Russian Chemical Reviews **65** (3) 249 – 277 (1996)
© 1996 Russian Academy of Sciences and Turpion Ltd

UDC 541.64

Cardo polyheteroarylenes. Synthesis, properties, and characteristic features

S V Vinogradova, V A Vasnev, Ya S Vygodskii

Contents

I. Introduction	249
II. Polyarylates	249
III. Aromatic polyethers	253
IV. Aromatic polyketones	255
V. Epoxide polymers	256
VI. Polyarylenephthalides	257
VII. Aromatic polyamides	258
VIII. Polyimides	261
IX. Poly-1,3,4-oxadiazoles	269

Abstract. The characteristic features of the synthesis and properties of cardo polyheteroarylenes (polyarylates, aromatic polyethers, polyamides, polyimides, polyoxadiazoles, and others) are examined and surveyed. It is shown that cardo polymers containing bulky side-groups, linked via cyclic groups to the polymer main chain, have enhanced thermal characteristics combined with a satisfactory solubility. Certain aspects of the practical applications of polymers of this kind are considered. The bibliography includes 309 references.

I. Introduction

Among polymers with an enhanced thermal stability, cardo polymers occupy a special place; the term cardo polymers is applied to those containing at least one element in the repeating group which is included in the cyclic side group. The term arose from the Latin word 'cardo', meaning loop, because such cyclic side groups can be regarded as loops in relation to the backbone of the macromolecule.[1-4]

Many years of study of the influence of chemical structure on the properties of polymers led to the idea that the asymmetry of the macromolecules, the incorporation of bridging units in the polymer chain, and the presence of bulky side substituents in the polymer chain may impart solubility in organic solvents to heat-resistant polymers, thereby facilitating their processing. An important factor in this connection is that the modification of the polymers in order to increase their solubility should not be accompanied by a decrease in their heat resistance. As will be shown in the present review, cardo polymers satisfy these requirements.

Data on the use of phenolphthalein for the synthesis of polyesters and alkyd, epoxide, phenolformaldehyde, and other polymers began to appear in patents and publications in the 1940s.[3,5] A characteristic feature of these polymers was that phenolphthalein was used simply as one of the diols without taking into account its specific influence on the properties of the polymers. The synthesis of high-molecular-mass polyarylates derived from phenolphthalein and various dicarboxylic acids, achieved in 1961, when attention was first directed to the specific contribution of the phthalide cardo group to the properties of the polymers, should be regarded as the start of systematic and deliberate studies on cardo polymers.[6,7]

In subsequent years, the studies on cardo polymers developed widely.

S V Vinogradova, V A Vasnev Heterochain Polymer Laboratory, Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 61 78 (S V Vinogradova).
Ya S Vygodskii Condensation Polymer Laboratory of the same Institute.

Received 11 September 1995
Uspekhi Khimii **65** (3) 266 – 295 (1996); translated by A K Grzybowski

II. Polyarylates

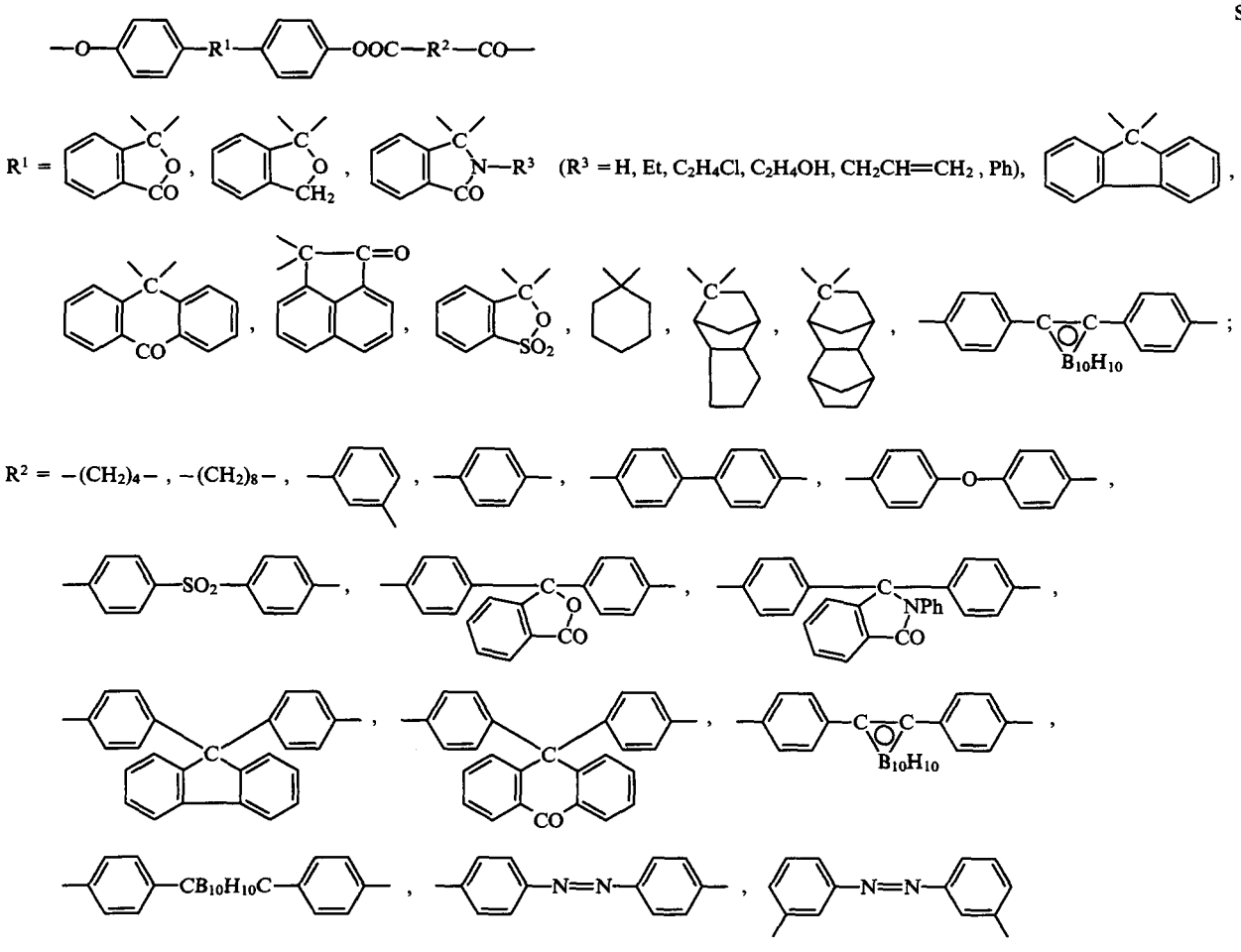
Data on the syntheses and the results of studies on cardo polyarylates have been published in a series of communications.[2-4,6-89] The most useful method for their synthesis is the polycondensation of dicarboxylic acid chlorides with dihydric phenols which contain cardo groups. Depending on the structure of the initial monomers, the polycondensation process can occur under high-temperature conditions in solution, under acceptor-catalytic conditions, or by the interfacial method.[8,10-12,14,15,49,50,55-58]

Scheme 1 presents examples of certain structures of cardo polyarylates.

Many cardo polyarylates have been synthesised successfully by the high-temperature polycondensation of the starting materials in solution in ditolylmethane, α-chloronaphthalene, Sovol(chlorinated biphenyl), nitrobenzene, etc. in the temperature range from 100 to 220 °C for ~10 h. The amount of starting materials used was 0.6 – 5 mol l^{-1}.[1,6,7,22,23,44,59,60] The polymers were obtained in nearly quantitative yields and had high molecular masses (for example, molecular masses of the order of 60 000 – 100 000 are attained in the case of polyarylates derived from phenolphthalein and aromatic dicarboxylic acids).

The kinetics of the process in the temperature range from 150 to 200 °C have been investigated in relation to the high-temperature polycondensation of 9,9-bis(4-hydroxyphenyl)fluorene (phenolfluorene) and bisphenols of the norbornane type with the chlorides of terephthalic and isophthalic acids in ditolylmethane. It was concluded that these reactions proceed in accordance with an ionic mechanism via an acylium ion.[54,61,62] The study of the influence of the nature of the reaction medium on the results of the polycondensation of phenolphthalein and its derivatives with the chlorides of aromatic dicarboxylic acid revealed an

Scheme 1



interesting feature. It was found that the reaction medium influences significantly the formation of the supermolecular structure and the properties of the amorphous vitreous polymers of this type.[59,60] The solvent power of the medium directs the process involving the formation of rigid macromolecules in the direction of either coiled or uncoiled conformations, as a consequence of which globular or fibrillar forms of supermolecular structures are produced. Thus, in the synthesis of the polyarylate derived from phenolphthalein and isophthalic acid in ditolylmethane, the polymer precipitates and has a globular supermolecular structure, whereas in the synthesis in solvents such as Sovol, α-chloronaphthalene, and nitrobenzene the polymer remains in solution throughout the reaction and a product with a predominantly fibrillar supermolecular structure and a better set of physicomechanical properties is formed.[50,59,60]

In the interfacial polycondensation of phenolphthalein anilide with terephthalic acid chloride (organic medium — benzene), where the polymer is formed at the interface between two liquid phases (the polymer is not soluble in either), the polyarylate has a distinct globular structure, whereas the polyarylate synthesised by the high-temperature polycondensation in a homogeneous medium (in α-chloronaphthalene) has a fibrillar supermolecular structure. Whereas the first polymer has a softening point of 280–285 °C, a tensile strength of 960 kgf cm^{-2}, a relative elongation at break of 13%, and a specific impact strength (A) of ~1 kgf cm cm^{-2}, the fibrillar specimen has a softening point of 315–320 °C, a tensile strength of 1000 kgf cm^{-2}, a relative elongation at break of 40%–50%, and a specific impact strength of 7–9 kgf cm cm^{-2}.[60]

In the synthesis of crystallising cardo polyarylates,[19,20,52] for example the polyarylate obtained from 9,9-bis(4-hydroxyphenyl)-10-anthrone (phenolanthrone) and terephthalic acid, the process conditions (reaction temperature, rate of heating and cooling of the reaction mass, concentration, etc.) influence not only the molecular mass of the polymer obtained but also its structure. This polymer is obtained with the highest percentage of the crystalline form when the polycondensation is carried out at 220 °C (in Sovol, α-chloronaphthalene, and nitrobenzene). When the process is carried out at a temperature above 220 °C, polyarylates with a lower degree of order are produced. An amorphous polyarylate is obtained when the reaction is performed in Sovol at 330 °C (with rapid heating and cooling of the reaction mass). The concentration of the initial monomers should be of the order of 0.6 M under these conditions; when the concentration is raised, an amorphous polymer cannot be obtained.

A series of studies[8,63–68] have been devoted to the characteristic features of the formation of phenolphthalein polyarylates by acceptor-catalytic polycondensation. One should note in the first place that the synthesis of polyarylates by this method is faster and proceeds under milder conditions than the synthesis by high-temperature polycondensation in solution. For example, the polycondensation of phenolphthalein with the terephthaloyl chloride in the presence of triethylamine in dichloroethane at 50 °C leads to the formation of a polymer after 5 min in a nearly quantitative yield, having a reduced (intrinsic) viscosity in tetrachloroethane of ~0.9 dl g^{-1}.[65] The study of the reaction of phenolphthalein with terephthaloyl chloride in the presence of triethylamine revealed the influence of the nature of the reaction medium on the acceptor-catalytic polycondensation.[66,67] It was established that the lack of the complete solubility of the initial compounds in the reaction medium is a significant obstacle to the formation of a high-molecular-mass polymer. The molecular mass of the polymer formed is greatly influenced by the properties of the reaction medium such as its polarity and its ability to dissolve the initial reactants and the polymer. In the study of the dependence of the molecular mass of the polymer formed on the composition of the binary reaction mixture (a mixture of acetone and benzene), it was found that the polyarylate with the highest molecular mass is obtained when the reaction mixture contains 30–40 vol% of acetone.[67] In this medium, it was possible to synthesise a polyarylate

with a very high molecular mass (250 000) and with a reduced viscosity in tetrachloroethane of 10 dl g^{-1}. In general, the optimum conditions for the synthesis of polyarylates by acceptor-catalytic polyesterification in heterogeneous systems are as follows: a high solubility of the initial compounds in the reaction medium and an appreciable swellability of the polymer in a weakly polar medium, or a high polarity of the medium where the swellability of the polymer in the solvent is insignificant.[58,66-70]

The cardo polyarylates based on trifunctional monomers such as 2-β-hydroxyethyl-3,3-bis(4-hydroxyphenyl)phthalimidine or phenolphthalein imide can be usefully synthesised by interfacial polycondensation because it is then possible to obtain linear high-molecular-mass polyarylates with free ethoxy- or imide groups when appropriate conditions are selected.[16,17,50,70] The synthesis of the same polyarylates by high-temperature polycondensation affords insoluble three-dimensional polymers owing to the reaction of the chlorocarbonyl groups with the ethoxy- or imino-group of the lactam at high temperatures.

Oligoarylates with a branched structure and an average functionality of 2, having terminal and side alcoholic hydroxy-groups, have been obtained by the acceptor-catalytic polyesterification reaction of terephthaloyl chloride with phenolphthalein, 2-β-hydroxyethyl-3,3-bis(4-hydroxyphenyl)phthalimidine, and ethylene glycol in dioxane at 30 °C in the presence of triethylamine.[64] It was shown that branched oligoarylates soluble in organic solvents may be obtained when 2-β-hydroxyethyl-3,3-bis(4-hydroxyphenyl)phthalimidine is introduced into their composition in an amount not exceeding 50 mol % of the sum of the bisphenols. An increase in the degree of branching of polyarylates entails an increase in their softening temperature. Thus, when the content of 2-β-hydroxyethyl-3,3-bis(4-hydroxyphenyl)phthalimidine in a mixture with phenolphthalein is increased from 3 to 25 mol %, the softening temperature increases from 280 to 340 °C. On the other hand, when the content of the first bisphenol is up to 50 mol %, the product does not soften up to 410 °C.[64]

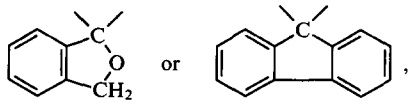
The properties of cardo polyarylates depend significantly on their chemical structure. The amorphous nature of the polyarylates with asymmetric cardo groups (for example, phthalide and acenaphthene groups) can be explained by the statistical nature of the polycondensation and the asymmetric form of the cardo groups, which lead to their different positions relative to the macromolecule.[21,49-51] The ability of cardo polyarylates to crystallise increases following the introduction of symmetrical cardo groups (the fluorene and anthrone groups) and when the cardo groups contain polar groups (for example, the anthrone group) and groups capable of forming hydrogen bonds [polyarylates derived from phenolphthalein imide and 2-β-hydroxyethyl-3,3-bis(4-hydroxyphenyl)phthalimidine].

Polyarylates containing cardo groups in both the bisphenol and acid fragments exhibit explicit signs of ordering. It has also been noted that the ability to crystallise is influenced significantly by the disposition of the cardo groups relative to the ester bond. Thus the phenolanthrone polyterephthalate, synthesised by high-temperature polycondensation at 220 °C, is crystalline to the extent of approximately 40%, while the isomeric polyarylate derived from hydroquinone and 9,9-bis(4-carboxyphenyl)-10-anthrone and obtained under similar conditions is amorphous.[33,51]

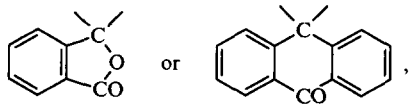
The softening temperatures of a series of amorphous cardo polyarylates and, for comparison, of certain polyarylates of the noncardo type are presented in Table 1.[29,51,52,54,72,73] It is seen from the data presented that the cardo polyarylates have significantly higher softening temperatures (compare, for example, polymers Nos 1 – 3, 5, and 6 with polymers Nos 12 and 13, etc.). Comparison of polymers Nos 7 and 8 with polymer No. 19 permits the conclusion that polyarylates with a cyclic acid fragment have appreciably higher softening temperatures than polyarylates with an acyclic, 'open-chain', structure of the isomeric acid fragment.[29,51] Thus the softening temperatures of the polyarylates obtained from bis(4-carboxyphenyl)phthalide and acyclic dihydric phenols [1,3- and 1,4-di(4-hydroxybenzyl)benzenes] are 250 and 270 °C respectively, whereas the softening temperature of the polyarylate obtained from phenolphthalein and bis(4-carboxyphenyl)phthalide is 340 °C.[29,51,62]

A high heat resistance is characteristic also of carborane-containing cardo polyarylates.[74-78] Thus the softening temperatures of the polyarylates obtained by the reaction of 1,2- and 1,7-bis(4-carboxyphenyl)carboranes with phenolphthalein, phenolfluorene, and phenolanthrone are 340 – 360 °C. It is noteworthy that, according to X-ray diffraction data, these polyarylates have crystalline structures with low or moderate degrees of order. One can only note a tendency towards the formation of an amorphous structure on transition to polyarylates based on the *m*-carborane-containing isomer. The softening temperature of the amorphous cardo polyarylate derived from 1,2-bis(4-hydroxyphenyl)carborane and bis(4-carboxyphenyl)phthalide is also high, being 330 °C.

There is no doubt that the high heat resistance of the cardo polyarylates and, incidentally, of other cardo polymers (see below) is due to the increased rigidity of the polymer chain. The cardo groups not only increase the rigidity of the main polymer chain but also loosen the structure of the polymer, diminishing thereby the interchain interaction, which ensures a high solubility of such polyarylates in many organic solvents. The majority of amorphous cardo polyarylates are readily soluble in methylene chloride, dichloroethane, chloroform, tetrachloroethane, tricresol, tetrahydrofuran, dioxane, cyclohexanone, nitrobenzene, and dimethylformamide, frequently with formation of highly concentrated solutions.[3,4,6,7,51] The chemical structure of polyarylates also influences their solubility. Thus polyarylates containing groups capable of forming hydrogen bonds, for example phenolphthalein imide polyarylates, do not dissolve in chlorinated solvents but are readily soluble in dioxane, tetrahydrofuran, tricresol, and dimethylformamide. In contrast to polyarylates with phthalide and anthrone cardo groups, i.e.



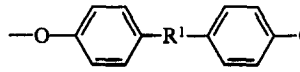
those with cardo groups not containing the CO group, i.e.

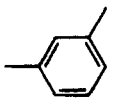
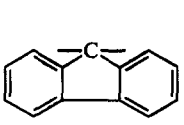
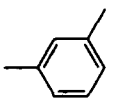
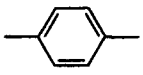
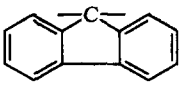
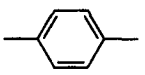
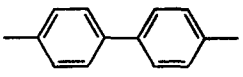
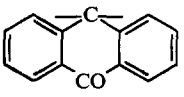
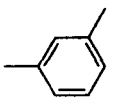
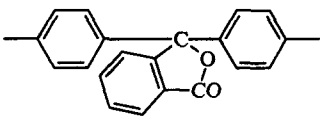
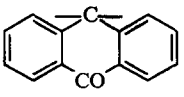
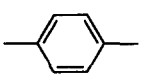
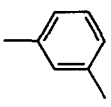
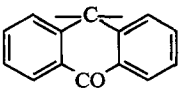
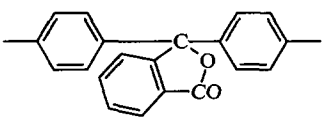
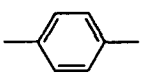
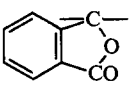
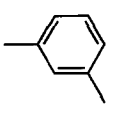
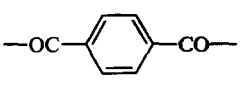
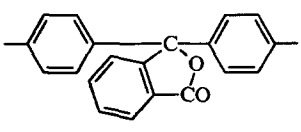
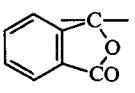
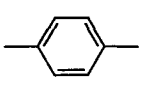
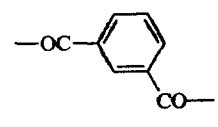
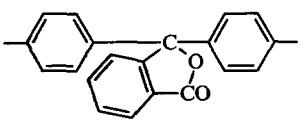
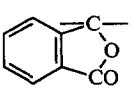
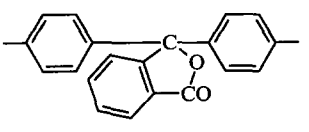
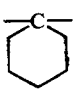
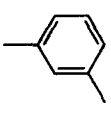
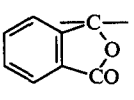
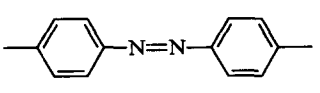
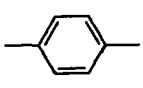
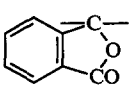
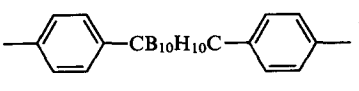
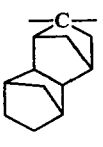
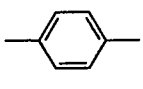
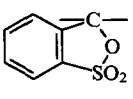
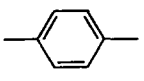


are soluble in chlorobenzene, toluene, and *o*- and *m*-xylenes.[51] Carbaborane-containing polyarylates derived from 1,2- and 1,7-bis(4-carboxyphenyl)carboranes and 1,2-bis(4-hydroxyphenyl)-carborane are readily soluble in aromatic hydrocarbons.[76,78] Amorphous phenolphthalein, phenolacenaphthene, and phenolanthrone polyarylates give rise to 35% solutions in chloroform, whereas phenolfluorene polyterephthalate gives only 5% solutions.[52]

The heat resistance and solubility of cardo polyarylates are also greatly influenced by their physical state. In particular, this has been clearly established for phenolanthrone polyterephthalate, the structure of which can be deliberately altered from amorphous to crystalline by changing the conditions of its synthesis or the subsequent treatment of the finished polymer.[21,51,52] Whereas the amorphous polyarylate softens at 335 – 365 °C and dissolves in a wide range of organic solvents, with increase in the degree of order in the structure of the polyarylate the range of solvents becomes narrower and the heat resistance increases. The crystalline polymer dissolves only in the phenol – tetrachloroethane mixture and is highly heat resistant (it does not melt before decomposition). Thus the heat resistance and solubility of cardo polyarylates can be varied specifically by varying their chemical and physical structures.

High thermal stability is characteristic of cardo polyarylates.[36,50,52] Under an inert atmosphere, the temperature of the onset of decrease in the mass of phenolphthalein, phenolfluorene,

Table 1. The softening temperatures of the polyarylates .

No	R^1	R^2	T/ °C	No	R^1	R^2	T/ °C
1	$-C(CH_3)_2-$		180	12			295
2	$-C(CH_3)_2-$		215	13			340
3	$-C(CH_3)_2-$		230	14			325
4	$-C(CH_3)_2-$		315	15			365
5	$-C(C_6H_5)_2-$		235	16			390
6	$-C(C_6H_5)_2-$		280	17			280
7			270	18			340
8			250	19			340
9			240	20			295
10			290	21			340
11			310	22			265

and phenolanthrone polyterephthalates is about 350–360 °C. The polymers decompose at a low rate, losing only 2%–3% of their mass before the onset of vigorous decomposition (at 460–470 °C). The chemical structure of the bisphenol does not influence significantly the temperature of the onset of the thermal decomposition of these polyarylates, which is determined mainly by the presence of the ester bond. The carborane-containing cardo polyarylates obtained by the reaction of 1,2- and 1,7-bis(4-carboxyphenyl)carboranes with phenolphthalein, phenol-fluorene, and phenolanthrone, as well as the polyarylates obtained from 1,2-bis(4-hydroxyphenyl)-carborane and bis(4-carboxyphenyl)phthalide have the best thermal characteristics.[74–79] The temperature of the onset of the change in their mass under an inert atmosphere and in air is 400–420 °C. After heat treatment for 3 h in air at 400 °C, these polymers give rise to large amounts of coke residues (86%–98%), whereas phenolfluorene polyterephthalate decomposes to an extent of 35% under these conditions.

The phenolphthalein, phenolfluorene, and phenolanthrone polyarylates are thermoplastic polymers. They can be processed by usual method for thermoplastic materials, which, combined with

their high thermal stability, give rise to extensive possibilities for their employment as constructional materials. By virtue of their effective dielectric properties, they can be used successfully in radio and electrical engineering. Filled materials, including antifriction materials with a low coefficient of friction and capable of working for a long time without a lubricant at high temperatures (250 °C) in a vacuum and under the conditions of high velocity gradients between the friction surfaces (sliding and roller bearings), are obtained from polyarylates.

The satisfactory solubility of cardo polyarylates in organic solvents and their compatibility with many polymers (in particular with epoxide polymers) makes it possible to convert them readily, both from solution and from mixtures, into coating films, fibrous materials, heat-resistant composite materials, and potting compounds and also permits their use as binders for reinforced plastics.[4, 10, 14, 49-51, 80-82] In particular, a promising procedure for the conversion of cardo polyarylates, for example phenolphthalein polyterephthalate, into monolithic articles involves its combination with a reactive epoxide oligomer and subsequent moderate heating. The chemical interaction of the epoxyoligomer with the polyarylate (via a mechanism involving the 'insertion' of an oxirane ring in the ester bond [80]) results in the formation of a network system having a specific set of properties and the region of mechanical usability of such compositions extends to more elevated temperatures compared with the traditional compositions based on oligoepoxides.[82] The part of the chemically reactive heat-resistant polymer in the composition with oligoepoxides which has not reacted serves as a filler. The presence of such a high-molecular-mass chemically reactive filler reduces significantly the density of the composition and improves its strength characteristics compared with compositions containing a usual mineral filler.[37]

The high glass points of cardo polyarylates ensure the retention at high temperatures of the effective mechanical and dielectric properties of articles made from these polymers. For example, nonoriented phenolanthrone polyterephthalate films have at 25 °C a tensile strength (σ_t) of 940 kgf cm^{-2}, and an elongation at break (ε) of 10%, whereas at 250 °C $\sigma = 470$ kgf cm^{-2} and $\varepsilon \leqslant 5\%$. After heating for 100 h at 300 °C or 500 h at 250 °C, the film retains about 50% of its initial strength. The tangent of the dielectric loss angle for this polymer hardly changes up to 250 °C; high specific volume resistivities ($\geqslant 1 \times 10^{15}$ Ω cm) are retained up to this temperature.[51, 52]

At 300 °C, phenolfluorene polyterephthalate films retain more than 50% of their initial strength. The tangent of the dielectric loss angle for this polymer is 0.0025 at 220 °C.[44, 45] Fibrous filtering materials based on phenolphthalein polyterephthalate, employed successfully for the purification of gases and liquids and for trapping aerosols, may be used up to 300 °C.[10, 14]

Cardo polyarylates can be converted also into heat-resistant strong monolithic articles. The bending strength (σ_b) of monolithic phenolanthrone polyterephthalate reaches 1700 kgf cm^{-2}.[52] The specific impact strengths of test specimens of phenolphthalein, phenolfluorene, and phenolanthrone polyterephthalates are 15-20 kgf cm cm^{-2}.[4] Monolithic articles made from the polyarylates of phenolphthalein and isophthalic acid, obtained by casting under pressure, have effective physicomechanical parameters (both in the initial state and after prolonged heat treatment).

Characteristic	Initial specimen	Heat-treated specimen (1000 h, 200 °C)
σ_t/ kgf cm^{-2}	940	800
A/ kgf cm cm^{-2}	30	70
σ_b/ kgf cm^{-2}	1300	1200
H/ kgf cm^{-2} [a]	1280	1250
tan δ [b]	2×10^{-2}	2×10^{-2}

[a] H is hardness. [b] tan δ is tangent of dielectric loss angle.

Articles made from phenolphthalein polyterephthalate, filled with talc or powdered quartz, exhibit a high resistance to repeated temperature changes from −60 to 250 °C and possess satisfactory electrical insulating properties.[83]

Cardo polyarylates are satisfactorily resistant to the action of ultraviolet and ionising radiations, retaining, for example, effective physicomechanical parameters after prolonged exposure to ^{60}Co γ-rays in air. Cardo polyarylates with fluorene groups are more stable than polymers with phthalide groups.[4] The partial or complete replacement of the lactone ring by a lactam ring in phenolphthalein polyarylates as well as the presence of fluorene groups in the bisphenol residues increase appreciably the resistance of the polyarylate to the action of light. The inclusion in the polymer chain of phenolphthalein polyarylates of small amounts (~1%) of sulfur, phosphorus, and hydroxy-groups by employing, for example, monomers such as phenolsulfophthalein, phloroglucinol, bis(4-carboxyphenyl)methylphosphine oxide, etc. promotes the formation of polyarylates with increased resistance to light-induced ageing.[72, 84-87]

The employment of chromophore-containing monomers (the chlorides of azobenzene-3,3′-dicarboxylic and azobenzene-4,4′-dicarboxylic acids, quinizarine, alizarine, Alizarine Blue, and others) in the synthesis of cardo polyarylates led to the possibility of obtaining coloured polyarylates with different colours, the colours exhibiting a high photostability. Colours with a high photostability can be achieved even in the presence of only a small amount (0.05 mol%) of the chromophore-containing monomer in the polyarylate chain.[49, 50, 88-91] It is also noteworthy that the introduction of even a small amount of a chromophore-containing monomer into mixed polyarylates derived from terephthalic acid and phenolphthalein greatly increases the resistance of the polymer to ultraviolet radiation.[80]

Thus cardo polyarylates have enhanced thermal characteristics, satisfactory solubilities, and effective physicomechanical properties.

III. Aromatic polyethers

Since the 1960s, aromatic polyethers have attracted the attention of investigators because of their high thermal stability and a number of other valuable properties.[92-94] However, their comparatively low heat resistance is a significant disadvantage of these polymers.

The positive influence of the cardo groups on the heat resistance of polyarylates stimulated the synthesis and study of aromatic cardo polyethers.[49, 51, 95-108]

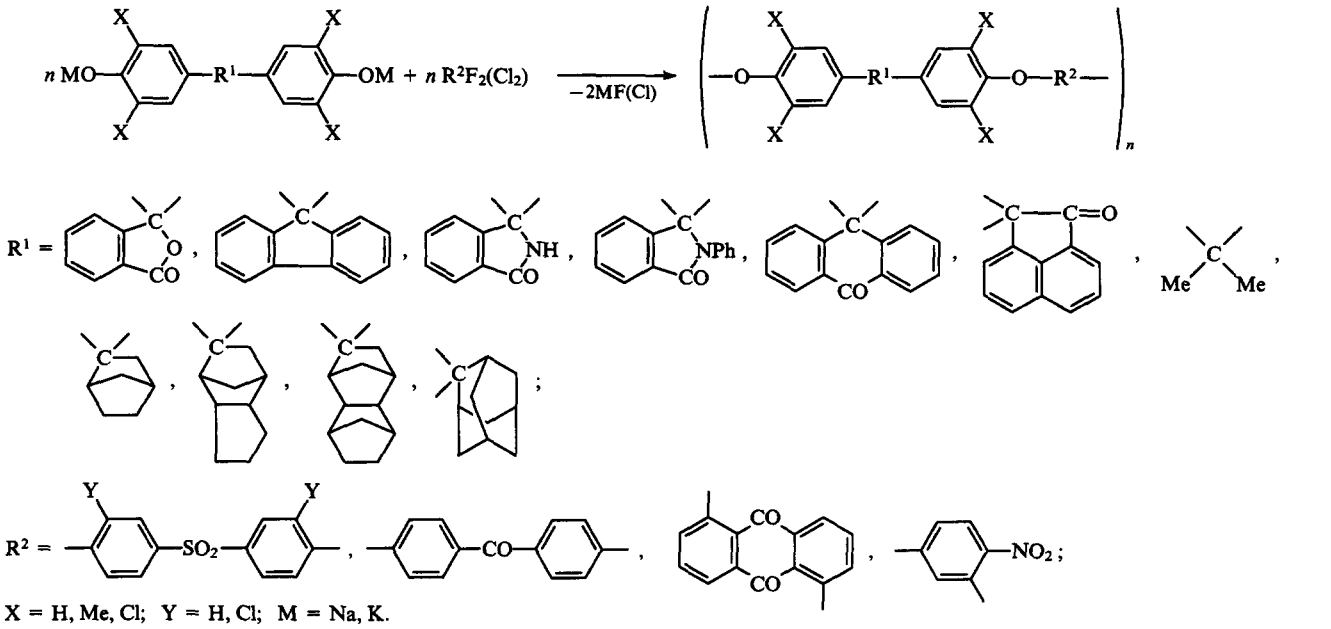
Aromatic cardo polyethers are obtained by the nucleophilic substitution reaction between phenoxides derived from bisphenols and activated aromatic dihalides (usually in dimethyl sulfoxide at 160-180 °C). Scheme 2 presents some of the structures of the polymers of this type which have been synthesised.

In the polycondensation of dihalo-derivatives with phenoxides derived from cardo bisphenols (with the exception of adamantane-containing bisphenols), only the difluoro-derivatives proved to be sufficiently reactive (for the formation of polymers with a high molecular mass). It has been suggested that the lower reactivity of the phenoxides obtained from cardo bisphenols compared with the phenoxide derived from 2,2-bis(4-hydroxyphenyl)propane is due in some cases to the greater acidity of the cardo bisphenols or the poorer solubility of the initial phenoxide in the reaction medium.[51, 95, 99] Polyethers based on phenolphthalein contain a phthalide ring,[97] although the lactone ring of phenolphthalein is opened in alkaline media.

It has been noted that, in the polycondensation of phenolphthalein imide with bis(4-fluorophenyl) sulfone, not only the phenoxide groups but also the mobile hydrogen atom at the nitrogen atom of the lactam ring can participate in the reaction, which leads to the formation of a structured fraction.[99]

A series of characteristics of the formation of cardo polyethers by the reactions of phenolphthalein and phenolfluorene with dihalobenzophenones in dimethylacetamide in the presence of potassium carbonate have been investigated.[97] It was established

Scheme 2



X = H, Me, Cl; Y = H, Cl; M = Na, K.

that 4,4′-difluorobenzophenone is much more reactive than the dichloro-derivative. Conditions have been found for the preparation of high-molecular-mass polymers (with a molecular mass >200 000). The addition of the monofunctional 4-fluorobenzophenone during the polycondensation process makes it possible to regulate the molecular masses of the polymers within wide limits (from 10 000 to 100 000).[97]

The study of the characteristic features of the synthesis of polyethers with polycyclic groups of the norbornane type from chlorobisphenols and bis(4-fluorophenyl) sulfone showed that best results are achieved when hexamethylphosphoramide is used as the reaction medium. The reaction takes place successfully under an inert atmosphere at a concentration of the starting materials of 1.7 M, at 130–180 °C, with a reaction time of 10–15 h, and for the equimolar ratio of the starting materials and leads to polymers with a molecular mass of the order of 60 000–80 000.[96]

It has been established that the interaction of polycyclic bisphenols of the norbornane type with 4,4′-difluorobenzophenone can be usefully carried out in dimethyl sulfoxide at a concentration of the starting materials of 1.5 M, for an equimolecular ratio of the starting materials, with a reaction time of 6–9 h, and at a temperature of 170–180 °C. In the synthesis of polyethers derived from polycyclic bisphenols of the norbornane type and 2,4-difluoronitrobenzene, best results were obtained when the reaction was carried out at 80–90 °C for 4–7 h.[96]

The majority of aromatic cardo polyethers are amorphous and readily soluble in organic solvents: chloroform, methylene chloride, tetrachloroethane, cyclohexanone, tricresol, nitrobenzene, dioxane, etc. However, a crystallisable polymer was obtained from bis(4-fluorophenyl) sulfone and phenolfluorene, which has a symmetrical cardo group.[51, 95, 98] The structure of this polymer may be varied both during the processing of the powdered polymer by treatment with various solvents and in the formation of films from various solvents.

Table 2 presents the softening temperatures of a series of cardo polyethers and the polyether based on 2,2-bis(4-hydroxyphenyl)propane obtained in thermomechanical tests.[51, 95, 96, 99] As can be seen from the data presented, it is possible to increase significantly (by 40–130 °C) their softening temperatures by introducing cardo groups into the macromolecules of aromatic polyethers. The heat resistance of the above polymers may be increased by replacing the CO group in the dihalo-derivative by the SO_2 group and by going over to structures with condensed rings.

Transparent strong films are obtained from solutions of aromatic cardo polyethers.[95–99] Thus the tensile strength of a polyether film based on 4,4′-difluorobenzophenone and phenolphthalein is 900 kgf cm^{-2} and its relative elongation at break is 40%–190%; the tensile strength of the corresponding phenolfluorene polyether film is 900 kgf cm^{-2} and the relative elongation at break is 70%.[97] Monolithic pressed specimens of cardo polyethers also exhibit effective mechanical parameters.[97]

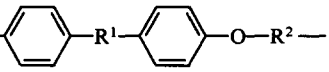
The study of the influence of the molecular mass of the polyether based on phenolphthalein and 4,4′-difluorobenzo-phenone on the physicomechanical properties showed that the latter properties of the polyethers hardly change from molecular masses of 40 000–60 000 up to 200 000. At the same time, for a molecular mass of 40 000–60 000, the polyethers can be readily moulded from the melt, since the polymer having this molecular mass still retains a satisfactory fluidity.[97]

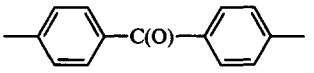
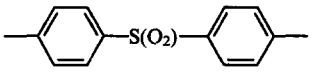
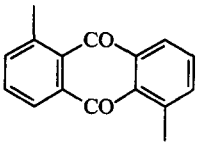
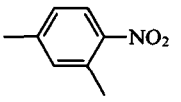
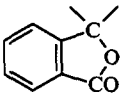
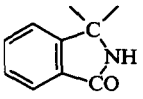
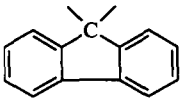
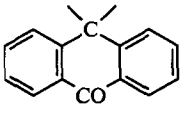
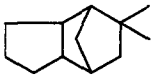
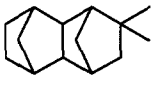
The chemical stabilities of aromatic cardo polyethers are greatly superior to those of polyarylates. Thus they are resistant to the action of water at 200–250 °C, concentrated 40% solutions of alkali at 100 °C, a 27% solution of ammonia, and a 36% solution of hydrochloric acid at 150 °C.[51, 95, 98] Aromatic polyethers with benzophenone fragments are distinguished by a greater hydrolytic stability compared with the polymers comprising diphenyl sulfone fragments.

Like the usual aromatic polyethers, the cardo polyethers exhibit a high thermal stability. According to the results of thermogravimetric analysis at a heating rate of 4 K min^{-1}, the decrease in the mass of aromatic polyethers based on phenolphthalein, phenolfluorene, and phenolanthrone in air begins at 450–500 °C.[98] The decrease in the mass of the polyether based on phenolphthalein and bis(4-fluorophenyl) sulfone on heating at 400 °C for 3 h in air was only 2.1%.[99] The temperatures of the onset of decrease in the mass of polyethers with norbornane cardo groups are in the range 400–460 °C. At temperatures above 580–600 °C, these polymers decompose without producing a coke residue.[96]

It is noteworthy that the thermal and chemical stabilities of aromatic cardo polyethers are superior to those of cardo polyarylates, but their heat resistances are lower than those of the latter polymers.

Fire-resistant aromatic polyethers have been synthesised from cardo bisphenols, bis(4-fluorophenyl) sulfone, and bis(4-chloromethyl)methylphosphine oxide.[103]

Table 2. The softening temperatures (°C) of the polyethers —O——O—R²—.

R¹	R²			
				
—C(CH₃)₂—	170	190	220	155
	230	260	280	–
	–	295	–	–
	240	270	285	–
	240	265	300	–
	240	250	–	210
	245	260	–	220
	265	270	–	235

Chemical modification of polyarylene ether-ketones and polyarylene ether sulfones, including those of the cardo type, has been achieved by treating them with chromium, molybdenum, and tungsten hexacarbonyls. Polymers containing 0.7 – 12 mass % of the metal (0.1 – 1.5 of a metal atom per polymer unit) were obtained. It was noted that the polymers containing arenemetal tricarbonyl fragments in the polymer chain can be worked into articles by employing a solution (for films and coatings) and a melt (for monolithic specimens). Such polymers have effective mechanical, optical, and adhesion properties.[109,110]

IV. Aromatic polyketones

The use for the synthesis of polymers of cardo monomers such as bis(4-carboxyphenyl)phthalide and 2-bis(4-carboxyphenyl)-*N*-phenylphthalimide led to the possibility of synthesising cardo polyketones.[49,111,112]

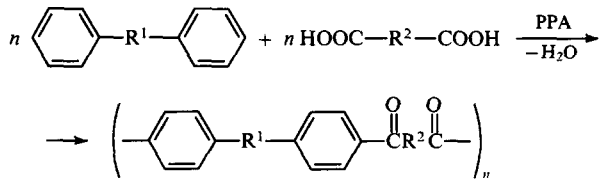
The study of the process characteristics showed that the polycondensation of the dicarboxylic acid with an aromatic hydrocarbon can be usefully carried out in polyphosphoric acid containing 85 mass % of phosphorus pentoxide at a concentration of the starting materials of ~0.5 M, a reaction temperature of 120 – 160 °C, and for a reaction time of 8 – 20 h. A series of polyketones of the noncardo type have also been synthesised for comparison. Scheme 3 presents examples of the structures of the polymers obtained.

In most cases, the polyketones were obtained in high yields (the reduced viscosity in sulfuric acid was 0.40 – 1.60 dl g^{-1}). The molecular mass of the polyketone based on bis(4-carboxyphenyl)phthalide and diphenyl ether and having a reduced viscosity of 0.68 dl g^{-1} was 44 000.

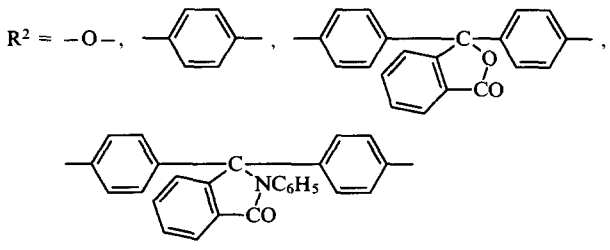
All the polyketones obtained were amorphous. The polyketones without cardo groups crystallise on heating above the softening temperature. The softening temperatures of the polyketones with phthalide and 2-(*N*-phenylphthalimidine) groups exceed by 60 – 80 °C those of the noncardo polyketones. Thus, whereas the softening temperatures of the polyketones based on diphenyl ether and bis(4-carboxyphenyl)phthalide and 2-bis(4-carboxyphenyl)-*N*-phenylphthalimidine are 250 and 270 °C, the softening temperatures of the polymers based on terephthalic acid and bis(4-carboxyphenyl) ether are 190 and 185 °C respectively.

The cardo polyketones dissolve readily in organic solvents (tetrachloroethane, chloroform, methylene chloride, dimethylacetamide, *N*-methylpyrrolidone, benzyl alcohol, etc.) to form 30% – 50% solutions, whereas the polyketones without cardo groups dissolve only in sulfuric acid. Colourless transparent films with a tensile strength of 690 kgf cm^{-2} and an elongation at break of ~10% were obtained from 30% solutions of the cardo polyketones

Scheme 3



R^1 = O, bond;



in chloroform. According to dynamic thermogravimetric data, the mass of the polyketone based on diphenyl ether and bis(4-carboxyphenyl)phthalide decreases by only 0.5% in air at 450 °C (the heating rate was 4.5 K min^{-1}), i.e. its thermal stability is extremely high. The significant difference between the softening and decomposition temperatures of the cardo polymers (180–200 °C) leads to the possibility of their successful working from the melt. A high fire resistance is characteristic of the polyketones under consideration.

V. Epoxide polymers

Data concerning the synthesis and study of epoxide polymers of the cardo type based on bisphenols have been published in a series of communications.[113–127]

Scheme 4 presents examples of the diglycidyl ethers of cardo bisphenols.

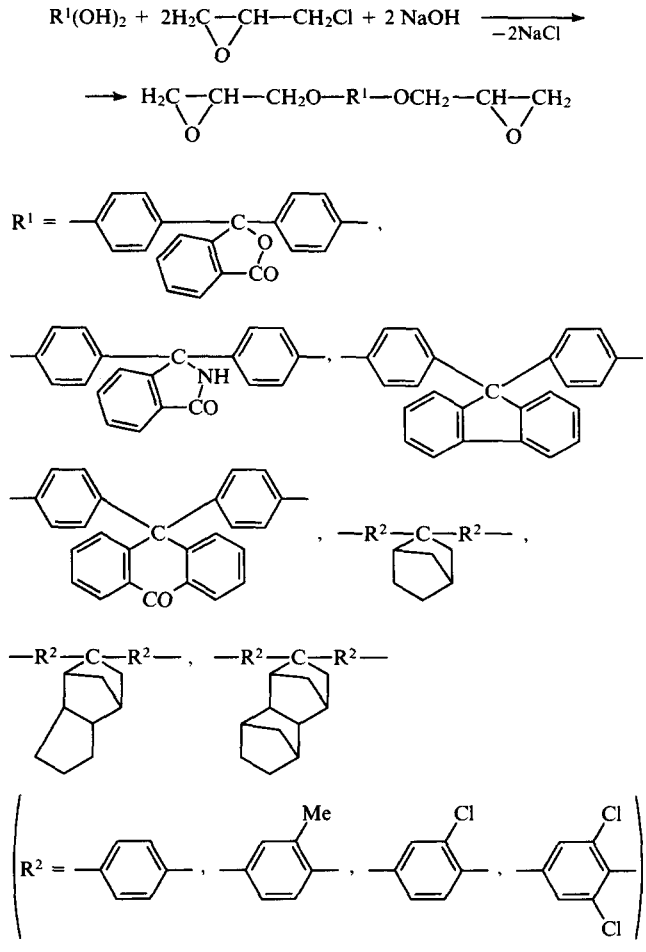
The study of the characteristics of the formation of epoxide oligomers in relation to the interaction of epichlorohydrin and 4,4′-(hexahydro-4,7-methyleneindan-5-ylidene)diphenol showed that their synthesis can be usefully carried out at 95 °C for 1 h in 50% aqueous solution of alkali with the molar ratios bisphenol : epichlorohydrin : alkali = 1 : 10 : 4. A product with a composition closest to that of diglycidyl ether is formed under these conditions in satisfactory yield (90%–95%).[114]

It has been shown that the interaction of phenolphthalein with epichlorohydrin in an alkaline medium results in the formation of a product containing a phthalide group with a lactone ring, although the formation of a compound with a quinonoid structure has been postulated in a number of studies.[115]

Oligoepoxides are readily soluble in acetone, benzene, toluene, dioxane, and ethyl acetate. The softening temperatures of the oligoepoxides based on phenolphthalein, phenolfluorene, and phenolanthrone are 36, 72, and 79 °C respectively [for comparison we may note that the softening temperature of the oligomer based on 2,2-bis(4-hydroxyphenyl)propane is –5 °C].[116]

Cardo oligoepoxides are very reactive and are easily hardened on treatment with various acid and basic hardening agents. The deformation heat resistance of the polyepoxides based on the diglycidyl ethers of phenolphthalein, phenolfluorene, and phenolanthrone, hardened by trimellitic anhydride, are 300, 330, and 315 °C respectively, while the decrements in mass after heating for 1 h at 300 °C are 14.8, 9.5, and 8.2% respectively [for comparison we may note that the deformation heat resistance and the decrease in mass of the polyepoxides based on bis(hydroxyphenyl)propane are 250 °C and 44.6%]. Hence it follows that the cardo epoxide polymers have more effective thermal characteristics.[116]

Scheme 4



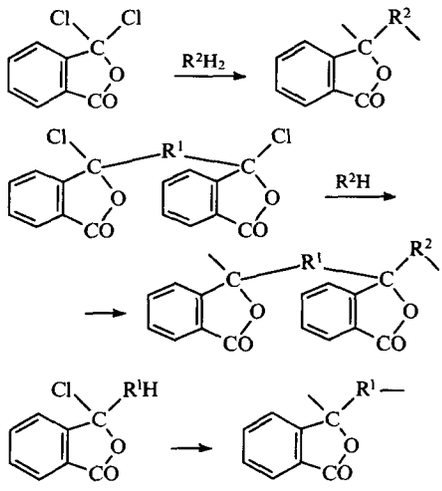
According to the results of thermomechanical and thermogravimetric studies, the introduction of cardo groups of the norbornane type does not have a significant influence on the heat resistance and thermal stability of epoxide polymers of this type. However, the presence of substituents (methyl, chlorine) in the benzene rings in such bisphenols impairs somewhat the thermal characteristic of the polymers. The diglycidyl ethers of polycyclic bisphenols of the norbornane type, hardened by bis(4-aminophenyl) sulfone and pyromellitic and maleic acid anhydrides, exhibit the highest heat resistance.[114] Thus the deformation heat resistance of the epoxide polymers based on the diglycidyl ether of 4,4′-(2-norbornylidene)diphenol, hardened with maleic anhydride, is 328 °C.[119] It has been noted that a characteristic feature of such polymers is their complete decomposition at high temperatures without the formation of a coke residue.[114]

Epoxide cardo polymers may be used as binders in the preparation of glass fibre-reinforced plastics, adhesives, and other composite materials,[114, 118, 119, 126, 127] which are characterised by an effective heat resistance and good physicomechanical and dielectric parameters.

VI. Polyarylenephthalides

Polyarylenephthalides are also cardo polymers.[128–142] Polymers of this type have been synthesised by electrophilic substitution with the aid of carboxylic acid pseudochlorides (Scheme 5).[128] The polycondensation was carried out in solution in chlorinated hydrocarbons (methylene chloride, dichloroethane, etc.) or in nitrobenzene at temperatures from –70 to 140 °C in the presence of Group III – V and VIII metal halides as catalysts (for example, $AlCl_3$, $FeCl_3$, and $SbCl_5$) in amounts ranging from 0.01 to 1.5 moles per acid chloride group. Certain properties of the polymers obtained in this way are presented in Table 3.[128]

Scheme 5

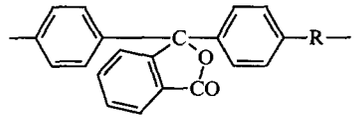


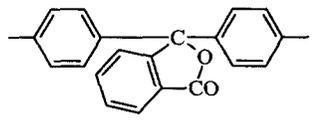
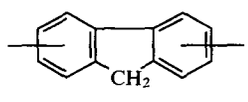
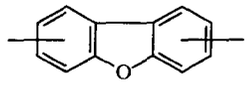
All the polymers presented in Table 3 are amorphous and readily soluble in methylene chloride, chloroform, tetrachloroethane, dimethylformamide, and other solvents. Nonoriented films with a tensile strength of 800 – 900 kgf cm^{-2} and a relative elongation at break of 10 – 20% have been obtained from the first three polymers by casting from solution. Table 3 shows that polyarylenephthalides have high heat resistances and thermal stabilities.

It is noteworthy that in a number of instances the synthesis of polyarylenephthalides may be accompanied by the formation of a gel.[129]

Special studies have been carried out to investigate the characteristic features of the formation of polydiphenylene-

Table 3. The properties of the polyarylenephthalides

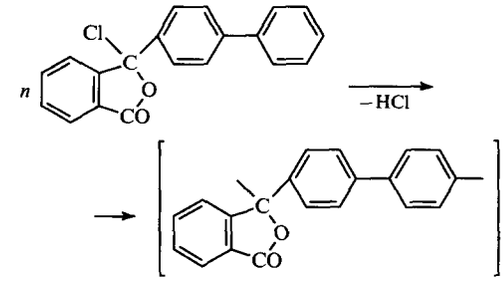


R	η_{red} /dl g^{-1} (tetrachloroethane	T/ °C softening	T/ °C onset of decomposition
Bond[a]	0.65	420	440
O	1.50	310	390
	0.55	> 300	380
S	0.50	> 250	380
	0.86	> 450	> 450
	0.72	> 400	> 450

Note. The softening temperature was determined from the thermomechanical curve obtained with a 1 kgf cm^{-2} load applied to the specimen and for a heating rate of 3 K min^{-1}. The temperature of the onset of decomposition was determined from the thermogravimetric curve at a heating rate in air of 5 K min^{-1}.

[a] The molecular mass of the polymer obtained by the light scattering method is 46 000.

Scheme 6



phthalide by the polycondensation of 4-(3-chloro-3-phthalyl)-biphenyl (Scheme 6).[130,131]

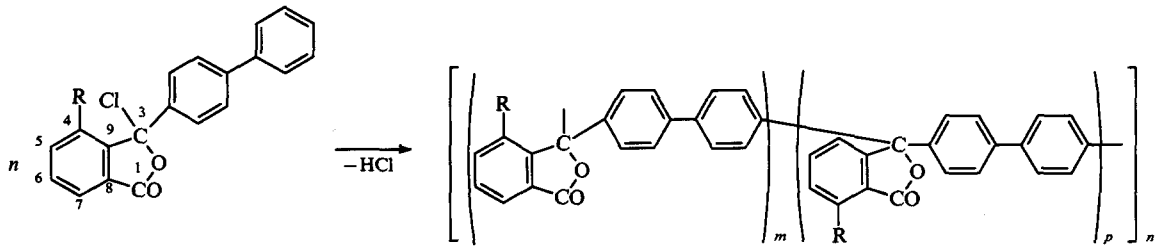
The influence of the type of solvent (chlorinated aliphatic hydrocarbons, aliphatic and aromatic nitro-compounds), temperature, reaction time, and the concentrations of the monomer and the catalyst has also been investigated. It has been noted that the polycondensation in nitro-compounds (especially in nitrobenzene) proved to be more universal and effective than in halo-derivatives, because it proceeds under the influence of catalysts of different types ($ZnCl_2$, $AlCl_3$, $AlBr_3$, $InCl_3$, $SnCl_4$, $TiCl_4$, $SbCl_5$, $SbCl_3$, SbF_3, $FeCl_3$) and leads to polymers with a higher molecular mass. The following are the most favourable conditions for the synthesis of polydiphenylenephthalide: monomer concentration 2 – 3 M, reaction temperature 100 – 110 °C, and $SbCl_3$ (7 – 10 mol %) or $InCl_3$ (3 – 10 mol %) as the catalyst. These ensure the selective formation of a polymer with a high molecular mass (46 000 – 60 000) and an intrinsic viscosity of 0.65 – 0.78 dl g^{-1} (in tetrachloroethane).[130] When the polycondensation is carried out under severe conditions (in the presence of large amounts of the catalyst and at high temperatures), in some cases the quality of the polymer and the process selectivity decrease and anomalous units, for example fragments with keto-groups, arise in the macromolecules.[130]

Polydiphenylenephthalide can also be obtained by precipitation polycondensation. In this case, the synthesis of the polymer proceeds in the initial stage in a homogeneous solution with subsequent segregation of the polymer in a separate phase.[131] For comparison, polydiphenylenephthalide has been synthesised in two variants: by polycondensation in solution in nitrobenzene (80 °C, 10 h) and by precipitation polycondensation in dichloroethane (20 °C, 24 h) with anhydrous aluminium chloride as the catalyst. It was found that the precipitation polycondensation affords a polymer with a higher molecular mass: its η_{red} in sulfuric acid was 1.02 dl g^{-1}, whereas in the case of the polymer obtained in nitrobenzene η_{red} was 0.64 dl g^{-1}. It has also been noted that nonoriented films of the 'precipitation' polydiphenylenephthalide, obtained by moulding from a solution of the polymer in chloroform, exhibit a higher optical anisotropy than the films of the 'solution' polymer and have a degree of crystallinity of 25% – 30%. The films of the 'solution' polymer are amorphous.[131]

The molecular mass characteristics of polydiphenylenephthalide have been investigated and the equilibrium rigidity of its macromolecules has been estimated. The length of the Kuhn segment of this polymer is 24 Å. It has been established[132] that, in order to obtain strong films, a polymer with a molecular mass $>3 \times 10^4$ is needed. The study of the chemical stability of polyarylenephthalides showed that they exhibit a satisfactory resistance to the action of corrosive media at elevated temperatures.[133] The thermal stability of the phthalide ring in polyarylenephthalide is determined by the nature of the groups joining the benzene rings in the main chain. The thermal stability of polydiphenylenephthalide is higher than that of poly(oxydiphenylene)phthalide.[134]

The thermal transformations of polydiphenylenephthalide and poly(diphenylene oxide)phthalide have been investigated over a wide temperature range (400 – 650 °C).[135] It was shown that the degradation of the polymers proceeds both via the end groups and via the phthalide ring and the hetero-bonds when such are present. The phthalide ring probably decomposes in three ways: without the evolution of carbon oxides (the formation of anthraquinone

Scheme 7



structures), with evolution of CO (the formation of compounds of the type of fluorenone), and with evolution of CO_2 (the formation of fragments of the anthracene, phenanthrene, and fluorene types), the last type of decomposition predominating. The first two reactions are accompanied by the rupture of the polymer chain, whilst the third leads to the formation of cross-linked structures.[135]

Certain electrophysical properties of polyarylenephthalides have been investigated and the possibility of the thermal initiation of conduction in aromatic polymers containing readily polarisable phthalide side groups has been demonstrated.[136]

Halo-substituted polyarylenephthalides have been synthesised by the Friedel–Crafts polycondensation of 3-aryl-3-chlorophthalides containing substituents in the 4-position relative to the phthalide ring. It was found that polymers containing two types of isomeric units in the polymer chain in the 4- and 7-positions can be obtained from such monomers (Scheme 7).[137]

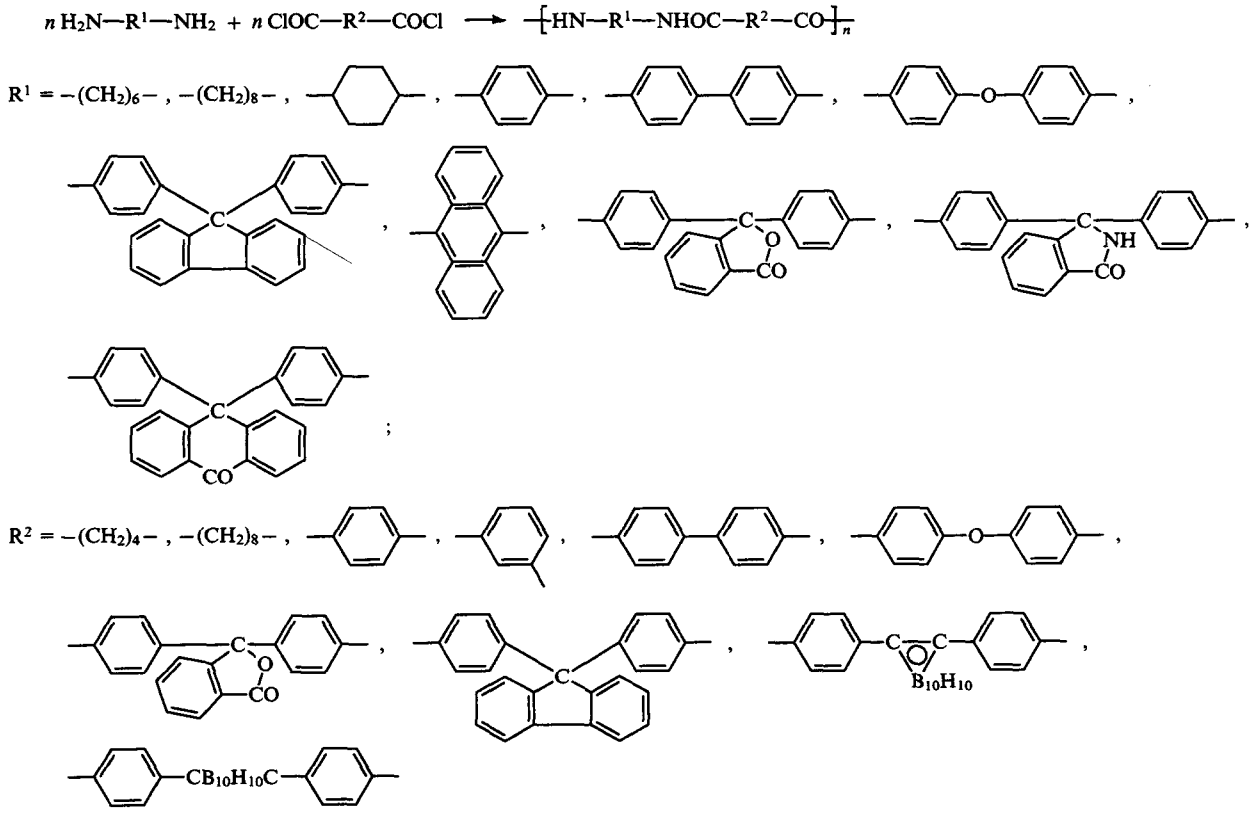
Effective thermal and physicomechanical parameters are characteristic of these polymers. Thus chloro-substituted polyarylenephthalides with a characteristic viscosity in tetrachloroethane of 1.52 dl g^{-1} have a softening temperature >450 °C, a temperature for the onset of decomposition of 450 °C, a degree of crystallinity of 30%, a tensile strength of the film of 900 kgf cm^{-2}, and an elongation at break of 85%.

Nitro-derivatives containing a controllable number of nitro-groups in the repeat unit (0.2–3.0 nitro-groups) have been obtained by nitrating polydiphenylenephthalide with potassium nitrate in nitric acid or with nitric acid in sulfuric acid.[138–140] It was found that the trinitro derivatives of polydiphenylenephthalide contain nitro-groups in the 6-position in the phthalide ring and in the 2- and 2′-positions in the biphenylene unit. They are soluble in nitrobenzene, dimethylformamide, dimethylacetamide, *N*-methylpyrrolidone, and cyclohexanone. The nitro-derivatives containing less than one nitro-group per repeat unit of the monomer are soluble in tetrachloroethane, aniline, and benzonitrile. The polymers containing more than one nitro-group per repeat unit are soluble in tetrahydrofuran, 1-chloro-2,3-epoxypropane, and dimethyl sulfoxide, in contrast to the initial polymer. Strong elastic films may be obtained from solutions of the polymers containing up to two nitro-groups in the repeat unit. The decomposition temperatures in air of nitro-substituted polyphenylenephthalides containing 0.2–2.6 nitro-groups in the repeat unit are in the range 320–340 °C. These polymers do not soften before they decompose.[140]

VII. Aromatic polyamides

The use of aromatic diamines and dicarboxylic acid chlorides with cardo groups for the synthesis of polyamides made it possible to obtain cardo polyamides.[2–4, 12, 27, 37, 38, 49, 76, 77, 127, 143–169] Scheme 8 presents examples of such polymers. The study of the characteristic features of the formation of cardo polyamides showed that satisfactory results are obtained when the low-temperature polycondensation is carried out in aprotic solvents

Scheme 8



(dimethylacetamide, *N*-methylpyrrolidone) at −10 to −30 °C for 15–60 min and at reactant concentrations of 0.6–0.7 M. The reaction is carried out by adding the solid acid chloride to a solution of the diamine.[27,143–147,154] The optimum polycondensation conditions for the polyamide based on 9,10-bis-(4-aminophenyl)-anthracene are as follows: temperature 20 °C, reaction time 2 h, solvent — 2:1 (vol%) *N*-methylpyrrolidone–hexamethylphosphoramide mixture, concentration of monomers 0.25 M, and concentration of LiCl 5% (relative to the solvent).[152]

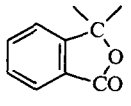
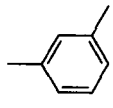
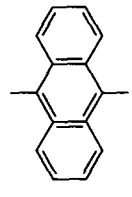
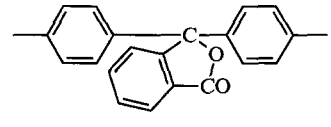
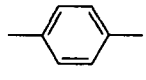
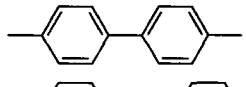
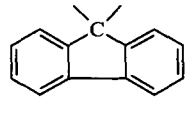
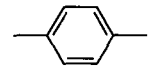
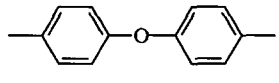
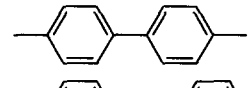
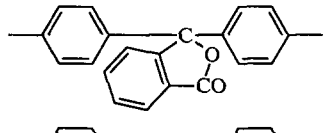
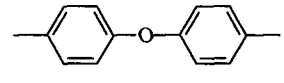
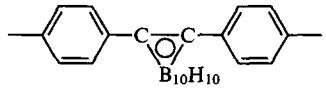
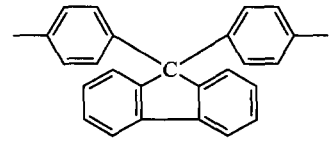
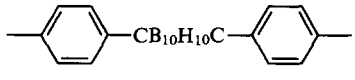
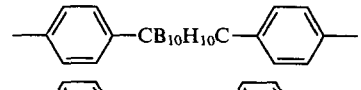
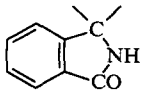
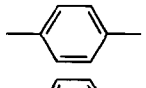
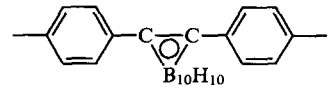
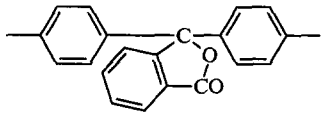
Electron microscope study of the films and pressed anilinephthalein polyamides, obtained by low-temperature polycondensation in solution, showed that such polymers contain supramolecular 500–1000 Å globular formations.[146] The majority of the cardo polyamides synthesised have an amorphous structure, although some of them exhibit a tendency towards ordered structures. This is characteristic of, for example, the polyamide based on anilinephthalein and terephthalic acid or bis(4-carboxyphenyl)phthalide and anilinefluorene polyterephthalamides and polyisophthalamides.[146,147,154]

When the fluorene cardo group with a dicarboxylic acid residue is introduced into the polyamide, the products are polyamides which show no tendency to crystallise.[154] According to the results of thermomechanical tests, the cardo polyamides derived from aliphatic dicarboxylic acids have comparatively low softening temperatures (210–240 °C),[147,154] exceeding somewhat the melting points of the widely familiar crystalline polyamides based on hexamethylenediamine and adipic and sebacic acids. Table 4 presents the softening temperatures (determined by the thermomechanical method) of a series of aromatic cardo polyamides.[27,147,152,155,161,162,164]

These polymers have a high heat resistance, which changes little on passing from isophthalic polyamides to the polyamides of terephthalic, biphenyl-4,4′-dicarboxylic, and carborane-dicarboxylic acids, or on replacement of the anilinephthalein residues in the repeat unit by anilinephthalein imide. An appreciable decrease in heat resistance is observed when bis(4-carboxyphenyl) ether residues are introduced into the polyamide, which is apparently due to the decreased rigidity of the main polymer chain owing to the presence of bridging units (oxygen atoms) in the hinge positions. The polyamide derived from 9,10-bis(4-aminophenyl)anthracene and bis(4-carboxyphenyl)phthalide as well as the copolymers of terephthalamide with diphenylanthracene and anilinefluorene, which do not soften up to the decomposition point, have exceptionally high heat resistances.[152] It is noteworthy that the softening temperature of cardo polyamides are always higher than those of the corresponding cardo polyarylates.[148,151]

The thermal and thermooxidative degradation of cardo polyamides has been investigated.[146,147,149,150,164] The temperature of the onset of mass decrease of these polymers is in the range 360–450 °C. It has been shown that the thermal stabilities of the cardo polyamides depend to some extent on the nature of the cardo group, whereas those of the polyarylates are limited mainly by the stability of the ester bond. Polyterephthalamides with anthrone and fluorene groups exhibit a higher stability than the polymers with phthalide groups. The study of the thermal degradation of anilinephthalein and anilinefluorene polyterephthalamides showed that the decomposition of these polymers begins at temperatures above 350 °C; the hydrolytic decomposition predominates at 350–400 °C, whereas the contribution of the homolytic decomposition increases above 400 °C. The homolytic

Table 4. The softening temperatures of the aromatic cardo polyamides —NH—R¹—NHOC—R²—CO —.

R¹	R²	*T*/ °C	R¹	R²	*T*/ °C
		385			Above decomposition temperature
		390			
		395			405
		340			430
		385			320
		380			420
		390			370
		395			380
		400			

decomposition of the amide bond is accompanied mainly by cross-linking processes in the polymers, which lead to the formation of tertiary amide and amine fragments in the polymeric structures.[149] The thermal oxidation of these polymers hardly differs from their thermal decomposition.[149] At temperatures preceding the decrease in the mass of the polymers (up to 350 °C), branching and cross-linking processes develop. During the isothermal heating of aromatic cardo polyamides at 300 °C in air and in vacuo for 3 h, no decrease in the mass and no appreciable impairment of the properties of these materials are observed.[147] According to the results of dynamic thermogravimetric analysis in air at a heating rate of 4–4.5 K min^{-1}, the temperatures of the onset of mass loss for a polyterephthalamide of anilinephthalein, anilinephthal-imidine, and anilinefluorene and the polyamide obtained from anilinefluorene and 9,9-bis(4-carboxyphenyl)fluorene are 400, 390, 405, and 410 °C respectively.[147,154]

Thermogravimetric study of the carborane-containing polyamides obtained from 1,2- and 1,7-bis(4-carboxyphenyl)-carboranes, anilinefluorene, and anilinephthalein showed that the principal difference in the nature of the degradation of these polymers and of the usual aromatic cardo polyamides consists in a lower rate of decomposition, while the temperature ranges of vigorous decomposition are comparatively the same. At the same temperature, the decrease in the mass of carborane-containing polyamides is 3–5 times less than for the usual aromatic polyamides.[163]

The use of cardo monomers for the synthesis of polyamides not only leads to the formation of heat-resistant and thermostable polymers but also greatly improves their solubility. In contrast to the majority of aromatic polyamides, sparingly soluble in organic solvents and soluble predominantly in solutions of inorganic salts in amide solvents,[170] cardo polyamides dissolve readily in dimethylformamide, dimethylacetamide, methylpyrrolidone, dimethyl sulfoxide, benzyl alcohol, and cresol with formation of highly concentrated solutions (in excess of 400 g l^{-1}).[4,147] Cardo polyamides dissolve in an unusual manner in cyclohexanone.[154] Whereas cardo polyamides with phthalide groups dissolve readily in cyclohexanone (this applies even to polyterephthalamide), anilinefluorene polyterephthalamide is almost insoluble in this solvent, while solutions of anilinefluorene polyisophthalamide are unstable, which is believed to be caused by the tendency of this amide to acquire an ordered structure. Anilinefluorene polyterephthalamide, which precipitates from solution in dimethylformamide, also exhibits a tendency towards ordering on standing at room temperature. This property of the chains can be suppressed by synthesising mixed polyamides derived from anilinefluorene and terephthalic and isophthalic acids with a molar ratio of the latter of 85 : 15. When the fluorene cardo group with a dicarboxylic acid residue is introduced into the polyamide, the products are also polyamides which do not exhibit a tendency towards ordering and which are readily soluble in cyclohexanone.[154] The study of solutions of anilinephthalein polyterephthalamide in dimethylformamide showed that such solutions are stable over a wide range of temperatures and compositions.[167]

Films with satisfactory strength parameters (tensile strength of 800–1500 kgf cm^{-2}, elongation at break 20%–70%) are obtained by moulding cardo polyamides from solutions.[4,27,49,147,154] Polyamide films, for example, anilinefluorene polyterephthalamide films, exhibit a high resistance to ultraviolet light and radiation. Thus the strength of a film made from this polyamide remains unchanged after exposure to ^{60}Co γ-rays in vacuo at a dose of 20 000 Mrad; 60% of the strength is retained on irradiation in air at a dose of 3500 Mrad.[154,166] The strength characteristics of the anilinefluorene polyterephthalamide film remain unchanged also after subsequent irradiation with UV light and electrons (50 MGy), while the relative elongation and the heat resistance increase.[158]

Aromatic cardo polyamides exhibit a satisfactory chemical stability.[146,147] Thus the molecular mass of anilinephthalein polyisophthalamide hardly changes after being kept for 40 h at room temperature in concentrated sulfuric acid or in a 40% sodium hydroxide solution. Films of this polyamide retain their strength and elasticity after heating in water for 4 h at 200 °C. The polymer is resistant to the action of boiling dimethylformamide and dimethylacetamide.

Cardo polyamides have satisfactory electrical characteristics, similar to those of other polyamides. Their stability is much higher by virtue of their high heat resistance.[4] Highly heat-resistant monolithic articles with effective mechanical and antifriction properties can be obtained by pressing filled and unfilled cardo polyamides.[4,147]

A number of studies [153,156,157] of the matrix polycondensation of the cardo polyanilinephthalein- and cardo polyanilinefluorene-terephthalamides with less rigid chains in a medium comprising the macromolecules of rigid-chain poly-*p*-phenyleneterephthalamide or polyphenylenebenzimidazoleterephthalamide have been carried out in order to be able to regulate the structures of cardo polyamides and hence their properties and to obtain polymer–polymer compositions. Thus blends of aromatic polyamides obtained by low-temperature polycondensation in solution of terephthaloyl chloride with anilinefluorene (cardo polyamide **1**) on a rigid-chain poly-*p* phenyleneterephthalamide matrix (matrix **2**) and by the retrosynthesis of poly-*p*-phenyleneterephthalamide (polyamide **2**) on a polyanilineterephthalamide matrix (matrix **1**) have been investigated.[156,157] Interesting results have been obtained in the synthesis of polyamide **1** on matrix **2**. The matrix polyanilinefluoreneterephthalamide has the highest coefficient of friction at elevated temperatures and the lowest intensity of linear wear of its specimens (obtained by compression pressing), amounting to 2×10^{-10}, which is five times smaller than for specimens of matrix poly-*p*-phenyleneterephthalamide (retrosynthesis) and is smaller by a factor of two than for a mechanical mixture of polyamides **1** and **2**. In contrast to polymer blends, obtained by retrosynthesis or by mechanical mixing of polyamides **1** and **2**, this polymer blend could not be separated quantitatively into the corresponding homopolymers by extraction with *N*-methylpyrrolidone. The content of polyamide **1**, which is as it were 'encapsulated' in matrix **2**, is 55%. These data indicate a definite influence of the method of synthesis of the polymer systems on their properties and also the possibility of employing such aromatic polyamides for the creation of antifriction materials with improved properties.[157]

The regulation of the properties of the polymers by varying the previous history of their synthesis, carried out in the presence of a matrix comprising one of the blend components, has also been demonstrated in relation to polymer blends of polyphenylene-benzimidazoleterephthalamide and polyanilinefluorenephthal-amide.[153] It was found that, depending on the structure of the polymer, the structure of the matrix can exert both disordering and ordering effects on the other polymer. This makes it possible not only to alter the mechanical properties of the films but also to obtain films from blends containing a large amount of the polymer which does not itself form films (in the given instance, this is polyphenylene-benzimidazoleterephthalamide, which is insoluble in organic solvents and has a high softening temperature).

The possibility of the formation of linear-network polymer systems based on a cardo polyamide and unsaturated cardo amides in which the linear cardo polyamide is enclosed in a network polymer matrix has been demonstrated.[168] In particular, the possibility of the polymerisation of amorphous and high-melting (T_m >350 °C) crystalline unsaturated cardo amides (for example, anilinefluorene bisacrylamide) in a matrix comprising the amorphous heat-resistant anilinefluorene polyterephthalamide has been investigated. Films were cast from solutions in dimethyl-formamide containing both the unsaturated bisamides and the polyamide. It was found that anilinefluorene and anilinephthalein bisacrylamides can be satisfactory blended with the polyamide and that, when the crystalline anilinefluorene bisacrylamide is blended with the cardo polyamide, it becomes amorphous. The crystalline anilinefluorene bisacrylamide does not itself polymerise in bulk up to 350 °C, but, when it is introduced into a matrix comprising a heat-resistant cardo polyamide in an amount of 10–100 mass %, it passes

to the amorphous state and polymerises effectively with formation of a network polymer in air at 250 °C in the course of 5 h. Such network systems, filled with amorphous cardo polymers, exhibit a high strength and heat resistance.[168]

Heat-resistant compositions based on cardo polyamides and oligoepoxides have also been described. It has been observed that at elevated temperatures epoxide compounds interact with aromatic cardo polyamides via a mechanism involving the 'insertion' of a fragment of an oxirane ring in the amide bond,[80, 81, 126, 127, 169] giving rise to three-dimensional polymer systems.

VIII. Polyimides

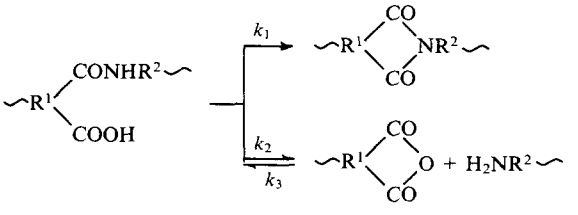
The cardo principle has been used successfully also for the synthesis of polymers with a cyclochain structure. In particular, cardo polyimides are the first representatives of heterocyclic cardo polymers. Numerous studies have been devoted to their synthesis and investigation (see, for example, Refs 2–4, 49, 146, and 171–269). Cardo diamines such as anilinephthalide, anilinephthalimide, anilinefluorene, anilineanthrone, anilinecyclohexane, and also the dianhydride of bis(3,4-dicarboxyphenyl)phthalide combined with various aromatic, aliphatic, and aliphatic-aromatic diamines as well as the dianhydrides of tetracarboxylic acids have been used as the starting materials for the synthesis of cardo polyimides.

It is noteworthy that the ready solubility of cardo polyimides has led to the possibility of their synthesis by different procedures: by the two-stage polycyclisation of tetracarboxylic acid dianhydrides and diamines [2–4, 49, 146, 174–177, 201, 210–213, 218–220, 223, 228, 250, 258, 262, 263, 265] with thermal and catalytic imidisation of polyamidoacids, by a single-stage polycyclisation in solution both in the presence of catalysts and without them (see, for example, Refs 2–4, 49, 146, 171–173, 178–183, 211–214, 217, 222, 223, 225, 250, 258, 261, 263), by the reaction of tetracarboxylic acid dichloride diesters and diamines,[2–4, 49, 183–185, 200, 211, 261] and by the polycyclisation of tetracarboxylic acid dianhydrides and trimethylsilyl derivatives of diamines.[211, 216, 258]

In the two-stage polycondensation, the first stage (the formation of polyamidoacids) is carried out under the conditions of low-temperature polycondensation in solution of solvents such as dimethylacetamide, dimethyl sulfoxide, *N*-methylpyrrolidone, etc. The study of the kinetics of the formation of cardo polyamidoacids from anilinefluorene and a number of dianhydrides in *N*-methylpyrrolidone [201, 262] showed that, in terms of decreasing reactivity, the dianhydrides can be arranged in the series presented in Scheme 9, the most reactive dianhydride being to a large extent involved in side reactions with the solvent or the impurities present in it. The rate of reaction increases on passing from a less polar solvent (dioxane) to a more polar one (methylpyrrolidone).[201] The formation of polyamidoacids involving the carboxy-groups arising on opening of the anhydride ring was found to be autocatalytic.[211, 262] This made it possible to develop catalytic procedures for the synthesis of polyamidoacids and polyimides in the presence of carboxylic acids. The catalytic method is extremely effective in the reactions of relatively unreactive diamines [for example bis(4-aminophenyl) sulfone] and tetracarboxylic acid dianhydrides [for example, bis(3,4-dicarboxyphenyl) ether].

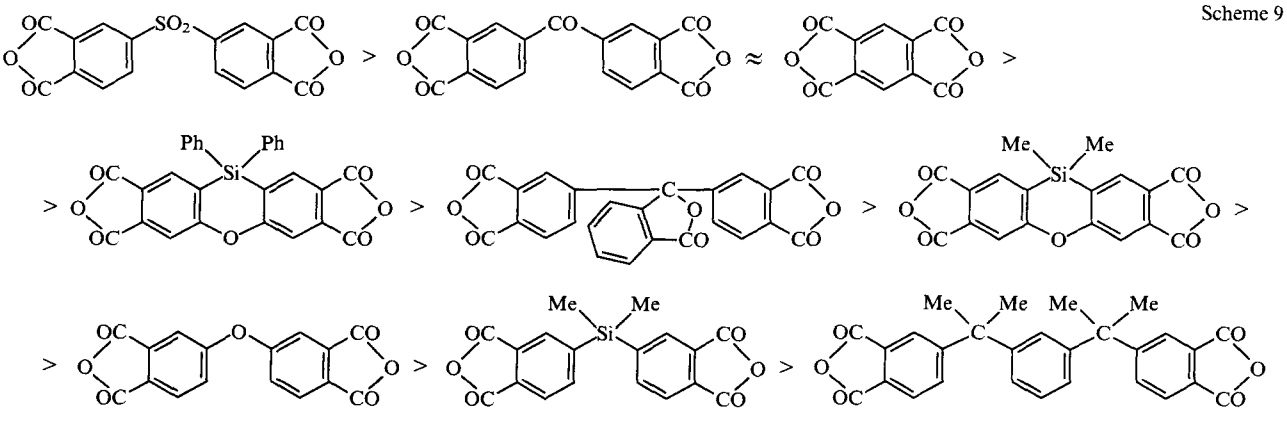
In the synthesis of polyimides, account must be taken of the reversibility of the formation of polyamidoacids.[69, 70, 211, 217–219] The reversibility is manifested particularly strongly in the thermal cyclisation of polyamidoacids, which leads to a sharp decrease in the molecular mass of the polymer in the initial instant of the cyclisation process. However, as the end groups accumulate, the resynthesis of the polyimides as a result of the condensation of the fragments formed via the terminal anhydride and amino-groups assumes an increasing importance. A mechanism has been proposed for the thermal imidisation of polyamidoacids (Scheme 10), taking into account the occurrence of consecutive-parallel cyclisation reactions of the *o*-carboxyamide units, their decomposition, and the condensation of the resulting fragments, i.e. this process must be described not by one but by at least three rate constants. The difficulties in the synthesis of polyimides associated with the instability of polyamidoacids and the reversibility of the imidisation stage can to some extent be overcome by carrying out the polycyclisation in the presence of catalytic systems [174, 211, 262] such as mixtures of acetic anhydride with various tertiary amines, alkali metal acetates, silazanes, mixtures of chlorotrimethylsilane with tertiary amines, etc. By virtue of the mild temperatures (20–100 °C) at which the catalytic cyclisation takes place, it is possible to obtain linear soluble polyimides with a reactive group, for example the cardo polyimides derived from benzophenone-3,3′,4,4′-tetracarboxylic acid, which are cross-linked via the ketogroup if synthesised by other methods. One should also note that polymers with extremely high molecular masses (up to 200 000) can be obtained by the chemical cyclisation of polyamidoacids, whereas thermal cyclodehydration affords polyimides with a molecular mass of ~20 000.

Scheme 10

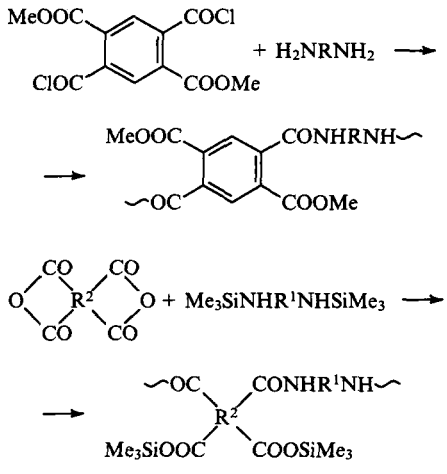


The formation of polyamidoacids may be avoided by employing as starting materials tetracarboxylic acid dichloride diesters and diamines or tetracarboxylic acid dianhydrides and bis-(trimethylsilyl) derivatives of diamines. Stable alkyl and silyl esters of polyamidoacids are then obtained at an intermediate stage, as shown in Scheme 11.

Scheme 9



Scheme 11



The cyclisation of polyamidoesters, which are hydrolytically more stable than polyamidoacids, leads to polyimides with higher molecular masses than those obtained by the cyclodehydration of the corresponding polyamidoacids. High-molecular-mass polyimides (molecular mass in the range 100 000 – 140 000) are formed on cyclisation of polyamidoesters in solution (for example, in nitrobenzene and sulfolane) at 210 °C and also on chemical cyclisation, which can be achieved directly in the film.

The solubility of cardo polyimides was a precondition for the development of a fundamentally new method of their synthesis — one-step high-temperature polycyclisation in an organic solvent (nitrobenzene, sulfolane, *p*-nitrotoluene, α-chloronaphthalene, cresol, etc.).[2-4,49,171-173,178-182,211,217,222] An equimolecular mixture of the starting materials in a solvent is heated rapidly to 200 – 210 °C in an inert gas stream and is maintained at this temperature for a specified time (3 – 10 h). The growth of the polymer chain (the formation of the polyamidoacid) and intramolecular cyclisation take place almost simultaneously. The one-step polycyclisation in the presence of acid catalysts proved extremely successful.[49,181,182,211-214] In this case, it is possible either to decrease significantly the reaction time (down to 1 – 3 h), with formation of polymers with extremely high molecular masses under these conditions, or to carry out the process at lower temperatures (140 – 160 °C).

Carboxylic acids (for example benzoic acid) are effective catalysts also in the synthesis of high-molecular-mass polyimides from monomers with a reduced reactivity such as the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid.[214]

Since, as mentioned above, the formation reaction of polyimides is reversible, it follows that in order to obtain high-molecular-mass polyimides, it is necessary to remove from the reaction sphere, as fully as possible, the water evolved during cyclisation, which is achieved by raising the reaction temperature, by carrying out the reaction in an inert gas stream, by binding the water with chemical reagents, etc. The simplicity of the one-step polycyclisation, its ready reproducibility, and the possibility of obtaining polyimides with a high molecular mass, which contain virtually no defective *o*-carboxyamide units, makes it possible to regard this method as promising for the synthesis of a wide variety of polyimides.[211]

In the synthesis of copolyimides, one must not forget that their formation reaction is reversible. There is also no doubt that one must take into account the involvement of polyimides in exchange reactions at elevated temperatures, in the first place aminolysis.[70,216,223-225,244,246,247,258] It has been shown that the formation of the microstructures of copolyimides may depend on three factors: the ratio of the reactivities of the comonomers, the rate of introduction of the intermonomer into the reaction vessel, and the occurrence or nonoccurrence of exchange reactions.

In the two-stage method of synthesis, the foundation of the microstructure of copolyimides is laid in the stage involving the formation of copolyamidoacids. Such a microstructure may be retained or damaged in the subsequent cyclisation. Since in the two-stage method of synthesis the polyamidoacids are formed close to room temperature, the exchange reactions are then virtually ruled out. For this reason, the formation of the copolyamidoacid microstructure is determined by the ratio of the rates of the interactions of the intermonomer with the comonomers, which depend on their reactivities and on the rate at which the intermonomer is introduced into the reaction. The formation of block copolyamidoacids when there is a significant difference between the reactivities of the comonomers is observed when the intermonomer is introduced into the reaction zone comparatively slowly, for example when it is added in the solid state (frequently in portions). On the other hand, in the synthesis of the copolyamidoacid by the rapid mixing of dianhydrides and diamines, statistical copolymers are produced.

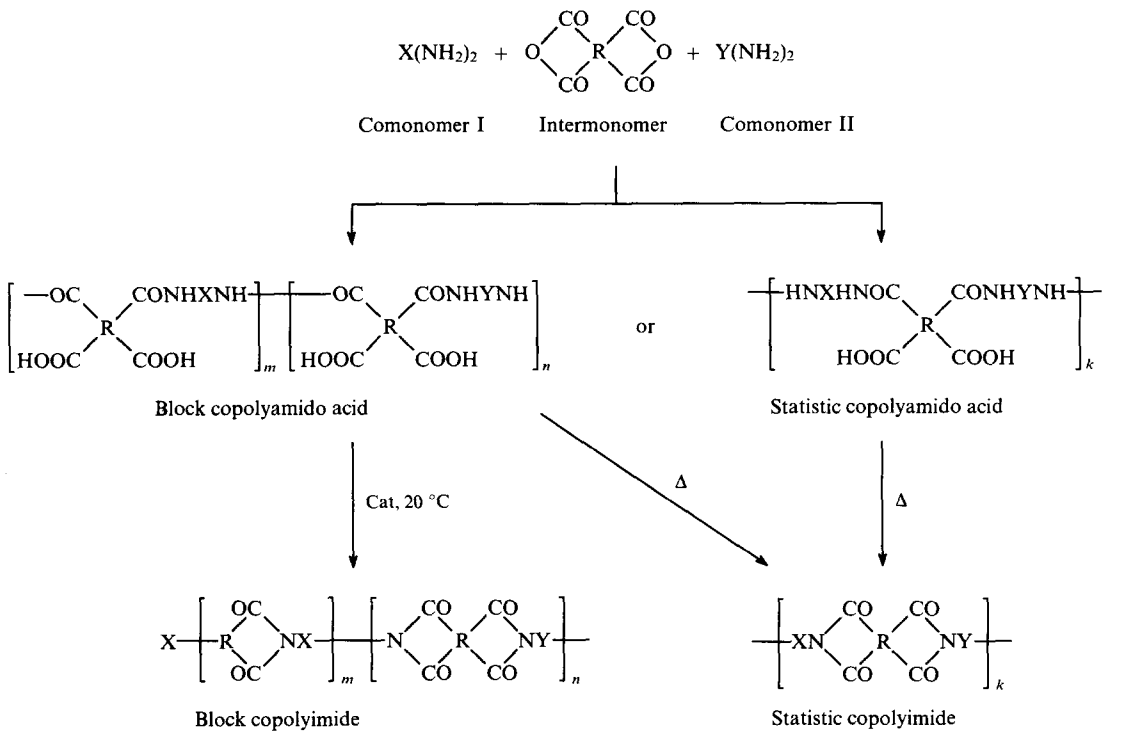
The microstructure of the copolyimides based on copolyamidoacids may be regulated by varying the cyclisation conditions. In the cyclisation under the influence of chemical reagents, occurring under mild conditions and not complicated by degradative or exchange reactions, the microstructure of the copolymer formed is identical with that of the corresponding copolyamidoacid. In thermal cyclisation, accompanied by exchange reactions, predominantly statistical copolyimides are formed from both block copolyamidoacids and from statistical copolyamidoacids.

A detailed study of the one-step copolycondensation showed that in this method of synthesis the copolymer microstructure depends on the relative reactivities of the comonomers, the differences between the reactivities of the functional groups of the intermonomer, the rate at which the intermonomer is introduced into the reaction, and the resistance of the imide rings to destructive exchange reactions and is in many respects determined by the ratio of the rates of the main polymer formation reaction and the exchange reactions, in the first place aminolysis.[70,216,223,225,258] When aliphatic and aromatic diamines (for example, hexamethylenediamine and anilinefluorene) are used as the comonomers, while the intermonomer is the dianhydride of bis(3,4-dicarboxyphenyl) ether, statistical copolyimides are obtained owing to the occurrence of effective aminolysis. The increase in the rate of formation of the polymer when the much more reactive pyromellitic dianhydride is used permits the formation of a copolyimide with a block structure. The microstructure of copoly(naphthoylene imide), which is more resistant to aminolysis, can be altered deliberately by varying the reaction conditions. Statistical copolyimides are obtained when the starting materials and the catalyst (benzoic acid) are introduced simultaneously into the reaction, whilst in the case where the intermonomer is added slowly together with the catalyst to a solution of a mixture of diamines, the product is a copolyimide with a block structure. Scheme 12 presents the overall mechanism of the formation of copolyimides by the one-step and two-stage methods.

The use of siloxane-containing diamines, together with cardo diamines, for the synthesis of copolyimides makes it possible to obtain high-molecular-mass siloxane-containing copolyimides with different numbers of dimethylsiloxane fragments in the repeat unit (Scheme 13). Such copolyimides have been synthesised by the low-temperature polycondensation of tetracarboxylic acid dianhydrides and diamines in solution with subsequent cyclodehydration of the copolyamidoacids in the presence of chemical reagents under conditions promoting the initial formation of siloxane-amidoacid and then arylene-amidoacid fragments.[198]

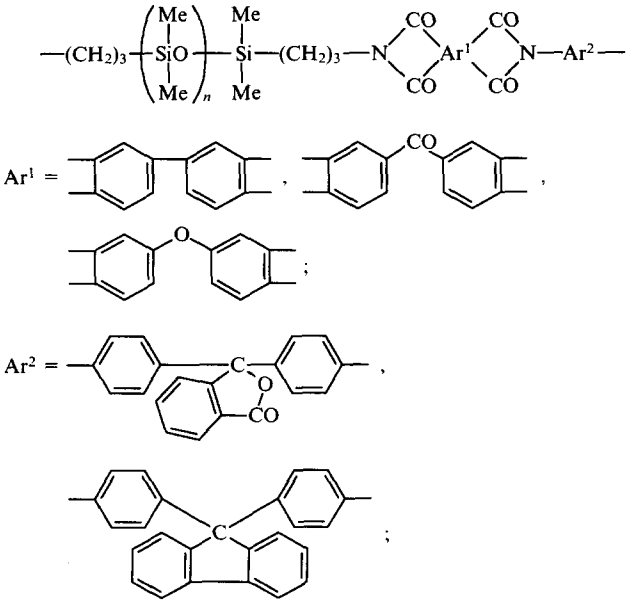
The presence of a cardo group in rigid-chain polymers such as polyimides affects primarily their solubility.[2-4,46,49,173,175,176,179,186,187,211,263,270] Many cardo polyimides are readily soluble in organic solvents: dimethylformamide, dimethylacetamide, methylpyrrolidone, dimethyl sulfoxide, hexafluoroisopropyl alcohol, sulfolane, chloroform, methylene chloride, tetrachloroethane, phenol, *m*-cresol, nitrobenzene, etc., while individual polyimides are soluble in dioxane and cyclohexanone. Among the cardo groups investigated, the asymmetric phthalide and phthalimidine groups impart the highest solubility to polymers. Their introduction

Scheme 12



X = alkylene or arylene, Y = arylene (cardo)

Scheme 13



n = 1, 29, 39, 99

increases the solubility of even the polyimides with a most rigid chain such as polypyromellitimide and poly(1,4,5,8-naphthoylene imide). The solubility of cardo polyimides is influenced appreciably also by the structure of the tetracarboxylic acid dianhydride. It has been found that the different groups entering into the composition of the main chain of the polymer can be arranged in a sequence, in terms of their influence on solubility, in which each successive group expands the range of the solvents for the polymer (Scheme 14).[211] Polyimides containing cardo groups in both the dianhydride and diamine components, (for example, phthalide or phthalide and fluorene) are more soluble than the polyimides containing only one such group in the elementary unit. (In particular, the former acquire solubility in cyclohexanone.[186]) The presence of the phthalide cardo group solubilises adamantane-containing polyimides based on the dianhydride of bis(3,4-dicarboxyphenyl)-phthalide, while their analogues based on the dianhydrides of pyromellitic and benzophenone-3,3′,4,4′-tetracarboxylic acids are insoluble.[234] The synthesis of cardo copolyimides has led to extensive possibilities for the variation of solubility. In particular, the formation of copolyimides is an effective method of imparting solubility to polyimides derived from naphthalenetetracarboxylic acid.[70, 225]

The effect of solvent antagonism has been observed for certain cardo polyimides. Such antagonists are dimethylformamide, dimethyl sulfoxide, dimethylacetamide, and methylpyrrolidone, on the one hand, and methylene chloride, chloroform, and tetrachloroethane, on the other.[211, 263] Thus the polyimide derived from anilinefluorene and bis(3,4-dicarboxyphenyl) ether does not dissolve in a 1:1 (vol%) dimethylformamide – chloroform mixture, but is readily soluble in each of these solvents. This effect is manifested even more strikingly in anilinephthalein poly(naphthoylene imide), which is insoluble in nitrobenzene – methylpyrrolidone mixtures with different proportions of the individual solvents.

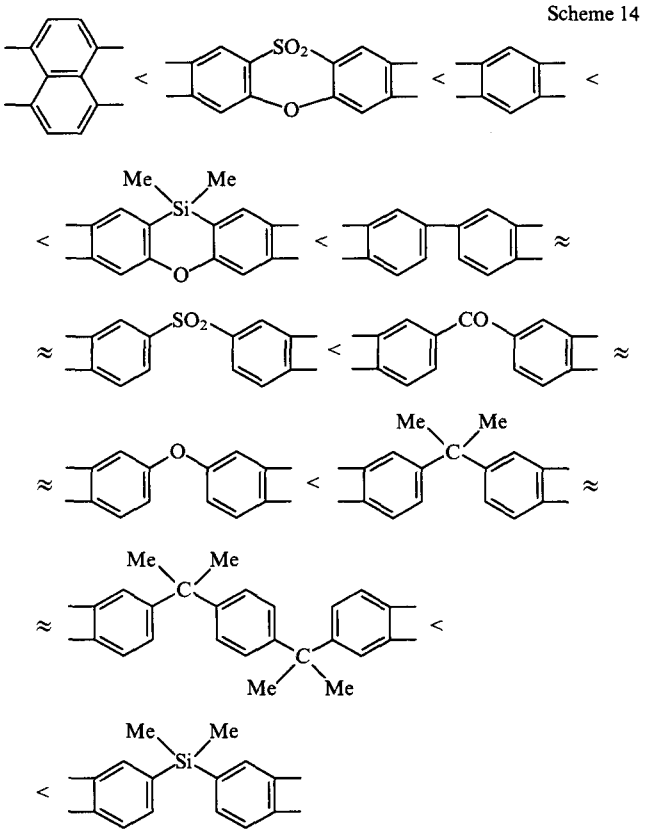
The majority of cardo polyimides are amorphous, but some of them tend to crystallise, which exerts a considerable influence on their solubility. Thus anilinefluorene and anilineanthrone polypyromellitimides and poly(naphthoylene imides) are weakly crystallising polymers which are insoluble in organic solvents (in contrast to the corresponding polyimides with phthalide groups).[211]

The ready solubility of cardo polyimides in organic solvents has led to the possibility of investigating their molecular mass characteristics and the determination of their constants in the Mark – Kuhn – Houwink equation (Table 5).[195, 202, 205, 211, 230, 263, 268]

$$[\eta] = KM_w^{\alpha}$$

A number of studies[167, 233, 235] have been devoted to the investigation of solutions of cardo polyimides in greater depth. Thus the study of solutions and gels of anilinephthalein polypyromellitimide in dimethylformamide showed that solutions of the polyimide lose their stability after a time, become turbid, and

Scheme 14

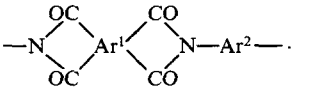


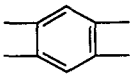
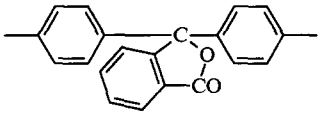
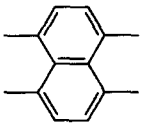
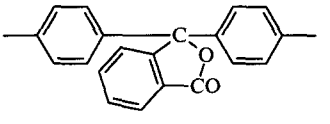
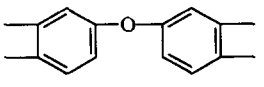
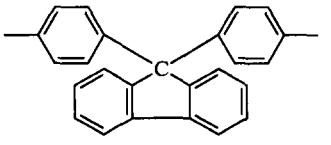
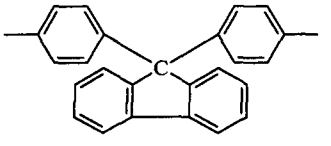
are converted into a gel, which can be explained by the poor thermodynamic affinity of the polyimide for dimethylformamide. It follows from X-ray diffraction and polarised light scattering data that the polyimide gels contain both isotropic and anisotropic regions having approximately the same dimensions (~400–600 nm).[167] The second virial coefficients of solutions of the polyimide derived from anilinephthalein and bis(3,4-dicarboxyphenyl) ether in *N*-methylpyrrolidone, dimethyl sulfoxide, chloroform, THF, and dimethylformamide have been determined. It has been shown that the molecular masses of this polymer in various solvents are virtually identical, which indicates the absence of association.[233] The phase diagram for solutions of cardo polypyromellitimides and poly(naphthoylene imides) with fluorene, phthalide, and anthrone groups in fused antimony trichloride has been investigated. The formation of spherulites of anilinefluorene polypyromellitimide and anilinefluorene poly(naphthoylene imide) solutions and of nonordered anisotropic rods has been established for the anilinephthalein pyromellitimide system in antimony trichloride. The results indicate the possibility of the crystallisation of cardo polypyromellitimides and cardo poly(naphthoylene imides) in antimony trichloride on phase separation of their solutions, which leads to new possibilities for the regulation of the properties of these polymers.[235]

Table 6 (see over) presents the softening temperatures of a series of cardo polyimides.[211, 265] It is seen from these data that polymers with three and five condensed rings in the dianhydride residue have the highest heat resistance, which is significantly higher than that of the polyimides with phthalimidine groups having similar chemical structures (cf, for example, polymers Nos 1 and 10, 5 and 4, or 6, 7, and 8).

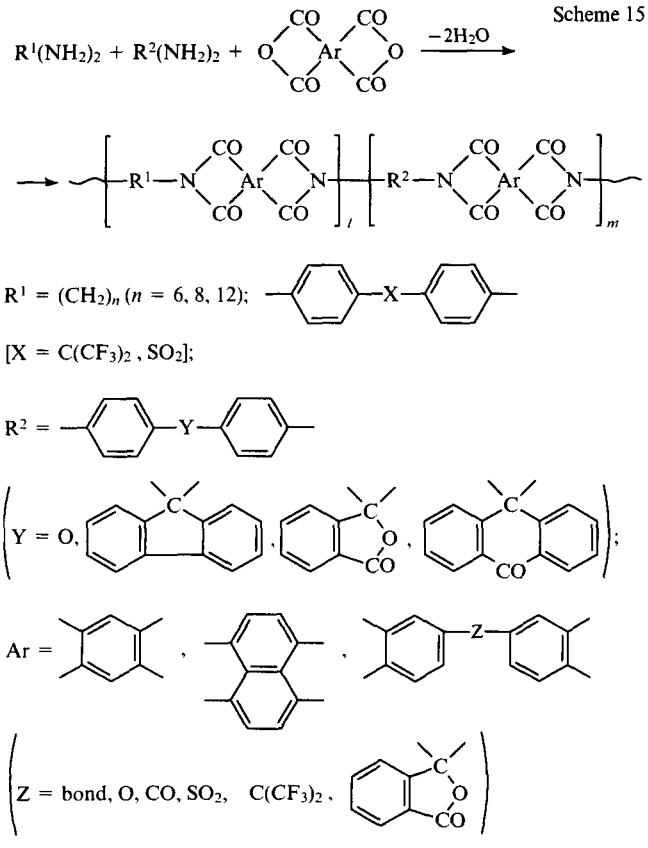
Scheme 15 presents examples of the structures of aliphatic-aromatic and aromatic cardo copolyimides.[49, 214, 216, 223, 225, 258] Their heat resistance may be varied within wide limits (160–500 °C) by varying the chemical structures and microstructures of the copolymers. The softening temperatures of the aliphatic-aromatic polyimides increase consistently with increase in the cardo diamine proportion in the macromolecule and on passing to polyimides with six-membered imide rings.

Like other aromatic polyimides, aromatic cardo polyimides have high thermal stability.[164, 179, 187, 191–193, 211, 250, 265] Polyimides with anthrone and fluorene groups are the most thermostable, the onset of decrease in their mass being observed at 500–520 °C. They retain 70% of their mass on heating to 900 °C under an inert atmosphere. The cardo groups in polyimides with anthrone and fluorene groups are stable virtually up to the same temperatures as the imide ring, whereas in the polyimides with phthalide and especially with cyclohexylidene groups, destruction affects primarily the cardo groups. According to the results of dynamic thermogravimetric analysis (heating rate 4.5 K min^{-1}), the polyimides with phthalide groups begin to decompose in air at

Table 5. The constants in the Mark–Kuhn–Houwink equation for the cardo polyimides .

Ar^1	Ar^2	Solvent	$K \times 10^{-4}$	α
		Dimethylformamide	0.71	0.88
		*N*-Methylpyrrolidone	1.28	0.77
		Dimethylformamide	8.91	0.56
		Dimethylacetamide	3.33	0.64

Scheme 15



450–490 °C. Saturation of the polymer chain by fragments with a large number of condensed rings in the system and replacement of the five-membered phthalimide groups by the six-membered naphthoylene imide groups increase the thermal stability of the cardo polyimides. On heating in helium (heating rate 5 K min^{-1}), the 'coke' residues from carborane-containing anilinefluorene cardo polyimides with 1,7- and 1,2-bis(3,4-dicarboxyphenyl)-carboranes amount to 92% and 80% respectively.[265]

The pyrolysis of the cardo polyimide obtained from anilinefluorene and the dianhydride of benzophenone-3,3′,4,4′-tetracarboxylic acid has been investigated in the temperature range from 450 to 3000 °C.[249, 253, 266] It was noted that thermochemical transformations begin in the polymer at a temperature above 450 °C. In argon, destructive processes take place most vigorously at 550–650 °C (with a 20–22% mass loss). At 700–750 °C, the formation of the polyimide coke residue, containing 92.5% carbon, is largely complete. It was of interest to note that, in contrast to a series of the usual polypyromellitimides, heat treatment of the cardo polyimide up to 3000 °C leaves a residue of up to 0.75% of the nitrogen forming part of the composition of condensed six-membered rings. As a result of pyrolysis, the electrical resistance of the system decreases by 12–13 orders of magnitude. The carbon materials thus obtained have a high mechanical strength, a low coefficient of friction, and, in contrast to graphite, a very low porosity. It was established that the electrical conductivity of the polyimide-based carbon materials may be increased still further by their thermal decomposition in various metal (copper, nickel, zinc, and iron) formates.[251]

The ability of soluble cardo polyimides to form charge-transfer complexes with low-molecular-mass (*N*-methylcarbazole) and high-molecular-mass (poly-*N*-vinylcarbazole) electron donors has been noted; in the latter case, a very distinct cooperative polymeric effect is observed.[252]

The radiolysis of anilinephthalein polypyromellitimide on prolonged γ-irradiation in vacuo has been investigated.[254] The high radiation stability of this polymer was demonstrated. The radiation-induced electrical conductivities of certain copolyimides have been studied in the course of their irradiation in vacuo by electron pulses with an energy of 65 keV. It was established that the macrostructure (block or statistical) of the copolyimide exerts a definite influence on the electrical conductivity.[256]

The high heat resistance, thermal stability, radiation resistance, and chemical stability of cardo polyimides, as well as the possibility of working many of them in the 'cyclised' form makes them promising for practical use in the manufacture of various articles designed for prolonged use at temperatures above 200 °C.

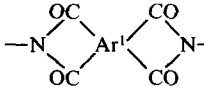
Virtually colourless strong films (tensile strength 1000–1100 kgf cm^{-2}, elongation at break 40%–70%), the electrical properties of which in the temperature range 20–300 °C are not inferior to the familiar Kapton H film, are obtained from solutions of cardo polyimides by casting.[211] The study of the optical properties of polyimide films obtained from anilinefluorene and bis(3,4-dicarboxyphenyl) ether showed that they exhibit a high optical transmittance at 500 nm (81%–87%) and are thermo-photoradiation-resistant. After heat treatment at temperatures up to 300 °C or after UV irradiation at a dose equivalent to a 300 h exposure to sunlight, the optical transmittance of the film diminishes by only 1%–3%.[158]

The cardo polyimide based on anilinefluorene and bis(3,4-dicarboxyphenyl) ether (PIR-2 brand) has been used successfully for the preparation and attachment by adhesive at room temperature of resistance strain gauges for the measurement of static deformations, operating over a wide temperature range (from −190 to 300 °C). A series of cardo polyimides can be worked in the fused state into strong plastics for various purposes. Thus the compressive strength of PIR-2 plastics is 1800 kgf cm^{-2} and their modulus of elasticity is 2.2×10^4 kgf cm^{-2}.[211] The strengths and moduli of elasticity on compression of plastics made from a series of cardo copolyimides reach 1400–2100 and (1.7 to 2.2) × 10^4 kgf cm^{-2} respectively, the strength characteristics remaining virtually unimpaired after preliminary heating of the plastics to 200–240 °C.[223] Monolithic plastics with an impact strength of 15 kgf cm cm^{-2} and a bending strength of 700–1000 kgf cm^{-2} have been moulded from cardo copoly(naphthoylene imides) by the hot pressing method.[225]

The satisfactory solubility of cardo polyimides and their compatibility with many polymers and oligomers, for example, with phenolformaldehyde and epoxide polymers, ensured their approval as heat-resistant fibre-forming materials, as binders for reinforced plastics, as coatings, and as adhesives.[126, 127, 211, 264] In particular, the modification of epoxide oligomers by cardo polyimides leads to the formation of cross-linked polymer systems superior as regards heat resistance, strength, and other properties to materials obtained with the aid of the usual hardening agents for epoxide oligomers. For example, the use of polyimide–epoxide compositions as binders for reinforced carbon plastics proved successful. The compressive strength of such plastics is 2900–4200 kgf cm^{-2} at 20 °C and remains virtually unchanged up to 250 °C.[264]

A linear-network system, in which the linear amorphous cardo polyimide is enclosed in a network polymer matrix, has been obtained by the polymerisation at 200–250 °C of anilinefluorene bisacrylamide in a matrix comprising a cardo polyimide based on anilinefluorene and bis(3,4-dicarboxyphenyl) ether. This system has a high strength and heat resistance.[168]

The high thermal stability of the imide rings combined with the valuable physicomechanical properties of the materials based on linear polyimides made it desirable to develop methods of synthesis of thermoreactive polyimides based on reactive oligomers having comparatively low softening temperatures. By imparting thermoreactive properties to polyimides, the possibilities for their processing into various materials are expanded. In particular, thermoreactive polymers containing imide rings have been synthesised from the dianhydrides of tetracarboxylic acids and the corresponding diamines with subsequent blocking of the terminal amino-groups by the acrylic or methacrylic acid chlorides in the oligomeric amidoacid stage (Scheme 16*a*) or the oligoimide stage (Scheme 16*b*).[206] A series of studies have been devoted to the preparation and study of certain oligomeric cardo imides with terminal unsaturated acrylamide and methacrylamide

Table 6. The softening temperatures of some polyimides  .

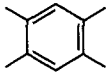
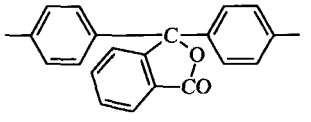
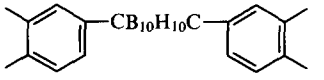
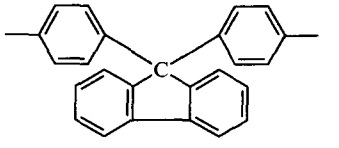
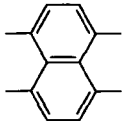
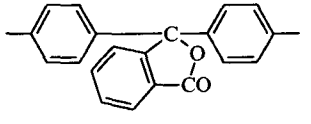
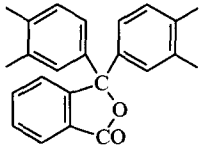
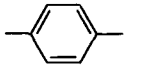
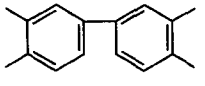
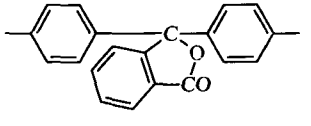
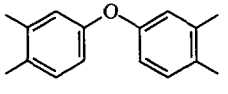
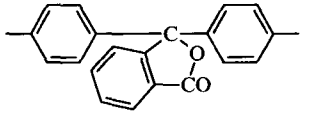
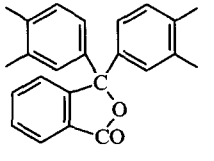
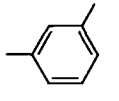
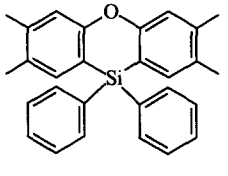
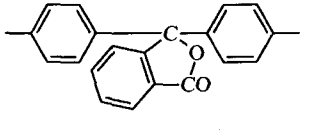
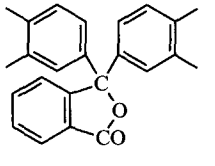
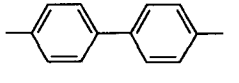
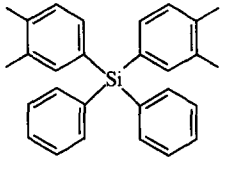
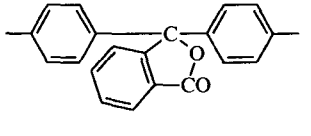
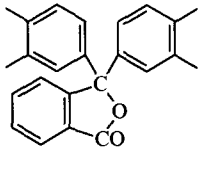
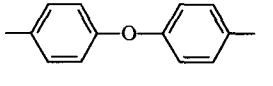
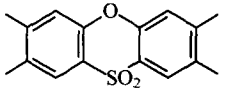
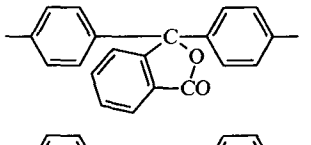
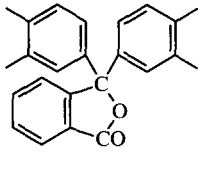
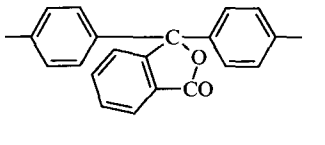
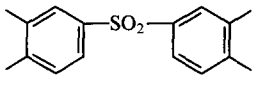
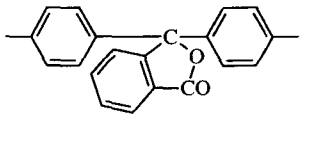
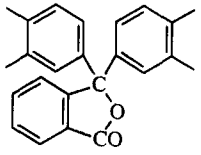
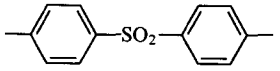
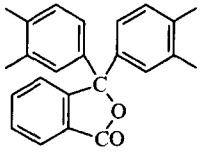
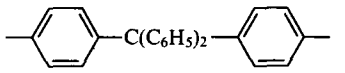
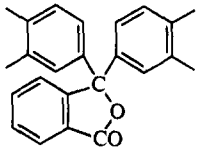
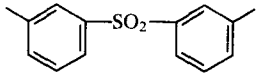
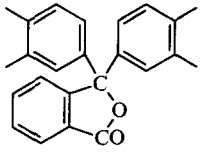
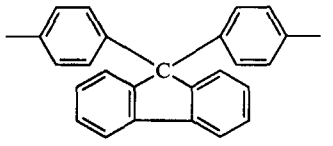
No	Ar^1	Ar^2	T/ °C	No	Ar^1	Ar^2	T/ °C
1			480	9			380
2			540	10			410
3			415				
4			375	11			360
5			460	12			415
6			330	13			345
7			Above decomposition temperatures	14			415
8			400				

Table 6 (continued)

No	Ar^1	Ar^2	T/ °C	No	Ar^1	Ar^2	T/ °C
15			370	17			380
16			315	18			425

groups.[49,168,203,204,206,207,211,245,259] They have been obtained in quantitative yields and with a specified degree of polymerisation.

Unsaturated oligoimides obtained from cardo diamines and having terminal acrylamide and methacrylamide groups are amorphous substances readily soluble in dimethylformamide, dimethylacetamide, and tetrachloroethane with formation of concentrated solutions. Their softening temperatures can be regulated by varying the nature of the cardo group and the degree of polymerisation of the oligomer. Thus, when the degree of polymerisation of the oligoimide obtained from anilinephthalein and benzophenone-3,3′,4,4′-tetracarboxylic acid and having terminal acrylamide groups is increased from 3 to 10, its softening temperature increases from 210 to 280 °C, remaining at the same time appreciably lower than the softening temperature of the corresponding high-molecular-mass linear polyimide (380 °C).

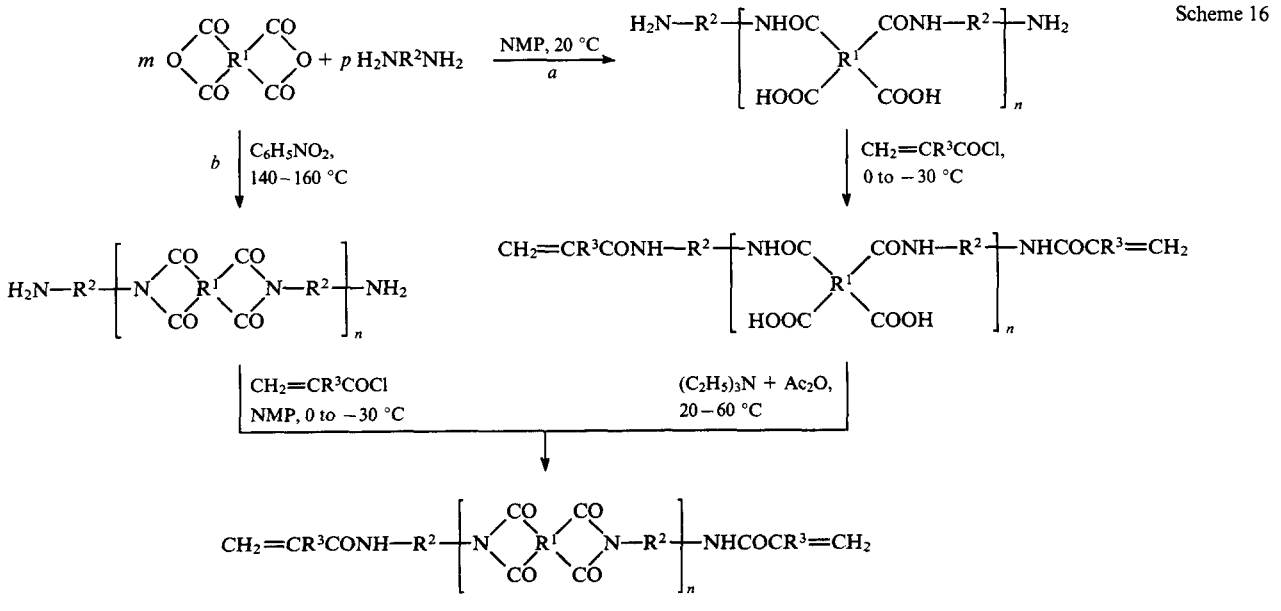
Cross-linked insoluble polymers which do not soften up to the onset of thermal destruction have been obtained by the thermal polymerisation in bulk of unsaturated cardo oligoimides in air at 250–310 °C. The thermal destruction develops vigorously only at temperatures above 400 °C.[206] Glass fibre-reinforced plastics with a low porosity and a high bending strength (4000–5000 kgf cm^{-2}) both at room and elevated temperatures have been prepared from solutions of unsaturated anilinefluorene- and anilineanthrone-benzophenone-3,3′,4,4′-tetracarboxylic acid oligoimides in *N*-methylpyrrolidone.[259]

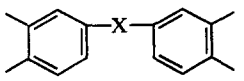
The above unsaturated oligoimides have been used successfully to prepare copolymers with monomers such as *N*-vinylpyrrolidone, *N*-phenylmaleimide, and the bismaleimides obtained from various aliphatic diamines, the oligomers being readily soluble in such monomers.[49,207,211,259] It was established that the cross-linked copolymers are formed at lower temperatures than the corresponding cross-linked homopolyimides. Thus the use of *N*-vinylpyrrolidone makes it possible to reduce the polymerisation temperature by 50–80 °C.[207] The cross-linked copolymers obtained in up to 90% yields by thermal polymerisation at 200–250 °C have high heat resistances and chemical and thermal stabilities.[207,211,259] Such copolymers begin to undergo deformation only at temperatures above 300 °C, and, according to dynamic thermogravimetric data, the onset of decrease in their mass in air is in the temperature range from 350 to 400 °C. The cross-linked copolymers of unsaturated polyoligoimides as well as the corresponding network homopolyimides undergo hardly any change in their mass on being kept for a week in sulfuric and nitric acids, 25% ammonia, and 10, 20, and 40% solutions of sodium hydroxide. In this respect, they are superior to their linear analogues, which undergo appreciable destruction under the conditions indicated.

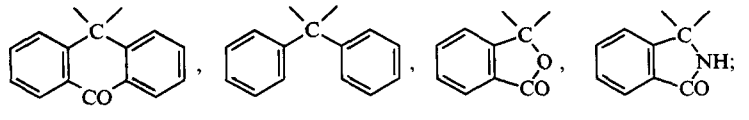
The satisfactory solubility of the unsaturated cardo oligoimides in a monomer such as *N*-phenylmaleimide makes it possible to obtain from them (without using an inert solvent as a binder) reinforced plastics (using organic and glass fibres) having a high mechanical strength both in the initial state and after prolonged maintenance at elevated temperatures. For example, the glass fibre-reinforced plastic based on the cross-linked copolymers of *N*-phenylmaleimide and the anilinefluorene–benzophenone-3,3′,4,4′-tetracarboxylic acid cardo oligoimide with terminal acrylamide groups and $n = 5$ (Scheme 16) has tensile strengths of 15500 and 15000 kgf cm^{-2} and bending strengths of 8500 and 14000 kgf cm^{-2} at room temperature and 250 °C.[211]

The cross-linked copolymers based on the unsaturated oligoimides considered and the bismaleimides obtained from aliphatic diamines have interesting properties These are solid, transparent, heat-resistant substances which do not undergo deformation up to the onset of thermal decomposition (the temperature of which in air is 400–450 °C according to thermogravimetric data). They have effective mechanical properties. At room temperature, the above substances have a compressive strength of 2000 kgf cm^{-2} and a modulus of elasticity on compression in the temperature range from 180 to 300 °C of $(4-7) \times 10^3$ kgf cm^{-2} which shows that such copolymers exhibit properties similar to those of leather over a wide range of elevated

Scheme 16



R^1 =  (X = O, CO);

R^2 = 

R^3 = H, Me; NMP is *N*-methylpyrrolidone

temperatures. This makes it possible to regard them as promising materials for high-temperature hermetic seals.[211, 259, 260]

Network cardo polymers of the polyaminoimide type[49, 208, 209, 260] have been synthesised by the interaction of *N,N'*-hexa-, octa-, nona-, deca-, and dodecamethylenebismaleimides with cardo diamines (anilinefluorene, anilinephthalein). The process may be regulated by varying the conditions under which it is carried out (temperature, reaction time, proportions of starting materials, addition of a catalyst and initiator) and by regulating the contribution of each of the two main reactions: migration polymerisation (addition of amino-groups to double bonds) and three-dimensional copolymerisation (via carbon – carbon double bonds). The density of the three-dimensional polymer network and the length of the fragments between its nodes change under these conditions. Network cardo polyimides of this type are solid monolithic materials insoluble in organic solvents and characterised by a valuable set of physicochemical properties: high heat resistances and chemical and thermal stabilities, and effective physicomechanical parameters.

We shall deal with yet another type of cardo polyimides, the so called functional cardo polyimides containing in their polymer chains free functional groups, which in a number of instances impart specific properties to the polyimides and give rise to the possibility of their further chemical modification.[269]

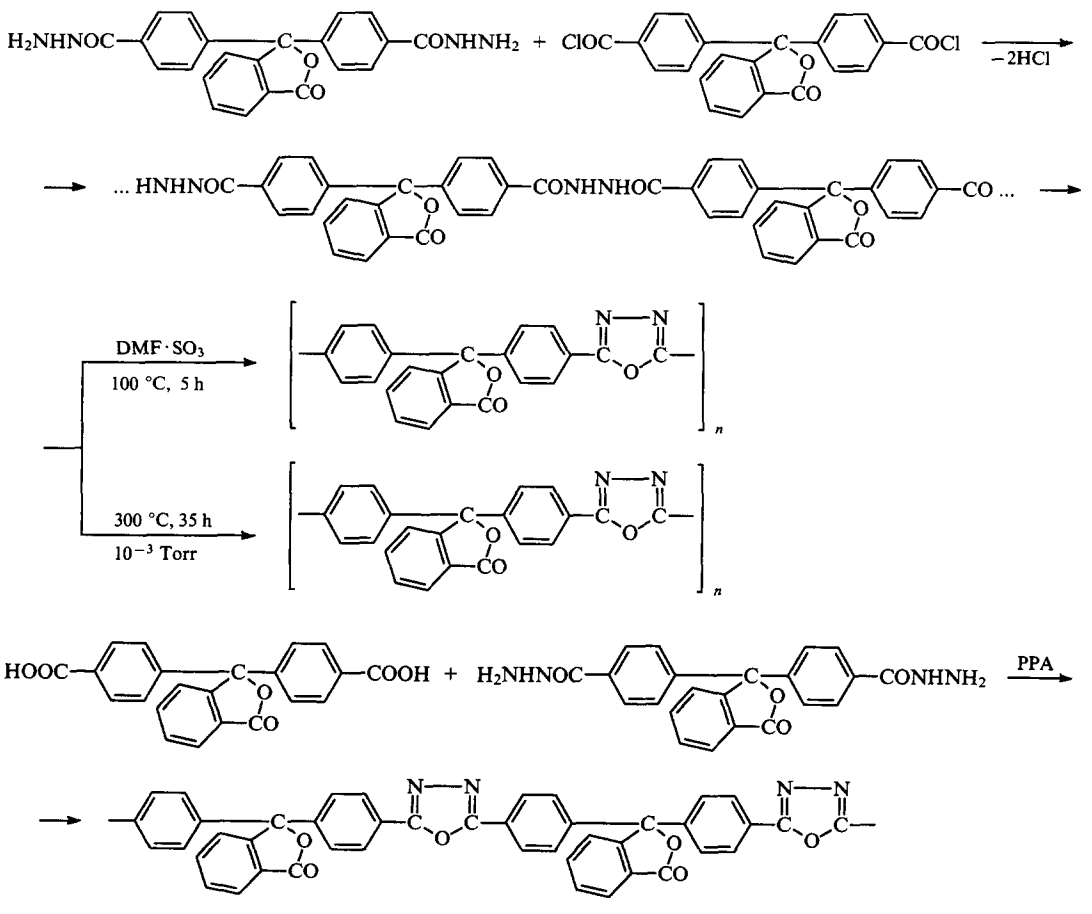
Thus the synthesis of cardo polyimides with free hydroxy-groups [the dianhydrides of bis(3,4-dicarboxyphenyl)methanol and cardo diamines were used as the starting materials] has been achieved. Copolyimides with benzimidazole rings, containing a free reactive NH group, in the main chain have been obtained by the polycondensation of various tetracarboxylic acid dianhydrides with a mixture of a cardo diamine and 5(6)-amino-2-(4-aminophenyl)benzimidazole. Aromatic polyimides with reactive quinuclidine cardo groups have been synthesised by the reaction of various tetracarboxylic acid dianhydrides with 3,3-bis(4-aminophenyl)quinuclidine. Polyimides with functional groups are readily soluble in organic solvents and have satisfactory heat resistances, thermal stabilities, and dielectric characteristics as well as enhanced adhesive properties and they form strong transparent films. The possibility of modifying epoxide oligomers by polyimides derived from bis(3,4-dicarboxyphenyl)methanol has been demonstrated. Such modification afforded cross-linked polymer systems with heat resistances and mechanical strengths superior to those of the epoxide oligomers hardened by the traditional methods. The presence of quinuclidine fragments in the polyimides gives rise to prospects for their employment as catalytic systems and for their further chemical modification at the tertiary nitrogen atoms of the quinuclidine ring system.

IX. Poly-1,3,4-oxadiazoles

The introduction of cardo groups also into polymers with a cyclochain structure such as poly-1,3,4-oxadiazoles has been successful.[2–4, 12, 49, 76, 77, 186, 270–296] The high heat resistances and thermal stabilities of aromatic polyoxadiazoles together with the comparatively ready availability of the initial compounds (dicarboxylic acids and their derivatives) used for their synthesis are responsible for the interest in these polymers.[297–300] However, aromatic polyoxadiazoles are in the main high-melting polymers insoluble in organic solvents. This limits the possibilities for the comprehensive investigation of such polymers and in many cases their practical applications.

Bis(4-carboxyphenyl)phthalide and its derivatives (the acid chloride and dihydrazide) containing a central carbon atom in the polar cyclic side group[270–275] and also 2-[3,3-bis(4-carboxyphenyl)]-*N*-phenylphthalimidine and its derivatives containing *N*-phenyl-2-phthalimidine cardo groups[293] were selected as the starting materials for the synthesis of cardo polyoxadiazoles.

Scheme 17



The polymers were synthesised by a two-stage polycyclisation method in which low-temperature polycondensation was employed in the first stage in order to produce a polyhydrazide with its subsequent cyclisation and by one-step polycyclisation in polyphosphoric acid (Scheme 17).

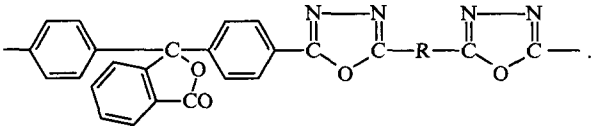
The ready solubility of the polyhydrazides based on bis(4-carboxyphenyl)phthalide and its derivatives owing to the presence of phthalide cardo groups permits their successful synthesis by low-temperature polycondensation not only in hexamethylphosphoramide, normally employed in the synthesis of aromatic polyhydrazides, but also in other organic solvents (*N*-methylpyrrolidone, dimethylacetamide).[271] Admittedly, polyhydrazides with a high molecular mass ($\eta_{red} = 2 \times 10$ dl g^{-1} in dimethylformamide) are obtained only in hexamethylphosphoramide apparently as a result of the much smaller tendency of this solvent (compared with dimethylacetamide and *N*-methylpyrrolidone) to undergo side reactions with acid chlorides.

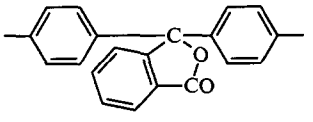
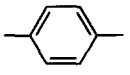
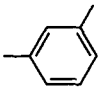
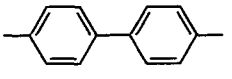
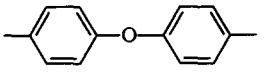
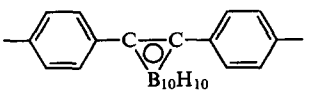
The thermal cyclodehydration of the polyhydrazide based on bis(4-carboxyphenyl)phthalide, like that of the polyhydrazides of aromatic dicarboxylic acids, requires extremely severe conditions as regards temperature in order to attain high degrees of cyclisation: prolonged (of the order of 30 h) heat treatment of the polymer at 300 °C *in vacuo* is needed. If the cyclodehydration of cardo polyhydrazides is carried out by treatment with the dimethylformamide – sulfur trioxide or dimethylacetamide – sulfur trioxide complex, it is possible to reduce the temperature (to 100 °C) and the reaction time (to 5 h).[49, 270, 271, 275]

The characteristic features of the formation of cardo polyoxadiazoles by one-step polycondensation in polyphosphoric acid have been investigated in detail.[49, 271, 275, 281] It was found that a side reaction involving the lactone ring takes place, leading to the formation of an insoluble cross-linked polymer, together with the growth of the polymer chain, in the one-step polycyclisation of the dihydrazide of bis(4-carboxyphenyl)phthalide in polyphosphoric acid and also in the interaction of bis(4-carboxyphenyl)phthalide with hydrazine sulfate. The side reaction may be avoided if the polyoxadiazole is synthesised from bis(4-carboxyphenyl)phthalide and its dihydrazide or the dihydrazides of other aromatic dicarboxylic acids, or from the dihydrazide of bis(4-carboxyphenyl)phthalide and various aromatic dicarboxylic acids.

A series of characteristics of the formation of polyoxadiazoles have been investigated in relation to the reaction of bis(4-carboxyphenyl)phthalide with its dihydrazide. It was established that the results of the polycondensation (yield and molecular mass of the polymer) and the possibility of the occurrence of side reactions are greatly influenced by the ratio of the starting materials, the reaction temperature, the reaction time, the concentration of the starting materials, and the content of phosphorus pentoxide in polyphosphoric acid. Thus a soluble polymer with a high molecular mass is obtained for the equimolecular ratio of the starting materials. An excess of the acid gives rise to a decrease in molecular mass, while an excess of the dihydrazide leads to the formation of an insoluble polymer as a result of the side reaction involving the lactone ring. When the process is carried out at 140 °C, it is desirable to continue it over a period of 5 h. Polymers with the highest molecular mass are obtained when the concentration of the starting materials is approximately 0.3 mole per kilogram of phosphoric acid. The molecular mass of polyoxadiazole depends greatly on the concentration of phosphorus pentoxide in polyphosphoric acid, increasing significantly with increase in the content of the pentoxide from 82% to 86%. However, polycondensation in polyphosphoric acid containing about 84% of

Table 7. The properties of the cardo polyoxadiazoles



R	Temperature/ °C		Mechanical properties of nonoriented films	
	softening	onset of decomposition	σ_r/kgf cm^{-2} [a]	ε (%)[b]
	390	400	1200	8
	390	430	2200	80
	360	400	1200	10
	400	430	2400	75
	340	430	1400	100
	335	420	–	–

[a] σ_r is tensile strength of the film. [b] ε is relative elongation at break.

phosphorus pentoxide is preferable on technological grounds. Mixed polyhydrazides and polyoxadiazoles were obtained when one of the initial components was replaced by the corresponding derivative of an aromatic dicarboxylic acid such as isophthalic, terephthalic, and biphenyl-4,4′-dicarboxylic acids, bis(4-carboxyphenyl) ether, benzophenone-4,4′-dicarboxylic acid, or 1,2- and 1,7-bis(4-carboxyphenyl)carboranes.

All three methods of synthesis (thermal dehydration, chemical dehydration in the presence of the dimethylformamide–sulfur trioxide complex, and one-step polycyclisation in polyphosphoric acid) can be used successfully for the synthesis of cardo polyoxadiazoles. However, polymers with a high molecular mass (up to 300 000) are obtained when the process is carried out in polyphosphoric acid.[49, 271, 275]

The homopolymers and copolymers of 1,3,4-oxadiazoles with *N*-phenyl-2,2-phthalimidine cardo groups have been synthesised successfully by one-step polycondensation in polyphosphoric acid.[293] In this case, the polyoxadiazoles were obtained by the interaction of salts of hydrazine or dicarboxylic acid dihydrazides with 2-[3,3′-bis(4-carboxyphenyl)]-*N*-phenylphthalimidine. The presence of the *N*-phenyl-2,2-phthalimide group in the initial monomer (in contrast to the phthalide group) rules out the occurrence of undesirable side reactions during synthesis. The synthesis of polyoxadiazoles from hydrazine sulfate involves the formation of polymeric adducts with sulfuric acid having high heat resistances and thermal stabilities and satisfactory solubilities even in solvents such as acetone, THF, ethyl methyl ketone, dioxane, and cyclohexanone.

Table 7 presents some properties of a series of cardo polyoxadiazoles with phthalide groups which have been obtained.[49, 271, 275] These polymers have high heat resistances and thermal stabilities. Thus the softening temperatures of polyoxadiazoles are from 340 to 400 °C. According to thermogravimetric data (heating rate 5 K min^{-1}), these polymers begin to decompose in air at 400–430 °C. Cardo polyoxadiazoles are resistant to the action of water and corrosive media at room temperature and to the action of water at 100 °C.[271, 291] Comparison of the thermomechanical curves for the polyoxadiazole derived from bis(4-carboxyphenyl)phthalide and the noncardo poly-2,5-(4,4′-diphenylene oxide)-1,3,4-oxadiazole in the amorphous state revealed the influence of the cardo group on the heat resistance of polymers of this type: the softening temperature of the cardo polymer exceeds by approximately 150 °C that for the noncardo polyoxadiazole.[49, 271]

Among various polyoxadiazoles with phthalide groups, poly 2,5-(4,4′-diphenylphthalide)-1,3,4-oxadiazole has the highest solubility. It is soluble in methylene chloride, tetrachloroethane, dimethylacetamide, hexamethylphosphoramide, pyridine, benzyl alcohol, methylpyrrolidone, etc. The solubility of cardo polyoxadiazoles gives rise to the possibility of obtaining different articles from them by moulding from solution. Strong transparent films, with effective physicomechanical and dielectric properties both at room and elevated temperatures, are formed from solutions of cardo polyoxadiazoles.[271, 275] Thus the strength of films of the homopolyoxadiazole obtained from bis(4-carboxyphenyl)phthalide is 1000 kgf cm^{-2} after heating at 250 °C for 500 h and 400 kgf cm^{-2} after heating at 300 °C for 1000 h (the initial strength is 1200 kgf cm^{-2}). At 20 °C and a frequency of 5000 Hz, the specific volume resistivity of this polymer is 6×10^{15} Ω cm, while the tangent of the dielectric loss angle is 3.2×10^{-2}; at 300 °C, these parameters are respectively 10^{13} Ω cm and 2.0×10^{-2}.

The solubility of cardo polyoxadiazoles made it possible to investigate for the first time the hydrodynamic properties, polydispersity, and the molecular mass characteristics of cyclochain polymers of this type.[178, 179, 270, 271, 282, 287] For the cardo polyoxadiazole obtained from bis(4-carboxyphenyl)phthalide in dimethylacetamide and THF, the Mark–Houwink equations are $[\eta] = 7.74 \times 10^{-4} M^{0.57}$ and $[\eta] = 4.00 \times 10^{-4} M^{0.66}$ respectively. The polydispersity coefficient for this polymer, synthesised by one-step polycyclisation in polyphosphoric acid, is 3.0–3.1.[270, 278, 279]

Polyoxadiazoles containing phthalide rings in the side chain have an amorphous structure regardless of the method of synthesis, whereas the familiar poly-1,3,4-oxadiazoles, synthesised in two stages, have a crystalline structure.[275] The radiation stability of the polyoxadiazole based on bis(4-carboxyphenyl)phthalide is fairly high and is superior to that of poly(ethylene terephthalate) and polycarbonate.[288]

The use in the synthesis of cardo polyoxadiazoles of phosphorus-containing monomers such as bis(4-carboxyphenoxymethyl)-methylphosphine oxide, bis(4-carboxyphenyl)methylphosphine oxide, and bis(1-carboxy-3,5-dichloro-4-phenoxymethyl)methylphosphine oxide together with bis(4-carboxyphenyl)phthalide and its hydrazide made it possible to obtain phosphorus-containing cardo polyoxadiazoles with a satisfactory solubility, high heat resistance and thermal stability, effective adhesive properties, and an enhanced resistance to combustion.[285, 294, 295]

Cardo polyoxadiazoles may be of interest for the electrical engineering industry, machine building, aircraft construction, and other industries employing materials in units and constructions designed for prolonged use at 200–300 °C. They have been used in the form of powders and solutions for the preparation of glass fibre-reinforced and carbon plastics, moulding materials, films, coatings, adhesives, filtering materials, including materials of the membrane type, and heat- and atmosphere-resistant anticorrosion coatings. Table 8 presents certain data on the properties of the moulding

Table 8. The properties of the 'Niplon 1' polyoxadiazole.

Parameter	Moulding material	Glass fibre-reinforced plastic	Carbon plastic
Density/g cm^{-3}	1.34	1.8	1.3
Tensile strength /kgf cm^{-2}			
at 20 °C	600	–	3500
at 325 °C	100	–	–
Young's modulus /kgf cm^{-2}	–	3×10^5	9×10^5
Bending strength /kgf cm^{-2} in the initial state			
at 20 °C	600	4000	5000
at 300 °C	400	3500	3700
after thermal ageing for 2000 h at 300 °C	–	1200	3000
Compressive strength /kgf cm^{-2}			
in the initial state			
at 20 °C	1900	–	–
at 300 °C	600	–	–
after thermal ageing for 200 h at 300 °C	700	–	–
Specific impact strength /kgf cm cm^{-2}	12	–	35
Brinell hardness /kgf cm^{-2}	1900	3300	3700
Vicat's temperature resistance / °C	330–340	–	–
Specific volume resistivity /Ω cm	10^{15}	2×10^{14}	–
Tangent of dielectric loss angle at 10^6 Hz	0.01	0.015	–
Dielectric constant at 10^6 Hz	3.7	4.0	–
Dielectric strength /kV mm^{-1}	18	–	–
Water absorption			
after 24 h (%)	1.2	–	–
after 1 month (%)	–	0.70	–

materials and glass fibre-reinforced and carbon plastics based on the 'Niplon l'cardo poly-1,3,4-oxadiazole.[301,302]

The data presented above show that cardo polyoxadiazoles have a set of valuable properties and are promising for practical employment.

* * *

Summarising the foregoing, one should note that the 'cardo' principle has been justified in a series of different types of polymers: polyarylates, aromatic polyethers, polyamides, polyarylenephthalides, epoxide polymers, polyheteroarylenes with a cyclochain structure (polyimides, polyoxadiazoles, polybenzoxazoles,[303-308] polybenzimidazoles[309]) etc. A characteristic feature of the cardo polymers, distinguishing them from their noncardoanalogues, is a combination of an enhanced heat resistance with a satisfactory solubility in organic solvents whilst retaining other valuable properties characteristic of the particular type of polymer to which they belong. This makes the employment of such polymers for practical purposes undoubtedly promising.

As shown above, the properties of cardo polymers depend on their chemical and physical structures and can be altered deliberately by varying the latter, including a transition from polymers of one class to another. For example, the heat resistances and the operating temperatures of cardo polymers and the materials based on them increase on passing from aromatic polyethers to polyarylates and aromatic polyamides and polyimides.

The solubility of cardo polymers in readily available organic solvents made it possible to investigate a series of common features of the formation of polymers with a cyclochain structure, which had not been possible previously owing to the insolubility of these polymers. The solubility of cardo polymers and their satisfactory compatibility with various monomers, oligomers, and polymers has also led to unlimited possibilities for the creation of new polymers in a matrix comprising cardo polymers and hence the creation of new valuable polymer systems.

References

1. S V Vinogradova, S N Salazkin, G Sh Chelidze, G L Slonimskii, A A Askadskii, K A Bychko, L I Komarova, I V Zhuravleva, V V Korshak *Plast. Massy* (8) 10 (1971)
2. S V Vinogradova, Ya S Vygodskii *Usp. Khim.* **42** 1225 (1973) [*Russ. Chem. Rev.* **42** 551 (1973)]
3. V V Korshak, S V Vinogradova, Ya S Vygodskii *J. Macromol. Sci., Rev. Macromol. Chem.* **C11** 45 (1974)
4. Ya S Vygodskii, S V Vinogradova, in *Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii*, T. 7 *(Ser. Itogi Nauki i Tekhniki)* [Chemistry and Technology of High-Molecular-Mass Compounds, Vol. 7 (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1975) p. 14
5. US P. 2 035 578; *Chem. Abstr.* **30** 3 542 (1936)
6. USSR P. 140 990; *Byull. Izobret.* (17) 51 (1961)
7. V V Korshak, S V Vinogradova, S N Salazkin *Vysokomol. Soedin.* **4** 339 (1962)
8. V V Korshak, S V Vinogradova *Neravnovesnaya Polikondensatsiya* (Nonequilibrium Polycondensation) (Moscow: Nauka, 1972)
9. V V Korshak, S V Vinogradova *Usp. Khim.* **39** 679 (1970) [*Russ. Chem. Rev.* **39** 308 (1970)]
10. V V Korshak, S V Vinogradova *Poliarilaty* (Polyarylates) (Moscow: Nauka, 1964)
11. A A Askadskii *Fiziko-Khimiya Poliarilatov* (Physical Chemistry of Polyarylates) (Moscow: Khimiya, 1968)
12. S V Vinogradova, in *Polymer Science Contemporary Themes* Vol. 2. (New Delhi: Tata McGraw-Hill, 1991) p. 658
13. V V Korshak, S V Vinogradova *Usp. Khim.* **37** 2024 (1968) [*Russ. Chem. Rev.* **37** 885 (1968)]
14. S V Vinogradova, in *Tekhnologiya Plasticheskikh Mass* (Technology of Plastics) (Moscow: Khimiya, 1985) p. 344
15. P W Morgan *Condensation Polymers by Interfacial and Solution Methods* (New York: Interscience, 1965)
16. S V Vinogradova, S N Salazkin, V V Korshak, S V Bereza, B V Lokshin, L I Komarova *Vysokomol. Soedin.* **9** 1792 (1967)
17. V V Korshak, S V Vinogradova, S N Salazkin, L I Komarova *Eur. Polym. J.* **10** 976 (1974)
18. V V Korshak *Termostoikie Polimery* (Heat-Resistant Polymers) (Moscow: Nauka, 1969)
19. USSR P. 203 891; *Byull. Izobret.* (21) 81 (1966)
20. S V Vinogradova, S N Salazkin, L A Beridze, A I Mzhel'skii, G L Slonimskii, A A Askadskii, V V Korshak *Izv. Akad. Nauk SSSR, Ser. Khim.* 931 (1969)
21. V V Korshak, S N Salazkin, L A Beridze, S V Vinogradova *Vysokomol. Soedin., Ser. A* **15** 841 (1973)
22. S V Vinogradova, V V Korshak, G Sh Papava, N A Maisuradze, P D Tsikarishvili *Izv. Akad. Nauk SSSR, Ser. Khim.* 434 (1969)
23. V V Korshak, S V Vinogradova, G Sh Papava, N A Maisuradze, P D Tsiskarishvili *Soobshch. Akad. Nauk Gruz. SSR* **51** 301 (1968)
24. USSR P. 507 595; *Byull. Izobret.* (11) 77 (1976)
25. USSR P. 241 013; *Byull. Izobret.* (13) 91 (1969); US P. 3 480 597 (1969); BRD P. 1 620 929 (1970); Jpn. P. 620 275 (1971); Br. P. 1 196 128 (1970)
26. USSR P. 172 492; *Byull. Izobret.* (13) 70 (1965)
27. V V Korshak, S V Vinogradova, G L Slonimskii, Ya S Vygodskii, S N Salazkin, A A Askadskii, A I Mzhel'skii *Vysokomol. Soedin., Ser. A* **10** 2058 (1968)
28. S V Vinogradova, S N Salazkin, L A Bereza, A I Mzhel'skii, A A Askadskii, G L Slonimskii, V V Korshak *Vysokomol. Soedin., Ser. A* **11** 27 (1969)
29. S V Vinogradova, V V Korshak, S N Salazkin, L A Beridze, G L Slonimskii, A A Askadskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 2554 (1969)
30. S V Vinogradova, S N Salazkin, L A Beridze, A I Mzhel'skii, A A Askadskii, G L Slonimskii, V V Korshak *Izv. Akad. Nauk SSSR, Ser. Khim.* 931 (1969)
31. G L Slonimskii, A A Askadskii, A I Mzhel'skii, V V Korshak, S V Vinogradova, S N Salazkin, L A Beridze *Vysokomol. Soedin., Ser. A* **11** 2265 (1969)
32. V V Korshak, S V Vinogradova, V G Danilov, L A Beridze, S N Salazkin *Vysokomol. Soedin., Ser. B* **12** 129 (1970)
33. S V Vinogradova, L A Beridze, T M Pavlova, S N Salazkin, V V Korshak *Vysokomol. Soedin., Ser. B* **13** 681 (1971)
34. V V Korshak, S N Salazkin, L A Beridze, S V Vinogradova *Vysokomol. Soedin., Ser. A* **15** 841 (1973)
35. V V Korshak, S V Vinogradova, V G Danilov, S N Salazkin *Dokl. Akad. Nauk SSSR* **202** 1076 (1972)
36. S A Pavlova, L V Dubrovina, N B Klimanova, S N Salazkin *Vysokomol. Soedin., Ser. B* **19** 175 (1977)
37. A A Askadskii *Struktura i Svoistva Teplostoikikh Polimerov* (The Structure and Properties of Heat-Resistant Polymers) (Moscow: Khimiya, 1981)
38. A A Askadskii, Yu I Matveev *Khimicheskoe Stroenie i Fizicheskie Svoistva Polimerov* (Chemical Structure and Physical Properties of Polymers) (Moscow: Khimiya, 1983)
39. USSR P. 159 030; *Byull. Izobret.* (23) 54 (1963)
40. USSR P. 176 401; *Byull. Izobret.* (22) 58 (1965)
41. S V Vinogradova, V V Korshak, S N Salazkin, S B Bereza *Vysokomol. Soedin.* **6** 1403 (1964)
42. P W Morgan *J. Polym. Sci., Part A* **2** 437 (1964)
43. USSR P. 231 120; *Byull. Izobret.* (35) 87 (1968)
44. V V Korshak, S V Vinogradova, V A Pankratov *Dokl. Akad. Nauk SSSR* **181** 1393 (1968)
45. V V Korshak, S V Vinogradova, V A Pankratov *Plast. Massy* (5) 21 (1967)
46. V V Rode, I V Zhuravleva, S R Rafikov, V V Korshak, S V Vinogradova, V A Pankratov *Vysokomol. Soedin.* **7** 1614 (1965)
47. Z Jedlinski (Ed.) *Advances in the Chemistry of Thermally Stable Polymers* (Warsaw: Pol. Sci. Publ., 1977)
48. Z Jedlinski *Thermal Stability of Polymers Containing Naphthalene Units in the Chain* (Warsaw: Pol. Sci. Publ., 1977)
49. S V Vinogradova, V A Vasnev *Chem. Rev. Harwood Acad. Publ., Part 2* **21** 1 (1996)
50. S V Vinogradova, V A Vasnev, P M Valetskii *Usp. Khim.* **63** 885 (1994) [*Russ. Chem. Rev.* **63** 833 (1994)]

51. S N Salazkin, Doctoral Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1979
52. L A Beridze, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1970
53. V V Korshak *Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov* (Chemical Structure and Temperature Characteristics of Polymers) (Moscow: Nauka, 1970)
54. N A Maisuradze, Candidate Thesis in Chemical Sciences, Institute of Physical Organic Chemistry, Academy of Sciences of the Georgia SSR, Tbilisi, 1970
55. S V Vinogradova *J. Prakt. Chem.* **313B** 359 (1971)
56. S V Vinogradova, in *Progress Polimernoi Khimii* (Progress in Polymer Chemistry) (Moscow: Nauka, 1969) p. 113
57. P W Morgan *Macromolecules* **3** 536 (1970)
58. V A Vasnev, S V Vinogradova *Usp. Khim.* **48** 30 (1979) [*Russ. Chem. Rev.* **48** 16 (1979)]
59. G L Slonimskii, V V Korshak, S V Vinogradova, A I Kitaigorodskii, A A Askadskii, S N Salazkin, E M Belavtseva *Dokl. Akad. Nauk SSSR* **156** 924 (1964); *Vysokomol. Soedin., Ser. A* **9** 402 (1967)
60. G L Slonimskii, V V Korshak, S V Vinogradova, A I Kitaigorodskii, A A Askadskii, S N Salazkin, E M Belavtseva *Dokl. Akad. Nauk SSSR* **165** 1323 (1965)
61. R S Velichkova, V V Korshak, S V Vinogradova, V V Ivanov, A T Ponomarenko, N S Enikolopyan *Izv. Akad. Nauk SSSR, Ser. Khim.* 858 (1969)
62. S V Vinogradova, V V Korshak, G Sh Papava, N A Maisuradze, R S Velichkova *Izv. Akad. Nauk SSSR, Ser. Khim.* 820 (1970)
63. V V Korshak, S V Vinogradova, V A Vasnev *Vysokomol. Soedin., Ser. A* **10** 1329 (1968)
64. S V Vinogradova, V A Vasnev, T S Simonenko, A M Tartakovskaya, V V Korshak *Vysokomol. Soedin., Ser. A* **23** 619 (1981)
65. S V Vinogradova, V A Vasnev, V V Korshak *Vysokomol. Soedin., Ser. B* **9** 522 (1967)
66. V V Korshak, S V Vinogradova, V A Vasnev, T I Mitaishvili *Vysokomol. Soedin., Ser. A* **11** 81 (1969)
67. T I Mitaishvili, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1970
68. V A Vasnev, Doctoral Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1975
69. S V Vinogradova, in *Advances in Polymer Chemistry* (Moscow: Mir, 1986) p. 75
70. S V Vinogradova, V A Vasnev *Chem. Rev. Harwood Acad. Publ., Part I* **21** 1 (1996)
71. S R Rafikov, S V Vinogradova, V V Korshak, Z Ya Fomina, B V Lokshin, V V Rode *Vysokomol. Soedin.* **8** 2189 (1966)
72. V V Korshak, S V Vinogradova, S A Siling, S R Rafikov, Z Ya Fomina, V V Rode *J. Polym. Sci. Part A, Polym. Chem.* **7** 157 (1969)
73. V V Korshak, S V Vinogradova, G L Slonimskii, S N Salazkin, A A Askadskii *Vysokomol. Soedin.* **8** 548 (1966)
74. V V Korshak, S V Vinogradova, A I Kalachev, P M Valetskii, N S Titova, V I Stanko *Vysokomol. Soedin., Ser. A* **14** 1306 (1972)
75. V V Korshak, S V Vinogradova, A I Kalachev, P M Valetskii, V I Stanko *Vysokomol. Soedin., Ser. A* **13** 848 (1971)
76. S V Vinogradova, P M Valetskii, N I Bekasova *Chem. Rev.* **18** 1 (1993)
77. S V Vinogradova, P M Valetskii, Yu A Kabachii *Usp. Khim.* **64** 390 (1995) [*Russ. Chem. Rev.* **64** 365 (1995)]
78. P M Valetskii, E K Lamenkova, S V Vinogradova *Vysokomol. Soedin., Ser. A* **16** 305 (1974)
79. P M Valetskii *Karbotsepnye i Geterotsepnye Polimery s Karboranovymi Gruppami v Tsepi* (Carbon-Chain and Heterochain Polymers with Carbaborane Groups in the Chain) (Gomel', 1972)
80. L I Komarova, S N Salazkin, Ya S Vygodskii, S V Vinogradova *Vysokomol. Soedin., Ser. A* **32** 1571 (1990)
81. V V Korshak, S V Vinogradova, I A Bulgakova, L I Komarova, Ya S Vygodskii, M A Yusufov, E E Zaborovskaya *Plast. Massy* (6) 47 (1986)
82. A A Askadskii, L N Belkina, K A Bychko, S N Salazkin, I A Bulgakova, L I Komarova, S V Vinogradova, G L Slonimskii, V V Korshak *Vysokomol. Soedin., Ser. A* **22** 1338 (1980)
83. S V Vinogradova, V V Korshak, E I Fridman, M A Andreeva, L N Baraboshkina *Plast. Massy* (9) 16 (1965)
84. Z Ya Fomina, Candidate Thesis in Chemical Sciences, Mendeleev Moscow Chemical Technological Institute, Moscow, 1967
85. S R Rafikov, V V Korshak, S V Vinogradova, Z Ya Fomina, V A Pankratov *Vysokomol. Soedin., Ser. A* **9** 1903 (1967)
86. S R Rafikov, S V Vinogradova, V V Korshak, Z Ya Fomina *Vysokomol. Soedin., Ser. A* **9** 98 (1967)
87. S V Vinogradova, S R Rafikov, V V Korshak, Z Ya Fomina *Vysokomol. Soedin., Ser. A* **9** 1797 (1967)
88. I P Antonova-Antipova, Candidate Thesis in Chemical Sciences, Mendeleev Moscow Chemical Technological Institute, Moscow, 1966
89. S V Vinogradova, V V Korshak, I P Antonova-Antipova *Vysokomol. Soedin.* **7** 2052 (1965)
90. S V Vinogradova, I P Antonova-Antipova, in *Progress Polimernoi Khimii* (Progress in Polymer Chemistry) (Moscow: Nauka, 1969) p. 375
91. V V Korshak, S V Vinogradova, I P Antonova-Antipova, V A Plakhov *Dokl. Akad. Nauk SSSR* **177** 120 (1967)
92. D M White, in *Comprehensive Polymer Science. The Synthesis, Characterization, Reactions, and Applications of Polymers* Vol. 5 (Oxford: Pergamon Press, 1989) p. 473
93. P A Staniland, in *Comprehensive Polymer Science. The Synthesis, Characterization, Reactions, and Application of Polymers* Vol. 5 (Oxford: Pergamon Press, 1989) p. 483
94. F Parodi, in *Comprehensive Polymer Science. The Synthesis, Characterization, Reactions, and Application of Polymers* Vol. 5 (Oxford: Pergamon Press, 1989) p. 561
95. A A Kul'kov, Candidate Thesis in Chemical Sciences, Mendeleev Moscow Chemical Technological Institute, Moscow, 1972
96. M K Kutateladze, Candidate Thesis in Chemical Sciences, Tbilisi State University, Tbilisi, 1981
97. V V Shaposhnikova, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 1993
98. V V Korshak, S V Vinogradova, S N Salazkin, A A Kul'kov *Dokl. Akad. Nauk SSSR* **208** 360 (1973)
99. S V Vinogradova, V V Korshak, S N Salazkin, A A Kul'kov *Vysokomol. Soedin., Ser. A* **14** 2545 (1972)
100. USSR P. 372 234; *Byull. Izobret.* (13) 77 (1973)
101. A A Kul'kov, S N Salazkin, G L Slonimskii, A A Askadskii, K A Bychko, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. A* **16** 1543 (1974)
102. V M Laktionov, I V Zhuravleva, S A Pavlova, S R Rafikov, S N Salazkin, S V Vinogradova, A A Kul'kov, V V Korshak *Vysokomol. Soedin., Ser. A* **18** 330 (1976)
103. G Sh Papava, S V Vinogradova, M K Kutateladze, K R Papava, G Borisov, S Verbanov *Acta Polymer.* **42** 74 (1991)
104. USSR P. 503 859; *Byull. Izobret.* (7) 67 (1976)
105. L A Beridze, G Sh Papava, M K Kutateladze, P D Tsiskarishvili *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **2** 226 (1976)
106. L A Beridze, M K Kutateladze, G Sh Papava, P D Tsiskarishvili *Soobshch. Akad. Nauk Gruz. SSR* **83** 269 (1976)
107. L A Beridze, M K Kutateladze, G Sh Papava, P D Tsiskarishvili *Soobshch. Akad. Nauk Gruz. SSR* **84** 401 (1976)
108. L A Beridze, M K Kutateladze, G Sh Papava *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **6** 232 (1980)
109. V M Agapov, S N Salazkin, V A Sergeev, L I Komarova, P V Petrovskii *Dokl. Akad. Nauk SSSR* **316** 126 (1991)
110. V M Agapov, S N Salazkin, V A Sergeev, L I Komarova, P V Petrovskii, G I Timofeeva *Vysokomol. Soedin., Ser. A* **34** 3 (1992)
111. USSR P. 403 705; *Byull. Izobret.* (43) 73 (1973)
112. V V Korshak, S V Vinogradova, D R Tur *Faserforsch. Textiltech.* **28** 339 (1977)
113. L K Solov'eva, Candidate Thesis in Chemical Sciences, Mendeleev Moscow Chemical Technological Institute, Moscow, 1969
114. N S Dokhturashvili, Candidate Thesis in Chemical Sciences, Tbilisi State University, Tbilisi, 1980

115. S N Salazkin, S V Vinogradova, L I Komarova *Izv. Akad. Nauk SSSR, Ser. Khim.* 144 (1973)
116. V V Korshak, L K Solov'eva, I V Kamenskii *Vysokomol. Soedin., Ser. A* **13** 150 (1971)
117. V V Korshak, L K Solov'eva *Vysokomol. Soedin., Ser. B* **13** 714 (1971)
118. V V Korshak, S V Vinogradova, L K Solov'eva, N S Dokhturashvili, G Sh Papava, P D Tsiskarishvili, L B Makina *Plast. Massy* (3) 74 (1975)
119. V V Korshak, G Sh Papava, N S Dokhturashvili, L K Solov'eva, L B Makina *Plast. Massy* (2) 17 (1974)
120. G Sh Papava, N S Dokhturashvili, N A Maisuradze, P D Tsiskarishvili, S V Vinogradova, V V Korshak, in *Sintez i Svoistva Nekotorykh Novych Polimernykh Materialov* (Synthesis and Properties of Some New Polymeric Materials) (Tbilisi: Metsniereba, 1974) p. 51
121. N S Dokhturashvili, G Sh Papava, P D Tsiskarishvili, L K Solov'eva, S V Vinogradova, V V Korshak, in *Sintez i Svoistva Nekotorykh Polimernykh Materialov* (Synthesis and Properties of Some New Polymeric Materials) (Tbilisi: Metsniereba, 1974) p. 66
122. USSR P. 454 228; *Byull. Izobret.* (47) 48 (1974)
123. G Sh Papava, N S Dokhturashvili, N A Maisuradze, P D Tsiskarishvili, B M Mgeladze, K S Kvaskhvadze *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **3** 121 (1977)
124. G Sh Papava, N S Dokhturashvili, N A Maisuradze, P D Tsiskarishvili, V V Korshak, S V Vinogradova *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **3** 249 (1977)
125. G Sh Papava, N A Maisuradze, N S Dokhturashvili, G G Andronikashvili *Soobshch. Akad. Nauk Gruz. SSR* **91** 349 (1978)
126. V V Korshak, S V Vinogradova, S N Salazkin, I A Bulgakova, L I Komarova, Ya S Vygodskii, M A Yusufov, E E Zaborovskaya *Issledovanie Vliyaniya Khimicheskogo Stroeniya Epoksidnykh Oligomerov Kardovykh Poligeteroarilenov na Ikh Sovmestimost' i Svoistva Poluchaemykh Kompozitsii* (Investigation of the Influence of the Chemical Structure of Epoxy-Oligomers of Cardo-Polyheteroarylenes on Their Compatibility and on the Properties of the Compositions Obtained) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No 7855, Moscow, 1984
127. I A Bulgakova, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1983
128. S N Salazkin, S R Rafikov, G A Tolstikov, M G Zolotukhin *Dokl. Akad. Nauk SSSR* **262** 355 (1982)
129. M G Zolotukhin, V D Skirda, V I Sundukov, S N Salazkin, E A Sedova, Kh G Mindiyarov, S R Rafikov *Vysokomol. Soedin., Ser. B* **29** 378 (1987)
130. M G Zolotukhin, V A Kovardakov, S N Salazkin, S R Rafikov *Vysokomol. Soedin., Ser. A* **26** 1212 (1984)
131. M G Zavarukhin, N G Gileva, E A Sedova, A E Egorov, Yu A Sangalov, S N Salazkin, Yu A Lebedev *Dokl. Akad. Nauk SSSR* **304** 378 (1989)
132. S N Salazkin, M G Zolotukhin, V A Kovardakov, S R Rafikov, L V Dubrovina, E A Gladkova, S A Pavlova *Vysokomol. Soedin., Ser. A* **29** 1437 (1987)
133. S R Rafikov, S N Salazkin, M G Zolotukhin *Plast. Massy* (10) 36 (1986)
134. V A Kraikin, S N Salazkin, V D Komissarov, M G Zolotukhin, S R Rafikov *Vysokomol. Soedin., Ser. B* **28** 264 (1986)
135. V A Kraikin, V A Kovardakov, A A Panasenko, R R Maslukhov, S N Salazkin, S R Rafikov *Vysokomol. Soedin., Ser. A* **34** 28 (1992)
136. S N Salazkin, M G Zolotukhin, A N Lachinov, Yu A Sangalov, G I Nikiforova, A A Panasenko, F A Valyamova *Dokl. Akad. Nauk SSSR* **302** 365 (1988)
137. S N Salazkin, M G Zolotukhin, E A Sedova, Yu L Sorokina, Yu A Sangalov, V S Sultanova, A A Panasenko, L M Khalilov, R M Muslakhov *Makromol. Chem.* **191** 1477 (1990)
138. A V Shitikov, M G Zolotukhin, S N Salazkin, S R Rafikov, V S Sultanova *Khimicheskaya Modifikatsiya Polidifenilenftalida* (Chemical Modification of Polydiphenylenephthalide) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No 6632, Moscow, 1985
139. V S Sultanova, L M Khalilov, A V Shitikov, M G Zolotukhin, A A Panasenko, S N Salazkin, S R Rafikov *Vysokomol. Soedin., Ser. B* **30** 659 (1988)
140. A V Shitikov, M G Zolotukhin, V S Sultanova, A A Panasenko, S N Salaskin, S R Rafikov *Makromol. Chem.* **190** 1837 (1989)
141. M G Zolotukhin, E A Egorov, E A Sedova, Yu L Sorokina, V A Kovardakov, S N Salazkin, Yu A Sangalov *Dokl. Akad. Nauk SSSR* **311** 127 (1990)
142. M G Zolotukhin, E A Sedova, Yu L Sorokina, S N Salazkin, Yu A Sangalov, V S Sultanov *Dokl. Akad. Nauk SSSR* **307** 617 (1989)
143. USSR P. 195 100; *Byull. Izobret.* (9) 120 (1967)
144. USSR P. 191 119; *Byull. Izobret.* (3) 93 (1967)
145. USSR P. 198 644; *Byull. Izobret.* (14) 95 (1967)
146. Ya S Vygodskii, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1968
147. S V Vinogradova, V V Korshak, Ya S Vygodskii, V I Zaitsev *Vysokomol. Soedin., Ser. A* **9** 658 (1967)
148. A A Askadskii, G L Slonimskii, Ya S Vygodskii, V V Korshak, S V Vinogradova, Ya S Vygodskii, S N Salazkin, V I Zaitsev *Vysokomol. Soedin.* **8** 2131 (1966)
149. V V Rode, P N Gribkova, Ya S Vygodskii, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. A* **10** 2550 (1968); *Izv. Akad. Nauk SSSR, Ser. Khim.* 85 (1969)
150. K A Reddy, M Srinivasan *Br. Polym. J.* **22** 333 (1990)
151. G L Slonimskii, A A Askadskii, V V Korshak, S V Vinogradova, Ya S Vygodskii, S N Salazkin *Vysokomol. Soedin., Ser. A* **9** 1706 (1967)
152. S V Vinogradova, Ya S Vygodskii, N A Churochkina, L B Tunik, V V Korshak, V I Berendyaev *Vysokomol. Soedin., Ser. A* **31** 45 (1989)
153. S V Vinogradova, Ya S Vygodskii, V V Korshak, G L Slonimskii, A A Askadskii, N A Churochkina, V V Kazanceva, H Raubach, B Falk *Acta Polymer* **41** 489 (1990)
154. S V Vinogradova, Ya S Vygodskii, G S Gurbich, V V Korshak, G Reinisch, U Gohlke *Faserforsch. Textiltech.* **29** 613 (1978)
155. USSR P. 513 051; *Byull. Izobret.* (47) 198 (1977)
156. V V Korshak, S V Vinogradova, Ya S Vygodskii, N A Churochkina *Issledovanie Obrazovaniya Kardovykh Poliamidov v Rastvore Poli-4-fenilentereftalamida* (Investigation of the Formation of Cardo Polyamides in Poly-4-phenyleneterephthalamide Solution) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No 837, Moscow, 1984
157. V V Korshak, S V Vinogradova, I A Gribova, Ya S Vygodskii, N A Churochkina, G I Gureeva, N Yu Krainova *Trenie Iznos* **10** 566 (1989)
158. N N Rukhlyada, N A Churochkina, Ya S Vygodskii, S V Vinogradova, T A Magula, E R Klinshpont, V K Milinchuk *Vysokomol. Soedin., Ser. A* **34** 94 (1992)
159. S N Salazkin, L I Komarova, I A Bulgakova, M I Melaniya, V I Nikolaichik, E E Zaborovskaya *Tezisy Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii, Tashkent, 1978* (Abstracts of the International Symposium on Macromolecular Chemistry, Tashkent, 1978) Vol. 6, p. 56
160. A P Khardin, I A Novakov, S S Radchenko, N A Brel', O A Kuznechikov, Ya S Vygodskii *Vysokomol. Soedin., Ser. B* **25** 433 (1983)
161. V V Korshak, P M Valetskii, L A Glivka, S V Vinogradova, N S Titova, V I Stanko *Vysokomol. Soedin., Ser. A* **14** 1043 (1972)
162. T N Balykova, P N Gribkova, L A Glivka, P M Valetskii, V V Korshak, S V Vinogradova *Vysokomol. Soedin., Ser. A* **15** 2441 (1973)
163. P M Valetskii, L A Glivka, L V Dubrovina, S V Vinogradova, V G Danilov, V I Stanko, V V Korshak *Vysokomol. Soedin., Ser. A* **15** 1227 (1973)

164. E P Krasnov, V P Aksenova, S N Khar'kov, in *Proizvodstvo Sinteticheskikh Volokon* (Production of Synthetic Fibres) (Moscow: Khimiya, 1971) p. 255
165. V V Rode, P N Gribkova, V V Korshak *Vysokomol. Soedin., Ser. A* **11** 57 (1969)
166. V V Lyashevich, V V Korshak, V V Rode, Ya S Vygodskii *Vysokomol. Soedin., Ser. A* **19** 581 (1977)
167. V M Andreeva, V I Konevets, A A Tager, Ya S Vygodskii, S V Vinogradova *Vysokomol. Soedin., Ser. A* **24** 1285 (1982)
168. Ya S Vygodskii, A A Askadskii, G S Gurbich, Yu S Kochergin, G L Slonimskii, V V Korshak, S V Vinogradova *Vysokomol. Soedin., Ser. A* **21** 161 (1979)
169. L I Komarova, Doctoral Thesis in Chemical Sciences, Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 1992
170. L Vollbracht, in *Comprehensive Polymer Science. The Synthesis, Characterization, Reactions, and Application of Polymers* Vol. 5 (Oxford: Pergamon Press, 1989) p. 375
171. Ya S Vygodskii, Z V Gerashchenko, S V Vinogradova, in *Preprints of the International Symposium Macromolecules, Helsinki, 1972* Vol. 2, p. 889
172. V V Korshak, S V Vinogradova, Ya S Vygodskii, B N Yudin *Izv. Akad. Nauk SSSR, Ser. Khim.* 1405 (1968)
173. S V Vinogradova, N A Churochkina, Ya S Vygodskii, G V Zhdanova, V V Korshak *Vysokomol. Soedin., Ser. A* **13** 1146 (1971)
174. S V Vinogradova, Ya S Vygodskii, V D Vorob'ev, N A Churochkina, T N Spirina, L I Chudina *Vysokomol. Soedin., Ser. A* **16** 506 (1974)
175. USSR P. 171 552; *Byull. Izobret.* (11) 76 (1965)
176. S V Vinogradova, V V Korshak, Ya S Vygodskii *Vysokomol. Soedin., Ser. A* **8** 809 (1966)
177. Ya S Vygodskii, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. B* **9** 587 (1967)
178. USSR P. 215 493; *Byull. Izobret.* (13) 80 (1968)
179. V V Korshak, S V Vinogradova, Ya S Vygodskii, S A Pavlova, L V Boiko *Izv. Akad. Nauk SSSR, Ser. Khim.* 2267 (1967)
180. S V Vinogradova, Ya S Vygodskii, V V Korshak *Vysokomol. Soedin., Ser. A* **12** 1987 (1970)
181. US P. 3 988 303 (1976); Fr. P. 7 442 536 (1977); Can. P. 1 043 940 (1978); Austral. P. 486 453 (1977); Aust. P. 340 685; Br. P. 1 489 933 (1977); Ital. P. 1 026 948 (1977); Jpn. P. 1 159 664 (1983); BRD P. 2 461 350 (1977)
182. *Vysokoteplostoikie Rastvorimye Kardovye Poliimidy* (Soluble Highly Heat-Resistant Cardo Polyimides) (Moscow: Nauka, 1977)
183. V V Korshak, S V Vinogradova, Ya S Vygodskii, Z V Gerashchenko *Vysokomol. Soedin., Ser. A* **13** 1190 (1971)
184. S N Khar'kov, E P Krasnov, Z N Lavrova *Vysokomol. Soedin., Ser. A* **13** 833 (1971)
185. V V Korshak, S V Vinogradova, Z V Gerashchenko, Ya S Vygodskii *Tr. Mosk. Khim.-Tekhnol. Int.* **70** 168 (1972)
186. S V Vinogradova, Ya S Vygodskii, V V Korshak, N A Churochkina, D R Tur, V G Danilov *Vysokomol. Soedin., Ser.A* **13** 1507 (1971)
187. S V Vinogradova, G L Slonimskii, Ya S Vygodskii, A A Askadskii, A I Mzhel'skii, N A Churochkina, V V Korshak *Vysokomol. Soedin., Ser. A* **11** 2725 (1969)
188. S V Vinogradova, S A Pavlova, V V Korshak, Ya S Vygodskii, L V Boiko, N A Golubeva *Vysokomol. Soedin., Ser. B* **10** 398 (1968)
189. V V Korshak, S A Pavlova, L V Boiko, T M Babchinitser, S V Vinogradova, Ya S Vygodskii, N A Golubeva *Vysokomol. Soedin., Ser. A* **12** 56 (1970)
190. G L Slonimskii, V V Korshak, A I Mzhel'skii, A A Askadskii, Ya S Vygodskii, S V Vinogradova *Dokl. Akad. Nauk SSSR* **182** 851 (1968)
191. USSR P. 257 010; *Byull. Izobret.* (35) 74 (1969)
192. E P Krasnov, V P Aksenova, S N Khar'kov, S A Baranova *Vysokomol. Soedin., Ser. A* **12** 873 (1970)
193. P N Gribkova, V V Rode, Ya S Vygodskii, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. A* **12** 220 (1970)
194. V V Korshak, S V Vinogradova, Ya S Vygodskii, Z V Gerashchenko, N I Lushkina *Vysokomol. Soedin., Ser. A* **14** 1924 (1972)
195. S A Pavlova, G I Timofeeva, V V Korshak, Ya S Vygodskii, S V Vinogradova, N A Churochkina *Vysokomol. Soedin., Ser. A* **15** 2650 (1973)
196. USSR P. 295 785; *Byull. Izobret.* (8) 69 (1971)
197. USSR P. 310924 SSSR; *Byull. Izobret.* (24) 89 (1971)
198. Ya S Vygodskii, N A Churochkina, L V Dubrovina, T P Bragina, S A Pavlova, S V Vinogradova, A E Travkin, V M Kopylov, M I Shkol'nik *Vysokomol. Soedin., Ser. A* **32** 2372 (1990)
199. S V Vinogradova, N A Churochkina, Ya S Vygodskii, V V Korshak *Vysokomol. Soedin., Ser. A* **15** 1713 (1973)
200. G L Slonimskii, Ya S Vygodskii, Z V Gerashchenko, F N Nurmukhametov, A A Askadskii, V V Korshak, S V Vinogradova, E M Belavtseva *Vysokomol. Soedin., Ser. A* **16** 2249 (1974)
201. Ya S Vygodskii, T N Spirina, P P Nechaev, L I Chudina, G E Zaikov, V V Korshak, S V Vinogradova *Vysokomol. Soedin., Ser. A* **19** 1516 (1977)
202. Ya S Vygodskii, E D Molodtsova, G I Timofeeva, S V Vinogradova, S A Pavlova, V V Korshak *Vysokomol. Soedin., Ser. B* **21** 100 (1979)
203. USSR P. 644 783; *Byull. Izobret.* (4) 86 (1979)
204. T Szekely, V V Korshak, S V Vinogradova, M Lengyel, Ya S Vygodskii, G S Gurbich *Acta Chim. Acad. Sci. Hung.* **100** 121 (1979)
205. E D Molodtsova, S A Pavlova, G I Timofeeva, Ya S Vygodskii, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. A* **16** 2183 (1974)
206. V V Korshak, S V Vinogradova, Ya S Vygodskii, G S Gurbich, I F Davydov, B A Kiselev *Vysokomol. Soedin., Ser. A* **22** 52 (1980)
207. V V Korshak, Ya S Vygodskii, G S Gurbich, S V Vinogradova *Vysokomol. Soedin., Ser. A* **23** 1023 (1981)
208. Ya S Vygodskii, V A Adigezalov, A A Askadskii, G L Slonimskii, Sh T Bagirov, V V Korshak, S V Vinogradova, Z M Nagiev *Vysokomol. Soedin., Ser. A* **21** 2672 (1979)
209. S V Vinogradova, Ya S Vygodskii, V A Adigezalov, V S Papkov, I I Dubovik, G L Slonimskii, Ya G Urman, S G Alekseeva, Sh T Bagirov, V V Korshak *Vysokomol. Soedin., Ser. A* **23** 1761 (1981)
210. S V Vinogradova, Ya S Vygodskii, T N Spirina, L I Chudina, V V Korshak *Vysokomol. Soedin., Ser. A* **21** 1064 (1979)
211. Ya S Vygodskii, Doctoral Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1980
212. S V Vinogradova, Ya S Vygodskii, N A Churochkina, V V Korshak *Vysokomol. Soedin., Ser. B* **19** 93 (1977)
213. S V Vinogradova, Ya S Vygodskii *Faserforsh. Textiltech.* **28** 581 (1977)
214. V V Korshak, S V Vinogradova, Ya S Vygodskii *Faserforsh. Textiltech.* **28** 439 (1977)
215. S V Vinogradova, V V Korshak, Ya S Vygodskii, B V Lokshin *Vysokomol. Soedin., Ser. A* **9** 1091 (1967)
216. V V Korshak, S V Vinogradova, Ya S Vygodskii, Z M Nagiev, Ya G Urman, S G Alekseeva, I Ya Slomnim *Makromol. Chem.* **184** 235 (1983)
217. S V Vinogradova, Z V Gerashchenko, Ya S Vygodskii, F B Sherman, V V Korshak *Dokl. Akad. Nauk SSSR* **203** 821 (1972)
218. P P Nechaev, Ya S Vygodskii, G E Zaikov, S V Vinogradova *Vysokomol. Soedin., Ser. A* **18** 1667 (1976)
219. E V Kamzolkina, P P Nechaev, V S Markin, Ya S Vygodskii, T V Grigor'ev, G E Zaikov *Dokl. Akad. Nauk SSSR* **213** 650 (1974)
220. S G Alekseeva, S V Vinogradova, V D Vorob'ev, Ya S Vygodskii, V V Korshak, I Ya Slonim, T N Spirina, Ya G Urman, L I Chudina *Vysokomol. Soedin., Ser. A* **21** 2207 (1979)
221. P P Nechaev, Yu V Moiseev, S V Vinogradova, Ya S Vygodskii, G E Zaikov, V V Korshak *Vysokomol. Soedin., Ser. A* **15** 702 (1973)
222. Z V Gerashchenko, Ya S Vygodskii, G L Slonimskii, A A Askadskii, V S Papkov, S V Vinogradova, V G Dashevskii, V A Klimova, F B Sherman, V V Korshak *Vysokomol. Soedin., Ser. A* **15** 1718 (1973)
223. Ya S Vygodskii, S V Vinogradova, Z M Nagiev, V V Korshak, Ya G Urman, G Reinisch, G Rafler *Acta Polymer* **33** 131 (1982)

224. G S Alekseeva, S V Vinogradova, V D Vorob'ev, Ya S Vygodskii, E I Efimova, V V Korshak, I Ya Slonim, P M Tanunina, Ya G Urman *Vysokomol. Soedin., Ser. B* **21** 883 (1979)
225. Ya S Vygodskii, Z M Nagiev, V V Korshak, S V Vinogradova, Ya G Urman, S G Alekseeva, I Ya Slonim, G Reinisch, E Bonatz, E Yakab, F Till, G Rafler *Acta Polymer* **35** 690 (1984)
226. P P Nechaev, Yu V Moiseev, G E Zaikov, Ya S Vygodskii, Z V Gerashchenko *J. Polym. Sci.* **42** 1425 (1973)
227. Ya S Vygodskii, in *Tekhnologiya Plasticheskikh Mass* (Technology of Plastics) (Moscow: Khimiya, 1985) p. 408
228. S G Alekseeva, S V Vinogradova, V D Vorob'ev, Ya S Vygodskii, V V Korshak, I Ya Slonim, T N Spirina, Ya G Urman, L I Chudina *Vysokomol. Soedin., Ser. B* **18** 803 (1976)
229. P P Nechaev, T N Simakina, Yu V Moiseev, Ya S Vygodskii, G E Zaikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2809 (1976)
230. E D Molodtsova, G I Timofeeva, S A Pavlova, Ya S Vygodskii, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. A* **19** 346 (1977)
231. E V Kamzolkina, P P Nechaev, Ya S Vygodskii, G E Zaikov *Dokl. Akad. Nauk SSSR* **233** 156 (1977)
232. S V Vinogradova, Ya S Vygodskii, V V Korshak, T N Spirina *Acta Polymer* **30** 3 (1979)
233. A A Tager, L K Kolmakova, S A Vshivkov, E V Kremlyakova, Ya S Vygodskii, S N Salazkin, S V Vinogradova *Vysokomol. Soedin., Ser. B* **19** 738 (1977)
234. V V Korshak, S S Novikov, S V Vinogradova, A P Khardin, I A Novakov, B S Orlinson, S S Radchenko *Vysokomol. Soedin., Ser. B* **21** 248 (1979)
235. S G Andreeva, A A Tager, V I Konevets, O V Glukhikh, Ya S Vygodskii, V V Korshak, S V Vinogradova *Vysokomol. Soedin., Ser. A* **21** 2229 (1979)
236. USSR P. 250 454; *Ref. Zh. Khim.* 19 S 309P (1970)
237. USSR P. 267 893; *Ref. Zh. Khim.* 5 S 338P (1971)
238. USSR P. 410 057; *Byull. Izobret.* (1) 89 (1974)
239. USSR P. 412 212; *Byull. Izobret.* (3) 100 (1974)
240. USSR P. 526 641; *Byull. Izobret.* (32) 78 (1976)
241. USSR P. 531 819; *Byull. Izobret.* (38) 77 (1976)
242. USSR P. 565 045; *Byull. Izobret.* (26) 50 (1977)
243. USSR P. 615 100; *Byull. Izobret.* (26) 81 (1978)
244. USSR P. 790 725; *Byull. Izobret.* (3) 279 (1983)
245. USSR P. 696 759; *Byull. Izobret.* (20) 259 (1981)
246. Ya S Vygodskii, S V Vinogradova, V V Korshak, Z M Nagiev, G Reinisch, G Rafler, Ya G Urman, in *Tezisy 8-go Mezhdunar. Simpoziuma po Polikondensatsii, Alma-Ata, 1981* (Abstracts of the Eighth International Symposium on Polycondensation, Alma-Ata, 1981) p. 91
247. Ya S Vygodskii, Z M Nagiev, V A Adigezalov, Sh T Bagirov, Ya M Nagiev, in *Tezisy 22-i Vsesoyuznoi Konferentsii po Vysokomolekulyarnym Soedineniyam, Alma-Ata, 1985* (Abstracts of the 22nd All-Union Conference on High-Molecular-Mass Compounds, Alma-Ata, 1985) p. 70
248. E M Belavtseva, L G Radchenko, Ya S Vygodskii, N A Churochkina *Vysokomol. Soedin., Ser. B* **24** 374 (1982)
249. L G Gladkova, E F Kolpikova, Ya S Vygodskii, A S Fialkov *Usp. Khim.* **57** 1742 (1988) [*Russ. Chem. Rev.* **57** 999 (1988)]
250. S N Khar'kov, Z N Lavrova, G A Tintsova, E P Krasnov, A S Chegolya, in *Proizvodstvo Sinteticheskikh Volokon* (Production of Synthetic Fibres) (Moscow: Khimiya, 1971) p. 289
251. L G Gladkova, E F Kolpikova, A S Fialkov, Ya S Vygodskii *Plast. Massy* (8) 70 (1989)
252. E V Lyamskaya, D V Pebak, B V Kotov, Ya S Vygodskii, A N Pravednikov *Vysokomol. Soedin., Ser. B* **29** 228 (1987)
253. A S Fialkov, E F Kolpikova, L G Gladkova, D S Konstantinova, Ya S Vygodskii, S V Vinogradova, V V Korshak *Vysokomol. Soedin., Ser. B* **27** 818 (1985)
254. V V Korshak, V V Lyashevich, V V Rode, Ya S Vygodskii *Vysokomol. Soedin., Ser. A* **22** 2559 (1980)
255. Ya S Vygodskii, L I Komarova, Yu V Antipov, V V Kazantseva, A V Davydov *Izuchenie Vzaimodeistviya Epoksidnykh Oligomerov s Poliimidami* (Investigation of the Interaction of Epoxy-Oligomers with Polyimides) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No 2342, Moscow, 1990
256. L I Titova, Z M Nagiev, A P Tyutnev, V S Saenko, Ya S Vygodskii *Acta Polymer* **35** 247 (1984)
257. V M Andreeva, A A Tager, B I Lirova, V I Konovets, O V Glukhikh, Ya S Vygodskii, S V Vinogradova, V V Korshak *Acta Polymer* **31** 727 (1980)
258. Z M Nagiev, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1983
259. G S Gurbich, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1981
260. V A Adigezalov, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1981
261. Z V Gerashchenko, Candidate Thesis in Chemical Sciences, Mendeleev Moscow Chemical Technological Institute, Moscow, 1972
262. T N Spirina, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1978
263. N A Churochkina, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1972
264. Yu V Antipov, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1990; Ya S Vygodskii, L I Komarova, Yu V Antipov *Vysokomol. Soedin., Ser. A* **37** 197 (1995)
265. V V Korshak, S V Vinogradova, T A Burtseva, P M Valetskii, V I Stanko, M S Klebanov *Vysokomol. Soedin., Ser. A* **17** 959 (1975)
266. Ya S Vygodskii, L G Gladkova, E F Kolpikova, in *Abstracts of the Fifth International Conference on Polyimides. New Trends in Polyimide Science and Technology* (New York, 1994) p. 116
267. A A Askadskii, in *Abstracts of the Fifth International Conference on Polyimides. New Trends in Polyimide Science and Technology* (New York, 1994) p. 105
268. E D Molodtsova, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1982
269. Ya S Vygodskii, T N Panova, S V Vinogradova *Vysokomol. Soedin.* **38** (1996) (in the press)
270. A L Rusanov, in *Advances in Polymer Chemistry* (Moscow: Mir, 1986) p. 159
271. D R Tur, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, Moscow, 1970; USSR P. 221 276; *Byull. Izobret.* (21) 92 (1968)
272. S V Vinogradova, D R Tur *Vysokomol. Soedin., Ser. A* **15** 284 (1973)
273. S V Vinogradova, V V Korshak, D R Tur *Vysokomol. Soedin., Ser. B* **10** 396 (1968)
274. S V Vinogradova, D R Tur, V V Korshak, E S Krongauz *Izv. Akad. Nauk SSSR, Ser. Khim.* 2827 (1968)
275. V V Korshak, S V Vinogradova, D R Tur *Izv. Akad. Nauk SSSR, Ser. Khim.* 439 (1969)
276. V V Rodez, E M Bondarenko, V V Korshak, S V Vinogradova, D R Tur *Izv. Akad. Nauk SSSR, Ser. Khim.* 1509 (1969)
277. V V Korshak, V M Mamedov, G E Golubkov, D R Tur *Vysokomol. Soedin., Ser. B* **12** 57 (1970)
278. G I Timofeeva, S A Pavlova, S V Vinogradova, D R Tur *Vysokomol. Soedin., Ser. A* **13** 2653 (1971)
279. S A Pavlova, G I Timofeeva, V V Korshak, S V Vinogradova, D R Tur, D Sharoshi *Vysokomol. Soedin., Ser. A* **13** 2643 (1971)
280. V V Korshak, G L Berestneva, S V Vinogradova, M S Gergaya, D R Tur *Khim. Geterotsikl. Soedin.* 1457 (1971)
281. S V Vinogradova, V V Korshak, D R Tur *Vysokomol. Soedin., Ser. A* **14** 915 (1972)
282. L A Pankratova, G I Timofeeva, V V Korshak, S A Pavlova, D R Tur, S V Vinogradova *Vysokomol. Soedin., Ser. A* **16** 2666 (1974)
283. V V Korshak, S A Pavlova, D R Tur, G I Timofeeva, L A Pankratova, S V Vinogradova *Vysokomol. Soedin., Ser. A* **17** 486 (1975)
284. I P Bragina, V V Korshak, G L Berestneva, S V Vinogradova, D R Tur, V A Khomutov, V V Krylov *Vysokomol. Soedin., Ser. A* **18** 2318 (1976)

285. G Borisov, S Sivriev, V V Korshak, S V Vinogradova, D R Tur *Faserforsh. Textiltech.* **28** 601 (1977)
286. P V Karyakin, V N Sapozhnikov, G P Kamelova, V V Korshak, G L Berestneva, D R Tur *Vysokomol. Soedin., Ser. A* **21** 18 (1979)
287. V V Korshak, G I Timofeeva, I A Ronova, D R Tur, S V Vinogradova *Vysokomol. Soedin., Ser. A* **21** 74 (1979)
288. V V Lyashevich, V V Korshak, D R Tur, V V Rode *Vysokomol. Soedin., Ser. A* **22** 2211 (1980)
289. I A Gribova, V V Korshak, L S Fedorova, L I Komarova, G E Morozova, D R Tur, N E Kolobova, Ya V Genin *Vysokomol. Soedin., Ser. A* **23** 2294 (1981)
290. V V Korshak, S A Pavlova, P N Gribkova, I A Gribova, O V Vinogradova, L L Chatova, S V Vinogradova, D R Tur, I V Zarubina *Vysokomol. Soedin., Ser. A* **27** 161 (1985)
291. V V Korshak, S V Vinogradova, D R Tur, V A Khomutov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2721 (1969)
292. V V Korshak, S A Pavlova, D R Tur, G I Timofeeva, L A Pankratova, S V Vinogradova *Issledovanie Nekotorykh Zakonomernostei Obrazovaniya Poligidrazidov na Primere Poli-(4,4′-difenilenftalid)digidrazida* [Investigation of Certain Characteristic Features of the Formation of Polyhydrazides in Relation to Poly(4,4′-diphenylenephthalide) Dihydrazide] Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) No 5876, Moscow, 1973
293. USSR P. 389 118; *Byull. Izobret.* (29) 95 (1973)
294. USSR P. 513 053; *Byull. Izobret.* (17) 86 (1976)
295. Bulg. P. 25 013; *Byull. Izobret.* (7) (1978); *Ref. Zh. Khim.* 18 S 370P (1979)
296. V V Korshak, S V Vinogradova, L A Glivka, P M Valetskii, V I Stanko *Vysokomol. Soedin., Ser. A* **15** 1495 (1973)
297. A N Frazer, F T Wallenberger, W G Sweeny *J. Polym. Sci., Part A* **2** 1157 (1964)
298. Y Iwakura, K Uno, S Hara *J. Polym. Sci., Part A* **3** 45 (1965)
299. A L Rusanov, V V Korshak, E S Krongauz, I B Nemirovskaya *Vysokomol. Soedin.* **8** 804 (1966)
300. E S Krongauz, V V Korshak, A L Rusanov, B V Lokshin *Vysokomol. Soedin., Ser. A* **9** 87 (1967)
301. *Novye Termostoikie Materialy "Niplon-1" i "Niplon-2"* (The New Heat-Resistant Materials 'Niplon-1' and 'Niplon-2') Exhibition of National Economic Achievement, USSR, Moscow, 1977
302. *Termostoikie Materialy "Niplon-1" i "Niplon-2"* (The Heat-Resistant Materials 'Niplon-1' and 'Niplon-2') (Moscow: Soyuzkhimeksport Vneshtorgizdat)
303. USSR P. 448 205; *Byull. Izobret.* (40) 50 (1974)
304. USSR P. 413 162; *Byull. Izobret.* (4) 67 (1974)
305. USSR P. 361 185; *Byull. Izobret.* (1) 59 (1973)
306. USSR P. 398 580; *Byull. Izobret.* (38) 77 (1973)
307. G I Timofeeva, V V Korshak, S A Pavlova, G M Tseitlin, N S Zabel'nikov, K A Krishtul *Vysokomol. Soedin., Ser. B* **15** 428 (1973)
308. V V Korshak, V A Khomutov, N S Zabel'nikov, V G Danilov, Yu E Doroshenko, G M Tseitlin *Vysokomol. Soedin., Ser. A* **16** 2671 (1974)
309. A A Izyneev, V P Mazurevskii, A D Markov, V V Korshak *Dokl. Akad. Nauk SSSR* **231** 1126 (1976)