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Polyarylates. Synthesis and properties

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Abstract. Data on the synthesis and properties of various types of polyarylates, including cardo-, self-coloured, self-protecting, carbaborane-containing, stereoregular, and block-polyarylates, etc., are examined and surveyed. It is shown that polyarylates represent a promising class of polymers with a valuable set of properties, which can be altered specifically by an appropriate design of the polymer chain. Certain aspects of the practical use of polyarylates are considered. The bibliography includes 320 references.

I. Introduction

In terms of their theoretical and practical importance, heterochain polyesters occupy an important place among synthetic high-molecular-mass compounds. The first representatives of these polymers had already been obtained in the last century.[1–4] Since then, there has been a continuous development of this field in polymer chemistry.

The study of the interrelation between the structure and properties of heterochain polyesters has led to the idea that the most interesting properties, and especially enhanced thermal characteristics, may be expected from polymers based on aromatic components. Thus the syntheses of a series of polyesters of aromatic dicarboxylic acids and aliphatic glycols have been achieved. Among these compounds, poly(ethylene terephthalates) and poly(butylene terephthalates) are of undoubted practical interest. The aromatic ring can be introduced into the polyester chain also via the diol component.

Polyarylates are heterochain polyesters of dihydric phenols. The first representatives of polyesters of this type were polycarbonates, i.e. polyarylates of dihydric phenols and carbonic acid, which were synthesised in 1898 by Einhorn[5] by the interaction of phosgene with resorcinol and hydroquinone. The study of polycarbonates developed during the 1960s because polymers of practical value were discovered among them, in particular the polycarbonate of 2,2-bis(4-hydroxyphenyl)propane.[6,7]

In 1957–1958 publications on the polyarylates of aromatic dicarboxylic acids, with a series of valuable properties, began to appear almost simultaneously in Belgium, the USSR, and the USA.[8–10] The studies on these polymers have continued to this day.

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II. Synthesis of polyarylates and their properties

Polyarylates can be obtained by the interaction of dicarboxylic acids with dihydric phenols (method I), of the diacetates of dihydric phenols with dicarboxylic acids (method II), and of dihydric phenols with dicarboxylic acid esters (method III), but the synthesis of polyarylates using the chlorides of dicarboxylic acids as the acid reagents (method IV) has assumed the greatest importance.

In the synthesis of polyarylates by the first three methods,[4,10–31] the polycondensation is usually carried out in the melt in an inert gas stream; in the final stage, the reaction mixture is heated in vacuo. A disadvantage of these methods is their unsuitability for the synthesis of polyarylates with high softening temperatures. Furthermore, the polyarylates obtained by polycondensation in the melt frequently acquire a colour during the reaction.[32]

The last method is best for the synthesis of high-melting polyarylates as well as polyarylates containing reactive groups in their chains. The employment of highly reactive dicarboxylic acid chlorides makes it possible to carry out successfully the polycondensation in solution. This method is of great importance in the synthesis of high-melting polyarylates, since it is then possible to achieve successful polycondensation up to a high degree of reaction without the decomposition of the polymer formed.

The polycondensation of dicarboxylic acid chlorides with dihydric phenols can be achieved in several versions: (1) at an elevated temperature in a high-boiling solvent; (2) as interfacial polycondensation; (3) as acceptor-catalytic polyesterification.

The characteristics of the polycondensation of dicarboxylic acid chlorides with dihydric phenols in a high-boiling solvent have been investigated in a number of studies.[4,11,14,33–40] It was established that the reactivity of the starting materials is greatly influenced by their structure.[33,37–45]

For example, when the condensation is carried out in dinyl (azeotropic mixture of diphenyl ether with biphenyl) in the temperature range 150–210 °C, it was found that isophthalic acid chloride reacts with 2,2-bis(4-hydroxyphenyl)propane at a higher rate than terephthalic acid chloride (at 170 °C, the rate constants are 10.7×10^{-5} and 6.6×10^{-5} litre mol^{-1} s^{-1} respectively). At 170 °C, dihydric phenols can be arranged in the following sequence in terms of the rate of their reaction with terephthalic acid chloride: hydroquinone > resorcinol > 2,2′-dihydroxybiphenyl > 2,2-bis(4-hydroxyphenyl)propane.[41]

The study of the kinetics of the polycondensation of terephthalic acid chloride with bis(4-hydroxyphenyl)methane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)-hexafluoropropane, bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxyphenyl)-2-phenylethane, bis(4-hydroxyphenyl)-trifluoromethylphenylmethane, and bis(4-hydroxyphenyl)-diphenylmethane in ditolylmethane in the temperature range 160–200 °C showed that the nature of the substituents at the central carbon atom of the bisphenol sometimes exerts a significant influence on the rate of polycondensation.[39] Thus the replacement of the electron-donating methyl groups in 2,2-bis-(4-hydroxyphenyl)propane by the strongly electron-accepting trifluoromethyl groups makes the rate of polycondensation of 2,2-bis(4-hydroxyphenyl)hexafluoropropane with terephthalic acid chloride higher by a factor of 2–2.5 than the rate of polycondensation of 2,2-bis(4-hydroxyphenyl)propane.

The introduction of side groups by substitution into the aromatic rings of the dihydric phenol in the *ortho*-position relative to the hydroxy-group diminishes the rate of reaction with aromatic dicarboxylic acid chlorides.[40,43] For example, when the extents of reaction of aromatic dicarboxylic acid chlorides with 2,2-bis(4-hydroxyphenyl)propane and 2,2-bis(3-allyl-4-hydroxyphenyl)propane are compared, it is found that the process is slower in the case of the diallyl-substituted bisphenol. Thus, whereas the degree of reaction of isophthalic acid chloride with 2,2-bis(4-hydroxyphenyl)propane at 220 °C (in dinyl) is 0.89 after only 1 h, in the case of the diallyl-substituted bisphenol the extent of reaction over the same period is only 0.34 and reaches 0.83 only after 9 h. Hence it follows that it is desirable to carry out the polycondensation of the diallyl-substituted bisphenol with terephthalic and isophthalic acid chlorides at an elevated temperature of the order of 220 °C over a long period.[43]

The rate of polycondensation of dicarboxylic acid chlorides with dihydric phenols containing substituents in the *ortho*-position relative to the hydroxy-group is influenced not only by the size but also by the chemical nature of the substituent. Thus the rate constants of the polycondensation of terephthalic acid chloride with 2,2-bis[3-methyl(propyl, chloro)-4-hydroxyphenyl] propanes are lower at the corresponding temperatures than the rate constants for the unsubstituted dihydric phenol in the same reactions.[40]

We shall also consider the synthesis of mixed block-polyarylates by high-temperature polycondensation in solutions of dicarboxylic acid chlorides, bis-phenols, and various low-molecular-mass polymers with terminal hydroxy-groups.[33,46–51] The block components employed were poly(ethylene oxide) $HO(CH_2CH_2O)_nH$, poly(propylene oxide) $HO[CH(CH_3).CH_2O]_nH$, poly[3,3-bis(chloromethyl)trimethylene oxide] $HO.[CH_2C(CH_2Cl)_2CH_2O]_nH$, and a silicon-containing oligomer having the structure $\{HOC_6H_4C(CH_3)_2C_6H_4[OSi(CH_3).(C_6H_5)]\}_2O$, i.e. polymers without reactive bonds in their chains with the exception of reactive terminal functional groups. Since the ether group is inert with respect to exchange reactions, such block components, used as one of the initial diols for the synthesis of the polyester, were introduced without change into the polymer chain of the final product, modifying it significantly. The properties of such mixed block-polyarylates are determined both by the composition and structure of the initial components and by the process conditions because the reactivities of the block component and of the dihydric phenol differ from one another. Comparative study of the kinetics of the polycondensation of terephthalic acid chloride with 2,2-bis(4-hydroxyphenyl)propane and the bifunctional block components listed above in ditolylmethane at 220 °C showed that these diols can be arranged in the following sequence in terms of their reactivity towards the acid chloride: poly(ethylene oxide) > poly(propylene oxide) > 2,2-bis(4-hydroxyphenyl)propane > poly[3,3-bis(chloromethyl)-trimethylene oxide] > silicon-containing oligomer.[47]

Apart from the synthesis of linear thermoplastic polyarylates, thermoreactive polymers can also be obtained by polycondensation in a high-boiling solvent. These include, for example, polyarylates containing free hydroxy-groups in the chain, obtained by the polycondensation of aromatic dicarboxylic acid chlorides with dihydric phenols and polyhydric aliphatic alcohols [glycerol, tris(hydroxymethyl)propane, pentaerythritol, tris(hydroxymethyl)ethane, etc.].[37,52–54]

Comparative study of the kinetics of the polycondensation of terephthalic and isophthalic acid chlorides with 2,2-bis(4-hydroxyphenyl)propane and tris(hydroxymethyl)ethane in dinyl showed that aromatic dicarboxylic acid chlorides react with polyhydric aliphatic alcohols much more vigorously than with dihydric phenols.[37] The extent of reaction is greatly influenced by the chemical nature of the diol component. Thus the extent of reaction of isophthalic acid chloride with tris(hydroxymethyl)-propane at 150 °C is 0.74 after 9 h, whereas in the case where 2,2-bis-(4-hydroxyphenyl)propane is used as the diol component it is only 0.21. In the latter case, the extent of reaction can be raised to 0.74 after 8 h only by carrying the polycondensation at 210 °C, i.e. at a higher temperature. In the polycondensation of isophthalic acid chloride with 2,2-bis(4-hydroxyphenyl)propane at 220 °C, the extent of reaction is 0.89 after only 1 h.

The above data show that it is desirable to synthesise mixed polyarylates containing free hydroxy-groups in the chain in two stages. The first stage — the polycondensation of the dihydric phenol with a dicarboxylic acid chloride — should be carried out at an elevated temperature (up to 220 °C). The second stage (after the entire dihydric phenol has reacted) — the polycondensation of the polyarylate formed with an aliphatic polyhydric alcohol — must be performed at lower temperatures (110–150 °C), which makes it possible to attain a fairly high degree of reaction without premature hardening of the product.[37,55]

Much attention has also been devoted to the study of processes occurring in the synthesis of polyarylates with the aid of interfacial and acceptor-catalytic polyesterification.[4,11,13,15,56–70]

Using all three variants, polymers with high molecular masses [for example up to 150 000 for the polyarylates obtained from 2,2-bis(4-hydroxyphenyl)propane and the chlorides of terephthalic and isophthalic acids by interfacial polycondensation, 60 000–100 000 for the polyarylates obtained by the high-temperature polycondensation in solution of phenolphthalein and aromatic dicarboxylic acid chlorides] can be obtained in nearly quantitative yields from dicarboxylic acid chlorides and dihydric phenols.[33,56]

The polycondensation of dicarboxylic acid chlorides with dihydric phenols has been used successfully for the synthesis of polyarylates having a wide variety of chemical structures.

As early as the 1930s, mention was made of the use of phenolphthalein for the synthesis of polyesters in a list of initial compounds published in an American patent.[71] Data on the synthesis of alkyd polymers using fluorescein and phenolphthalein were published in 1946.[72] However, a characteristic feature of these studies is that phenolphthalein was used simply as one of the representatives of the enormous number of diols without taking into account its specific contribution to the properties of the polymers.

Polyarylates derived from phenolphthalein and aromatic dicarboxylic acids were first obtained in 1961 and attention was turned to the specific contribution of the phthalide side group to a valuable set of properties of these polymers: the combination in the latter of an increased thermal stability with an effective solubility in organic solvents.[73,74] It was subsequently suggested that polymers of this type, i.e. those containing in the repeat unit at least one element entering into the composition of the cyclic side group, be called cardo-polymers,[75] from the Latin word 'cardo', which means loop, because such groups can be regarded as loops in relation to the main chain of the macromolecule. In subsequent years, the studies in the field of cardo-polyarylates developed extensively.[11,12,33,56,57,73–113]

In the synthesis of cardo-polyarylates, various dihydric phenols containing closed cyclic groups at the central carbon atom were used as the starting materials: phenolphthalein, phenolfluorene, phenolanthrone, phenolacenaphthylene, phenolphthalein imide, its *N*-β-hydroxyethyl and allyl derivatives, etc. The acid chlorides of aromatic dicarboxylic acids of the cardo-type, for example diphenylnaphthalide-4,4′-dicarboxylic acid, have also been used in a number of cases. For example, phenolphthalein polyarylates with a high molecular mass (up to ~100 000) have been obtained successfully by acceptor-catalytic polyesterification in an organic solvent at moderate temperatures (up to ~50 °C) in the presence of a tertiary amine or by polycondensation in an inert medium at an elevated temperature (100–200 °C) in a high-boiling solvent. Since the process takes place in the absence of a catalyst in the latter case, its completion requires approximately 10 h.

An interesting feature was discovered in the study of the formation reactions of phenolphthalein polyarylates in a high-boiling solvent. It was established that the properties of the polyarylate obtained from isophthalic acid and phenolphthalein varied appreciably depending on the nature of the solvent in which the process was carried out.[114]

The chemical structure of the polyarylates obtained from phenolphthalein and aromatic dicarboxylic acids ensures a high rigidity of their macromolecules. For this reason, in the synthesis of such polyarylates in ditolylmethane, which is not a solvent for the polymer obtained, the free energy of formation of the coiled macromolecules should be smaller than the free energy of formation of the uncoiled macromolecules. This results in the selection, during the synthesis, of globular forms of the macromolecules and ensures the globular type of supermolecular structure of the phenolphthalein polyarylates synthesised in ditolylmethane. On the other hand, in the synthesis of the phenolphthalein polyarylate in α-chloronaphthalene or nitrobenzene, which are solvents also for the polymer formed, uncoiled (extended) macromolecules are formed preferentially. Fibrillar supermolecular structures arise as a result of this. The polymers with such supermolecular structure have a better set of physicochemical properties. This follows from Table 1, which presents the characteristics of the isophthalic–phenolphthalein polyarylates synthesised in various media.

Table 1. The properties of phenolphthalein–isophthalic acid polyarylate.

Properties of polyarylate	Medium in which the polyarylate has been synthesised			
	ditolyl-methane	α-chloro-naphthalene		nitro-benzene
Molecular mass	28 000	28 000	48 000	26 000
Softening temperature/°C	270	290	300	275
Tensile strength/ kgf cm^{-2}	640	740	780	650
Elongation at rupture (%)	10–20	80	100	40–70
Specific impact strength/ (kgf cm) cm^{-2}	2–3	10	20	14

The synthesis of polyarylates based on 2-(β-hydroxyethyl)-3,3′-bis(4-hydroxyphenyl)phthalimidine or phenolphthalein imide at elevated temperatures is nonspecific, since infusible and insoluble polymers with a three-dimensional structure are then formed owing to the trifunctional nature of the initial bisphenols. At the same time, the interfacial polycondensation of these bisphenols with dicarboxylic acid chlorides, carried out under mild conditions, leads to linear high-molecular-mass polyarylates containing free hydroxy- or NH groups in the chain,[81,82,115] which do not interact with the acid chloride groups under the conditions of the given reaction.

The use of such bisphenols in the synthesis of polyarylates in a mixture with the usual bisphenols leads, for example, to the possibility of a clear-cut regulation of the content of the reactive group along the polymer chain. Such polymers have advantages over the widely known alkyd polymers because of their linear structure, high softening temperature, high molecular mass, and a uniform distribution of the free functional groups NCH_2CH_2OH or NH along the chain.

The development of the theory of nonequilibrium (irreversible) polycondensation and the advances in the field of its preparative methods of synthesis have created broad preconditions for the synthesis of block-copolymers of the polycondensation type. This applies in the first place to acceptor-catalytic polycondensation,[33,68,116,117] the mild conditions of which make it possible to synthesise block-copolymers with virtually complete suppression of exchange reactions. When the process characteristics are known adequately, this makes it possible to produce block-copolymers directly from the monomers.[68] Even greater prospects for controlling the microstructure of the polymer chain in block-copolymers and hence their properties arise when oligomers and polymers with terminal functional groups are used as the starting materials for their synthesis.[116–148]

At least three methods of synthesis of polycondensation block-copolymers are realistic, for example the synthesis of polyarylate-arylene sulfone oxide block-copolymers.

(1) The synthesis in two reaction volumes of oligomers, having different chemical structures, with a specified molecular mass and heterofunctional groups followed by their copolycondensation (Scheme 1).

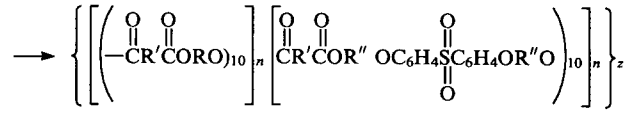
Scheme 1

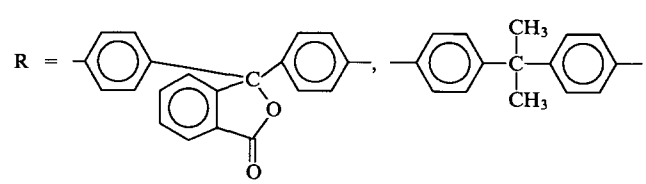
$$10n\,HOROH + 11n\,ClOCR'COCl \longrightarrow$$

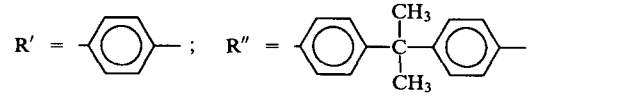
$$\longrightarrow n\,Cl(OCR'COORO)_{10}OCR'COCl$$

A

$$A + HOR''(OC_6H_4SO_2C_6H_4OR'')_{10}OH \xrightarrow{-2n\,HCl}$$

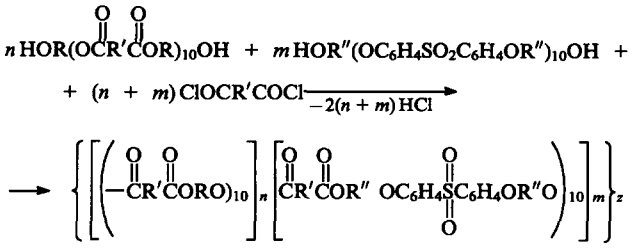






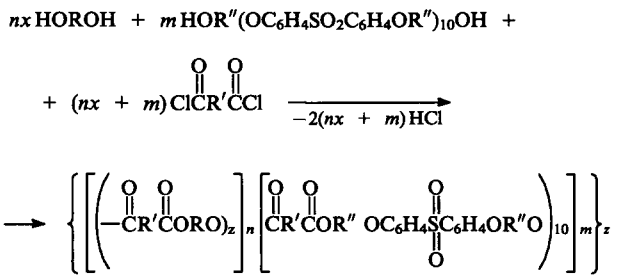
(2) The synthesis in two reaction volumes of oligomers, having different chemical structures, with a specified molecular mass and homofunctional end groups and their copolycondensation with the aid of an intermonomer (a chain lengthening agent) (Scheme 2).

Scheme 2



(3) The synthesis of an oligomer having a specified molecular mass and its copolycondensation with a low-molecular-mass monomer and an intermonomer, the interaction of which gives rise to polymer blocks having a different chemical structure (Scheme 3).

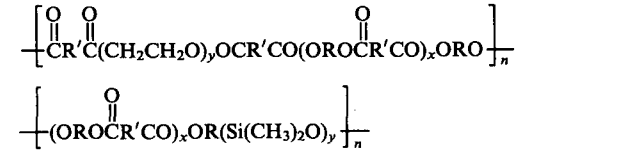
Scheme 3



Naturally, depending on the method of synthesis of the block-copolymers, the chemical structure of the monomers and the block components, their molecular mass, the length of blocks having different chemical structures and their distribution along the macrochain all vary, i.e. the nonuniformity of the composition of the block-copolymer and hence its properties vary. It follows from the three schemes presented above that the block-copolymers having the most regular structure are obtained as a result of acceptor-catalytic polyesterification in accordance with Scheme 1.

The polycondensation method makes it possible to vary widely the position of the block-copolymers. Thus various block-copolymers containing both polymer blocks having similar chemical structures (for example, polyarylate-arylene sulfone oxides [119-123,136,137]) and polymer blocks differing appreciably in their structure and properties from polyarylates [for example, polyarylate-ethylene oxides [120,131,137,140,141] or polyarylate-organosiloxanes [125-129,137-139] (Scheme 4)] have been obtained (and investigated) on the basis of cardo-polyarylates incorporating terephthalic and isophthalic acids (polyarylate F-1 in the case of isophthalic acid) and the polyarylate obtained from 2,2-bis-(4-hydroxyphenyl)propane and terephthalic and isophthalic acids (polyarylate D).

Scheme 4



Deeper study of nonequilibrium condensation processes, especially acceptor-catalytic polyesterification, created theoretical preconditions for the synthesis of stereoregular polyarylates the molecules of which contain regular sequences of stable rotational isomers. [68,145,149-160]

The fundamental novelty of the synthesis of conformationally regular polyarylates consists in the fact that their regular steric microstructure is formed directly during the growth of the macromolecule when monomers which are neither conformational nor configurational isomers but their molecules contain fragments with hindered internal rotation are used in the reaction. An example of polyarylates of this kind is provided by the stereoregular polyterephthalates based on disubstituted 2,2-bis-(4-hydroxyphenyl)propanes, for example 2,2-bis(3-chloro-4-hydroxyphenyl)propane.

Comparison of the stereotacticities of the polymers obtained with the conditions of their synthesis made it possible to formulate a series of rules governing the formation of such macromolecules. Thus in the presence of weakly basic heterocyclic tertiary amines (nucleophilic catalysis), mainly polyarylates with the *cis*-disposition of the substituents in the bisphenol fragment are formed, whereas in the presence of highly basic trialkylamines (general base catalysis) polyarylates with the *trans*-isomers are produced, which is associated with the different geometries of the transition complexes. The presence of regular sequences of isomeric forms in the macromolecules of polyarylates influences significantly their properties. In particular, an increase in the stereotacticity of the polymers increases the degree of their crystallinity and their softening temperatures and diminishes their solubility. The synthesis of stereoregular polyarylates is illustrated schematically (Scheme 5).

A special series of studies have been carried out on the so called 'self-coloured' polyarylates. [161-166] Aromatic polyesters are known to be extremely difficult to dye. [161,166] It has been found that in the case of polyarylates this problem can be solved by synthesising polymers the macromolecules of which contain chemically bound dye molecules.

The construction of such a polymer chain is achieved by employing chromophore-containing dihydric phenols and dicarboxylic acid chlorides together with the usual phenols and acids for the synthesis of polyarylates. Thus homogeneous and mixed polyarylates, containing anthraquinone residues or azo-groups in the chain, have been synthesised, and their properties investigated, from compounds such as the chlorides of azobenzene-3,3'- and azobenzene-4,4'-dicarboxylic acids, 2,2' and 4,4'-dihydroxy-, 4,4'-dihydroxy(ethoxy), and 4,4'-dihydroxy-(propoxy)-azobenzenes, quinizarin, alizarin, and Alizarin Blue. The use of fumaric acid chloride as the acid reagent in the synthesis of such polyarylates made it possible to obtain coloured polyarylates capable of copolymerising with various monomers. Table 2 (page 838) presents examples of the polymers obtained.

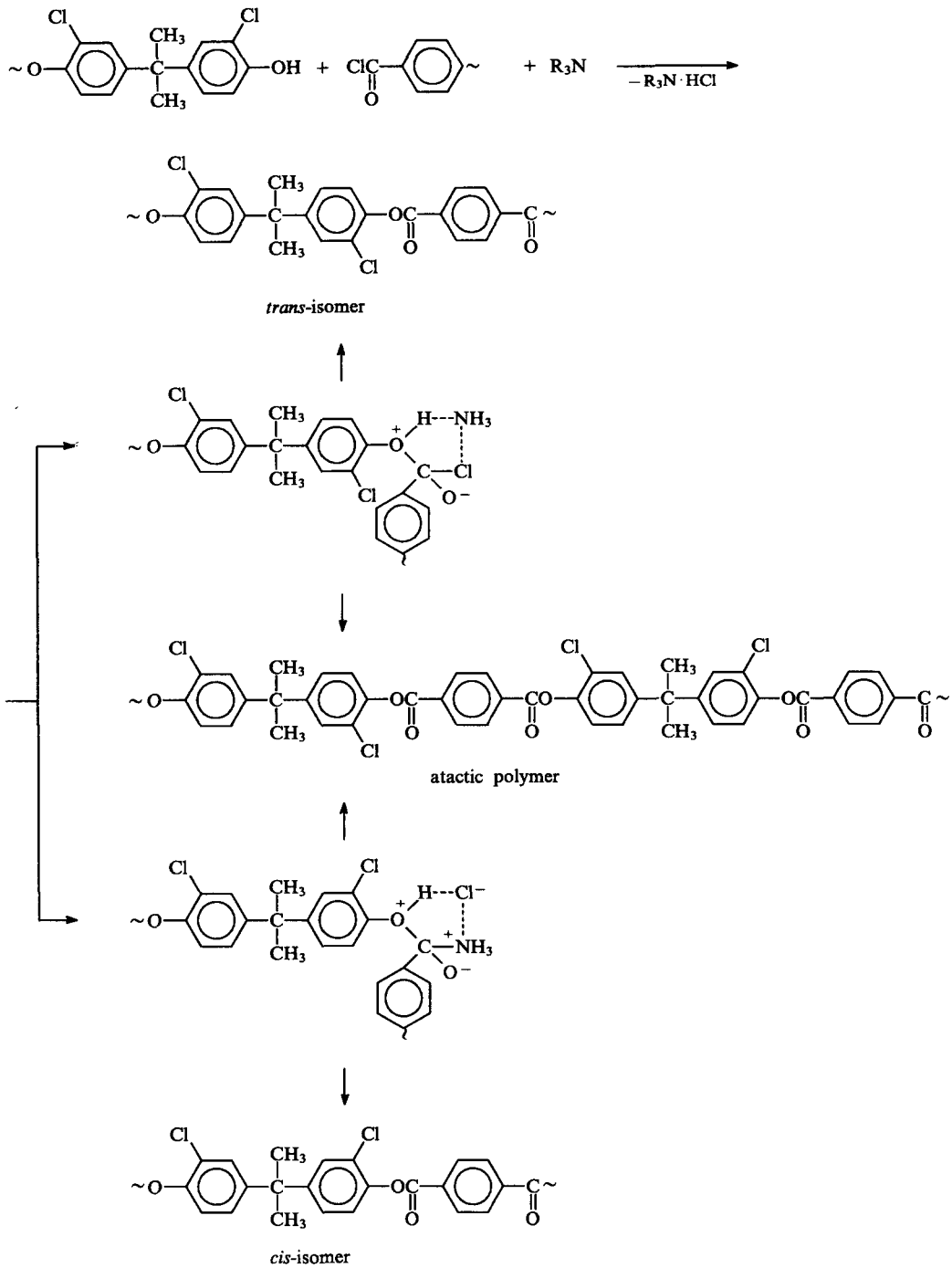
All these polyarylates are substances having colours corresponding to that of the starting material. It is noteworthy that, as part of the coloured component in the homopolyarylate is replaced by a colourless monomer, the colour of the polyarylate is usually retained and the intensity of the absorption in the visible region varies in proportion to the concentration of the coloured component in the polymer. The relatively high intensity of the absorption in the visible spectra of self-coloured polyarylates with even small amounts (for example 0.1-0.05 mole) of coloured chromophore-containing monomers in the mixture of the initial components suggests a technologically extremely simple solution of the problem of dyeing the known polyarylates. [163,166]

The fact that molecules of the coloured substance in the self-coloured polyarylates are covalently linked to other components renders their colour stable towards various influences, including the action of light, which is one of the most important characteristics of the colour. For example, in the case of self-coloured homopolyarylates and copolyarylates containing only 0.05 mol.% (2-3 mass%) of a chromophore-containing substance, the photostability proved to be satisfactory.

It has been observed that the introduction of even small amounts of a chromophore-containing monomer into the polyarylate chain appreciably increases the resistance of solutions and films of these polymers to the action of UV radiation. [161]

Transparent coloured films, the tensile strength of which in the nonoriented state at room temperature varies in the range from 800 to 1300 kgf cm^{-2}, have been obtained from a series of coloured polyarylates containing different amounts of a chromophore-containing substance. Tests on these films at

Scheme 5



elevated temperatures showed that at 250 °C they retain up to 40% of the initial strength. The coloured polyarylates can be worked to produce cast and moulded articles. The specific impact strength of moulded specimens of the 4,4'-dihydroxyazobenzene polyarylate is 25 (kgf cm) cm^{-2}.[166]

A series of coloured polyarylates containing fumaric acid fragments in their macromolecules are satisfactorily compatible with various monomers (styrene, methyl methacrylate, diallyl isophthalate), forming with the latter under appropriate conditions coloured copolymers in the form of transparent coloured monolithic substances. Compositions comprising self-coloured unsaturated polyesters with unsaturated monomers have been used successfully in the preparation of yellow and red vitreous plastics possessing a high photostability and an effective chemical stability in addition to good mechanical parameters.[161,166]

Thus chromophore-containing bisphenols and dicarboxylic acids are of interest not only from the standpoint of the synthesis of new heat-resistant coloured polyesters but also from the standpoint of imparting a predetermined colour with a specified intensity to colourless polyarylates most interesting from the practical point of view and of an appreciable improvement of the photochemical stability of these polymers.[161]

In order to find polyarylate structures with an increased photostability, a study has been made of the effect of ultraviolet radiation on specifically synthesised homogeneous and mixed polyarylates based on phenolphthalein, phenolsulfophthalein, bis(4-hydroxyphenyl) sulfone, phenolphthalein anilide, phenolphthalein imide, phloroglucinol, and the chlorides of terephthalic, isophthalic, and methylphosphinic acids, bis(4-carboxyphenyl)-methyl ether, and a number of others.[167-174]

It has been found that the partial or complete replacement of the lactone ring by a lactam ring in phenolphthalein polyarylates as well as the presence of a cyclic substituent with a conjugated bond system (for example, the fluorenyl substituent) at the central

Table 2. Certain properties of coloured polyarylates.

Starting material		Temperature/°C		Colour of powdered polymer
acid chloride	dihydric phenol	softening	onset of decomposition[a]	
Azobenzene-3,3'-dicarboxylic acid	phenol-phthalein	250	310	yellow
Azobenzene-4,4'-dicarboxylic acid	"	295	360	red
Azobenzene-3,3'-dicarboxylic acid	2,2'-dihydroxy-azobenzene	230	350	bright yellow
Azobenzene-4,4'-dicarboxylic acid	"	235	380	orange
Azobenzene-3,3'-dicarboxylic acid	4,4'-dihydroxy-azobenzene	350	385 (380)	"
Azobenzene-4,4'-dicarboxylic acid	"	400[b]	410 (410)	yellow
Terephthalic acid	"	400[b]	415 (415)	yellow
	1,4-dihydroxy-anthraquinone	400[b]	420 (390)	green-yellow
	1,2-dihydroxy-anthraquinone	150	360 (360)	green
	7,8-dihydroxy-5,6-phthalyl-quinoline	190	300	blue-violet

[a] Obtained from the results of thermogravimetric analysis at a heating rate of 17 °C per minute; the values in brackets were obtained at a heating rate of 3 °C per minute.
[b] Softening takes place with decomposition.

carbon atom in the bisphenol residues appreciably increase the resistance of the polymer to the action of light. The inclusion of small amounts (~1%) of sulfur, phosphorus, and free phenolic groups in the polyarylate chain afforded polyarylates with increased resistance to light-induced ageing.

As shown above, the photostability of polyarylates can be increased also by introducing into their polymer chain the residues of bifunctional chromophore-containing substances (for example, 1,3-dihydroxyanthraquinone). It is also noteworthy that the high photostability of polyarylates, exhibited when their solutions are irradiated, may be due to the occurrence under these conditions of the Fries rearrangement, which leads to the appearance in the polymer chain of hydroxyketone groups stabilising the polymer.

The introduction of sulfur and phosphorus into the structure of phenolphthalein polyarylates increases not only the photostability of the polymers but also their thermal stability and in the case of phosphorus their fire resistance.

Thus polymers with 'self-protecting' properties as regards the action of light and heat can be obtained with the aid of specific design of the polyarylate chain.[174]

Polyarylates containing reactive groups in their chain, for example hydroxy-groups, and double bonds possess thermoreactive properties. They are capable of long-range chemical reactions and of undergoing a transition to an infusible three-dimensional state as a result of both heat treatment and various chemical reactions.

Thus polyarylates based on polyhydric alcohols containing free hydroxy-groups in their chain are capable of undergoing a transition to a three-dimensional state on additional heat treatment and as a result of their interaction with pyromellitic, maleic, and phthalic anhydrides, diisocyanates, metal derivatives, and other reagents,[52-54,175,176] whereupon the properties of the polymers are modified significantly, for example their thermal characteristics are improved.

The double bond-containing polyarylates based on 2,2-bis(3-allyl-4-hydroxyphenyl)propane (with added 2-allylphenol) and fumaric acid may be hardened on heating or as a result of copolymerisation with other unsaturated compounds.[177-186] This made it possible to modify within wide limits the properties of the polymers, in particular to improve their thermal characteristics. For example, high elastic deformation over a wide temperature range is characteristic of the hardened polyarylate obtained from isophthalic acid and 2,2-bis(3-allyl-4-hydroxyphenyl)propane; the decomposition of this polymer is observed at temperatures exceeding 500 °C.[11]

Polyarylates derived from aromatic dicarboxylic acids possess a valuable set of properties: high heat resistance and thermal stability, effective insulating properties over a wide temperature range, and resistance to the action of many chemical reagents, UV light, and ionising radiation.

The physicochemical properties of these polymers are closely related to their structure and depend on the disposition of the functional groups in the initial components and also on the presence and nature of substituents. The highest melting points are observed for polyarylates whose monomers contain functional groups in the *para*-positions and have no aliphatic units. Thus poly(hydroquinone terephthalate) and *o*-hydroxybenzoic acid polyarylate (econol) do not melt up to 500 °C, and the softening temperatures of phenolphthalein–terephthalic acid and phenolphthalein–isophthalic acid polyarylates are 340 and 275 °C respectively.

The high heat resistance of cardo-polyarylates[11,12,56,76-79,82,92,99,102] greatly exceeds that of polyarylates with similar chemical structures but not containing cardo-groups. For example, the softening temperatures of polyarylates of terephthalic acid combined with phenolphthalein, phenolfluorene, and phenolanthrone are 340, 350, and 360 °C respectively, whereas that of poly[bis(4-hydroxyphenyl)diphenyl methane terephthalate] is 280 °C. The heat resistance of polyarylates increases significantly with increase in the number of aromatic rings in the initial components.

The presence of alkyl substituents in the *ortho*-positions relative to the hydroxy-group of the bisphenol as it were promotes the 'internal' plasticisation of the polyarylates based on them.[187-191] Polyarylates obtained from terephthalic acid and such bisphenols have lower softening temperatures [for example, the softening temperature of the 2,2-bis(4-hydroxy-3-methylphenyl)propane polyarylate is 180 °C] and a greater impact resistance and they can be more readily worked to form monolithic articles than the polyarylates derived from the corresponding ring-unsubstituted bisphenols.

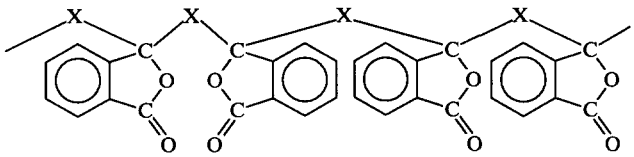
The properties of polyarylates are also closely related to the nature of the side substituents at the central carbon atom of the dihydric phenol.[192-199]

The decrease in the packing density of the polymer chains as a consequence of the presence of functional groups in the initial components in the *meta*- or *ortho*-positions rather than *para*-positions and the presence of side substituents in dihydric phenols promote the formation of amorphous polyarylates. The tendency of polyarylates to crystallise also diminishes with the appearance of an asymmetric substituent at the central carbon atom of the bisphenol.[4,11]

Since polyarylates based on phenolphthalein and an acid such as terephthalic it had always been obtained in the amorphous form, the impression was created initially that this is a specific feature of the cardo-polymers due to the large bulk of their cyclic substituents. However, deeper study of polyarylates with different cardo-groups made it necessary to revise this idea. It was found that, despite the large bulk of the cardo-group, these polymers are capable of crystallising. The conditions facilitating their crystallisation are the symmetry of the shape of the cardo-group (fluorene and anthrone groups) and the presence in the polymers of polar components (the anthrone group).

This made it necessary to look again at the lack of capacity for crystallisation in cardo-polyarylates containing cardo-groups with an asymmetric shape (phthalide and acenaphthene groups) and to attempt an explanation of this feature in terms of the atactic nature of the polyarylates obtained. As a consequence of the asymmetry of their shape and the statistical nature of the polycondensation reaction, the cardo-groups in such polymers are arranged in different nonordered ways relative to the main axis of the macromolecule (Scheme 6).

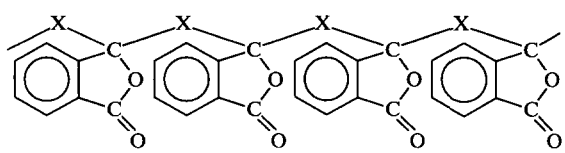
Scheme 6



Subsequently it was demonstrated for polyarylates with phthalimidine groups that polyarylates with asymmetric cardo-groups can also crystallise. This is apparently achieved by virtue of the presence of hydrogen bonds promoting a definite disposition and orientation of the macromolecules. A greater crystallinity can be achieved when the orientational mobility of the hydrogen is facilitated to the maximum extent (the H atom at the nitrogen atom is replaced by the CH_2CH_2OH group).[82]

The crystallisation of polyarylates with phthalimidine groups gives rise to the hope that, by an appropriate selection of the conditions in the synthesis or by subsequent treatment of the finished polymer, it may be possible to achieve the crystallisation also of polyarylates containing asymmetric cardo-groups such as the phthalide group. It is quite logical to suppose that this would be promoted by a regular disposition of the groups along the polymer chain (Scheme 7).

Scheme 7



The possibility of a deliberate change in structure is undoubtedly an important factor which will make it possible to achieve the desired modification of the properties of the polymers. For example, the heat resistance of the polyarylate obtained from phenolanthrone and terephthalic acid may be varied by altering the conditions in the synthesis and in the subsequent treatment of the polymer.[84,85,99] It increases significantly on passing from an amorphous polymer to one with an ordered structure: the amorphous polyarylate softens at ~340–360 °C, whilst the crystalline one does not soften before decomposition.[86]

Polyarylates with a definite structure also exhibit liquid crystal properties.[200–211]

The solubility of polyarylates is likewise associated with their chemical structure. Polyarylates derived from aromatic dicarboxylic acids such as terephthalic and isophthalic acids and biphenyl-4,4′-dicarboxylic acid and bisphenols such as hydroquinone and resorcinol are almost insoluble in organic solvents. The presence of side substituents in the bisphenol increases the solubility of the polyarylates. The polyarylates obtained from isophthalic acid, on the one hand, and 2,2-bis(4-hydroxyphenol)-propane, 2,2-bis(4-hydroxyphenyl)butane, and bis(4-hydroxy-phenyl)diphenylmethane, on the other, are soluble in cresol and chlorinated hydrocarbons. Compared with noncardo-polymers, cardo-polymers are much more readily soluble in organic solvents.[11,102] For example, the polyarylates obtained from phenolphthalein and aromatic dicarboxylic acids dissolve readily in methylene chloride, chloroform, dichloroethane, *sym*-tetra-chloroethane, tetrahydrofuran, cyclohexanone, etc., forming highly concentrated (> 25%) solutions.

The presence of mobile hydrogen atoms in the cardo-groups (for example, in the polyarylates of phenolphthalein imide), which are capable of involvement in the formation of hydrogen bonds, narrows the range of solvents. Such polyarylates no longer dissolve in chlorinated solvents but are readily soluble in solvents capable of forming hydrogen bonds with the mobile hydrogen atoms in the polyarylates (in dimethylformamide, tricresol, etc.).[81,82] Mixed polyarylates are more soluble than the homopolymers.[11]

Polyarylates possess film- and fibre-forming properties. In order to exhibit film-forming properties, the polymers must have an intrinsic viscosity (η_{int}) (in dichloroethane or tetrachloro-ethane) of the order of 0.4–0.5 dl g^{-1}, while the value required for fibre formation is approximately 1.0 dl g^{-1}. The breaking stress on extension of nonoriented polyarylate films is 600–1000 kgf cm^{-2}. The orientation of films in both directions can increase this value to 1500–2000 kgf cm^{-2}.

A valuable property of polyarylate films is their ability to retain effective mechanical parameters after prolonged heating at elevated temperatures. The breaking stresses on extension of nonoriented films of the cardo-polyarylates obtained by the reaction of diphenylphthalide-4,4′-dicarboxylic acid with phenol-phthalein and phenolphthalein anilide at 300 °C are 330 and 250 kgf cm^{-2} respectively. Films of mixed polyarylates obtained from 2,2-bis(4-hydroxyphenyl)propane and terephthalic and isophthalic acids withstand prolonged heating (for 1000 h) at 150–200 °C, retaining satisfactory mechanical parameters.

Polyarylates have effective dielectric parameters which do not change over a wide temperature range.[4,11,212,213] The relative permittivity of films of 2,2-bis(4-hydroxyphenyl)propane–phenolphthalein polyarylates is close to that of poly(ethylene terephthalate). The advantage of polyarylates over poly(ethylene terephthalate) and poly[2,2-bis(4-hydroxyphenyl)propane carbonate] consists in a smaller change in the dielectric loss angle and in the specific resistance of the bulk-phase material in the temperature range from −60 to 200 °C and above. The dielectric loss angle does not exceed $(4-5) \times 10^{-3}$ for 2,2-bis(4-hydroxy-phenyl)propane polyarylates and $(5-8) \times 10^{-3}$ for phenol-phthalein polyarylate in the same temperature range. Whereas the maximum in the dielectric loss angle is observed at 140 °C for poly(ethylene terephthalate) and at 200 °C for poly[2,2-bis-(4-hydroxyphenyl)propane carbonate], in the case of phenol-phthalein polyarylates it has not been observed even at 300 °C. The bulk-phase value of the resistivity of 2,2-bis(4-hydroxy-phenyl)propane and phenolphthalein polyarylate films is about $(1-3) \times 10^{13}$ Ω cm at 200 °C, which is 1.5–2 orders of magnitude higher than for poly(ethylene terephthalate) and the polycarbonate.

Polyarylates are resistant to the prolonged action of inorganic and organic acids (with the exception of sulfuric acid), oxidants, and dilute alkalis, but are inadequately resistant to the action of concentrated solutions of alkali and ammonia.[214]

The polyarylates of aromatic dicarboxylic acids are char-acterised by high thermal stability.[43,215] The polyterephthal-ates of 2,2-bis(4-hydroxyphenyl)propane, phenolphthalein,

phenolanthrone, and phenolfluorene under an inert atmosphere begins to lose mass at 350–360 °C for a heating rate of 5 °C per minute. The decrease in the mass of the phenolphthalein–biphenyl-4,4'-dicarboxylic acid polyarylate during isothermal heating in air at 400 °C for 1 h is about 7%.

Polyarylates burn but do not support combustion. The polymers containing chlorine (up to 13%) and phosphorus in the macromolecule exhibit an enhanced fire resistance and also a high resistance to the action of ionising radiation. The radiation yield of the gaseous products of the radiolysis of these polymers, obtained by the polycondensation of isophthalic acid chloride with 2,2-bis(4-hydroxyphenyl)propane and hydroquinone, is of the order of 0.02 of a molecule per 100 eV, which is appreciably less than the yield of gases on irradiation of poly(ethylene terephthalate) and the polycarbonate. The molecular structure of polyarylates does not change significantly for doses of the order of 10^{23} eV cm^{-3}.[216]

Table 3 presents certain properties of the phenolfluorene–terephthalic acid polyarylate. Evidently high heat resistance, thermal stability, and dielectric parameters are characteristic of this polymer over a wide temperature range.[108,109] Films of this polymer retain an appreciable strength even at 350 °C.

Table 3. The properties of the 9,9-bis(4-hydroxyphenyl)fluorene–terephthalic acid polyarylate.

Property	Value
Molecular mass	50000
Softening temperature/°C	~360
Glass point/°C	~290
Temperature of onset of decomposition (from thermogram)/°C	465
Tensile strength (of film), σ/kgf cm^{-2}, at	
20 °C	840
300 °C	440
350 °C	250
Elongation at rupture, ε (%), at	
20 °C	15
300 °C	32
Modulus of elasticity, E/kgf cm^{-2}, at	
20 °C	26000
300 °C	5400
Specific impact strength/(kgf cm) cm^{-2}	15–20
Tangent of dielectric loss angle at	
25 °C	0.0037
220 °C	0.0025
Relative permittivity at	
25 °C	3.3
200 °C	3.0
Bulk-phase specific resistance/Ω cm, at	
25 °C	10^{17}
200 °C	5×10^{13}

The cardo-polyarylates based on polycyclic bisphenols containing norbornane groups at the central carbon atom also possess a high heat resistance, effective physicomechanical and dielectric parameters, and a high solubility.[78,87,88]

The synthesis of mixed polymers based on several dicarboxylic acid chlorides or bisphenols as well as the synthesis of block-copolymers with polyarylate fragments in the chain have given rise to extensive possibilities for specific regulation of the properties of polyarylates. One of the methods for synthesis of the block-copolymers with polyarylate fragments involves, as mentioned above, their preparation from oligomers, previously synthesised, with a specific molecular mass and functional groups of different nature. By varying the molecular mass of the initial block components and their chemical nature, it is possible to regulate within wide limits the properties of such block-copolymers. We shall consider certain examples.

It is of interest that, despite the polyblock nature of their construction, polyarylate–siloxane block-copolymers possess a distinct microheterogeneous structure ensuring the retention of the high-temperature properties of the rigid block and the low-temperature properties of the flexible block. All the polyarylate–dimethylsiloxane copolymers have two glass points corresponding to the polydimethylsiloxane (−120 °C) and the polyarylate (for example, 320 °C in the case of the phenolphthalein–terephthalic acid polyarylate) and combine the properties of both homopolymers (strength, elasticity, gas-separating properties, etc.). Nonvulcanised films of such block-copolymers retain high ultimate strengths and relative elongations over a wide temperature range, which is related to the glass point of the rigid block and the phase incompatibility of the two blocks in the polyblock system. Table 4 shows that, after exposure to air at 250 °C for 10 h, the films of the block-copolymers remain elastic.[124]

Table 4. Mechanical properties of the polyarylate-siloxane block-copolymers $-[OROC(O)R'CO]_{10}ORO[Si(CH_3)_2O]_y-$.

y	σ/kgf cm^{-2}, at		ε (%), at	
	20 °C	200 °C	20 °C	200 °C
20–40	400–300	200–150	30–80	80–100
80–100	250–150	120–100	120–220	150–250
180–200	80–120	200–300	200–250	2–3
180–200[a]	40	–	120–150	–

[a] After ageing for 10 days at 250 °C.

In the case of polyarylate–arylene sulfone oxides,[119–123,136,137] microphase separation is difficult and a monotonic variation of the properties takes place over a wide range of compositions, as happens in the case of statistical copolymers. However, it has been found that, when the polyarylate–arylene sulfone oxide contains 10–15 mass% of arylene sulfone oxide blocks, a seemingly abrupt change in properties takes place, being manifested, in particular, by a sharp increase in the viscosity of their concentrated solutions and melts. This decrease reaches several orders of magnitude, the viscosity approaching the value for the poly(arylene sulfone oxide) melt. Thus, whereas the viscosities are $10^{4.0}$ P for the poly(arylene sulfone oxide) melt, $10^{7.0}$ P for the polyarylate F-1, and $10^{6.0}$ P for the polyarylate D, the viscosity of the block-copolymer based on the polyarylate F-1 and poly(arylene sulfone oxide) [obtained from 2,2-bis-(4-hydroxyphenyl)propane and bis(4-chlorophenyl) sulfone], in which the content of the latter is 10 mass%, amounts to $10^{4.5}$ P and that of the block–copolymer based on the polyarylate D and the same polysulfone for a content of the latter of 12 mass% is 10^4 P. This leads to the possibility of successful working of such block-copolymers by casting under pressure (which constitutes their advantage over homopolyarylates) whilst retaining a higher heat resistance than that of the initial polysulfone.

Table 5. Properties of polyarylate-arylene sulfone oxide block-copolymers.

Parameter	Brand of block-copolymer	
	FS-10	DS-12
Breaking stress/kgf cm^{-2}		
on extension	600–700	700–800
on compression	700–800	800–900
on static bending	800–900	900–1000
Relative elongation at rupture (%)	80	130
Modulus of elasticity in extension/kgf cm^{-2}	17000	14000
Specific impact strength/(kgf cm)cm^{-2}	30–40	70–90
Microhardness/kgf mm^{-2}	21–23	14–16
Absorption of water in 24 h (%)	0.20	0.18
Bulk phase resistivity/Ω cm	1×10^{15}	2×10^{16}
Tangent of dielectric loss angle at		
60 Hz	0.015	0.015
10^6 Hz	0.020	0.018
Insulating strength/kV mm^{-1}	25–30	25–30
Relative permittivity	4.2	4.0

Table 5 shows that polyarylate-arylene sulfone oxides have effective mechanical and electrophysical properties.[136] The properties of these block-copolymers can be altered specifically by varying the microstructure of the polymer chain and its chemical structure and composition.

A complex transformation of the phase composition from single-phase to three-phase takes place in polyblock polyarylate-ethylene oxide block-copolymers containing relatively short individual blocks with a definite compatibility.[140] In contrast to the block-copolymers with full phase separation, such as polyarylate-dimethylsiloxanes,[126,128] the phase separation in polyarylate-ethylene oxide block-copolymers depends on the mass ratios of the individual blocks and also on their molecular masses.[140]

Table 6 presents certain mechanical properties of polyarylate-ethylene oxide block-copolymers.[141] They show that, by varying the ratio of block sizes, it is possible to vary the properties of the block-copolymers within wide limits. Thus the strength of the films varies from 90 to 1000 kgf cm^{-2}, the deformation at rupture varies from 30% to 700%, and the modulus of elasticity varies from 400 to 17 000 kgf cm^{-2}. It is also noteworthy that the ratio of the reversible and irreversible deformations of the films likewise varies significantly under these conditions. For example, the high elastic deformation reaches 50% in the block-copolymer having the composition $x:y = 5:91$ (the molecular mass ratio is 2500:4000) and in terms of all their properties the block-copolymers having this composition approach an elastomer.[141]

Together with the synthesis of polycondensation block-copolymers containing block sequences of various heterochain polymers, block-copolymers based on block components comprising carbochain polymers have been synthesised. In particular, polyarylate-butadiene and polyarylate–arylene sulfone oxide–butadiene block-copolymers have been obtained and investigated using oligobutadiene and its derivatives as one of the block components.[142–144,147,148] Such construction of the polymer chain leads to new possibilities for the modification of polyarylate polymers. Thus it is known[12] that the deformation of

Table 6. Properties of the polyarylate-ethylene oxide block-copolymers $-OCR'CO(CH_2CH_2O)_yOCR'CO[OROC(O)R'CO]_xORO-$.

Composition of block-copolymers			η_{int}/dl g^{-1} (in $CHCl_3$)	σ/kgf cm^{-2}	ε (%)	E/kgf cm^{-2}
x	y	content of oligo-(ethylene oxide) (mass%)				
5	9	12.7	0.82	840	90	14000
5	14	17.9	0.98	800	110	9500
5	91	59.2	1.14	220	700	400
5	340	84.5	1.34[a]	90	5	3500
10	9	7.3	0.91	860	75	15000
10	14	10.6	0.96	880	94	13500
10	91	44.2	1.22	530	370	2000
10	340	74.8	1.45	200	15	4000
20	9	4.0	0.84	1000	110	17000
20	91	29.5	1.02	530	120	–
20	340	61.1	1.26	290	30	2800

[a] Molecular mass 70 000.

polyarylates takes place without the formation of a 'neck'. The appearance of a 'neck' has been observed in the deformation of polyarylate-butadiene block-copolymers containing up to 30% of polybutadiene blocks, which is associated with the increased mobility of the polyarylate phase owing to a kind of plasticisation of the latter by the polybutadiene blocks.[142]

We shall consider yet another type of polymer—carbaborane-containing polyarylates. The most interesting carbaborane-containing polyarylates have been synthesised from 1,2- and 1,7-bis(4-carboxyphenyl)carbaboranes combined with various bisphenols[216-229] or from 1,2-bis(4-hydroxyphenyl)-carbaborane (phenolcarbaborane) combined with the chlorides of various aromatic dicarboxylic acids.[230-233] These polyarylates have been synthesised by acceptor-catalytic and high-temperature polyesterification in solution.

Table 7 presents as an example data on the polyarylates derived from 1,2- and 1,7-bis(4-carboxyphenyl)carbaboranes. Polyarylates with diphenylcarbaborane fragments in the chain dissolve in a wide range of organic solvents. It must be emphasised that, in contrast to the usual cardo-polyarylates which are also readily soluble, many carbaborane-containing polyarylates exhibit a high solubility in solvents such as aromatic hydrocarbons (benzene, toluene, xylene), polyarylates derived from the less symmetrical and more polar isomer of bis(4-carboxyphenyl)-*o*-carbaborane being somewhat more soluble.[219] Like the usual polyarylates, strong colourless films can be obtained from the carbaborane-containing polyarylates by casting from solutions.

The softening temperatures of the polyarylates obtained from the *ortho*- and *meta*-isomers of bis(4-carboxyphenyl)carbaborane and dihydric phenols having the same composition are virtually identical under the conditions of a comparable phase state. The polyarylates derived from dihydric phenols of the cardo-type have the highest softening temperatures (340–360 °C).

In the case of a mononuclear dihydric phenol of the type of hydroquinone or a dinuclear one of the type of bis(hydroxyphenyl)propane the structure of the polyarylates derived from the more symmetrical *meta*-isomer of bis(4-carboxyphenyl)carbaborane is more ordered than that of the polyarylates of the *ortho*-isomer. Thus, whereas the polyarylate obtained from 1,2-bis-(4-carboxyphenyl)carbaborane and 2,2-bis(4-hydroxyphenyl)propane by acceptor-catalytic polycondensation is amorphous, the corresponding polymer based on the *meta*-isomer has a crystalline structure with a high degree of order. The polyarylates synthesised from 1,7-bis(4-carboxyphenyl)carbaborane and dihydric phenols of the cardo-type differ little from the analogous polymers based on the *ortho*-isomer as regards the degree of order. According to X-ray diffraction data, these polyarylates have a crystalline structure with an average degree of order.

The thermal properties of the polyarylates with the diphenylcarbaborane fragments in the chain described above have been considered in a number of studies.[217-219,221-225] According to the results of thermogravimetric analysis, in air the mass of the carbaborane-containing polyarylates begins to change at a temperature higher by 20–60 °C than for the usual polyarylates. Slower degradation processes are characteristic of the carbaborane-containing polyarylates and in a number of cases sections corresponding to the retardation or cessation of the degradation in the temperature range between 600 and 650 °C are observed on the thermogravimetric curve. The high 'coke' residue (from 50%

Table 7. The properties of polyarylates obtained by the acceptor-catalytic (A) and high-temperature (B) polycondensation of 1,2-bis-(4-carboxyphenyl)carbaborane (*ortho*) and 1,7-bis(4-carboxyphenyl)carbaborane (*meta*) with various dihydric phenols.

Dihydric phenol	Acid chloride	η_{int}/dl g^{-1} (in tetrachloroethane, 25 °C)		Softening temperature/°C[a]	σ/kgf cm^{-2}	ε (%)	Temperature of onset of decrease in mass/°C[b]	'Coke' residue on heating	
		A	B					to 900 °C[b]	to 400 °C[c]
Hydroquinone	*ortho*	0.6	–	320	brittle film		380	88	94
	meta	0.6	0.9	320	brittle film		380	85	91
Bis(4-hydroxy-phenyl) ether	*ortho*	0.6[d]	0.9	290	500	23	390	85	90
	meta	2.0	1.9	280	990	10	390	81	85
2,2-Bis(4-hydroxy-phenyl)-propane	*ortho*	0.9	–	290	570	4	400	62	96
	meta	0.6	2.3	320	650	2	420	50	86
9,9-Bis(4-hydroxy-phenyl)-fluorene	*ortho*	0.9	2.3	350	680	4	420	60	95
	meta	1.3	1.2	360	1050	5	400	58	90
9,9-Bis(4-hydroxy-phenyl)-10-anthrone	*ortho*	0.9	–	350	470	–	410	70	96
	meta	1.1	0.7	340	920	4	400	–	98
Phenolphthalein	*ortho*	1.2	–	350	570	2	400	78	98
	meta	2.0	2.4	340	1100	7	400	80	98

Remarks. All the polymers A were obtained in the presence of triethylamine in acetone over a period of 1 h at 45–50 °C. The polymers B were obtained in α-chloronaphthalene over a period of 10–16 h at 220 °C. The yields of the polymers were nearly quantitative. All the properties other than η_{int} are quoted for polymers obtained by method A.

[a] The temperature corresponding to the point of intersection of the tangents to the thermomechanical curve in the region of the onset of flow for a load of 0.8 kgf cm^{-2} was adopted as the softening temperature.

[b] The temperature was determined from the thermogravimetric curve at a heating rate of 4.5 °C per minute in air.

[c] Isothermal conditions in air over a period of 3 h.

[d] The molecular mass, determined by the light scattering method, was 116000.

to ~90% relative to the initial mass of the polymer), characteristic of the bis(4-carboxyphenyl)carbaborane polyarylates when the latter are heated in air to 900 °C should also be mentioned, as the usual polyarylate burns completely at 650–700 °C.

This difference is manifested even more clearly when carbaborane-containing polyarylates and the polyterephthalate of phenolfluorene are heated under isothermal conditions in air. Thus, after being heated at 400 °C for 3 h, the mass of the carbaborane-containing polyarylates (Table 7) diminishes by 2%–15%, whereas the polyterephthalate of phenolfluorene begins to decompose even before 400 °C is attained and the degree of decomposition increases monotonically, reaching 35% of the initial mass after 3 h.

Under an inert atmosphere, the mass of all the bis(4-carboxyphenyl)carbaborane polyarylates begins to change at the same temperature as in air, while the 'coke' residue amounts to ~80%–90% after thermal degradation, in many instances actually at higher temperatures than on heating in air.[219]

An appreciably lower content of carbon oxides and a high content of hydrogen in the gaseous products together with a lower degree of decomposition are characteristic of the thermal degradation processes involving polyarylates with diphenylcarbaborane fragments (compared with the usual polyarylates).[217,223,224] This difference is more striking for polyarylates with *o*-carbaborane groups in the chain. The evolution of hydrogen at comparatively low temperatures and with a low activation energy (~20 kcal mol^{-1}) and the results of the analysis of the thermal behaviour of compounds modelling fragments of the molecules of carbaborane-containing polyarylates and the products of the possible reactions led to the assumption that this phenomenon is due to heterolytic and not homolytic processes. The carbaborane ring exerts a stabilising influence on the thermal stability of the ester linkage. It has been noted that the thermal decomposition of the polyarylate obtained from bis-(4-carboxyphenyl)-*o*-carbaborane and phenolfluorene proceeds via two mechanisms: heterolytic reactions predominate up to 450 °C, whilst radical processes predominate at higher temperatures.[223]

Derivatives of dicarbaundecaborate have been detected in the products of the thermal degradation of carbaborane-containing polyarylates and the corresponding model systems in the presence of nucleophiles, including water.[221,223] This suggests that water, a certain amount of which is always present in polymers, behaves as a nucleophile disrupting the carbaborane ring to form the dicarbaundecaborate anion in the first stage of the degradation of the carbaborane-containing polyarylate. The consumption of water in this reaction with the carbaborane ring rules out the hydrolysis of the ester linkage, which plays the main role in the initial stage of the degradation of the usual polyarylates. This promotes in the case of the carbaborane-containing polyarylates the retention of the weak polyarylate link (the ester group) at higher temperatures.

Comparative study of the thermal and thermooxidative degradation of the 1,2-bis(4-carboxyphenyl)carbaborane–phenolfluorene polyarylate and the polyterephthalate of phenolfluorene revealed yet another characteristic feature of the behaviour of these polymers.[222] In vacuo, the onset of gel formation occurs sooner in the case of the *o*-carbaborane-containing polymer and a 100% degree of reaction is attained already at 350 °C, whereas the gel content in the case of the terephthalic acid polyarylate is only 2.7%. Under oxidation conditions, the *o*-carbaborane-containing polyarylate begins to lose its solubility much sooner and is fully cross-linked already at 275 °C, whereas the terephthalic acid polyarylate contains only 30% of the gel even at 350 °C.

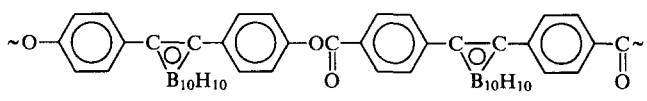
In the synthesis of polyarylates based on phenolcarbaborane and the chlorides of terephthalic, isophthalic, biphenyl-4,4′-carboxylic oxybis(benzene-4-carboxylic), and diphenylphthalide-4,4′-dicarboxylic acids, polyarylates with relatively high intrinsic viscosities were obtained only in the last two cases (0.92 and 0.62 dl g^{-1} respectively in tetrachloroethane).[230] Regardless of the conditions in the synthesis, the polyarylates derived from these dicarboxylic acids have an amorphous structure, whereas the terephthalic and biphenyl-4,4′-dicarboxylic acid polyarylates, obtained by high-temperature polycondensation, have a crystalline structure with a high degree of order according to X-ray diffraction data and are insoluble. The polymer obtained from isophthalic acid, which is less ordered and more soluble, occupies an intermediate position, but it too was obtained with low intrinsic viscosities of the solutions (0.20–0.31 dl g^{-1} in tetrachloroethane). In all cases, these polymers precipitated during polycondensation even for low degrees of conversion and subsequent polycondensation could take place only under heterogeneous conditions. The limited solubility, caused by the crystallisation of the polymers during their formation, is apparently the reason for their low molecular mass.

In comparing the properties of polyarylates derived from phenolcarbaborane polyarylates based on its carboxyl analogue — 1,2-bis(4-carboxyphenyl)carbaborane — one should note that the latter are readily soluble and are amorphous or are comparatively little ordered when dihydric phenols such as hydroquinone, 2,2-bis(4-hydroxyphenyl)propane, and bis(4-hydroxyphenyl) ether are used. Conversely, they are more ordered when dihydric cardo-phenols are employed: phenolphthalein, phenolfluorene, and phenolanthrone.[231] The softening temperatures of the amorphous polyarylates obtained by the polycondensation of phenolcarbaborane with oxybis(benzene-4-carboxylic) and diphenylphthalide-4,4′-dicarboxylic acids are 275 and 330 °C. The isomeric amorphous polyarylate obtained from 1,2-bis(4-carboxyphenyl)carbaborane and bis(4-hydroxyphenyl) ether softens at 290 °C, i.e. whether the *o*-carbaborane group is linked to the hydroxyphenyl or carboxyphenyl residues is immaterial as regards the softening temperatures of the amorphous polyarylates with an isomeric structure.

Under the conditions of dynamic thermogravimetric analysis, the mass of phenolcarbaborane polyarylates begins to change at 350–400 °C in air and at 360–410 °C in an inert medium. All these polymers contain a large 'coke' residue on heating to 900 °C both in air (70%–85%) and in an inert medium (85%–90%).

A polyarylate the polymer chain of which was made up only of alternating ester and 1,2-diphenylcarbaborane fragments has been synthesised by the polycondensation of 1,2-bis(4-hydroxyphenyl)-carbaborane with the acid chloride of 1,2-bis(4-carboxyphenyl)-carbaborane (Scheme 8).[232]

Scheme 8



It was found that, regardless of whether the polymer was synthesised by acceptor-catalytic polycondensation in acetone in the presence of triethylamine or by high-temperature polycondensation in chlorinated biphenyl or α-chloronaphthalene, the polymer formed had a crystalline structure (degree of crystallinity is 35%–55%) and was insoluble in any of the solvents known for polyarylates with the exception of tetrahydrofuran. The polymers obtained by high-temperature polycondensation in α-chloronaphthalene at 220 °C over a period of 15–18 h have the highest crystallinity. As already mentioned, by varying the polycondensation condition and also the subsequent treatment of the polymer, it is possible to alter its physical structure. Thus it has been observed that, after reprecipitation from solution in tetrahydrofuran in cold water or methanol, the polymer becomes amorphous and soluble in solvents such as chloroform, tetrachloroethane, cyclohexanone, and benzene. Depending on the degree of conversion into the amorphous form, the polymers soften at 260–290 °C, whereas the crystalline specimens do not melt up to 400 °C. Above this temperature, their thermal degradation begins.

Interesting results have been obtained in the study of the thermal stability of the polyarylate obtained from phenolcarbaborane and 1,2-bis(4-carboxyphenyl)carbaborane with different degrees of crystallinity [232,233] under the conditions of dynamic thermogravimetric analysis in air, under an inert atmosphere, and also under isothermal conditions at 400 °C for 3 h.

The highest-melting specimen usually has the highest thermal stability among polymers of the same or similar chemical structure which pass to the highly elastic or fused state at different temperatures. This can be accounted for by the diffusional inhibition of the degradative processes in the solid phase of the polymer. The opposite behaviour has been observed for the carbaborane-containing polyarylate considered: under the conditions of both dynamic (in the temperature range 400–500 °C) and isothermal (400 °C, 3h) thermogravimetric analysis, the specimen converted into the amorphous form exhibits the smallest weight loss.

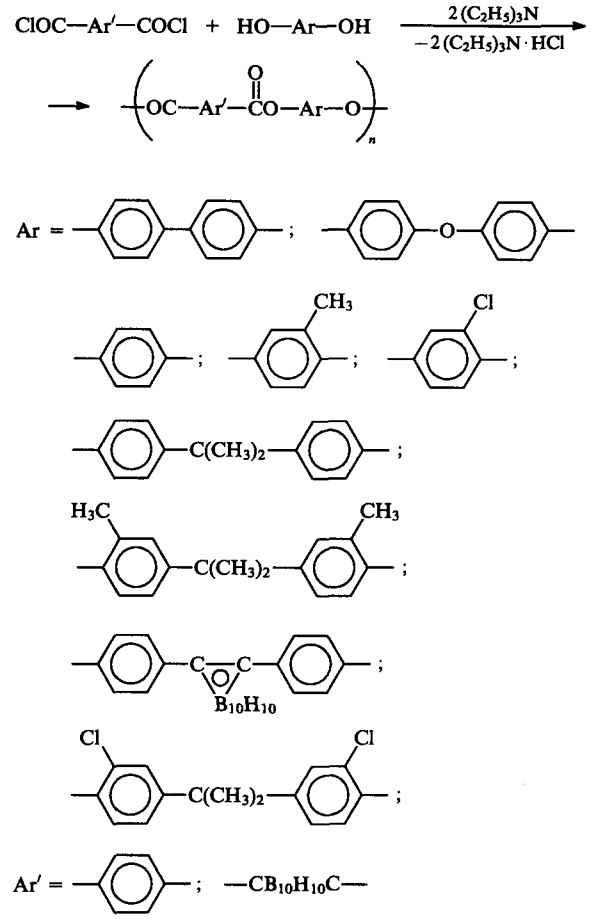
With increase in the degree of crystallinity of the polymer, the weight loss increases in all cases. Thus the mass of the specimen converted into the amorphous form does not change up to 650 °C, while the mass of the crystalline polymers diminishes already at 400 °C. It has been suggested that the different types of behaviour on heating of the crystalline carbaborane-containing polyarylate specimen and the specimen converted into the amorphous form may be caused by the difference between their molecular mobilities in the range 280–380 °C. [233] The increased thermal stability of the amorphous polymer with a relatively low softening temperature is caused either by the enhanced stabilising influence of the carbaborane groups in the polymer melt or by the formation of thermally more stable secondary structures as a result of the interaction of the carbaborane groups, the occurrence of which in the melt or in the highly elastic state is facilitated. In highly crystalline polymers with a high melting point, the manifestation of these effects is evidently hindered. [232]

The possibility of obtaining organoelement liquid crystal polymers from carbaborane-containing polyarylates has recently attracted the attention of investigators. [146,210,211,234]

Thus the polyarylates whose structures are presented in Schemes 9 and 10 have been obtained [146,234,235] by acceptor-catalytic polycondensation from bis(4-hydroxyphenyl)-*o*-carbaborane, the chloride of carbaborane-*m*-dicarboxylic acid (as the carbaborane-containing components), terephthalic acid chlorides, and various bisphenols.

The properties of carbaborane-containing polymers such as retarded thermal and thermo-oxidative degradation, effective mechanical properties, and high yields of the 'coke' residues in the products on heating, due to the involvement of the carbaborane fragments in the formation of three-dimensional structures, constitute a positive factor in the creation of thermostable and heat resistant materials. [229] Therefore one of the approaches to the preparation of new copolyarylate liquid crystal carbaborane-containing structures with an improved thermal stability involves the introduction of carbaborane-*m*-dicarboxylic acid and phenylcarbaborane fragments into the structures of various homo- and copolyarylates.

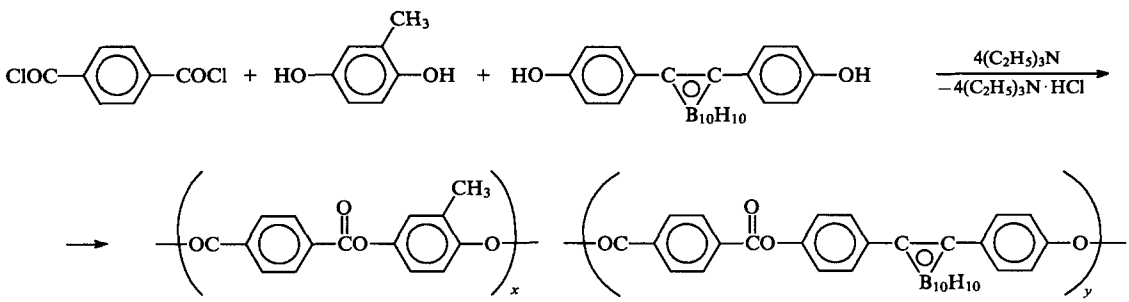
Scheme 9



The study of the properties of the polymers and copolymers obtained showed that, on passing from the high-melting polyterephthalate of 4,4′-dihydroxybiphenyl (does not melt up to 500 °C) to the carbaborane-*m*-dicarboxylic acid copolyarylates (i.e. on replacing some of the terephthalic acid units by the carbaborane-*m*-dicarboxylic acid units in the polyarylate structure), the softening temperature of the polymer falls appreciably (to 140 °C). A solid–liquid crystal transition (the temperature range of the mesophase is 260–350 °C) then appears in the copolymer with a molar content of the carbaborane-*m*-dicarboxylic acid (relative to the sum of the dicarboxylic acids) of 90 mol.% at 260 °C. On the other hand, the complete replacement of terephthalic acid residues by carbaborane-*m*-dicarboxylic acid residues in the polyester structure leads to the formation of poly(4,4′-dihydroxybiphenyl carbaborane-*m*-dicarboxylate) with a softening temperature of 240 °C and lacking liquid crystal properties.

The introduction of carbaborane-*m*-dicarboxylic acid fragments into the structure of the polyterephthalates of 2,2-bis-(4-hydroxyphenyl)propane, hydroquinone, or their chloro- or

Scheme 10



methyl-substituted derivatives leads to an appreciable decrease in the softening temperatures of the polymers. The presence or absence of the mesophase in the three-component copolyarylate structures depends on their quantitative content of carbaborane-*m*-dicarboxylic acid fragments. For example, the copolyarylate based on chlorohydroquinone and the chlorides of terephthalic and carbaborane-*m*-dicarbocyclic acids, introduced into the reaction in molar proportions of 1:0.8:0.2, has a softening temperature of 220 °C and the temperature range of the mesophase is 250–350 °C. In the case of four-component copolyarylates containing hydroquinone, 2,2-bis(4-hydroxyphenyl)-propane, and their chloro- or methyl-substituted derivatives, the introduction of small amounts of carbaborane-*m*-dicarboxylic acid (for example, 20 mol.%) leads to the loss of liquid crystal properties by the copolyarylates.

Table 8 presents as an example data on the homo- and co-polytetraphthalates of chlorohydroquinone and bis(4-hydroxyphenyl)-*o*-carbaborane.

It is noteworthy that the copolyterephthalates based on chlorohydroquinone and hydroxyphenylcarbaborane have lower softening temperatures than the copolyterephthalate of hydroquinone and hydroxyphenylcarbaborane owing to the introduction into the polymer structure of asymmetrically constructed fragments in the form of chlorohydroquinone residues. The transition to the mesophase occurs at a higher temperature the smaller the amount of hydroquinone introduced into the copolymer structure.

The temperature corresponding to the formation of the mesophase in carbaborane-containing copolyarylates based on hydroxyphenylcarbaborane shifts towards higher values (by 70–80 °C) compared with the copolyarylates containing carbaborane-*m*-dicarboxylic acid fragments.

The liquid crystal properties of carbaborane-containing copolyarylates based on asymmetric monomers having, as it were, a 'head' and a 'tail', in particular chlorohydroquinone and methylhydroquinone, are influenced not only by the ratio of the initial components in the copolymer structure but also by the microstructure of the copolymer: the sequence in which the comonomers alternate in the polymer chain and the direction in which the 'heads' and 'tails' of the asymmetric monomer are arranged. Thus, among the copolymers obtained from methylhydroquinone and the chlorides of terephthalic and carbaborane-*m*-dicarboxylic acids in molar proportions of 1.0:0.4:0.6[146] only those with a block structure are capable of undergoing a transition to a liquid crystal melt.

In order to investigate the effect of thermal influences on the structure and properties of copolymers containing carbaborane-*m*-dicarboxylic acid units, the copolyterephthalate of chlorohydroquinone carbaborane-*m*-dicarboxylate, containing 20 mol.% of carbaborane-*m*-dicarboxylic acid, was heated in air at 200 °C for 6 h. It was then found that the specimen retained its original composition, structure, and properties after the heat treatment.[146]

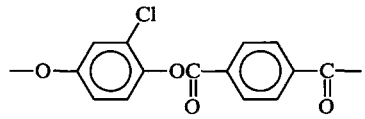
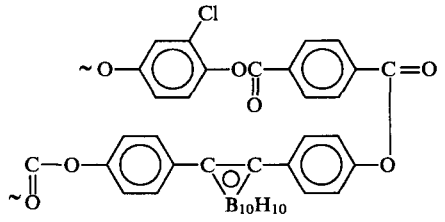
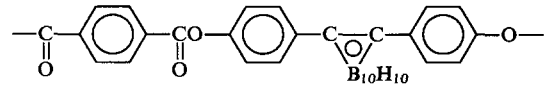
According to the results of a thermogravimetric study, chlorohydroquinone polyterephthalate decomposes totally in air at 600 °C (heating rate 5 °C min^{-1}), while the copolyarylate containing 20 mol.% of carbaborane-*m*-dicarboxylic acid affords a 65% yield of the 'coke' residue at the same temperature; the 'coke' residue of the copolyarylate containing 60 mol.% of carbaborane-*m*-dicarboxylic acid is 80%. Thus the presence of the carbaborane nucleus has a positive effect on the thermal properties of the liquid crystal copolyarylates obtained.

Together with their influence on the thermal characteristics, the carbaborane fragments in the macromolecules also alter the solubilities of the polymers. Thus the presence of 20 and 50 mol.% of carbaborane-*m*-dicarboxylic acid fragments (relative to the total acids) in the structure of the insoluble methylhydroquinone polyterephthalate led to the formation of soluble copolyarylates. Similarly, the introduction of bis(4-hydroxyphenyl)-*o*-carbaborane fragments into the structure of insoluble polyterephthalates of hydroquinone and its chloro- and methyl-substituted derivatives promotes an improvement in solubility and all the copolyarylates indicated are soluble in organic solvents.[146,234]

Thus the presence of carbaborane-containing fragments in the polymer structures lowers the softening temperatures of the copolyarylates and the temperatures corresponding to the transition to the liquid crystal state, improves their thermal properties, and helps to make them soluble.

It is useful to carry out further studies on carbaborane-containing liquid crystal polyarylates in order to establish the possibility of detecting the mesophase in the polymer on heating to 250 °C and above as a result of the thermal transformations of the *o*- and *m*-carbaborane nuclei which lead to the formation of a three-dimensional cross-linked structure.[229]

Table 8. The results of the synthesis and of the study of the properties of homo- and co-polyterephthalates of chlorohydroquinone and bis(4-hydroxyphenyl)-*o*-carbaborane.

Structure of homo- and co-polyarylates	Molar monomer ratio	η_{int}/dl g^{-1}	X-Ray diffraction data	T_{decomp}/ °C	Temperature range of mesophase/ °C
	1.0:1.0	insoluble	crystalline	160	none
	0.6:1.0:0.4	0.34	weakly-crystalline	195	230–400
	0.5:1.0:0.5	0.37	"	200	235–400
	0.4:1.0:0.6	0.40	"	210	245–400
	1.0:1.0	0.15	amorphous	215	none

The syntheses and properties of polyarylates of different structure were examined above and it was shown that the most promising method for their synthesis is the polycondensation of dicarboxylic acid chlorides with bisphenols carried out in different versions. However, attempts have been made to obtain polyarylates also in other ways.[146]

The new methods for synthesis of polyarylates include their preparation by the method of 'carbonylation' polycondensation resulting from the use of carbon monoxide and aromatic dihalocompounds combined with bisphenols in the presence of palladium catalysts, in place of the traditional dicarboxylic acids or their derivatives, as the acid component in the polycondensation process. Thus polyarylates with average intrinsic viscosities have been obtained by the reaction of 2,2-bis-(4-hydroxyphenyl)propane (or other bisphenols), bis(4-bromophenyl) ether, and carbon monoxide in the presence of palladium catalysts at 115 °C in chlorobenzene.[236-241]

The synthesis of polyarylates was also tried by comparatively new polycondensation methods such as 'direct',[69,146,242-258] 'activated',[69,146,259,260] and 'silylated'[146,261-271] polycondensation.

The 'direct' polycondensation leads to the possibility of carrying out the polycondensation process directly between the dicarboxylic acid (and not its derivatives) and the bisphenol in solution at a moderate temperature by employing special condensing agents (for example, triphenylphosphine dichloride, arenesulfonyl chloride, or hexachlorocyclotriphosphazene frequently in combination with other compounds).

The 'activated' polycondensation is based on the activation of the process by employing in the latter monomers having the appropriate structure [for example bis(2,5-dinitrophenyl) isophthalate or adipate, bis(pentachlorophenyl) isophthalate, etc.], containing groups which activate the terminal functional groups of the monomer in the part of the molecule which enters into the composition of the low-molecular-mass product during polycondensation and does not participate in the construction of the chain. This method makes it possible to carry out the process under comparatively mild conditions and is characterised by little tendency towards side reactions.

The 'silylated' polycondensation is based on the use of silylated nucleophilic monomers, in particular bisphenols and carboxylic hydroxyacids, as the starting materials in the polycondensation process. The silylation of the monomers leads to the possibility of altering their reactivity, frequently increasing it appreciably. The employment of silylated monomers instead of 'free' monomers makes it possible in a number of instances to carry out the polycondensation process under milder conditions, avoiding undesirable side reactions. However, in many cases the new methods do not lead to the desired results. There is no doubt that they still require further development and improvement.

III. Applications of polyarylates

Polyarylates are worked to produce articles by cast moulding, moulding under pressure, extrusion, vortical sputtering and, in the case of soluble polyarylates, also by employing their solutions.[11,56,214,272-278]

It was found that an infusible and insoluble polyarylate such as econol, can be used successfully to produce monolithic articles by sintering at 425–450 °C under a pressure of 350–1400 kgf cm^{-2} and also by high-speed forging. Econol coatings can be obtained by a plasma method (in a helium atmosphere).

The high heat resistance of polyarylates combined with their effective strength parameters have led to extensive possibilities for the use of these polymers as constructional articles (components for automation and other mechanisms); by virtue of their effective insulating properties, they are used successfully in radio engineering and electrical engineering (shells for coils, plugs, disconnecting devices, etc.) and in the electronic industry.[11,56,273,277,279,280]

Heat-resistant polyarylate films are obtained by extrusion or casting from solution and are used as electrically insulating materials. Polyarylates are also employed for the preparation of varnishes. By virtue of their high solubility and compatibility with various polymers, cardo- and other polyarylates are used successfully for the preparation of valuable composite materials.

For example, oligoepoxide-polyarylate compositions are used as casting compounds, sealing coatings, binders for reinforced plastics, etc. They exhibit enhanced heat resistance (~250 °C); the ultimate compressive strength of such systems reaches 800 kgf cm^{-2} and the ultimate bending strength is up to 1700–2000 kgf cm^{-2}, which is almost twice as high as the analogous parameters of systems hardened without using polyarylates.[309] In terms of their properties, such compositions are not inferior to materials containing mineral fillers and, in terms of a series of parameters, they are superior to them. Thus they are distinguished by a significantly higher specific gravity (by ~40%) and a high capacity to resist repeated thermal shocks following changes in temperature from −60 to 250 °C.

The introduction of a polymer such as the terephthalic acid–phenolphthalein polyarylate into an epoxide composition leads to the formation of not only strong and lighter materials but also of materials capable of being employed over a wide range of temperatures and loads.[310,311] The study of the properties of oligoepoxide-polyarylate compositions has demonstrated the extensive possibilities for the regulation of the mechanical properties of these network systems, including those associated with vibroabsorption.[310,312,313] Materials based on oligoepoxide polyarylate compositions exhibit a low creep when subjected to high loads.[313]

Filled materials such as antifriction products, which have a low coefficient of friction and can be employed for a long time without a lubricant at high temperatures (250 °C), *in vacuo*, and for high velocity gradients between friction surfaces (sliding and roller bearings) are also obtained from polyarylates. It has been suggested that highly heat-resistant antifriction self-lubricating coking plastics, ensuring the operation of dry friction units at temperatures in the range 350–500 °C, be prepared by employing in such plastics carbaborane-containing polymers including carbaborane-containing polyarylates which can be converted during preparation into a high-strength coke, constituting a sterically structured polymeric system, without altering the initial mass and shape of the article.[229,314-316]

For example, heat-treated materials comprising carbaborane-containing polyarylates [obtained from the acid chloride of 1,2-bis(4-carboxyphenyl)carbaborane and phenolfluorene or 1,2-bis(4-hydroxyphenyl)carbaborane] and graphite have the following physicomechanical parameters: coefficient of friction 0.05–0.09, intensity of linear wear $(2.5-5) \times 10^{-9}$, and limiting working temperature 500 °C.

It has been noted that compositions containing polyarylate, polyester imide, and a filler are technologically suitable for moulding and the preparation of impact-resistant articles.[281] The glass-reinforced polyarylates based on 2,2-bis(4-hydroxyphenyl)-propane and mixtures of terephthalic and isophthalic acid chlorides containing also a mineral filler possess a valuable set of properties.[290] Impact-resistant compositions with improved low-temperature properties (worked on a casting machine), which are used to manufacture motorcar components, are obtained from mixtures of polyarylates with poly(alkylene terephthalates) and other polymers.[292] Electrically conducting transparent polymer compositions have been developed. They were obtained by the crystallisation in situ of tetraselenatetracene chloride in a polyarylate matrix.[299]

It is noteworthy that filled polyarylate materials can be obtained not only by processing finished polyarylates with a filler but also directly during the synthesis of the polymer by polycondensation in the presence of fillers, which may play the role of a homogeneous or heterogeneous matrix.[270,317-320] For example,

mixtures of polyterephthalates of 2,2-bis(3-chloro-4-hydroxyphenyl)propane with graphite, obtained by polycondensation, are superior to blends obtained by the mechanical mixing of a finished polyarylate with a filler in terms of many properties (thermal characteristics, specific impact stength, specific electrical resistance, and a lower coefficient of friction).

The solubility of cardo-polyarylates leads to the possibility of their successful conversion from a solution into films and fibrous materials, which are used for the purification of gases and liquids and for the trapping of aerosols. Depending on the operating conditions, such filter materials can be employed at temperatures up to 300 °C.[11,56]

Polycondensation block-copolymers with a polyarylate base also possess useful properties.[56,145,146] Thus films of polyarylate-siloxane block-copolymers of the Silar type have a valuable set of physicomechanical and gas-separating properties. Their tensile strength reaches 500 kgf cm^{-2} in many cases. They possess a high elasticity and permeability to gases, the latter approaching that of polydimethylsiloxane, but their mechanical strength is higher than that of the latter material. This leads to the successful employment of such polymers in engineering and medicine (for example, as membrane gas oxygenators).

Polyarylate-arylene sulfone oxides with a small content of arylene sulfone oxide (~15%) exhibit a high heat resistance, which is close to that of polyarylates, but the viscosity of their melts is appreciably lower than that for the latter compounds, which significantly facilitates the working of such block-copolymers. Heat-resistant (prolonged heat resistance at 200–230 °C) polyarylate-arylene sulfone oxide cast thermoplastics, designed for constructional and electrical insulating purposes, can be used for the manufacture of articles for electronic engineering electrically insulating materials, and components subjected to appreciable loads at elevated temperatures.[136]

* * *

The foregoing review shows that polyarylates constitute an extremely promising class of polymers, which can be used successfully in many branches of engineering where a high heat resistance, photostability, and effective electrical insulating, mechanical, etc. parameters are needed.

The knowledge of the characteristic features of the formation of polyarylates and of the relation between their structure and properties leads to extensive prospects for the specific design of the polyarylate chain and hence for imparting a set of desired properties to such polymers.

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