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Aromatic polyimides with flexible and rigid chains

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Abstract. The results of studies in recent years on the synthesis of polyimides with chains which are both flexible and rigid to the maximum extent are surveyed. The characteristic features of the formation of these polymers, their properties, and certain aspects of their practical applications are considered. It is shown that the thermodynamic rigidity of the macromolecules is one of the principal factors which determines the most important properties of polyimides and the materials based on them. The bibliography includes 85 references.

I. Introduction

The development of the chemistry of aromatic polyimides (API)[1–5] led to the formation of a large number of polyheteroarylenes exhibiting significantly different properties. One of the most important factors influencing the properties of API is the rigidity of their macromolecules. In terms of this feature, the API may be divided into two principal groups — flexible-chain and rigid-chain polyimides.

The development of the flexible-chain polyimides was stimulated by the need to obtain easily processed polyimides soluble in the usual organic solvents and having wide gaps between the glass transition and decomposition temperatures.[6–8] The development of the chemistry of the rigid-chain polymers was in its turn determined by the need to create very strong and high-modulus materials.[9,10]

The molecular designs of the flexible-chain and rigid-chain polyimides are different. The flexible-chain API contain in the main chain asymmetric phenylene (*m*-phenylene) rings and groups which increase the flexibility of the chain (ether, thioether, isopropylidene, hexafluoroisopropylidene, etc.),[6–8] whereas in the rigid-chain API the macromolecular chains are extended to the maximum extent and contain predominantly symmetrical *p*-phenylene fragments and heterocycles without any groups increasing the flexibility of the chains.[11]

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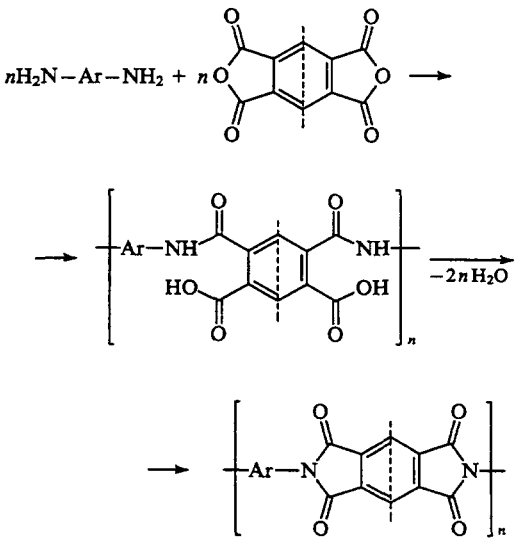
II. Flexible-chain aromatic polyimides

The most important flexible-chain API are polyimides with ether groups in the main chain, the so called polyetherimides (PEI). A wide range of PEI have been obtained as a result of the interaction of various aromatic diamines containing ether groups and the dianhydrides of aromatic tetracarboxylic acids without the same groups[1,12,13] in accordance with Scheme 1.

The values of the Kuhn segment (A_f/Å), calculated and determined experimentally[14,15] for certain PEI based on the dianhydride of oxybis(benzene-3,3′,4,4′-dicarboxylic) acid (OBBDCA) as well as the properties of these PEI are presented in Table 1.

The use of diamines with *p*-phenylene fragments and of dianhydrides containing only one ether group led to PEI with a 30–37 Å Kuhn segment and a glass transition temperature of 255–290 °C. When the 'dianhydride R' was used instead of OBBDCA, the PEI **3a–e** with a 26–32 Å Kuhn segment and a glass transition temperature of 175–215 °C were synthesised (Table 2).

Scheme 1



1–3

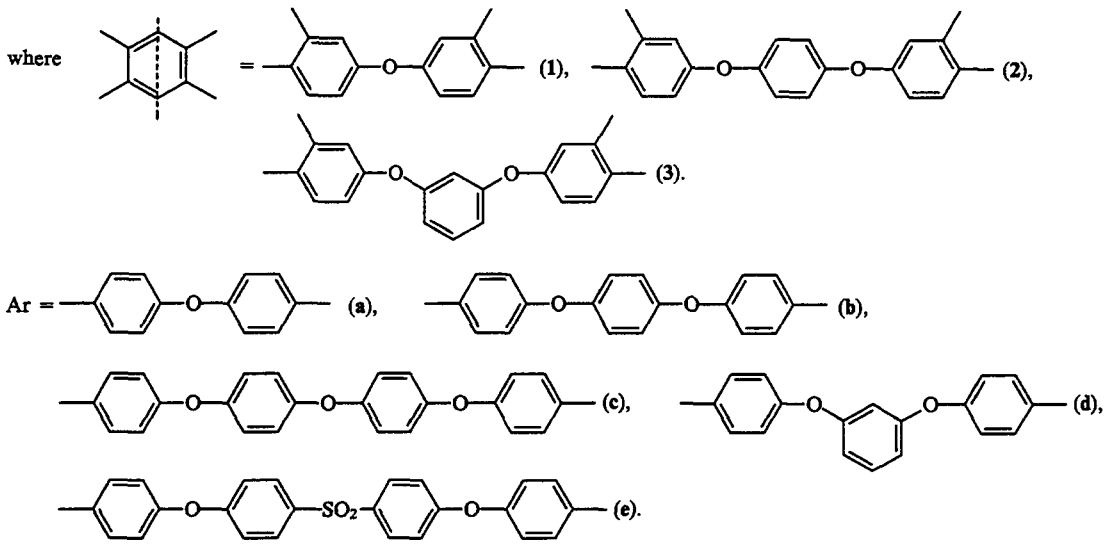
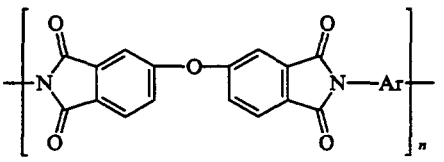


Table 1. The properties of polyimides based on the dianhydride of oxybis(benzene-3,3′,4,4′-dicarboxylic) acid.[14,15]



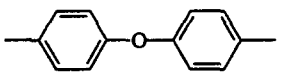
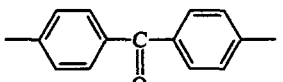
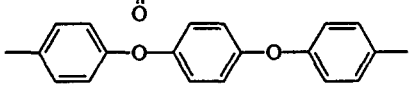
–Ar–	T_g / °C	$T_{10\%}$ / °C (TGA)	Properties of films			A_f / Å
			σ / MPa	ε (%)	E / GPa	
	270	450–500	160–200	50–100	3.2	36.4
	290	445	141	16	3.1	36.3
	255	460	140–170	50–75	2.7–3.2	29.9

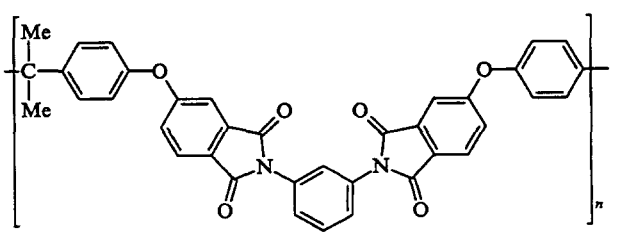
Table 2. Some properties of the polyetherimides **3a–e**.

Poly-etherimide	T_g / °C	$T_{10\%}$ / °C (TGA)	Properties of films σ / MPa	ε (%)	E / GPa
3a	215	540	120	20	2.6
3b	202	560	125	160	–
3c	174	510	120	90	2.3
3d	197	577	120	160	3.4
3e	205	510	100	60	2.4

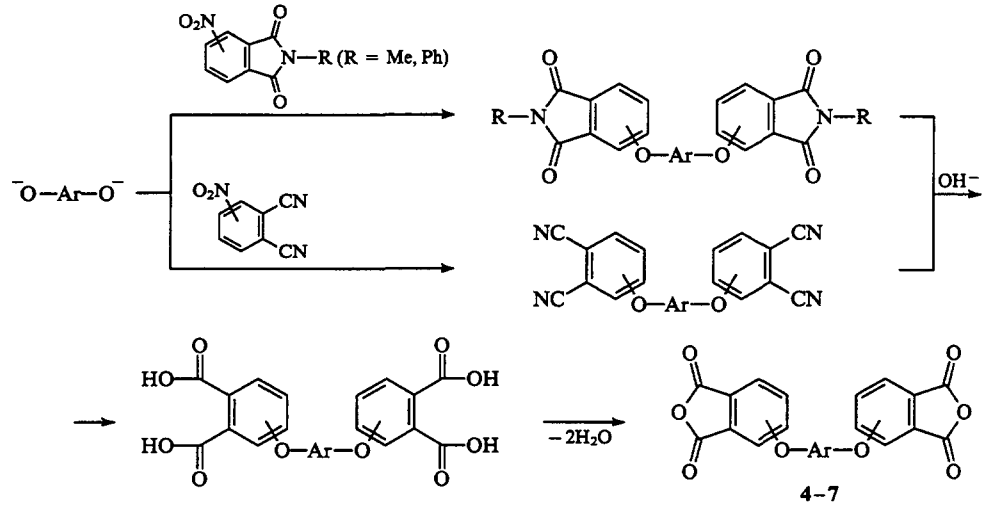
In order to obtain PEI with a smaller Kuhn segment and lower glass transition temperatures it appeared useful to introduce into the macromolecule the largest possible number of ether groups, which increase the flexibility of the chain, as well as *m*-phenylene fragments. A large group of bis(phthalic anhydrides), containing at least two ether groups — bis(etherphthalic anhydrides) (BEPA) — were synthesised. The dianhydrides were obtained by the aromatic nucleophilic nitro-displacement reaction between bisphenoxides and nitrophthalimides or nitrophthalonitriles (Scheme 2).[6–8,16–21]

The reactions of the BEPA **4–7** with aromatic diamines [*m*-phenylenediamine, bis(4-aminophenyl)ether, bis(4-aminophenyl)methane, etc.] were carried out in accordance with Scheme 3.[22–34] The PEI were synthesised in the melt,[22–26] in amide solvents (high-temperature polycondensation),[27,28] or in nonpolar organic[22,23,29,30] and phenolic[31–34] solvents. Particular attention was concentrated on the polymers obtained on the basis of the cheap and readily available *m*-phenylenediamine. Certain properties of these polymers are presented in Table 3.

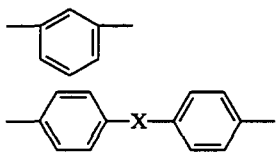
Among the PEI listed in Table 3, the polymer synthesised from the 'dianhydride A' is the most important and most readily available.



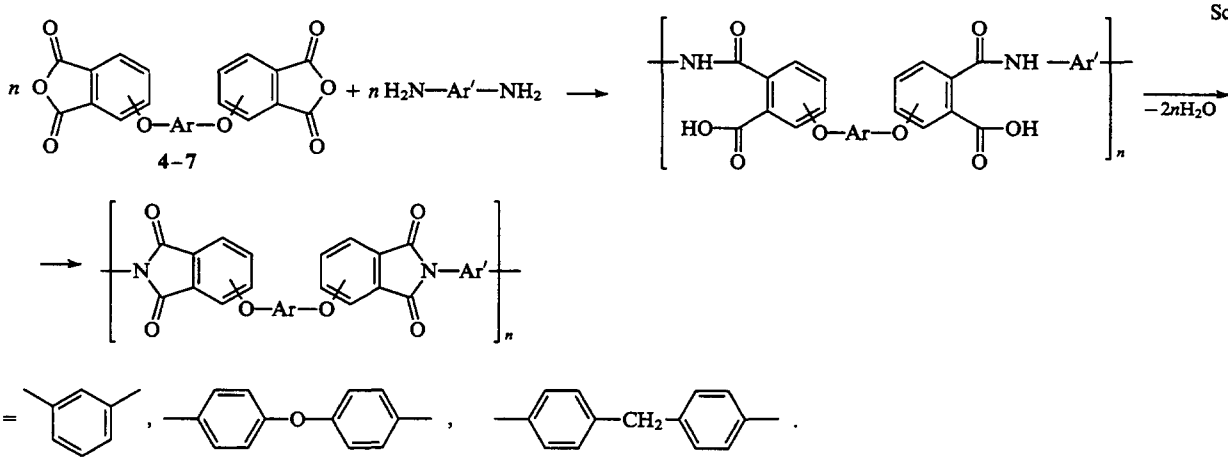
Scheme 2



4-7

Ar	BEPA	Isomer	Yield (%)	T_m / °C
	4	3,3′	100.0	228–229.5
		4,4′	89.9	284.5–286
X = O	5	3,3′	98.9	254–255.5
		4,4′	100.0	238–239
X = S	6	3,3′	46.6	257–257.5
		4,4′	97.0	189–190
X = CMe_2	7	3,3′	97.0	186.5–187.5
		4,4′	85.0	189–190

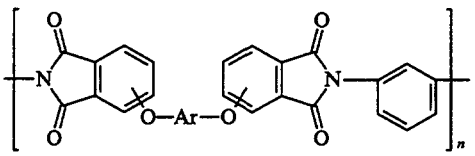
Scheme 3



This polymer, containing *m*-phenylene ring, ether, and isopropylidene groups in the main chain, is extremely flexible — its Kuhn segment is 19 Å long.[35] It was selected as the starting material for the preparation of the ULTEM plastic, which is produced by the General Electric Company.[6] Certain properties of ULTEM are listed in Table 4. A high transparency and rigidity combined with a high decomposition temperature and fire resistance as well as the absence of smoke formation or combustion are characteristic of this polymer.[6]

Another approach to the synthesis of flexible-chain readily processable PEI is based on the use of aromatic diamines containing several ether groups and *m*-phenylene fragments in the structure of the molecule. A large group of these diamines have been obtained by the interaction of various bisphenoxides with unsubstituted and substituted *m*-dinitrobenzenes[36–57] by the aromatic nucleophilic nitro-displacement reaction (Scheme 4).

Table 3. The properties of polyetherimides having the general formula [6,18]



Initial BEPA	Isomer PEI	$[\eta]$/dl g^{-1} [a]	T_g/ °C (DSC)	$T_{10\%}$/ °C (TGA)		Solubility [b]		
				air	N_2	*N*-MP	DMF	$CHCl_3$
4	3,3′	0.57	241	460	500	S	S	IS
	4,4′	0.70	224	500	515	S	IS	IS
5	3,3′	0.53	238	480	480	S	S	S
	4,4′	1.04	227	500	490	S	IS	PS
6	3,3′	0.39	236	446	470	S	S	S
	4,4′	0.50	215	460	480	S	S	S
7	3,3′	0.52	231	470	470	S	S	S
	4,4′	0.45	209	480	490	S	IS	S

[a] The viscosity η was measured in *m*-cresol at 25 °C. [b] Notation adopted: S = soluble, IS = insoluble, PS = partially.

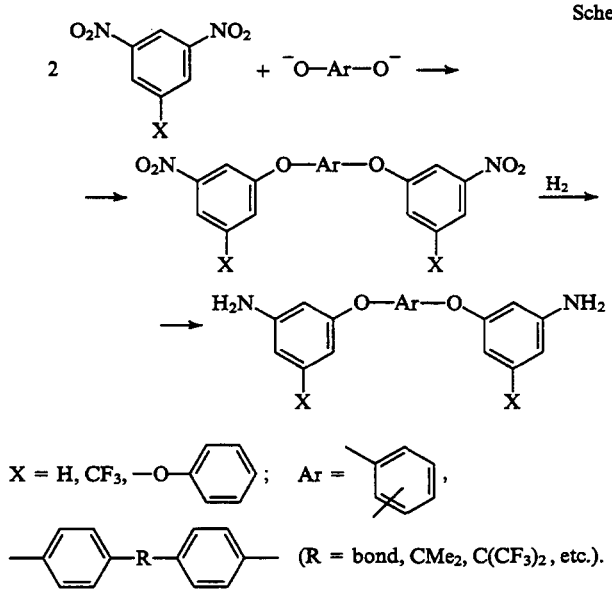
Table 4. The properties of the ULTEM polyimide.[6]

Mechanical properties		Thermal properties	
Tensile strength at yield (yield point)	105 MPa	Glass transition temperature	217 °C
Tensile modulus	3000 MPa	Heat deflection temperature	
Tensile elongation, ultimate	60% – 80%	1.85 MPa	200 °C
		0.46 MPa	210 °C
Flexural strength	145 MPa	Limited oxygen index	47
Flexural modulus	3300 MPa	Burn bending UL 94 (vertical)	v-O at 0.64 mm
Compressive strength	140 MPa		
Compressive modulus	2900 MPa	Smoke evolution according to the NBS method	
Gardner impact strength	36 Nm	D_s after 4 min	0.7
		D_{max} after 20 min	30
Izod impact strength			
notched	50 J m^{-1}		
unnotched	1300 J m^{-1}		

As a rule, the aromatic nucleophilic nitro-displacement reaction takes place readily, provided that the activating groups are located in the *ortho*- and *para*-positions relative to the nitro-group, but in certain cases *meta*-substituted dinitro-compounds can also be involved in the reaction.[4,6,7]

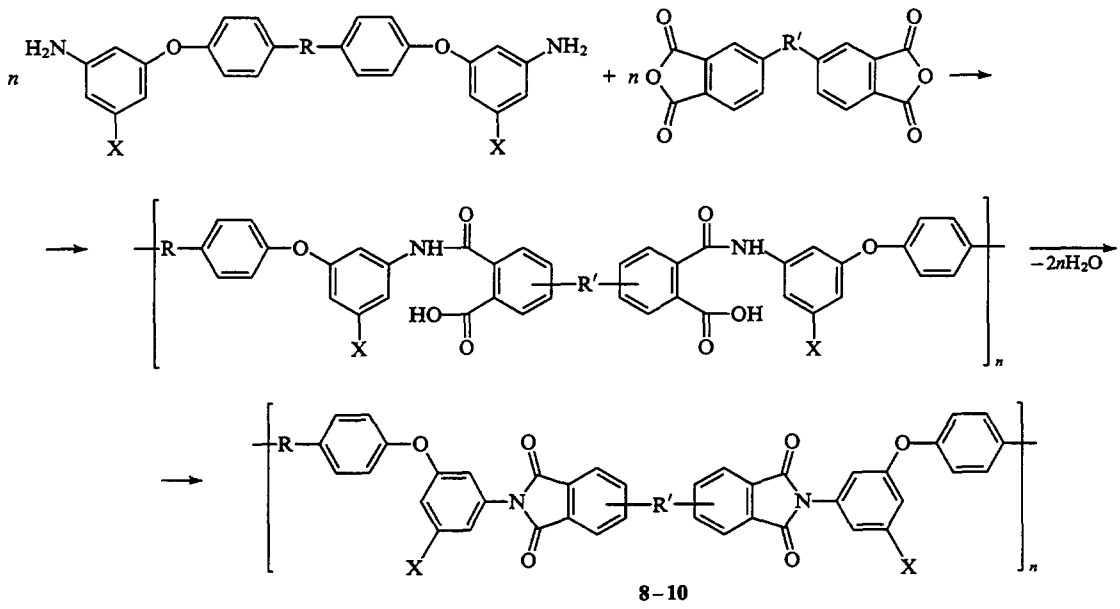
Numerous studies [36–49] have been devoted to the preparation of diamines from *m*-dinitrobenzene. Among them, products with the isopropylidene and hexafluoroisopropylidene 'bridging' groups are of greatest interest. The PEI involving these diamines have been synthesised in accordance with Scheme 5.

Scheme 4



The reactions were carried out in *N*-methylpyrrolidone (*N*-MP) at room temperature; the intermediate poly(*o*-carboxy)amides were cyclised directly in the reaction solution using as the catalyst either a 1 : 1 pyridine – acetic anhydride mixture or orthophosphoric acid or adding compounds which form azeotropic mixtures with the water evolved during cyclisation. All the reactions took place under homogeneous conditions. Under the conditions of catalysis by orthophosphoric acid or without the use of any catalyst, as a rule high-molecular-mass PEI with a high degree of cyclisation were obtained. Certain properties of the PEI **8** and **9** are presented in Table 5. It follows from the data in Table 5 that the PEI **8** and **9** are characterised by relatively low glass transition temperatures (180 – 225 °C) and high decomposition temperatures. The melt viscosity of these polymers is fairly low, which makes them suitable for processing by injection moulding.

Scheme 5



8–10

X = H: R = CMe_2 (8), $C(CF_3)_2$ (9); X = CF_3: R = CMe_2 (10)

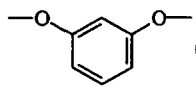
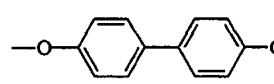
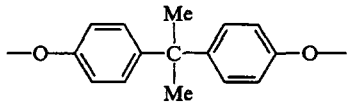
R′ = bond (a), C(O) (b), –O– (c),  (d),  (e),  (f).

Table 5. The properties of the polyimides **8** and **9**.[46,48]

Polyimide	η_{red} [a] /dl g^{-1}	T_g/°C	$T_{5\%}$/°C (TGA)	$10^{-3}\eta_{eff}$ /dl g^{-1} [b]	
				A	B
8a	0.78	210	438	3.9	9.0
8b	0.71	225	443	8.7	28.0
8c	0.69	200	443	5.4	15.0
8d	0.42	180	508	1.8	4.7
8e	0.50	200	484	2.4	5.4
8f	0.59	190	447	2.7	3.5
9a	1.23	220	492	8.6	23.0
9b	0.55	220	492	2.8	4.9
9c	0.55	180	505	0.4	–
9d	0.68	200	517	2.8	7.7
9e	1.07	220	498	5.4	1.5
9f	0.78	200	507	2.9	6.4

[a] The viscosity η measured in *m*-cresol at 25 °C. [b] The effective viscosity of the melt (capillary viscosimetry) measured at $v = 2912\ s^{-1}$ (A), $v = 728\ s^{-1}$ (B) (v is rate of shearing).

The polyimides obtained are readily soluble in organic solvents — *N*-MP, *m*-cresol, methylene chloride, chloroform, etc. The ready solubility of the polymers is determined by their structure and method of synthesis. The polymers synthesised under mild conditions are known to be more soluble than the polymers obtained at high temperatures.[58] Thus the polyimides **9a–c**, obtained in accordance with Scheme 5, are readily soluble in *N*-MP and dimethylacetamide (DMA) while the polyimides based on 2,2-[bis(*p*-aminophenoxy)phenylene]propane,[59] obtained using solid-phase high-temperature cyclisation of polyamido-acids, are insoluble in these solvents. The polyimides based on diamines with trifluoromethyl groups in the benzene ring are even more soluble.[51,52] The corresponding diamines were obtained in accordance with Scheme 4; 3,5-dinitro-1-trifluoromethylbenzene and various bisphenoxides were used as the starting compounds.[50–52] Attention has been concentrated on the diamine with the isopropylidene bridging group.

The polyimides were synthesised from this diamine and the dianhydrides of the simplest dinuclear tetracarboxylic aromatic acids in *N*-MP without a catalyst in accordance with Scheme 5.[52] The principal properties of the polyimides **10a–c** are presented in Table 6. As can be seen, the polyimides have low glass transition temperatures (180–210 °C) combined with high decomposition temperatures. The polymers **10a–c** are soluble not only in amide, phenolic, and chlorinated solvents (like the polymers **8** and **9**) but also in cyclohexanone and butyrolactone.

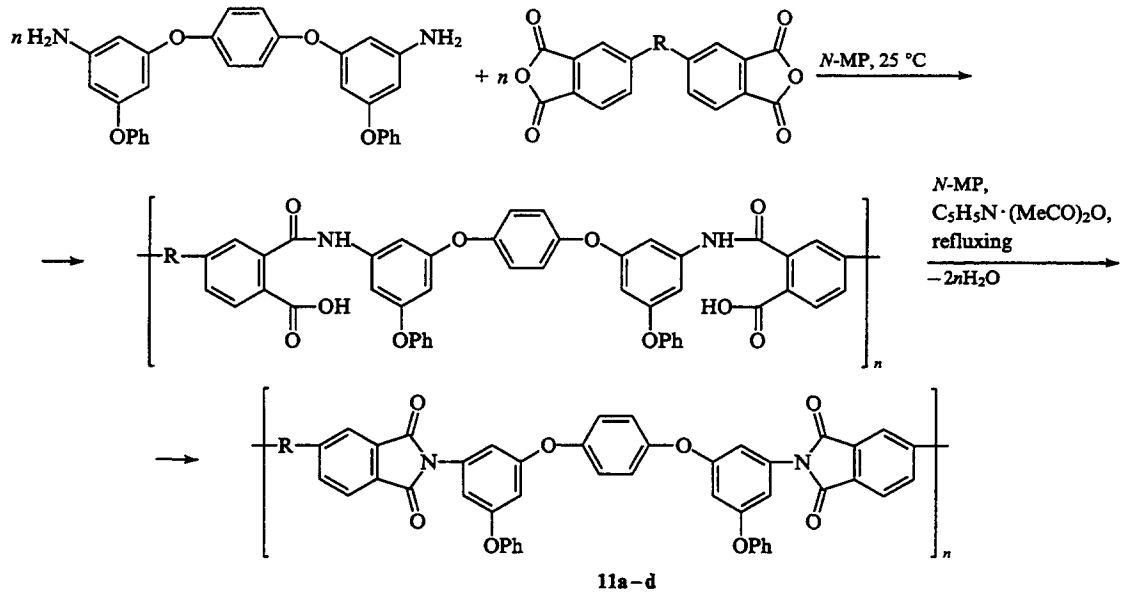
Table 6. The properties of the polyimides **10a–c**.[52]

Polyimide	η_{red} /dl g^{-1} [a]	T_g/°C	$T_{10\%}$/°C (TGA)
10a	0.46	193	523
10b	0.37	190	502
10c	0.31	180	511

[a] The viscosity η measured in *m*-cresol at 25 °C.

3,5-Dinitrodiphenyl ether can also be used to obtain the diamines. The interaction of the ether with various bisphenoxides leads to nitro-compounds with phenoxide side groups,[53,54] the reduction of which results in the formation of the corresponding amines with phenoxide side groups.[56] The polyimides **11a–d** have been synthesised from a diamine containing a hydroquinone residue.[57] The synthesis was based on Scheme 6. All the reactions were carried out homogeneously and led to high-molecular-mass polyimides with a high degree of cyclisation. The properties of the polyimides **11a–d** are presented in Table 7. The polyimides obtained were distinguished by relatively low glass transition temperatures combined with high decomposition temperatures and a ready solubility in organic solvents, which led to their being easily processed into articles.

Scheme 6



11a–d

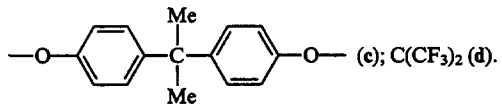
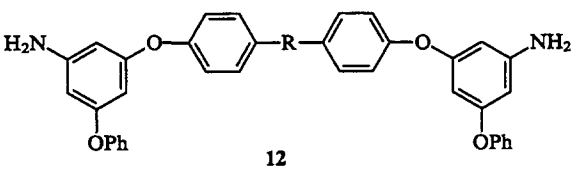
R = O (a), C(O) (b),  (c); $C(CF_3)_2$ (d).

Table 7. The general properties of the polyimides **11a–d**.[57]

Poly-imide	η_{red} / dl g^{-1}	T_g / °C	$T_{10\%}$ / °C (TGA)	Molecular mass	Properties of films	
					σ / MPa	ε (%)
11a	0.67	170	520	47000	890	4
11b	1.00	190	520	77000	760	5
11c	0.95	188	500	–	540	5
11d	0.65	205	470	–	530	4

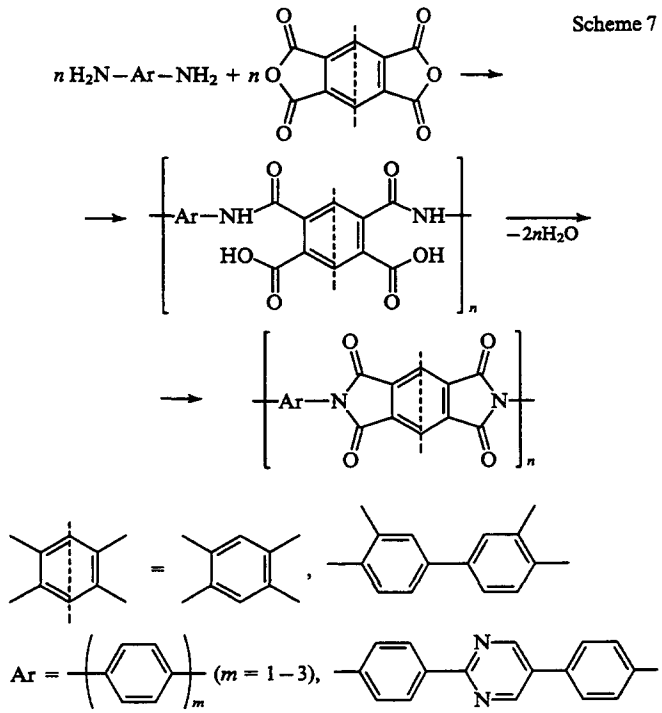
Almost all the polymers are soluble in amide, phenolic and chlorinated solvents, and also in cyclohexanone, acetone, and butyrolactone. The polyimides based on the diamines having the general formula **12** are even more easily processed into articles.



12

R = CMe_2, $C(CF_3)_2$.

Scheme 7



III. Rigid-chain aromatic polyimides

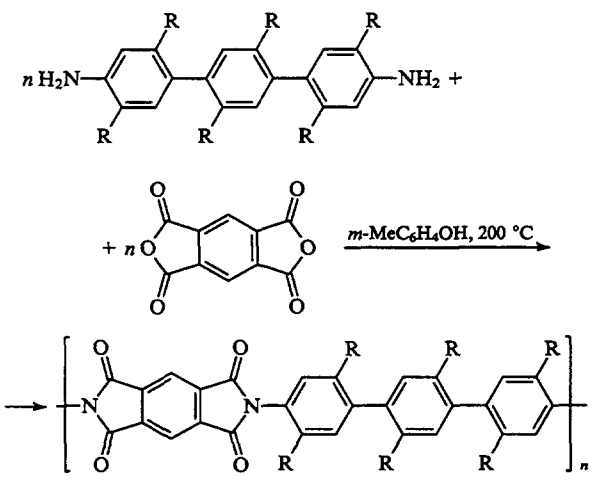
As mentioned above, the macromolecules of rigid-chain aromatic polyimides must be extended to the maximum extent and must contain symmetrical *p*-phenylene fragments and heterocyclic units without 'flexibilising bridges'. The simplest aromatic polyimides with a 'rod' geometry may be obtained from pyromellitic dianhydride or the dianhydride of biphenyl-3,3′,4,4′-tetracarboxylic acid and carbocyclic (*p*-phenylenediamine, benzidine, 4′,4″-diaminoterphenyl, etc.) or heterocyclic [2,5-bis(*p*-aminophenyl)pyrimidine]diamines [60–64] in accordance with Scheme 7.

The high-molecular-mass poly(*o*-carboxy)amides formed in the first stage (in various amide solvents) undergo chemical or thermal cyclodehydration in the second stage, which results in the formation of insoluble polyimides. The value of the Kuhn segment was 625 Å for the polypyromellitimide based on 4′,4″-diaminoterphenyl and 1750 Å for the polypyromellitimide based on 2,5-bis-(*p*-aminophenyl)pyrimidine, which indicates a high rigidity of the macromolecules.[62]

It is noteworthy that the evolution of gaseous products during the high-temperature thermal cyclodehydration limits the use of these materials in the industrial manufacture of thick-walled articles.[60]

The studies by various research groups on the problem of the removal of water stimulated investigations of the synthesis of rigid-chain polyimides soluble in organic solvents. Bulky side groups are usually introduced into the macromolecule in order to improve the solubility of polymers. Typical representatives of such groups are long aliphatic segments, for example dodecyl fragments.[65-68] The reaction of 4,4″-diamino-2,5,2′,5′,2″,5″-hexadodecyl-*p*-terphenyl with pyromellitic dianhydride in *m*-cresol at 200 °C using isoquinoline as the catalyst was carried out in accordance with Scheme 8. The polyimide **13** obtained as a result of this reaction was soluble in various organic solvents. However, it is noteworthy that the introduction of aliphatic fragments into the molecules of aromatic polyimides appreciably lowers their thermal stability — the polymers rapidly lose weight starting from 380 °C.

Scheme 8



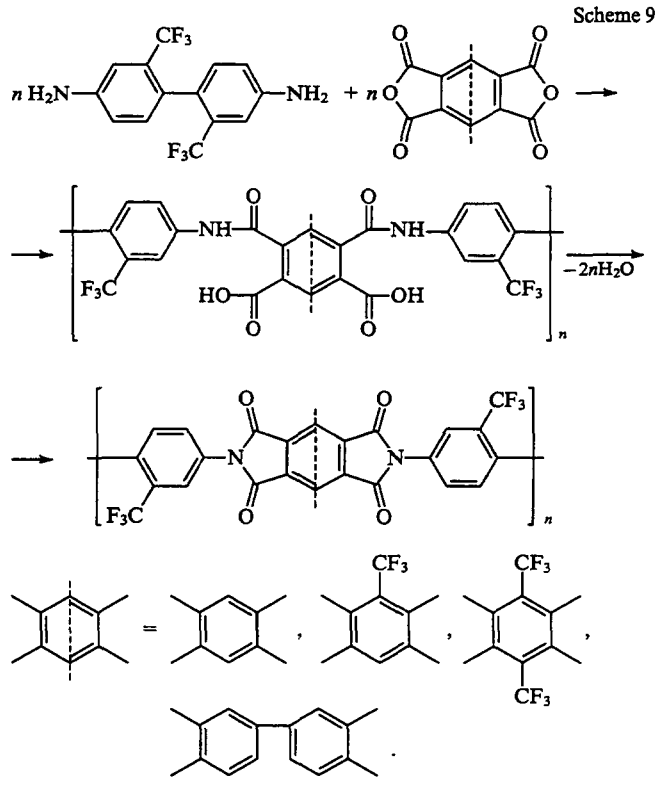
13

R = $(CH_2)_{11}CH_3$.

Better results were obtained when diamines and/or dianhydrides with trifluoromethyl side groups were used as the starting components.[69-76] Polyimides based on 2,2′-bis-(trifluoromethyl)-4,4′-diaminobiphenyl and the dianhydrides of pyromellitic, biphenyl-3,3′,4,4′-tetracarboxylic, 1-(trifluoromethyl)benzene-2,3,5,6-tetracarboxylic, and 1,4-bis(trifluoromethyl)benzene-2,3,5,6-tetracarboxylic acids have been synthesised by this procedure (Scheme 9).

The synthesis is carried out in two ways — by a two-stage reaction involving the low-temperature synthesis of poly(*o*-carboxy)amides in DMA with subsequent thermal cyclisation in the solid state at 350 °C[70,71] and by a single-stage polycyclocondensation in boiling *m*-cresol.[72-76] The polyimide obtained from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl and the dianhydride of biphenyl-3,3′,4,4′-tetracarboxylic acid by polycondensation in *m*-cresol is of greatest interest.[72-76] This polymer is soluble in hot *m*-cresol. Fibres with a low strength and low elasticity modulus have been obtained by spinning its isotropic solution, but after tenfold drawing at a temperature above 380 °C the strength and the modulus of elasticity improved greatly when a load was applied. The fibres drawn in this way had a tensile strength of 3.2 GPa and an initial modulus of elasticity in excess of 130 GPa. The fibres had excellent thermal stability and retained a high strength and modulus of elasticity at elevated temperatures.

Scheme 9



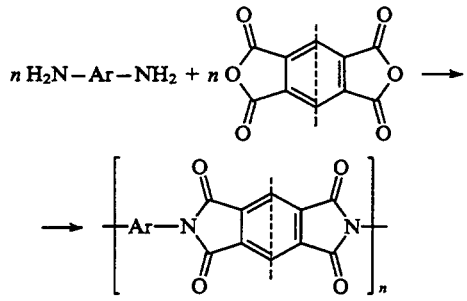
Rigid-chain polymides soluble in phenolic solvents have been obtained by the interaction of the dianhydride of biphenyl-3,3′,4,4′-tetracarboxylic acid with 2-phenyl-*p*-phenylenediamine and 4,4′-diamino-1,1′-binaphthyl[77] in accordance with Scheme 10. The reaction was carried out in *m*-cresol or *p*-chlorophenol at 200 °C using isoquinoline or tertiary amines as catalysts. The polyimides **14** and **15** are soluble in *m*-cresol and *p*-chlorophenol and have a high viscosity combined with high glass transition temperatures and decomposition temperatures. The same diamines have been used in the reactions with the dianhydrides of 3-phenyl- and 3,6-diphenylpyromellitic acids (Scheme 10).[78] The properties of the polyimides obtained under the conditions described above are presented in Table 8.

Table 8. The properties of the polyimides **14**–**19**.[77,78]

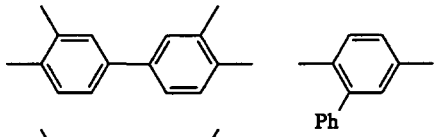
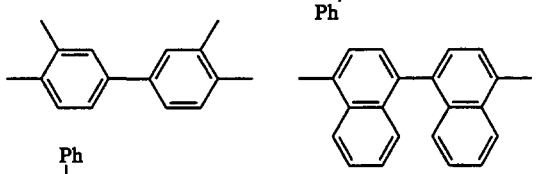
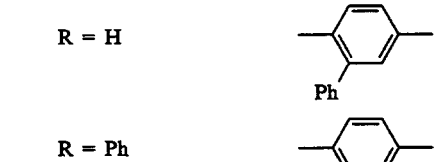
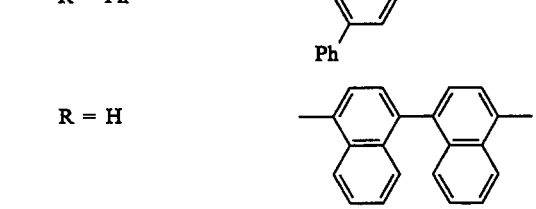
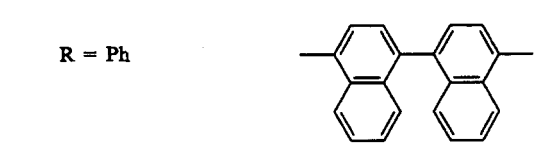
Polyimide	η_{log} / dl g^{-1}	T_g / °C	$T_{5\%}$ / °C (TGA)	
			N_2	air
14	0.96	341	565	572
15	4.54	–	585	498
16	0.70	–	560	501
17	2.32	–	557	555
18	1.21	–	578	557
19	3.15	404	546	467

The dianhydride of 3,6-diphenylpyromellitic acid was also made to react with *p*-phenylenediamine, 1,4-diamino-2,3,5,6-tetramethylbenzene, benzidine, 4,4′-diamino-3,3′,5,5′-tetramethylbiphenyl, 4,4′-diamino-3,3′-dimethoxybiphenyl, and 4,4′-diamino-2,2′-bis(trifluoromethyl)biphenyl.[79] The corresponding polyimides were obtained in two ways — by a two-stage synthesis (low-temperature synthesis of poly-*o*-carboxyamides in *N*-MP with subsequent chemical or thermal imidisation) and a single-stage high-temperature polycyclocondensation in boiling *m*-cresol with isoquinoline as the catalyst. Best results were achieved when the single-stage process was used.

Scheme 10



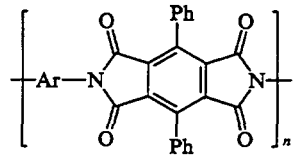
14–19

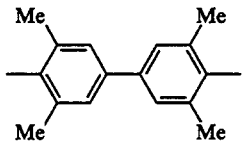
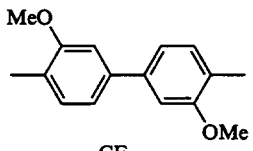
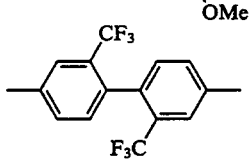
Compound	—Ar—
14	
15	
16	R = H 
17	R = Ph 
18	R = H 
19	R = Ph 

Among the rigid-chain polyimides synthesised in this way, three polymers (based on dinuclear diamines) proved soluble in *m*-cresol. It is most likely that the improvement of the solubility of these polymers is associated with the nonplanarity of the bisphenylene fragments (especially 2,2′-substituted ones).[80]

The intrinsic viscosities of the polymers soluble in *m*-cresol (Table 9) are in the range 0.91–2.63 dl g^{-1}; these are relatively low values for rigid-chain polymers. The mass-average molecular masses of these polymers are 10 000–12 000.

Table 9. Some properties of polyimides having the general formula.[79]



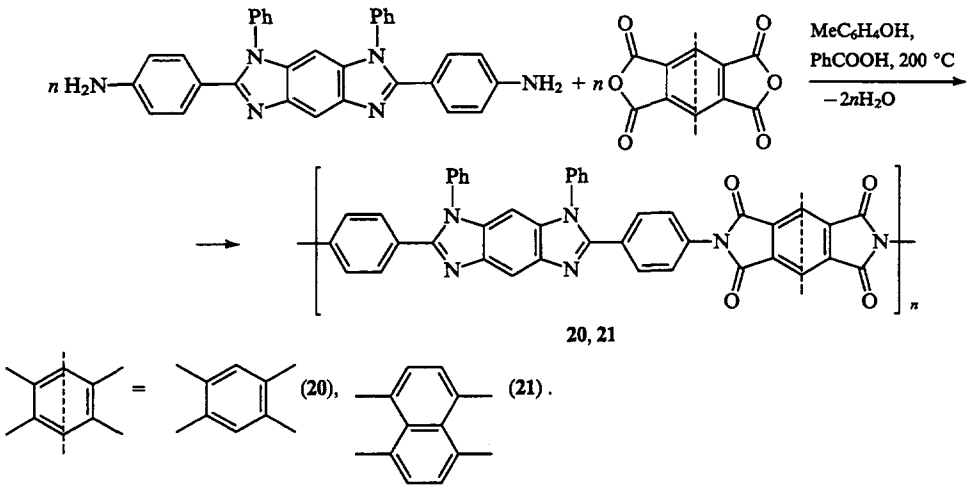
Ar	$[\eta]$ / dl g^{-1}	$T_{5\%}$ / °C (TGA)	
		N_2	air
	0.91	520	440
	2.63	475	425
	2.40	585	585

Fibres have been obtained from the polyimide with trifluoromethyl side groups by wet spinning from a hot *m*-cresol solution. The thermooxidative stability of the polyimides synthesised from 4,4′-diamino-3,3′,5,5′-tetramethylbiphenyl and 4,4′-diamino-3,3′-dimethoxybiphenyl is relatively low — thermograms indicate 5% weight losses in air at 425 and 440 °C respectively. The low thermal stability of these polymers may be associated with the lack of resistance of the methoxy and methyl groups to oxidation. The thermal stability of the same polymers under nitrogen is much higher (the thermograms indicate 5% weight losses at 475 and 520 °C respectively in this instance). The presence of trifluoromethyl side groups in polyimides increases the thermooxidative and thermal stabilities of the polymers. Thermograms indicate a 5% weight loss at 585 °C in air and under nitrogen.[79]

The rigid-chain polypyromellitimide **20** was obtained from 2,6-di(*p*-aminophenyl)-1,7-diphenylbenzo[1,2;4,5′]biimidazole[81] by high-temperature polycondensation in phenolic solvents (Scheme 11). Despite the presence of phenyl substituents, the polyimide **20** hardly dissolves in organic solvents. A polymer with a better solubility was synthesised by the interaction of the same diamine and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid.[81] The resulting polynaphthylimide **21** dissolved not only in sulfuric but also in trifluoroacetic acid as well as the tetrachloroethane — phenol mixture. The ready solubility of the polyimide is combined with a high viscosity of the solution and a very high glass transition temperature and decomposition temperature (540 °C).

Polynaphthylimides have a series of advantages over polyphthalimides (for example, they are more stable under conditions of hydrolysis and thermolysis),[82] so that investigators have devoted much attention to the synthesis of soluble polynaphthylimides. The most significant and to some extent unexpected result was obtained in the synthesis of the polyimide from the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid and an asymmetric diamine — 2-(*p*-aminophenyl)-5(6)-aminobenzimidazole in accordance with Scheme 12.[83]

Scheme 11

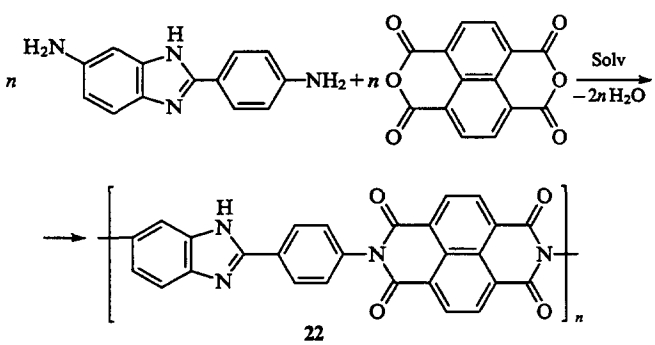


20, 21

(20), (21).

Despite the absence of substituents of any kind in the diamine and the dianhydride, the reaction occurred homogeneously and led to the high-molecular-mass polymer **22** (M = 120 000),[84] which is soluble (before isolation from the reaction solution) in phenolic solvents. The polymer **22** is moderately rigid — its Kuhn segment is 320 Å.[84] Strong and elastic films have been cast from the reaction solutions of the polyimide **22** (Table 10). After heat treatment at 140 °C for 12 h with subsequent maintenance in vacuo at 250 °C for 3 h, the properties of the films improved and after stretching the tensile strength was 930 ± 10 MPa and the modulus of elasticity was 20 ± 1 GPa.

Scheme 12



22

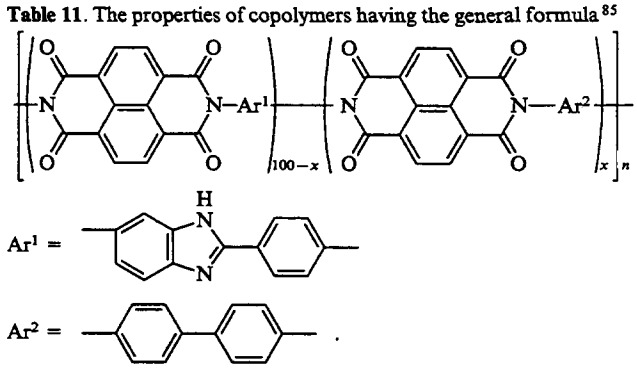
Solv = MeC_6H_4OH, PhCOOH (200°C)

Table 10. The properties of a polynaphthylimidobenzimidazole film (polyimide **22**).[83]

Test specimen	σ / MPa	ε (%)	10^{-3} E / MPa
Film after casting	320±10	25±5	4.5±0.5
Film after heating (140 °C / 12 h and 250 °C / 3 h in vacuo)	470±10	35±5	4.6±0.5
Stretched film	930±10	8±1	20±1

The partial replacement of 2-(*p*-aminophenyl)-5(6)-aminobenzimidazole by benzidine led to a polymer with a larger Kuhn segment and a greater strength and modulus of elasticity (Table 11).[85]

Table 11. The properties of copolymers having the general formula[85]



Ar¹ =

Ar² =

x (mol %)	[η] / dl g^{-1} (H_2SO_4)	σ / MPa	ε (%)	10^{-3} E / MPa
0	9.8	320±10	25±5	4.5±0.5
5	11.5	384±21	17±4	10.0±0.5
10	13.0	443±9	17±1	12.9±0.5
15	8.9	417±19	17±2	12.0±0.8
20	11.2	446±19	17±2	15.2±1.6
20	11.2	1174[a]	4[a]	29.9[a]
25	9.4	418±14	20±4	10.7±0.3
30	15.3	418±33	20±4	10.4±0.2
30	15.3	1500[a]	4[a]	38.0[a]

[a] Data for oriented (60%) films are presented.

IV. Conclusion

The data considered above indicate considerable advances in the chemistry and technology of the flexible- and rigid-chain polyimides achieved during recent years. Novel methods of synthesis of various bifunctional and tetrafunctional aromatic monomers have been developed and the reactions involving the formation from them of high-molecular-mass polyimides have been investigated. Certain polyimides are of practical as well as academic interest. Further development of this field of polymer chemistry makes it possible to hope that new results will be obtained in the immediate future.

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