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Synthesis and thermal properties of poly(amideimide)s based on tricarboxylic acid anhydrides containing aryloxy groups

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Thermostable poly(amideimide)s (PAIs) were synthesized according to a 'one-pot/two-step' direct polycondensation of flexible aromatic diamines with monoesters of isomeric tricarboxylic acid anhydrides containing an aryloxy group or with the monoesters of trimellitic anhydride (TMA). The prepared PAIs have inherent viscosity values of 0.46–0.95 dl g^{-1}, are soluble in strongly polar aprotic solvents and form tough and transparent films. The molecular structure of the polymers was investigated by Fourier transform infrared and ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy. A constitutional disorder due to a random sequence of amide and imide groups was found. Measurements by wide-angle X-ray diffraction indicated that the prepared PAIs are amorphous. The thermal behaviour was studied by differential scanning calorimetry and dynamic thermogravimetric analysis. The glass transition temperatures (T_g) of the PAIs obtained from monoesters of tricarboxylic acid anhydrides containing an aryloxy group range between 262 and 213°C, and are lower than those of the corresponding PAIs derived from TMA. The prepared PAIs have high thermal resistance in nitrogen as shown by their temperatures of 10% of weight loss (T_d), which are higher than 500°C. Both T_g and T_d depend on the orientation of the aryloxy group in the tricarboxylic acid anhydride moiety. © 1997 Elsevier Science Ltd.

(Keywords: poly(amideimide)s; thermostable polymers; tricarboxylic acid anhydrides)

INTRODUCTION

There is a growing interest in aromatic poly(amideimide)s (PAIs) for a variety of applications as they retain good mechanical properties at high temperatures and show easier processability when compared with other aromatic thermostable polymers[1–3]. Commercial PAIs are obtained from trimellitic anhydride (TMA) or a TMA derivative, and aromatic diamines such as 4,4′-oxydianiline or 4,4′-methylenedianiline. Several attempts have been made to modify the PAI structure, introducing into the diamine moiety other functional groups or ring substituents capable of reducing the chain rigidity and further increasing their tractability[4–9]. Less attention has been devoted to the study of PAIs derived from aromatic tricarboxylic acid anhydrides, different from TMA, which have hinge bridging groups between the aromatic rings[10–13].

We recently reported on the structure–properties relationships of PAIs based on TMA and diamines containing thermally stable bisaryloxy groups[9]. It was found that most of these PAIs are amorphous thermoplastic materials and exhibit good thermal resistance up to 500°C. In this work we describe the synthesis of two-ring tricarboxylic acid anhydrides having an ether bridging group and different ring orientations and of the PAIs prepared from their monoesters and aromatic diamines according to a 'one-pot' straightforward method recently described[14,15]. The thermal properties of these novel PAIs have been also investigated and compared with those of the corresponding polymers based on TMA.

EXPERIMENTAL

Materials

1-Methyl-2-pyrrolidone (NMP) and triphenylphosphite (TPP) (Fluka), *N*,*N*-dimethylacetamide (DMAc) and *N*,*N*-dimethylformamide (DMF) (Aldrich), were dried by vacuum distillation over 4 Å molecular sieves. Toluene was dried by elution on aluminium oxide, and pyridine (Py) was distilled over potassium hydroxide pellets. Lithium chloride and potassium carbonate were dried under vacuum for 6 h at 160 and 100°C, respectively.

Monomers

4,4′-Oxydianiline (**1**), 4,4′-methylenedianiline (**2**) (Aldrich) and 4,4′-(1,4-phenylenedioxy)dianiline (**3**) (Chriskev) were recrystallized from tetrahydrofuran (THF), toluene and ethanol, respectively. 3,4-Dimethylphenol (Aldrich), 3-cyanophenol, 4-cyanophenol, 3-nitrophthalonitrile and 4-nitrophthalonitrile (TCI Tokio) were used as received. A mixture of 1,2,4-benzentricarboxylic-acid-1-ethylester and 2-ethylester (**4**), with a molar ratio of 57/43, was prepared according to a previously reported procedure[14].

4-4′-(2-Carboxy)oxydibenzoic acid (5), 3-4′-(2-carboxy)oxydibenzoic acid (6) and 4-3′-(2-carboxy)oxydibenzoic acid (7). These acids were synthesized via two procedures:

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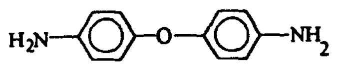
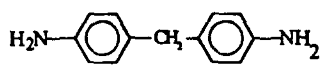
Procedure A. 3,4-Dimethylphenol (24.4 g, 0.200 mol) and KOH (12.3 g, 0.220 mol) in 40 ml of toluene were refluxed in a flask fitted with a Dean–Stark trap and inlet for nitrogen until the water/toluene azeotrope was completely removed. The solvent was evaporated, and 32.4 g (0.200 mol) of 4-bromotoluene, 1.0 g of copper powder, 1.0 g of cuprous chloride and 60 ml of DMF were added. The reaction mixture was refluxed at 170°C for 11 h. After cooling, the suspension was filtered on Celite, DMF was removed under vacuum and the recovered brown liquid was purified by vacuum distillation (95°C, 10 mmHg), affording 33.0 g of 4,4′-(2-methyl)oxyditoluene (78% yield). $KMnO_4$ (19.8 g, 0.125 mol) was added to a solution of 4,4′-(2-methyl)oxyditoluene (16.1 g, 0.078 mol) in 1.15 litres of a Py/water (2 : 1 v/v) solution, and the mixture was refluxed for 1.5 h. A further 60.0 g (0.38 mol) of $KMnO_4$, divided into three portions, was added successively during 1.5 h. After refluxing for an additional hour, the excess of permanganate was destroyed with ethanol, and the hot suspension was filtered on Celite. Py was distilled off and, after cooling, the solution was acidified with HCl and stirred overnight. The white precipitate was collected on a filter and repeatedly washed with water. After drying at 140°C, 2.45 g of **5** was recovered (10% yield).

Procedure B. 4-Cyanophenol (7.1 g, 0.060 mol) and K_2CO_3 (16.5 g) were suspended in 200 ml of a DMF/toluene solution (4 : 1 v/v) and placed in a flask fitted with a Dean–Stark trap and an inlet for nitrogen. The mixture was refluxed at 150°C until the water/toluene azeotrope was completely removed. After removing the residual toluene, 10.3 g (0.060 mol) of 4-nitro-1,2-dicyanobenzene were added, and the reaction mixture was refluxed at 100°C for 6 h. DMF was then distilled under vacuum, and the recovered compound was ground, washed with water and dried at 120°C. Crystallization from acetone gave 13.5 g of white crystals (82% yield; m.p. = 154.3°C). KOH (75.0 g) was added to 5.39 g (0.0220 mol) of the tricyano compound dissolved in 270 ml of a water/ethanol solution (1 : 1 v/v), and the mixture was refluxed for 48 h at 90°C. After cooling, ethanol was completely removed and the solution was acidified with HCl to pH 1.



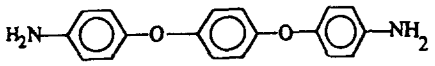
4,4'-Oxydianiline

(1)



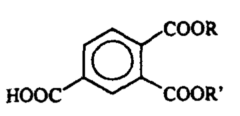
4,4'-Methylenedianiline

(2)



4,4'-(1,4-Phenylenedioxy)dianiline

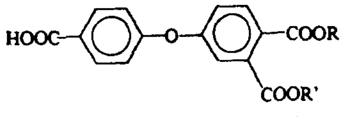
(3)



R = H; R' = Et
or
R = Et; R' = H

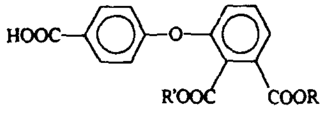
1,2,4-benzentricarxylic-acid-1-ethylester and 2-ethylester

(4)



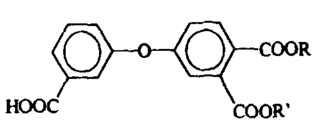
4,4'-(2-carboxy)oxydibenzoic-ethylester

(11)



3,4'-(2-carboxy)oxydibenzoic-ethylester

(12)



4,3'-(2-carboxy)oxydibenzoic-ethylester

(13)

2-ethylester: R = H, R' = Et
1-ethylester: R = Et, R' = H

Figure 1 Monomers used in the preparation of the aromatic PAIs studied in this work

The white precipitate was collected on a filter, repeatedly washed with water, and dried at 140°C, giving 5.61 g (83% yield) of **5**. This procedure was also followed to prepare the acids **6** and **7**.

5: m.p. = 180°C; i.r. (nujol)—1699 cm^{-1} (C=O, s). **6**: m.p. = 214°C. **7**: m.p. = 213°C.

4-4′-(2-Carboxy)oxydibenzoic anhydride (8), 3-4′-(2-carboxy)oxydibenzoic anhydride (9), 4-3′-(2-carboxy)-oxydibenzoic anhydride (10). Anhydrides were obtained by heating the corresponding triacids *in vacuo* at 200–210°C for 1 h. The crude products were dissolved in acetone and filtered on Celite. By evaporation of the solvent the pure anhydrides were recovered in high yields (95%) as white powders.

8: m.p. = 243°C. **9**: m.p. = 256°C; i.r. (KBr)—1846 and 1796 cm^{-1} (C=O), s), 1290 and 1219 cm^{-1} (C–O–C, s). **10**: m.p. = 185°C.

4-4′-(2-Carboxy)oxydibenzoic-acid-1-ethylester and 2-ethylester (11), 3-4′-(2-carboxy)oxydibenzoic-acid-1-ethylester and 2-ethylester (12), 4-3′-(2-carboxy)oxydibenzoic-acid-1-ethylester and 2-ethylester (13). The synthesis of **11** is reported as an example: 2.07 g (7.30 mmol) of the anhydride **8** was refluxed in 10 ml of ethanol for 4 h under nitrogen. After cooling, the ethanol was distilled off and the resulting solid product was dissolved in diethyl ether and filtered on Celite. The solution was evaporated to dryness, yielding 2.04 g of **11** (85% yield, m.p. = 157 and 178°C).

^{1}H n.m.r. (CD$_3$OD): 2-ethylester (70%)—$\delta = 1.33$ (t, 3H), $\delta = 4.32$ (q, 2H), $\delta = 7.14$ (d, 2H), $\delta = 7.21$ (m, 2H),

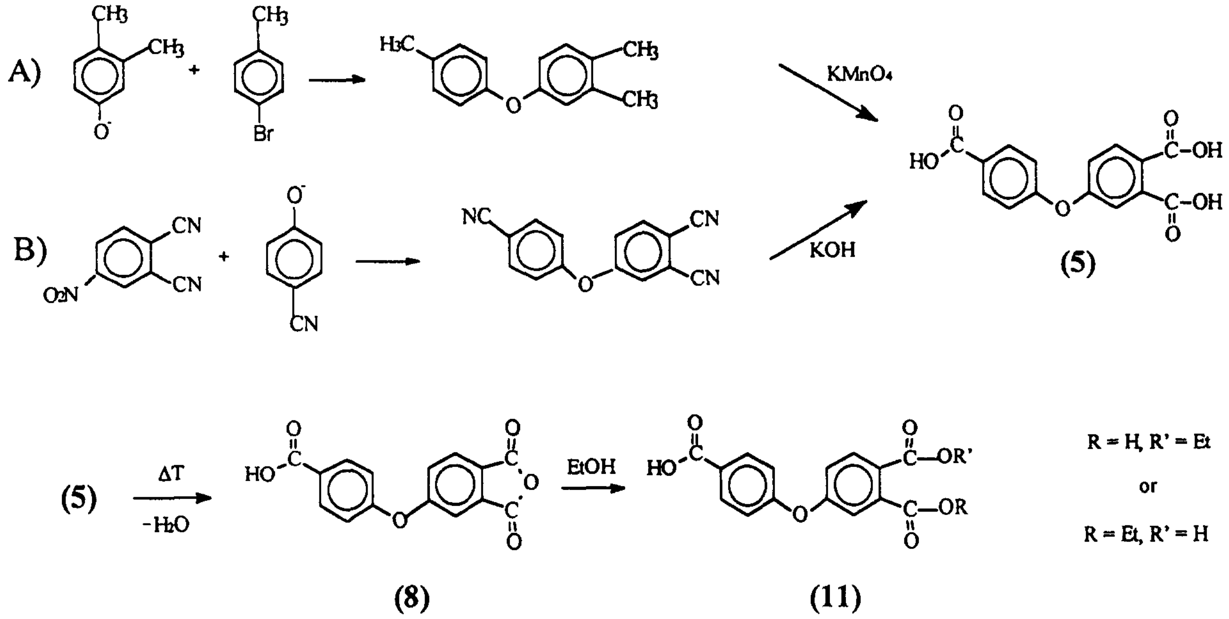


Figure 2 Reaction patterns followed to obtain the mixtures of monoethyl esters of the tricarboxylic acids **5**, **6** and **7**

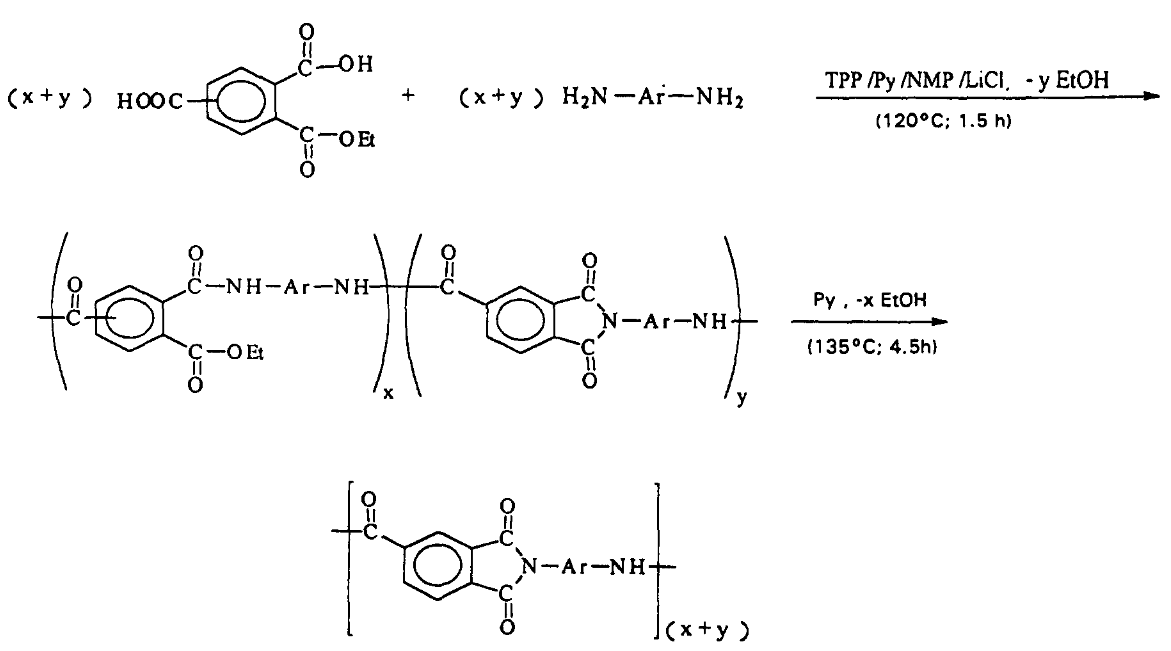


Figure 3 Scheme of the 'one-pot/two-step' polymerization method used in the preparation of aromatic PAIs

$\delta = 7.90$ (d, 1H), $\delta = 8.08$ (d, 2H); 1-ethylester (30%)—$\delta = 1.34$ (t, 3H), $\delta = 4.33$ (q, 2H), $\delta = 7.14$ (d, 2H), $\delta = 7.21$ (s, 1H), $\delta = 7.34$ (d, 1H), $\delta = 7.77$ (d, 1H), $\delta = 8.08$ (d, 2H).

12: m.p. = 169°C. **13**: m.p. = 143 and 150°C.

General polymerization procedure

Equimolar amounts of a tricarboxylic acid monoethylester and a diamine (4.20 mmol) were reacted at 120°C in an NMP (33.6 ml)/Py (8.4 ml) solution in the presence of TPP (8.82 mmol) and LiCl (8% w/v) for 1.5 h. Additional Py (14 ml) was added, and the reaction was continued for 4.5 h at 135°C. The polymers were recovered from the reaction mixture by precipitation in methanol, and near quantitative yields were obtained.

Table 1 Inherent viscosity and solubility of the prepared PAIs

Polymer code	Monomers	η_{inh} (dl g^{-1})^a	Solubility^b NMP	DMAc	DMF	DMSO	THF
PAI A1	4 + 1	0.85	+	+	+	+^{c}	−
PAI A2	4 + 2	0.77	+	+	+	+	−
PAI A3	4 + 3	0.95	+	+	+*	+*^{c}	−
PAI B1	11 + 1	0.92	+	+	+	+^{c}	−
PAI B2	11 + 2	0.85	+	+	+	+^{c}	−
PAI B3	11 + 3	0.72	+	+	+	+	−
PAI C1	12 + 1	0.46	+	+	+	+	−
PAI C2	12 + 2	0.46	+	+	+	+	−
PAI C3	12 + 3	0.51	+	+	+	+	−
PAI D1	13 + 1	0.60	+	+	+	+	−
PAI D2	13 + 2	0.56	+	+	+	+^{c}	−
PAI D3	13 + 3	0.56	+	+	+	+	−

[a] Inherent viscosity at 25°C in NMP, $c = 0.5\ \mathrm{g\,dl^{-1}}$

[b] +, soluble; +*, soluble with added LiCl; −, insoluble

[c] Soluble when heated

Characterization

The inherent viscosities were measured with an Ubbelhode viscosimeter in NMP at 25°C ($c = 0.5\ \mathrm{g\,dl^{-1}}$). Glass transition temperatures and melting temperatures were determined using a Mettler TA-3000 differential scanning calorimeter in the temperature range from 50 to 450°C with a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Thermal stability was tested by t.g.a. using a Mettler TC-10 thermobalance at a heating rate of 10°C min^{-1} from 50 to 750°C in a nitrogen atmosphere. The infrared spectra were obtained using a Bruker IFS 66 *FT*i.r. spectrophotometer on films obtained by solution casting. The ^{1}H n.m.r. spectra were recorded at 25°C using a Bruker WH-270 instrument operating at 270 MHz in dimethyl sulfoxide-d_6 (DMSO-d_6), acetone-d_6 or chloroform-d solutions. The ^{13}C n.m.r. spectra were recorded at 50.3 MHz by means of a Varian Gemini spectrometer. Wide-angle X-ray diffraction patterns were recorded on a Philips diffractometer equipped with a continuous scan attachment and a proportional counter, using Ni-filtered Cu K$_\alpha$ radiation (1.5418 Å).

RESULTS AND DISCUSSION

Synthesis of the monomers

The structure of the monomers used in the synthesis of PAIs containing arylether groups are reported in *Figure 1*. The diamines **1–3** are commercially available. A mixture of 1,2,4-benzenetricarboxylic-acid-1-ethylester

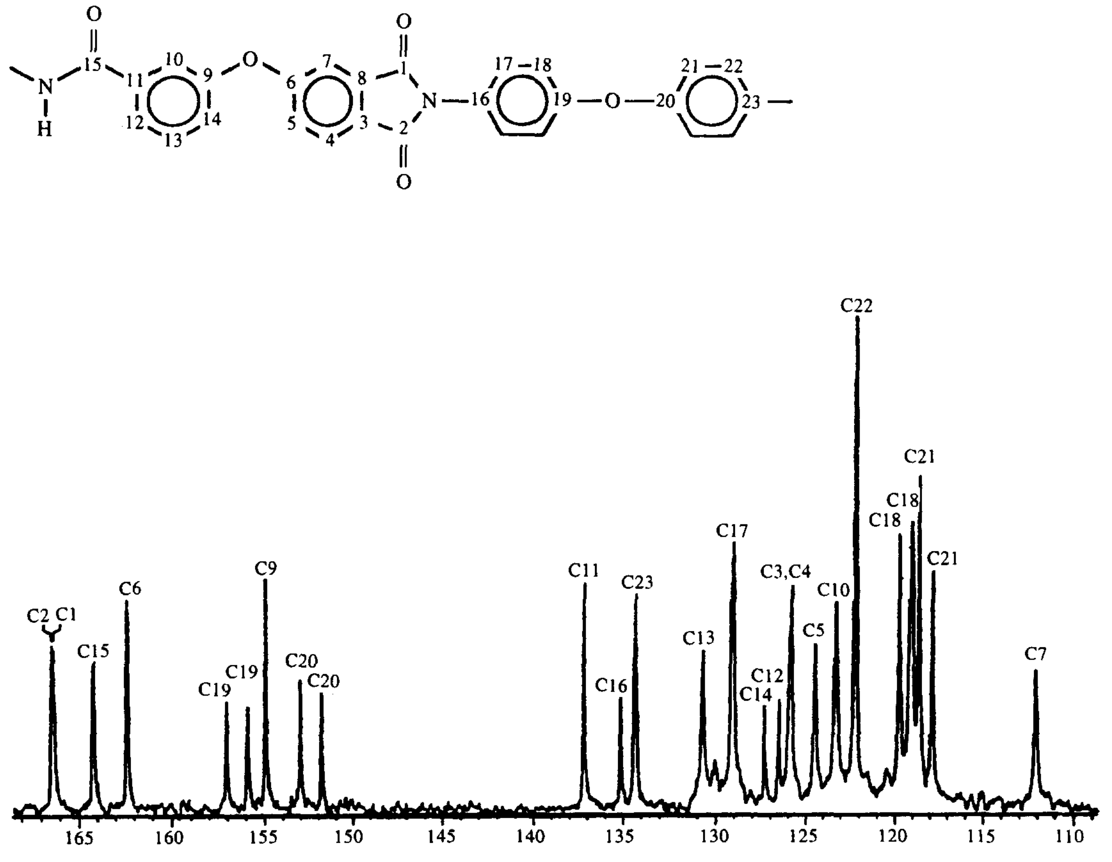


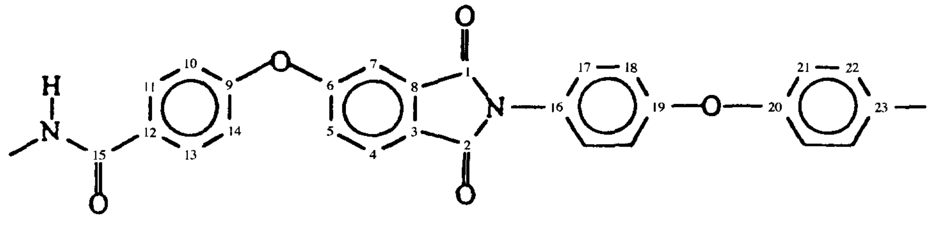
Figure 4 ^{13}C n.m.r. spectrum (50.3 MHz, DMSO-d_6, 298 K) of PAI D1

and 2-ethylester **4** was prepared according to a previously reported procedure[14]. The triacid **5** was obtained according to two different reaction routes A and B illustrated in *Figure 2*:

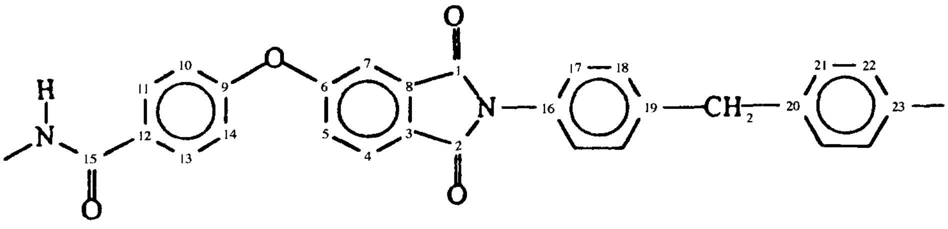
Route A. Condensation of 4-bromotuoluene with the 3,4-dimethylphenoxy ion under Ullman's synthesis conditions and subsequent oxidation of the 4,4′-(2-methyl)-oxyditoluene intermediate with potassium permanganate afforded **5** in low yields.

Route B. Nucelophilic nitrodisplacement of 4-nitro-1,2-dicyanobenzene by the 4-cyanophenoxy ion gave 4,4′-(2-cyano)oxydibenzonitrile, which by alkaline hydrolysis of the cyano groups followed by acidification afforded **5** in high yields. Triacids **6** and **7**, therefore, were prepared following route B. Thermal dehydration of **5**, **6** and **7** gave the corresponding anhydrides **8**, **9** and **10**. The mixture of monoethyl esters **11**, **12** and **13** were then obtained by refluxing the anhydrides in dry ethanol. The

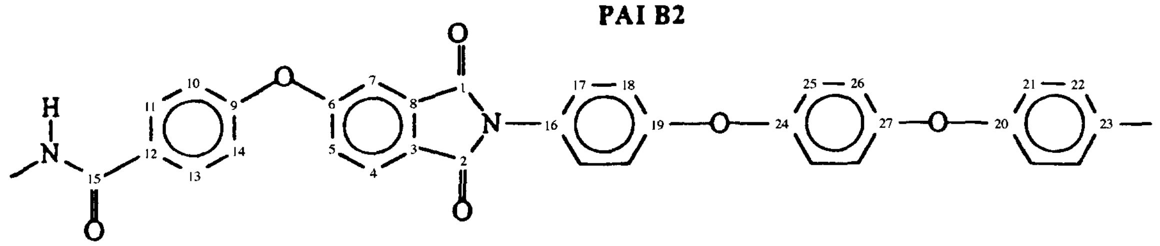
Table 2 ^{13}C n.m.r. chemical shifts of aromatic PAIs^{a}



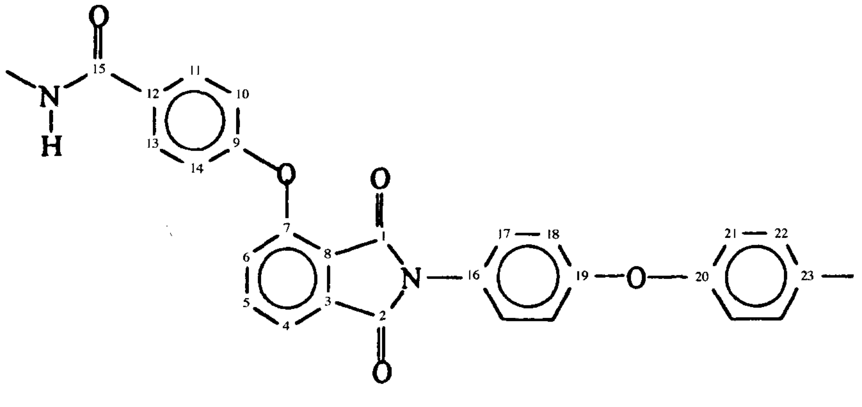
PAI B1



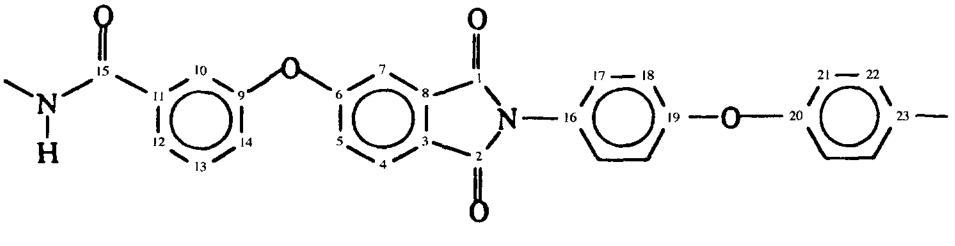
PAI B2



PAI B3



PAI C1



PAI D1

Table 2 (continued)

Atom	PAI B1	PAI B2	PAI B3	PAI C1	PAI D1
C-1	167.3	166.4	162.2	166.5	166.3
C-2	167.5	166.2	166.3	164.7	166.4
C-3	126.0	123.9	123.7	134.1	125.8
C-4	126.1	126.2	126.1	120.4	125.8
C-5	124.0	126.0	125.9	137.1	124.5
C-6	161.8	161.9	161.7	127.2	162.3
C-7	112.5	112.6	112.4	152.3	112.1
C-8	134.3	134.3	134.2	126.4	134.3
C-9	157.7	157.7	157.5	158.5	154.9
C-10	119.4	119.4	119.3	118.3	123.2
C-11	130.3	130.3	130.2	130.1	137.2
C-12	131.6	131.6	131.4	130.7	126.5
C-13	130.3	130.3	130.2	130.1	130.7
C-14	119.4	119.4	119.3	127.3	127.3
C-15	164.5	164.6	164.4	164.5	164.1
C-16	135.4	137.2	135.0	135.2	135.2
C-17	129.1	127.3	128.9	129.3	129.0
	129.0			129.2	
C-18	119.9	129.2	121	119.9	119.7
	119.0	129.1		119.1	119.0
C-19	157.2	137.4	156.9	157.2	157.0
	156.2	136.9	157.1	156.0	155.9
C-20	153.0	141.7	152.5	152.9	153.0
	151.7	141.1	152.8	151.6	151.8
C-21	118.7	129.8	119.8	117.8	117.9
	117.8	128.8		118.6	118.6
C-22	122.1	120.6	120.0	122.2	122.2
C-23	136.4	136.3	134.6	134.7	134.3
C-24	–	–	153.5	–	–
			153.0		
C-25	–	–	118.8	–	–
			118.6		
C-26	–	–	118.0	–	–
			117.8		
C-27	–	–	151.3	–	–
			152.0		

[a] Solvent: DMSO-d_6. Chemical shifts in ppm from tetramethylsilane

novel monomers, as well as their intermediates, were characterized by *FT*i.r. and ^{1}H n.m.r. spectroscopy. The esters are thermally stable up to 200°C, where they start to cyclize back to the anhydrides with loss of ethanol.

Synthesis of the polymers

The use of the TPP/Py system as a condensing agent for dicarboxylic acids and aromatic diamines to form amide bonds is an efficient way to obtain polyamides of moderate polymerization degree on a laboratory scale[16]. This method has been extended to the preparation of PAIs from diacids containing preformed imide groups and aromatic diamines as an alternative route to the well-known polycondensation of aromatic diamines and the acyl chloride of trimellitic anhydride followed by the chemical cyclodehydration of the resulting polyamic acid. We recently reported a 'one-pot/two-step' polymerization procedure which affords PAIs according to the reaction scheme reported in *Figure 3*[14,15]. During the polycondensation step the *o*-ethylester-amide groups partially cyclize to imide rings up to an imidization degree of 60–70%. The cyclization step is then completed by adding more Py and increasing the temperature to 135°C. Imidization degrees higher than 90% were generally obtained, as revealed by t.g.a. and proton n.m.r. spectroscopy (*vide infra*). This synthetic approach does not require the preparation of imide-containing monomers, and has several advantages over conventional two-step procedures. The most important advantage is that the PAI structure is obtained directly in solution, thus avoiding the thermal or chemical imidization of poly(amide-amic acid)s.

Four series of PAIs, denoted A, B, C and D, were prepared starting from the monoesters **4**, **11**, **12** and **13** (monomer **4** → A, **11** → B, **12** → C, **13** → D). The PAIs were obtained in almost quantitative yields, and have inherent viscosity values ranging between 0.46 and 0.95 g dl^{-1}. These are reported in *Table 1* along with the solubilities in polar aprotic solvents such as NMP, DMAc, DMSO, DMF and THF. All PAIs are soluble at room temperature in NMP and DMAc, and are insoluble in THF. PAIs of the C and D series show greater solubility in DMSO. All PAIs show outstanding film-forming properties. Transparent, flexible and tough films are obtained by slowly evaporating the solvent from NMP or DMAc solutions.

The molecular structure of PAIs was checked by i.r. analysis and ^{1}H n.m.r. spectroscopy. The i.r. spectra show characteristic absorptions of the imide ring at 1780 cm^{-1} and 1720 cm^{-1} (C=O stretching) and at 1379 cm^{-1} (C–N–C stretching), and those of the amide group at 3300, 1657–1650 and 1553–1540 cm^{-1}. The C–O–C stretching bands were observed at 1275–1273, at 1241–1238 and at 1218–1215 cm^{-1} in the case of PAIs belonging to the B, C and D series, respectively. The ^{1}H n.m.r. spectra of the polymers are in agreement with the proposed structures. The resonances of ethyl ester hydrogen atoms were used to quantitatively evaluate the cyclization of the *o*-ethylester-amide groups to imide rings. The n.m.r. analysis also made it possible to highlight the PAI enchainment. In fact, in the spectra of PAI A1, B1, C1 and D1 the amide hydrogen gives rise to two close peaks of equal intensity at about 10.3–10.4 δ, and this splitting is related to the formation of amide-amide, A-A, or amide-imide, A-I, sequences for each diamine moiety. Such splitting is barely observable in the spectra of PAIs derived from diamine **2**, and cannot be detected in the case of PAIs derived from **3** because of the increased distance between the nitrogen atoms. Moreover, the spectra of PAI A2, B2, C2 and D2 show three peaks, due to the $-CH_2-$ protons, centred at 3.92, 4.00 and 4.10 δ (intensity ratio 1 : 2 : 1), which are related to A-A, A-I (I-A) and I-I sequences, respectively. These results are indicative of a random distribution of amide and imide linkages in the polymer chain and suggest an equal or quite similar reactivity of the two chemically different carboxylic groups of monomers in the amidation reaction. The molecular structure was confirmed by analysing the ^{13}C n.m.r. spectra of selected PAIs whose chain repeat units are representative of the structural features of all used monomers. *Figure 4* shows the spectrum of PAI D1 as an example. The ^{13}C chemical shift values of PAI B1, B2, B3, C1 and D1 are reported in *Table 2*. The resonance assignments were made using literature data on PAIs[15,17,18] and related polymers[19] and comparing the experimental chemical shifts with those calculated according to the group contribution method. The resonances of the C-17, C-18, C-19, C-20 and C-21 atoms are split into two peaks of the same intensity, in agreement with the constitutional randomness of the PAIs obtained by our method.

Thermal properties

The thermal properties of PAIs were investigated by means of d.s.c. and dynamic t.g.a., and the thermal data are summarized in *Table 3*. All the investigated PAI are amorphous as obtained from the synthesis. However, the PAIs prepared from **4** and diamines **1** and **3**, which contain *p*-oxyphenylene groups, crystallize during heating to high-melting materials, as shown by the presence in their d.s.c. thermograms of exotherms at 281 (PAI A1) and 245°C (PAI A3) followed by melting endotherms at 431 and 441°C, respectively. These findings were confirmed by X-ray diffraction powder patterns of 'as-polymerized' and annealed samples.

The glass transition temperatures, T_g, of the investigated polymers are spread over a wide temperature range, from 213 to 279°C. The values reported in *Table 3* were determined in second heating runs of d.s.c. measurements and are slightly higher than those obtained in the first runs. Some structure–properties relations can be inferred from these data. Firstly, taking the PAI A series as a reference, the presence of the aryloxy group in the anhydride-acid moiety of the PAIs belonging to the B, C and D series lowers the glass transition temperature of the polymers. Secondly, the replacement of *para*-oriented rings with *meta*-oriented ones enhances the chain rotational freedom and increases the chain flexibility, thus lowering the T_g. In fact, PAI D polymers show T_g values which are approximately 30°C lower than those of the corresponding polymers of the B series. Finally, it is worth noting that the position of the aryloxy group with respect to the imide group, 4 in the B PAIs and 3 in the C PAIs, does not significantly affect the glass transition temperature. On the basis of these results, the investigated PAIs can be ordered according to their T_gs in the following way:

$$\text{PAI A} > \text{PAI B} \approx \text{PAI C} > \text{PAI D}$$

Table 3 Thermal data of aromatic PAIs

Polymer code	T_g (°C)[a]	T_m (°C)[b]	ΔH_m ($J\,g^{-1}$)[b]	T_d (°C)[c]	T_{max} (°C)[d]	Residue at 750°C (wt%)
PAI A1	274	431	27	550	471–620	56
PAI A2	279	–	–	510	470–605	63
PAI A3	250	441	41	523	480–588	59
PAI B1	262	–	–	552	444–617	54
PAI B2	250	–	–	526	477–600	59
PAI B3	242	–	–	552	450–585	62
PAI C1	253	–	–	525	420–597	52
PAI C2	258	–	–	500	428–578	60
PAI C3	244	–	–	520	450–574	60
PAI D1	231	–	–	522	475–590	65
PAI D2	243	–	–	525	468–600	59
PAI D3	213	–	–	518	473–590	59

[a] Glass transition temperature measured by d.s.c.

[b] Melting temperature and melting enthalpy measured by d.s.c.

[c] Temperature of 10% weight loss in nitrogen

[d] Temperatures of maximum rate of weight loss corresponding to two decomposition steps determined from the differential thermogravimetric curve in nitrogen

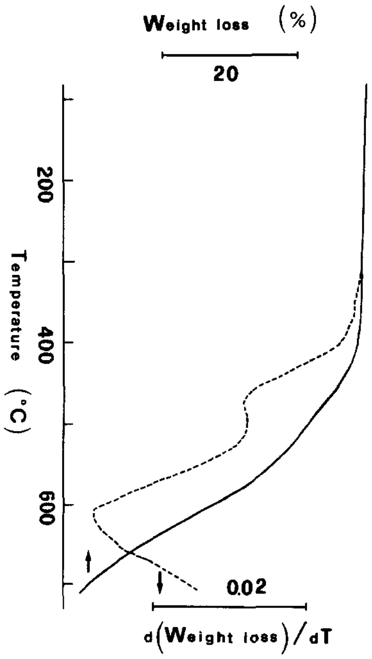


Figure 5 T.g.a. thermogram (10 K min^{-1}, under nitrogen) of PAI D2

As far as the dependence of the T_gs on the structure of the diamine component is concerned, it is observed that the oxygen atom and the methylene group, as hinges, have a similar effect on the chain flexibility (cf. the T_gs of PAI 1 and PAI 2 within each series), whereas the introduction of a further aryloxy group causes a lowering of the glass transition temperature of 10–20°C, as can be seen by comparing the T_g values of PAI A3, B3, C3 and D3 with those of the corresponding PAIs derived from **1**.

All the synthesized PAIs show excellent resistance to thermal degradation. Under dynamic t.g.a. in a nitrogen atmosphere, they do not in fact show significant weight loss up to temperatures close to 400°C, and the T_d values (temperatures which correspond to a 10% weight loss) range from 496 to 552°C (see *Table 3*). Two decomposition steps were generally found in the t.g.a. thermograms, as shown in *Figure 5* in the case of PAI D2 as an example. This behaviour has been observed in the case of other PAI polymers[9,10]. It is generally assumed that the first step, which is characterized by a maximum in the weight loss rate occurring in the 420–480°C range, is related to the thermal degradation of the weakest amide bond, while extensive chain degradation, also involving the imide ring, takes place at $T \geq 500°C$[9]. For all polymers the residual weights at 750°C are still higher than 52%. A comparison of the T_d values, used as a criterion for thermostability, indicates that the polymers containing methylene bridging groups are less stable than those containing oxygen bridging atoms. Moreover, when the PAIs of the A series are taken as a reference, the incorporation of the *para*-aryloxy group in position 4 with respect to the imide group (PAI B) improves the thermostability of the acid-anhydride moiety. A shift of this group to position 3 (PAI C), on the other hand, induces chain distortion from linearity and leads to lower thermal resistance. A similar but less significant effect is caused by a *meta*-orientation of the aryloxy group (PAI D). The polymers, therefore, can be arranged in the following series of decreasing thermostability:

$$\text{PAI B} > \text{PAI A} > \text{PAI D} > \text{PAI C}$$

A comparison of the T_g and T_d values indicates for the PAIs belonging to the B, C and D series a wide 'processing window', T_d–T_g, and, therefore, suggests easy melt processability.

CONCLUSIONS

Isomeric tricarboxylic anhydrides which have a hinge ether group connecting two phenyl rings can be prepared in high yields, and when used together with flexible multiring diamines, a series of amorphous and soluble aromatic PAIs can be obtained. These polymers are characterized by T_g values lower than those of the corresponding PAIs derived from TMA and by high thermal stability. Such monomers, therefore, appear to be a useful tool with which to design thermal resistant processable PAIs.

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REFERENCES

1. Cassidy, P. E., *Thermally Stable Polymers*. Dekker, New York, 1980.
2. Hergenrother, P. M., *Encyclopedia of Polymer Science and Technology*, 2nd edn. Wiley, New York, 1987.
3. Yang, H. H., *Aromatic High-Strength Fibers*. Wiley, New York, 1989.
4. Venkatesan, D. and Srinivasan, M., *Polym. Int.*, 1992, **29**, 275.
5. Adduci, J., Chapoy, L. L., Jonsson, G., Kops, J. and Shinde, B. M., *J. Appl. Polym. Sci.*, 1983, **28**, 2069.
6. Yang, C. P. and Chen, W. T., *J. Polym. Sci. A: Polym. Chem.*, 1994, **32**, 435.
7. Hsiao, S. H. and Yang, C. P., *J. Polym. Sci. A: Polym. Chem.*, 1990, **28**, 1149.
8. Hsiao, S. H. and Yang, C. P., *J. Polym. Sci. A: Polym. Chem.*, 1990, **28**, 2169.
9. Avella, N., Maglio, G., Palumbo, R. and Vignola, M. C., *Polymer*, 1996, **37**, 4615.
10. Fetodova, O. Ya., Kolesnikov, H. S., Gorokhov, V. I. and Fedyna, V. N., *Vysokomol. Soyed.*, 1971, **A13**, 1886.
11. Tagle, L. H., Neira, J. F., Diaz, F. R. and Ramirez, R. A., *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13**, 2827.
12. Tagle, L. H. and Diaz, F. R., *Polymer*, 1982, **23**, 1057.
13. Adduci, J. M. and Sikka, S. K., *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 1321.
14. Avella, N., Maglio, G., Palumbo, R. and Vignola, M. C., *Makromol. Chem. Rapid Commun.*, 1994, **15**, 95.
15. Avella, N., Maglio, G. and Palumbo, R., *J. Polym. Science A: Polym. Chem.*, 1996, **34**, 1219.
16. Yamazaki, N., Matsumoto, M. and Higashi, F., *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 1321.
17. De la Campa, J. G. and De Abajo, J., *Eur. Polym. J.*, 1983, **19**, 667.
18. Sintès-Zydowicz, N., Pham, Q. T. and Michaud, P., *Makromol. Chem.*, 1993, **194**, 2295.
19. Wang, J., Zhang, J., Li, B., Ding, M. and Feng, Z., *Macromol. Chem. Phys.*, 1996, **197**, 651.