963).

290. J. W. Hill, U.S. Patent 2,484,508 (1949); *Chem. Abs.* **44,** 5899 (1950).

291. R.-H. Wang, M.-C. Hong, J.-H. Luo, R. Cao, J.-B. Weng, *Eur. J. Inorg. Chem.* 2082 (2002).

292. R.-G. Xiong, J.-L. Zuo, X.-Z. You, H.-K. Fun, S. S. S. Raj, *Organometallics* **19,** 4183 (2000).

293. C. E. Carraher, Jr., C. Deremo Reese, *Angew. Makromol. Chem.* **65,** 95 (1977).

294. C. E. Carraher, Jr., C. Deremo Reese, *J. Polym. Sci., Polym. Chem.* **16,** 491 (1978).

295. C. E. Carraher, Jr., C. Deremo Reese, *Organometallic Polymers,* Academic Press: New York, 1978, p. 101.

296. A. K. Brimah, P. Schwarz, R. D. Fischer, N. A. Davies, R. K. Harris, *J. Organomet. Chem.* **568,** 1 (1998).

297. F. T. Edelmann, I. Haiduc, C. Silvestru, H.-G. Schmidt, M. Noltemeyer, *Polyhedron* **17,** 2043 (1998).

Subject Index