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Cardopolymers (Loop Polymers)

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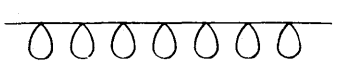
Polymers containing bulky side groups linked in ring form to the main chain are distinguished by a specific set of properties (cardopolymers). The review deals with the characteristics of the synthesis and with the physicochemical properties of cardopolycarbonates, cardopolyarylates, cardopolyamides, cardopolyimides, cardopoly-1,3,4-oxadiazoles, carbonchain cardopolymers, etc. The bibliography includes 232 references.

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I. INTRODUCTION

The set of physicochemical properties of polymers is in many ways determined by their chemical structure. Recently studies have been made in the field of polymers containing in the repeat units of the chain at least one element entering into the composition of a cyclic side group. It has been suggested[1] that such polymers be called cardopolymers from the latin word "cardo" (loop), since such groups can be regarded as loops in relation to the main chain of the macromolecule:



Naturally the properties of cardopolymers are influenced also by the structure of the main polymer chain. However, the presence in various types of heterochain and carbonchain polymers of cardo-groups imparts to them specific properties: a combination of enhanced heat resistance with excellent solubility, which is particularly important for rigid-chain aromatic heterocyclic polymers.

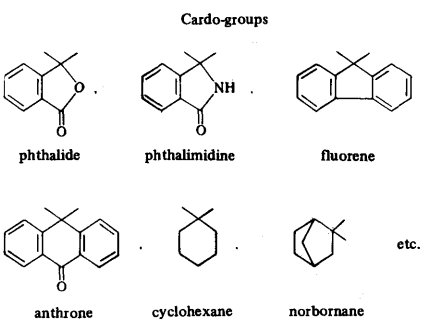
As early as the 1930's, Wagner[2] mentioned in his list of different initial compounds (diols) the possibility of employing phenolphthalein for the synthesis of polyesters. Data concerning the synthesis of resin-like products of complex composition from phenolphthalein were published in a number of reports[3-5].

A few of the early studies dealt with the products of the condensation of formaldehyde and phenolphthalein[6-10]. In 1946 a report was published on the synthesis of alkyd polymers of fluorescein and phenolphthalein[11] and two years later polymers were obtained by the polymerisation of diallylphenolphthalein dicarbonate[12]. Later data were published on the semiconductor properties of polymers prepared by heating phenolphthalein with $ZnCl_2$ at 256° and 306°C[13] and also on the epoxy-polymers based on phenolphthalein[14-18].

A characteristic feature of the above investigations is that phenolphthalein—the starting material for the synthesis of particular polymers—was used as a member of the enormous class of diols without taking into account its specific contribution to the properties of the polymer.

Systematic studies on cardopolymers as such probably began with the synthesis of high-molecular-weight polyarylates from phenolphthalein and various dicarboxylic acids in 1961 when, essentially for the first time, attention was turned to the specific contribution of the phthalide cardo-group to the formation of the set of properties of heterochain polymers[19,20].

So far numerous cardopolymers with ester, amide, imide, 1,3,4-oxadiazole, ether, etc. groups have been synthesised:



The introduction of cardo-groups into polyesters, polyethers, aromatic polyamides, heterocyclic polymers[21-25], and carbonchain polymers imparted to them many specific properties and made it possible to investigate characteristics which could not be estimated using polymers without such groups. In recent years the manufacture of first examples of cardopolymers (cardopolyarylates) has begun in the USSR on an experimental industrial scale.

Among the monomers with cardo-groups, perhaps only phenolphthalein [3,3-bis-(*p*-hydroxyphenyl)phthalide] is an industrial product employed in analytical chemistry and as a medicinal preparation. Other bi- or poly-functional compounds of the cardo-type have been studied much less, and frequently the information about them (before their employment in the synthesis of polymers) was restricted to one or two reports. Many cardomonomers were altogether unknown previously and were synthesised specially for the preparation of cardopolymers, for example 9,9-bis-(*p*-carboxyphenyl)-10-anthrone[26], the dianhydride of 3,3-bis-(3′,4′-dicarboxyphenyl)phthalide[27], and 2-(β-hydroxyethyl)-3,3-bis-(*p*-hydroxyphenyl)phthalimidine[28].

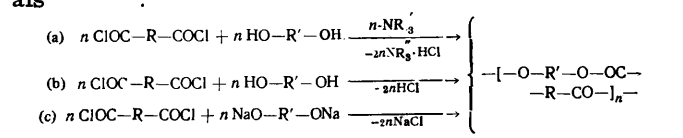
II. SYNTHESIS

The usual methods for the formation of polymers of a particular type are used as a rule to synthesise cardopolymers. Therefore in the present review attention has been

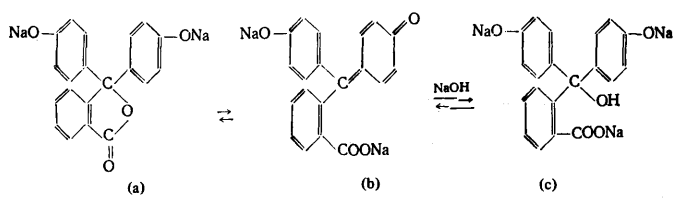
concentrated on those characteristics of the synthesis which are due to the specific features of the structure and behaviour of cardomonomers and cardopolymers. In addition certain general characteristics of the synthesis of the polymers of various classes have been traced using cardopolymers as an example and phenomena useful for the understanding of the reaction mechanism have been discovered; these findings have also been reflected in the review.

1. Bisphenol Polyesters

Bisphenol polyesters are obtained nowadays with the aid of different types of non-equilibrium polycondensations such as (a) low-temperature (acceptor-catalytic) polycondensation, (b) high-temperature polycondensation in solution, and (c) interfacial polycondensation using dicarboxylic acid chlorides and bisphenols as the starting materials[2,25,29-32]:



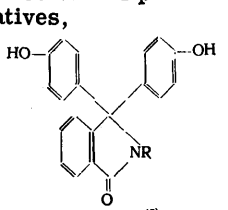
All these methods are also applicable to the preparation of cardopolyarylates. In many cases, when these polymers are synthesised by interfacial polycondensation, account must be taken of the specific features of the behaviour of cardomonomers such as phenolphthalein in aqueous alkaline media. The structure of phenolphthalein in an aqueous alkaline solution is known to depend on the amount of alkali present:



The formation of polyarylates without quinonoid structures in the interfacial polycondensation of phenolphthalein and dicarboxylic acid chlorides shows that a rearrangement or a shift of equilibrium between forms (B) and (A) takes place during the reaction and leads to the retention of the lactone ring in phenolphthalein[25,33,34].

The phthalide structure is characteristic of the glycidyl ether of phenolphthalein[35], which is formed in an alkaline medium, and of aromatic phenolphthalein polyethers obtained by the nucleophilic substitution of activated halogen-containing aromatic compounds[36,37]. The existence of cardobisphenols such as fluorescein or phenolsulphophthalein in the form of a mixture of isomers (in the quinonoid and lactone forms) even in a neutral medium hinders the synthesis of high-molecular-weight polymers based on them.

The replacement of phthalide derivatives by phthalimidine derivatives,



(R=H; Ph, ETOH etc.).

(I)

which do not undergo changes in an alkaline medium associated with formation of a quinonoid structure, makes it possible to synthesise high-molecular-weight polyarylates by interfacial polycondensation under the usual conditions[38]. One should only note that in the interfacial polycondensation of 2-(β-hydroxyethyl)-3,3-bis-(*p*-hydroxyphenyl)phthalimidine and isophthalic or terephthalic acid chlorides[39] in the presence of more than two moles of alkali, not only the phenolic but also the alcoholic hydroxyl is acylated, which leads to the formation of a cross-linked polymer.

Cardopolyarylates are usually synthesised by acceptor-catalytic polycondensation whereby it is possible to obtain high-molecular-weight polymers under mild conditions in a short time[25,39,40,41]. Much attention has been devoted to the study of the mechanism and characteristics of this process[31,32,40-47]. In contrast to interfacial polycondensation, where the behaviour of phenolphthalein is unusual, in acceptor-catalytic polycondensation in anhydrous solvents the structure of phenolphthalein does not change even in the presence of highly basic tertiary amines.

The greatest number of cardopolyarylates have been synthesised by the high-temperature polycondensation of dicarboxylic acid chlorides and bisphenols in organic solvents. The kinetics of this reaction have been investigated for the interaction of terephthalic acid chloride and 9,9-bis-(*p*-hydroxyphenyl)fluorene and other polycyclic bisphenols, which led to the suggestion of an ionic mechanism for this reaction, including the formation of an acylium ion[48,49]. Cardopolyarylates are synthesised in ditolylmethane[19,20], sovol[50-56] (a mixture of tetra- and pentachlorobiphenyls), α-chloronaphthalene[56], *o*-dichlorobenzene[57], 1,2,4-trichlorobenzene[57], nitrobenzene[57], etc. at a concentration of the starting materials in the range 0.6–5.0 M in the temperature range 180–220°C for several hours and in many cases also at higher temperatures (see below).

It is noteworthy that, whereas in the polycondensation of phenolphthalein and aromatic dicarboxylic acid chlorides in ditolylmethane the polyarylate precipitates from the reaction medium during its formation in the form of a thick sparingly soluble mass, in the synthesis of polyarylates in a medium which dissolves the polymer unfolded rigid macromolecular conformations are produced preferentially which results in the formation of fibrous structures, while the polymer synthesised in ditolylmethane is made up of not altogether regular globular ~ 1000 Å particles, which in turn consist of still smaller also nearly spherical 30–40 Å particles[57].

Thus in the synthesis of polymers with rigid macromolecular chains, it is necessary to make a correct choice of the reaction medium bearing in mind its influence on the selection of particular macromolecular conformations during the synthesis.

In the synthesis of crystallisable cardopolyarylates[59,60], particularly the polyarylate produced from 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone and terephthalic acid, the process conditions affect not only the molecular weight but also the structure of the polymer. It is most crystalline when the polycondensation is carried out at 220°C in Sovol, 1,2,4-trichlorobenzene, and similar solvents; the polymer is obtained in amorphous form on rapid heating of a 0.6 M solution of the starting materials in Sovol at 330°C, the solution being kept at this temperature for 1 h with subsequent rapid cooling of the reaction mass to room temperature[60].

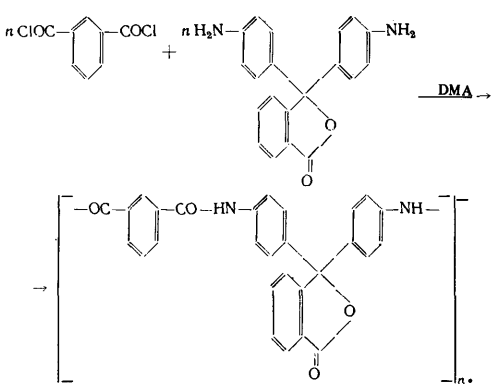
High-molecular-weight thermoreactive mixed polyarylates based on phenolphthalein, aromatic dicarboxylic acid chlorides, trihydric alcohols (for example trishydroxymethylpropane), the chlorides of unsaturated dicarboxylic

acids, for example fumaric acid, or 2,2-di-(3-allyl-4-hydroxyphenyl)propane[61,62] have been synthesised.

2. Aromatic Polyamides

The low basicity of aromatic diamines, including cardodiamines, and the high softening temperatures of cardopolyamides rule out the possibility of their successful formation by polycondensation in the melt. The method of interfacial polycondensation is also relatively unsuitable owing to the low solubility of cardodiamines and even their hydrochlorides in water. Cardopolyamides have been obtained by interfacial polycondensation only on the basis of 3,3-bis-(*p*-carboxyphenyl)phthalide and aliphatic diamines[63,64].

Cardopolyamides are usually synthesised by the low-temperature polycondensation of dicarboxylic acid chlorides and primary diamines in aprotic dipolar solvents, for example *NN*-dimethylacetamide (DMA) and *N*-methylpyrrolidinone (NMP) which function both as solvents for the starting materials and the polymers and as acceptors for the hydrogen chloride liberated[63-67], for example:



Polymers with the highest molecular weight are obtained by adding the solid acid chloride to a solution of the diamine between −10° and −30°C and stirring the reaction mixture at this temperature for 15–60 min. Although the high solubility of cardoamides makes it unnecessary to introduce into the reaction medium inorganic salts (LiCl), which are often used in the synthesis of other aromatic polyamides and when they are extruded as fibres from solutions.

3. Polyimides

Cardopolypyromellitimides obtained from anilinephthalein [3,3-bis-(*p*-aminophenyl)phthalide] and its imide were the first soluble examples of these extremely heat-resistant polymers[68,69]. Like other polyimides, they are synthesised by two-stage polycondensation with thermal cyclodehydration of the high-molecular-weight polyaminoacid obtained beforehand[68,69]. In the synthesis of cardopolyimides, it was shown that the heat treatment of polyaminoacids entails, together with intramolecular cyclisation, also solid-phase polycyclisation involving the terminal anhydride and amino-groups, leading to an increase of the molecular weight of the polyimide[70].

Single-stage high-temperature polycyclisation in an organic solvent (nitrobenzene, benzonitrile, α-chloronaphthalene, sulpholane, cresol, etc.) has been used successfully to synthesise high-molecular-weight soluble cardopolyimides[71-74]. The difference of this method from the two-stage version is that in the single-stage polycyclisation the growth of the polymer chain (the polymerisation reaction proper) takes place simultaneously with ring closure. This has been demonstrated both by kinetic studies (the rate of reaction is limited by the formation of the amidoacid and not by its cyclodehydration[75,76]) and by the discovery that the molecular weight of the polyimide increases slowly and gradually with duration of the reaction[73,74]. It has been shown for the reaction of anilinephthalein with pyromellitic anhydride and also of anilinephthalein and 9,9-bis-(*p*-aminophenyl)fluorene with the dianhydride of di-(3,4-dicarboxyphenyl) ether in nitrobenzene at 180°C that the rate of reaction is more sensitive to the change in the nature of the tetracarboxylic acid dianhydride than in the diamine[75,76].

It is noteworthy that single-stage high-temperature polycyclisation is applicable also to the synthesis of other high-molecular-weight soluble or insoluble and fusible or infusible polyimides[77,78].

The formation of polyimides from tetracarboxylic dianhydrides and primary diamines is a reversible reaction[72,73,76]. Therefore, in order to obtain high-molecular-weight polyimides, it is necessary to remove from the reaction medium as far as possible the water formed on cyclisation, which is achieved in high-temperature cyclisation by raising the reaction temperature and by carrying out the process in a stream of an inert gas, by binding the water with chemical agents (acid anhydrides and chlorides, carbodi-imides, etc.), and by employing a vacuum in the two-stage process.

High-molecular-weight cardopolyimides are also obtained by the cyclisation in solution of high-molecular-weight polyamidoacids in the presence of a mixture of carboxylic acid anhydrides and tertiary amines at 20–100°C without the intermediate formation of the final moulded objects from the polyamidoacids[79].

Cardopolyimides have also been successfully synthesised[80,81] by two-stage polycyclisation of the dichlorides of tetracarboxylic acid diesters and primary diamines. Cyclisation of the intermediates (polyamidoesters) which are much more resistant to hydrolysis than polyamidoacids, leads to the formation of carbopolyimides with higher molecular weight than those obtained by the cyclodehydration of the corresponding polyamidoacids, best results being obtained by the cyclisation of polyamidoesters in nitrobenzene at 210°C or by treatment in solution in amide-type solvents with a mixture of acetic anhydride and pyridine. The cyclisation of polyamidoesters is also a reversible process[80] since polyimides readily undergo methanolysis.

The study of the kinetics of the solid-phase polycyclisation of cardopolyamidoesters in films showed that the process follows first-order kinetics in the initial stage, the rate of cyclisation increasing with the basicity of the diamine used to prepare the polyamidoester ($k_c = 7.10 \times 10^{-2}$ and 3.10×10^{-2} min^{-1} at 200°C for the polypyromellitamidoesters derived from 9,9-bis-(*p*-aminophenyl)fluorene and anilinephthalein respectively[82]).

4. Poly-1,3,4-oxadiazoles

Cardopoly-1,3,4-oxadiazoles have been synthesised using 3,3-bis-(*p*-carboxyphenyl)phthalide and its derivatives (the dichloride and the dihydrazide) as the starting materials[83-86]. Two methods were chosen for its synthesis and investigated: a two-stage method designed to

prepare high-molecular-weight polyhydrazides with subsequent cyclodehydration and single-stage polycyclisation in polyphosphoric acid (PPA).

The characteristics of the low-temperature polycondensation of the dihydrazide and the dichloride of 3,3-bis-(*p*-carboxyphenyl)phthalide and also of either of these compounds coupled with the corresponding derivatives of other dicarboxylic acids are similar to those of the formation of other polyhydrazides with the sole difference that the high solubility of cardopolyhydrazides makes it possible to carry out the reaction not only in hexamethylphosphoramide but also in solvents such as NMP and DMA. It is also noteworthy that in the synthesis of mixed polyhydrazides the reaction takes place more successfully when one of the initial dihydrazides is that of 3,3-bis-(*p*-carboxyphenyl)phthalide coupled with the chloride of another acid. This is probably due to the higher solubility of the dihydrazide compared with the dihydrazides of many other aromatic dicarboxylic acids, the higher rate of the main process, and the consequent decrease of the contribution by side reactions.

Apart from the thermal cyclisation of polyhydrazides, which requires extremely high temperatures, the chemical cyclisation method for the conversion of cardopolyhydrazides into poly-1,3,4-oxadiazoles has become possible and has proved extremely effective. It consists in the treatment of the polyhydrazide in solution at 100°C for 5 h with the dimethylformamide (DMF)–sulphur trioxide complex[86]. The resulting polymer is identical in structure to the poly-1,3,4-oxadiazole obtained by the thermal cyclodehydration of the polyhydrazide at 300°C for 35 h in a vacuum of 10^{-3} mmHg.

A particularly successful method of synthesising solid cardopoly-1,3,4-oxadiazoles is single-stage polycyclisation in PPA at 140–150°C for 5 h.[86] An unusual feature of the synthesis of cardopoly-1,3,4-oxadiazoles in PPA consists in the fact that soluble linear polymers are formed only when equimolar amounts of 3,3-bis-(*p*-carboxyphenyl)phthalide and its dihydrazide interact. This is because in the reactions according to other generally adopted schemes, based on the acid and hydrazinium sulphate or the acid dihydrazide alone, there are side reactions between the lactone ring and hydrazine or the dihydrazide[86]. The molecular weight of the polymer depends on the concentration of phosphorus pentoxide in PPA, increasing markedly with the latter, starting from about 82%.

The study of the formation of poly-1,3,4-oxadiazoles also shows that the method of synthesis affects the structure of the polymer[87]. Thus, in contrast to the insoluble crystalline poly(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneoxy-1,4-phenylene) obtained by the thermal cyclisation of the corresponding polyhydrazide, in the single-stage polycyclisation in PPA the product is an amorphous polymer soluble in a *sym*-tetrachloroethane–phenol mixture (3 : 1, w/w).[87]

5. Other Polymers

Aromatic cardopolyethers derived from phenolphthalein, obtained by the nucleophilic substitution of activated aromatic dihalogeno-compounds and alkali metal bisphenoxides in dimethyl sulphoxide (DMSO)[36], were already mentioned above. The formation of polyethers from cardobisphenols (phenolphthalein, 9,9-bis-(*p*-hydroxyphenyl)fluorene proceeds less vigorously than the reaction with bisphenols such as 2,2-di-(*p*-hydroxyphenyl)propane, which may be due both to the reduced reactivity of the former owing to the high acidity of cardobisphenols and to the heterogeneity of the reaction medium owing to the low solubility of such alkali metal bisphenoxides. High-molecular-weight polyethers based on cardobisphenols have been obtained using as the initial dihalogeno-compound di-(*p*-fluorophenyl) sulphone and 4,4′-difluorobenzophenone, which are more reactive than their chlorinated analogues, and at higher temperatures (170–185°C) than other polyethers[36].

Despite the opening of the lactone ring of phenolphthalein in alkaline media (see above), aromatic polyethers based on it are soluble, have high molecular weights, and their lactone rings remain unaffected, which rules out the possibility of reaction between the dihalogeno-compound and the carboxy anion of the open-chain form of phenolphthalein [(B) and (C), see p.552]. Owing to the reactivity of the NH-group of the lactim ring of 3,3-bis-(*p*-hydroxyphenyl)phthalimidine in the formation of the polyester from it and di-(4-fluorophenyl) sulphone, the NH group is also involved in the reaction, which results in the formation of an insoluble and probably structured polymer.

The preparation of soluble and fusible aromatic homo- and mixed cardopolyanhydrides from 3,3-bis-(*p*-carboxyphenyl)phthalide by low-temperature polycondensation in solution has been described[88]. The chloride of 3,3-bis-(*p*-carboxyphenyl)phthalide or a mixture of this chloride with 3,3-bis-(*p*-carboxyphenyl)phthalide are employed for the synthesis of homopolyanhydrides. In the first case, the polycondensation is achieved in the presence of water.

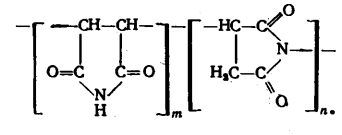
Cardobisphenols [phenolphthalein, fluoroscein, *o*-cresolphthalein, 1,1-bis-(*p*-hydroxyphenyl)cyclohexane, etc.] have been used successfully to synthesise thermoreactive polymers of the phenol-formaldehyde type[89–92]. Owing to the insolubility of such bisphenols in water, the polymers were formed in solvents such as DMF and n-propyl alcohol[89] in the presence of aqueous ammonia as a catalyst. The polymers become infusible and insoluble on heating at 160–180°C.

Many high-molecular-weight (with M_W up to 100 000 and above) carbon chain cardopolymers have also been synthesised: polymethylenephthalide, polymethylenephthalimidine, polyacenaphthene, etc.[92–98] They are synthesised by the usual polymerisation methods: the high melting point of the monomers hinders polymerisation in bulk, since such polymerisation requires the initial fusion of the monomer.

It has been shown that the resistance of methylenephthalimidines to polymerisation is lower than that of methylenephthalide, which is probably due to the greater steric hindrance in the former monomer.

An unusual monomer of the cardo-type is maleic anhydride the capacity of which for homopolymerisation was clearly demonstrated as late as 1961–1963.[99–103] It was established that maleic anhydride polymerises via a radical mechanism under the influence of γ-radiation or in the presence of a high sensitiser concentration (for example 5% benzoyl peroxide).

Maleimide, the nitrogen analogue of maleic anhydride, polymerises via radical and ionic mechanisms[104,105], the ionic polymerisation proceeding partly with migration of hydrogen atoms and the formation of a polymer with the following structure[105]:



III. PROPERTIES

We shall consider initially the effect of the chemical structure of the polymer on its heat resistance and solubility. The joint examination of such seemingly different properties is not fortuitous, since the effect of cardo-groups has the greatest influence precisely on these polymer characteristics.

One of the ways of obtaining heat resistant polymers is the synthesis of rigid-chain macromolecules with large segments, which leads to high glass temperatures. In many cases the glass temperature of rigid-chain polymers may be above the temperature of the onset of their vigorous decomposition and the latter then determines the temperature range in which the polymer may be used.

Thus there is a serious contradiction between the attempt to create the most heat resistant polymer and the possibility of moulding it into finished articles: the higher the heat resistance of the polymer the more difficult it is to mould its melt by the usual methods. One of the ways of overcoming this difficulty involves the formation of articles from highly heat-resistant polymers in solution, which requires the creation of polymers combining a high rigidity of its component macromolecules and a high solubility†.

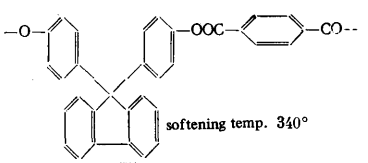
The introduction of various rings into the main macromolecular chain, the enhancement of the intermolecular interaction owing to polar groups and hydrogen bonds, the introduction of cyclic side groups, the crystallisation of the polymer, an increase in the degree of order in the supermolecular structure, the employment of starting compounds with a symmetrical structure (for example the replacement of isophthalic acid by terephthalic acid), the formation of chemical cross-links between linear macromolecules, a regular distribution of chain units, conversion into stereoregular polymers, etc. lead to an increase of the heat resistance of linear polymers.

Solubility is improved mainly by the conversion of the polymer into an amorphous form, an increase of the rigidity of the macromolecular chain, the introduction of polar groups with an affinity for the solvent (i.e. leading to a positive heat of mixing), the introduction of various substituents "loosening" the polymer structure, the introduction of cyclic side groups containing polar groups with an affinity for the solvent, the breakdown in the order of alternation of chain units and the introduction of units of different kinds, etc. In many cases one of these factors is insufficient for a significant improvement of the solubility—a combination of various factors is necessary.

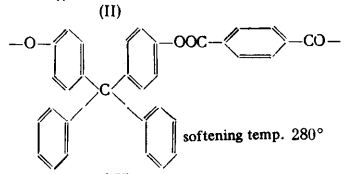
Comparison of the factors leading to an improvement of heat resistance and of solubility shows that some of these improve one property and impair the other (for example a decrease of rigidity improves solubility but lowers heat resistance, etc.) It would be most interesting to achieve a simultaneous increase of the heat resistance of polymers and of their solubility. This can be done by introducing cyclic side groups into the macromolecule. An appreciable effect is obtained when cardo-groups are introduced.

† Therefore infusible and insoluble, as a rule heterocyclic, polymers are moulded mainly at an intermediate stage of their synthesis—the soluble pre-polymers (polyamidoacids, polyhydrazides, etc.)—which has its disadvantages relating to the removal of water and the solvent, which impairs the integrity of the finished article, and a number of other unfavourable complications[72,106].

The superior heat resistance of the polyterephthalate of 9,9-bis-(*p*-hydroxyphenyl)fluorene (II) compared with the polyterephthalate of 4,4′-dihydroxytetraphenylmethane (III) is instructive in this sense:



(II)



(III)

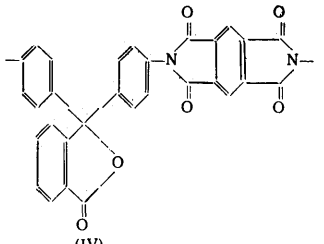
As already stated, one of the ways of increasing heat resistance is crystallisation of the polymer. Since many cardopolymers have an amorphous structure, it has come to be believed that the increase of the rigidity of the polymer chain as a result of the introduction of cardo-groups and crystallisation are largely mutually exclusive factors, since crystallisation requires the presence of chains with a symmetrical structure and a powerful interaction between the chains, while bulky substituents, such as cardo-groups in particular, hinder it[106]. That this is a mistaken view was demonstrated subsequently by the synthesis of crystallisable polyarylates derived from 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone, the structure of which may be varied both by the conditions of synthesis and by the conditions in the subsequent treatment of the polymer[59,60]. Other cardopolymers in different structural forms can also be obtained, for example polyarylates derived from 9,9-bis-(*p*-hydroxyphenyl)fluorene and 1,1-bis-(*p*-hydroxyphenyl)-cyclohexane[107]. These factors, in conjunction with the finding that polyarylates from phenolphthalein as well as other cardopolyheteroarylenes containing phthalide groups are amorphous non-crystallisable polymers lead to the hypothesis, based on the asymmetric structure of the phthalide group, that the structure of such polymers resembles that of atactic polymers. Like atactic polymers, cardopolymers with phthalide groups in the chain contain an asymmetric substituent distributed at random.

Presumably under certain conditions it is possible to achieve a stereoregular distribution of the phthalide groups and the formation of a crystalline polymer is then possible.

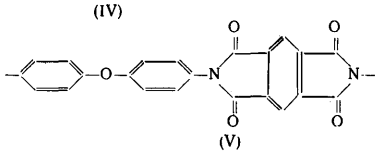
The crystallinity of cardopolymers and others must be taken into account when their properties are compared, since it affects[107] the heat resistance and the thermal stability of the polymers, their solubility, etc. Therefore, in order to compare polymers with different chemical structures, it is best to employ data for amorphous polymers.

As already stated, cardo-groups increase the rigidity of the main chain and loosen the polymer, which improves the solubility. The solubilisation of rigid-chain polymers such as polypyromellitimides due to cardo-groups appears particularly striking. Thus the polypyromellitimide derived from anilinephthalein (IV), which has a glass temperature of 485°C, is readily soluble in DMF, DMA, nitrobenzene, *sym*-tetrachloroethane, cresol, hexafluoroacetone sesquihydrate, etc., in contrast to the familiar

polyoxydiphenylenepyromellitimide (V), which is insoluble in known organic solvents:

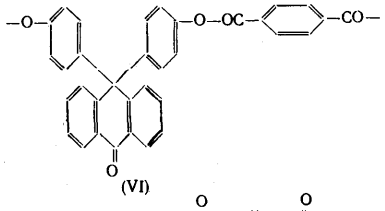


(IV)

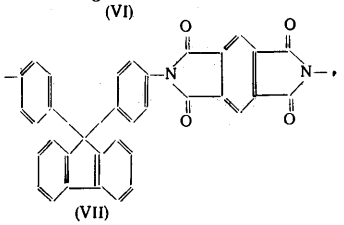


(V)

The solubility of cardopolymers with polar groups is much higher than that of polymers with less polar cardo-groups while their heat resistance is approximately the same. Thus the 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone polyarylate (VI) are more soluble than the 9,9-bis-(*p*-hydroxyphenyl)-fluorene polyarylate (II) despite their higher tendency towards crystallisation while the polypyromellitimide derived 9,9-bis-(*p*-aminophenyl)fluorene (VII) does not dissolve in any of the known organic solvents in contrast to the polyimide (IV):



(VI)



(VII)

1. Polycarbonates

The properties of cardopolycarbonates derived from bisphenols and based on 2-norbornanone and analogous ketones, cyclohexanone, etc. have been investigated in greatest detail[108-114]. Such polycarbonates have an amorphous structure and dissolve in chlorinated and saturated aliphatic hydrocarbons: CH_2Cl_2, $CHCl_3$, 1,2-dichloroethane, aromatic hydrocarbons (benzene and toluene), cyclohexanone, and dioxan; they swell in aliphatic ketones. Their enhanced solubility is probably associated with the large size of the non-planar cardo-group, which leads to an appreciable loosening of the polymer. At the same time, the presence of cardo-groups leads to an increase of the heat resistance of the polymers and it is interesting that the glass temperature increases with the dimensions of the cardo-group of the norbornane type. The high glass temperatures of such polycarbonates are due to the fact that the non-coplanar groups of the norbornane type, which are very bulky in various directions, cannot be oriented in any particular direction and therefore cannot "migrate" in the small space between the molecular chains to the same extent as, for example, alkyl or phenyl groups[108].

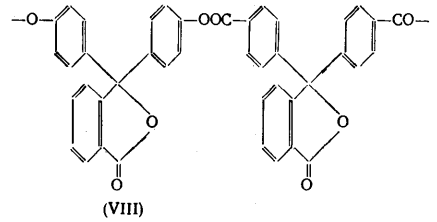
Polycarbonates derived from phenolphthalein and its derivatives show an even higher heat resistance while retaining a high solubility. The somewhat greater range of solvents for the polycarbonate from phenolphthalein compared with the polycarbonate from 3,3-bis-(*p*-hydroxyphenyl)phthalimidine is striking; this is probably due to intermolecular hydrogen bonds in the second polymer. At the same time it dissolves in chloroform, while the corresponding polyterephthalate is insoluble in chlorinated solvents owing to hydrogen bonding[115].

2. Polyarylates

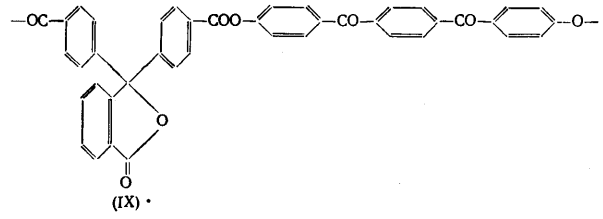
As already stated, the characteristics of cardopolymers were discovered for the first time for polyarylates; it is therefore natural that their properties have been investigated in greatest detail, which in turn required the synthesis of a wide variety of examples of this class of polymers differing in the nature of the cardo-group and other moieties of the macromolecule. They include polyarylates derived from phenolphthalein[19,20,34,54,116-127], 4,5,6,7-tetrachlorophenolphthalein[128], 3,3-bis-(*p*-hydroxyphenyl)phthalimidine[34,129-131], 3,3-bis-(*p*-hydroxyphenyl)-2-phenylphthalimidine[37,52,53,132], 2-ethyl-3,3-bis-(*p*-hydroxyphenyl)-phthalimidine[133], 2-(β-chloroethyl)-3,3-bis-(*p*-hydroxyphenyl)phthalimidine[134], phenolsulphophthalein[135], 9,9-bis-(*p*-hydroxyphenyl)fluorene[113,136-139], 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone[59,95,113,114,132], and many other cardobisphenols and dicarboxylic acids[56,140-149].

The main characteristic feature of these polymers is heat resistance, greatly exceeding the heat resistance of polyarylates which have a similar structure but do not contain cardo-groups. The polyarylates devised from 9,9-bis-(*p*-hydroxyphenyl)fluorene and 4,4'-dihydroxytetraphenylmethane were already compared above in this sense.

Another clear example is provided by the much higher heat resistance of polyarylate (VIII) (softening temperature 340°C)[150] compared with the isomeric polyarylate (IX) (270°C)[142]:



(VIII)

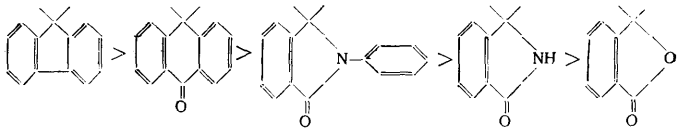


(IX)

The influence of the cardo-group on the softening temperature is shown particularly clearly in polyarylates synthesised from aliphatic dicarboxylic acids. Thus the softening temperatures of polyarylates from phenolphthalein

and 2,2-di-(*p*-hydroxyphenyl)propane on the one hand and sebacic acid on the other are 100° and 36°C respectively.

Estimation of the "intrinsic" contribution of various cardo-groups to a heat resistance of polyarylates showed that they can be arranged in the following series in terms of the decrease of their contribution[114]:



K_i/M 1.58 1.56 1.55 1.43 1.40

where K_i/M is the ratio of the "reduced" volume of the ring to its molecular weight[151]. Above it was stated that, depending on the nature of the solvent in which the polyarylates are synthesised, coiled or uncoiled conformations are produced, which entails the formation of globular (synthesis in a non-solvent medium) or fibrous (synthesis in a medium dissolving the polymer) forms of supermolecular structures respectively[50,51,57,152]. The supermolecular structure of polyarylates has a significant influence on the entire set of their physical properties. Table 1 shows that, for identical molecular weights, the specific impact strength of a polyarylate synthesised in "good" solvents (Sovol, α-chloronaphthalene, nitrobenzene) is higher by a factor of 4–10 than that of the same polyarylate synthesised in ditolylmethane. The elongation on rupture also increases severalfold.

Table 1. Properties of the polyarylates synthesised from phenolphthalein and isophthalic acid by high-temperature polycondensation in various media[51].

Property	Medium used in synthesis				
	ditolylmethane	Sovol	α-chloronaphthalene		nitrobenzene
Structure	globular	← fibrous →			
Molecular weight M_w	28000	33000	28000	48000	26000
Softening temperature, °C*	270	280	290	300	275
Tensile strength (film), kgf cm^{-2}	640	640	740	780	650
Elongation on rupture (film), %	10—20	85	80	100	40—70
Specific impact strength (monolithic specimen), kgf cm^{-2}	2—3	11	10	20	14

* The temperature at which the strain in the monolithic specimen relaxes to zero was adopted[150].

The more satisfactory physicomechanical parameters of the fibrous polyarylate obtained from 3,3-bis-(*p*-hydroxyphenyl)-2-phenylphthalimidine by high-temperature polycondensation in a medium dissolving the polymer compared with the corresponding polyarylate having a globular supermolecular structure and obtained by interfacial polycondensation (Table 2) suggests that high-temperature polycondensation is perhaps a more successful method of synthesising polyarylates[51].

Although the majority of cardopolyarylates are amorphous, many of them have a distinct tendency to become ordered. Among the latter, the polyarylate obtained from 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone and terephthalic acid, which can be synthesised with a high degree of crystallinity[60], is outstanding. The structure and hence the properties of this polymer can be regulated both by varying the conditions of synthesis and by appropriate treatment of the finished polymer. The polymer is obtained in the most crystalline form on polycondensation at 220°C in solvents such as Sovol, 1,2,4-trichlorobenzene, nitrobenzene, and α-chloronaphthalene.

Table 2. Properties of the polyarylates synthesised from 3,3-bis-(*p*-hydroxyphenyl)-2-phenylphthalimidine and terephthalic acid[51].

Property	Method of synthesis	
	interfacial	high-temperature, in solution
Softening temperature, °C	280–285	315–320
Tensile strength (film), kgf cm^{-2}	960	1000
Elongation on rupture (film), %	13	40–50
Specific impact strength (monolithic specimen), kgf cm^{-2}	1	7–9

By successive treatment of such a polymer by various solvents, it is possible to crystallise the amorphous polyarylate and conversely to obtain the amorphous polymer from a crystalline specimen. For example, when amorphous polyarylate is treated with chloroform in a swollen state, it crystallises, while reprecipitation of crystalline polyarylate with the same chemical structure from solution in a 3 : 1 (by weight) tetrachloroethane (TCE)–phenol mixture results in the formation of an amorphous polymer[107]. The crystalline polyarylate does not soften up to the onset of its decomposition and dissolves only in a 3 : 1 (by weight) tetrachloroethane–phenol mixture, while in the amorphous form it softens at 325–365°C and dissolves readily in various organic solvents[107,118]. Polyarylates obtained from 9,9-bis-(*p*-hydroxyphenyl)fluorene also show a tendency to crystallise, albeit to a smaller extent[107,118].

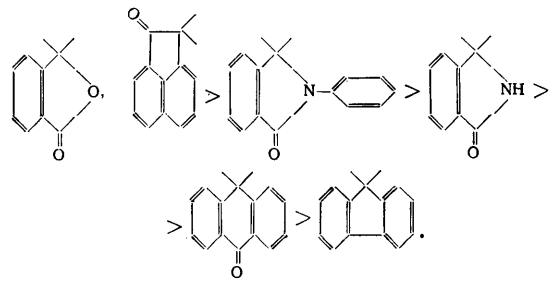
The crystallisability of cardopolyarylates depends not only on the nature of the cardo-group but also on the component in which it is introduced into the macromolecule. Thus the polyarylate obtained from hydroquinone and 9,9-bis-(*p*-carboxyphenyl)-10-anthrone, which is isomeric with the polyarylate 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone and terephthalic acid, has an amorphous structure, in contrast to the latter[132]. Cardopolyarylates derived from phenolphthalein have a certain degree of order only when an acid with a cardo-group in the molecule is employed as the initial component[119], for example polyarylate (VIII), which may be due to the fact that, while the phthalide group itself is asymmetric, the macromolecule as a whole becomes more symmetrical.

Certain cardopolyarylates derived from 3,3-bis-(*p*-hydroxyphenyl)phthalimidine and 2-(β-hydroxyethyl)-3,3-bis-(*p*-hydroxyphenyl)phthalimidine also show some tendency towards becoming ordered, which may be consequence of hydrogen bonds influencing also the solubility of such polymers[129–131].

The presence in the polymer chain of cardo-groups results in a high solubility of such polyarylates in many organic solvents. Polyarylates from phenolphthalein and aromatic dicarboxylic acids are soluble in methylene chloride, chloroform, 1,2-dichloroethane, *sym*-tetrachloroethane, tetrahydrofuran (THF), cyclohexanone, DMF, and others with formation of highly concentrated solutions

(> 25%).[19,20] The increase of solubility as a result of the introduction of cardo-groups (for example the phthalide group) is also achieved when they are present at a very low concentration in the macromolecules of copolymers. For example, the mixed polyarylate obtained from terephthalic acid, phenolphthalein, and 2,2-di-(*p*-hydroxyphenyl)propane (in molar proportions of 1.0 : 0.15 : 0.85) is readily soluble in chloroform[20]. An analogous enhancement of solubility is achieved by the introduction of the phthalide group into the polymer chain as part of the acid component[56,119].

Comparison of the contributions of various cardo-groups to the increase of the solubility of polyarylates suggests that they can be arranged in the following sequence:



The highest solubility of polymers with phthalide and phthalimidine groups is probably due to the greater dimensions, polarity, and asymmetry of the structure of such groups. The somewhat lower solubility of polyarylates containing fluorene and anthrone cardo-groups is probably due to their greater symmetry, which leads to the crystallisation of such polymers.

The solubility of polymers containing phthalimidine cardo-groups is due to the presence or absence of mobile hydrogen atoms. Thus polyarylates from 3,3-bis-(*p*-hydroxyphenyl)phthalimidine or 2-(β-hydroxyethyl)-3,3-bis-(*p*-hydroxyphenyl)phthalimidine dissolve only in solvents which rupture intermolecular hydrogen bonds[39,129-131], while polyarylates from 3,3-bis-(*p*-hydroxyphenyl)-2-phenylphthalimidine in which the mobile hydrogen atom is replaced by the phenyl group, dissolve even in chloroform and methylene chloride[38,52,53].

The solubility of cardopolyarylates makes it possible to determine their molecular weight and to establish the relation between the intrinsic viscosity of their solutions and the molecular weight (Table 3). The properties of solutions of cardopolyarylates have been described in dissertations and in a monograph[152-155]. The method of synthesis affects not only the physicochemical properties of polyarylates but also their molecular-weight characteristics (Table 3).

The study of thermal and thermo-oxidative degradation of polyarylates showed[162-172] that, according to dynamic thermogravimetric (TG) data (in an atmosphere of helium at a heating rate of 5 deg min^{-1}), the onset of the decrease of the weight of various polyterephthalates occurs at 350–360°C and their vigorous decomposition takes place at 460–470°C.[172] The polyarylate obtained from terephthalic acid and 9,9-bis-(*p*-hydroxyphenyl)fluorene begins to decompose at a temperature higher by 10–15 deg than the other polymers. Cardopolyarylates differ from one another mainly in the amount of carbon residue at 900°C. Polyarylates from 9,9-bis-(*p*-hydroxyphenyl)-10-anthrone, 9,9-bis-(*p*-hydroxyphenyl)fluorene, and 2,2-bis-(*p*-hydroxyphenyl)-1-acenaphthenone, in which there are two aromatic rings in the cardo-group, decompose in an inert atmosphere to the extent of 43–44% regardless of the presence of absence of a carbonyl group, while the polyterephthalate synthesised from phenolphthalein loses 50% of its weight.

Table 3. The values of the parameters K and a in the Mark–Houwink equation for cardopolyarylates.

Polymer	Method of synthesis	Solvent for determination of $[\eta]^{20°}$	$K \times 10^{4}$	a	References
Polyarylate from phenolphthalein and isophthalic acid	High-temperature polycondensation in ditolylmethane	*sym*-Tetrachloroethane	16.4	0.53	152,156
		Tetrahydrofuran	52.3	0.39	152,156
Ditto	Interfacial polycondensation	*sym*-Tetrachloroethane	3.35	0.67	152,156
		Tetrahydrofuran	21.3	0.46	152,156
Polyarylate from phenolphthalein and terephthalic acid	High-temperature polycondensation in ditolylmethane	*sym*-Tetrachloroethane	2.42	0.696	156
		Tetrahydrofuran	6.357	0.596	156
		Dioxan	10.30	0.549	156
Ditto	High-temperature polycondensation in Sovol	*sym*-Tetrachloroethane	6.36	0.596	156
Ditto	Acceptor-catalytic polycondensation in dichloroethane	*sym*-Tetrachloroethane	5.09	0.69	157
Ditto	Acceptor-catalytic polycondensation in acetone	*sym*-Tetrachloroethane	4.42	0.73	157
Ditto	Interfacial polycondensation	*sym*-Tetrachloroethane	0.266	0.938	152-154
		Tetrahydrofuran	0.724	0.828	152-154
		Dioxan	0.883	0.800	152-154
Polyarylate from 3,3-bis-(*p*-hydroxyphenyl)-2-phenylphthalimidine and terephthalic acid	High-temperature polycondensation in Sovol	*sym*-Tetrachloroethane	6.7	0.59	158
		Tetrahydrofuran	25.85	0.488	158
Ditto	Interfacial polycondensation	*sym*-Tetrachloroethane	1.114	0.84	158
		Dioxan	3.64	0.706	
Polyarylate from 3,3-bis(*p*-hydroxyphenyl)-2-phenylphthalimidine and isophthalic acid	High-temperature polycondensation in Sovol	Tetrahydrofuran	29.20	0.415	159
Ditto	Interfacial polycondensation	*sym*-Tetrachloroethane	6.820	0.615	159
Polyarylate from 9,9-bis-(*p*-hydroxyphenyl)-fluorene and isophthalic acid	High-temperature polycondensation in ditolylmethane	*sym*-Tetrachloroethane	23.05	0.495	160,161
		Tetrahydrofuran	50.24	0.407	
Ditto	Interfacial polycondensation	*sym*-Tetrachloroethane	5.22	0.640	160,161

The study of the ageing processes of polyarylates for low degrees of conversion (250–350°C) showed that structure-formation processes predominate on heat treatment alone and on thermo-oxidation[166,168,170]. Degradation of the polymers takes place at 300–350°C together with structure formation, as shown by the splitting of the maximum on the molecular-weight distribution curve[166-168]. At higher temperatures (350–500°C), more far-reaching changes take place, accompanied by the formation of solid and gaseous low-molecular-weight products and of a solid carbonised residue[165-170].

The resistance of cardopolyarylate based on phenolphthalein and 9,9-bis-(*p*-hydroxyphenyl)fluorene to the action of ionising and ultraviolet radiation in films and solutions has been studied[121,173-176].

3. Aromatic Polyamides

Another type of cardopolymers which exhibit all the specific features are aromatic polyamides (Table 4). In contrast to many aromatic polyamides, cardopolyamides have an amorphous structure. A tendency has been noted towards the ordering of polyamides derived from 9,9-bis-(*p*-aminophenyl)fluorene and terephthalic acid (when the solution of the polymer in DMF is allowed to stand) and from 9,9-bis-(*p*-aminophenyl)fluorene and isophthalic acid (when its solution in cyclohexanone is allowed to stand). Despite their amorphous structure, the heat resistance of cardopolyamides is much higher than that of other polyamides. Thus the polyamide from 9,9-bis-(*p*-aminophenyl)fluorene and isophthalic acid softens at 385°C,[65] while the widely familiar poly-*m*-phenyleneisophthalamide has a glass temperature of 270°C. The softening temperature of the cardopolyamide is always higher than that of the corresponding cardopolyarylate[186].

Table 4. Cardopolyamides[a]

No.	Starting materials		Polymer			References
	diamine	dicarboxylic acid chloride	d, g cm^{-3}	$\eta_{ln}^{25°}$ in DMF, dl × g^{-1}	softening temp.[b], °C	
1	2	3	4	5	6	7
1	3,3-Bis-(4'-aminophenyl) phthalide	Adipic	1.213	0.57	240	65,177,178
2	Ditto	Sebacic	1.195	0.94	220	65,177,178
3	»	Fumaric	—	0.19	530 (decomp.)	65,177,178
4	»	Isophthalic	1.298	1.14	385	65,177,178
5	»	Terephthalic	1.302	1.45	390	65,177,178
6	»	Biphenyl-4,4'-dicarboxylic	1.271	0.79	395	65,177,178
7	»	Di-(*p*-carboxyphenyl) ether	1.281	1.22	340	65,177,178
8	»	3,3-Bis-(*p*-carboxyphenyl)-phthalide	1.280	0.41	385	63,64
9	»	2,2-Bis-(*p*-carboxyphenyl)-hexafluoropropane	—	0.44	390	179
10	3,3-Bis-(*p*-aminophenyl)-phthalimidine	Adipic	—	0.23	245	65,177
11	Ditto	Sebacic	1.193	0.57	225	65,177,178
12	»	Isophthalic	1.297	0.41	390	65,177,178
13	»	Terephthalic	1.297	0.74	395	65,177,178
14	»	3,3-Bis-(*p*-carboxyphenyl) phthalide	1.278	0.50	400	63, 64
15	9,9-Bis-(*p*-aminophenyl) fluorene	Isophthalic	—	1.30	350	67
16	Ditto	Terephthalic	—	1.58	405	67
17	9,9-Bis(*p*-aminophenyl)-10-anthrone	Isophthalic	—	0.75	—	
18	Ditto	Terephthalic	—	1.06	400	180
19	»	3,3-Bis-(*p*-carboxyphenyl)-phthalide	—	0.41	—	

Table 4 (continued).

No.	Starting materials		Polymer			References
	diamine	dicarboxylic acid chloride	d, g cm^{-3}	$\eta_{ln}^{25°}$ in DMF, dl × g^{-1}	softening temp.[b], °C	
1	2	3	4	5	6	7
20	1,1-Bis-(*p*-aminophenyl) cyclohexane	Terephthalic	—	1.26[c]	305	181
21	Hexamethylenediamine	3,3-Bis-(*p*-carboxyphenyl)-phthalide	—	0.26	200	63,64
22	Octamethylenediamine	Ditto	—	0.25	195	63,64
23	Piperazine	»	—	0.18	305	63,64
24	*p*-Phenylenediamine	»	1.300	0.57	380	63,64
25	Benzidine	»	1.270	0.81	385	63,64
26	Di-(*p*-aminophenyl) ether	»	1.287	0.54	320	63,64
27	Di-(*m*-aminophenyl)-sulphone	3,3-Bis-(*p*-carboxyphenyl)-phthalide	—	0.57	310	
28	Di-(*p*-aminophenyl)-sulphone	Ditto	—	0.75	365	
29	3,3-Bis-(aminomethyl)-oxacyclobutane	Adipic	—	1.04[d]	170	182,183
30	Ditto	Sebacic	—	2.82[d]	170	182,183
31	»	Terephthalic	—	1.96[d]	300	182,183
32	9,9-(Bis-(3-aminopropyl) fluorene	Ditto	—	0.97[e]	—	184
33	Di-(*p*-aminophenyl) ether	1,2-Bis-(*p*-carboxy-phenyl)carborane	—	0.50[f]	350	185
34	Bis-(*p*-aminophenyl)-ether of hydroquinone	Ditto	—	0.52[f]	350	185
35	*m*-Phenylenediamine	»	—	0.20[g]	350	185

a. All the polymers except Nos. 21 and 22 were synthesised by low-temperature polycondensation in solution and polymers Nos. 21 and 22 were obtained by interfacial polycondensation.
b. The softening temperature was determined as the point of intersection of tangents to the branches of the thermochemical curve in the region of polymer flow (heating rate 150 deg h^{-1}, pressure 0.8 kgf cm^{-2}).
c. In a DMF–5% LiCl mixture.
d. In formic acid.
e. In *m*-cresol.
f. In *N*-methylpyrrolidinone.
g. In sulphuric acid.

The activation energy for the relaxation process in polyamides is always higher than in the analogous polyarylates[178] (Table 5). This suggests that the rearrangement processes in polyamide superstructures and their elements are more difficult than in polyarylates. It has been suggested[186] that this is mainly due to the presence of hydrogen bonds between the polyamide macromolecules and to some extent also to a change in the mobility of the elements of the macromolecule caused by the replacement of the ester linkage by the amide linkage.

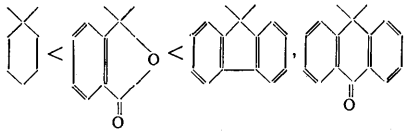
In contrast to the majority of aromatic polyamides, which are sparingly soluble in organic solvents and are mainly soluble in solutions of inorganic salts in amide

solvents, cardopolyamides are highly soluble in various amide solvents, DMSO, and cresol with formation of highly concentrated solutions (25–35%).[177] The somewhat lower solubility of polyamides with fluorene cardo-groups compared with polyamides from 9,9-bis-(*p*-aminophenyl)-10-anthrone is shown by the fact that the polyterephthalamide derived from 9,9-bis-(*p*-aminophenyl)-10-anthrone is soluble in cyclohexanone while the polyterephthalamide from 9,9-bis-(*p* -aminophenyl)fluorene does not dissolve in this solvent.

Table 5. Activation energies for the relaxation process (U_0) and molar structural constants (γ) cardopolyamides and cardopolyarylates[178].

Parameter	Polyamides from 9,9-bis-(*p*-aminophenyl) fluorene and various acids				Polyarylates from phenolphthalein and various acids	
	sebacic	isophthalic	terephthalic	diphenyl-4,4′-dicarboxylic	isophthalic	terephthalic
U_0, kcal mole^{-1}	47.5	76.3	79.5	78.9	62.7	73.0
γ, kcal mm^2 mole^{-1} kg^{-1}	1.300	0.834	1.290	1.286	1.13	1.74

A detailed study of the thermal and thermo-oxidative degradation of many cardopolyamides showed that their thermal stability depends to a high degree on the nature of the cardo-group[180,187,188], while that of polyarylates is limited mainly by the stability of the ester linkage. Cardo-groups can be arranged in the following series in terms of increasing thermal stability of polyterephthalamides[180]:



It has been shown for the highly soluble polyterephthalamides derived from anilinephthalein and 9,9-bis-(*p*-aminophenyl)fluorene[189] that branching and structure-formation processes develop at temperatures preceding the decrease in their weight (up to 350°C).

4. Aromatic Polyimides

Aromatic polyimides (Table 6) are the first examples of heterocyclic cardopolymers. The characteristics of the structure of rigid-chain cardopolymers such as polyimides affect in the first place their solubility. The only example of such polymers with the most rigid chains (polypyromellitimides), which are soluble in organic solvents while retaining their high heat resistance, are the polypyromellitimides derived from anilinephthalein and 3,3-bis-(*p*-aminophenyl)phthalimidine[68,69,72]. It is noteworthy that in the series of cardopolyimides solubility is determined not only by the chemical structure of the cardo-group but to a considerable degree also by the nature of the bridging group between the phenyl groups of the second component. Thus, in contrast to cardopolypyromellitimides, the cardopolyimides derived from biphenyl-3,3′,4,4′-tetracarboxylic acid do not dissolve in amide solvents. On the other hand, the introduction of a

Table 6. Properties of cardopolyimides.

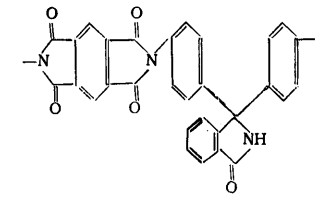
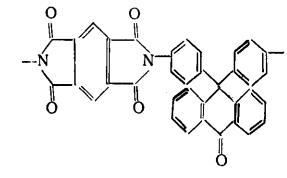
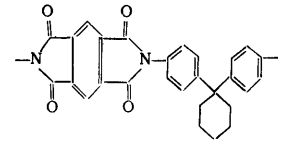
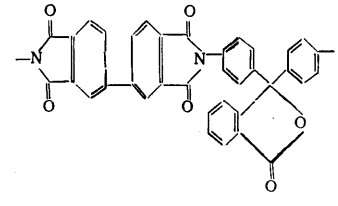
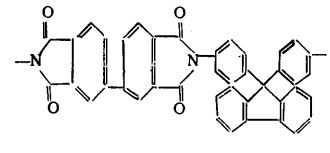
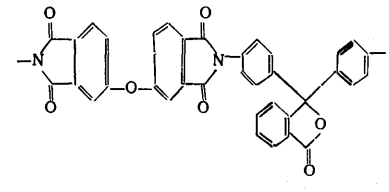
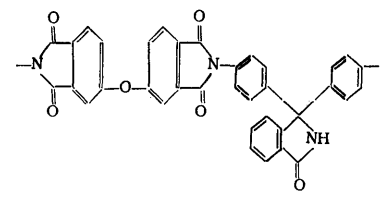
No.	Elementary unit of polyimide	$\eta_{ln}^{25°}$ in DMF, dl g^{-1}	Density, g cm^{-3}	Softening temp., °C	References
1	2	3	4	5	6
1	IV	2.15	1.326	490[b]	68,69, 190
2		0.57	—	—	69,190
3	VII	0.65[d]	1.278	515[b]	67,69, 190
4		0.41[d]	—	—	190
5		0.35[d]	—	—	190,191
6		0.52[e]	1.325	415[c]	190
7		0.75[e]	1.260	425[b]	190
8		1.66	1.346	375[b] 360[c]	190
9		0.62	—	385[c]	190

Table 6 (contd.)

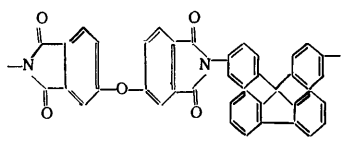
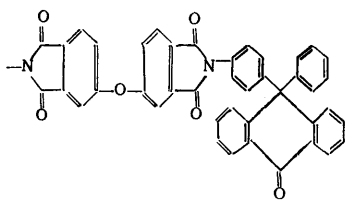
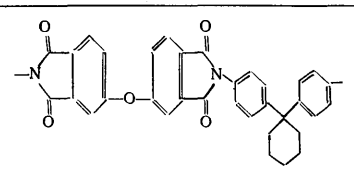
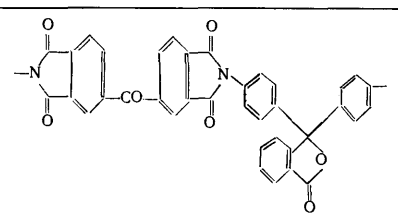
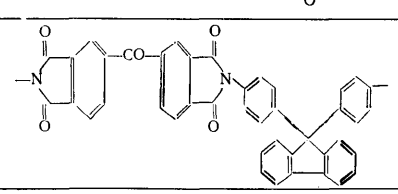
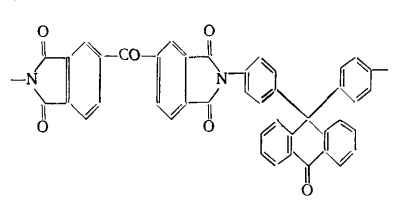
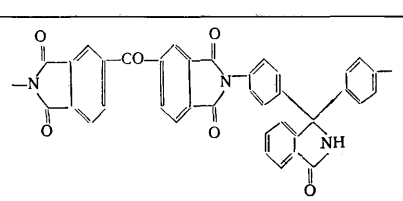
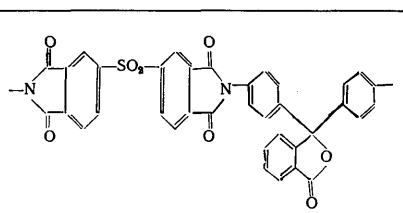
No.	Elementary unit of polyimide	$\eta_{in}^{25°a}$ in DMF, dl g^{-1}	Density g cm^{-3}	Softening temp., °C	References
1	2	3	4	5	6
10		1.20	1.280	405[b] 385[c]	190
11		1.35[c]	1.380	385[b]	190,192
12		0.33	—	285[c]	190,191
13		0.75	—	360[b] 365[c]	190
14		1.20	—	370[c]	190
15		0.64	—	370[c]	190, 192
16		0.66	—	380[c]	190
17		1.00	—	400[c]	190

Table 6 (contd.)

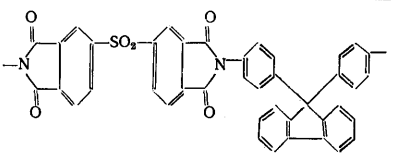
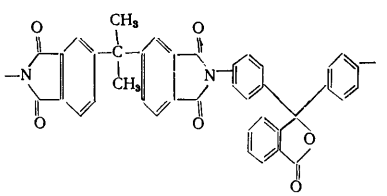
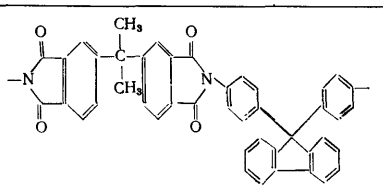
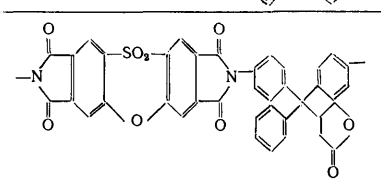
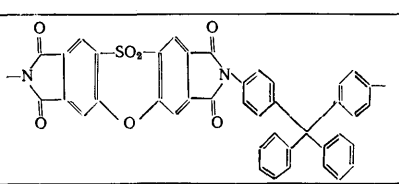
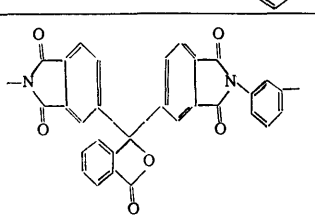
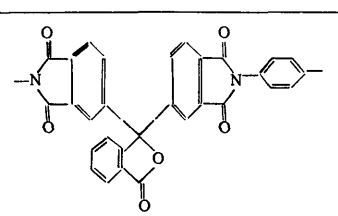
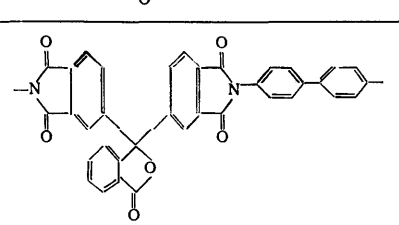
No.	Elementary unit of polyimide	$\eta_{in}^{25°a}$ in DMF, dl g^{-1}	Density, g cm^{-3}	Softening temp., °C	References
1	2	3	4	5	6
18		0.92	—	400[c]	190
19		1.01	—	355[c]	193
20		0.74	—	350[c]	193
21		1.86	—	500[c] (de-comp.)	193
22		—	—	—	193
23		0.47	—	360[c]	194
24		0.47	—	410[c]	194
25		1.17[c]	—	415[c]	194,195

Table 6 (contd.)

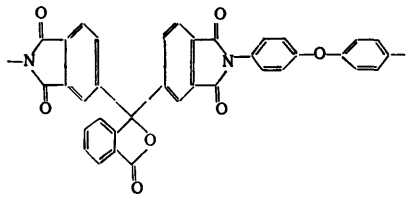
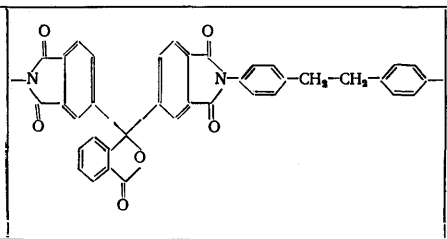
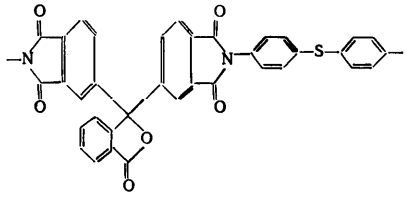
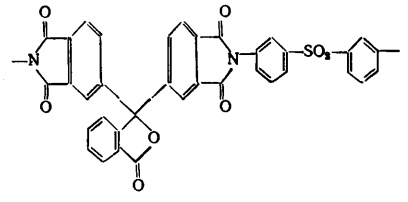
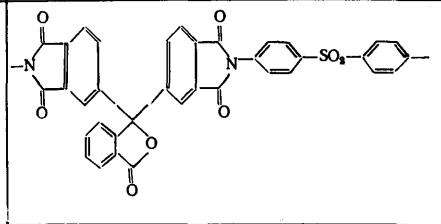
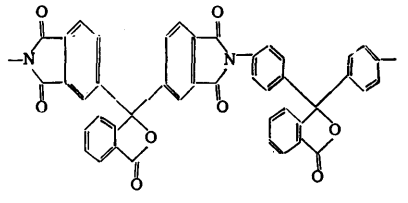
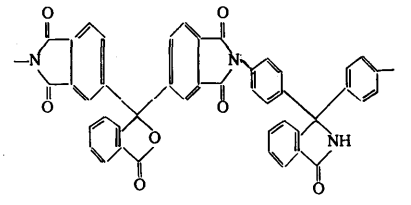
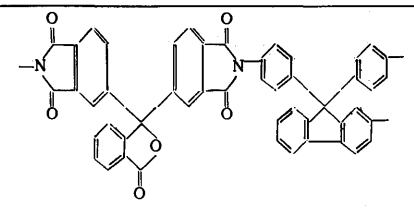
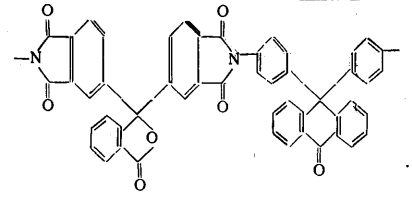
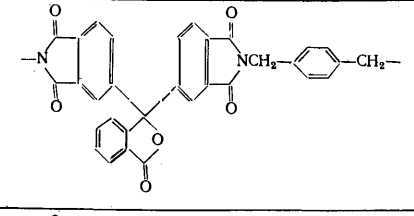
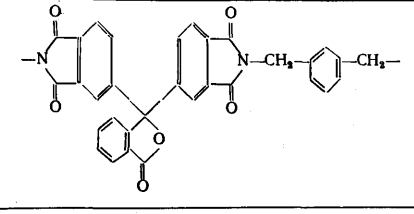
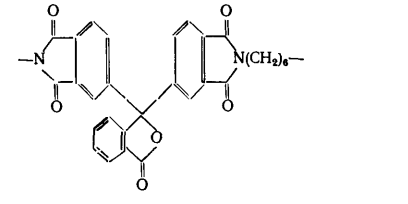
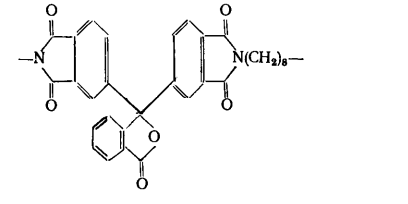
No.	Elementary unit of polyimide	$\eta_{ln}^{25°}$ a in DMF, dl g^{-1}	Density, g cm^{-3}	Softening temp., °C	References
1		3	4	5	6
26		1.36	—	345[c]	194,195
27		0.92[e]	—	315[c]	196
28		0.69	—	320[c]	194
29		0.42	—	315[c]	194
30		0.34	—	370[c]	194,19
31		1.04	—	415[c]	194,195
32		0.38	—	410[c]	194

Table 6 (contd.)

No.	Elementary unit of polyimide	$\eta_{ln}^{25°}$ a in DMF, dl g^{-1}	Density, g cm^{-3}	Softening temp., °C	References
1	2	3	4	5	6
33		1.15	—	425[c]	194
34		0.93	—	425[c]	194
35		0.37[f]	—	305[c]	78
36		0.32[f]	—	240[c]	78
37		0.86[f]	—	205[c]	78
38		0.64[f]	—	195[c]	78

a. Concentration of polymer solution 0.5 g/100 ml.
b. The softening temperature was determined in the useful operating range[150].
c. The softening temperature was assumed to be the point of intersection of tangents to the thermomechanical curve in the region of polymer flow (load 100 g, disc diameter 4 mm).
d. In sulphuric acid.
e. In *sym*-tetrachloroethane.
f. In tricresol.

carboxylic acid residue, on either group, or a carbonyl group between the phenyl rings restores the solubility of the polyimides in DMF, DMA, DMSO, and NMP and makes them soluble in methylene chloride and chloroform, while retaining their solubility in TCE.[190] An unusual feature of cardopolyimides from aliphatic diamines is that they do not dissolve in DMF but do dissolve in DMA and many chlorinated solvents[78]. The presence of two cardo-groups (phthalide or phthalide and fluorene) in the elementary unit of polyimides promotes an even greater increase of solubility, making them soluble in cyclohexanone, in which other known polyimides do not dissolve[194].

An antagonistic effect in mixtures of a number of solvents[190] has been observed for cardopolyimides obtained from di-(3,4-dicarboxyphenyl) ether, of the type which has been noted also for the polyarylate from phenolphthalein and terephthalic acid[34]. Certain cardopolyimides have a lower consolute in DMF and chloroform.

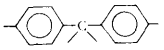
The molecular weight distribution for the polypyromellitimide obtained from anilinephthalein has been estimated and the relation between $[\eta]$ of its solution in DMF and M_w has been found[72,197,198]:

$$[\eta]^{20^\circ} = 32.83 \cdot 10^{-4}\,\bar{M}_w^{0.516}$$

together with the analogous characteristics for the polyimide from di-(3,4-dicarboxyphenyl) ether and 9,9-bis-(*p*-aminophenyl)fluorene[199]:

$$[\eta]^{20^\circ}_{DMF} = 8.91 \cdot 10^{-4}\,\bar{M}_w^{0.56},$$
$$[\eta]^{20^\circ}_{DMA} = 3.33 \cdot 10^{-4}\,\bar{M}_w^{0.65}.$$

Electron microscope and viscometric studies have shown[198] a relatively higher rigidity of the macromolecules of the polypyromellitimide obtained from anilinephthalein, which exist in solution in a coiled form. The diphenylphthalide group, where the rotation about the



linkage is hindered, is responsible for the rigid coiling of the chain[198].

Cardopolyimides can be arbitrarily divided into several groups on the basis of their heat resistance[190,200]. Polyimides from pyromellitic and naphthalenetetracarboxylic acids exhibit the highest heat resistance. An unusual feature of these polymers is that their elementary units are made up of 3–4 condensed rings. As regards this feature, they occupy an intermediate position between the usual polycondensation systems, such as aromatic polyesters and polyamides, and ladder-type polymers. As a result of this feature, these polyimides have higher softening temperatures, which are sometimes not attained owing to degradation. Monolithic specimens of cardopolyimides[200] have operating characteristics at high temperatures and stresses which are unusual for organic polymers. Thus at 300°C polypyromellitimide devised from 9,9-bis-(*p*-aminophenyl)fluorene withstands a load of 500 kgf cm^{-2}, while at 400°C it withstands a load of 200 kgf cm^{-2}.

Polyimides obtained from dinuclear and polynuclear tetracarboxylic acids with phthalimide groups (Table 6, polymers Nos. 6–20) have a high heat resistance (although lower than that of polypyromellitimides), and their softening temperature can be regulated within wide limits by varying the nature of the bridging group between the phenyl rings of the tetracarboxylic acid or diamine residues[190,194].

Polyimides from aliphatic diamines show the lowest heat resistance among cardopolyimides but, even when the polymer chain contains long aliphatic fragments [$(CH_2)_6$ or $(CH_2)_8$], the softening temperature of the polymers reaches about 200°C.[78]

Like other polyimides, cardopolyimides have a high thermal stability[72,190] and in a series of polyimides thermal stability depends to an even greater extent on the nature of the cardo-group than among polyamides. Polyimides with fluorene and anthrone cardo-groups show the highest thermal stability[190,192]; on heating to 1000°C in an inert atmosphere (under the conditions of dynamic thermogravimetric measurements, the heating rate was 5 deg min^{-1}), they retain 68–70% of the weight of the initial specimen and the decrease in weight begins at 480–500°C.[72] The lowest thermal stability is characteristic of cardopolyimides with cyclohexyl groups[190,191], which, like aliphatic polyimides, begin to decompose in air at about 400°C. This has been explained by the initial degradation of the cyclohexyl groups. Polyimides with phthalide groups[72,190,191,201], the thermal stability of which is lower than that of the imide rings, occupy an intermediate position.

It has been shown that, at temperatures (300–350°C) preceding the onset of decrease in weight, processes leading to a change of molecular weight characteristics and solubility develop in polyimides[202].

Certain chemical properties of cardopolyimides (the data obtained are probably valid also for other polyimides) have been estimated. On heating, polyimides are resistant to acidolysis and exchange reactions involving the imide ring but decompose under the influence of amines and other bases[203,204]. Compared with the corresponding aromatic polyamides, polyimides are less resistant to hydrolysis[73,74]; their hydrolysis is accelerated in the presence of DMF, DMA, and DMSO[73,74] and depends on the chemical structure of the polymer and on its physical structure[196,205,206].

5. Poly-1,3,4-Oxadiazoles

Another class of heterocyclic cardopolymers are poly-1,3,4-oxadiazoles (Table 7). The use of aromatic dicarboxylic acids and their derivatives containing cardo-groups in the molecule for the synthesis of such polymers made it possible to obtain highly soluble amorphous polymers[71,73,86], poly[1,3,4-oxadiazole-2,5-diyl-1,4-phenylene-(3,3-phthalidylene)-1,4-phenylene] among which contains two phthalide groups per elementary polymer unit, shows the highest solubility; it is soluble in methylene chloride, TCE, DMA, HMP, NMP, pyridine, benzyl alcohol, etc.

The polydispersity of cardopoly-1,3,4-oxadiazoles synthesised in polyphosphoric acid has been estimated[208,209]. The polydispersity coefficient ($\bar{M}_w/\bar{M}_n$) of the linear poly-1,3,4-oxadiazole based on 3,3-bis-(*p*-carboxyphenyl)phthalide and its dihydrazide is 3.0–3.1. The variation of the viscosity of solutions of this polymer with molecular weight is of the following type[208]:

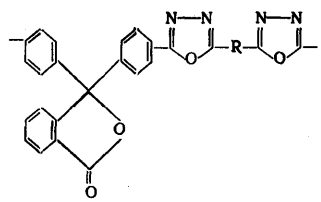
$$[\eta]^{25^\circ}_{DMA} = 7.74 \cdot 10^{-4}\,\bar{M}_w^{0.57},$$
$$[\eta]^{25^\circ}_{TCE} = 4.00 \cdot 10^{-4}\,\bar{M}_w^{0.66}.$$

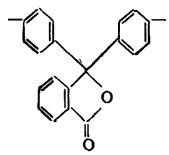
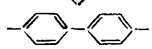
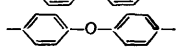
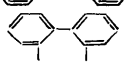
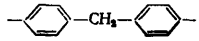
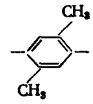
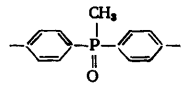
As in other cases, the introduction of phthalide cardo-groups into poly-1,3,4-oxadiazoles increases significantly the thermal stability of the polymer. Thus poly[1,3,4-oxadiazole-2,5-diyl-1,4-phenylene-(3,3-phthalidylene)-1,4-phenylene] softens at a temperature approximately 150 deg above that of amorphous poly(1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneoxy-1,4-phenylene).[86]

Cardopoly-1,3,4-oxadiazoles are resistant at room temperature to the action of organic solvents, water, and

corrosive media; they are slightly degraded at elevated temperatures in amide solvents[210]. Poly-1,3,4-oxadiazoles are degraded at room temperature in 98% sulphuric acid[210]. The polymers have been found to be stable in water at 100°C; poly-1,3,4-oxadiazoles are hydrolysed at higher temperatures, the hydrolysis being accelerated in acid and basic media.

Table 7. Properties of cardopoly-1,3,4-oxadiazoles



№ №	R	$\eta_{int}^{25°}$, dl g^{-1}	d, g cm^{-3}	Softening temp.[b], °C	References
1		3.00	1.320	390	83,84
2		1.90	1.316	390	83,84
3		1.00	1.309	360	83,84
4		4.75	—	400	83,84
5		3.50	1.340	340	83,84
6		0.68	—	280	84
7		0.88	—	315	207
8		0.50	—	300	207
9		0.98	—	380	207
10	$-(CH_2)_8-$	1.66	—	160	207

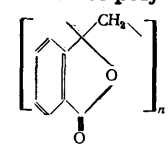
a. Concentration of polymer solution 0.5 g per 100 ml of TCE–phenol mixture (3 : 1 by weight).
b. See footnote b to Table 6.

Poly-1,3,4-oxadiazoles do not enter into exchange reactions involving the oxadiazole ring up to 200°C but decompose under the influence of carboxylic acids and their hydrazides.

Cardopoly-1,3,4-oxadiazoles obtained from 3,3-bis-(*p*-carboxyphenyl)phthalide begin to decompose in air according to dynamic thermogravimetric data obtained at a heating rate of 5 deg min^{-1} at 400–430°C, i.e. the thermal stabilities of the 1,3,4-oxadiazole and phthalide rings are approximately the same[194].

6. Carbon Chain Cardopolymers

Cardopolymers of the polymerisation type have been investigated in less detail, although the number of known examples of such polymers is very large. These include polyacenaphthylene[95,211–219], polyindene[85,220], polybiindenyl[221], poly(vinylene carbonate), poly(maleic anhydride)[100], polymaleimide[222], poly-*N*-phenylmaleimide[223,224], and polymethylenefluorene[225]. Systematic studies on carbon chain cardopolymers of methylenephthalide[93] and many methylenephthalimidines[94] and their copolymers with monomers of the vinyl type[1,226] have shown that such polymers are amorphous highly heat-resistant substances soluble in polar solvents. Thus polymethylenephthalide softens at about 300°C and dissolves in trifluoroacetic acid, formic acid, DMSO, the monohydrate of 1,3-dichloro-1,1,3,3-tetrafluoroacetone, trifluoroethanol, sulpholane, NMP, DMF, tricresol, etc., the solvent depending appreciably on the molecular weight of the polymer. It is distinguished from the majority of carbon chain polymers by a high density (d = 1.3462 g cm^{-3}). In a study of the glass temperatures of the copolymers of methylenephthalide with styrene, methyl methacrylate, and methyl acrylate, it was shown experimentally and by calculation[226] that the glass temperature of polymethylenephthalide should be 370–380°C, but is not attained owing to the depolymerisation process at temperatures in excess of 300°C.[1] Consequently the heat resistance of polymethylene phthalide



(X)

surpasses that of the majority of other carbon chain polymers and many heterochain polymers (polyarylates and aromatic polyamides).

The heat resistance of the carbon chain cardopolymers polymethylenephthalide, polymethylenefluorene, and polymethylenephthalimidine is independent of the chemical structures of the cyclic groups and is determined in this instance by the nature of the bonds in the main polymer chain[1,94]. All these polymers are depolymerised at temperatures in the range 250–300°C, while heterochain cardopolymers with similar groups remain thermally stable up to 350–450°C, the thermal stability of the latter depending on the nature of the cardo-groups (see above).

Comparison of the cardopolymers and other carbon chain polymers showed that the presence in the macromolecule of phthalide or phthalimidine groups improves the solubility of the polymer (for example, compared with polyethylene) in highly polar solvents[93]. However, the above carbon chain polymers do not dissolve in many polar solvents incapable of intense intermolecular association (for example in *sym*-tetrachloroethane) in which polystyrene dissolves readily, although it is insoluble in highly polar solvents such as trifluoroacetic and formic acids and DMSO. Such differences between the solubilities are probably due to the greater rigidity of the cardopolymers compared with polystyrene and the presence in the former of highly polar groups capable of intermolecular interaction.

Polymethylenephthalimidine and also copolymers of methylenephthalide and methylenephthalimidine dissolve in formic and trifluoroacetic acids, i.e. in solvents capable of rupturing intermolecular hydrogen bonds, but are insoluble in amide and chlorinated solvents[94].

In contrast to the cardopolymers mentioned above, polymethylenefluorene does not involve in the known organic solvents, which may be due to a definite albeit slight ordering of the structure of this rigid-chain polymer.

IV. APPLICATIONS

Films of various cardopolymers have been obtained by casting from solution in various organic solvents. The high heat resistance and thermal stability of such polymers ensures the stability of the physicomechanical and particularly the dielectric characteristics of such films up to 300°C.[21,86,138,152,193,227,228] Highly heat-resistant fibres of cardopolyarylates and certain other cardopolymers, which have an isotropic amorphous structure with traces of crystallinity, have been obtained by extrusion from solutions[113,180]. The use of cardopolymers as varnish coatings for plastics, as binders for fibreglass, as antifriction self-lubricating materials, and other products is also promising[229-232].

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