Polymer Vol. 37 No. 20, pp. 4615–4619, 1996
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0032-3861/96/$15.00 + 0.00

S0032-3861(96)00301-1

Poly(amideimide)s based on diamines containing bisaryloxy groups: structure–properties relationships

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(Received 10 January 1996; revised 21 February 1996)

A series of random poly(amideimide)s (PAIs) were prepared from 1,2,4-benzenetricarboxylic acid monoesters and multi-ring diamines containing bisaryloxy groups by a 'one pot' method using the triphenylphosphite/pyridine system. The diamines differ because of the *para* or *meta* catenation and because of the presence of lateral substituents or bulky isopropylidene or perfluoroisopropylidene groups connecting two phenyl rings. The prepared PAIs were characterized by Fourier transform infra-red and ^{1}H nuclear magnetic resonance spectroscopy. Thermal analysis and X-ray diffraction experiments indicated that all PAIs 'as polymerized', are amorphous and that polymers having a prevailing *para*-orientation and no substituents crystallize upon thermal treatments. The glass transition temperatures (T_gs) determined by differential scanning calorimetry and dynamic mechanical thermal analysis, range between 178°C and 253°C. Both the T_g and the solubility, in polar aprotic solvents, are strongly affected by the chemical structure of the polymers. Flexible and tough films were obtained by solution casting or, in the case of amorphous PAIs, by compression moulding. The PAIs investigated exhibit thermostability–10% weight loss at $T \geq 495$°C–as shown by dynamic thermogravimetric analysis. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(amideimides)s; bisarylether diamines; thermostable polymers)

INTRODUCTION

Aromatic poly(amideimide)s (PAIs) are considered useful high-performance materials which show better processing properties when compared with polyimides of analogous structures. The increased solubility in polar aprotic solvents and the lowering of the glass transition temperature (T_g) can, in fact, be attributed to the incorporation of amide linkages in the polyimide backbone[1–6].

In previous papers[7,8] we reported a 'one pot' synthesis procedure which brings about high molecular weight PAIs. This method uses triphenylphosphite (TPP) and pyridine as condensing agents to form amide bonds from aromatic diamines and a mixture of isomeric 1,2,4-benzenetricarboxylic acid monoethyl esters (BTE). Under the reaction conditions used, both condensation and cyclization to imide rings occur. The feasibility of this straightforward synthesis method prompted us to employ it in the preparation of a series of aromatic processable PAIs with the aim being to correlate their structural features with solubility, crystallinity and T_g.

In this work we report the results of a study on poly(amideimide)s prepared from BTE and multi-ring aromatic diamines containing thermally stable bisaryloxy groups which increases chain flexibility. These PAIs have different structures due to the presence of: (a) *para*- or *meta*-oriented rings; (b) pendent ring substituents; (c) bulky isopropylidene or hexafluoroisopropylidene groups connecting phenylene rings.

EXPERIMENTAL

Materials

1-Methyl-2-pyrrolidinone (NMP) and TPP (Fluka) were dried by refluxing over 4-Å molecular sieves followed by vacuum distillation. Pyridine (Py) from Fluka was distilled over potassium hydroxide pellets. Lithium chloride (Aldrich) was dried under vacuum at 160°C for 6 h.

Monomers

4,4′-(1,4-Phenylendioxy)dianiline (**3**), 4,4′-(1,4-phenylendioxy-2-methyl)dianiline (**4**), 4,4′-(1,4-phenylenedioxy-2-phenyl)dianiline (**5**), and 4,4′-(1,3-phenylendioxy)-dianiline (**6**) were prepared by reacting 4-fluoronitrobenzene with the potassium salt of hydroquinone, methylhydroquinone, phenylhydroquinone and resorcinol, respectively. The dinitro derivatives obtained were subsequently reduced to diamines with hydrazine hydrate. The procedure is reported in the literature[9]. 4,4′-[Hexafluoroisopropylidene-bis(1,4-phenylene)dioxy]dianiline (**1**) and 4,4′-[isopropylidene-bis(1,4-phenyleneoxy)]dianiline (**2**) were obtained in a similar way[10].

A mixture of 1,2,4-benzentricarboxylic-acid-1-ethylester and 1,2,4-benzenetricarboxylic-acid-2-ethylester (BTE), with a molar ratio of 57/43, was prepared according to a previously reported procedure[7].

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Measurements

The inherent viscosities were determined with a Ubbelhode viscosimeter in NMP at 25°C ($c = 0.5\,\mathrm{g\,dl^{-1}}$). T_gs and melting temperatures (T_ms) were determined using a Mettler TA-3000 differential scanning calorimeter (d.s.c.) in the temperature range from 50 to 450°C and with a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ in a nitrogen atmosphere. Thermal stability was tested by thermogravimetric analysis (t.g.a.) using a Mettler TC-10 thermobalance at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ from 50 to 750°C, in a nitrogen atmosphere. Dynamic mechanical thermal analysis (d.m.t.a.) was performed using a DMTA analyser (Polymer Laboratories) on 0.4–0.5 mm thick specimens obtained by compression moulding. Infra-red spectra were recorded using a Bruker IFS66 Fourier-transform infra-red (*FT*i.r.) spectrophotometer on films obtained by solution casting. The ^1H nuclear magnetic resonance (n.m.r.) spectra were recorded at 25°C using a Bruker WH-270 instrument operating at 270 MHz in dimethylsulfoxide-d_6 or N,N'-dimethylacetamide-d_9 solutions. Wide-angle X-ray diffraction (WAXD) patterns were recorded on a Philips diffractometer, equipped with a continuous scan attachment and a proportional counter, using Ni-filtered Cu-K_α radiation (1.5418 Å).

General procedure of polymerization

Equimolar amounts of BTE and diamine, 4.20 mmol, were reacted at 120°C in a NMP (33.6 ml)/Py (8.4 ml) mixture in the presence of TPP (8.82 mmol) and LiCl (8% w/v) for 1.5 h. Additional pyridine (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. The details of the procedure have been previously reported[8].

RESULTS AND DISCUSSION

Synthesis and characterization

All PAIs were prepared by reacting BTE with the appropriate diamine in a NMP/LiCl solution in the presence of the condensing system TPP/Py[11] according to the reaction pattern reported in *Figure 1*.

Analysis of the polymers obtained after 1.5 h at 120°C indicated fair inherent viscosity values and cyclization degrees to the imide ring of approximately 75%. The latter was tested by ^1H n.m.r. spectroscopy and t.g.a.[8]. We successfully obtained cyclization degrees ≥95%, without detrimentally affecting the molecular weight values, by adding more pyridine to the solution containing the poly(amide-amic ethylester) intermediate and by increasing the temperature to 135°C. A detailed study of the polymerization procedure was reported in a previous work[8]. The diamines used have the structures reported in *Figure 2*.

In the polymer code, PAI X ($X = 1,\ldots,7$), the number indicates the diamine used in the preparation of the poly(amideimide). The PAIs were obtained in almost quantitative yields and have typical inherent viscosity values ranging between 0.39 and $0.95\,\mathrm{g\,dl^{-1}}$ as reported in *Table 1*, where are also shown the solubilities in polar aprotic solvents such as N,N'-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), N,N'-dimethylformamide (DMF), NMP and tetrahydrofuran (THF). It was found that all PAIs are soluble at room temperature in NMP, whereas their solubility in other organic solvents is related to their structural features. In

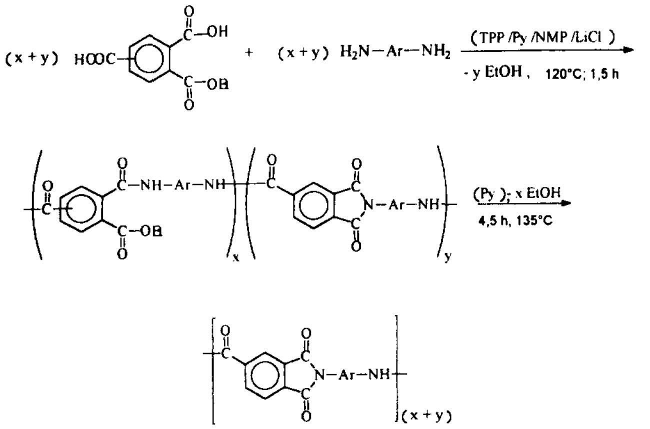


Figure 1 Scheme of the 'one-pot' synthesis of poly(amideimide)s

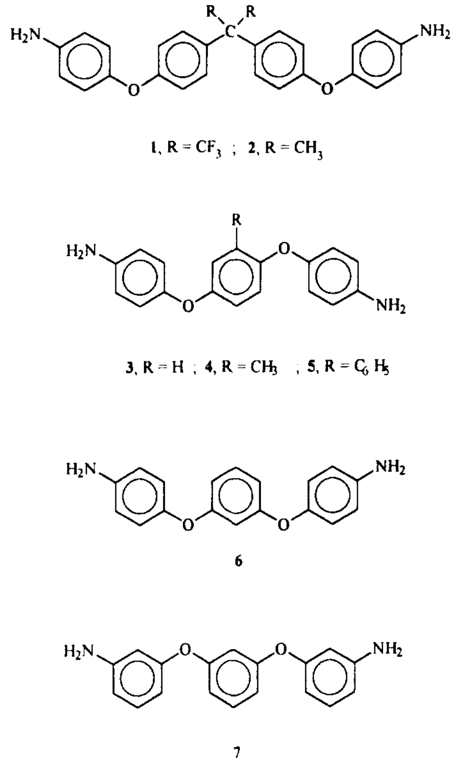


Figure 2 Structure of the diamine monomers **1–7**

Table 1 Inherent viscosity and solubility of poly(amideimide)s from 1,2,4-benzenetricarboxylic monoethylesters

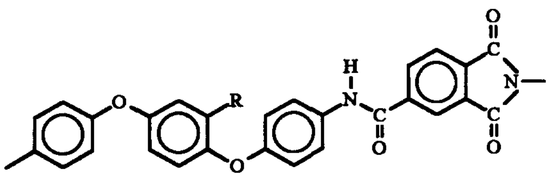
Diamine	Polymer code	η_{inh}[a] ($\mathrm{dl\,g^{-1}}$)	Solubility[b] NMP	DMAc	DMF	DMSO	THF
1	PAI 1	0.70	+	+	+	+	−
2	PAI 2	0.88	+	+	+	+	−
3	PAI 3	0.95	+	+*	−	−	−
4	PAI 4	0.91	+	+	+	+	+−
5	PAI 5	0.39	+	+	+	+	+
6	PAI 6	0.69	+	+*	−	−	−
7	PAI 7	0.43	+	+	+	+	+

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

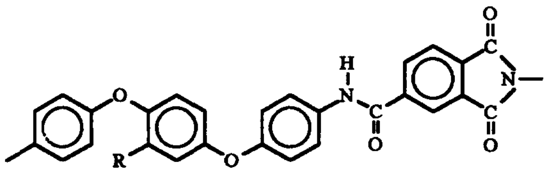
[b] (+) Soluble, (+−) swollen, (+*) soluble with added LiCl, (−) insoluble

particular it is worth noting that the substituted PAI 4 and PAI 5 and the all-*meta*-oriented PAI 7 have an improved solubility when compared to PAI 3. A feasible explanation for this is that chain packing is affected by the presence of the methyl or the phenyl substituent on the central phenyl ring, or by the *meta* catenation, thus allowing the solvent to penetrate and solubilize the polymers. The same considerations also account for the solubility of PAI 1 and PAI 2 related to the presence of isopropylidene and hexafluoroisopropylidene groups. All the PAIs show outstanding film forming properties. Transparent and flexible films are obtained by slowly evaporating the solvent from DMAc or NMP solutions.

The structural characterization was carried out by means of *FT*i.r. and ^{1}H n.m.r. spectroscopy. The i.r. spectra confirm the expected structures. Absorption bands at 1717 and 1779 cm^{-1}, due to asymmetrical and symmetrical C = O stretching vibrations, were assigned to the imide ring. Absorptions at 3302–3323 cm^{-1} (NH st), at 1670–1698 cm^{-1} (CO st) and 1539–1578 cm^{-1} (NH def and CN st) were assigned to the amide group. The structure of the PAIs was also verified by analysing their ^{1}H n.m.r. spectra. The hyrdogen resonances of the 1,2,4-benzenetricarboxylic acid moiety at 8.1–8.6 δ are well separated from those of the other aromatic hydrogens which appear at 7.0–7.8 δ and from the amide hydrogen signals at 10.2–10.6 δ. Due to previous ^{1}H and ^{13}C n.m.r. investigations which allowed us to shed some light on the polymer microstructure[7], we found that the PAIs obtained according to the 'one pot' procedure have no constitutional regularity, i.e. they have a random enchainment of amide and imide groups,. In the case of PAI 4 and PAI 5 the presence of a methyl or phenyl substituent on the central phenyl ring is a further element of constitutional disorder. Accordingly, two well separated resonances of the same intensity were found for the amide hydrogens in the proton n.m.r. spectra of PAI 5 (10.60–10.69 δ) and PAI 4 (10.23 and 10.26 δ), while a single resonance was observed for all other PAIs. This splitting is due to the different chemical environment of amide hydrogens in the structures (a) and (b):



(a)



(b)

In the PAI 4 spectrum the methyl resonance split into two signals at 2.23 and 2.26 δ depending on whether the substituent was closer to an amide or an imide group.

All the PAIs, as obtained from the polymerization, are amorphous as indicated by the absence of crystallinity peaks in their WAXD spectra (*vide infra*).

Thermal behaviour

The thermal behaviour was investigated by means of d.s.c., t.g.a. and d.m.t.a. The thermal data are summarized in *Table 2*. *Figure 3* shows some representative d.s.c. traces of the investigated PAIs in the temperature range from 50 to 470°C. Only a second order transition is observed in the thermograms of PAI 2, PAI 5 and PAI 7 at 239, 223 and 178°C, respectively (curves a, b and c), Analogous d.s.c. traces were found in the case of PAI 1 and PAI 4. PAI 3 and PAI 6, on the contrary, exhibit quite a different thermal behaviour as illustrated for PAI 6, as an example, by curves d, d′ and d″. The first heating run of an 'as polymerized' sample (curve d) reveals an exotherm at 215°C, attributed to a crystallization process, followed by a first order transition at 378°C ($\Delta H = 31\ \mathrm{J\,g^{-1}}$). In all probability the glass transition is likely masked by the crystallization exotherm; in fact, the thermogram of a sample previously heated up to 300°C shows a second order transition at 216°C before the melting endotherm (curve d′). The apparent heat of

Table 2 Thermal properties of the prepared poly(amideimides)s

Polymer code	T_g[a] (°C)	T_m[b] (°C)	ΔH_m[b] ($\mathrm{J\,g^{-1}}$)	T_d[c] (°C)	T_{max}[d] (°C)	Char yield[e] (%)
PAI 1	253 (238)	–	–	542	553	54
PAI 2	239 (230)	–	–	495	522	57
PAI 3	250	441 (449)	41 (52)	523	482–588[f]	59
PAI 4	242 (237)	–	–	503	470–617[f]	56
PAI 5	223	–	–	536	472–587[f]	64
PAI 6	216	378 (380)	31 (45)	527	478–593[f]	63
PAI 7	178 (193)	–	–	512	475–588[f]	68

[a] T_g measured by d.s.c.; values in brackets refer to T_g measured by d.m.t.a.
[b] T_m and apparent melting enthalpy measured by d.s.c.; values in brackets refer to samples annealed at $T = 300$°C for 1 h
[c] Temperature of 10% weight loss
[d] Temperature of maximum rate of weight loss determined from the differential thermogravimetric curve
[e] Residue at 750°C (weight %)
[f] Two decomposition steps

fusion is increased up to 45 J g^{-1} by annealing for 1 h at 300°C. It is worth noting that after heating up to 420°C, only a very small melting endotherm ($\Delta H \approx 4$ J g^{-1}) can be detected in the second run (curve d″), even after annealing at 300°C. As the T_g value increases in the second run from 216 to 230°C, we suggest that a partial crosslinking occurs after melting, thus preventing a subsequent crystallization. The insolubility of PAI 6 samples after a melting–cooling cycle supports this hypothesis. PAI 3 is characterized by a similar behaviour showing a T_m of 441°C. The higher T_m value ($\Delta T = 63$°C) is related to the fact that macromolecular chains are better packed in a tight structure if the phenylene rings have a linear *p-p-p* orientation. *Figure 4* shows X-ray diffraction diagrams obtained from PAI 3 and PAI 6 samples, 'as polymerized' (a and b) and after 1 h annealing at 300°C (a′ and b′). They are characterized by a broad amorphous halo centered at $2\theta \cong 19°$ in the case of the polymers obtained from the synthesis. Crystalline patterns were obtained from annealed specimens, with strongest reflections at 18.8° and 20.2° of 2θ (PAI 3) and at 19.4° and 21.6° of 2θ (PAI 6). Crystallinity degrees of 39% (PAI 3) and 36% (PAI 6) were calculated. The results of X-rays diffraction experiments are consistent with d.s.c. data and indicate that PAIs are amorphous in origin and, rather surprisingly, that PAI 3 and PAI 6 develop crystallinity upon thermal treatments in spite of their constitutional disorder. Thus, for random PAIs containing bisaryloxy groups, the formation of ordered structures requires an all *para* or a prevailing *para* ring orientation, provided that no ring substituents or flexible joints are present.

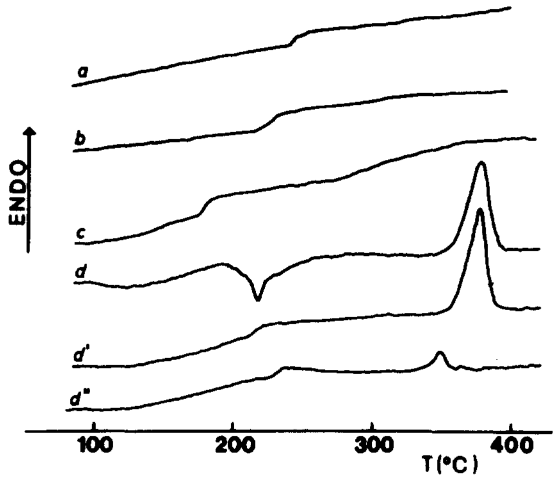


Figure 3 D.s.c. traces of PAI 2 (a), PAI 5 (b), PAI 7 (c) and PAI 6 (d, d′, d″) poly(amideimide)s; (d) as polymerized, (d′) second run after a first heating–cooling cycle up to 300°C, (d″) second run after a first heating–cooling cycle up to 420°C

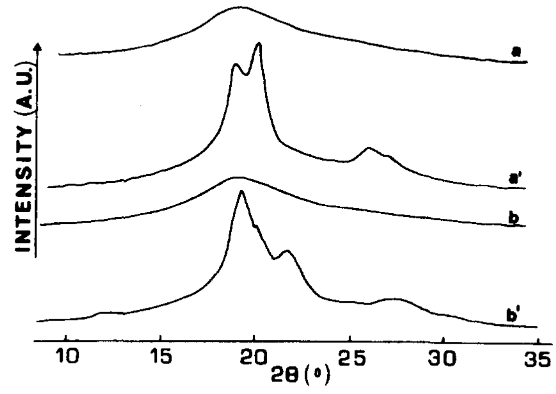


Figure 4 X-ray diffraction powder patterns obtained for PAI 3 (a, a′) and PAI 6 (b, b′) poly(amideimide)s as polymerized (a, b) and after 1 h annealing at 300°C (a′, b′)

In the case of PAIs which give films by melt casting, T_gs were also measured by d.m.t.a. giving values fairly close to those determined by d.s.c. The glass T_gs occur between 178 and 253°C and are significantly lower than that of Torlon®, a commercial PAI obtained from trimellitic anhydride chloride and 4,4′-methylenedianiline ($T_g = 279$°C). This finding can be expected in light of the increased chain flexibility imparted by the two bisaryloxy groups present in all investigated PAIs. The relationships between T_g and structure can be discussed more easily by using PAI 3 as a reference, as it is made from diamine 3 which has the most regular structure. This diamine, in fact, contains all *para*-oriented unsubstituted rings which are only connected by means of ether bridges. Thus, the thermal data indicate that, with respect to PAI 3, a lowering of the T_g is caused by structural features which distort the chain from linearity and/or decrease the interchain forces, and in particular by: (a) *meta*-oriented rings (PAI 6 and PAI 7) and (b) bulky phenyl substituent on the central ring (PAI 5). A negligible influence on T_g is exerted by the methyl substituent (PAI 4) and by isopropylidene bridging groups (PAI 2). The polar trifluoromethyl groups present in PAI 1, on the other hand, leads to a higher T_g as they increase interchain attractive forces.

Thermal stability was investigated by means of dynamic t.g.a. in a nitrogen atmosphere. Most PAIs display two-step decomposition patterns. Accordingly, two close maxima were found in the differential t.g.a. curves. The results reported in *Table 2* show high thermal resistance for all the PAIs. In fact, the decomposition temperatures (T_d), i.e. the temperature taken when a 10% weight loss occurs, range from 495 to 542°C, and the char yield values range from 54 to 68%. The lowest T_d values are found in the presence of methyl groups in the central ring (PAI 4, $T_d = 503$°C) or in the isopropylidene group (PAI 2, $T_d = 495$°C). When the methyl groups of PAI 2 are replaced with trifluoromethyl groups (PAI 1) a significant increase of T_d is observed ($\Delta T_d = 47$°C). A comparison between the thermal degradation behaviour of the investigated PAIs and that of the polyamides of related structures[10,12] confirms that the imide group has a higher thermal stability with respect to the amide group.

CONCLUSION

Incorporation of aromatic ether bridges into the main chain of structurally disordered poly(amideimide)s produces processable polymers characterized by a high thermal stability. Amorphous and easily soluble PAIs were obtained in the presence of *meta*-oriented phenylene rings, flexible joints and ring substituents. These structural features also cause a lowering of T_g. Due to the large difference between decomposition temperatures and T_gs, the amorphous PAIs can be melt processed into transparent and flexible films.

ACKNOWLEDGEMENTS

The authors wish to thank M.U.R.S.T. (Fund 60%) and the Strategic Project on 'Innovative Chemical Technologies' of the Italian *Consiglio Nazionale delle Ricerche* for financial support.

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