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# Polyimides Based on Heterocyclic Monomers

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Data concerning polyimide macromolecules, containing various heterocyclic fragments in their main chains, which are obtained using monomers incorporating the required heterocyclic systems as well as groups capable of giving rise to such systems, are discussed.
The bibliography includes 189 references.

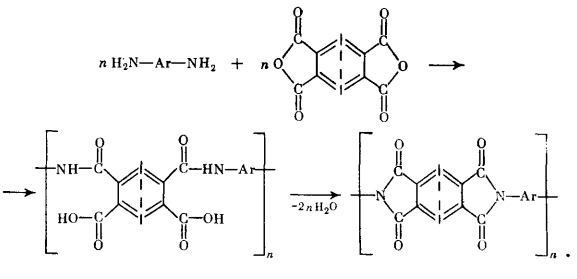
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## I. INTRODUCTION

The vigorous development of new branches of engineering, aviation, cosmonautics, electronics, etc. has imposed increasingly stringent requirements on the polymers employed in these fields. In particular, increasing operating temperatures of polymeric materials are needed—polymeric materials capable of being used at temperatures of 300 °C and above are nowadays of considerable interest. The solution of the problem of synthesising such materials is related directly to the development of new thermostable polymers.

Studies during the last 20 years in the USSR and abroad led to the creation of a series of polymers with high thermal and deformation-strengths[1-9]. In the various examples of new thermostable polymers polyheteroarylenes—polymers containing aromatic heterocycles in the main chains of the macromolecules—are most widely used[1-15]. Despite the great structural variety of the polyheteroarylenes synthesised, only a few of them have emerged from the area of academic research and have acquired industrial importance. Such polyheteroarylenes include in the first place aromatic polyimides—the product of the interaction of aromatic diamines with aromatic tetracarboxylic acid dianhydrides[16,17]:



Polyimides are usually synthesised by a two-stage process involving the interaction of the initial compounds in polar organic solvents, the conversion of the resulting pre-polymers [polyamidoacids (PAA), also referred to as poly(*o*-carboxy)amides] into articles, and thermal cyclisation of the PAA resulting in the formation of articles made of insoluble and infusible polyimides which do not require additional treatment. This method of synthesis of polyimides, which permits the formation of articles from polymers of different structure, has become very common and is nowadays used widely to make polyimide films, fibres, binders, adhesives, varnish coatings, plastics, etc.[16,17].

The majority of the polyimides known at present have been obtained from carbocyclic aromatic monomers, but in recent years polyimides based on heterocyclic monomers have attracted the attention of investigators to an increasing extent.

The great variety of the known heterocycles led to the possibility of formulating completely different projects designed to modify the properties of polyimides:

1. The introduction of highly condensed heterocyclic fragments permitted an increase in the thermal stability and heat resistance of the polyimides.

2. Heterocycles containing bulky side groups have been introduced in order to make polyimides soluble in organic solvents[18-21].

3. The high resistance of the majority of aromatic heterocycles to hydrolysis and the action of nucleophiles compared with imide rings has made it possible to use heterocyclic monomers with a comparatively high molecular weight, which reduced the content of imide rings per unit molecular weight of the polymer, increasing the hydrolytic stability of the polyimides.

Naturally, not every task enumerated above was solved to an equal extent, because all the approaches indicated are formal; nevertheless, definite successes have been achieved in the solution of these problems.

Heterocycles can be introduced into polyimides by employing monomers containing the required heterocycles and also monomers containing groups capable of giving rise to the required heterocyclic systems. Each of these methods has a number of advantages and disadvantages and merits separate consideration.

## II. POLYIMIDES BASED ON MONOMERS CONTAINING THE REQUIRED HETEROCYCLIC SYSTEMS

The synthesis of polyimides using monomers containing particular aromatic heterocycles has a significant advantage over the synthesis based on monomers containing groups capable of giving rise to the corresponding heterocyclic systems, which arises because imidisation processes, i.e. cyclisation processes with formation of an imide ring, proceed under milder conditions than the processes leading to the formation of other heterocyclic systems. As a result, this procedure can yield polymers with a higher degree of cyclisation[22,23], i.e. with a less heterounit structure[24-28], which makes it possible to achieve more fully the properties designed into polymers of this type.

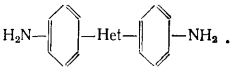
The heterocyclic monomers employed in most studies are isotypical products obtained as a result of complex reactions. This is true also of heterocyclic diamines, particularly of diamines containing azole and benzazole rings, which are synthesised by reactions widely used in the chemistry of polyazoles and polybenzazoles[29-34].

The simplest diamines containing azole rings are of the type

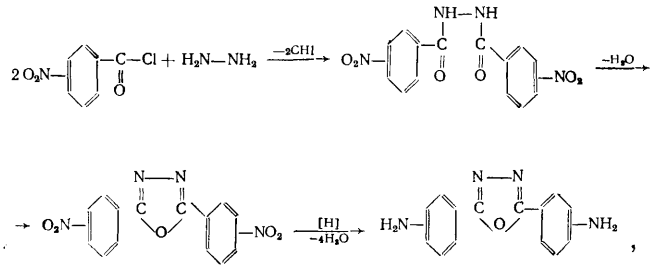
$$H_2N—Het—NH_2 ,$$

some of which (Het = 1,3,4-oxazole, 1,2,4-triazole, 1,3,4-thiadiazole, etc.) have attracted the attention of investigators[35,36] because of the possibility of synthesising from them (by reaction with the dianhydride of pyrazine-2,3,5,6-tetracarboxylic acid) polyimides without hydrogen atoms and possessing as a result an increased thermal stability[37-39]. However, according to some workers[35,36], the low basicity of diamines of this type and the tendency of pyrazine-2,3,5,6-tetracarboxylic acid to decarboxylate precluded the realisation of this possibility. The polyimides obtained had low molecular weights and contained a considerable number of amide fragments formed as a result of the decarboxylation of the PAA; it is noteworthy that these data[35,36] conflict with others[37-39].

More unambiguous results were obtained using azole-containing diamines of the type

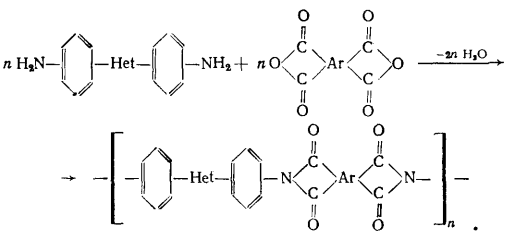


In the series of compounds of this kind the isomeric 2,5-(diaminophenyl)-1,3,4-oxadiazoles[40-47] and 3,5-(diaminophenyl)-4-phenyl-1,3,4-triazoles[41-45,47] are the most common. The former, obtained in accordance with the scheme



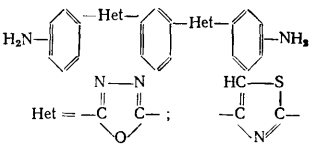
have been most widely used because of their availability.

Poly(*o*-carboxy)amides, the thermal cyclodehydration of which led to polyimides containing 1,3,4-oxadiazole rings, have been synthesised by the reaction of the above diamines with the dianhydrides of aromatic tetracarboxylic acids[41-49]:



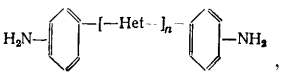
The authors of the above studies do not present data on the basicity of the diamines employed, but the viscosities of the fore-polymers ($\eta_{log} = 1.0-2.0$) indicate a high reactivity of the compounds used. The high molecular weights of the resulting PAA made it possible to obtain from them strong films and fibres, the thermal imidisation of which led to products insoluble in organic solvents and having melting points (485–520 °C) close to the temperatures of the onset of the degradation of these polymers (500–520°).

Polymers of analogous structure, characterised by the same set of properties, have been obtained by a number of other workers[50-52]. The same group of investigators achieved the synthesis of aromatic diamines containing 1,3,4-oxadiazole[51] and thiazole rings[4,45,47] and having the general formula

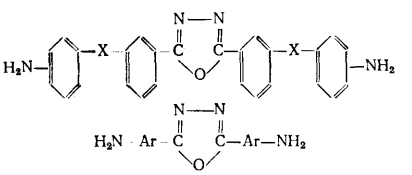


as well as polyimides based on them. Since such diamines are less readily available than di(aminophenyl)-1,3,4-oxadiazoles and the polymers based on them do not have appreciable advantages over the polyimides based on 2,5-(diaminophenyl)-1,3,4-oxadiazoles, these studies were not developed further.

Various modifications of the structure of diamines containing 1,3,4-oxadiazole rings have been carried out in studies[50-52] in which diamines of the following type were synthesised:



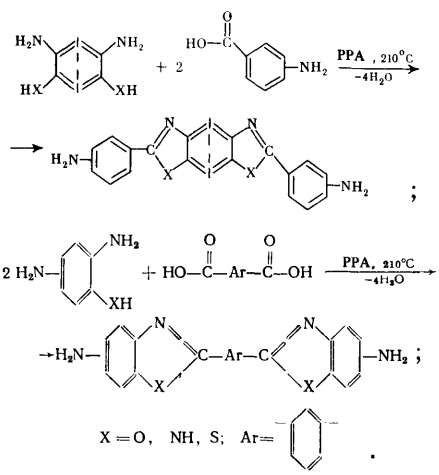
where $n = 2$ or 3 and Het = 1,3,4-oxadiazole or another heterocycle and



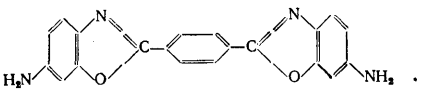
where Ar = naphthyl or a substituted phenyl group and X = O, S, or $CH_2$. Polyimides based on these diamines were also obtained.

A number of diamines containing benzazole rings were synthesised together with the azole-containing diamines with a symmetrical structure enumerated above. Among these compounds, symmetrical diamines formed in accordance with one

of the following schemes[40,53-59] in polyphosphoric acid (PPA) have come to be most widely used:

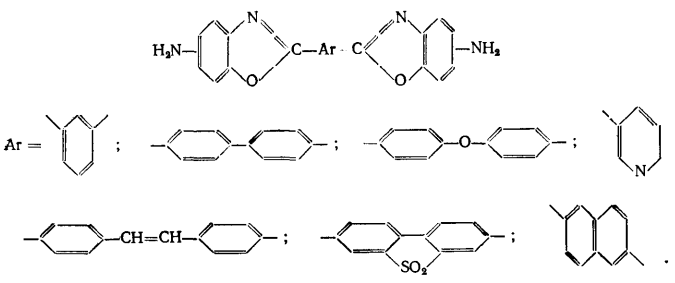


These reactions are employed successfully for the synthesis of diamines containing all three types of the most common benzazole rings—benzoxazole, benzimidazole, and benzothiazole, but, in the series of monomers synthesised, only 2,2-phenylenebis(5-aminobenzoxazole) is promising according to a number of investigators[60]:



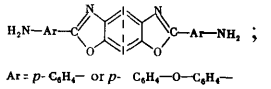
The interaction of this diamine with tetracarboxylic acid dianhydrides under the conditions of a two-phase process yielded high-molecular-weight (the viscosity of the solution of the fore-polymers was $\eta_{log} = 1.24-1.50$) polybenzoxoxazole imides, which can be made into strong elastic films and fibres, best results being obtained when the dianhydride of benzophenone-3,3',4,4'-tetracarboxylic acid is used[22,46,61]. The polymers obtained had high melting points (560–570 °C) and high temperatures for the onset of degradation in the range 560–595 °C (DTGA†, $N_2$, $\Delta T = 15$ K min$^{-1}$).

Polymers having comparable thermal characteristics have been obtained on the basis of a series of other benzoxazole-containing diamines having the general formula



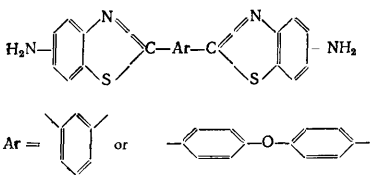
† DTGA = differential thermogravimetric analysis (Ed. of Translation).

Symmetrical benzoxazole-containing diamines derived from bis(*o*-aminophenols) and having the general formula



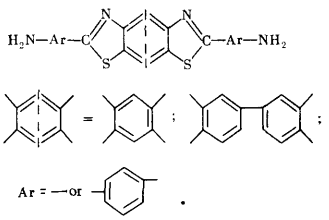
have been used successfully by a number of investigators[22,62-68] to obtain polyimides differing slightly in their characteristics from the polymers discussed above.

Compounds containing benzothiazole rings are much less readily available than the benzoxazole-containing diamines. Compounds of this type, having the general formula

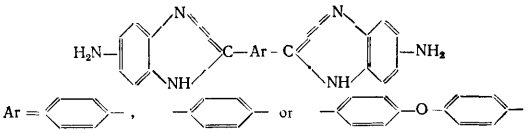


were used by Preston and coworkers[22,46,60] to obtain polyimides on the basis of pyromellitic and benzophenone-3,3',4,4'-tetracarboxylic acids. According to Korshak and Maksimov[69], an appreciable increase in the thermal stability of the systems under consideration might have been expected following the introduction of the benzothiazole ring into the main chains of the macromolecules, but the benzothiazole-containing polyimides did not in fact differ from their benzoxazole-containing analogues[22] and benzothiazole-containing diamines having the above structure have not therefore been widely used in the synthesis of polyimides.

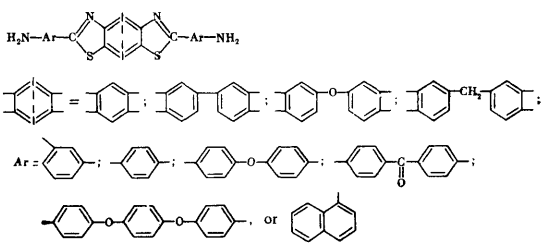
All the above considerations are valid also for benzothiazole-containing diamines having the general formula[22,61,70]



In the series of benzazole-containing aromatic diamines compounds containing benzimidazole rings have attracted most attention. Diamines having the general formula



have been comparatively little used[50], while products based on bis(*o*-phenylenediamines) and having the general formula

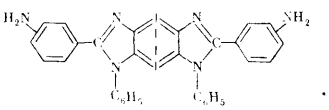


have been used to synthesise polyimides by a number of Soviet and foreign investigators[44,45,47,49,55,57-59,68,71-74].

Detailed studies of polyimides based on benzimidazole-containing diamines[55] showed that, under the classical conditions of the two-stage synthesis of aromatic polyamides, i.e. when a solid dianhydride is added to a solution of the diamine, high-molecular-weight film-forming PAA are formed ($\eta_{log} = 0.48-3.3$). Thermal imidisation of the resulting films at 280–320 °C yielded polyimide films with comparatively high tensile strengths (1225–1900 kgf cm$^{-2}$), but giving rise to small elongations on rupture (1.5–3.8%).

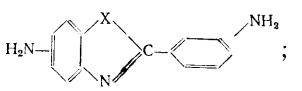
The study of the thermal stability of the polyimides by the DTGA method (air, $\Delta T = 5$ K min$^{-1}$) showed that weight losses corresponding to 15% are observed in the temperature range 620–630 °C; however, one should note that such high values of the thermal characteristics of benzimidazole-containing polyimides conflict with the results of Preston and Black[45].

Korshak et al.[75] synthesised a series of symmetrical diamines containing *N*-phenylbenzimidazole rings:



The interaction of these diamines with the dianhydrides of aromatic tetracarboxylic acids under the conditions of one- and two-stage polycyclocondensation yielded polyimides containing *N*-phenylbenzimidazole rings[76–79]. In contrast to the polyimides examined above, which are obtained from diamines containing unsubstituted benzimidazole rings, these polymers are in most cases soluble in organic solvents, which makes it possible to make them into articles in the final stage. The polymers obtained in a number of investigations[76–79] exhibited high viscosities ($\eta_{int} = 0.2-2.00$), which makes it possible to convert them into films with interesting electrophysical properties[76]. The polyimides synthesised under the conditions of DTGA ($\Delta T = 5$ K min$^{-1}$, air) lost 10% of their weight at 520–550 °C and had softening temperatures between 300° and 540 °C depending on their structure.

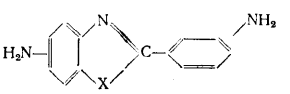
Together with symmetrical benzazole-containing diamines, asymmetric diamines containing benzoxazole, benzimidazole, and benzothiazole rings have attracted much attention[51,80,81]:



X = O; S; NH .

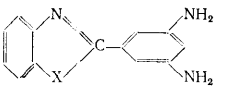
The interaction of asymmetric diamines with the dianhydrides of tetracarboxylic acids under the conditions of a two-stage process gave rise to benzazole-containing polyimides[51,74,80,82–86].

In contrast to the symmetrical diamines examined above, compounds having the general formula



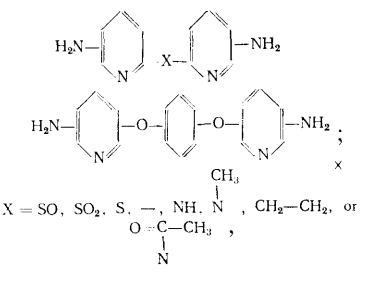
contain amino-groups with non-equivalent nucleophilic properties, which makes it possible to obtain from them polymers with a limited degree of order[82]; the few data available in the literature[87] indicate a comparatively low basicity of such compounds, which is nevertheless sufficient to obtain from them PAA with fairly high viscosity characteristics ($\eta_{log} = 0.6-2.5$). Despite their lack of order, the final structures—polyimides containing benzazole rings—hardly differ from polyimides obtained from symmetrical benzazole-containing diamines: their melting points are in the range 540–575 °C and the temperatures of the onset of their decomposition are in the range 525–575 °C (DTGA, $N_2$, $\Delta T = 15$ K min$^{-1}$).

Polyimides based on the benzazole-containing symmetrical and asymmetric diamines listed above contain benzazole heterocycles in the main macromolecular chains, which gives rise to the insolubility of the majority of these polyimides in organic solvents. When the benzazole ring is introduced as a side group into the macromolecular chains of polyimides, which is achieved by employing diamines with a specific structure[51,88]



conditions are created for imparting solubility in organic solvents to polyimides, although information concerning the realisation of this possibility is not available in the literature.

Somewhat less systematic studies have been made on polyimides based on diamines containing six-membered aromatic heterocycles. The simplest diamine of this kind—2,6-diaminopyridine—attracted the attention of a number of research groups[35,36,89–91], but the weak nucleophilic properties of the second amino-group ($pK_{a2} = 1.67$) in this compound constituted a serious obstacle to the synthesis of high-molecular-weight polymers from it. Monomers of the bipyridyl series having the structural formulae

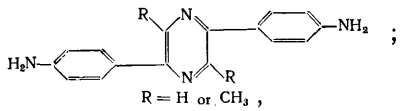


X = SO, $SO_2$, S, —, NH, , $CH_2$—$CH_2$, or ,

which are less readily available but are more nucleophilic compared with 2,6-diaminopyridine, have been used to synthesise polyimides[92,93]. Because of the relatively high nucleophilicities of diamines of this kind, they can interact with the dianhydrides of pyromellitic and benzophenone-3,3',4,4'-tetracarboxylic acids under the conditions of low-temperature polycondensation in dimethyl sulphoxide (DMSO) to yield high-molecular-weight ($\eta_{log}$ up to 2.26) film-forming PAA, whose cyclisation *in vacuo* at 190–200 °C for 2–2.5 h yielded polyimides.

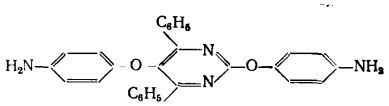
It is of interest to note that, according to the data of Kurita and Williams[92], the introduction of heteroatoms into aromatic rings increases significantly the solubility of polyimides in organic solvents. Polyimides obtained from bipyridyl-containing diamines, incorporating as groups X sulphide, sulphoxide, or sulphone fragments, are readily soluble in dimethylacetamide (DMAA) and *m*-cresol. On the other hand, the thermal stability of polyimides of this kind is appreciably lower than that of their carbocyclic analogues. It may be that these properties of bipyridyl-containing polyimides are due to the unduly mild imidisation conditions, which do not lead to a high degree of completion of this process.

A series of pyrazine-containing diamines having the general formula



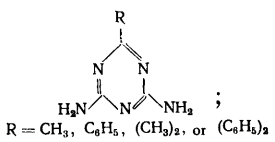
as well as isomeric compounds have been used[94] to obtain polyimides under the conditions of two-stage polycyclocondensation. PAA with logarithmic viscosities in the range 0.22–1.86 have been obtained in DMAA at 20 °C, those with highest molecular weights exhibiting film-forming properties. The thermal imidisation of these products at 250–270 °C led to the formation of polyimides soluble only in sulphuric and methanesulphonic acids and suffering a 5% weight loss (DTGA, $N_2$, $\Delta T = 5$ K min$^{-1}$) at 485–595 °C.

Polyimides soluble in amide solvents have been obtained[95] by the interaction of 2,5-bis(4-amino phenoxy)-4,6-diphenylpyrimidine



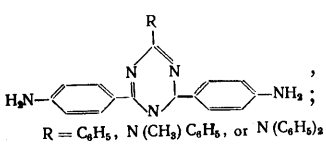
with a series of dianhydrides of aromatic tetracarboxylic acids. The polyimides synthesised exhibit an anomalous thermal stability—their decomposition temperatures do not exceed 310 °C.

Polyimides based on diamines containing symmetrical triazine rings have attracted much attention. The simplest compounds of this series—products having the general formula



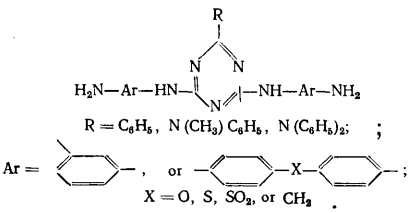
have a weakly nucleophilic second amino-group according to some data[35,36] ($pK_{a2} = 1.90$), which prevents the formation of polyamides with high molecular weights on the basis of these compounds[35,36,96,97]. Nevertheless, polyimides have been successfully synthesised as a result of the two-stage interaction of the above compounds with the dianhydrides of pyromellitic and benzophenone-3,3′,4,4′-tetracarboxylic acids, yielding polyimides which began to lose structure, according to DTGA data[96], at 390–420 °C in air and at 440–460 °C in $N_2$.

Triazine-containing diamines having the general formula



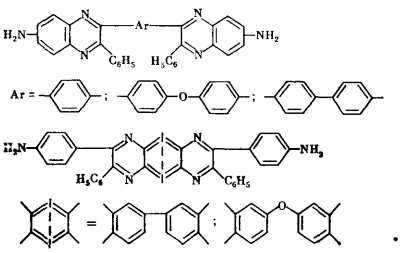
have been used[98,99] to obtain high-molecular-weight film-forming polyimides with high thermal stability and fire resistance.

Analogous results have been achieved by a number of investigators[100–103], who synthesised polyimides from diamines having the general formulae



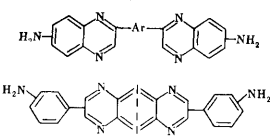
The presence of bulky side groups in the triazine-containing diamines discussed above makes it possible, in principle, to render the final polyimide soluble in organic solvents; however, only some of the investigators concerned have reported the realisation of this possibility[96,100,101].

A much more unambiguous influence of the introduction of a bulky substituent into the diamine molecule on the solubility of polyimides has been traced in the studies by Korshak and coworkers[104–107], who synthesised polyimides from diamines containing quinoxaline rings[107–109]:

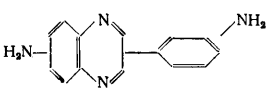


The large set of diamines makes it possible to vary the properties of the final polyamides[105], which combine a high thermal stability with solubility in *m*-cresol, *N*-methyl-2-pyrrolidinone, and the 3 : 1 tetrachloroethane–phenol mixture.

The decisive influence of the phenyl substituent on the solubility of polyimides has been confirmed by the finding that polyimides based on symmetrical diamines containing unsubstituted quinoxaline rings[110,111],

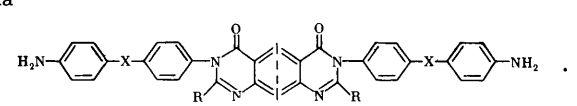


as well as asymmetric diamines having the general formula[77, 110–112]



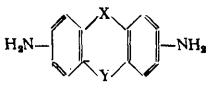
are insoluble in organic solvents.

Results confirming the increased solubility of the final polyimides under the influence of side groups in the diamines have been obtained also using as the starting compounds quinazolinone-containing diamines[113–115] having the general formula



The polyimides obtained from such diamines dissolved in *m*-cresol and exhibited thermal characteristics comparable to those of the usual polyamides.

In the series of diamines containing highly condensed heterocycles (tricyclic and tetracyclic systems) compounds having the general formula



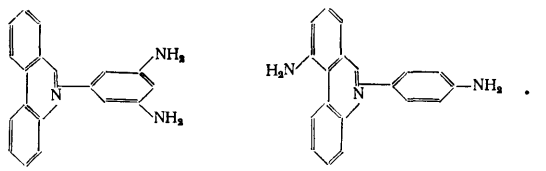
X = O, Y = S, $SO_2$, or CO; X = $SO_2$, Y = O, S, $SO_2$, or $CH_2$

have attracted most attention. The interaction of diaminophenoxathiine with the dianhydrides of aromatic tetracarboxylic acids yielded polyimides[116-118] with a higher thermal stability than that of polyimides based on di(4-aminophenyl) ether[118].

Polypyromellitimides[119], obtained using 2,7-diaminoxanthone as the initial compound, undergo an appreciable weight loss (under the conditions of DTGA) only at 500 °C.

High-molecular-weight film-forming polyimides have been synthesised by the two-stage interaction of diaminocyclosulphones with the dianhydrides of aromatic tetracarboxylic acids[120].

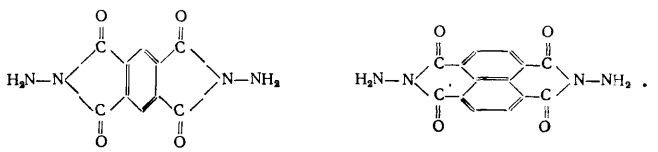
Polyimides based on aromatic diamines containing phenanthridine rings also exhibit high thermal characteristics[121-134]:



It is of interest to note that polyimides obtained from phenanthridine-containing diamines did not dissolve in organic solvents regardless of the location of the heterocycle (in the main chain or as a side group) and of the method of imidisation.

The attempts to employ 3,9-acridine as the monomer[91] did not lead to high-molecular-weight polymers as a consequence of the weak nucleophilic properties of this monomer.

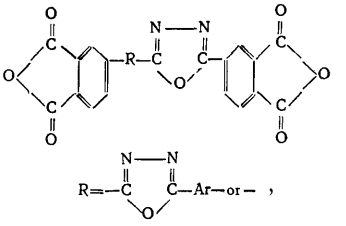
In the series of heterocyclic diamines monomers containing imide rings were of special interest, since one may hope to obtain, by an appropriate selection of those compounds, macromolecules consisting of imide rings only. An attempt to create such structures was undertaken by Dine-Hart[125], who used *N,N'*-diamino(pyromellitimide) and *N,N'*-diamino-(tetracarboxynaphthalene diimide):



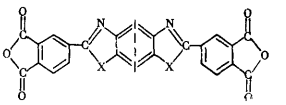
The attempt to synthesise high-molecular-weight polyimides was unsuccessful. Even the feasibility of the above solution of the problem of synthesising high-molecular-weight polymers of this type, capable of being worked, is controversial in view of the weakness of the N–N bonds in the main macromolecular chains.

The structural set of dianhydrides of heterocyclic aromatic tetracarboxylic acids, used to synthesise polyimides, is much smaller than the set of heterocyclic diamines discussed above. In the series of dianhydrides of the tetracarboxylic acids derived from the simplest aromatic heterocycles the dianhydrides of furan-2,3,4,5-tetracarboxylic[126] and thiophen-2,3,4,5-tetracarboxylic acids[100,126,132] attracted attention, but the properties of polyimides based on these monomers have not been studied in detail.

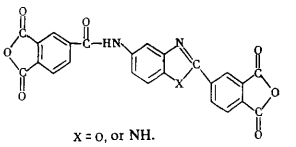
In the series of azole-containing dianhydrides of tetracarboxylic acids only 1,3,4-oxadiazole-containing compounds having the formula[44,133-135]



and in the series of benzazole-containing dianhydrides compounds having the general formulae[136-139]



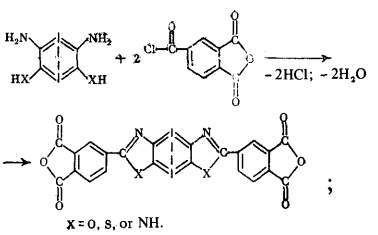
X = O, S, or NH;



X = O, or NH.

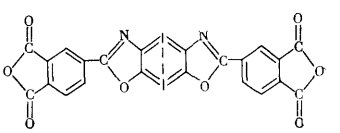
have been widely used.

In most cases, the dianhydrides of tetracarboxylic acids containing azole and benzazole heterocycles can be obtained by the interaction of tetra- or tri-functional nucleophiles with the 4-chloroformyl derivatives of phthalic anhydride[140]:



X = O, S, or NH.

Dianhydrides containing benzoxazole rings[140], particularly compounds having the formula



have been most widely used. Their interactions with di(4-aminophenyl) ether under the conditions of low-temperature polycondensation yielded PAA with $\eta_{log} \geq 0.4$; poly(benzoxazole-imides), obtained by the heat treatment of PAA at 200–380 °C *in vacuo* for 1 h, exhibited high thermal characteristics.

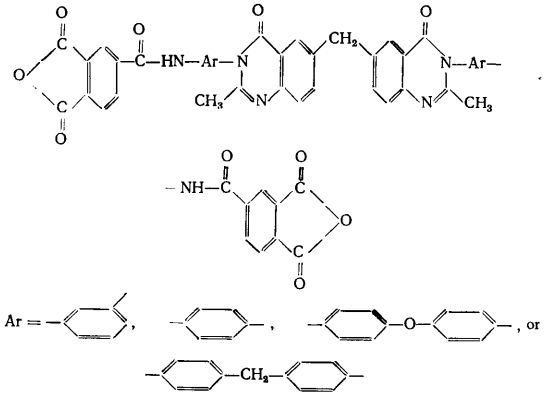
Poly(benzoxazole-imide) films are very strong and last for a long time at 300 °C. The study of the resistance of poly(benzoxazole-imides) to alkalis showed that, on being boiled for 30 min in 10% aqueous solutions of sodium hydroxide, the films hardly changed, their chemical stability being much superior to that of the usual polyimide films.

In the series of dianhydrides of aromatic heterocyclic tetracarboxylic acids containing six-membered heterocycles detailed studies have been made of the dianhydrides of pyridine-2,3,5,6-tetracarboxylic[126,141] and pyrazine-2,3,5,6-tetracarboxylic acids[35-39,90,100,126,127-131,142-146]. The second

dianhydride attracted the attention of numerous investigators in view of the possibility, in principle, of using it to synthesise hydrogen-free polyimides, although, as stated previously, the problem of applying this idea in practice remains open.

The dianhydrides of tetracarboxylic acids containing substituted symmetrical triazine rings[99,147,148] have been used, by analogy with diamines containing identical fragments, to synthesise polyimides soluble in organic solvents[99,147,148].

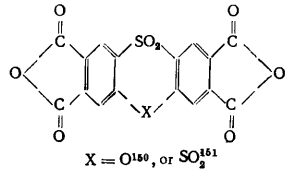
The interaction of the dianhydrides of tetracarboxylic acids containing substituted quinazolinone rings and amide groups and having the general formula



with various aromatic diamines yielded polyimides incorporating amide and quinazolinone groups[149]; these polyimides are soluble in *m*-cresol, but their thermal stability is somewhat lower than that of polyimides obtained from quinazolinone-containing diamines[113-115].

A number of investigators[150,151] attempted to synthesise polyimides from the dianhydrides of tetracarboxylic acids containing highly condensed (tricyclic and polycyclic) heterocycles. The aim in introducing such fragments was usually to increase the thermal stability and heat resistance of the polyimides, which, however, is not achieved in all cases.

When initial compounds having the general formula



were used under the conditions of two-stage processes, polyimides giving rise to strong elastic films and stable up to 440 °C were obtained according to patent data[151].

The syntheses of polymers based on monomers containing heterocyclic units discussed above have not only significant advantages (see above) but also suffer from considerable disadvantages. The latter include the following.

(1) An increased rigidity of the PAA containing certain (particularly highly condensed) heterocycles, which precludes a high solubility of these fore-polymers and a high capacity for being worked into articles.

(2) The reduced reactivity of certain monomers containing aromatic heterocyclic units, which precludes the synthesis of high-molecular-weight polymeric products from these compounds.

In view of the above disadvantages of the method, investigators became interested in monomers, containing groups leading to the final heterocyclic systems, as the initial compounds for the synthesis of polyimides.

## III. POLYIMIDES BASED ON MONOMERS CONTAINING GROUPS CAPABLE OF GIVING RISE TO THE REQUIRED HETEROCYCLIC SYSTEMS

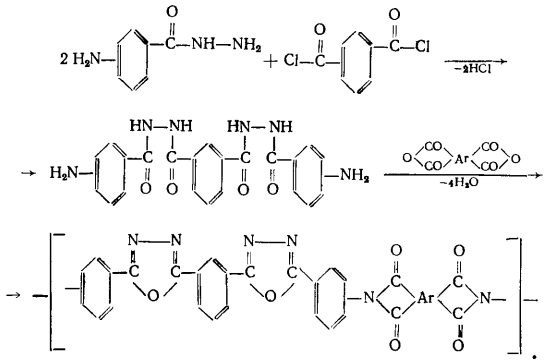
The simplest diamines of this type, containing groups capable of forming the 1,3,4-oxadiazole rings[51] (hydrazide fragments), have been obtained by the interaction of isomeric nitrobenzoic acid chlorides and hydrazides with subsequent mild reduction of the di(nitroaryl)hydrazides.

When the hydrazides of nitrobenzoic acids and the dichlorides of aromatic dicarboxylic acids were used as the comonomers (with subsequent reduction of the nitro-groups), diamines containing two hydrazide groups were obtained[51,152]. The reaction of these compounds with the dianhydrides of pyromellitic and benzophenone-3,3',4,4'-tetracarboxylic acids in DMAA led to the synthesis of PAA containing hydrazide groups, the heat treatment of which led to ordered copolyimido-1,3,4-oxadiazoles[51,152].

Solutions of PAA containing hydrazide fragments had fairly high viscosities ($\eta_{log} = 0.53-0.92$ dl $g^{-1}$), which made it possible to obtain strong and elastic films from them. Heating the polymers to 150 °C led to their imidisation and the formation of polyimidohydrazides, while heating to higher temperatures (up to 325 °C) resulted in the cyclisation of the hydrazide fragments to the 1,3,4-oxadiazole groups.

A study of the thermal stability of simple copoly(oxadiazole-imides) containing two imide groups per oxadiazole group showed that it is comparable to that of the best polyimide structures, while polymers with the same numbers of imide and oxadiazole rings proved to be less thermally stable[51].

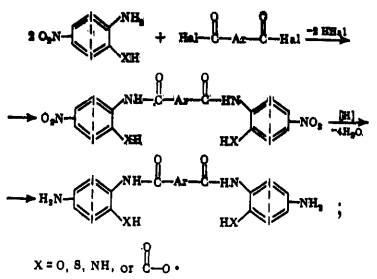
Preston chose a somewhat different approach to the synthesis of diamines containing hydrazide fragments[153,154] using the difference between the nucleophilic reactivities of the amino- and hydrazide groups of *p*-aminobenzohydrazide. The diamines obtained in this way, containing two hydrazide fragments, can be made to react directly with the dianhydride of a tetracarboxylic acid:



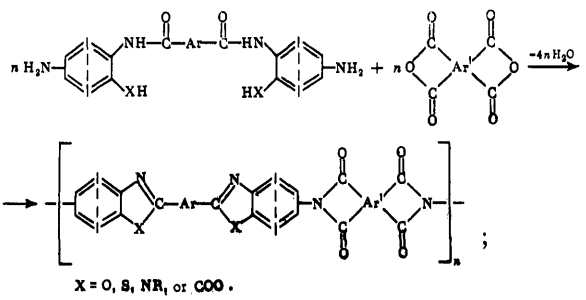
The structure of the resulting diamines is in this case less unambiguous than in the case where nitro-derivatives are used—apparently the interaction of the acid chloride groups can involve partially also the amino-group of the aminobenzohydrazide with formation of amide and amidoimide fragments in the final copolyimido-1,3,4-oxadiazoles, which have an unfavourable effect on various properties of these systems.

A general approach to the synthesis of symmetrical diamines incorporating groups capable of giving rise to benzazole and benzoxazinone rings has been proposed by Kurihara et al.,[155] who achieved the interaction of nitroamines containing various substituents with the dihalides of dicarboxylic acids and the

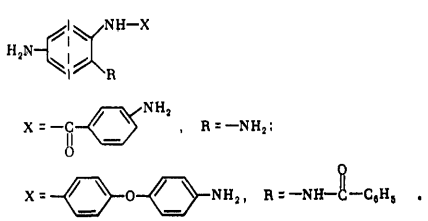
reduction of the resulting dinitro-compounds to the corresponding diamines:



The interaction of the resulting diamines with the dianhydrides of tetracarboxylic acids and subsequent heat treatment of the resulting pre-polymers led to the synthesis of polyimides containing benzoxazole, benzothiazole, benzimidazole, and benzoxazinone rings in the main chains of the macromolecules:



Asymmetric diamines containing groups capable of giving rise to benzimidazole and *N*-phenylbenzimidazole rings have been used[156-158] to synthesise film- and fibre-forming polyimides containing imidazole and *N*-phenylbenzimidazole rings:



A much larger number of studies were designed to synthesise polyimides from the dianhydrides of tetracarboxylic acids containing groups capable of giving rise to various, primarily azole and benzazole, heterocycles. The extensive development of such investigations was due mainly to the fact that the initial compounds can be obtained by a standard procedure involving the interaction of various tetrafunctional compounds, which have found applications in the chemistry of polyazoles[29-32], with the 4-chloroformyl derivatives of phthalic anhydride, which is a derivative of the readily available trimellitic acid[140].

Dianhydrides containing acylamidoxime fragments, capable of giving rise to 1,2,4-oxadiazole rings, have been obtained by the reaction of the bisamidoximes of dicarboxylic acids with the 4-chloroformyl derivatives of phthalic anhydride. The reaction of these compounds with aromatic diamines under the conditions of two-stage polycyclocondensation led to polyimides with 1,2,4-oxadiazole rings[135,160].

Polyimides containing isomeric 1,3,4-oxadiazole rings, whose thermal stability is higher than that of the compounds with 1,2,4-oxadiazole rings, have been obtained by the reaction of dicarboxylic acid dihydrazides with the 4-chloroformyl derivative of phthalic anhydride; the reaction of the dianhydrides containing hydrazide groups, obtained in this way, with diamines and the thermal cyclisation of the resulting copolyhydrazidoamidoacids[161] led to the synthesis of copolyimido-1,3,4-oxadiazoles.

A large series of studies were devoted to the synthesis of dianhydrides containing groups capable of giving rise to benzazole and benzoxazinone rings[162-166]. The interaction of these dianhydrides with aromatic diamines yielded high-molecular-weight ($\eta_{log}$ up to 1.9) PAA containing groups capable of giving rise to benzazole and benzoxazinone rings; subsequent heat treatment at 250–400 °C converts these PAA into polyimides containing benzoxazole[137,162-175], benzothiazole[162-166,174], benzoxazinone[162-166,175], as well as unsubstituted[162-166,176,177] and *N*-substituted[178] benzimidazole rings.

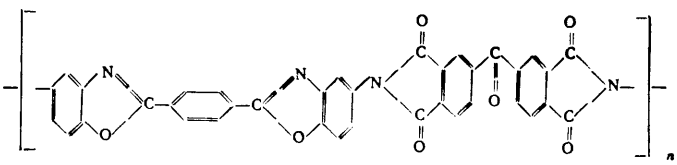
The synthesis of poly(benzoxazoleimides) proceeds most smoothly owing to the ease of the selective acylation of bis(*o*-aminophenols) by the 4-chloroformyl derivative of phthalic anhydride, while the acylation of bis(*o*-phenylenediamines) and bis(*o*-aminothiophenols) by this compound is accompanied by side reactions and ultimately by gel formation. The more nearly ideal structure of poly(benzoxazoleimides) is responsible for their higher thermal characteristics compared with the remaining systems.

A number of studies were undertaken to synthesise copolymers from mixtures of traditional dianhydrides of aromatic tetracarboxylic acids with dianhydrides containing groups capable of giving rise to benzimidazole[179], benzothiazole[180], and benzoxazinone[181] rings.

The fact that almost all reactions using dianhydrides containing groups capable of forming azole, benzazole, and benzoxizinone rings have been carried out without isolating the dianhydrides from the reaction mixture merits attention; this approach is undoubtedly of considerable interest, since it makes it possible to eliminate the laborious and expensive processes involving the isolation and purification of the monomers and hence simplifies the technological synthesis of polymers and also reduces the cost of the latter. Evidently, this approach deserves the widest possible development, particularly in those cases where the syntheses of monomers proceed with a high selectivity and lead to homogeneous initial compounds and not mixtures of products containing various functional groups.

A critical examination of the foregoing data shows that the vast majority of studies on polyimides, obtained from heterocyclic monomers or monomers containing groups capable of giving rise to the required heterocycles, have been purely of their synthesis. Despite the large amount of evidence (particularly in patents) concerning the possibility of obtaining on the basis of polymers of this kind a wide range of materials for all purposes, specific data on the properties of the resulting articles are very few. The properties of materials obtained from polyimides containing azole and benzazole rings, introduced into these polymers as part of the initial diamines, have been examined in greatest detail. In particular, reinforced plastics, obtained using polyimides based on diamines containing 1,3,4-oxadiazole and benzimidazole rings, have been investigated in detail[182,183]. The properties of articles made from polyimides based on diamines and benzoxazole rings have been studied in even greater detail. In particular, fibres whose resistance to thermo-oxidative degradation is superior to that of the poly(*p,p'*-oxydiphenylenepyromellitimide) fibre[186] and the polypyromellitimide fibre based on 2,5-di(*p*-aminophenyl)-1,3,4-oxadiazole

have been obtained[184-189] from the polyimide



synthesised by the reaction of a benzoxazole-containing diamine with the dianhydride of benzophenone-3,3',4,4'-tetracarboxylic acid[187]; the copoly(benzoxazole-imide) fibres have a unique ability to retain acceptable strength characteristics up to temperatures of 500 °C.

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