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New bis(naphthalic anhydrides) and polyheteroarylenes based on them with improved processability

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ABSTRACT. New bis(naphthalic anhydrides) containing 'hinge' groups and/or bulky substituents are considered. It has been shown that the majority of these monomers may be synthesised from derivatives of naphthalic anhydride or acenaphthene with subsequent oxidation of the bisacenaphthyls obtained. Reaction of these compounds with aromatic diamines and bis(*o*-phenylenediamines) gives polynaphthalimides and polynaphthoylenebenzimidazoles combining solubility in organic solvents with high thermal and chemical stability.

The bibliography contains 154 references.

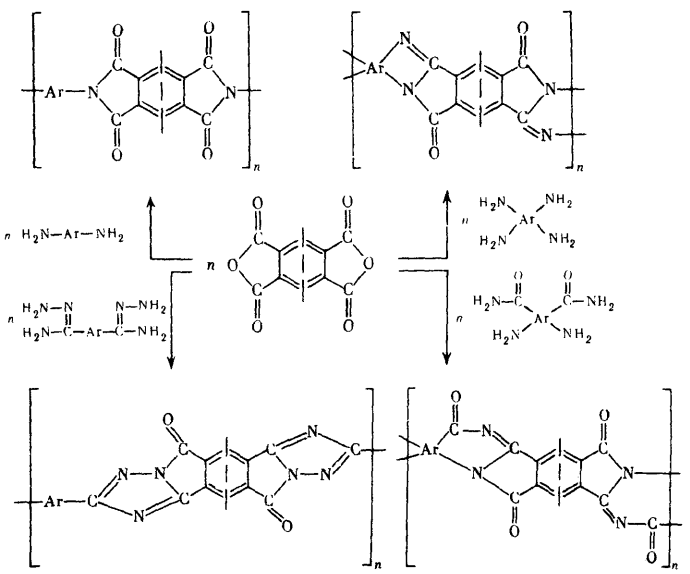
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I. Introduction

The rapidly developing variety of modern techniques present ever-increasing requirements for the polymers used in them. Investigations on thermally and chemically stable polymers are fairly widespread[1–9] and in some of these the polyheteroarylenes, aromatic polymers containing heterocycles in the main chains of the macromolecule, have attracted particular interest. This interest is explained by the spectrum of valuable, occasionally unique, physicochemical and mechanical properties possessed by these polymers and the materials based on them.[1–21]

A significant portion of the studies on the synthesis of polyheteroarylenes is devoted to polymers based on bis(phthalic anhydrides). These monomers are widely used in the synthesis of polyimides[22–25] and of the completely and partially 'ladder' polyheteroarylenes,[26] the polybenzoylenebenzimidazoles, polybenzoylene-S-triazoles, polyisoindoloquinazolinediones,[27] etc., which are illustrated by the following scheme:

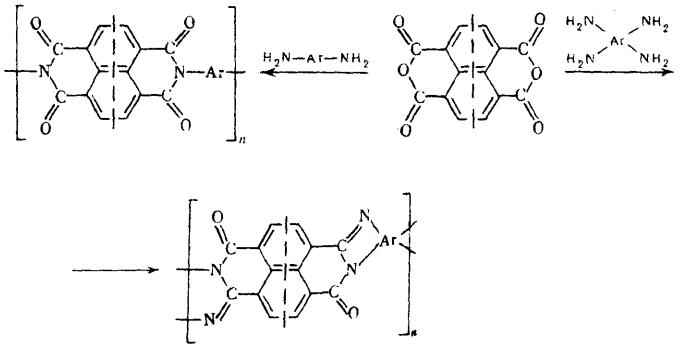


Practically all these polyheteroarylenes are obtained using stepwise processes with the possibility of stopping the reaction at the stages of formation, of prepolymers soluble in organic solvents, processing of the prepolymers into a product and subsequent cyclisation of them in the form of the finished products with the formation of the desired infusible and insoluble polyheteroarylenes as the already finished goods.

It must however be noted that both the polyimides and the ladder polyheteroarylenes based on bis(phthalic anhydrides) possess comparatively low thermal and chemical stability.[27] This is caused to a significant extent by the strain of the five-membered imide fragments of the resulting heterocycles and the high positive charges on the carbon atoms of the carbonyl groups of these systems.

The logical route leading to a potential increase in the thermal and chemical stability of the polyheteroarylenes is the replacement of the bis(phthalic anhydrides) in the above-mentioned reactions by bis(naphthalic anhydrides) the structure of which should be determined by the formation of systems containing six-membered imide rings, either on their own or condensed with other heterocyclic fragments.

Previous investigations[28–37] have shown that on using bis(naphthalic anhydrides) as monomers polynaphthalimides and polynapht'ioylenebenzimidazoles are obtained which possess high chemical and thermal stability and fire resistance compared with analogous systems based on the bis(phthalic anhydrides).[28–40]

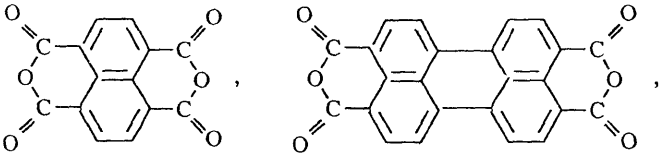


The polymers based on bis(naphthalic anhydrides) are therefore more promising than those based on bis(phthalic anhydrides) from the point of view of creating materials with improved properties.

It must however be noted that the polyheteroarylenes based on bis(naphthalic anhydrides) are generally systems with a low ability to be processed into articles. On the one hand the final polyheteroarylenes are infusible and are soluble in strong acids, such as sulphuric, methanesulphonic or polyphosphoric, and on the other the reactions using bis(naphthalic anhydrides) as stepwise processes are difficult due to the reduced electrophilic reactivity of bis(naphthalic anhydrides) and the ease of forming six-membered naphthalimide systems.

Hence it follows that the development of polyheteroarylenes based on bis(naphthalic anhydrides) characterised by a satisfactory processability into articles is an important and urgent problem in the chemistry of thermostable polymers. One of the most common routes of improving the processability of polyheteroarylenes is the conferring on them of solubility in organic solvents. The main ways to solve this problem are:

1. The synthesis of polyheteroarylenes based on the most common bis(naphthalic anhydrides), i.e. the anhydrides of naphthalene-1,4,5,8-tetracarboxylic and perylene-3,4,9,10-tetracarboxylic acids



and nucleophilic co-monomers differing in the structure which causes an improved processability of the desired polyheteroarylenes.

2. The development of bis(naphthalic anhydrides) containing structural elements causing improved processability of the polyheteroarylenes based on them and the use of the indicated bis(naphthalic anhydrides) in reactions with di- and tetra-functional nucleophilic comonomers.

Since the first of the above-mentioned approaches has been considered previously,[24,41,42] attempts will be undertaken in the present review to analyse the results obtained in the second direction.

The main approaches[43,44] to the conferment of solubility in organic solvents to the polyheteroarylenes by modifying the initial dianhydrides are:

a) the introduction of 'hinge' bonds into the molecules which facilitate to a maximal extent the rotation of the individual fragments of the macromolecule relative to one another and b) the introduction into the molecule of anhydrides with bulky substituents.

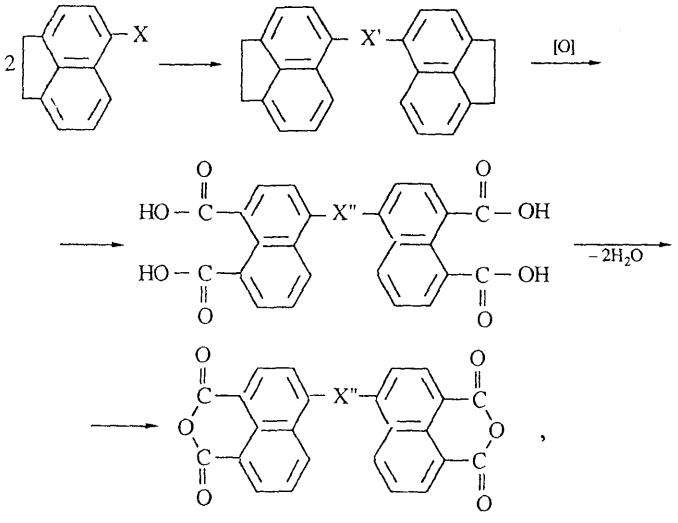
A combined approach is frequently used, i.e. both hinges and bulky substituents are introduced into the anhydride molecule.

These approaches and combinations of them were used in the development of new bis(naphthalic dianhydrides) intended for the preparation of polyheteroarylenes soluble in organic solvents.

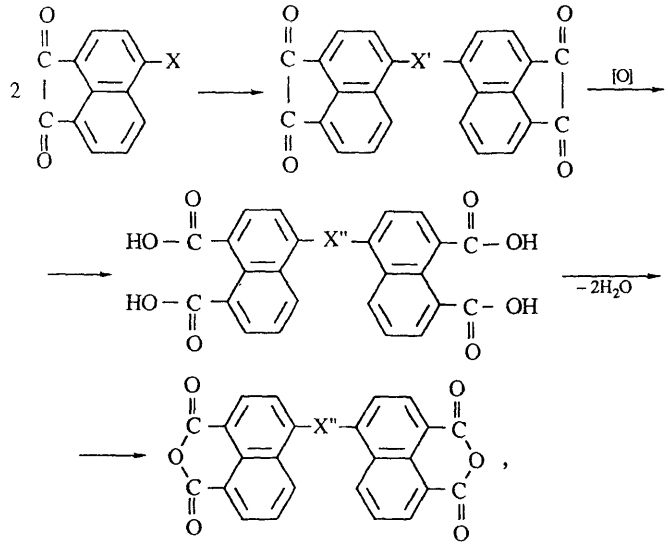
II. Bis(naphthalic anhydrides) containing structural elements causing improved solubility of the polyheteroarylenes based on them

The simplest modification of the most common bis(naphthalic anhydrides) directed towards improving the processability of the polyheteroarylenes derived from them is the introduction of a single bond or a hinge group between two naphthalic anhydride residues. Analogous bis(naphthalic anhydrides)[42] are most frequently obtained from acenaphthene[45] or its simplest derivatives using such approaches as:

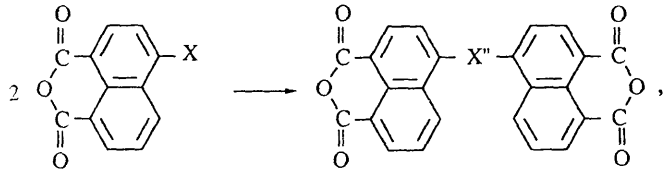
– the reaction of two molecules of acenaphthene or a derivative with the appropriate compounds leading to the formation of bis-acenaphthenes, subsequent oxidation[46] of them and dehydration of the resulting bis(naphthalic acids):



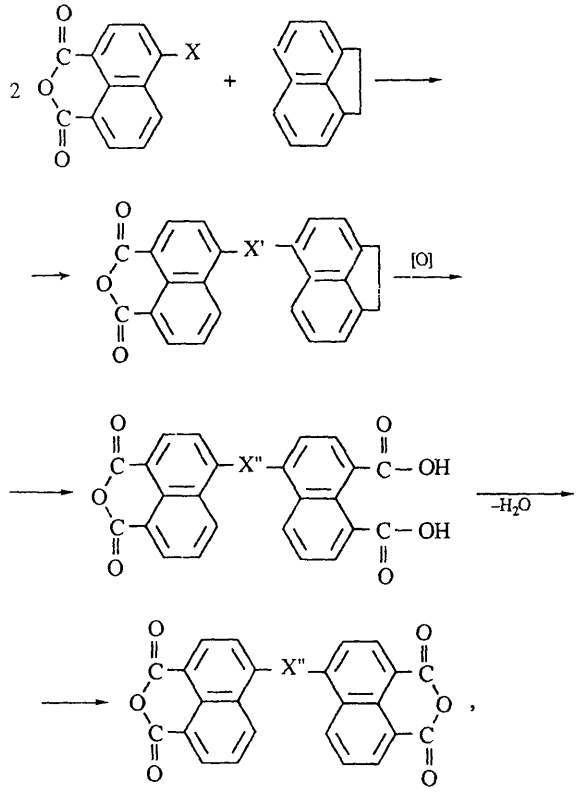
– the reaction of two molecules of acenaphthoquinone derivatives (product of partial oxidation of acenaphthene) with appropriate compounds and subsequent oxidation of the resulting bis-acenaphthoquinones to bis(naphthalic anhydrides):



– the reaction of two molecules of the naphthalic anhydride derivative (derived from acenaphthene[45]) with appropriate compounds leading to the formation of bis(naphthalic anhydrides):

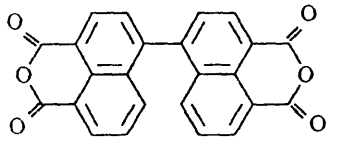


– the reaction of naphthalic anhydride derivatives with acenaphthene or a derivative of it leading to the formation of compounds containing both an acenaphthyl and an anhydride function with subsequent oxidation of the acenaphthyl group and dehydration of the resulting acid function:

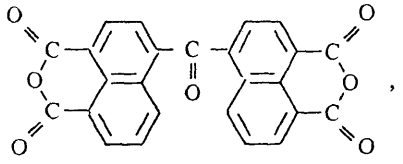


Certain monomers of this type containing separate naphthalic anhydride residues were obtained a fairly long time ago. Their simplest representatives are as follows:

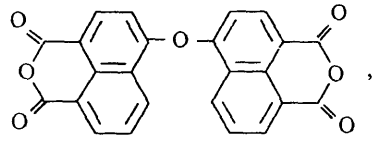
4,4′-Bis(naphthalic anhydride)[47,48]



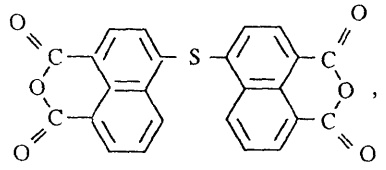
4,4′-Ketobis(naphthalic anhydride)[49,50]



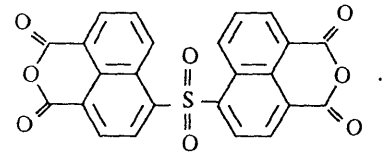
4,4′-Epoxybis(naphthalic anhydride)[51–54]



4,4′-Thiobis(naphthalic anhydride)[55,56]



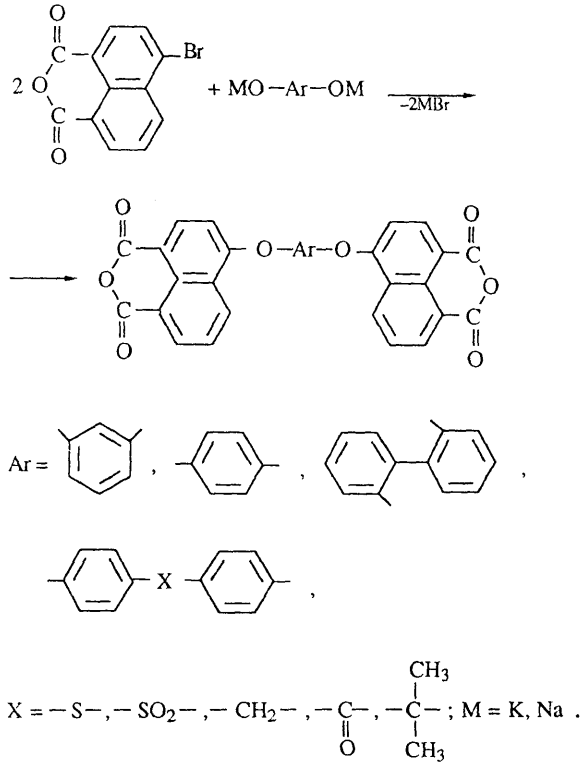
4,4′-Sulphonylbis(naphthalic anhydride)[56,57]



It must however be noted that polyheteroarylenes, primarily polynaphthoylenebenzimidazoles, obtained from bis(naphthalic dianhydrides) containing no more than one hinge group and the simplest bis(*o*-phenylenediamines), proved to be soluble only in strong acids and were practically insoluble in a single organic solvent.[55,57–61]

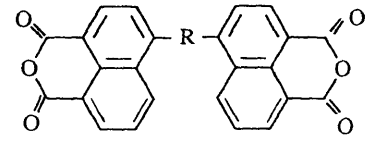
The simplest change in the structure of the bis(naphthalic dianhydrides) directed towards obtaining the desired polyheteroarylenes soluble in organic solvents is the introduction of additional hinge groups.

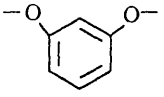
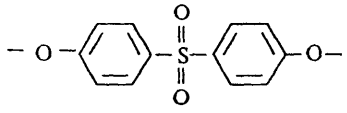
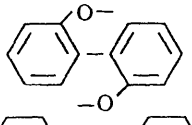
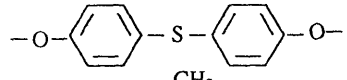
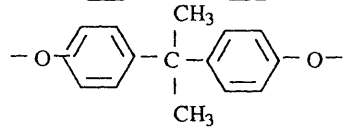
Significant attention has been paid to systems containing at least two ether bonds in several bis(naphthalic anhydrides) containing more than one hinge group. These monomers are obtained by the reaction of two moles of 4-bromonaphthalic anhydride with an alkali metal bisphenoxide in dipolar aprotic solvents[55,62–68] according to the following scheme:



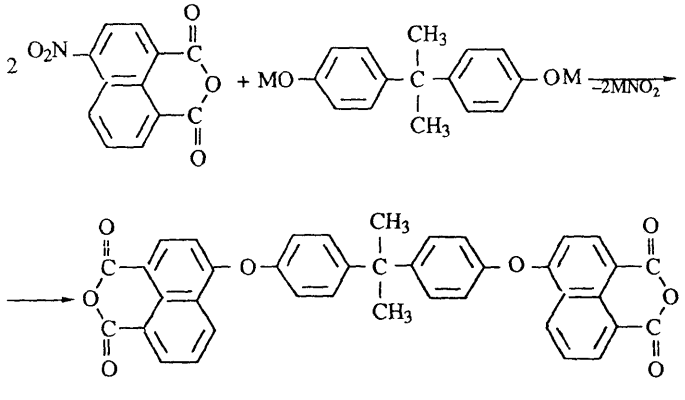
Some characteristics of individual bis(naphthalic anhydrides) containing ether groups are shown in Table 1.

Table 1. Bis(naphthalic anhydrides) of general formula

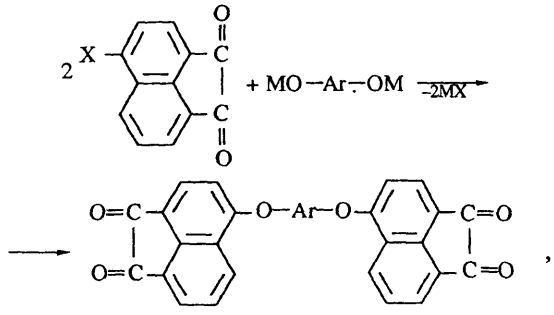


R	Mp, °C	Yield, %	Ref.
	271–272	81.6	[63]
	300	93.0	[63]
	287.5–287.6	95.0	[63]
	274.4–275.5	96.7	[63]
	294–295	70.0	[65]

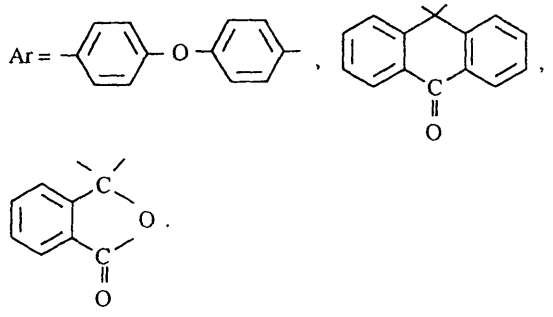
An alternative method of synthesising similar bis(naphthalic anhydrides) is the use of 4-nitronaphthalic anhydride in place of 4-bromonaphthalic anhydride,[69] however this process has only been considered in an extremely fragmentary manner.



The 4-bromo and 4-nitro derivatives of acenaphthoquinone[66,70,72] also react with alkali metal bisphenoxides in the reactions considered above. In these cases bisacenaphthoquinones are formed in the first stage.



X = Br, NO_2;



Individual bisacenaphthoquinones were then oxidised further to bis(naphthalic acids) and then converted into bis(naphthalic anhydrides).[71,72]

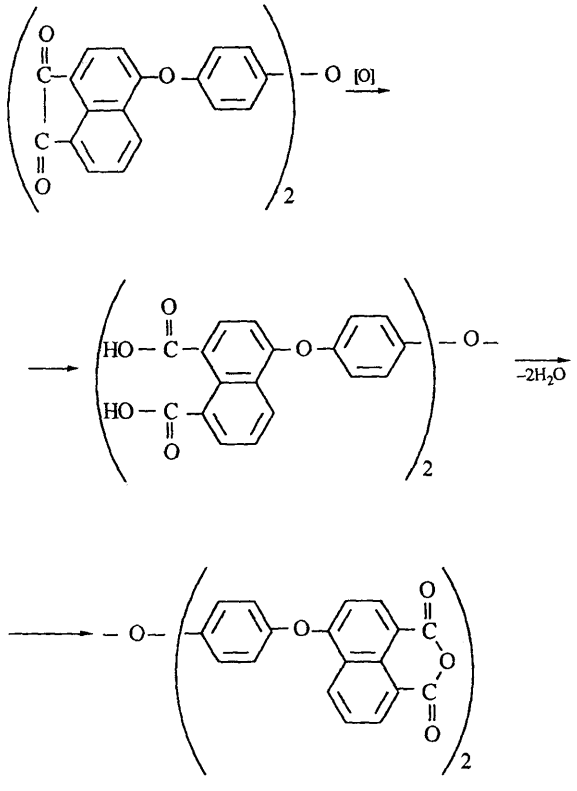
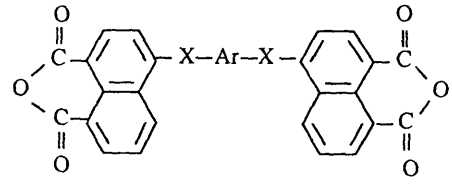
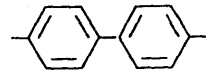
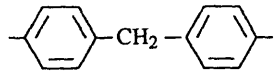
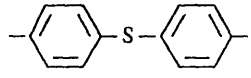
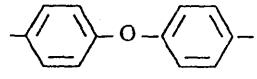
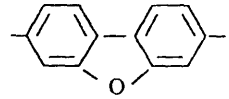
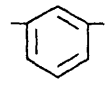
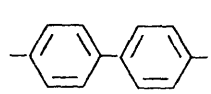
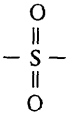
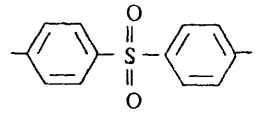
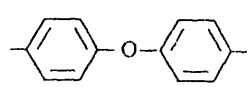
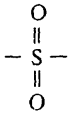
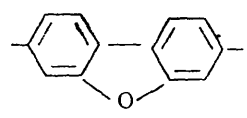
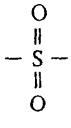
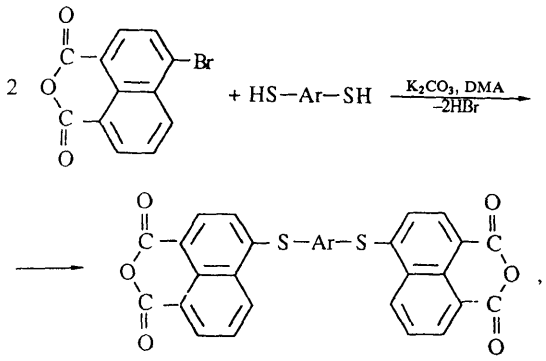


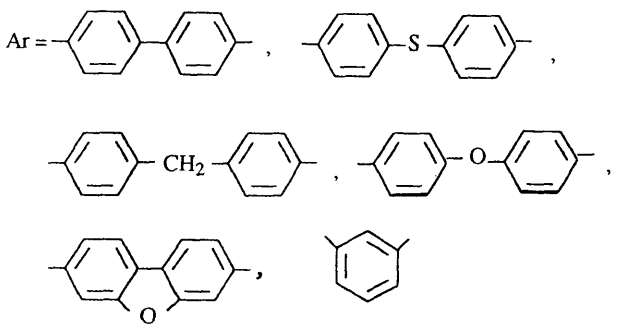
Table 2. Some characteristics of bis(naphthalic anhydrides) of general formula



Ar	X	Mp, °C	Yield, %	Ref.
	—S—	370–372	70	[73, 74]
	—S—	294–296	82	[73, 74]
	—S—	250–251	56	[55, 73, 74]
	—S—	289–291	80	[73, 74]
	—S—	372–374	73	[73, 74]
	—S—	222.5–223	75	[63]
		400–401	92	[73, 74]
		395–396	85	[73, 74]
		358–362	87	[73, 74]
		341–342	91	[73, 74]

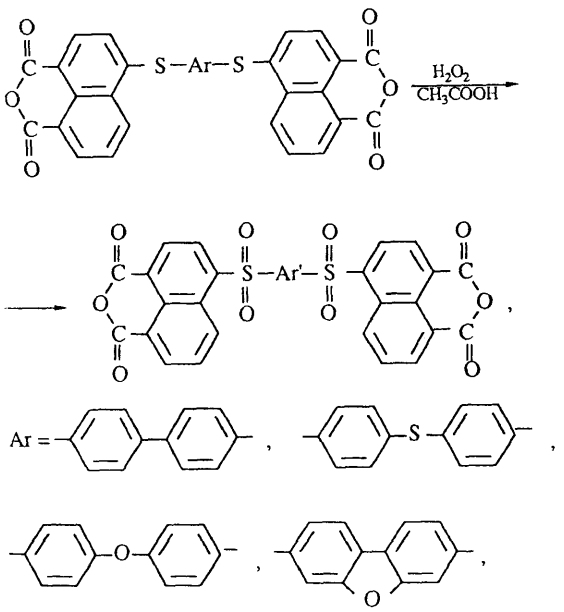
Practically all the reactions considered above for the synthesis of bis(naphthalic anhydrides) containing ether groups may be used for the preparation of bis(naphthalic anhydrides) containing thioether linkages.[55,63,73,74] In these reactions bis(thiophenoxides) are used as starting materials instead of alkali metal bisphenoxides.

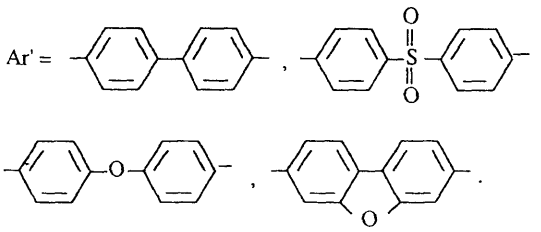




Some characteristics of bis(naphthalic anhydrides) containing thioether groups are given in Table 2.

The bis(naphthalic anhydrides) are characterised by a lower electrophilic reactivity than the bis(phthalic anhydrides). The introduction into them of ether and thioether groups, which are electron-donating substituents, causes a further reduction in their electrophilic reactivity. This led to a switch from electon-donating to electron-accepting hinge groups and in particular to the transition from dianhydrides containing thioether groups to dianhydrides with sulphone fragments. Synthesis was effected by the following scheme:[73,74]





Some characteristics of the bis(naphthalic anhydrides) containing sulphone groups are given in Table 2.

Another large group of bis(naphthalic anhydrides), the so-called bis(ketonaphthalic anhydrides), were obtained by the Friedel–Craft reaction of the diacid chlorides of aromatic dicarboxylic acids with two moles of acenaphthene with subsequent oxidation of the bis(acenaphthyls) to bis(ketonaphthalic acids) which undergo further dehydration to bis(ketonaphthalic anhydrides)[77–81] according to the following scheme:

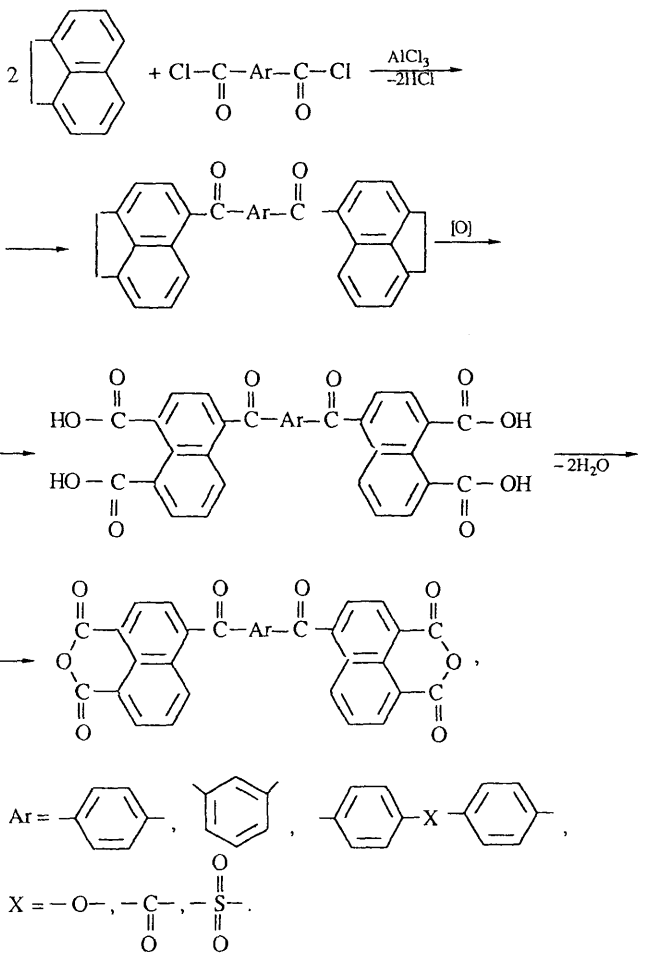
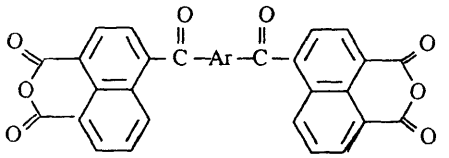
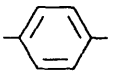
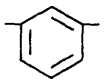
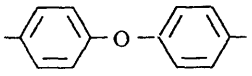
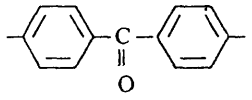
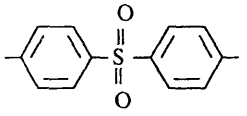
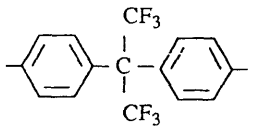
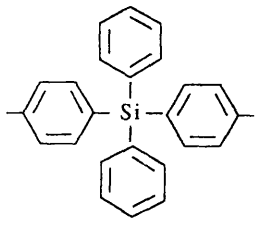


Table 3. Properties of aroylenebis(naphthalic anhydrides)



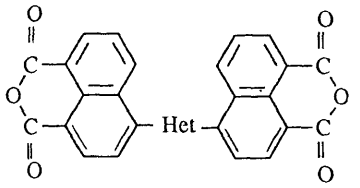
Ar	Mp, °C	Yield, %	Ref.
	> 450	70.8	[77, 78, 80]
	434–436	90.2	[77,80]
	309–311	93.0	[77,80]
	313–314	94.0	[77, 80]
	341–342.5	89.1	[77, 80]
	288–290	96	[77]
	308–309	57	[82, 84]
$-CB_{10}H_{10}C-$	278–280	35	[83, 84]

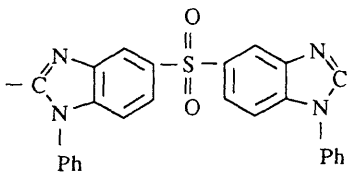
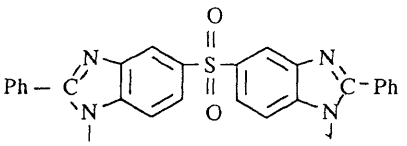
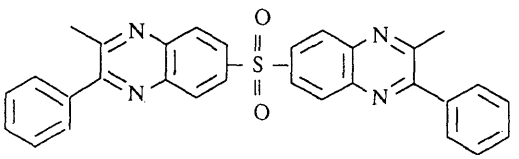
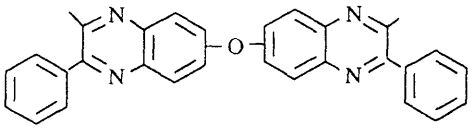
Some characteristics of the bis(ketonaphthalic anhydrides) synthesised are given in Table 3.

The same synthetic approach was used for obtaining bis(ketonaphthalic anhydrides) containing a heteroorganic central grouping, such as hexafluoroisopropylidene, diphenylsilyl and *m*-carboranylene (Table 3).[82–84]

An alternative method of synthesising the bis(ketonaphthalic anhydrides) considered above and systems isomeric with them is the Friedel–Craft reaction of a 4-chloroformylnaphthalic anhydride with aromatic hydrocarbons.[85]

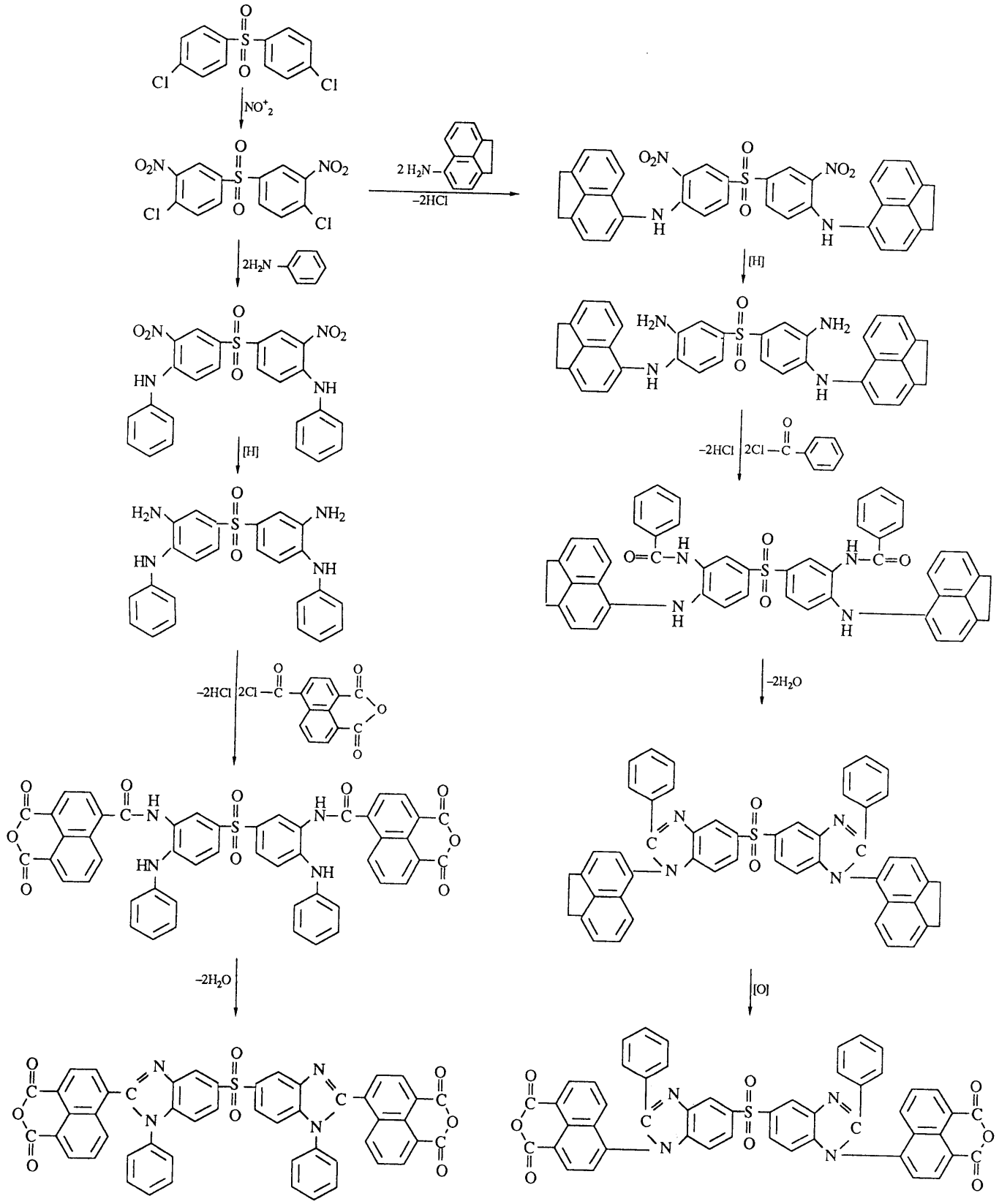
Table 4. Some characteristics of heteryl-containing bis(naphthalic anhydrides) of general formula



Het	Mp, °C	Yield, %	Ref.
	377–379	40	[86]
	355–356	42	[87]
	352–364	73	[89]
	315–335	68	[89]

4-Chloroformylnaphthalic anhydride was also used for obtaining bis(naphthalic anhydrides) containing phenyl substituted heterocycles. The dianhydride of bis[1-phenyl-2-(4,5-dicarboxynaphthyl)-benzimidazol-5-yl] sulphone was obtained by treating bis[(3-amino-4-phenylamino)phenyl] sulphone, a product from 4,4′-dichlorodiphenyl sulphone produced on an industrial scale, with two moles

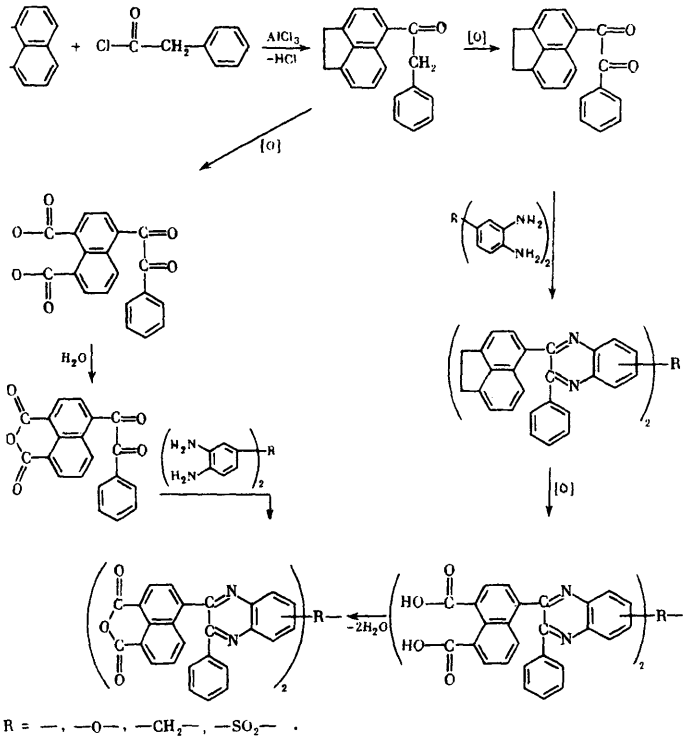
of 4-chloroformylnaphthalic anhydride and subsequent cyclodehydration of the compound obtained.[86,87]



The dianhydride of bis[2-phenyl-1-(4,5-dicarboxynaphthyl)benzimidazol-5-yl] sulphone, isomeric with this compound, was obtained by treating 4,4'-dichloro-3,3'-dinitrodiphenyl sulphone with 4-aminoacenaphthene, reduction of the nitro groups of the obtained 4,4'-di(aminoacenaphthyl)-3,3'-dinitrodiphenyl sulphone to primary amino groups, benzoylation of these amino groups, cyclodehydration of the 2-benzamido-imine fragments into 2-phenyl-1-acenaphthylbenzimidazole rings, oxidation of the acenaphthyl groups to peri carboxyl groups and anhydride formation of the latter.[87]

Individual characteristics of the synthesised bis(naphthalic anhydrides) containing various heterocycles are given in Table 4.

The derivatives of acenaphthene and naphthalic anhydride containing α-diketone groups in the 4 position have been used for obtaining bis(naphthalic anhydrides) containing phenylquinoxaline fragments.[88–91] The synthesis of these monomers was effected by the following scheme:

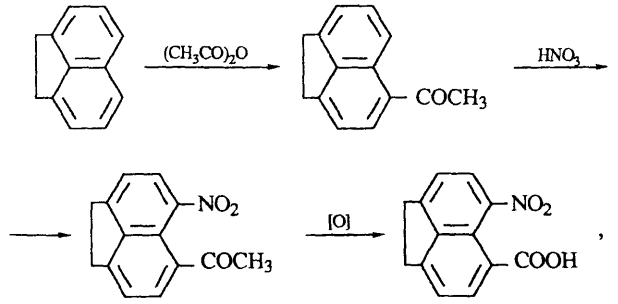


R = —, —O—, —CH_2—, —SO_2— .

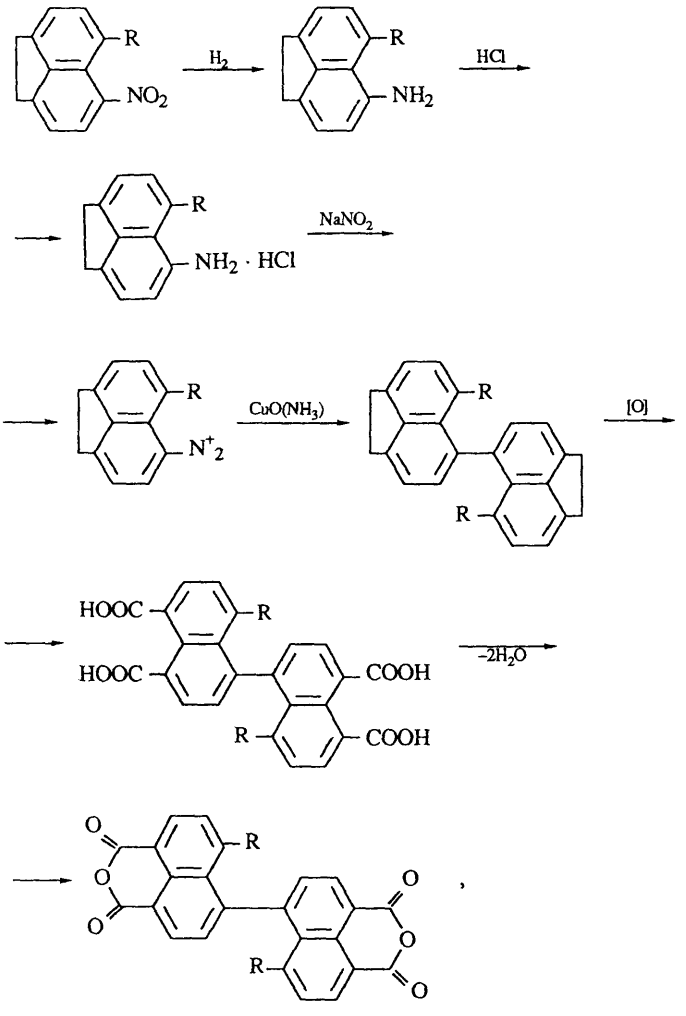
Some characteristics of the bis(phenylquinoxalinylnaphthalic anhydrides) are given in Table 4.

The diffuse melting points of the bis(phenylquinoxalinylnaphthalic anhydrides) are probably due to these products being mixtures of isomers, which is usual when forming bis and polyphenylquinoxaline systems.[92–94] In addition to phenyl, acetyl and carboxyl substituents, capable of increasing the solubility of the target polyheteroarylenes,[95] were also introduced into the bis(naphthalic anhydrides).

The diacetyl and dicarboxyl derivatives of bis(naphthalic anhydride) were obtained by the acetylation of acenaphthene, nitration of the 4-acetylacenaphthene obtained[96] and oxidation of the resulting acetylnitroacenaphthene[97]



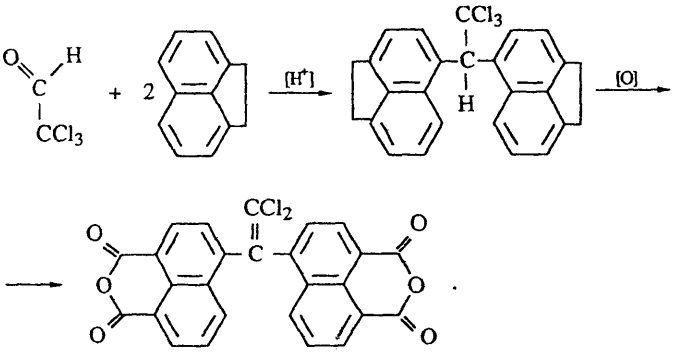
and subsequent formation and dimerisation of the diazo compounds.[98–100]



R = $COCH_3$, COOH .

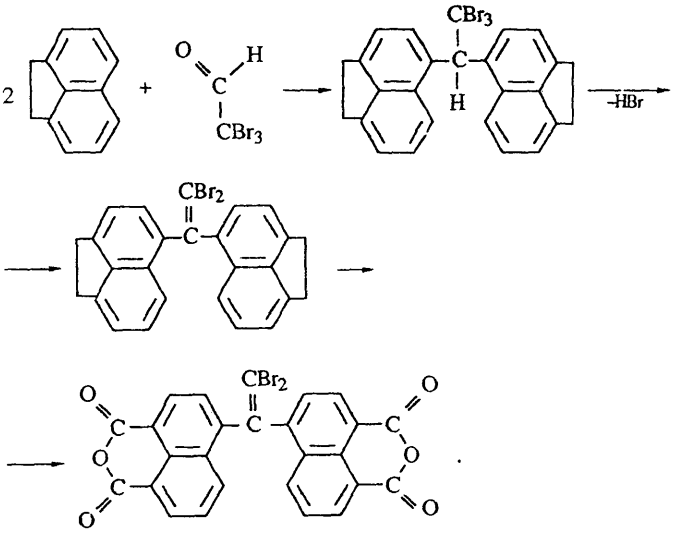
The dianhydride of 1,1′-bis(naphthyl)-4,4′,5,5′,8,8′-hexacarboxylic acid is manufactured in the USSR on a semi-industrial scale at the present time for the production of cubogens.[101,102]

Bis(naphthalic anhydrides) containing 1,1-dihaloethylene groups have been synthesised since it is known that the introduction of these fragments into macromolecules of various polyheteroarylenes are capable of improving the solubility of the latter.[102,108] Proceeding from the general chemistry of chloral derivatives,[103,114] it might be expected that the condensation of chloral with two molecules of acenaphthene must lead to di(acenaphth-4-yl)trichloroethane and this was found to be so. The oxidation of diacenaphthyltrichloroethane with potassium and sodium dichromate in glacial acetic acid at 90–110 °C was accompanied by dehydrochlorination of the central grouping and simultaneous anhydride formation of the peri dicarboxyl groups.[77,110,111]



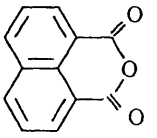
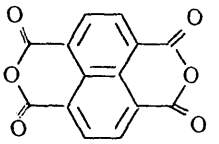
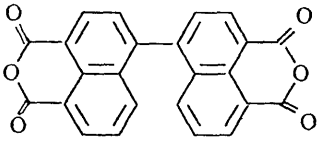
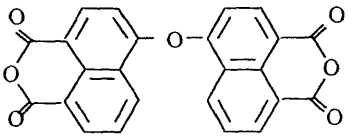
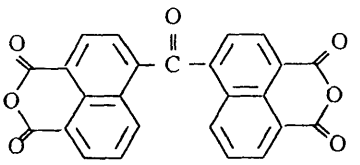
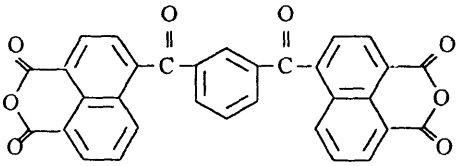
Neither dehydrochlorination of the 1,1,1-trichloroethane groups to 1,1-dichloroethylene nor oxidation of the 1,1-dichloroethylene group to carbonyl occurred when the usual conditions of carrying out these processes were applied to this system.

It is interesting to note that on replacing chloral by bromal the reactions considered occurred totally as expected[103,107,109,113] and led to the formation of the dianhydride of 1,1-bis(1,8-dicarboxynaphth-4-yl)-2,2-dibromoethylene.[80,112]



Since there are no literature data on the relative reactivities of bis(naphthalic anhydrides) a quantum chemical calculation of certain parameters was carried out by the PPP method,[113] particularly of the value of the electron affinity (A) which is a measure of the electrophilic reactivity of the dianhydrides in reactions with amines.[114] The results of the calculations of the values of A for various bis(naphthalic anhydrides) are given in Table 5.

Table 5. Electronic characteristics of bis(naphthalic anhydrides).

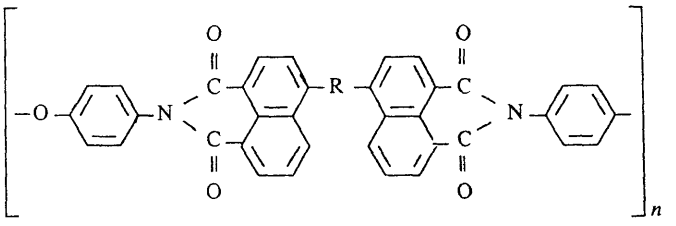
Compound	A, eV		q_1	q_2
	from Koopmans' theorem	from energy difference		
	3.1493	1.7426	0.2478	0.2478
	4.0102	2.6044	0.2477	0.2477
	3.7990	2.4770	0.2474	0.2469
	3.4488	2.0819	0.2097	0.2184
	3.8704	2.4896	0.2486	0.2475
	3.6475	2.1878	0.2490	0.2475

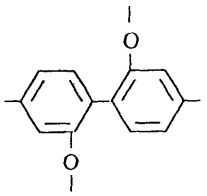
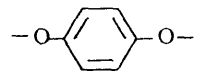
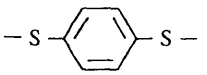
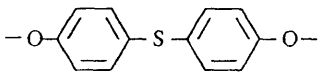
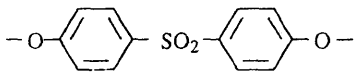
Note: q_1 is the positive charge on the 5 and 5′ carbon atoms, q_2 is the positive charge on the 4 and 4′ carbon atoms.

As in the case of the bis(phthalic anhydrides) the greatest value of A was found for the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid and the values of A for bis(naphthalic anhydrides)

containing electron-accepting hinge groups were greater than those for the bis(naphthalic anhydrides) with electron-donating groups. Comparison of the absolute values of A shows that the values of A for the bis(naphthalic anhydrides) were significantly greater than for the bis(phthalic anhydrides), which agrees with the literature[114] and is explained by the high aromaticity of the bis(naphthalic anhydrides). However the high values of A are not linked with the higher reactivity of the bis(naphthalic anhydrides) compared with the bis(phthalic anhydrides) since the reactivity depends on the strain in the anhydride ring.

Table 6. Some characteristics of polynaphthoylenebenzimidazoles of general formula[62,63]



R	η_{inh}(H_2SO_4, 30 °C)	T_g, °C
	0.15	260
	0.20	260
	0.26	253
	0.30	269
	0.29	317

Values have been calculated for the positive charges on the carbonyl carbon atoms to determine the reaction centre primarily subject to nucleophilic attack.[113] In the bis(naphthalic anhydrides) containing electron-donating hinge groups a high positive charge q is characteristic of the carbonyl carbon atoms at positions 5 and 5′. In bis(naphthalic anhydrides) with electron-accepting hinge groups the high positive charge is a characteristic of the carbonyl carbon atoms in the 4 and 4′ positions.

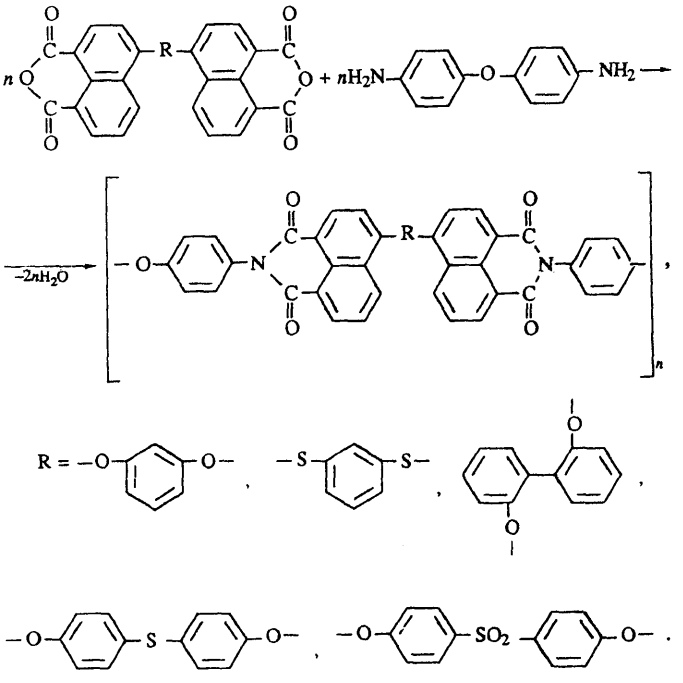
The fact that all the bis(naphthalic anhydrides) possess a lower reactivity than the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid points to the expediency of synthesising polyheteroarylenes from them using catalytic processes which are being used more in polycondensation and polycyclocondensation reactions.[115]

III. Polyheteroarylenes from bis(naphthalic anhydrides)

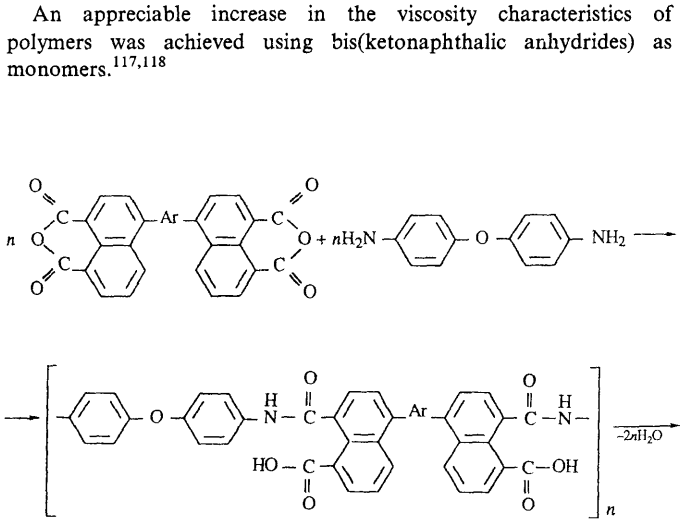
1. Polynaphthalimides

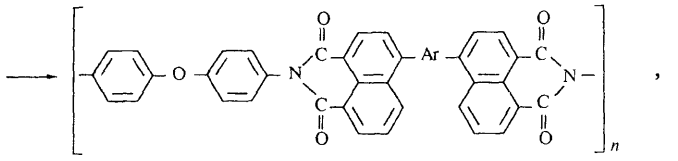
The majority of polynaphthalimides described in the literature are products of the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with various diamines.[116] Several bis(naphthalic anhydrides) containing hinge groupings have been used for the synthesis of polynaphthalimides.

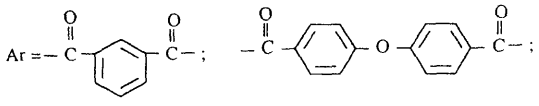
Polynaphthalimides containing ether and thioether groups, which are soluble in phenolic solvents, have been obtained by the reaction of ether- and thioether-containing bis(naphthalic anhydrides) with 4,4′-diaminodiphenyl oxide.[62,63] Reactions were carried out in *m*-cresol at 10% concentration (calculated on the final polymer) using quinoline or isoquinoline as catalyst. In contrast to the tougher polymer from the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid, which is precipitated from *m*-cresol at this concentration, the polyimides obtained were soluble in *m*-cresol up to 15% concentration though their molecular weights were fairly low (η_{inh} = 0.15–0.30 dlitre g^{-1}). The logarithmic viscosities and glass points of the polynaphthalimides synthesised are given in Table 6. Thermogravimetric analysis of the polymers showed the start of a mass loss at 450 °C in air and at 500 °C in a nitrogen atmosphere.

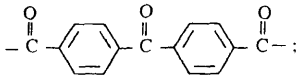


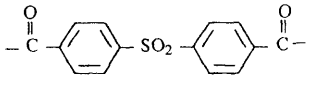
An appreciable increase in the viscosity characteristics of polymers was achieved using bis(ketonaphthalic anhydrides) as monomers.[117,118]





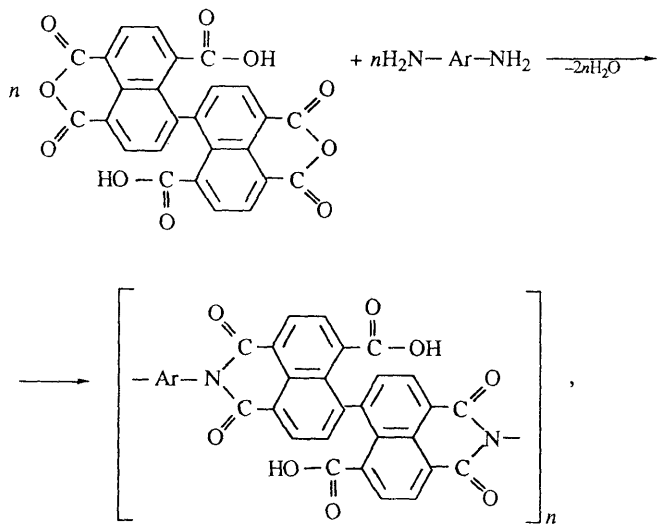


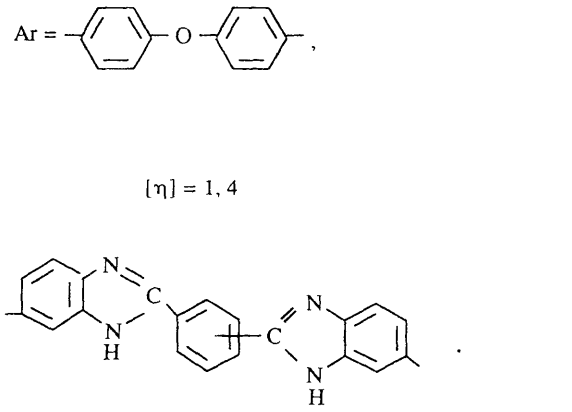




Synthesis of the polynaphthalimides was effected in *m*-cresol using benzoic acid as catalyst. The polynaphthalimides dissolved in H_2SO_4, phenolic solvents and mixtures of tetrachloroethane with phenol but polymers from dianhydrides containing ether bonds in the central group dissolved in tetrachloroethane as well. Some characteristics of the polynaphthalimides are given in Table 7.

Polynaphthalimides containing free carboxyl groups were obtained by the reaction of the dianhydride of 1,1-dinaphthyl-4,4′,5,5′,8,8′-hexacarboxylic acid with 4,4′-diaminodiphenyl oxide and benzimidazole-containing aromatic diamines.[119–121]





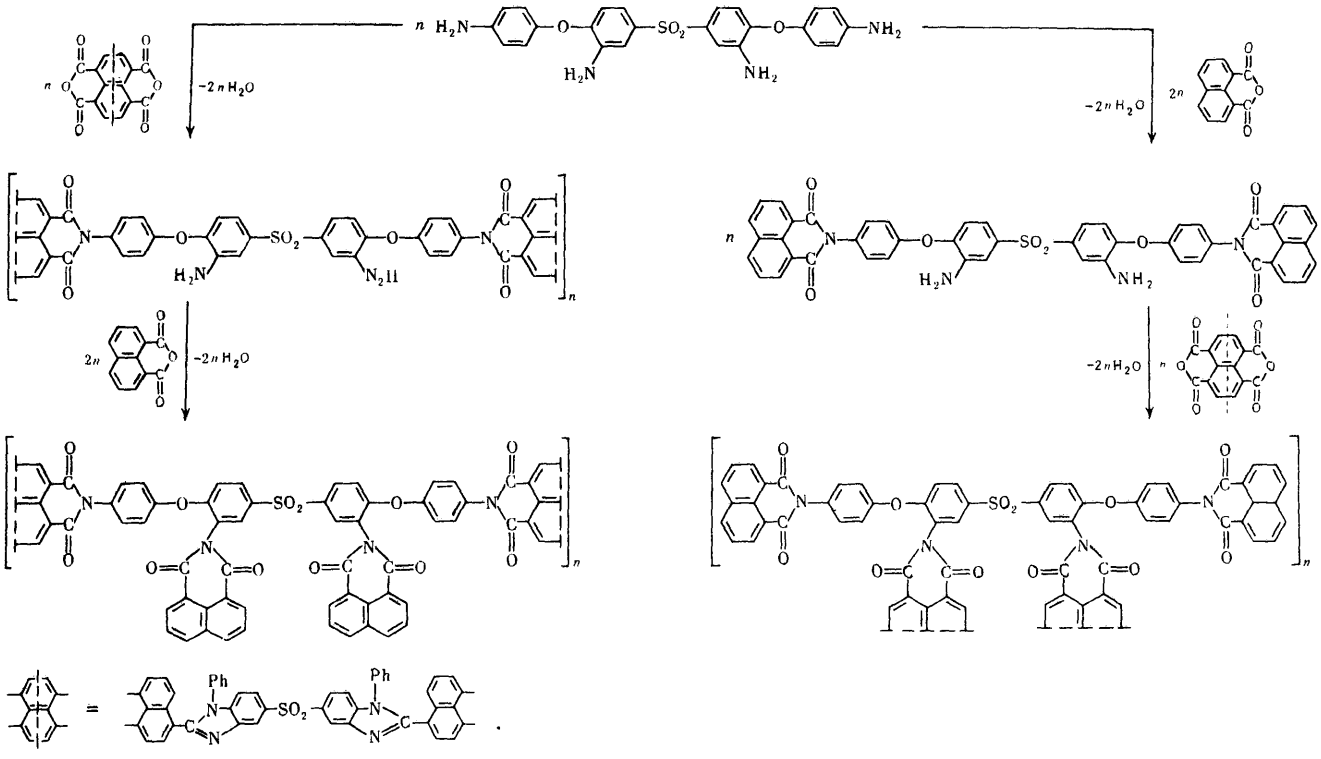
$[\eta] = 1,4$

$[\eta] = 2,0$

High temperature (125–130 °C) polycyclocondensation was carried out in dipolar organic solvents with the addition of base. The polycondensation proceeds best of all in DMSO on adding sodium acetate in equimolar quantities. This is linked with the better solubility and stability of the monosodium salts formed at the strongly acidic carboxyl group of the dianhydride and the polynaphthalamide.[122] The remaining free carboxyl groups are probably catalysts of the polycyclocondensation process. The high molecular polynaphthalamides obtained dissolve readily in the presence of base in organic solvents (DMSO, DMAA) and in water. The polynaphthalimides do not soften until decomposition begins at 520–525 °C according to TGA (ΔT = 10 °C min^{-1}). When preparing polynaphthalimides in a chloride precipitating bath they form films and filaments with a strength up to 35 cN tex^{-1} and an elongation at break of up to 20%.

High solubility in organic solvents is also inherent of polynaphthalimides containing *N*-naphthylimide or *N*-(4-phenoxy)-naphthylimide substituents and which are synthesised as described[123]

by the following scheme:



Polynaphthalimides with *N*-naphthalimide *o*-substituents are obtained by the reaction of 3,3′-diamino-4,4′-di-(4-aminophenoxy)-diphenyl sulphone with an equimolar quantity of the bis(naphthalic anhydride) with subsequent treatment with two moles of the naphthalic anhydride under high temperature catalytic polycyclo-condensation conditions in *m*-cresol with benzoic acid. This polymer dissolves in phenolic solvents, in *N*-methyl-2-pyrrolidone (N-MP) and also in tetrachloroethane, it has a molecular weight of the order of 60000, softens at 340 °C and has a 10% weight loss temperature of 480 °C.

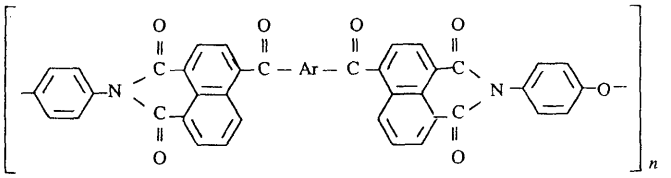
When the alternative sequence of adding mono- and dianhydride to the reaction is used a polynaphthalimide with even more bulky *N*-(4-phenoxy)naphthalimide *ortho* substituents is obtained which is soluble in a wide range of solvents, including those mentioned above and chloroform. The thermal characteristics of the polynaphthalimide synthesised were assessed from a thermomechanical curve and from dynamic TGA data and were comparable with the thermal characteristics of the polynaphthalimides with *N*-naphthalimide substituents (Table 8). The molecular weight of the synthesised polymer was of the order of 25000 but it was not possible to obtain films from it with satisfactory characteristics.

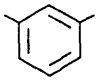
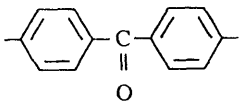
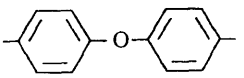
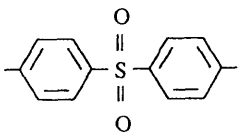
The high solubility of the systems obtained by both the first and second routes is seemingly determined by the lack of symmetry of the polymer molecules, by the presence of bulky side substituents, which aid its solubility by breaking up the polymer structure, and by the positive effect of the SO_2 group and the mild cyclisation conditions.

2. Polynaphthoylenebenzimidazoles

Significantly more attention has been paid to the polynaphthoylenebenzimidazoles based on the bis(naphthalic anhydrides) described above than to the polynaphthalimides. This is readily explainable even allowing for the fact that the bis(*o*-phenylenediamines), which are used to obtain the polynaphthoylenebenzimidazoles, are less accessible and more expensive than the aromatic diamines used in the synthesis of polynaphthalimides. The naphthoylenebenzimidazole ring is one of the most stable heterocycles (both thermally and hydrolytically),[124] and polynaphthoylenebenzimidazoles from naphthalene-1,4,5,8-tetracarboxylic acid dianhydride have been used successfully to obtain fibres with a unique set of properties.[125–135]

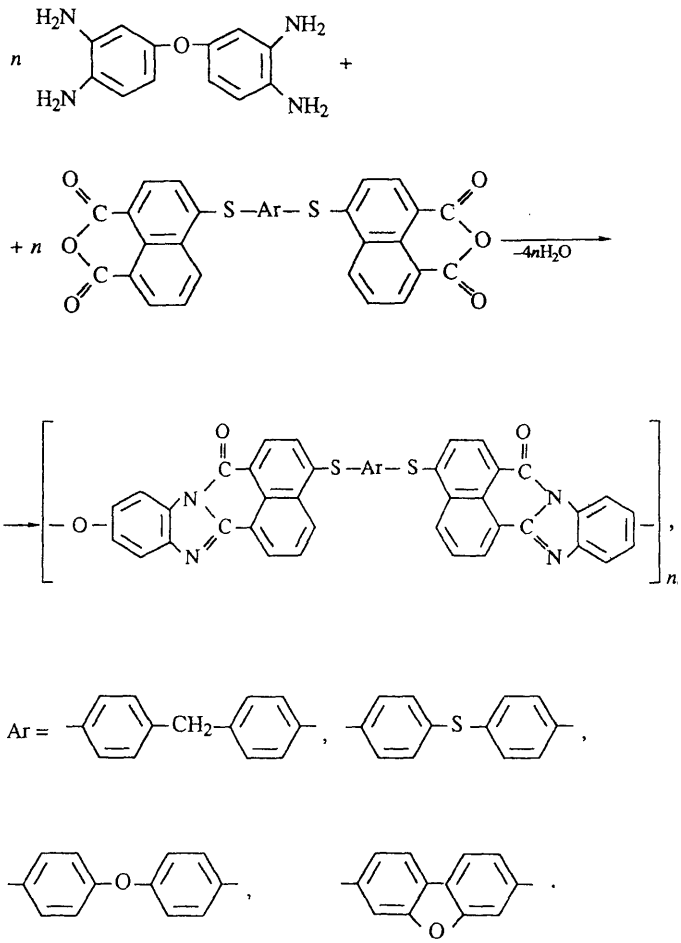
Table 7. Some characteristics of polynaphthalimides of general formula[117]



Ar	η_{red}*, dlitre g^{-1}	T_{soft}**, °C	$T_{10\%}$***, °C	Solvent**** H_2SO_4	*m*-cresol	TCE: phenol (3 : 1)	TCE
	0.72	310	500	+	+	+	+/-
	0.53	300	515	+	+	+	+/-
	0.78	275	490	+	+	+	+/-
	0.78	335	520	+	+	+	+/-

*Reduced viscosities of 0.5% solutions of polymers in H_2SO_4 at 25 °C.
**Softening points of polymers from thermomechanical analysis.
***10% Weight loss temperatures from dynamic TGA in air, ΔT = 5 °C min^{-1}.
****+ signifies soluble, − insoluble, +/− partially soluble.

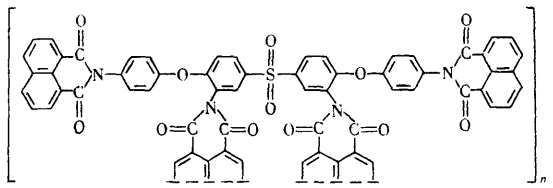
Sulphide-containing polymers were among the first to be synthesised among the polynaphthoylenebenzimidazoles from bis(naphthalic anhydrides) containing more than one hinge group.[55,73–76] These polymers were obtained by high temperature catalytic polycyclocondensation in *m*-cresol using benzoic acid as catalyst. The reaction proceeds as follows:

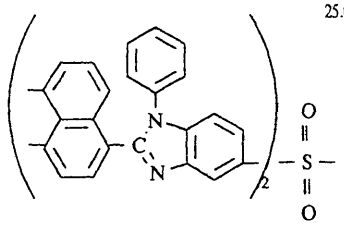
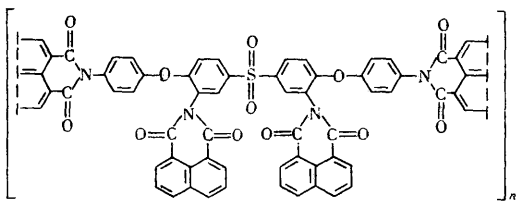


All the polycyclocondensations proceeded in solution (homogeneously) and led to the preparation of well cyclised polymers, the individual characteristics of which are given in Table 9.

The sulphide-containing polynaphthoylenebenzimidazoles synthesised were soluble in H_2SO_4 and in phenolic solvents (*m*-cresol, phenol : tetrachloroethane mixture) which in conjunction with high temperatures for softening (T_{soft} = 310−380 °C) and decomposition (T_{dec} = 450−470 °C) determine the well-known practical value of these systems. At the same time all the sulphide-containing polynaphthoylenebenzimidazoles have low viscosity characteristics (η_{red} = 0.4−0.9 dlitre g^{-1}) which do not permit materials with usable deformational strength characteristics to be obtained from them.

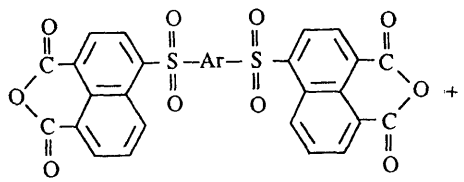
Table 8. Some characteristics of polynaphthalimides of general formula

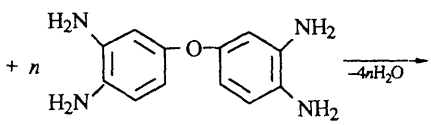


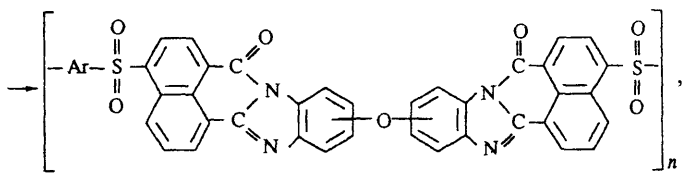
	$\bar{M}^*_w$	T_{soft}, °C	$T_{10\%}$, °C	Solvent			
				N-MP	*m*-cresol	TCE	$CHCl_3$
	25.000	340	480	+	+	+	+
	60.000	340	480	+	+	+	–

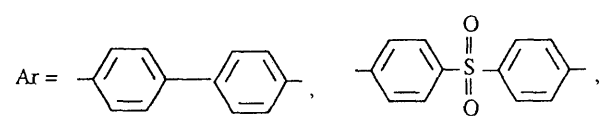
*Determined by sedimentation equilibrium.

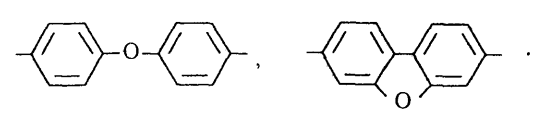
The low viscosity and corresponding molecular weight characteristics of the sulphide-containing polynaphthoylenebenzimidazoles may be due to the presence of the electron-donating sulphide groups in the initial bis(naphthalic anhydrides) which determines the reduced electrophilic reactivity of these monomers. With the aim of increasing the latter, attempts were undertaken to obtain polynaphthoylenebenzimidazoles using bis(naphthalic anhydrides) containing at least two sulphonyl groups in the molecule.[55,73–76]











These systems were synthesised by high temperature catalytic polycyclocondensation in *m*-cresol using benzoic acid as catalyst as in the preparation of the polynaphthoylenebenzimidazoles from sulphide-containing bis(naphthalic anhydrides).[55,73–76]

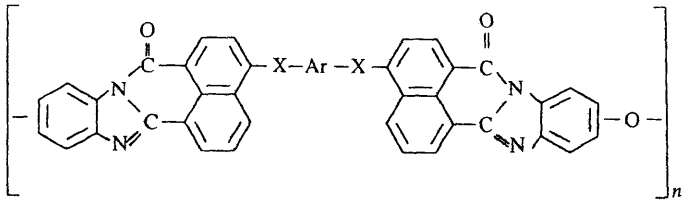
All the reactions for polyheteroarylene synthesis with the exception of processes using the dianhydride of 4,4′-bis(1,8-dicarboxynaphthalene-4-sulphonylphenyl) sulphone took place under homogeneous conditions and led to the preparation of the desired polyheteroarylenes in close to quantitative yield.

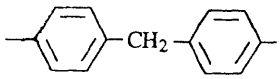
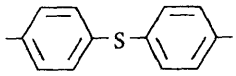
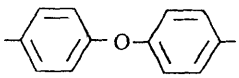
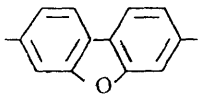
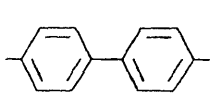
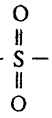
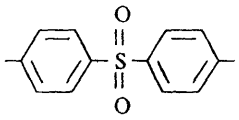
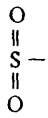
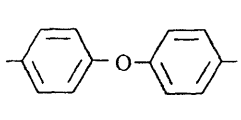
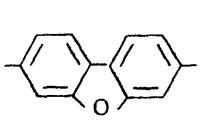
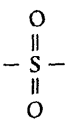
Some characteristics of the synthesised polynaphthoylenebenzimidazoles are given in Table 9.

The synthesised polynaphthoylenebenzimidazoles are more soluble than the polymers of this class obtained previously from 4,4′-sulphonylbis(naphthalic anhydride),[55] which indicates the positive effect of the introduction of a second sulphonyl group into the dianhydride and correspondingly into the main chain of the macromolecule. An exception is the polymer with three sulphonyl groups in the chain. The lack of solubility of this polynaphthoylenebenzimidazole in the solvents listed is explained by its crystallinity which was 20–30% according to X-ray data.

On the other hand the polynaphthoylenebenzimidazoles containing two or more sulphonyl groups were less soluble than the analogous systems containing sulphide groups.

Table 9. Some characteristics of polynaphthoylenebenzimidazoles of general formula[73–76]



Ar	X	η_{red}, dlitre g^{-1} (25 °C)		T_{soft}, °C	$T_{10\%}$, °C
		H_2SO_4	TCE, phenol		
	—S—	0.4	0.5	330	450
	—S—	0.5	0.5	310	470
	—S—	0.8	0.7	330	460
	—S—	–	0.4	380	460
		0.4	–	380	430
		0.4	–	–	400
		–	0.3	350	420
		0.4	–	370	410

The low viscosity characteristics of the polymers, which are somewhat unexpected for systems based on dianhydrides activated by sulphonyl groups, are probably explained by the occurrence of side reactions breaking the naphthoylenebenzimidazole rings by *o*-phenylenediamine fragments of the monomers or by the end groups of the growing chains of the macromolecule.

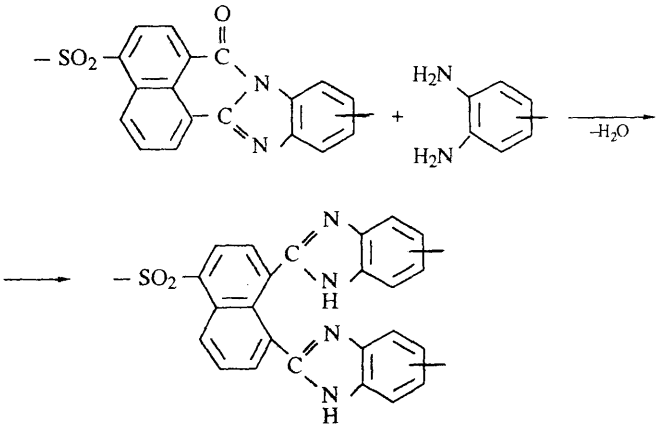
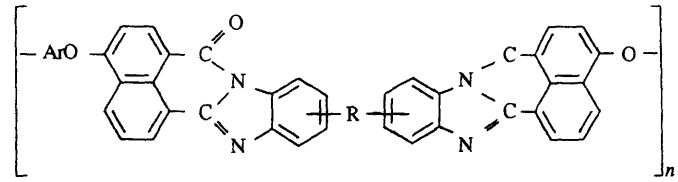
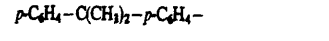
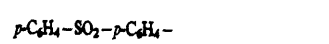
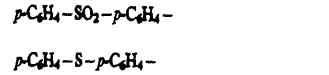


Table 10. Reduced viscosities of polynaphthoylenebenzimidazoles of formula



synthesised in mixtures of *m*-cresol with P_2O_5 (method *a*) and *m*-cresol with benzoic acid (method *b*), reaction time 30 h.[137]

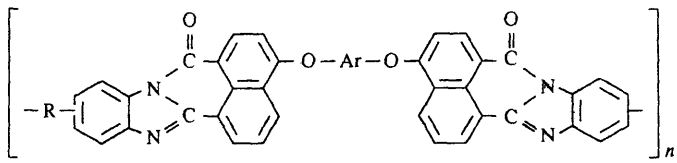
Ar	R	η^*_{red}, dlitre g^{-1}	
		method *a*	method *b*
	–	1.10	1.00
	-O-	0.94	0.75
	–	3.95	1.10
	-O-	1.18	0.68
	–	1.00	0.49
	-O-	0.97	0.30
	–	1.89	1.03
	-O-	1.03	0.62

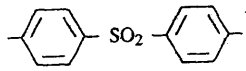
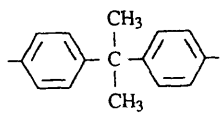
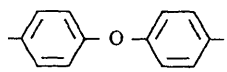
*η_{red} was measured in tetrachloroethane : phenol mixture at 25 °C.

This hypothesis is in complete agreement with the concept of a correlation between the electrophilic reactivity of the initial anhydrides and the sensitivity of the desired carbonyl-containing heterocycles towards hydrolysis and the action of nucleophilic reagents.[136] The same circumstance determines the low thermal stability of the synthesised polynaphthoylenebenzimidazoles during TGA in air. As is seen from Table 9 the 10% weight loss temperature was 400–430 °C under these conditions. The

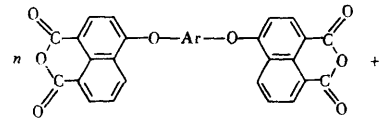
unsatisfactory properties of the synthesised polyheteroarylenes indicates the inexpediency of using bis(naphthalic anhydride) systems containing sulphonyl groupings bound directly to the anhydride rings.

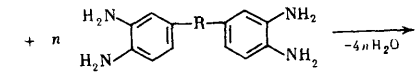
Table 11. Some characteristics of polynaphthoylenebenzimidazoles of general formula

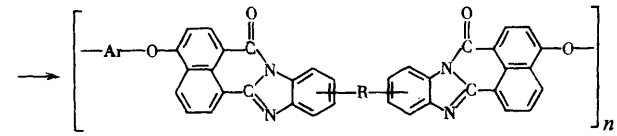


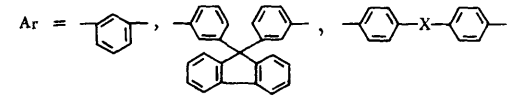
Ar	R	η_{red}, dlitre g^{-1}	T_g, °C	T_{dec}, °C		Solvent		
				argon	air	CF_3COOH	*m*-cresol	TCE: phenol (1 : 3)
	–	1.10	395	490	470	+	–	–
	-O-	0.68	368	490	490	+	+/–	+/–
	$-CH_2-$	0.29	–	460	440	+	+	+
	–	0.49	404	450	430	+	+	+
	-O-	0.30	360	460	430	+	+	+
	$-CH_2-$	0.20	380	450	340	+	+	+
	–	1.00	373	460	450	+	+	+
	-O-	0.75	312	460	450	+	+	+
	$-CH_2-$	0.37	355	460	440	+	+	+
	–	0.40	340	–	520	–	+	+
	-O-	0.50	320	–	500	–	+	+
	$-CH_2-$	0.70	320	–	380	–	+	+

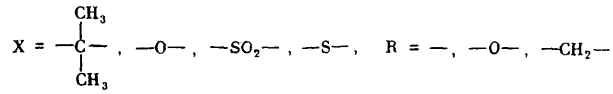
Significantly better results were obtained in the synthesis of polynaphthoylenebenzimidazoles from bis(naphthalic anhydrides) containing ether bonds.[65–68] These reactions were effected under conditions traditional for the synthesis of similar systems, viz. high temperature polycondensation in *m*-cresol using benzoic acid as catalyst,[65] and in other solvents[137] (mixtures of *m*-cresol with polyphosphoric acid, *m*-cresol with di-*m*-cresyl phosphate, *m*-cresol with P_2O_5, phenol with P_2O_5 and *p*-chlorophenol with P_2O_5).







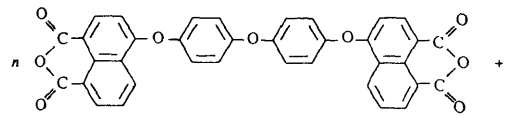


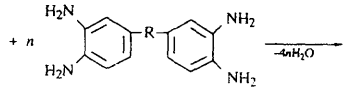


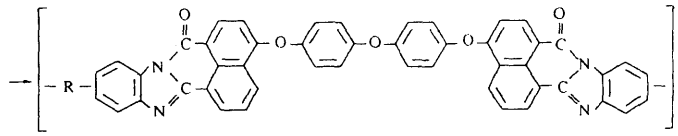
The best of the systems studied proved to be *m*-cresol with P_2O_5 which is particularly obvious from the comparative data given in Table 10 on the viscosity characteristics of the polynaphthoylenebenzimidazoles obtained in mixtures of *m*-cresol with P_2O_5 and *m*-cresol with benzoic acid.[137] Nevertheless the polynaphthoylenebenzimidazoles synthesised in other solvents and particularly in a mixture of *m*-cresol and benzoic acid possessed viscosity characteristics (Table 11) and molecular weights which are sufficiently high for obtaining strong and elastic films (Table 12) possessing interesting electrical and physical properties.

The thorough investigations on the thermal,[138] dynamic, mechanical[138] and relaxation[139,140] characteristics of the polynaphthoylenebenzimidazoles of this series showed that these systems are of significant practical interest.

A logical evolution and continuation of the studies in this field is the development of polynaphthoylenebenzimidazoles from the dianhydride of 4,4′-epoxybis[(*p*-phenyloxy)dinaphthalene-1,1′,8,8′-tetracarboxylic acid].[71] Reaction of this with bis(*o*-phenylenediamine), 3,3′,4,4′-tetra-aminodiphenyl oxide, 3,3′,4,4′-tetra-aminodiphenylmethane and 3,3′-diaminobenzidine occurred according to the following scheme:



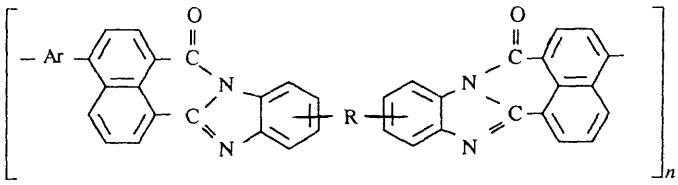


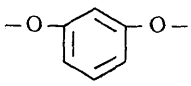
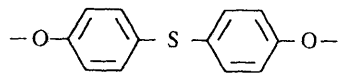
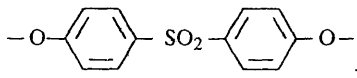
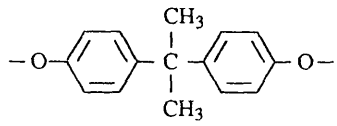


R = –, –O–, $-CH_2-$.

under conditions of high temperature catalytic polycyclisation in phenolic solvents. All the reactions in the synthesis of the polynaphthoylenebenzimidazoles proceeded from beginning to end under homogeneous conditions and led to the formation of polymers with moderate viscosity characteristics (Table 12).

Table 12. Properties of films based on polynaphthoylenebenzimidazoles of general formula



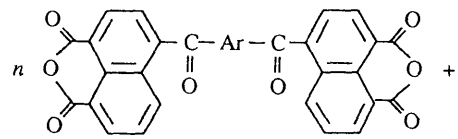
Ar	R	Mechanical properties, 25 °C		Electrical properties	
		σ, kg cm^{-2}	ε, %	$10^{-16}\rho^{*}$, Ω.cm	$10^{-3}\tan\delta^{**}$
	–	1120	85	2	1.7
	–O–	1080	85	7	1.4
	–	1350	70	3	1.2
	–O–	910	75	4	1.4
	–	920	60	1	1.5
	–O–	1110	80	3	1.4
	–	950	70	6	0.94
	–O–	980	113	1	1.6

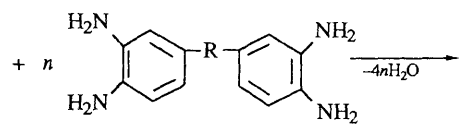
*ρ is the bulk resistance, **tan δ is the loss factor.

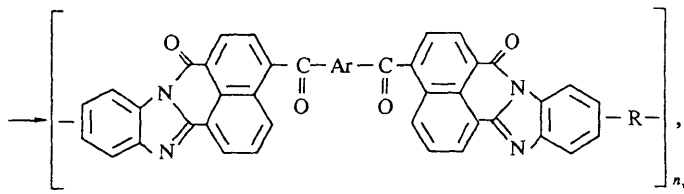
The introduction of an additional oxygen atom did not lead to an improvement in polymer solubility. The polymers were soluble in acidic and phenolic solvents but were insoluble in DMSO and N-MP.

Comparison of the softening temperatures and the region of marked thermal destruction indicated that these polymers may be successfully processed into objects by pressing.

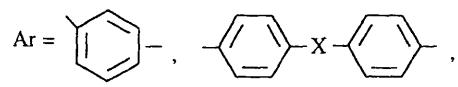
Polynaphthoylenebenzimidazoles based on aroylene-bis(naphthalic anhydrides) are of significant interest and are obtained according to the following scheme:[77,80,81]

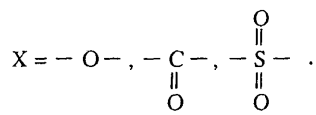






R = –, –O–, $-SO_2-$, $-C(CF_3)_2-$, $-CH_2-$;

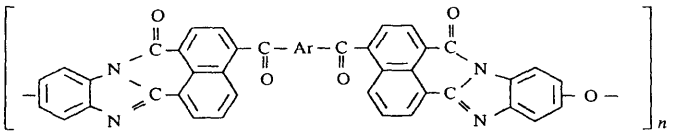


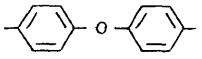
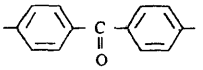
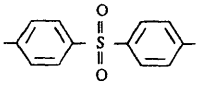
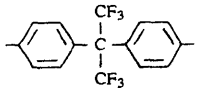
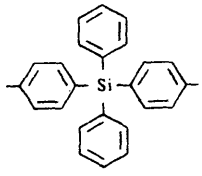


The synthesis of these polynaphthoylenebenzimidazoles was effected by high temperature polycondensation in *m*-cresol using benzoic acid as catalyst. All the reactions to synthesise polynaphthoylenebenzimidazoles occurred in a homogeneous manner and led to the preparation of fully cyclised high molecular polymers. Some characteristics of the polynaphthoylenebenzimidazoles based on aroylene-bis(naphthalic anhydrides) and 3,3',4,4'-tetra-aminodiphenyl oxide are given in Table 13.

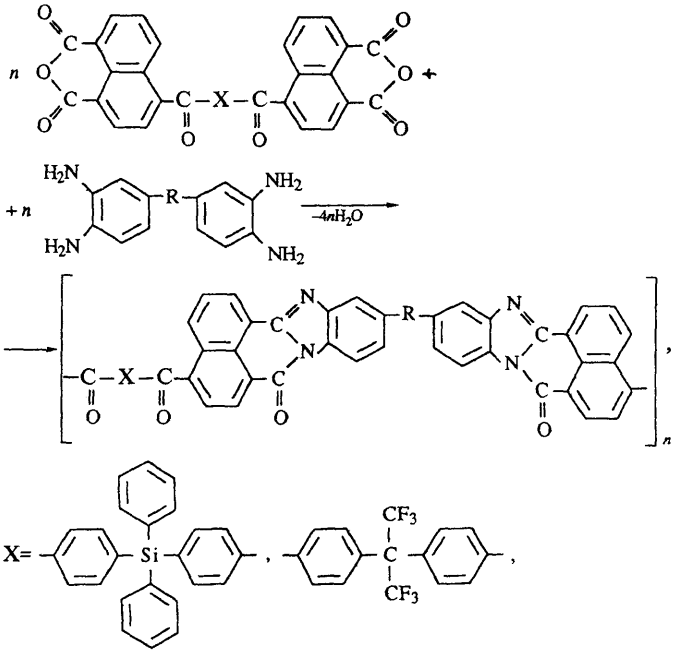
As is evident from the data of Table 13 the polynaphthoylenebenzimidazoles synthesised are soluble in H_2SO_4 and in phenolic solvents. The molecular weights of the polymers were sufficiently high to make stable films from them and the decomposition temperature (490–550 °C) was sufficiently large for these polymers to be processed into objects by pressing.

Table 13. Some characteristics of polynaphthoylenebenzimidazoles of general formula[77,80,82–84]



Ar	η_{red}, dl litre g^{-1} (H_2SO_4)	T_{soft}, °C	$T_{10\%}$, °C	Solvent				Film properties, 25 °C	
				m-cresol	TCE: phenol (3 : 1)	H_2SO_4	N-MP	σ, kg cm^{-2}	ε, %
	1.00	345	550	+	+	+	–	1260	15
	1.40	355	520	+	+	+	–	1100	13
	1.35	375	525	+	+	+	–	1000	11
	3.90	370	530	+	+	+	–	1040	11
	0.53	–	490	+/–	+	+	–	–	–
	1.80	360	545	+	+	+	–	1080	13
	1.57	375	550	+	+	+	–	920	10
$-CB_{10}H_{10}C-$	0.40	–	550	+	+	+	+	–	–

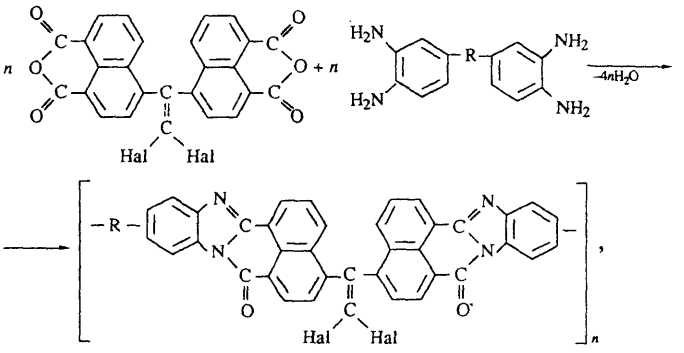
Even better solubility was a characteristic of the polynaphthoylenebenzimidazoles based on bis(naphthalic anhydrides) with a heteroorganic central group, such as hexafluoroisopropylidene,[82,84] diphenylsilyl[83,84] and *m*-carboranylene.[82,84] These polymers were synthesised by the following scheme:



$-CB_{10}H_{10}C-$, R = –, –O–.

The synthesis of these polymers was effected by high temperature catalytic polycyclocondensation in *m*-cresol using benzoic acid as catalyst. Some characteristics of the polynaphthoylenebenzimidazoles containing heteroorganic central groupings are given in Table 13. The introduction of diphenylsilyl and hexafluoroisopropylidene groups led only to a quantitative increase in the solubility of the polynaphthoylenebenzimidazoles in phenolic solvents[82–84] while the introduction of the *m*-carboranylene group into the macromolecule was accompanied by conferment of solubility in N-MP to the polymer.[83,84]

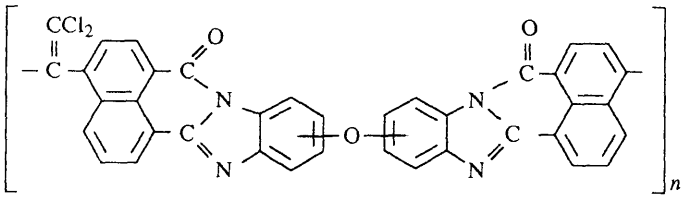
The introduction of the 1,1-dichloroethylene and 1,1-dibromoethylene groups into the macromolecule by the use of the appropriate bis(naphthalic anhydrides) has an extremely important effect on the properties of the polynaphthoylenebenzimidazoles.[111,112,141]



R = –, –O–, ; Hal = Cl, Br.

The synthesis of polynaphthoylenebenzimidazoles with 1,1-dichloroethylene and 1,1-dibromoethylene bridge groups[77,80,111,112,141] was effected in *m*-cresol with benzoic acid fulfilling the function of catalyst. In every case the synthesis of the polynaphthoylenebenzimidazoles took place homogeneously and led to the formation of fully cyclised and in some cases high molecular systems.

Table 14. Viscosity and molecular weight characteristics of polynaphthoylenebenzimidazoles of formula[141]

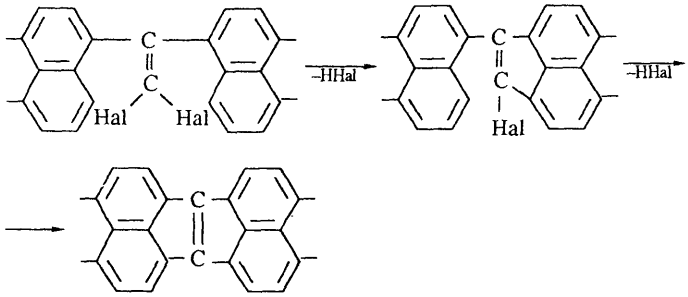


η_{sp}, H_2SO_4, 25 °C	10^{-3}M
0.39	33
0.73	80
0.98	108
1.14	117

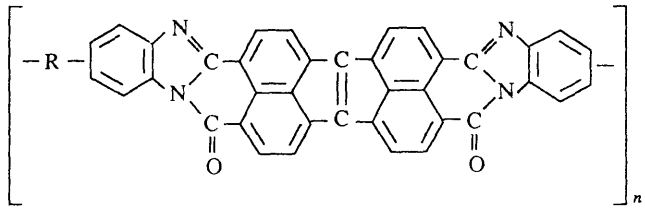
Comparison of the viscosity and molecular weight characteristics[142] of one of the similar polynaphthoylenebenzimidazoles is shown in Table 14.

Some characteristics of the synthesised polynaphthoylenebenzimidazoles containing 1,1-dihaloethylene groups are given in Table 15. It follows from an analysis of these data that all the polynaphthoylenebenzimidazoles synthesised are soluble in sulphuric acid and in phenolic solvents. High softening temperatures and high decomposition points under conditions of dynamic TGA are characteristic of the majority of these systems.

Under conditions of isothermal storage at temperatures exceeding 300 °C all the polymers considered underwent significant weight loss mainly with evolution of hydrogen halide. Among the alternative dehydrohalogenation reactions, monomolecular and intramolecular, the latter is more probable since in the heat treatment process the polymers do not lose their solubility in H_2SO_4. In view of the high lability of the peri protons[143] it might be suggested that the most probable course for the dehydrohalogenation is that expressed by the following scheme:

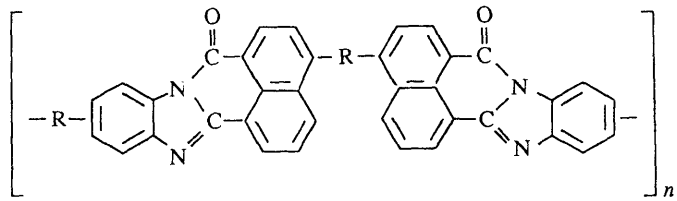


Similar 'naphtho-(9,10)-acenaphthyl' structures have been described in the literature.[144] When applied to the polymers their formation may lead to a new highly condensed system of general formula



which enables the results obtained to be considered as a new approach to the synthesis of ladder or double-chain polymers.[26,27]

Table 15. Some characteristics of polynaphthoylenebenzimidazoles of general formula

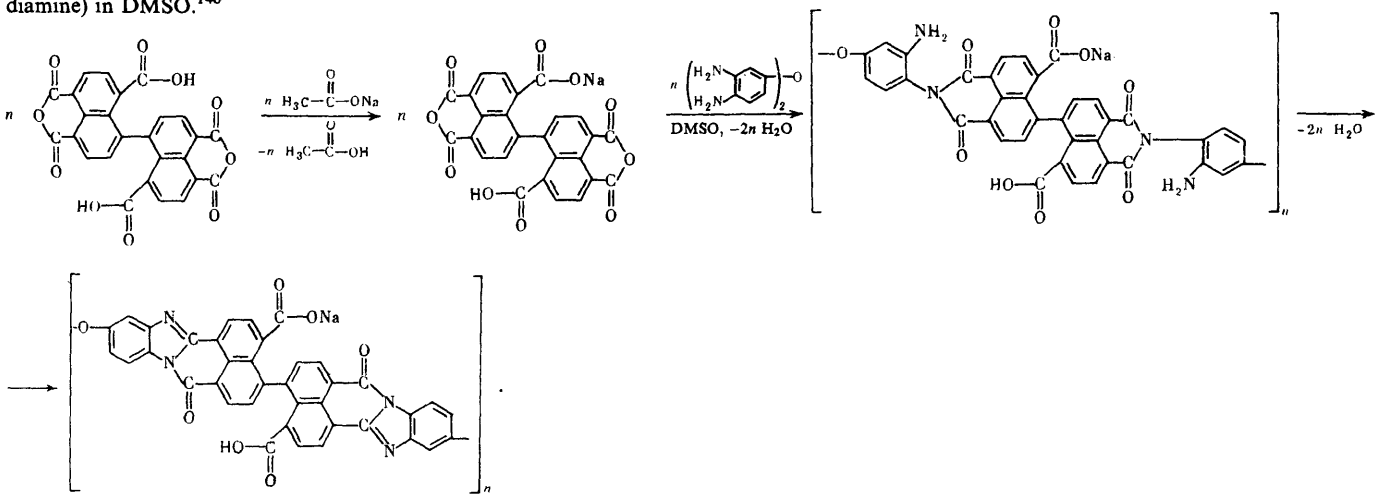


R	R'	η_{red}, dl/litre g^{-1}	T_{soft}, °C	$T_{10\%}$, °C	Solvent		
					m-cresol	TCE, phenol	H_2SO_4
–	$-C(=CCl_2)-$	0.80	450	500	+	+	+
-O-	$-C(=CCl_2)-$	2.00	380	500	+	+	+
$-SO_2-$	$-C(=CCl_2)-$	0.50	410	490	+	+	+
$-CH_2-$	$-C(=CCl_2)-$	0.70	370	490	+	+	+
$-C(CF_3)_2-$	$-C(=CCl_2)-$	0.80	380	500	+	+	+
-O-	$-C(=CBr_2)-$	0.30	380	490	+	+	+

In appearance the polymers based on 1,1'-bisnaphthyl-4,4',5,5',8,8'-hexacarboxylic acid[145–148] are systems extremely close to the polynaphthoylenebenzimidazoles containing 1,1-dihaloethylene groups.

The polynaphthoylenebenzimidazole based on 3,3',4,4'-tetraaminodiphenyl oxide and the dianhydride of 1,1'-binaphthyl-4,4',5,5',8,8'-hexacarboxylic acid has been studied in most detail. The optimum method of synthesising this polymer is the reaction of the

monosodium salt of the acid component with the bis(*o*-phenylenediamine) in DMSO.[146]



As a result of the increased basicity of the tetramine compared with the diamines[149] the reaction to prepare the polynaphthoylenebenzimidazole took 3–5 h at 115–120 °C, i.e. was more rapid than the synthesis of the polynaphthalimides, leading to the preparation of a polymer with $[\eta] \geqslant 1.3$ dlitre g^{-1}. Carrying out the synthesis of the polynaphthoylenebenzimidazole at higher temperatures led to gel formation and an increase in polymer viscosity.

This polynaphthoylenebenzimidazole dissolved in organic solvents only on addition of concentrated alkali solutions (10% KOH). After precipitation in an acid bath the polymer underwent 10–15% destruction.

Stable films were obtained by drying solutions of the monosodium salts of the polynaphthoylenebenzimidazole. The formation of fibres took place in a stable manner in baths of composition DMSO–water–conc. HCl.

Significant attention has been paid to the product of converting polynaphthoylenebenzimidazole into perylene-[147] and anthanthrone-containing[148] systems.

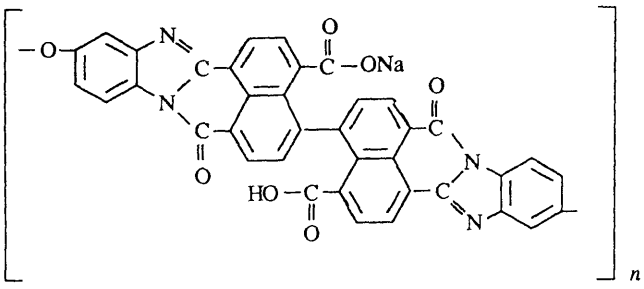
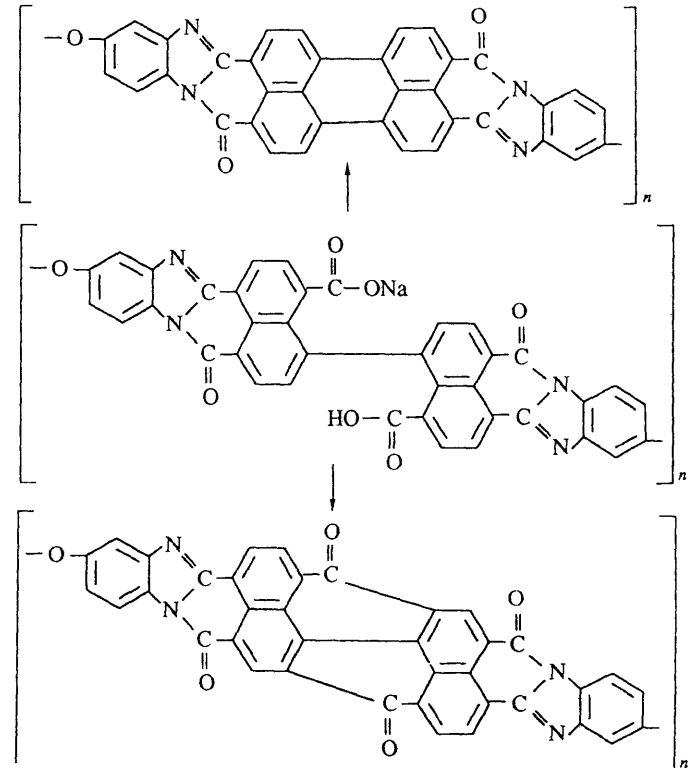


Table 16. Characteristics of the threads and elementary fibres from the initial polynaphthoylenebenzimidazole and of the products of its chemical and thermal cyclisation.

Characteristic	Initial polymer	Chemical cyclisation products		Thermal treatment product
		perylene-containing	anthanthrone-containing	
σ_{thr}, sR tex^{-1}	20–25	7	12	20–25
Elongation to break thread, %	20–25	13	15–27	15–30
Tensile strength *E*, GPa	5.7	–	–	6.9
T_{dec}, °C				
in air	530	540	550	550
in inert medium	600	610	620	610
Zero tensile strength temperature T_0, °C	580	–	–	630
OI, %	–	–	–	65



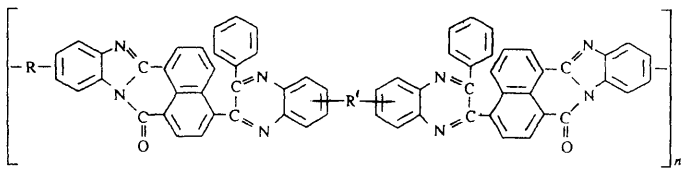
In order to convert the initial polynaphthoylenebenzimidazole into a perylene-containing structure it was decarboxylated in 10% KOH solution (attempts to prepare a 1% solution of the polymer in a less alkaline medium were unsuccessful). The conversion of the dicarboxydinaphthyl into perylene fragments produced 70% but [η] for the polymer solutions reached 0.8 dlitre g^{-1} which is significantly greater than the viscosity of the polynaphthoylenebenzimidazoles from the dianhydride of perylene-3,4,9,10-tetracarboxylic acid.[150,151]

A cyclisation reaction with H_2SO_4 was used to convert the initial polynaphthoylenebenzimidazole into an anthranthrone-containing structure. The process proceeded efficiently in 2% oleum at 40 °C giving 80% cyclisation after 2 h and the reduction of [η] of the polymer did not exceed 0.1 dlitre g^{-1}.

In addition to cyclisation by alkaline and acidic reagents the highly condensed systems may be obtained by thermal treatment of the initial polynaphthoylenebenzimidazoles in an inert medium. Not only was cyclodehydration observed but in addition cyclodecarboxylation processes occurred as a result of which the thermally treated systems contain both perylene and anthanthrone rings. Thermal treatment is the optimum method of cyclisation of polynaphthoylenebenzimidazole fibres which is confirmed by the data of Table 16.

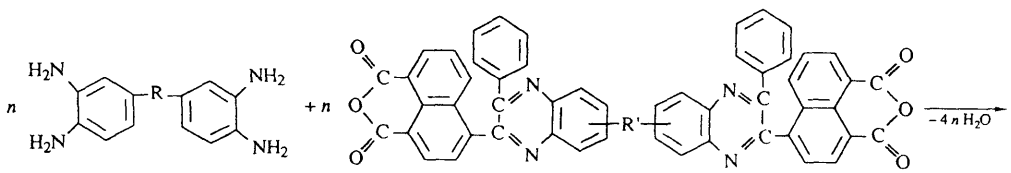
The products of thermal treatment of the initial polynaphthoylenebenzimidazole exceed the threads 'Arimid-PM' and 'LOLA' in the magnitude of the oxygen index (OI). In decomposition point they are superior to 'LOLA' however they are inferior to it in thermal stability assessed by heat treatment and are inferior to 'Arimid-PM' threads in strength. Polynaphthoylenebenzimidazoles soluble in organic solvents were obtained by the reaction of various bis(*o*-phenylenediamines) with bis(naphthalic anhydrides) containing phenylquinoxaline rings[88,90] according to the following scheme:

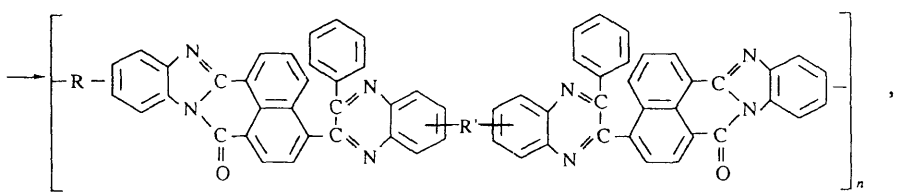
Table 17. Some characteristics of polynaphthoylenebenzimidazoles of general formula



R	R'	η_{red}, dlitre g^{-1} (H_2SO_4, 25 °C)	T_{soft}, °C	$T_{10\%}$, °C	Solvent			Film properties, 25 °C	
					m-cresol	TCE: phenol	phenol	σ, kg cm^{-2}	ε, %
–	–O–	1.4	340	455	+	+	+/–	1020	18
–O–	–O–	2.1	320	470	+	+/–	+/–	950	24
$–CH_2–$	–O–	1.0	320	455	+	+	+/–	1080	20
$–SO_2–$	–O–	0.8	340	460	+	+	+/–	990	20
–	$–SO_2–$	1.6	360	480	+	+	+/–	1100	20
–O–	$–SO_2–$	2.3	340	470	+	+	+	1300	25
$–CH_2–$	$–SO_2–$	1.8	340	460	+	+	+/–	1050	23
$–SO_2–$	$–SO_2–$	0.4	350	490	+	+	+/–	980	23

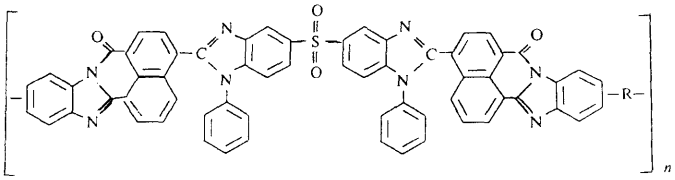
The synthesis of these polynaphthoylenebenzimidazoles was effected in *m*-cresol using benzoic acid as catalyst. The polycondensation reaction occurred in a homogeneous manner and led to the formation of high molecular (Table 17) polymers with a high degree of cyclisation.





R = –, –O–, $–CH_2–$, $–SO_2–$; R' = –, –O–, $–CH_2–$, $–SO_2–$

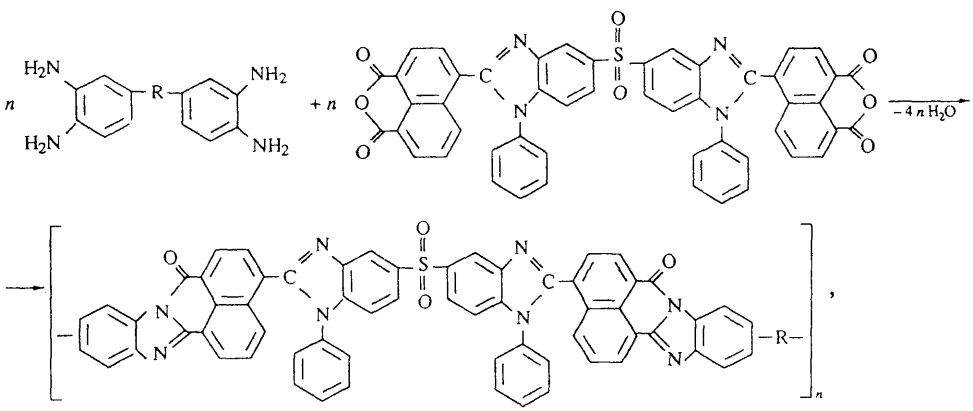
Table 18. Some characteristics of polynaphthoylenebenzimidazoles of general formula[152]



R'	η_{red}, dlitre g^{-1} (H_2SO_4, 25°C)	T_{soft}, °C	$T_{10\%}$, °C	Solvent				Film properties, 25 °C	
				m-cresol	TCE: phenol	N-MP	TCE	σ, kg cm^{-2}	ε, %
–	2.50	460	550	+	+	+/–	–	1000	7
–O–	1.20	420	500	+	+	+/–	–	1020	7
$-CH_2-$	0.90	430	500	+	+	+/–	–	1080	6.5
$-C(=O)-$	–	430	500	+	+	+/–	–	1000	7
$-C(CF_3)_2-$	0.60	420	520	+	+	+	+	–	–

Polynaphthoylenebenzimidazoles based on other bis(naphthalic anhydrides) containing phenylquinoxaline rings also possess characteristics closely similar to those given in Table 17.

These systems combine high (350 ± 20 °C) softening temperatures with high viscosity characteristics (sufficient for reliable film formation) and solubility in organic solvents. It must however be noted that these polymers are only soluble in phenolic solvents or mixtures of the latter with halogenated hydrocarbons. From this point of view there is considerable interest in polynaphthoylenebenzimidazoles obtained from bis(*o*-phenylenediamines) and bis[1-phenyl-2-(1,8-dicarboxynaphth-4-yl)benzimidazol-5-yl] sulphone[152] by the following scheme:



R = R = –, –O–, $-CH_2-$, –CO–, $-C(CF_3)_2-$.

The polynaphthoylenebenzimidazoles were synthesised in *m*-cresol using benzoic acid as catalyst at 160–190 °C. The polycondensation reactions were carried out under homogeneous conditions and led to the formation of the desired polymers possessing high viscosity characteristics (Table 18) and a high degree of cyclisation.

A distinctive feature of the polynaphthoylenebenzimidazoles considered is their solubility in N-MP which is a most acceptable solvent.

It is interesting to note that the polynaphthoylenebenzimidazoles are more soluble than the corresponding polynaphthalimides which is explained by the presence in their molecules of a 'pyridine' nitrogen atom[153,154] which is readily protonated (being the first stage of the solution of these polymers in protogenic solvents) and also by the amorphous nature of these systems caused by the presence in them of a broad set of isomeric structures.[153,154]

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Analysis of the data given in this review indicates the emergence during the last two decades of many new accessible bis(naphthalic anhydrides) characterised by the presence in their structures of elements determining improved solubility (and general processability) of the polyheteroarylenes based on them. The bis(naphthalic anhydrides) containing ether groups may be used for preparing systems related to the polyesterimides but differing from them in a higher glass point. At the same time the majority of the new bis(naphthalic anhydrides) may be used for preparing new polynaphthoylenebenzimidazoles combining satisfactory processability with very high thermal, fire and chemical resistance.

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