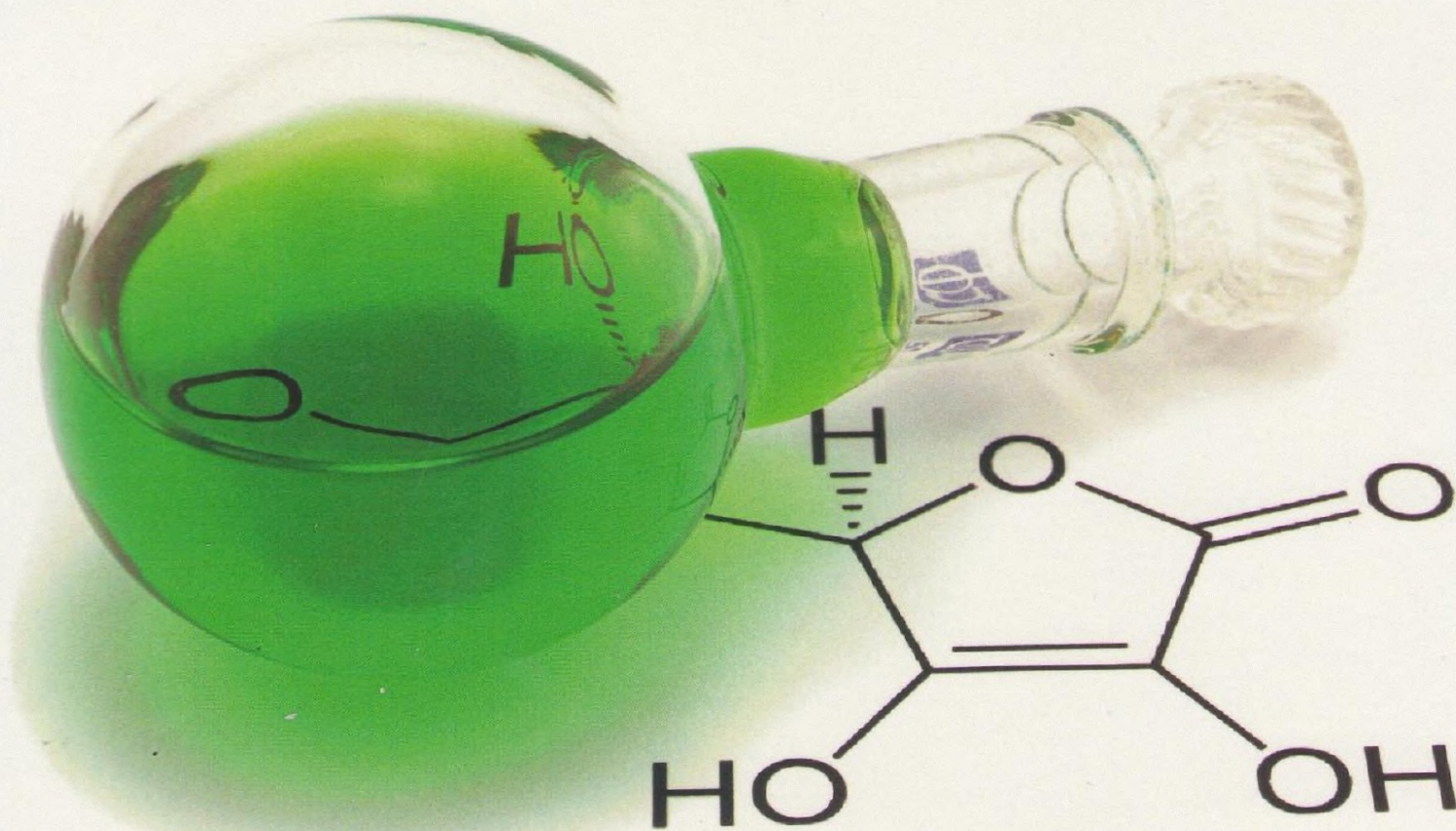


Zinaida S. Khasbulatova
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DERIVATIVES OF AROMATIC POLYESTERS BASED ON n-OXYBENZOIC AND PHTHALIC ACID (REVIEW)



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AROMATIC POLYESTERS OF *n*-OXYBENZOIC AND PHTHALIC ACID DERIVATIVES (REVIEW)

ABSTRACT

The data on aromatic polyesters based on phthalic and *n*-oxybenzoic acid derivatives have been presented and various methods of synthesis of such polyesters developed by Russian and foreign scientists for last 50 years have been reviewed.

Keywords: monomers, polycondensation, synthesis, oligoesters, tere- and isophthalic acids, *n*-oxybenzoic acid, polyesters.

INTRODUCTION

The important trend of modern chemistry and technology of polymeric materials is the search for the possibilities of producing materials with novel properties based on given combination of known polymers.

One of the most interesting ways in this direction is the creation of block-copolymers macromolecules of which are the “hybrids” of units differing in chemical structure and composition. Thermodynamical incompatibility of blocks results in stable microphase layering in the majority cases what, finally, allows one to combine the properties of various fragments of macromolecules of block-copolymers in an original way.

Depending on diversity of chemical nature of blocks, their length, number and sequence as well as their ability to crystallize one can obtain materials of structure and properties distinguishing from that of initial components. Here are the huge potential possibilities the practical realization of which has already been started. The most evident is the creation of thermoplastic elastomers (TPEs) – high-tonnage polymeric materials synthesized on the base of principle of block-copolymerization: joining of properties of both thermoplastics and elastomers in one material. The great potentials of block-copolymers caused considerable attention to them within the last years.

Nowadays, all the main problems of physics and physic-chemistry of polymers became closely intertwined when studying block-copolymers: the nature of ordering in polymers, the features of phase separation in polymers and the influence of general molecular parameters on it, the stability of phases at exposing to temperature and power impacts, the features of physical and mechanical properties of microphases and the role of their conjugation.

Existing today numerous methods of synthesis of block-copolymers give the possibility to combine unlimited number of various macromolecules, what already allowed people to synthesize multiple block-copolymers. The thermal and

mechanical properties and also the stability of industrial block-copolymers vary in broad limits.

The range of operating temperatures and the thermal stability of TPEs have lately been extended owing to the use of solid blocks of high T_{glass} (of polysulfones or polycarbonates for instance) combined with soft blocks of low T_{glass} . Moreover, the incompatibility of those blocks results in independence of elasticity modulus on temperature in broad temperature range. Applying appropriate selection of chemical nature of blocks one can also improve the other properties.

Some limitations and unresolved issues still exist in areas of synthesis, analysis and characterization of properties and usage of block-copolymers. This is a good stimulus for the intense researches and development of corresponding fields of industry.

The most preferred methods of synthesis of block-copolymers are the three following. The polymerization according to the mechanism of “live” chains with the consecutive addition of monomers has been used in the first one. The second is based on the interaction of two preliminary obtained oligomers with the end functional groups. The third one is the polycondensation of the second block at expense of end group of primarily obtained block of the first monomer. The second and the third methods allow one to use great variety of chemical structures.\

So, to produce block-copolymers one can avail numerous reactions allowing one to bind, within the macromolecule, blocks synthesized by means of polycondensation at expense of joining or cycloreversion.

The second method of synthesis of block-copolymers allows one to produce polymers after various combinations of initial compounds, one among which is that monomers able to enter the reaction of condensation are added to oligomers obtained by polycondensation.

Generally, the bifunctional components are used for creating the block-copolymers of $(-AB-)_n$ type. The necessary oligomers could be obtained by means

of either condensation reactions or usual polymerization. The end groups of monomer taken in excess are responsible for the chemical nature of process in case of condensation.

Until now, the morphological studies have been performed mainly on block-copolymers containing two chemically different blocks *A* and *B* only. One can expect the revelation of quite novel morphological structures for three-block copolymers, including three mutually incompatible units $(ABC)_n$. And there are few references on such polymers.

Russian and foreign scientists remarkably succeeded in both areas of creation of new inflammable, heat- and thermal resistant polycondensation polymers and areas of development of methods of performing polycondensation and studying of the mechanism of reactions grounding the polycondensation processes [1-6].

The reactions of polycondensation are the bases of producing the most important classes of heterochain polymers: polyarylates, polysulfones, polyarylenesterketones, polycarbonates, polyamides and others [7-12].

Non-equilibrium polycondensation can be characterized by a number of advantages amongst the polycondensation processes. These are the absence of exchange destructive processes, high values of constants of speed of growth of polymeric chain, et cetera. However, some questions of non-equilibrium polycondensation still remain unanswered: the mechanism and basic laws of formation of copolymers when the possibility of combination of positive properties of two, three or more initial monomers can be realized in high-molecular product.

The simple and complex aromatic polyesters, polysulfones and polyaryleneketones possess the complex of valuable properties such as high physic-mechanical and dielectric properties as well as increased thermal stability.

There is a lot of foreign scientific papers devoted to the synthesis and study of copolysulfones based on oligosulfones and polyarylenesterketones based on

oligoketones.

Because of importance of the problem of creation of thermo-stable polymers possessing high flame- and thermal resistance accompanied with the good physic-mechanical properties, the study of the regularities of formation of copolyesters and block-copolyesters based of oligosulfoneketones, oligosulfones, oligoketones and oligoformals appeared to be promising depending on the constitution of initial compounds, establishing of interrelations between composition, structure and properties of copolymers.

To improve the basic physic-mechanical parameters and abilities to be re-used (in particular, to be dissolved), the synthesis of copolyesters and block-copolyesters has been performed through the stage of formation of oligomers with end reaction-able functional groups.

As the result of performed activities, the oligomers of various chemical compositions have been synthesized: oligosulfones, oligoketones, oligosulfoneketones, oligoformals, and novel aromatic copolyesters and block-copolyesters have been produced.

Obtained copoly- and block-copolyestersulfoneketones, as well as polyarylates based of dichloranhydrides of phthalic acids and chloranhydride of 3,5-dibromine-*n*-oxybenzoic acid and copolyester with groups of terephthaloyl-bis(*n*-oxybenzoic) acid possess high mechanical and dielectric properties, thermal and fire resistance and also the chemical stability. The regularities of acceptor-catalyst method of polycondensation and high-temperature polycondensation when synthesizing named polymers have been studied and the relations between the composition, structure and properties of polymers obtained have been established. The synthesized here block-copolyesters and copolyesters can find application in various fields of modern industry (automobile, radioelectronic, electrotechnique, avia, electronic, chemical and others) as thermal resistant construction and layered (film) materials.

CHAPTER I. Literature review

1.1. Aromatic polyesters

Aromatic polyesters are polycondensation organic compounds containing complex ester groups, simple ester links and aromatic fragments within their macromolecule in different combination.

Aromatic polyesters (AP) are thermo-stable polymers; they are thermoplastic products useful for reprocessing into the articles and materials by means of formation methods from solutions and melts.

Mainly, plastics and films are produced from aromatic copolyesters. APs can be used also as lacquers, fibrous binding agents for synthetic paper, membranes, hollow fibers, as additions for semiproducts when obtaining materials based on other polymers.

Many articles based on APs appear in industry. The world production of APs increased from 38 millions of tons in 2004 to 50 in 2008, or on 32%. The polymers referred to the class of constructional plastics are distinguished among APs.

Until now, the technical progress in many fields of industry, especially in engineering industry, instrument production, was circumfused namely by the use of constructional plastics. Such exploitation properties of polymers as durability, thermal stability, electroisolation, antifriction properties, optical transparency and others determine their usage instead of ferrous and nonferrous metals, alloys, wood, ceramics and glass [13]. 1 ton of polymers replace 5-6 tons of ferrous and nonferrous metals and 3-3,5 tons of wood while the economy of labor expenses reaches 800 man-hours per 1 ton of polymers. About 50% of all polymers used in engineering industry are consumed in electrotechnique and electronics. The 80% of all the production of electrotechnique and up to 95% of that of engineering industry has been produced with help of polymers.

The use of construction plastics allows one to create principally new

technology of creation the details, machine knots and devices what provides for the high economical efficiency. The construction polymers are well utilized by means of modern methods: casting and extrusion to the articles operating in conditions of sign-altering loads at temperatures 100-200°C.

The modern chemical industry gave constructional thermoplastic materials with lowered consumption of material and weight of the machines, devices, mechanisms, reduced power capacities and labor-intensity when manufacturing and exploiting, increased stint.

Nowadays, the radioelectronics, electrotechnical, avia, shipbuilding and fields of industry can not develop successively without using the modern progressive polymers such as polyarylates, polysulfones, polyesterketones and others which are perspective construction materials. Only Russian industry involves 50 types of plastics including more than 850 labels and various modifications [14]. As a result, the specific weight of products of engineering areas and several other branches of industry produced with help of plastics grew from 32-35% in 1960 till 85-90% in 1990.

The specific weight of construction plastics among the total world production of plastics reached only 5% in 1975 [15]. But plastics of constructional use prevailed in world production of plastics in 1981-1985 [16].

The introduction of polymers has not only positive effect on the state of already existing traditional areas of industry but also determined the technical progress in rocket and atomic industries, aircraft industry, television, restorative surgery and medicine as a whole et cetera. The world production of construction polymers today is more than 10 million tons.

The thermal and heat-resistant constructional plastics take special place among the polymers. The need for such ones arises from fact that the use of traditional polymeric materials of technological assignment is limited by insufficient working thermal resistance, which is usually less than 103-150°C.

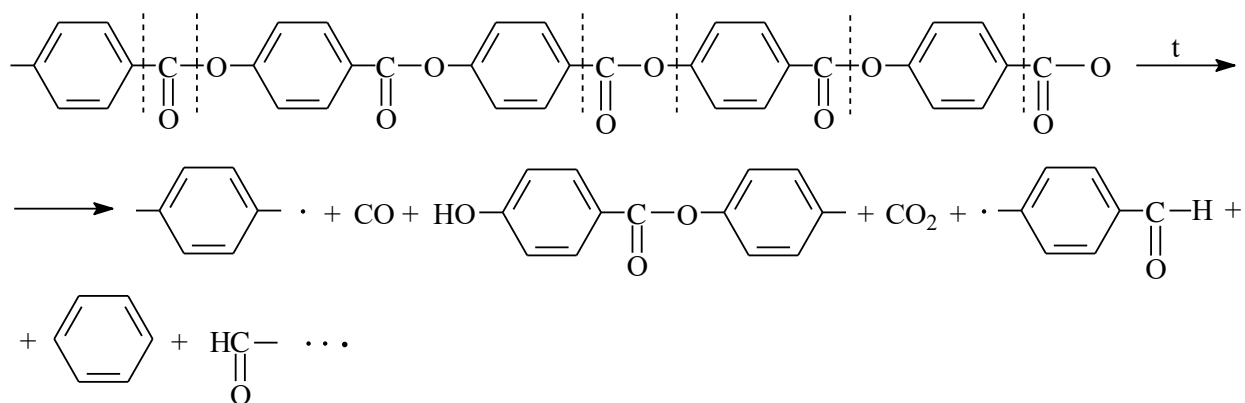
Two classes of polymers have been used for producing high-tonnage thermally resistant plastics: aromatic polyarylates and polyamides [17]. Starting with these and mutually complementing the properties, materials of high operation properties, and thermo-stable plastics of constructional assignment in the first turn, have been produced.

Some widely used and attractive classes of polymers of constructional assignment are considered in detail below.

1.2. Aromatic polyesters of *n*-oxybenzoic acid

The *n*-hydroxybenzoic (*n*-oxybenzoic) acid has been extensively used at polymeric synthesis for the improvement of thermal stability of polymers for the last years [18, 19]. The aromatic polyester “ECONOL”, homopolymer of poly-*n*-oxybenzoic acid, possesses the highest thermal resistant amongst the all homopolymeric polyethers [20] and attracts attention for the industry.

The poly-*n*-oxybenzoic acid is the linear high-crystalline polymer with decomposition temperature in inert environment of 550°C [20]. Below this point decomposition goes extremely slow. The loss in weight at 460°C in air is 3% during 1 hour of thermal treatment and than number is 1% at 400°C. The CO, CO₂ and phenol are released when decomposing in vacuum at temperatures 500-565°C, the coke remnant is of almost polyphenylene-like structure. It is assumed [27], that decomposition starts from breaking of ester bonds. The energy of activation of the process of fission of up to 30% of fly degradation products is 249,5 kJ/mol. The following mechanism for the destruction of polymer has been suggested:



The high ordering of polymer is kept till temperature 425°C. The equilibrium value of the heat of melting of polymers of *n*-oxybenzoic acid is found to be 5,4 kJ/mol [21].

Several methods for the producing the poly-*n*-oxybenzoic acid have been proposed [20, 23-30], which are based of the high-temperature polycondensation, because the phenol hydroxyl possesses low reaction ability. Usually more reactive chloranhydrides are used. The polycondensation of *n*-oxybenzoic acid with blocked hydroxyl group (or of corresponding chloranhydride) happens at temperature of 150°C and greater. The *n*-acetoxybenzoic acid [23, 24] or the *n*-oxybenzoic acid mixed with acylation agent Ac₂O [25-27] at presence of standard catalyst (in two stages: in solution at temperature 180-280°C and in solid phase at temperature 300-400°C) as well as chloranhydride of *n*-oxybenzoic acid [34], or the reaction of *n*-oxybenzoic acid with acidic halogenating agent (for example, SOCl₂, PCl₃, PCl₅) [29] have been used at synthesis of high-molecular polymer aiming to increase the reactivity.

Besides the *n*-oxybenzoic acid, its replaced in core derivatives (with F, Cl, Br, J, Me, Et etc. as replacers) can be used as initial materials in polycondensation processes. However, the low-molecular polymer of logarithmic viscosity equal to 0,16 is formed at polycondensation of methyl-replaced *n*-oxybenzoic acid in presence of triphenylphosphite [37] which is associated to the elapsing of adverse reaction of intramolecular etherification with triphenyl phosphite, resulting in termination of chain. This reaction does not flow when using PCl₃. High heat- and

thermo-stable polyesters of *n*-oxybenzoic acid of given molecular weight containing no edge COOH-groups can be obtained by heating of *n*-oxybenzoic acid mixed with dialkylcarbonate at 230-400°C [20].

The high-molecular polymer can be produced from phenyl ester of *n*-oxybenzoic acid at presence of butyltitanate in perchloroligophenylene at heating in current nitrogen during 4 hours at temperatures 170-190°C and later after 10 hours of exposure to 340-360°C [20]. Usually [32], Ti, Sn, Pb, Bi, Na, K, Zn or their oxides, salts of acetic, chlorohydratic or benzoic acid are used as catalysts of polycondensation processes when producing polyesters. The polycondensation of polymers of oxybenzoic acids and their derivatives has been performed at absence of catalysts [33] in current nitrogen at temperatures 180-250°C and pressure during 5-6 hours either. The temperature of polycondensation can be lowered [34] if it is carried out in polyphosphoric acid or using activating COOH- group of the substance.

Interesting investigation on study of structure characteristics of polyesters and copolyesters of *n*-oxybenzoic acid have been performed in [35, 36]. The introduction of links of *n*-oxybenzoic acid results in high-molecular compounds of ordered packing of chains, similar to the structure of high-temperature hexagonal modification of homopolymer of *n*-oxybenzoic acid [37, 38]. The presence of fragments of *n*-oxybenzoic acid in macromolecular chain of the polymer not only increases the thermal resistance but improves the physic-chemical characteristics of polymeric materials. Obtained polyesters, consisting of monomers of *n*-oxybenzoic acid and *n*-dioxyarylene (of formula HO-Ar-OH, where Ar denotes bisphenylene, bisphenylenoxide, bisphenylensulfone), possess higher breaking impact strength, than articles from industrial polyester [39]. The data on thermogravimetric analysis of homopolymer of *n*-oxybenzoic acid and its polyesters with 4,4'-dioxybisphenylpropane, tere- or isophthalic acids are presented in [21]. The temperature of 10% loss of mass is 454,482, 504°C for them correspondingly.

Highly durable, chemically inert, thermo-stable aromatic polyesters can be produced by interaction of polymers containing links of *n*-oxybenzoic acid, aromatic dioxy-compounds, for example of hydroquinone and aromatic dicarboxylic acids [40]. Thermo- and chemically resistant polyesters of improved mechanical strength can be obtained by the reaction of *n*-oxybenzoic acid, aromatic dicarboxylic acids, aromatic dioxy-compounds and diaryl carbonates held in solid phase or in high-boiling solvents [41] at temperature 180°C and lowered pressure, possibly in the presence of catalysts [42]. Some characteristics of aromatic polyesters based on *n*-oxybenzoic acid are gathered in Table 1 [20].

As mentioned above, the thermal stability of polymers is closely tied to the manifestation of fire-protection properties. Many factors causing the stability of the materials to the exposure of high temperatures are characteristic for the fire-resistant polymers too.

Thermally stable polyesters can be produced on the basis of *n*-oxybenzoic acid involving stabilizer (triphenylphosphate) introduced on the last stage. The speed of the weight loss decreases two times, after 3 hours of exposure to 500°C polymer loses 0,87% of mass [43].

The high strength high-modular fiber with increased thermo- and fire-resistance can be formed from liquid-crystal copolyester containing 5-95 mol % of *n*-oxybenzoic acid.

The phosphorus is used as fire-resistant addition, in such a case the oxygen index of the fiber reaches 65% [44].

40-70 mol % of the compound of formula $\text{Ac-}n\text{-C}_6\text{H}_4\text{COOH}$ are used to produce complex polyesters of high mechanical strength [45]. The polyesters with improved physic-chemical characteristics can be obtained by single-stage polycondensation of the melt of 30-60 mol % of *n*-oxybenzoic acid mixed with other ingredients [46].

Table 1

**Physic-mechanical properties of aromatic polyesters
based on *n*-oxybenzoic acid**

Composition of polyesters	Heat resistance on vetch, C, °C	Bending strength, MPa	Flex modulus, N/sm ²	Breaking strength, MPa	Elasticity modulus when break, N/sm ²
<i>n</i> -oxybenzoic acid, terephthalic acid,	-	-	-	35,5	35000
4,4'-bisphenylquinone				157	47000
<i>n</i> -oxybenzoic acid, isophthalic acid, hydroquinone, 4,4'-benzophenon dicarboxylic acid	141	163	10270	-	-
<i>n</i> -oxybenzoic acid, isophthalic acid, hydroquinone, bisphenylcarbonate	-	-	493	120,5	-
<i>n</i> -oxybenzoic acid, isophthalic acid, hydroquinone, 4,4'-bis-hydroxydiphenoxide or bisphenol S	130	160	6100	-	-
<i>n</i> -oxybenzoic acid, isophthalic acid, hydroquinone, 3-chlor- <i>n</i> -oxybenzoic acid and bisphenol D	133	232	10260	-	-

The most used at synthesizing aromatic polyesters are the halogen-replaced anhydrides of dicarboxylic acids and aromatic dioxy-compounds of various constitutions. However, the growing content of halogens in polyesters obtained from mono-, bis- or tetra-replaced terephthalic acid [46] results in lowering of temperatures of glassing, melting as well as of the degree of crystallinity and to some decrease in mechanical strength for halogen-replaced bisphenols. Chlorine- and bromine-containing antipyrenes worsen the thermal resistance of polyesters and are usually used in a company with stabilizers [47, 48]. (Antipyrenes are

chemical substances, either inorganic or organic, containing phosphorus, halogen, nitrogen, boron, metals which are used for the lowering of the flammability of polymeric materials).

Besides, the usage of halogen-replaced bisphenols and dicarboxylic acids for synthesizing polyesters of lowered flammability considerably increases the cost of the latter. Consequently, the aromatic inhibiting flame additions are necessary for creating thermally and fire resistant polymeric materials. The introduction of such agents in small amounts would not diminish properties of polyesters.

Accounting for the aforesaid, one can assume that the chemical modification of known thermally resistant polyesters, by means of introduction of solid component (halogen-containing *n*-oxybenzoic acid) can help to solve the problem of increasing of fire safety of polyesters without worsening of their properties. It is obvious [49], that to replace one should intentionally use bromine atoms which are more effective in conditions of open fire compared to atoms of other halogens.

So, as it comes from the above, the reactive compound involving halogens are widely used for imparting fire-protection properties to aromatic polyesters, as well as oligomer and polymeric antipyrenes.

The liquid-crystal polyesters (LQPs) became quite popular within the last decades. Those differ in their ability to self-arm, possess low coefficient of linear thermal expansion, have extreme size stability, are very chemically stable and almost do not burn.

LQPs can be obtained by means of polycondensation of aromatic oxy-acids (*n*-oxybenzoic one), dicarboxylic acids (iso- and terephthalic ones) and bisphenols (static copolymers) and also by peretherification of polymers and monomers.

Depending on the degree of ordering, LQPs are classified as smectic, nematic and cholesterol ones. Compounds, able to form liquid-crystal state, consist of long flat and quite rigid, in respect to the major axis, molecules.

LQPs can be obtained by several cases:

- Polycondensation of dicarboxylic acids with acetylic derivatives of aromatic oxy-acids (*n*-oxybenzoic one) and bisphenols.
- Polycondensation of phenyl esters of aromatic oxy-acids (*n*-oxybenzoic one) and aromatic dicarboxylic acids with bisphenols.
- Polycondensation of dichloranhydrides of aromatic dicarboxylic acids and bisphenols.
- Copolycondensation of dicarboxylic acids, diacetated of bisphenols and/or acetated of aromatic oxy-acids (*n*-oxybenzoic one) with polyethyleneterephthalate.

Liquid crystal copolyesters have been synthesized [50-56] on the basis of *n*-acetoxybenzoic acid, acetoxybisphenol, terephthalic acid and *m*-acetoxybenzoic acid by means of polycondensation in melt. All the copolyesters are thermotropic and form nematic phase. The types of LQPs of *n*-oxybenzoic acid are given in Table 2.

LQPs can be characterized by high physic-chemical parameters, see Table 3.

The fiber possessing high strength properties is formed from the melt of such copolyesters at high temperatures.

The synthesis of totally aromatic thermo-reactive complex copolyesters based on *n*-oxybenzoic acid, terephthalic acid, aromatic diols and alyphatic acids has been performed by means of polycondensation in melt [57-61].

Complex copolyesters are nematic static copolyesters.

The analysis of patents shows that various methods have been proposed for the production of liquid-crystal complex copolyesters [62-64].

Table 2

Label assortment of thermotropic liquid-crystal polyesters of *n*-oxybenzoic acids

Company	Country	Trade label	Remarks
1	2	3	
Dartco Manufacturing Inc.	USA	Xydar	Polyester based on <i>n</i> -oxybenzoic acid, terephthalic acid and <i>n,n</i> -bisphenol
		SRT – 300	Unfilled with normal fluidity
		SRT – 500	Unfilled with high fluidity
		FSR – 315	50 % of talca
		MD – 25	50 % of glass fiber
		FC – 110	Glass-filled
		FC – 120	Glass-filled
		FC – 130	Mineral filler
		RC – 210	Mineral filler
		RC – 220	Glass-filled
LNP Corp.		Thermocomp	Xydar + 150 polytetrafluorethylene (antifriction)

RTP Co		FDX - 65194	Xydar compositions: glass-filled with finishing and thermal-stabilizing additions, mineral fillers
Celanese Corp.		Vectra	Polyesters based on <i>n</i> -oxybenzoic acid and naphthalene derivatives
Celanese Corp.		A – 130	30 % of glass fiber
		B – 130	30 % of glass fiber
		A – 230	30 % of carbon fiber
		B - 230	30 % of glass fiber
		A – 540	40 % of mineral filler
		A – 900	Unfilled
		A – 950	Unfilled
Eastman Kodak Co	USA	Vectron	Copolyesters based on <i>n</i> -oxybenzoic acid and polyethyleneterephthalate
		LCC – 10108	
		LCC – 10109	
BASF	Germany	Ultrax	Re-replaced complex aromatic polyester
Bayer A.G.	Germany	Ultrax	Aromatic polyester

1	2	3	4
ICI	Great Britain	Victrex	Polyester based on <i>n</i> -oxybenzoic acid and acetoxynaphtoic acid
		SRP – 1500G	Unfilled
		SRP – 1500G–30	27 % of glass fiber
		SRP – 2300G	Unfilled (special design)
		SRP – 2300G- 30	27 % of glass fiber (special design)
Sumimoto kagaku koge K.K	Japan	Ekonol – RE -6000	Polyester based on <i>n</i> -oxybenzoic acid, isophthalic acid and bisphenol
Japan Elano Co		Ekonol	Fiber
Mitsubishi chemical Co		Ekonol	Aromatic polyester
Unitica K.K.		LC – 2000	Polyesters based on <i>n</i> -oxybenzoic acid and terephthalic acid
		LC – 3000	
		LC - 6000	

Table 3

**Physic-mechanical properties of some liquid-crystal polyesters
of *n*-oxybenzoic acid**

Property	Xydar			Vectra				
	SRT-300	SRT-350	FSR-315	A-625 (chem. stable)	A-515 (highly fluid)	A-420 (wear resistant)	A-130 (filled with glass fiber)	C-130 (highly thermal resistant)
Density, g/cm ³	1,35	1,35	1,4	1,54	1,48	1,88	1,57	1,57
Tensile limit, MPa	115,8	125,5	81,4	170	180	140	200	165
Modulus in tension, GPa	9,65	8,27	8,96	10	12	20	17	16
Transverse strength, MPa	131,0	131,0	111,7	-	-	-	-	-
Izod impact, J/m of samples with cut	128,0	208	75	130	370	100	135	120
of samples without cut	390,0	186	272	-	-	-	-	-
Tensile elongation, %	4,9	4,8	3,3	6,9	4,4	1,3	2,2	1,9
Deformation heat resistance (at 1,8 MPa), °C	-	-	-	185	188	225	230	240
Heat resistance on vetch, °C	366	358	353	-	-	-	-	-
Arc resistance, sec	138	138	-	-	-	-	-	-
Dielectric constant at 10 ⁶ Hz	3,94	3,94	-	-	-	-	-	-
Dielectric loss tangent at 10 ⁶ Hz	0,039	0,039	-	-	-	-	-	-

The description of methods for production of copolymers (having repetitive links from derivatives of *n*-oxybenzoic acid, 6-oxy-2-naphthoic acid, terephthalic acid and aromatic diol) formable from the melt is reported in papers [65-68]. Each repetitive link is in certain amounts within the polymer. All these copolymers are used as protective covers.

The thermotropic liquid-crystal copolyesters can be synthesized also on the basis of *n*-oxybenzoic and 2,6-oxynaphthoic acid at presence of catalysts (sodium and calcium acetates) [69, 70]. The catalyst sodium acetate accelerates the process of synthesis. Calcium acetate accelerates the process only at high concentration of the catalyst and influences on the morphology of complex copolyesters.

The syntheses of copolymers of *n*-oxybenzoic acid with polyethyleneterephthalate and other components are possible too [71-75]. It is established that copolymers have two-phase nature: if polyethyleneterephthalate is introduced into the reaction mix then copolymers of block-structure are formed.

The properties of liquid-crystal copolyesters based on *n*-oxybenzoic acid and oxynaphthoic acid (in various ratios and temperatures) are described in papers [76-81]. It was shown therein that the plates from such polymers formed by die casting are highly anisotropic which results in appearance of the layered structure. Those nematic liquid crystals had ferroelectric ordering. Following substances are characterized in [82-85]: aromatic copolyesters of *n*-oxybenzoate/bisphenol A; those based on *n*-oxybenzoic acid, bisphenol and terephthalic acid; based on 40 molar % *n*-oxybenzoic acid, 30 molar % *n*-hydroquinone and isophthalic acid; and those based on *n*-oxybenzoic acid, *n*-hydroquinone and 2,6-naphthalenedicarboxylic acid. The influence of temperature, warm-up time and heating rate on the properties of copolyesters was studied: the glass-transition temperature was shown to increase with warm-up expanded. The number of works is devoted to the study of the complex of physic-chemical properties of liquid-

crystal copolyesters based on *n*-oxybenzoic acid and polyethyleneterephthalate [86-97]. It was established that mixes up to 75% of liquid-crystal compound melt and solidify like pure polyethyleneterephthalate. Copolyesters, containing less than 30% of *n*-oxybenzoic acid, are in isotropic glassy state while copolyesters of higher concentration of the second compound are in liquid-crystal phase and can be characterized by bigger electric inductivity, than in glassy state. This distinction is caused by the existence of differing orientational distribution of major axes in relation to the direction of electric field in various structure instances of copolyesters. The data of IR-spectroscopy reveal that components of the mix interact in melt by means of re-etherification reaction. Increasing pressure, decreasing free volume and mobility in the mix, one can delay the reaction between the compounds.

The investigation of the properties of liquid-crystal copolyesters based on *n*-oxybenzoic acid / polyethyleneterephthalate and their mixes with isotactic polypropylene (PP), polymethylmethacrylate, polysulfone, polyethylene-2,6-naphthalate, copolyester of *n*-oxybenzoic acid 6,2-oxynaphthoic acid continues in papers [98-106]. Specific volume, thermal expansion coefficient α and compressibility β were measured for PP mixed with liquid-crystal copolymer *n*-oxybenzoic acid / polyethyleneterephthalate. The high pressure results in appearance of ordering in melted PP. The increase of α and β for all mixes studied (100-25% PP) has been observed at temperatures about melting point of PP having those parameters for liquid-crystal copolyester changed inconsiderably. Increasing content of liquid-crystal copolyester in the mix remarkably decreases the value of α both in solid state and in area of melting PP. The latter has to be accounted for when producing articles. The liquid-crystal compound is grouped in shape of concentric cylinders of various radii in mixes with polysulphones. It becomes responsible for the viscous properties of the mixes at above conditions.

Piezoelectric can be produced from liquid-crystal polymers based on *n*-oxybenzoic acid / polyethyleneterephthalate and *n*-oxybenzoic acid / oxynaphthoic

acid. Time-stability and temperature range of efficiency of piezoelectric from polymer made of 6,2-oxynaphthoic acid are higher compared to that of polyethyleneterephthalate.

It was found that the use of 30% liquid-crystal copolyester of *n*-oxybenzoic acid / polyethyleneterephthalate makes polymethylmethacrylate 30% more durable and increases the elasticity modulus on 110%, with the reprocessibility being the same.

The structure and properties of various liquid-crystal copolymers are studied in papers [107-112]. For example, copolymers based on *n*-oxybenzoic acid, polyethyleneterephthalate, hydroquinone and terephthalic acid, are studied in [107]: the introduction of the mix hydroquinone / terephthalic acid accelerates the process of crystallization and increases the degree of crystallinity of polyesters.

The existence of two structure areas of melts of copolyesters, namely of low-temperature one (where high-melting crystals are present in nematic phase) and high-temperature other (where the homogeneous nematic alloy is formed) is revealed when studying the curves of fluxes of homogeneous and heterogeneous melts of copolyesters based on polyethyleneterephthalate and acetoxybenzoic acid [108].

The curves of flux of liquid-crystal melt are typical for viscoplastic systems while the trend for the flow limit to exist becomes more evident with increasing molar mass and decreasing temperature. Essentially higher quantities of molecular orientation and strength correspond to extrudates obtained from the homogeneous melt compared to extrudates produced from heterophase melt. The influence of high-melting crystallites on the process of disorientation of the structure and on the worsening of durability of extrudates becomes stronger with increasing contribution of mesogenic fragment within the chain.

When studying structure of liquid-crystal copolymers based on *n*-oxybenzoic acid / polyethyleneterephthalate and *m*-acetoxybenzoic acid by means

of IR-spectroscopy, ^1H nuclear magnetic resonance and large angle X-ray scattering, the degree of ordering in copolymers was shown [109] to increase if concentration of *n*-oxybenzoic units went from 60 till 75%.

When studying properties of copolymers *n*-oxybenzoate / ethyleneterephthalate / *m*-oxybenzoate with help of thermogravimetry [110] the thermo-decomposition of copolymers was found to happen at temperatures 450-457°C in N_2 and 441-447 °C in air. The influence of the ratio of *n*- and *m*-isomers was regarded, the coal yield at $T > 500$ °C found to be 42,6% and increasing with growing number of *n*-oxybenzoic units.

The mixing of melts poly-4,4'-oxybenzoic acid / polyethyleneterephthalate was studied in paper [111]: the kinetic characteristics of the mix became incompatible at re-etherification.

The measurement of glassing temperature T_{glass} [112] of thermotropic liquid-crystal polyesters synthesized from 4-acetoxybenzoic acid (component *A*), polyethyleneterephthalate (component *B*) and 4-acetoxy-hydrofluoric acid revealed that the esters could be characterized by two phases, to which two glassing temperatures correspond: $T_{\text{glass}} = 66\text{-}83$ °C and $T_{\text{glass}} = 136\text{-}140$ °C. The lower point belongs to the phase enriched in *B*, while higher one – to phase enriched in *A*.

Liquid-crystal polymers are most applicable among novel types of plastics nowadays. The chemical industry is considered to be the one of perspective areas of using liquid-crystal polymers where they can be used, because of their high thermal and corrosion stability, for replacement of stainless steel and ceramics.

Electronics and electrotechnique are considered as promising areas of application of liquid-crystal polymers. In electronics, however, liquid-crystal polymers meet acute competition from cheaper epoxide resins and polysulfone. Another possible areas of using high-heat-resistant liquid crystal polymers are avia, space and military technique, fiber optics (cover of optical cable and so on), auto industry and film production.

The question of improving fire-resistance of aromatic polyesters is paid more attention last time. Polymeric materials can be classified on criterion of combustibility: noncombustible, hard-to-burn and combustible. Aromatic polyesters enter the combustible group of polymers self-attenuating when taken out of fire.

The considerable fire-resistance of polymeric materials and also the conservation of their form and sizes are required when polymers are exploited to hard conditions such as presence of open fire, oxygen environment, exposure to high-temperature heat fluxes.

On the assumption of placed request, the extensive studies on both syntheses of aromatic polyesters of improved fire-resistance and modification of existing samples of polymers of given type have been carried out. The most used methods of combustibility lowering are following:

- coating by fireproof covers;
- introduction of filler;
- directed synthesis of polymers;
- introduction of antipyrenes;
- chemical modification.

The chemical modification is the widely used, easily manageable method of improving the fire resistance of polymers. It can be done synthetically, simultaneously with the copolymerization with reactive modifier via, for example, introduction of replaced bisphenols, various acids, other oxy-compounds. Or it can be done by addition of reactive agents during the process of mechanic-chemical treatment or at the stage of reprocessing of polymer melt [113].

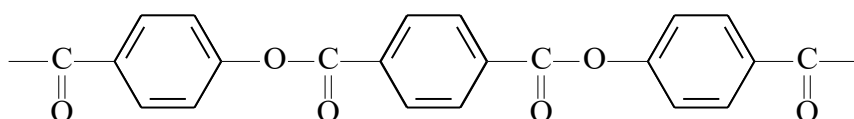
The most acceptable ways of modification of aromatic polyesters aimed to get self-attenuating materials of improved resistance to aggressive media are the

condensation of polymers from halogen-containing monomers, the combination of aromatic polyesters with halogen-containing compounds and the use of halogen-involving coupling agents [114, 115].

Very different components (aromatic and aliphatic) can become modifiers. They inhibit the processes of combustion and are able to not only to attach some new features to polymers but also improve their physical properties.

1.3. Aromatic polyesters of terephthaloyl-bis-(*n*-oxybenzoic) acid

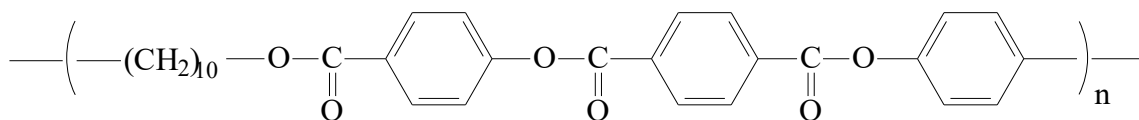
Among known classes of polymers the aromatic polyesters with rigid groups of terephthaloyl-bis-(*n*-oxybenzoic) acid in main chain of next formula attract considerable attention:



The polymers with alternating terephthaloyl-bis(*n*-oxybenzoic) rigid (R) mesogenic groups and flexible (F) decouplings of various chemical structure within the main chain (RF-copolymers) are able to form liquid-crystal order in the melt. The interest to such polymers is reasoned by fact that dilution of mesogenic “backbone” of macromolecule by flexible decouplings allows one to change the temperature border of polymer transfer from the partially-crystalline state into the liquid-crystal one and also to change the interval of existence of liquid-crystal melt. The typical representatives of such class of polymers are polyesters with methylene flexible decouplings.

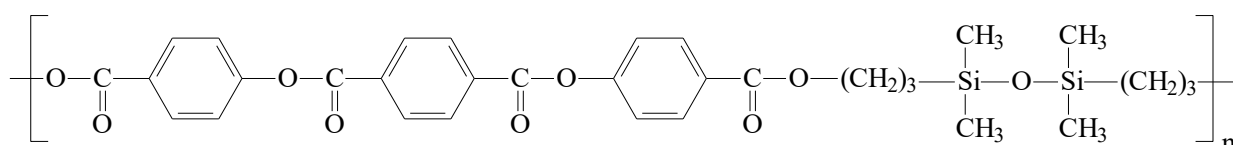
These polymers have been synthesized by high-temperature polycondensation of terephthaloyl-bis(*n*-oxybenzoylchloride) with appropriate diols in high-boiling dissolvent under the pressure of inert gas. Bisphenyloxide is used as dissolvent.

The features of conformation, orientation order, molecular dynamics of mentioned class of polymers are studied in [116-119] on the basis of polydecamethyleneterephthaloyl-bis(*n*-oxybenzoate), P-10-MTOB, which range of liquid-crystallinity is from 230 °C till 290 °C.



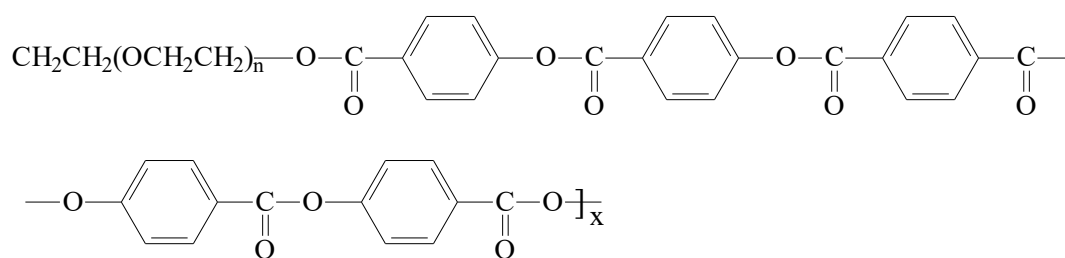
The study of polyesters with terephthaloyl-bis(*n*-oxybenzoate) groups continues in papers [120-123]. The oxyethylene (CH₂CH₂O)_{*n*} and oxypropylene (CH₂CHCH₃O)_{*n*} groups are used as flexible decouplings. It was found for oxyethylene decouplings that mesophase did not form if flexible segment was 3 times longer than rigid one. The folding of flexible decoupling was found to be responsible for the formation of ordered mesophase in polymers with long flexible decoupling. It was observed that polymers are able to form smectic and nematic liquid-crystal phases, the diapason of existence of which is determined by the length of flexible fragments.

The reported in [124] were the data on polymers containing methylene siloxane decouplings in their main chain:



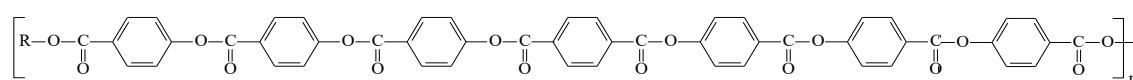
The polymer was produced by heating of dichloranhydride of terephthaloyl-bis(*n*-oxybenzoic) acid, 1,1,3,3-tetramethylene-1,3-bis-(3-hydroxypropyl)-bis-siloxane and triethylamine in ratio 1:1:2 respectively in environment of chloroform in argon atmosphere. The studied were the fibers obtained by mechanical extrusion from liquid-crystal melt when heating initial sample. The polymer's characteristic structure was of smectic type with folding location of molecules within layers.

The study of liquid-crystal state was performed in [125] on polymers with extended (up to 5 phenylene rings) mesogenic group of various lengths of flexible oxyethylene decouplings:



All polymers were obtained by means of high-temperature acceptor-free polycondensation of terephthaloyl-bis(*n*-oxybenzoylchloride) with bis-4-oxybenzoyl derivatives of corresponding polyethylene glycols in solutions of high-boiling dissolvent in current inert gas. Copolyesters with mesogenic groups, extended up to 5 phenylene cycles and up to 15-17 oxyethylene links, are able to form the structure of nematic type.

Polymers can also form the systems of smectic type [126]. The studied in paper [127] was the mesomorphic structure of polymer with extended group polyethylene glycol-1000-terephthaloyl-bis-4-oxybenzoyl-bis-4'-oxybenzoyl-bis-4''-oxybenzoate:



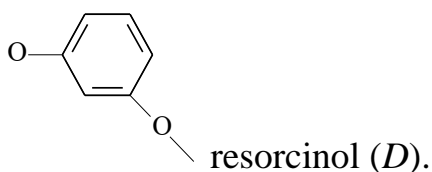
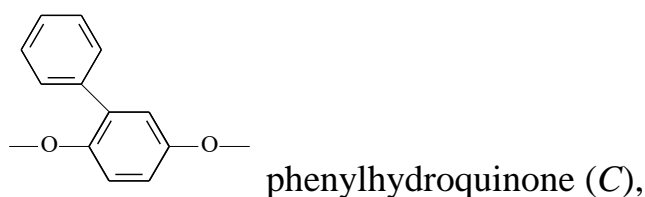
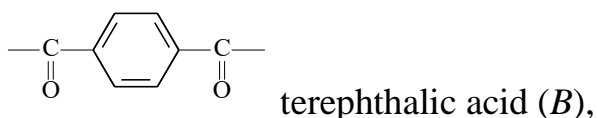
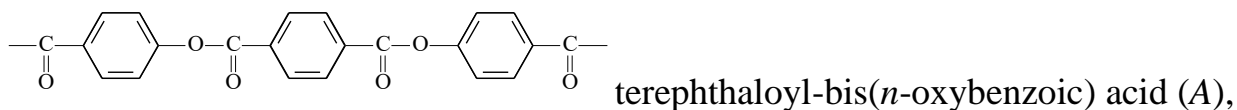
This polymer (of formula $R=CH_2CH_2(OCH_2CH_2)_{18-20}$) was synthesized by means of high-temperature acceptor-free polycondensation of terephthaloyl-bis-4-oxybenzoate with bis-(4-oxybenzoyl-4'-oxybenzoyl) derivative polyethylene glycol-1000 in the environment of bisphenyloxide [128]. The X-ray diffraction pattern revealed that the regularity of layered order weakened with rising temperature while ordering between mesogenic groups in edge direction kept the same. That type of specific liquid-crystal state in named polymer formed because of melting of layers including flexible oxyethylene decouplings at keeping of the ordering in transversal direction between mesogenic groups.

The paper [129] was devoted to the study of the molecular mobility of polymer which formed mesophase of smectic type in temperature range 223-298 °C. Selectively deuterated polymers were synthesized to study the dynamics of different fragments of polymer in focus. That polymer was found to have several co-existing types of motion of mesogenic fragment and decoupling at the same

temperature. There were massive vibration of phenylene cycles with varying amplitude and theoretically predicted movements of polymethylene chains [130]: trans-gosh-isomerization and translation motions involving many bonds. Such coexistence was determined by the phase micro-heterogeneity of polymers investigated.

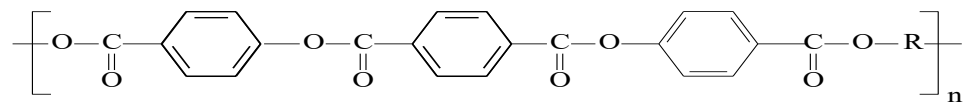
The process of polycondensation of terephthaloyl-bis(*n*-oxybenzoylchloride) with decamethyleneglycol resulting in liquid-crystal polyester was studied in [131]. The monomers containing groups of complex esters entered into the reaction with diols at sufficiently high temperature (190 °C).

The relatively low contribution of adverse reactions compared to the main one led to regular structure of final polyester. The totally aromatic polyesters of following chemical constitution were studied in [132]: polymer “ΦTT-40” consisting of three monomers (terephthaloyl-bis(*n*-oxybenzoic) acid, terephthalic acid, phenylhydroquinone and resorcinol) entering to the polymeric chain in quantities 2:3:5. Terephthalic acid was replaced with monomer containing phenylene cycle in meta-place in polymer “ΦΓP-80”.



The monomers entered to the polymeric chain in ratio $A:C:D=5:4:1$. These polymers melted at temperatures 300-310 °C and switched to liquid-crystal state of nematic type. The monomers in “ΦTT-40” were found to be distributed statistically.

The influence of chemical structure of flexible decouplings in polyterephthaloyl-bis(*n*-oxybenzoates) on their mesogenic properties was studied in [131]. The studied were the polymers which had asymmetrical centers introduced into the flexible methylene decoupling and also complex ester groups:



$\text{R}=\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ (I); $\text{R}=\text{CH}(\text{R}')\text{COOCH}_2\text{CH}_2$ (II, I)

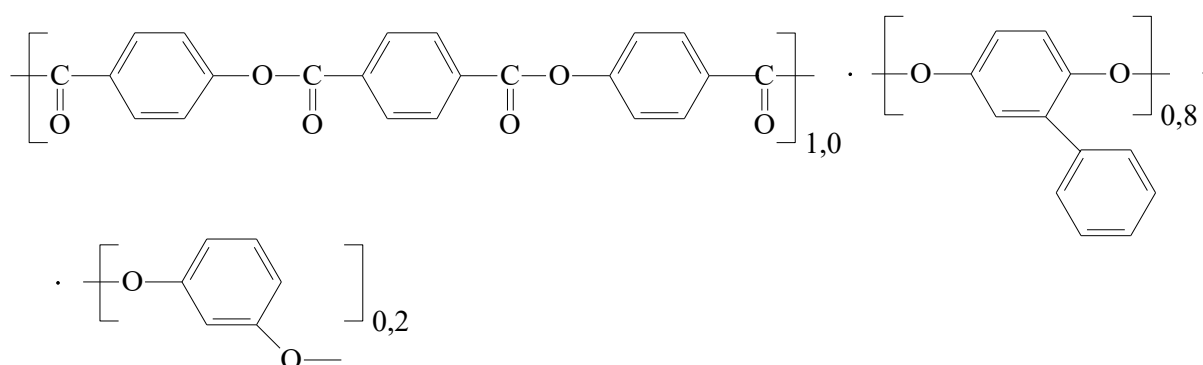
where $\text{R}'=\text{CH}(\text{CH}_3)_2$ (II) or $\text{CH}_2\text{CH}_2(\text{CH}_3)$ (III).

The polymer I was synthesized by means of high-temperature acceptor-free polycondensation from dichloranhydride of terephthaloyl-bis(*n*-oxybenzoic) acid and 2-methylhexa-methylene-1,5-diol in inert dissolvent (bisphenyloxide at 200 °C). The phase state of polymer I at room temperature was found to depend on the way of sample preparation. The samples obtained from polymer immediately after synthesis and those cooled from melt were in mesomorphic state, but dried from the solutions in trifluoroacetic acid were in partially-crystalline state.

The polymers II and III were in partially-crystalline state at room temperature irrespective from the method of production.

So, the introduction of asymmetrical center into the flexible pentamethylene decoupling did not change the type of the phase state in the melt and did not influence on the temperature of the transitions into the area of existing of liquid-crystal phase. However, increasing of the rigidity of methylene decouplings via the introduction of complex-ester groups and enlarging of the volume of side branches considerably influenced on the character of intermolecular interaction what resulted in the formation of mesomorphic state of 3D structure during the melting of polymers.

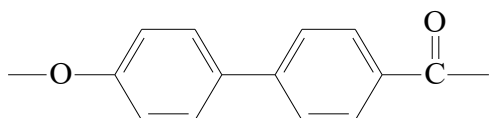
The conformational and optic properties of aromatic copolyesters with links of terephthaloyl-bis(*n*-oxybenzoic) acid, phenylhydroquinone and resorcinol, containing 5% (from total number of para-aromatic cycles) of m-phenylene cycles within the main chain were studied in [134]. The polymer had the structure:



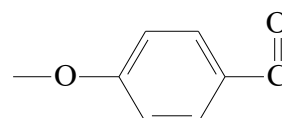
It was determined that the length of statistic Kuhn segment A was $200 \pm 20 \text{ \AA}$, the degree of dormancy of intramolecular rotations $(\sigma^{-2})^{1/2} = 1,08$, the interval of molar masses started with 3,1 and ended $29,9 \times 10^3$.

The analysis of literature data shows that the use of bisphenyl derivatives as elements of structure of polymeric chain allows one to produce liquid crystal polyesters, reprocessable from the melt into the articles of high deformation-strength properties and high heat resistance.

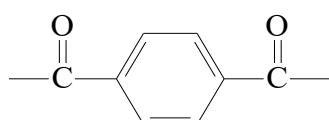
The polyethers containing mesogenic group and various bisphenylene fragments were synthesized in [135]:



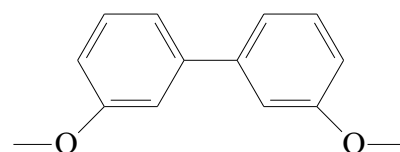
links of 4-oxybisphenyl-4-carbonic acid,



links of *n*-oxybenzoic acid,

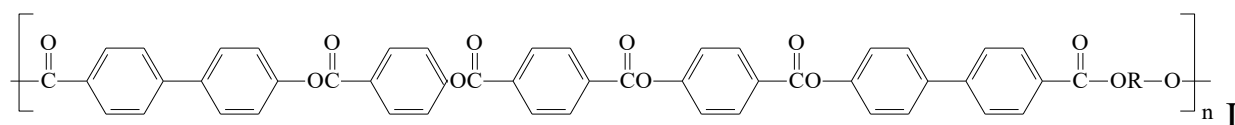


links of terephthalic acid,



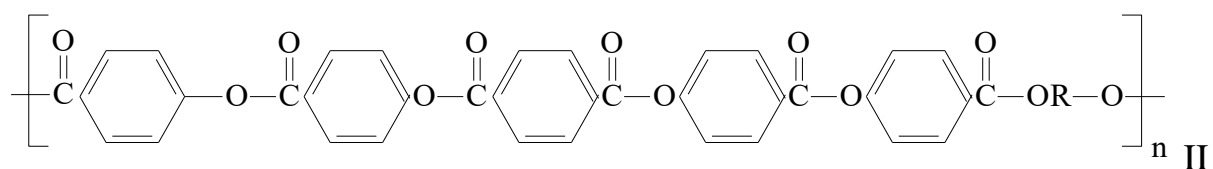
links of dihydroxylic bisphenyls of (3,3'-dioxylbisphenyl).

All were linked with various decouplings within the main chain of next kinds:



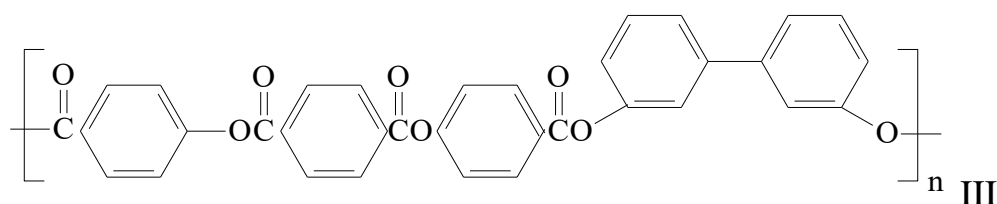
poly(alkyleneterephthaloyl-bis-4-oxybisphenyl-4'-carboxylate)

$[\eta] = 0,78$ deciliter/gram $T_{\text{glass}} = 160 \text{ }^\circ\text{C}$, $T_{\text{vapor}} = 272 \text{ }^\circ\text{C}$, where $R = (\text{CH}_2)_6$; $(\text{CH}_2)_{10}$

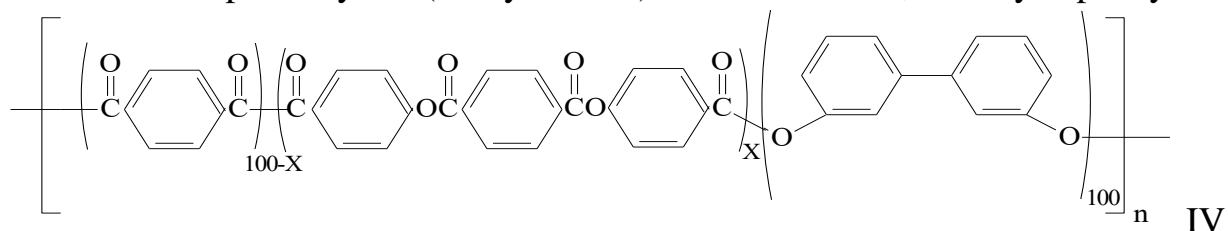


poly(oxyalkyleneterephthaloyl-bis-4-oxybenzoyl-4'-oxybenzoate,

where $\text{R} = -\text{CH}_2-\text{CH}_2\text{OCH}_2-\text{CH}_2-$; $-(\text{CH}_2\text{CH}_2\text{O})_2-\text{CH}_2\text{CH}_2-$ oxyethylene decouplings; polyethylene glycols (PEG) PEG 200, PEG 300, PEG 400, PEG 600, PEG 1000 – polyoxyethylene decouplings of various molecular weights and copolymers based on 3,3'-dioxybisphenyl with elements of regularity within the main chain:



links of terephthaloyl-bis(*n*-oxybenzoic) acid – links of 3,3'-dioxybisphenyl



links of terephthalic acid – links of terephthaloyl-bis(*n*-oxybenzoic) acid – links of 3,3'-dioxybisphenyl.

The synthesized in [136] were the block-copolymers containing the links of terephthaloyl-bis(*n*-oxybenzoate) and polyarylate. It was found that such polymers had liquid-crystal nematic phase and the biphasic separation occurred at temperatures above 280 °C.

The thermotropic liquid-crystal copolyester of polyethyleneterephthalate and terephthaloyl-bis(*n*-oxybenzoate) was described in [137]. The snapshots of polarized microscopy revealed that copolyester was nematic liquid-crystal one.

When studying the reaction of re-etherification happening in the mix 50:50 of polybutyleneterephthalate and complex polyester, containing mesogenic sections from the remnants of *n*-oxybenzoic (I) and terephthalic (II) acids separated by the tetramethylene decouplings the content of four triads with central link (I)

and three triads with central link II was determined in [138]. The distribution of triad sequences approximated to the characteristic one for statistical copolymer with increasing of the exposure time.

The relaxation of liquid-crystal thermotropic polymethyleneterephthaloyl-bis(*n*-oxybenzoate) was studied in [139]: the β -relaxation occurred at low temperatures while α -relaxation took place at temperatures above 20 °C (β -relaxation is associated with local motion of mesogenic groups while α -relaxation is caused by the glassing in amorphous state). It was established that the presence of ordering both in crystals and in nematic mesophase expanded relaxation.

So, the liquid-crystal nematic ordering is observed, predominantly, in considered above polymeric systems containing links of terephthaloyl-bis(*n*-oxybenzoic) acid [140] and combining features of both polymers and liquid crystals. Such ordering can be characterized by the fact that long axes of mesogenic groups are adjusted along some axis and the far translational ordering in distribution of molecules and links is totally absent.

The analysis of references demonstrates that polyesters with links of terephthaloyl-bis(*n*-oxybenzoic) acid can be characterized by the set of high physico-mechanical and chemical properties.

That is why we have synthesized novel copolymers on the basis of dichloranhydride of terephthaloyl-bis(*n*-oxybenzoic) acid and various aromatic oligoesters.

1.4. Aromatic polyarylenesterketones

The acceleration of technical progress, the broadening of assortment of chemical production, the increment of the productivity of labor and quality of items from plastics are to a great extent linked to synthesis, mastering and application of new types of polymeric materials. New polymers of improved resistance to air, heat form-stability, longevity appeared to meet the needs of air and space technique. Filling and reinforcement can help to increase the heat resistance on about 100 °C. Plastics enduring the burden in temperature range 150-180 °C are called

The paper [202] reports on the synthesis of liquid-crystal polysulfone with mesogenic link – cholesteryl pentoatesulfone.

The effect of compatibility, morphology, rheology, mechanical properties of mixes of polysulfones and liquid-crystal polymers are studied in papers [203-205]. There are several contributions on the methods of synthesizing of copolymers of polysulfones and polyesterketones and on the production of mixes [206-210]. The method for the synthesis of aromatic copolyestersulfoneketones proposed in [206] allows one to decrease the number of components used, to lower the demands to the concentration of moist in them and to increase the safety of the process. The method is in the interaction without azeotrope former in environment of dimethylsulfone of bisphenols, dihalodarylenesulfones and (or) dihalodaryleneketones and alkali agents in the shape of crystallohydrated of alkali metal carbonated and bicarbonates. All components used are applicable without preliminary drying.

The novel polyarylenestersulfoneketone containing from the cyclohexane and phthalasynone fragments is produced via the reaction of nucleophilic replacement of 1-methyl-4,5-bis(4-chlorobenzoyl)cyclohexane, 4,4'-dichlorobisphenylsulfone and 4-(3,5-dimethyl-4-hydroxyphenyl)-2,3-phthalasine-1-one. The polymer is described by means of IR-spectroscopy with Fourier-transformation, ^1H nuclear magnetic resonance, differential scanning calorimetry and diffraction of X-rays. It is shown that the polymer is amorphous and has high glassing temperature (200 °C), it is soluble in several dissolvents at room temperature. The by-products are the “sewn” and graft copolymers [207].

The block copolymers of low-molecular polyesterketoneketone and 4,4'-bisphenoxybisphenylsulfone (I) can be produced [208] by the reaction of polycondensation. The glassing temperatures increase and melting points lower of copolymers if the concentration of (I) increases. Block copolymers, containing 32,63-40,7% of (I) have glassing temperature and melting point 185-193 and 322-346 °C respectively; the durability and modulus in tension are 86,6-84,2 MPa and 3,1-3,4 GPa respectively; tensile elongation reaches 18,5-20,3%. Block-

copolymers possess good thermal properties and reprocessability in melt.

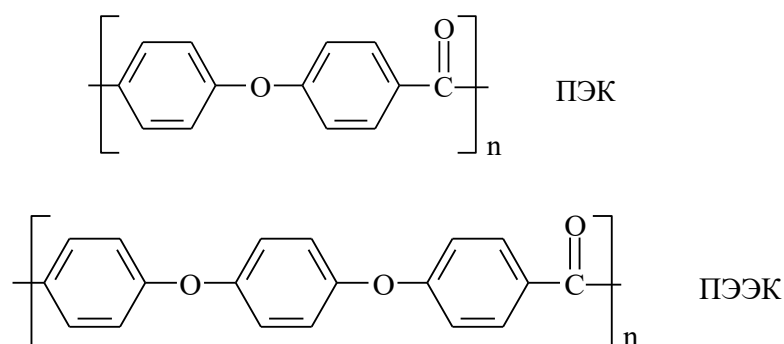
The analysis of literature data and patent investigation has revealed that the production of such copolymers as polyestersulfoneketones, liquid-crystal polyestersulfones as well as the preparation of the mixes and melts of polysulfones with liquid-crystal polyesters of certain new properties are of great importance.

With the account for the upper-mentioned, we have synthesized polyestersulfones on the basis of oligosulfones and terephthaloyl-bis(*n*-oxybenzoic) acid [174, 186, 434] and polyestersulfoneketones on the basis of aromatic oligosulfoneketones, mixes of oligosulfones with oligoketones of various constitution and degree of polycondensation and different acidic compounds [211, 212, 435].

1.5. Aromatic polysulfones

The stormy production development of polymers, containing aromatic cycles like, for example, the polyarylenesterketones has happened within the past decades. The polyarylenesterketones represent the family of polymers in which phenylene rings are connected by the oxygen bridges (simple ester) and carbonic groups (ketones). The polyarylenesterketones include polyesterketone, polyesteresterketone and others distinguishing in the sequence of elements and ratio E/K (of ester groups to ketone ones). This ratio influences on the glassing temperature and melting point: the higher content of ketones increases both temperatures and worsens reprocessability [213].

The elementary units of polysteresterketones contain two simple ester and one ketone groups, while those of polyesterketone – only one ester and one ketone [214].



Polyesteresterketone is partially-crystalline polymer the thermo-stability of which depends on glassing temperature (amorphosity) and melting point (crystallinity) and increases with immobilization of macromolecules. The strong valence bonds define the high thermo-stability and longevity of mechanical and electrical properties at elevated temperature.

The polyesterketone labeled "Victrex^R" was firstly synthesized in Great Britain by company «Imperial Chemical Industries» in 1977. The industrial manufacture of polyesteresterketones started in 1980 in Western Europe and USA and in 1982 in Japan [215].

The polyesteresterketone became the subject of extensive study from the moment of appearance in industry. The polyesteresterketone possesses the highest melting point among the other high-temperature thermoplasts (335 °C) and can be distinguished by its highly durable and flexible chemical structure. The latter consists of phenylene rings, consecutively joined by para-links to ester, ester and carboxylic groups. There is a lot of information available now on the structure and properties of polyesteresterketones [216, 217].

The polyesteresterketone is specially designed material meeting the stringent requirements from the point of view of heat resistance, inflammability, products combustions and chemical resistance [218, 219]. "Victrex^R" owns the unique combination of properties: thermal characteristics and combustion parameters quite unusual for thermoplastic materials, high stability to effect of different dissolvents and other fluids [220, 221].

The polyesteresterketone can be of two types: simple (unarmored) and reinforced (armored) by glass. Usually both types are opaque though they can become transparent after treatment at certain conditions. This happens due to the reversible change of material's crystallinity which can be recovered by tempering. The limited number of tinges of polyesteresterketones has been produced for those areas of industry where color articles are used.

The structure crystallinity endows polyesteresterketones by such advantages as

- stability to organic solvents,
- stability to dynamical fatigue,
- improved thermal stability when armoring with glass,
- ability to form plasticity at short-term thermal aging,
- orientation results in high strength fibers.

“Vitrex^R” loses its properties as elasticity and solidity moduli with increasing temperature, but the range of working temperatures of polyesteresterketones is wider in short-term process (like purification) than that of other thermoplastic materials. It can be exploited at 300 °C or higher. The presumable stint at 250 °C is more than 50 thousand hours for the given polyesteresterketone. If one compares the mechanical properties of polyesteresterketone, polyestersulfone, nylon and polypropylene then he finds that the first is the most resistant to wear and to dynamic fatigue. The change of mechanical characteristics was studied in dependence of sorption of CH_2CCl_2 .

Polyesteresterketones, similar to any other thermoplastics, is isolation material. It is hard-burnt and forms few smoke and toxic odds in combustion, the demand in such materials arises with all big hardening requirements to accident prevention.

If one compares the smoke-formation in combustion of 2-3 mm of samples from ABC-plastics, polyvinylchloride, polystyrene, polycarbonate, polytetrafluorethylene, phenolformaldehyde resin, polyestersulfone, polyesteresterketone then it occurs that the least smoke is released by polyesteresterketone, while the greatest amount of smoke is produced by ABC-plastic.

“Vitrex^R” exhibits good resistance to water reagents and pH-factor of different materials starting with 60% sulphuric acid and 50% potassium hydroxide. The polyesteresterketone dissolves only in proton substances (such as concentrated sulphuric acid) or at the temperature close to its melting point. Only α -chlornaphthalene (boiling point 260 °C) and benzophenone influence on “Vitrex^R” among organic dissolvents.

The data on the solubility have revealed that two classes of polyesteresterketones coexist: “amorphous” and crystalline [222].

The division of these polymers into two mentioned classes is justified only by that the last class, independent of condensation method, crystallizes so fast in conditions of synthesis that the filtering of combustible solution is not possible. It may be concluded from results obtained that “amorphous” class of polyesteresterketones is characterized by bisphenols, which have hybridized sp^3 -atom between phenyl groups.

From the point of view of short-term thermal stability the polyesteresterketones do not yield most steady materials - polyestersulfones - destruction of which is 1% at 430 °C. Yet and still their long-term stability to UV - light, oxygen and heat must be low due to ketone-group [222].

The influence of environment on polyesteresterketones is not understood in detail, but it has proven that polyesteresterketone fully keeps all its properties within 1 year. Polyesteresterketones exhibit very good stability to X-ray, β - and γ -radiations. Wire samples densely covered with polyesteresterketones bear the

radiation 110 Mrad without essential destruction.

The destroying tensile stress of polyesteresterketone is almost nil at exposure to air during 100 hours at 270 °C. At the same time the flex modulus at glassing temperature of 113 °C falls off precipitously, however remains sufficiently high compared to that of other thermoplasts.

When placed into hot water (80 °C) for 800 hours the tensile stress and the permanent strain after rupture of polyesteresterketones decreases negligibly. The polyesteresterketone overcomes all the other thermoplasts on stability to steam action. The articles from polyesteresterketone can stand short exposure to steam at 300 °C.

On fire-resistance this polymer is related to hard-to-burn materials.

The chemical stability of polyesteresterketone “Victrex^R” is about the same as of polytetrafluorethylene while its long-term strength and impact toughness are essentially higher than those of nylon A-10 [223].

The manufacture of the polyesteresterketones in Japan is organized by companies “Mitsui Toatsu Chem” under the labels “Talpa-2000”, “ICI Japan”, “Sumitoma Kogaku Koge”. The Japanese polyesteresterketones have glassing temperature 143 °C and melting point 334 °C [224, 225].

The consumption of polyesteresterketones in Japan in 1984 was 20 tons, 1 kilogram cost 17000 Yen. The total consumption of polyestersulfones and polyesteresterketones in Japan in 1990 was 450-500 tons per year [226].

Today, 35% of polyesteresterketones produced in Japan (of general formula $[-OC_6H_4-O-C_6H_4-CO-C_6H_4-]_n$) are used in electronics and electrotechnique, 25% - in aviation and aerospace technologies, 10% - in car manufacture, 15% - in chemical industry as well as in the fields of everyday life, for example at producing the buckets for hot water, operating under pressure and temperature up to 300 °C. The Japanese industrial labels of polyesteresterketones have good physical-

mechanical characteristics: the high impact toughness; the heat resistance (152 °C, and 286 °C with introduction of 20% of glass fiber); the chemical resistance (bear the influence of acids and alkalis, different chemicals and medicines), the tolerance for radiation action; the elasticity modulus 250-300 kg/mm²; the rigidity; the lengthening of 100%; the negligible quantity of smoke produced. The polyesteresterketone can be reprocessed by die casting at 300-380 °C (1000-1400 kg/cm²), extrusion, formation and others methods [224]. High physical-mechanical properties remain the same for the long time and decrease on 50% only after 10 years.

The polymer is expensive. One of the ways for reducing the product price is compounding. The company “Kogaku Sumitoma” created compounds “Sumiploy K” on the basis of polyesteresterketones by their original technology. The series “Sumiploy K” includes the polymers with high strength and of improved wear resistance. The series “Sumiploy SK” is based on the polyesteresterketone alloyed with other polymers [224]. The series includes polymers, the articles of which can be easily taken out from the form, and products are of improved wear resistance, increased high strength, good antistatic properties, can be easily metalized.

The company “Hoechst” (Germany) produces unreinforced polyesteresterketones “Hoechst X915”, armored with 30 weight% of glass fiber (X925) and carbon fiber (X935), which are characterized by the good physical-mechanical properties (Table 4). The unreinforced polymer has the density almost constant till glassing temperature (about 160 °C). The reinforcing with fibers permits further to increase the heat resistance of polyesteresterketone. At the moment the polyesteresterketones labeled “Hostatec” are being produced with 10, 20 and 30 weight % of glass and carbon fibers. Several labels of polyesteresterketones are under development which involve mineral fillers, are not reinforced and contain 30 weight % of glass and carbon fibers.

The constructional thermoplast “Hostatec” dominates polyoxymethylene, polyamide and complex polyesters on many parameters.

The polyesteresterketones can be easily processed by pressing, die cast and extrusion. They can be repeatedly crushed to powder for secondary utilization. They are mainly used as constructional materials but also can be used as electroinsulation covers operating at temperatures of 200 °C and higher for a long time [225].

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Physic-mechanical properties of polyesteresterketones of company “Hoechst”

Property	unreinforced	containing 30 weight %	
		glass fiber	carbon fiber
Density, g/cm ³	1,3	1,55	1,45
Linear shrinkage, %	1,5	0,5	0,1
Tensile strength, N/mm ²	86	168	218
Breaking elongation, %	3,6	2,2	2,0
Modulus in tension, kN/mm ²	4	13,5	22,5
Impact toughness notched, J/m	51	71	60
Heat resistance, °C	160	Above 320	320

The polyesteresterketone found application in household goods (in this case its high heat resistance and impact toughness are being used), in lorries (joint washers, bearings, probes bodies, coils and other details, contacting fuel, lubricant and cooling fluid).

The big attention to polyesteresterketones is paid in aircraft and space industries. The requirements to fire-resistance of plastics used in crafts have

become stricter within the last years. Unreinforced polyesteresterketones satisfy these demands having the fire-resistance category U-O on UL 94 at thickness 0,8 mm. In addition, this polymer releases few smoke and toxic substances in combustion (is used in a subway). The polyesteresterketone is used for coating of wires and cables, used in details of aerospace facility (the low inflammability, the excellent permeability and the wear stability), in military facility, ship building, on nuclear power plants (resists the radiation of about 1000 Mrad and temperature of water steam 185 °C), in oil wells (pillar stand to the action of water under pressure, at a temperature of 288 °C), in electrical engineering and electronics. Polyesteresterketone offer properties of thermoreactive resin, can be easily pressed, undergoes overtone, resists the influence of alkalis.

Since January 1990, the Federal aviation authority have adopted the developed at Ohio State University method, in which the heat radiation (HR) and the rate of heat release (RHR) are determined. The standard regulates the HR level at 65 kJ. Many aircraft materials do not face this demand: for example, the ternary copolymer of acrylonitrile, butadiene and styrene resin, the polycarbonate, phenol and epoxide resins. It is foreseen to substitute these materials by such polymers, which meet these requirements. The measurements in combustion chamber of Ohio State University indicated that polyesteresterketone fulfills this standard.

The heightened activity in creating and evaluation of composite properties on the basis of polyesteresterketones occurs recent years [228]. The thermoplastic composites have the number of advantages regarding the plasticity, maintainability and ability for secondary utilization compared to epoxy composites. These polymers are intended to be applied in alleviated support elements. In the area of cable insulation, polyesteresterketones can be reasonably used when thermo-stability combined with fire-resistance without using of halogen antipyrenes where is desired.

The “Hostatec” has low water absorption. Dielectric properties of films from polyesteresterketone “Hostatec” are high. This amorphous polymer has the electric

inductivity 3,6, loss factor 10^{-3} and the specific volume resistance 10^{17} Ohm \times cm, these values remain still up to 60 °C.

Growth of demand for polyesteresterketones is very intense. In connection with growing demands on heat resistance and stability to various external factors the polyesteresterketones find broader distribution. The cost of one kilogram of such polymer is 5-20 times larger than the cost of usual constructional polymers (polycarbonates, polyamides, and polyformaldehydes). But, despite the high prices the polyesteresterketones and compositions on their basis, owing to the high level of consumer characteristics, find more and more applications in all industries. The growth of production volumes is observed every year.

It is known, that the paces of annual growth of polyesteresterketones consumption were about 25% before 1995, and its global consumption in 1995 was 4000 tons. The polyesteresterketone do not cause ecological problems and is amenable to secondary processing.

In connection with big perspectiveness of polyarylesterketones, the examining of the most popular methods for their production was of interest. The literature data analysis shows that the synthesis of aromatic polyesterketones can be done by the acylation on Friedel-Crafts reaction or by reaction of nucleophylic substitution of activated dihalogen-containing aromatic compounds and bisphenolates of alkali metals [224, 229].

In the majority cases, the polyesterketones and polyesteresterketones are produced by means of polycondensation interaction of bisphenols with 4,4'-dihalogen-substituted derivatives of benzophenone [230-263], generally it is 4,4'-difluoro- or dichlorobisphenylketone. The introduction of replacers into the benzene ring of initial monomer raises the solubility of polyesterketones and polyesteresterketones. So, polyesterketone on the basis of 3,3',5,5'-tetramethylene and 4,4'-difluorobenzophenone is dissolved at 25 °C [211-214] in dimethylsulfoxide, the reduced viscosity of melt with concentration

0,5 gram/deciliter is 0,79 deciliter/gram.

The polyesterketone based on 4,4'-dioxybenzophenone and dichloromethylenized benzene derivatives is soluble in chloroform and dichloroethane [264]. The logarithmic solution viscosity of polyesterketone obtained on the basis of 4,4'-dioxybisphenylsulfone and 4,4'-dichlorobenzophenone in tetrachloroethane of concentration 0,5 gram/deciliter is 0,486; the film materials from this polyester (of thickness 1 mm) are characterized by the high light transmission (86%) and keep perfect solubility and initial viscosity after exposure to 320 °C during 2 hours.

The high-boiling polar organic solvents – dimethylsulfoxide, sulfolane, dimethylsulfone, dimethylformamide, dimethylacetamide – are generally used for synthesizing the polyesterketones and polyesteresterketones by means of polycondensation; in this case the reaction catalysts are the anhydrous hydroxides, carbonates, fluorides and hydrides of alkali metals. The polymers synthesis is recommended to be carried out in inert gas atmosphere at temperatures 50-450 °C. If catalysts used are the salts of carbonic or hydrofluoric acids then oligomers appear. Chain length regulators when producing polyesterketones based on difluoro- or dichlorobenzophenone and bisphenolates of alkali metals and dihydroxynaphthalenes can be the monatomic phenols [251-253].

The synthesis of polyesterketones and polyesteresterketones according to the Friedel-Crafts reaction is lead in mild conditions [265-283]. So, solidifying thermo-stable aromatic polyesterketonesulfones, applied as binding agents when laminating, can be produced [278] in the presence of aluminium chloride by the interaction of 1,4-di(4-benzoylchloride)butadiene-1,3-dichloranhydrides of iso- and terephthalic acids, bisphenyl oxide and 4,4'-bisphenoxybisphenylsulfone.

The aromatic polyesterketones and their thioanalogs are synthesized [266-281, 284] with help of polycondensation of substituted and not-substituted aromatic esters and thioesters with choric anhydrides of dicarboxylic acids in

environment of aprotone dissolvents at temperatures from -10 till 100 °C in the presence of Lewis acids and bases.

The aromatic polyesterketones and polyesterketonesulfonamides based on 4,4'-dichloranhydride of bisphenyloxidebicarboxylic acid and 4-phenoxybenzoylchloride can be produced by means of Friedel-Crafts polycondensation in the presence of AlCl_3 [270]. The reduced viscosity of the solution in sulphuric acid of concentration 0,5 gram/deciliter is 0,07-1,98 deciliter/gram. The Friedel-Crafts reaction can also be applied to synthesize the copolyesterketones from bisphenyl ester and aromatic dicarboxylic acids or their halogenanhydrides [274]. The molecular mass of polymers, assessed on the parameter of melt fluidity, peaks when bisphenyl ester is used in abundant amount (2-8%).

The polyarylesterketones can be produced by means of interaction between bisphenylsulphide, dibenzofurane and bisphenyloxide with monomers of electrophilic nature (phosgene, terephthaloylchloride) or using homopolycondensation of 4-phenoxybenzoylchloride and 4-phenoxy-4-chlorcarbonyl-bisphenyl in the presence of dichloroethane at 25 °C [282-285]. Aromatic polyesterketones form after the polycondensation of 4-phenoxybenzoylchloride with chloranhydrides of tere- and isophthalic acids, 4,4'-dicarboxybisphenyloxide in the environment of nitrobenzene, methylchloride and dichloroethane at temperatures from -70 till 40 °C during 16-26 hours according Friedel-Crafts reaction.

The synthesis of polyesterketones based on aromatic ether acids is possible in the environment of trifluoromethanesulfonic acid [249, 287]. The data of ^{13}C nuclear magnetic resonance have revealed [249] that such polyesterketone comprise only the *n*-substituted benzene rings. When using the N-cyclohexyl-2-pyrrolidone as a solvent when synthesizing polyphenylenesterketones and polyphenylenethioesterketones the speed of polycondensation and the molecular mass of polymers [288] increase.

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The synthesis of polyesterketones based on aromatic ether acids is possible in the environment of trifluoromethanesulfonic acid [249, 287]. The data of ^{13}C nuclear magnetic resonance have revealed [249] that such polyesterketone comprise only the *n*-substituted benzene rings. When using the N-cyclohexyl-2-pyrrolidone as a solvent when synthesizing polyphenylenesterketones and polyphenylenethioesterketones the speed of polycondensation and the molecular mass of polymers [288] increase.

So, the polymer is produced, the reduced viscosity of 0,5% solution of which in sulphuric acid is 1,0 deciliter/gram, after the interaction of 4,4'-difluorobenzophenone and hydroquinone at 290 °C in the presence of potassium carbonate during 1 hour. Almost the same results are obtained when synthesizing polyphenylenethioesterketones. However, the application of the mix bisphenylsulfone / sulfolane as a solvent during the interaction of 4,4'-difluorobenzophenone with sodium sulfide within 2-13 hours provides for the production of polymer with reduced viscosity 0,23-0,25 deciliter/gram. The high-molecular polyarylenesulphideketones, suitable for the preparation of films, fibers and composite materials are formed during the interaction of 4,4'-dihalogenbenzophenone with sodium hydrosulfide in solution (N-methylpyrrolidone) at 175-350 °C within 1-72 hours [289].

For the purpose of improving physical-mechanical properties and increasing the reprocessibility of polyesterketones and polyesteresterketones their sulfonation by liquid oxide of hexavalent sulfur in environment of dichloroethane has been carried out [290]. In this case the polymer destruction does not happen, which is observed at sulfonation by concentrated sulphuric or chlorosulfonic acid. The abiding flexible film materials can be produced from sulfonated materials using the method of casting. The aromatic polyesterketones could also be produced by oxidative dihydropolycondensation (according to the Scolla reaction) of 4,4'-bis-(1-naphthoxy)-benzophenone at 20 °C in the presence of trivalent iron chloride in environment of nitrobenzene [291]. The mix of pentavalent phosphorus oxide and methylphosphonic acid in ratio 1:10 can be used as a solvent and dehydrate agent [292, 293] when synthesizing the aromatic polyesterketones on the basis of bisphenylester of hydroquinone, 4,4'-bisphenyloxybicarboxylic acid, 1,4-bis(m-carboxyphenoxy)benzene, and also for homopolycondensation of 3- or 4-phenoxybenzoic acid at 80-140 °C.

The sulfur-containing analogs of polyesterketones, i.e. polythioesterketones and copolythioesterketones can be synthesized [294-303] by polycondensation of dihalogenbenzophenols with hydrothiophenol or other bifunctional sulfur-involving

compounds, and also of their mixes with different bisphenols in environment of polar organic solvents. As in case of polyesterketones, the synthesis of their thioanalogs is recommended to be carried out in inert medium at temperatures below 400 °C in the presence of catalyst (hydroxides, carbonates and hydrocarbonates of alkali metals).

The aromatic polyesterketones can also be produced by polycondensation or homopolycondensation of compounds like halogen-containing arylketonephenols and arylenedihalogenides of different functionality at elevated temperature and when the salts of alkali and alkali-earth metals in environments of high-boiling polar organic solvents are used as catalysts [222, 304-312]. The 4-halogen-3-phenyl-4-hydroxybenzophenone, 4-(*n*-haloidbenzoyl)-2,6-dinethylphenol and others belong to monomers with mixed functional groups.

The polycondensation process when synthesizing polyesterketones and polyesteresterketones can be performed in the melt [223, 313-317] too. So, it is possible to produce the aromatic polyesterketones by means of interaction in melt of 4,4'-difluorobenzophenone with trimethylsiloxane esters of bisphenols with different bridged groups in the presence of catalyst (cesium fluoride – 0,1% from total weight of both monomers) at 220-270 °C [318]. The monomers do not enter the reaction without catalyst at temperatures below 350 °C. The reduced viscosity of 2% solution of polymer in tetrachloroethane at 30 °C is 0,13-1,13 deciliter/gram, the molecular weight - 3200-60000, glassing temperature is 151-186 °C, melting point is 240-420 °C. According to the data of thermogravimetric analysis in the air the mass loss of polymer is less than 10%, when temperature elevates from 422 °C to 544 °C with the rate 8 degrees per minute.

To increase the basic physical-mechanical characteristics and reprocessibility (the solubility, in particular), the polyesterketones and polyesteresterketones are synthesized [319-329] through the stage of formation of oligomers with end functional groups accompanied with the consequent production of block-

copolyesterketones or by means of one-go-copolycondensation of initial monomers with production of copolyesterketones.

The polyesteresterketones, their copolymers and mixes are used for casting of thermally loaded parts of moving transport, instrument, machines, and planes. They are used in articles of space equipment: for cable insulation, facings (pouring) elements. For instance, the illuminators frames of planes and rings for high-frequency cable are made of polyesterketone “Ultrapek”. It is widely used in electronics, electrician, for extrusion of tubes and pipes operating in aggressive media and at low temperatures. The polyesteresterketones and polyesterketones are used for multilayer coating as the basis of printed planes. The conservation of mechanical strength in conditions of high humidity and temperature, the stability to radiation forwards their application to aerospace engineering.

The compositions on the basis of polyesteresterketones already compete with those based on thermoreactive resins when making parts of military and civilian aircrafts. Sometimes it is possible to cut the weight on 30% if produce separate parts of plane engines from reinforced polyesteresterketones.

It is proposed to use the polyesteresterketones in the manufacture of fingers of control rod and cams of brake system, motors buttons in car industry. The piston cap of automobile engine, made from polyesteresterketone “Viktrex”, went through 1300 hours of on-the-road tests.

The advantage of using this material, contrary to steel, lays in wearout decrease, noise reduction, 40% weight reduction of the article. The important area of application of polyesteresterketones can be the production of bearings and backings. The polyesteresterketones are recommended to be used for piece making of drilling equipment (zero and supporting mantles) and timber technique, in different joinings of electric equipment of nuclear reactors, layers and valves coverings, components of sports facility.

The fibers of diameter 0,4 mm (from which the fabric is weaved in shape of

tapes and belts used in industrial processes where the temperature-resistant, the high-speed conveyers are needed) are produced from polyesteresterketone melt at temperatures of 350-390 °C. The fabric from polyesteresterketone or polyesterketone keeps 90% of the tensile strength after thermal treatment at 260 °C, does not change its properties after steaming at 126 °C for 72 hours under the load, and resists alkalis action with marginal change. The medical instruments, analytical, dialysis devices, endoscopes, surgical and dental tools, containers made of polyarylesterketones can be sterilized by steam and irradiation [330].

The manifold methods of synthesizing polyarylenesterketones have been devised by Russian and foreign scientists within the last twenty years.

For example, the method for production of aromatic polyketones by means of Friedel-Craft polycondensation of bis(arylsilanes) with chlorides of aromatic dicarboxylic acids (isophthaloyl-, terephthaloyl-, 4,4'-oxydibenzoylchloride) at 20 °C in environment of dissolvent (1,2-dichlorethane) in the presence of aluminium chloride is proposed in [331]. The polyketones have the intrinsic viscosity more than 0,37 deciliter/gram (at 30 °C, in concentrated H₂SO₄), glass transition temperature is 120-231 °C and melting point lies within 246-367 °C. The polyketones start decomposing at a temperature of 400 °C, the temperature of 10% loss of mass is 480-530 °C.

It is possible to produce polyketones by the reaction of aromatic dicarboxylic acid and aromatic compound containing two reactive groups [332]. The reaction is catalyzed by the mix of phosphoric acid and carboxylic acid anhydride having the formula of RC(O)O(O)CR (R stands for not-substituted or substituted alkyl, in which one, several or all hydrogen atoms were replaced by functional groups and each R has the Gamet constant $\sigma_m \geq 0,2$). The pressed articles can be created from synthesized polyketones.

The aromatic polyketones can be synthesized [333] when conducting the Friedel-Craft polymerization with acylation by means of the interaction of

2,2{ }bis(arylphenoxy)bisphenyls with chlorides of arylenebicarboxylic acids in the presence of AlCl_3 . The polyketones obtained using the most efficient 2,2{ }bis(4-benzoylphenoxy) bisphenyl are well soluble in organic solvents and possess high heat resistance.

Also, the aromatic polyketones are produced [334] by the reaction of electrophilic substitution (in dispersion) of copolymer of aliphatic vinyl compound (1-acosen) with N-vinylpyrrolidone, at ratio of their links close to equimolar.

The other method of synthesizing aromatic polyketones includes the interaction of monomer of formula $[\text{HC}(\text{CN})(\text{NR}_2)]\text{Ar}$ with 4,4'-difluorobisphenylsulfone in dimethylsulfoxide, dimethylformamide or N-methylpyrrolidone at 78-250 °C in the presence of the base [335]. The soluble polyaminonitrile of formula $[\text{C}(\text{CN})(\text{NR}_2)\text{ArC}(\text{CN})(\text{NR}_2)\text{C}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4]_n$ is thus produced (Ar denotes $m\text{-C}_6\text{H}_4$, NR_2 – stands for group $-\text{NCN}_2\text{CH}_2\text{OCH}_2\text{CH}_2$). When acid hydrolysis of polyaminonitrile is carried out the polysulfoneketone of formula $[\text{COArCOC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4]_n$ forms with glassing temperature of 192 °C, melting point 257 °C and when 10% mass loss happens at 478 °C. The acid hydrolysis can be performed in the presence of *n*-toluenesulfoacid, trifluoroacetic acid, and mineral acids.

The synthesis of aromatic polyketone particles has been carried out [336] by means of precipitation polycondensation and is carried out at very the low concentration of monomer [0,05 mol/liter]. The polyketones are produced from bisphenoxybenzophenone (0,005 mole) or isophthaloylchloride (0,005 mole) in 100 milliliters of 1,2-dichloroethane. Some of obtained particles have highly organized the needle-shaped structure (the whisker crystals). The use of isophthaloyl instead of terephthaloyl at the same low concentration of monomer results in formation of additionally globular particles, the binders of strip structures gives rise. The average size of needle-shaped particles is 1-5 mm in width and 150-250 mm in length.

The synthesis of aromatic high-molecular polyketones by the low-temperature solid-state polycondensation of 4,4'-bisphenoxybenzophenone and isophthaloylchloride in the presence of AlCl_3 in 1,2-dichlorethane is possible [337]. Obtained polymers are thermoplasts with glass transition temperature $160\text{ }^\circ\text{C}$ and melting point $382\text{ }^\circ\text{C}$.

The polyesterketones are synthesized [338] from dichlorbenzophenone and Na_2CO_3 in the presence of catalyst $\text{SiO}_2\text{-Cu-salt}$. The polymer has the negligible number of branched structures and differs from polyesterketones synthesized on the basis of 4-hydroxy-4'-fluorobenzophenone on physical properties (its pressed samples have higher crystallinity and orientation).

There exist reports on syntheses of fully aromatic polyketones without single ester bonds [339-349].

The fully aromatic polyketones without ether bonds were produced [339] on the basis of polyaminonitrile, which was synthesized from anions of bis(aminonitrile) and 4,4'-difluorobenzophenone using the sodium hydride in mild conditions. The acid hydrolysis of synthesized polyaminonitrile avails one to obtain corresponding polyketone with high thermal properties and tolerance for organic solvents.

They are soluble only in strong acids such as concentrated H_2SO_4 . The polyketones have glassing temperature $177\text{-}198\text{ }^\circ\text{C}$. Their melting points and temperature of the beginning of decomposition are respectively $386\text{-}500\text{ }^\circ\text{C}$ and $493\text{-}514\text{ }^\circ\text{C}$ [340].

The aromatic polyketones without ester bonds can also be produced by the polymerization of bis(chlorbenzoyl)dimethoxybisphenyls in the presence of nickel compounds [341]. The polymers have the high molecular mass, the amorphous structure, the glass transition temperature $192\text{ }^\circ\text{C}$ and $218\text{ }^\circ\text{C}$ and form abiding flexible films.

The known aromatic polyketones (the most of them) dissolve in strong acids, or in trifluoroacetic acid mixed with methylenechloride, or in trifluoroacetic acid mixed with chloroform.

It is known that the presence of bulk lateral groups essentially improves the solubility of polyketones, and also improves their thermo-stability. In connection to this, dichloranhydride of 3,3-bis-(4'-carboxyphenyl)phthalide (instead of chloranhydride) was used as initial material for condensation with aromatic hydrocarbons [350]. According to the Friedel-Crafts reaction of electrophilic substitution in variant of low-temperature precipitation polycondensation the high-molecular polyarylenephthalidesterketones have been synthesized. Obtained polymers have greater values of intrinsic viscosity 1,15-1,55 deciliter/gram (in tetrachloroethane). The softening temperatures lies within 172-310 °C, the temperature of the beginning of decomposition is 460 °C. Polyarylenephthalidesterketones dissolve in wide range of organic solvents, form colorless, transparent, abiding ($\sigma = 85\text{-}120$ MPA) and elastic ($\epsilon = 80\text{-}300\%$) films when formed from the melt.

The soluble polyketones – polyarylemethylketones – can be produced [351] by condensation polymerization of 1,4-dihalogenarenes and 1,4-diacetylbenzols in the presence of catalytical palladium complexes, base and phosphoric ligands. The high yield of polymer is seen when using the tetrahydrofurane, o-dichlorobenzole and bisphenyl ester as solvents. The synthesized polymers dissolve in tetrahydrofurane, dichloromethane and hexane, has the decomposition point 357 °C (in nitrogen). It has luminescent properties: emits the green light (490-507 nm) after light irradiation with wavelength of 380 nm.

The works [352-355] report on syntheses of carding aromatic polyketones.

The ridge-like polyarylesterketones have been synthesized by means of one-stage polycondensation in solution of bis(4-nitrophenyl)ketone with phenolphthalein, o-cresolphthaleine, 2,5,2'-5'-tetramethylphenolphthaleine and timolphthaleine [352].

Authors have shown that the free volume within the macromolecule depends on position, type and number of alkyl substitutes.

The homo- and copolyarylenesterketones of various chemical constitution (predominantly, carding ones) have been produced by the reaction of nucleophylic substitution of aromatic activated dihaloid compound [353], and also the “model” homopoyarylenesterketones on the basis of bisphenol, able to crystallize, created. The tendency to crystallization is provided by the combination of fragments of carding bisphenols with segments of hydroquinone (especially, of 4,4'-dihydroxydiphenyl) and increases with elongation of difluoro-derivative (the oligomer homologues of benzophenone), and also in the presence of bisphenyl structure in that fragment. Owing to the presence of carding group, the glass transition temperature of copolymer reaches 250 °C, and the melting point – 300-350 °C.

The crystallizing carding polyarylenesterketones, in difference from amorphous ones, dissolve in organic solvents very badly, they are well soluble in concentrated sulfuric acid at room temperature and when heating to boiling in m-cresol (precipitate on cooling) [354, 355].

There are contributions [356, 357] devoted to the methods of synthesis of aromatic polyketones on the basis of diarylidenecycloalkanes.

The polyketones are produced [356] by the reaction of 2,7-dibenzylidenecyclopentanone (I) and dibenzylideneacetone (II) with dichlorides of different acids (isophthalic, 3,3'-azodibenzoic and others) in dry chloromethane in the presence of AlCl_3 . The “model” compounds from I and II and benzoylchloride are also obtained. The synthesized polyketones have intrinsic viscosity 0,36-0,84 deciliter/gram (25 °C, H_2SO_4). They do not dissolve in most organic solvents, dissipate in H_2SO_4 . It is determined that the polyketones containing the aromatic links are more stable than those involving aliphatic and azo group. The temperature of 10% and 50% mass loss is 150-250 °C and 270-540 °C for these polyketones.

The polyketones, possessing intrinsic viscosity 0,76-1,18 deciliter/gram and

badly dissolving in organic solvents, can be produced by Friedel-Crafts polycondensation of diarylidenecyclopentanone or diarylidenecyclohexanone, chlorides of aromatic or aliphatic diacids, or azodibenzoylchlorides. The temperature of 10% mass loss is 190-300 °C. The in polyketones have the absorption band at wavelength 240-350 nm in ultraviolet spectra (visible range). [357].

The metal-containing polyketones, which do not dissolve in most of organic solvents and easily dissipate in proton dissolvents, have been produced by the reaction of 2,6[bis(2-ferrocenyl)methylene]cyclohexane with chlorides of dicarboxylic acids [358]. The intrinsic viscosity of metal-containing polyketones is 0,29-0,52 deciliter/gram.

The papers [359, 360] report on different syntheses of isomeric aromatic polyketones. Three isomeric aromatic polyketones, containing units of 2-trifluoromethyl- and 2,2{ }-dimethoxybisphenylene were synthesized in [326] by means of direct electrophilic aromatic acylated polycondensation of monomers. Two isomers of polyketone of structure “head-to tail” and “head-to head” contain the links of 2-trifluoromethyl-4,4/{ }-bisphenylene and 2,2{ }-dimethoxy-5,5{ }-bisphenylene.

There exist several reports on syntheses of polyarylketones, containing bisphthalasinone and methylene [361, 362], naphthalene [363-367] links; containing sulfonic groups [368], carboxyl group in side chain [369], fluorine [370-372] and on the basis of carbon monoxide and styrol or *n*-sthylstirol [373]. It is shown that methylene and bisphthalasinone links in main chain of polyketones are responsible for its good solubility in *m*-cresol, chloroform. The links of bisphthalasinone improve thermal property of polymer.

The synthesis of temperature-resistant polyketone has been carried out in [362] by means of polycondensation of 4-(3-chlor-4-oxyphenyl)-2,3-phthalaoasine-1-one with 4,4/-difluorobisphenylketone.

The polymer is soluble in chloroform, N-methylpirrolydone, nitrobenzene and tetrachloroethane, its glass transition temperature is 267 °C.

The aromatic polyketones, containing 1,4-naphthalene links were produced in [363] by the reaction of nucleophilic substitution of 1-chlor-4-(4'-chlorobenzoyl)naphthalene with 1) 1,4-hydroquinone, 2) 4,4'-isopropylidenediphenol, 3) phenolphthalein, 4) 4-(4'-hydroxyphenyl)(2H)-phthalazine-1-one, respectively. All polymers are amorphous and dissolve in some organic solvents. The polymers have good thermo-stability and the high glassing temperatures.

Fluorine containing polyarylesterketone was synthesized on the basis of 2,3,4,5,6-pentafluorobenzoylbisphenyl esters in [370]. The polymers possess good mechanical and dielectric properties, has impact strength, solubility and tolerance for thermooxidative destruction.

The just-produced polyketones are stabilized by treating them with acetic acid solution of inorganic phosphate [371].

The simple fluorine containing polyarylesterketones was obtained in [372] on the basis of bisphenol AF and 4,4'-difluorobenzophenone. The polymer has the glass transition temperature 163 °C and temperature of 5% mass loss 515 °C, dielectric constant 1,69 at 1 MHz, is soluble well in organic solvents (tetrahydrofurane, dimethylacetamide and others).

The works [374, 375] are devoted to the synthesis of polyesterketones with lateral methyl groups.

The polyarylesterketones have been produced by the reaction of nucleophilic substitution of 4,4'-difluorobenzophenone with hydroquinone [374]. The synthesis is held in sulfolane in the presence of anhydrous K_2CO_3 . The increasing content of methylhydroquinone links in polymers leads to increasing of glass transition temperature and lowering of crystallinity degree, melting temperature and activation energy.

The methyl-substituted polyarylesterketones have been produced in [375] by means of electrophilic polymerization of 4,4'-bis-(0-methylphenoxy)biphenylketone or

1,4-bis(4-(methylphenoxy)benzoyl)benzene with terephthaloyl or isophthaloyl chloride in 1,2-dichloroethane in the presence of dimethylformamides and AlCl_3 . The polymers have glassing temperature and melting point 150-170 °C and 175-254 °C.

The simple aromatic polyesterketones, which are of interest as constructional plastics and film materials, capable of operating within the long time at 200 °C, have been synthesized [376-381] by means of polynitrosubstitution reaction of 1,1-dichloro-2, 2-di(4-nitrophenyl)-ethylene and 4,4'-dinitrobenzophenone with aromatic bisphenols.

The simple esterketone oligomer can be synthesized [378] also by polycondensation of aromatic diol with halogen-containing benzophenone at 150-250 °C in organic solvent in the presence of alkali metal compound as catalyst and water.

The particles of polyesterketone have a diameter ≤ 50 micrometers, intrinsic viscosity 0,5-2 deciliter/gram (35 °C, the ratio *n*-chlorphenol : phenol is 90:10).

The simple polyesterketone containing lateral side cyano-groups, possessing the glass transition temperature in range 161-179 °C, has been produced [379] by low-temperature polycondensation of mix 2,6-phenoxybenzonitrile and 4,4'-bisphenoxybenzophenone with terephthaloylchloride in 1, 2-dichloroethane.

The simple polyarylesterketones, containing the carboxyl pendent groups [380] and flexible segments of oxyethylene [381] have been synthesized either.

Russian and foreign scientists work on synthesis of copolymers [382-393] and block copolymers [394-399] of aromatic polyketones.

So, the high-molecular polyketones, having amorphous structure and high values of glassing temperature, have been produced by copolymerizing through the mechanism of aromatic combination of 5,5-bis(4-chlorbenzoyl)-2,2-dimethoxybisphenyl and 5,5-bis(3-chlorbenzoyl)-2,2-dimethoxybisphenyl with help of nickel complexes [382].

Terpolymers on the basis of 4,4'-bisphenoxybisphenylsulfone, 4,4'-bisphenoxybenzophenone and terephthaloylchloride were produced in [383] by low-temperature polycondensation. The reaction was lead in solution of 1,2-dichloroethane in the presence of AlCl_3 and N-methyl-2-pyrrolidone. It has been found that with increasing content of links of 4,4'-bisphenoxybisphenylsulfone in copolymer their glassing and dissipation temperatures increase, but melting point and temperature of crystallization decrease.

The new copolyesterketones have been produced in [384] also from 4,4'-difluorobenzophenone, 2,2{ },3,3{ },6,6{ }-hexaphenyl-4,4'-bisphenyl-1,1{ }-diol and hydroquinone by the copolycondensation in solution (sulfolane being the dissolvent) in the presence of bases (Na_2CO_3 , K_2CO_3). The synthesized copolyesterketones possess solubility, high thermal stability; have the good breaking strength and good gas-separating ability in relation to CO_2/N_2 and O_2/N_2 .

The random copolymers of polyarylesterketones were produced by means of nucleophylic substitution [385] the basis of bisphenol A and carding bisphenols (in particular, phenolphthalein).

The simple copolyesterketones (copolyesterketonearylates) are synthesized [386] and the method for production of copolymers of polyarylates and polycarbonate with polyesterketones is patented [387]. The reaction is held in dipolar aprotone dissolvent in the presence of interface catalyst (hexaalkylguanidinehalogenide).

The statistical copolymers of polyarylesterketones, involving naphthalene cycle in the main chain, can be produced [388] by low-temperature polycondensation of bisphenyloxide, 4,4'-{ }-bis(β -naphtoxy)benzophenone with chloranhydrides of aromatic bicarbonic acids – terephthaloylchloride and isophthaloylchloride (I) in the presence of catalytical system AlCl_3/N -methylpirrolydone/ $\text{ClCH}_2\text{CH}_2\text{Cl}$ (copolymers are characterized by improved thermo- and chemical stability), and also by the reaction of hydroquinone with 1,4-bis(4,4'-flourobenzoyl)naphthalene (II) in the presence of sodium and potassium carbonates in bisphenylsulfone [389].

The glass transition temperature of polyarylesterketones is going up, and melting point and temperature of the beginning of the destructions are down with increasing concentration of links of 1,4-naphthalene in main chain of copolymers.

The polyarylesterketone copolymers, containing lateral cyano-groups, can be synthesized [390] on the basis of bisphenyl oxide, 2,6-bisphenoxybenzonitrile (I) and terephthaloylchloride in the presence of AlCl_3 , employing 1,2-dichloroethane as the dissolvent, N-mthyl-2-pyrrolidon as the Lewis base. With increasing concentration of links of I the crystallinity degree and the melting point of copolymers decrease while the glass transition temperature increase. The temperature of 5% of copolymers mass loss is more than 514 °C (N_2).

Copolymers, containing 30-40 weight % of links of I, possess higher therm0-stability (350 ± 10 °C), good tolerance for action of alkalis, bases and organic solvents.

The copolymers of polyarylesterketones, containing lateral methyl groups, can be produced by low-temperature polycondensation of 2,2{ }-dimethyl-4,4{ }-bisphenoxybisphenyleneketone (I) or 1,4-[4-(2-methylphenoxy)benzoyl]benzene (II) and bisphenylester, terephthaloylchloride [391]. The synthesis is held in 1,2-dichloroethane in the presence of dimethylformamides and AlCl_3 as catalyst. With increasing concentration of links of I or II in copolymers the glass transition temperature increases, and the melting point and the crystallinity degree decreases.

The copolymers of polyarylketones, containing units of naphthalenesulfonic acid in lateral links, are use in manufacturing of proton-exchange membranes [392].

The polymeric system, suitable as proton-exchanged membrane in fuel cells, was developed in [393] on the basis of polyarylenesterketones.

The polyarylesterketones are firstly treated with metasulfonic acid within 12 hours at 45 °C up to sulfur content of 1,2%, and then sulfonize with oleum at 45 °C up to sulfur content 5 % (the degree of sulfonation 51%).

The high-molecular block-copolyarylenesterketones have been synthesized on the basis of 4,4'-difluorobenzophenone and number of bisphenols by means of reaction of nucleophylic substitution of activated arylhalogenide in dimethylacetamide (in the presence of potassium carbonate) [394, 395]. It has been identified the cutback of molecular weight of polymer when using bisphenolate of 4,4'-(isopropylidene)bisphenol.

The block-copolyesterketones are synthesized [396] on the basis of dichloranhydride-1,1'-dichlor-2,2'-bis(*n*-carboxyphenyl)ethylene and various dioxy-compounds with complex of worthy properties. It is possible to create, on the basis of obtained polymers, the constructive and film materials possessing lower combustibility and high insulating properties. Some synthesized materials are promising as modifiers of high density polyethylene.

The block copolymers, containing units of polyarylesterketones and segments of thermotropic liquid-crystal polyesters of different length, are synthesized by means of high-temperature polycondensation in solution [397, 398]; the kinetics, thermal and liquid-crystal properties of block-copolymers have been studied.

The polyarylenesterketones have been obtained [399], which contain blocks of polyarylesterketones, block of triphenylphosphite oxide and those of binding agent into the cycloaliphatic structures. The film materials on their basis are used as polymer binder in thermal control coatings.

The works [400-402] informed on production of polyester- α -diketones using different initial compounds.

Non-asymmetrical polyester- α -diketones are synthesized [400] on the basis of 4-flouru-4'(*n*-fluorophenylglyoxalyl)benzophenone. Obtained polymers are amorphous materials with glassing temperature 162-235 °C and have the temperatures of 10% mass loss in range of 462-523 °C.

The polyester- α -diketones synthesized in [401] on the basis of 2,2-bis[4-(4-

fluorophenylglyoxalyl)phenyl]hexafluoropropane are soluble polymers. They exhibit the solubility in dimethylformamide, dimethylacetamide, N-methylpyrrolidone, tetrahydrofuran and chloroform. The values of glassing temperature lie in interval 182-216 °C, and temperatures of 10% mass loss are within 485-536 °C and 534-556 °C in air and argon respectively.

The number of new polyester- α -diketones in the form of homopolymers and copolymers has been produced [402]. Polyester- α -diketones have the amorphous structure, include α -diketone, α -hydroxyketone and ester groups, they are soluble in organic solvents. The films with lengthening of 5-87%, solidity and module under tension respectively 54-83 MPa and 1,6-3 GPa are produced by casting from chloroform solution.

The quinoxaline polymers, possessing higher glassing and softening temperatures and better mechanical properties compared to initial polymers, have been produced by means of interaction of polyester- α -diketones with α -phenylenediamine at 23 °C in m-cresol. Polyquinoxalines are amorphous polymers, soluble in chlorinated, amide and phenol dissolvents with $\eta_{\text{lim}} = 0,4-0,6$ deciliter/gram (25 °C, in N-methylpyrrolidone of 0,5 gram/deciliter).

It is reported [403] on liquid-crystal polyenamineketone and on mix of liquid-crystal thermotropic copolyester with polyketone [404]. The mix is prepared by melts mixing. It has been found that the blending agents are partially compatible; the mixes reveal two glass transition temperatures.

The transitions of polyketones into complex polyesters are possible.

So, when conducting the reaction at 65-85 °C in water, alcohol, ester, acetonitrile, the polyketone particles of size 0,01-100 micrometers transform the polyesters by the oxidation under the peroxide agents: peroxybenzoic, m-chloroperoxybenzoic, peroxyacetic, trifluoroperoxyacetic, monoperoxyphthalic, monoperoxymaleine acids, combinations of H₂O₂ and urea or arsenic acid [405, 406].

For increasing of basic physical-mechanical characteristics and reprocessing, in particular of solubility, the synthesis of aromatic polyketones is lead through the stages of formation of oligomers with end functional groups accompanied by the production of block-copolyketones or through the one-stage copolycondensation initial monomers with production of copolyketones.

So, unsaturated oligeketons are produced [407, 408] by the condensation of aromatic esters (for example, bisphenyl ester, 4,4'-bisphenoxybisphenyl ester and others) with maleic anhydride in the presence catalyst AlCl_3 .

The oligoketones with end amino groups can be produced [409] on the basis of dichloranhydride of aromatic dicarboxylic acid, aromatic carbohydrate and telogen (N-acylanylode) according Friedel-Crafts reaction in organic dissolvent.

The oligoketones can be produced [410] by polycondensation of bisphenyloxide and 4-fluorobenzoylchloride in solution, in the presence of AlCl_3 . It has been found that the structure of synthesized oligomer is crystalline.

The synthesis of oligoketones, containing phthaloyl links, can be implemented [411] by the Friedel-Craft reaction of acylation.

The cyclical oligomers of phenolphthalein of polyarylenestersulfoneketone can be produced [412] by cyclical depolymerization of corresponding polymers in dipolaraprotic solvent (dimethylformamide), dimethylacetate in the presence of CsF as catalyst.

The aromatic oligoesterketones can be produced by means of interaction between 4,4'-dichlorbisphenylketone and 1,1-dichlor-2,2-di(3,5-dibrom-*n*-oxyphenyl)ethylene in aprotic dipolar dissolvent (dimethylsulfoxide) at 140 °C in inert gas [413]. The copolyesterketones of increased thermo-stability, heat- and fire-resistance can be synthesized on the basis of obtained oligomers.

The works on production of oligoketones and synthesis of aromatic polyketones on their basis are held in Kh.M. Berbekov Kabardino-Balkarian State

University.

So, availing the method of high-temperature polycondensation in environment of dimethylsulfoxide, the oligoketones are produced with edge hydroxyl groups with the degree of condensation 1-20 from bisphenols (diane or phenolphthalein) and dichlorobenzophenone. The condensation on the second stage is carried out at room temperature in 1,2-dichloroethane in the presence of HCl as acceptor and triethylamine as catalyst with introduction of the diacyldichloride of 1,1-dichlor-2,2-(*n*-carboxyphenyl)ethylene into the reaction. The reduced viscosity of copolyketones lies within 0,78-3,9 deciliter/gram for polymers on the basis of diane oligoketones and 0,50-0,85 deciliter/gram for polymers on the basis of phenolphthalein oligoketones. The mix of the tetrachloroethane and phenol in molar ratio 1:1 at 23 °C was taken as a solvent [414].

The aromatic block-copolyketones have been synthesized by means of polycondensation of oligoketones of different composition and structure with end OH-groups on the basis of 4,4'-dichlorobenzophenone and dichloranhydrides mixed with iso- and terephthalic acids in environment of 1, 2-dichloroethane [415-418].

The synthesis is lead via the method of acceptor-catalyst polycondensation. The double excess of triethylamine in respect to oligoketones is used as acceptor-catalyst. Obtained block-copolyketones possess good solubility in chlorinated organic solvents and can be used as temperature-resistant high-strength durable constructional materials.

1.6. Aromatic polyestersulfoneketones

Along with widely used polymer materials of constructional assignment such as polysulfones, polyarylates, polyaryleneketones et cetera, the number of researches has recently, within the last decades, appeared which deal with production and study of properties of polyestersulfoneketones [290, 419-433]. The

advantage of given polymeric materials is that these simultaneously combine properties of both polysulfones and polyaryleneketones and it allows one to exclude some or the other disadvantages of two classes of polymers. It is known, that high concentration of ketone groups results in greater T_{glass} and T_{flow} respectively, or – in better heat stability. On the other hand, greater concentration of ketone groups results in worsening of reprocessibility of polyarylenesterketones. That is why the sulfonation of the latter has been performed. The solubility increases with increasing of the degree of sulfonation. Polyestersulfoneketones gain solubility in dichloroethane, chloroform, dimethylformamide. The combination of elementary links of polysulfone with elementary links of polyesterketone also improves the fluidity of composition during extrusion.

The papers [424-433] report on various methods of production of polyestersulfoneketones.

The 4,4'-bis(phenoxy)bisphenylsulfone has been synthesized by means of reaction of phenol with bis-(4-chlorophenyl)sulfone and the low-temperature polycondensation of the product has been carried out in the melt with tere- and isophthaloylchloride resulting in the formation of polyarylenestersulfonesterketoneketones. The polycondensation is conducted in 1,2-dichloroethane at presence of $AlCl_3$ and N-methylpyrrolidone. Compared to polyesterketoneketones synthesized polymers have greater temperatures of glassing and decomposition and lower melting point and also possess higher thermal resistance [424].

The block-copolymers have been created by means of polycondensation of low-molecular polyesterketone containing the remnants of chloranhydride of carbonic acid and 4,4'-bisphenoxybisphenylsulfone (I) as end groups. The increase in concentration of component I result in greater glassing temperature and lower melting point of block-copolymers.

The block-copolymers containing 32,63-40,7% of component I have glassing

temperature and melting point respectively 185-193 °C and 322-346 °C, durability and modulus in tension respectively 86,6-84,2 MPa and 3,1-3,4 GPa and tensile elongation 18,5-20,3%.

Block-copolymers have good thermal properties and could be easily reprocessed in melt [425].

Polyestersulfoneketones have been produced by means of electrophilic Friedel-Crafts acylation in the presence of dimethylformamides and anhydrous AlCl_3 in environment of 1,2-dichlorethane on the basis of simple 2- and 3-methylbisphenyl esters and 4,4'-bis(4-chloroformylphenoxy)bisphenylsulfone. The copolymer has the molecular weight of 57000-71000, its temperatures of glassing and decomposition are 160,5-167,0 °C and >450 °C respectively, the coke end is 52-57 % (N_2). Copolyestersulfoneketones are well soluble in chloroform and polar dissolvents (dimethylformamide and others) and form transparent and elastic films [426].

Some papers of Chinese researchers are devoted to the synthesis and study of properties of copolymers of aryleneestersulfones and esterketones [427-429].

The block-copolyesters based on oligoesterketones and oligoestersulfones of various degree of condensation have been produced in paper [430] by means of acceptor-catalyst polycondensation; the products contain simple and complex ester bonds.

Polyestersulfoneketones possessing lower glassing temperatures and excellent solubility have been synthesized in [431] by means of low-temperature polycondensation of 2,2', 6,6'-tetramethylbisphenoxybisphenylsulfone, iso- and terephthaloylchloride in the presence of AlCl_3 and N-methylpyrrolidone in environment of 1,2-dichlorethane. The increasing concentration of iso- and terephthaloylchloride results in greater glassing temperatures of statistical copolymers.

The manufacture of ultrafiltration membranes is possible on the basis of mix polysulfone-polyesterketone [432, 433]. Transparent membranes obtained by means

of cast from solution have good mechanical properties in both dry and hydrated state and keep analogous mechanical properties after exposition in water (for 24 hours at 80 °C). The maximal conductivity of membranes at 23 °C is $4,2 \times 10^{-2}$ Sm/cm while it increases to 0,11 Sm/cm at 80 °C.

In spite of a number of investigations in the area of synthesis and characterization of polyestersulfoneketones, there are no data in literature on the polyestersulfoneketones of block-composition based on bisphenylolpropane (or phenolphthalein), dichlorbisphenylsulfone and dichlorbenzophenone, terephthaloyl-bis(*n*-oxybenzoylchloride).

Russian references totally lack any researches on polyestersulfoneketones, not speaking on the production of such polymers in our country. Accounting for this, we have studied the regularities of the synthesis and produced block-copolyestersulfoneketones of some valuable properties [423]. The main structure elements of the polymers are rigid and extremely thermo-stable phenylene groups and flexible, providing for the thermoplastic reprocessibility, ester, sulfone and isopropylidene bridges.

Synthesized, within given investigation, polyestersulfoneketones on the basis of phthalic acid; polyarylates on the basis of 3,5-dibromine-*n*-oxybenzoic acid and phthalic acids and copolyesters on the basis of terephthaloyl-bis(*n*-oxybenzoic) acid are of interest as heat-resistant and film materials which can find application in electronic, radioelectronic, avia, automobile, chemical industries and electrotechnique as thermo-stable constructional and electroisolation materials as well as for the protection of the equipment and devices from the influence of aggressive media.

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