

The synthesis of a 1,1'-bi-2-naphthol-based bis(ether anhydride) and aromatic polyimides derived therefrom*

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2,2'-Bis(3,4-dicarboxyphenoxy)-1,1'-binaphthyl dianhydride was used as a new monomer with various aromatic diamines to obtain polyimides by the usual two-step method. The bis(ether anhydride) was prepared by a nucleophilic substitution of 1,1'-bi-2-naphthol with *N*-phenyl-4-chlorophthalimide, *N*-methyl-4-nitrophthalimide or 4-nitrophthalonitrile in aprotic polar solvent, and subsequent hydrolysis of the resulting bis(ether imide)s or bis(ether dinitrile), and then dehydration of the corresponding tetracarboxylic acid to afford the dianhydride. Most of the obtained polyimides were soluble in chloroform, pyridine, DMF, etc. The polyimide prepared from *p*-phenylene diamine was partial crystalline, whereas the others showed amorphous patterns in a WAXD study. These polymers have glass transition temperatures between 255–294°C and 5% weight loss temperatures in the range of 502–541°C in nitrogen and 473–537°C in air. © 1997 Elsevier Science Ltd.

(Keywords: bis(ether anhydride); polyimides; 1,1'-bi-2-naphthol)

INTRODUCTION

Aromatic polyimides, as high performance polymers, have been of great interest in the applications of engineering plastics, matrix resins for advanced composites, electric insulating materials and functional materials, such as membrane for gas separation, photo-sensitive resins, alignments for liquid crystal display as well as optoelectronics owing to the outstanding properties^{1–4}. To meet the requirements for these applications, structurally widely varied polyimides have been designed and synthesized in the past decades^{5–13}. Among them, the polyimides with aromatic rings in the twisted planes, such as that from 3,3',4,4'-biphenyl dianhydride and 2,2'-di(trifluoromethyl)benzidine reported by Harris and his coworkers⁵ are specially attractive because of the good solubility in common organic solvents, high thermal stability and the outstanding optical properties¹⁴. In this work, we chose 1,1'-bi-2-naphthalene as the units of the macromolecular chain under the consideration that the rotary axis of two naphthalene rings was perpendicular to that of the macromolecular chain which may cause interesting physical behaviours for the polymers. To be an analogue in this aspect, Imai and his coworkers¹⁵ have recently reported the polyimides prepared from aromatic diamine containing 1,1'-binaphthyl-2,2'-diyl unit. In this paper, we would like to describe the synthesis and characterization of aromatic polyimides from bis(ether anhydride) containing 1,1'-binaphthyl-2,2'-diyl unit.

EXPERIMENTAL

Materials

N-Phenyl-4-chlorophthalimide (mp 194–196°C) and *N*-methyl-4-nitrophthalimide (mp 178–180°C) were prepared as described in the literature¹⁶. 4-Nitrophthalonitrile (mp 141°C) was prepared as described in the literature¹⁷. 1,1'-Bi-2-naphthol (mp 215–217°C) was recrystallized from toluene before use. *m*-Phenylene diamine (*m*-PDA, mp 62.5–64.5°C) and *p*-phenylene diamine (*p*-PDA, mp 139–141°C) were purified by distillation under reduced pressure. 4,4'-Methylenedianiline (MDA, mp 89–91°C) and 1,4-bis(4-aminophenoxy)benzene (BAB, mp 173–174°C) were recrystallized from ethanol. 4,4'-Oxydianiline (ODA, mp 189–190°C) was used as received. Anhydrous grades of solvents such as DMAc, DMF were distilled under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Common reagents, e.g. potassium carbonate, sodium hydroxide, acetic anhydride, and methanol were used without further purification.

Monomer synthesis

2,2'-Bis(*N*-phenylphthalimid-4-oxy)-1,1'-binaphthyl (**3a**). Aqueous potassium hydroxide (4.5 ml of 50 wt%, 40 mmol) was added to a solution of 1,1'-bi-2-naphthol (5.72 g, 20 mmol) in DMAc (80 ml) and toluene (20 ml) in a three-neck flask equipped with a Dean–Stark trap. The mixture was heated with stirring to remove water by azeotropic distillation under nitrogen. After being cooled, *N*-phenyl-4-chlorophthalimide (11.07 g, 43 mmol) was added. The reaction was carried out with stirring at 160–165°C for 20 h. The white solid generated with time. The reaction mixture was cooled to 60–65°C

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and then added to ethanol (100 ml) with stirring. The white solid was collected by filtration, washed with water and ethanol in turn to afford crude product (8.69 g). Recrystallization was taken from DMF to afford white powders (7.13 g, 49% yield), mp 316–318°C. ¹H n.m.r. (400 MHz, DMSO-*d*₆): δ 8.35 (*d*, 2H, *J* = 8.8 Hz), 8.24 (*d*, 2H, *J* = 8.4 Hz), 7.80 (*d*, 2H, *J* = 8.4 Hz), 7.70 (*t*, 2H, *J* = 7.6 Hz), 7.65–7.50 (*m*, 10H), 7.44–7.34 (*m*, 6H), 7.25 (*d*, 2H, *J* = 8.4 Hz), 6.94 (*s*, 2H). M.s.: 729. Anal. calcd for C₄₈H₂₈N₂O₆: C, 79.10; H, 3.88; N, 3.84. Found: C, 78.95; H, 4.01; N, 3.94.

2,2'-Bis(*N*-methylphthalimid-4-oxy)-1,1'-binaphthyl (3b). A mixture of 1,1'-bi-2-naphthol (5.72 g, 20 mmol), *N*-methyl-4-nitrophthalimide (9.15 g, 43 mmol) and anhydrous potassium carbonate (7.72 g, 56 mmol) was reacted in dried DMAc (35 ml) under nitrogen at 120°C for 20 h. The white solid generated with time. After being cooled, the mixture was poured into ethanol–water (v/v 1/1, 100 ml) with stirring. The precipitate was collected by filtration and recrystallization from DMF/ethanol to give white powder (5.72 g, 47% yield), mp 258–259°C. ¹H n.m.r. (400 MHz, DMSO-*d*₆): δ 8.32 (*d*, 2H, *J* = 8.8 Hz), 8.23 (*d*, 2H, *J* = 8.0 Hz), 7.69 (*t*, 2H, *J* = 8.4 Hz), 7.59 (*d*, 2H, *J* = 8.4 Hz), 7.58 (*d*, 2H, *J* = 8.8 Hz), 7.55 (*t*, 2H, *J* = 8.4 Hz), 7.22 (*d*, 2H, *J* = 8.0 Hz), 7.20 (*d*, 2H, *J* = 8.4 Hz), 6.72 (*s*, 2H), 2.99 (*s*, 6H). M.s.: 605. Anal. calcd for C₃₈H₂₄N₂O₆: C, 75.48; H, 4.01; N, 4.63. Found: C, 75.88; H, 4.21; N, 4.61.

2,2'-Bis(3,4-dicyanophenoxy)-1,1'-binaphthyl (7). A mixture of 1,1'-bi-2-naphthol (5.72 g, 20 mmol), 4-nitrophthalonitrile (7.44 g, 43 mmol) and potassium carbonate (7.72 g, 56 mmol) was reacted under nitrogen with stirring in dried DMF (35 ml) at room temperature for 20 h. The pale yellow solid generated with time. The reaction mixture was slowly poured into cold dilute hydrochloric acid (2 N, 100 ml). The solid was collected by filtration and washed with water until the washings were neutral, and then recrystallized twice from methanol/acetonitrile (1/1) to yield white product (9.68 g, 90% yield), mp 257.5–258.3°C. ¹H n.m.r. (400 MHz, CDCl₃): δ 8.03 (*d*, 2H, *J* = 8.8 Hz), 7.93 (*d*, 2H, *J* = 8.0 Hz), 7.51 (*t*, 2H, *J* = 7.2 Hz), 7.46 (*d*, 2H, *J* = 8.4 Hz), 7.36 (*t*, 2H, *J* = 7.2 Hz), 7.28 (*dd*, 2H, *J* = 8.8 Hz), 7.20 (*d*, 2H, *J* = 8.4 Hz), 7.00–7.05 (*m*, 4H). M.s.: 539. FTi.r. (KBr): 2232 cm⁻¹ (C≡N). Anal. calcd for C₃₆H₁₈N₄O₂: C, 80.27; H, 3.37; N, 10.40. Found: C, 80.61; H, 3.34; N, 10.49.

2,2'-Bis(3,4-dicarboxyphenoxy)-1,1'-binaphthyl (4). From bis(ether imide)s: A mixture of 2,2'-bis(*N*-phenylphthalimid-4-oxy)-1,1'-binaphthyl (7.29 g, 10 mmol) or 2,2'-bis(*N*-methylphthalimid-4-oxy)-1,1'-binaphthyl (6.10 g, 10 mmol), sodium hydroxide (8.0 g) and distilled water (50 ml) were refluxed with stirring for 60 h during the time the large amount of white salts precipitated. After being cooled, the resulting mixture was acidified with cold dilute hydrochloric acid. The solid was collected by filtration, washed with distilled water and dried at 100°C to give product (5.50 g, 89% yield). ¹H n.m.r. (400 MHz, CDCl₃): δ 13.01 (wide peak, 4H), 8.01 (*d*, 2H, *J* = 8.8 Hz), 7.91 (*d*, 2H, *J* = 8.0 Hz), 7.69 (*d*, 2H, *J* = 8.4 Hz), 7.48 (*t*, 2H, *J* = 7.2 Hz), 7.33 (*t*, 2H, *J* = 8.4 Hz), 7.30 (*d*, 2H, *J* = 8.8 Hz), 7.25 (*d*, 2H, *J* = 8.0 Hz), 7.18–7.20 (*m*, 4H).

From bis(ether dinitrile): A mixture of 2,2'-bis(3,4-dicyanophenoxy)-1,1'-binaphthyl (5.39 g, 10 mmol), sodium hydroxide (8.0 g), hydrogen peroxide (30%, 10 ml) and water (50 ml) was stirred at 80°C for 12 h, then refluxed for an additional 48 h during the time the large amount of white salts precipitated. The resulting mixture was diluted with distilled water and acidified with concentrated hydrochloric acid to give product (5.53 g, 90% yield).

2,2'-Bis(3,4-dicarboxyphenoxy)-1,1'-binaphthyl dianhydride (5). **4** (6.14 g, 10 mmol) dissolved in acetic anhydride (10 ml) and stirred at reflux for 30 min during the time white solid precipitated. After being cooled, the solid was removed by filtration and washed twice with a small amount of glacial acetic acid and then dried under vacuum at 140°C (4.63 g, 80% yield), mp 228–230°C. ¹H n.m.r. (400 MHz, DMSO-*d*₆): δ 8.15 (*d*, 2H, *J* = 9.2 Hz), 8.03 (*d*, 2H, *J* = 8.4 Hz), 7.80 (*d*, 2H, *J* = 8.8 Hz), 7.49 (*td*, 2H, *J* = 7.2 Hz), 7.39 (*d*, 2H, *J* = 9.2 Hz), 7.35 (*t*, 2H, *J* = 7.2 Hz), 7.27 (*td*, 2H, *J* = 8.4 Hz), 7.10–7.23 (*m*, 4H). M.s.: 579. Anal. calcd for C₃₆H₁₈O₈: C, 74.74; H, 3.14. Found: C, 74.50; H, 3.10.

Polymer synthesis

Polyimide 9a from 5 and ODA by the usual two-step method. To a 10 ml round bottom flask was added **5** (1.1571 g, 2 mmol), 4,4'-oxydianiline (0.4004 g, 2 mmol) and DMAc (7.5 ml). The mixture was stirred under nitrogen at room temperature for 12 h to obtain a viscous solution.

Chemical cyclodehydration was carried out by adding a mixture of acetic anhydride (0.6 ml) and triethylamine (0.3 ml) into the poly(amic acid) solution with stirring at room temperature for 12 h and then heated at 80°C for 1 h. The polymer solution was poured into ethanol, and the white fibrous precipitate was collected by filtration, washed thoroughly with ethanol and hot water and then dried at 100°C. The yield of the polymer was 1.463 g (99%) and the intrinsic viscosity was 0.50 dl g⁻¹ measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C. ¹H n.m.r. (400 MHz, DMSO-*d*₆): δ 8.2 (*s*, 2H), 8.1 (*s*, 2H), 7.3–7.7 (*m*, 12H), 7.0–7.3 (*m*, 8H), 6.9 (*s*, 2H). FTi.r. (KBr): 1776 and 1721 cm⁻¹ (carbonyl groups of imide), 1373 cm⁻¹ (C–N), and 1240 cm⁻¹ (C–O–C). U.v./vis (*M* = 1 × 10⁻⁵, DMF, nm): 260 (weak), 268 (strong), 327 (weak).

All other homopolyimides **9b–e** and random copolymers **10a** from equimolar *p*-PDA/BAB and **10b** from equimolar *m*-PDA/BAB were prepared by the same procedure as mentioned above.

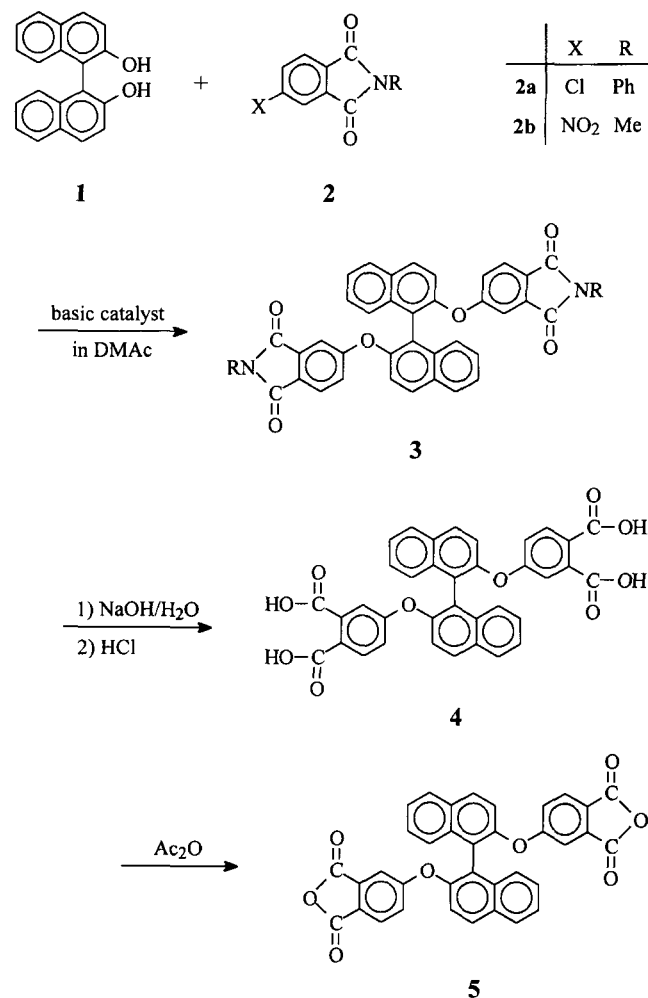
Measurements

The melting points were obtained with open capillary tubes on a Mel-Temp apparatus. The ¹H n.m.r. spectra were recorded on a Varian Unity-400 (400 MHz) spectrometer. The FTi.r. spectra were measured using Biorad FTS-7 spectrometer. The u.v. spectra were recorded on a (Varian) Cary 1/3 E spectrometer. The mass spectra were recorded on a VG-7070E spectrometer. Elemental analyses were performed on an Elemental Analyzer MOD-1106 (Italy). Intrinsic viscosities of polymers were determined at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C using a Cannon–Fenske viscometer, except the polyimide from *p*-PDA. The polymer molecular weights were determined relative to

polystyrene by g.p.c. in THF on Shimadzu HPLC LC-4A instrument. D.s.c. analyses were performed on Perkin-Elmer DSC-7 at a heating rate of $20^{\circ}\text{C min}^{-1}$ in nitrogen. T.g.a. were recorded on a Perkin-Elmer TGS-2 thermal analyser at a heating rate of $10^{\circ}\text{C min}^{-1}$ in air or nitrogen.

RESULTS AND DISCUSSION

Recently there has been a considerable effort directed



Scheme 1

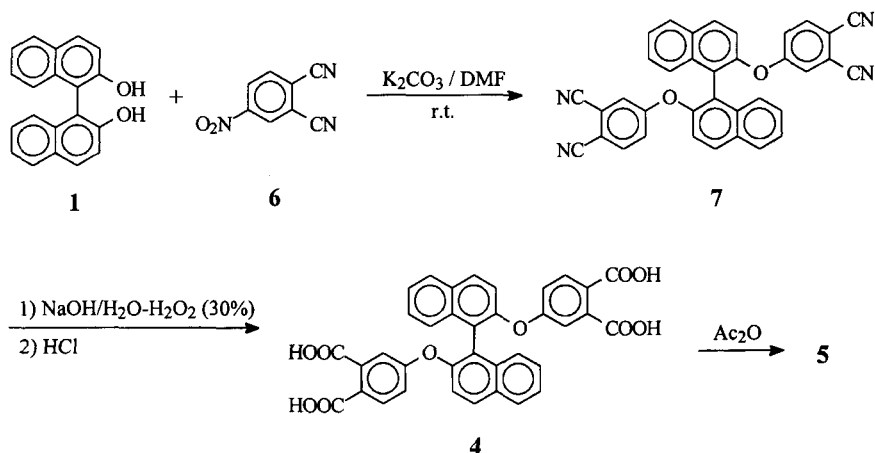
at the synthesis and characterization of polyimides with 2,2'-substituted, 4,4'-linked biphenylene units in the backbone^{3,5,18}. The noncoplanarity of the sterically hindered biphenylene rings destroyed the conjugation in macromolecular chain but still endowed with rigidity of the main chain. Therefore, these kinds of polymers possess some valuable properties, such as high thermal stability, good solubility in common solvents, excellent mechanical properties, transparent to visible light, etc. But so far most polyimides synthesized of this kind had coaxial structure between the axis laying on the macromolecular main chain and the axis linking two phenyl rings in biphenylene. In this paper, the obtained polyimides have the axes perpendicularity between the axis in 1,1'-binaphthyl-2,2'-diyl unit and the axis laying on the macromolecular main chain.

There were two synthetic routes¹⁹⁻²² that have been used to prepare bis(ether anhydride) **5**. In route 1 (see Scheme 1), 4-substituted phthalimide was reacted with 1,1'-bi-2-naphthol to obtain bis(ether imide)s which were then hydrolysed and dehydrated to obtain bis(ether anhydride). In route 2 (see Scheme 2), 4-nitrophthalonitrile was used instead of 4-substituted phthalimide. The results are listed in Table 1. From the data shown in Table 1, we can obviously see that route 2 was superior to route 1 for the low reaction temperature and the high yield. The high reaction temperature may cause the cleavage of the imide ring in the alkaline medium²³, especially when potassium carbonate was used since the potassium bicarbonate, generated during the reaction proceeding, would decompose to generate water.

The sodium salts of tetracarboxylic acid either from bis(ether imide)s or from bis(ether dinitrile) precipitated in hot aqueous sodium hydroxide while redissolved at low temperature. This soluble behaviour was quite different from other sodium salts of tetracarboxylic acid²⁴.

The structures of intermediates were confirmed by ¹H n.m.r., i.r., m.s. and elemental analysis in the Experimental section and the results are in good agreement with proposed structures.

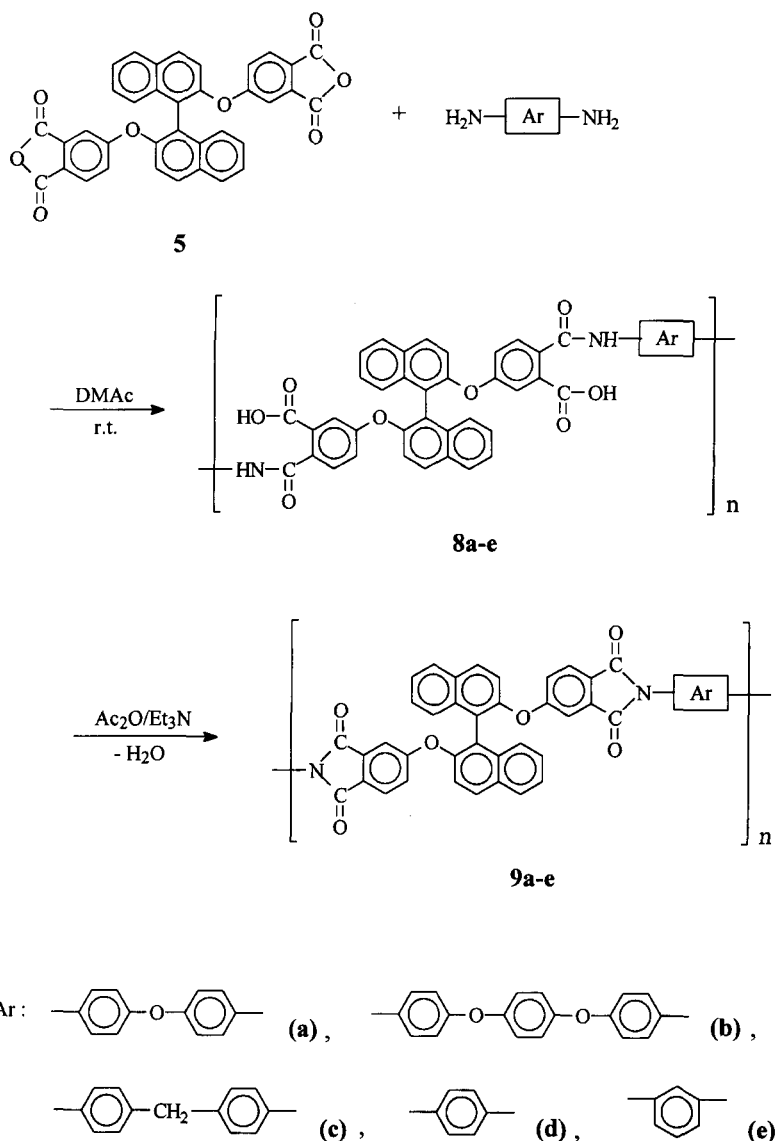
Polyimides (**9a-e**) and random copolymers (**10a-b**) were synthesized by a conventional two-stage process in DMAc involving the ring opening polycondensation and subsequent chemical cyclodehydration by treatment of acetic anhydride and triethylamine (see Scheme 3). All the polyimides were obtained in almost quantitative yields with intrinsic viscosities 0.30–0.50 dl g⁻¹, respectively.



Scheme 2

Table 1 Preparation of bis(ether imide)s and bis(ether dinitrile)

Entry	Starting materials	Basic condition	Solvent	React. temp./time (°C h ⁻¹)	Yield (%)	Product
1	1/2a	KOH/toluene	DMAc	160–165/20	49, white solid	3a
2	1/2a	K ₂ CO ₃	DMAc	160–165/20	5, brown powder	3a
3	1/2b	K ₂ CO ₃	DMAc	115–120/20	47, white solid	3b
4	1/2b	K ₂ CO ₃	DMAc	160–165/20	0.5, yellow powder	3b
5	1/2b	K ₂ CO ₃	DMAc	85–90/20	10, white solid	3b
6	1/6	K ₂ CO ₃	DMF	20–25/20	90, white solid	7


Scheme 3

The formation of polyimides were also confirmed by i.r., u.v., elemental analysis and ¹H n.m.r. The appearance of the characteristic absorption of 1776 and 1721 cm⁻¹ (asymmetric C=O stretching of imide ring) and the disappearance of 3400, 1650 and 1400 cm⁻¹ in i.r. spectra for **9a** indicated the complete cyclodehydration in the polymers. The maximal absorption of u.v./vis at 268 nm for **9a** showed excellent transparent to visible light. The ¹H n.m.r. and elemental analysis also supported the transformation.

An early precipitation of **9d** and **9e** were observed during the reaction proceeding whereas **10e** was still soluble in DMAc at high temperature. Copolymerization using BPA and *p*- or *m*-PDA as the comonomer could improve the solubility²⁵.

The solubility of the obtained polyimides is summarized in Table 2. All polyimides, except polyimides **9d–e** were soluble in variety of organic solvents such as CH₂Cl₂, pyridine, DMAc and NMP. The insolubility of polyimides **9d–e** may be due to their rigid structure

Table 2 Solubility of aromatic polyimides containing 1,1'-binaphthyl-2,2'-diyl units

Polymers	Solvent ^a								
	CH ₂ Cl ₂	CHCl ₃	Py	THF	DMF	DMSO	NMP	Acetone	conc. H ₂ SO ₄
9a	++	++	++	++	++	++	++	--	++
9b	++	++	++	++	++	+-	++	--	++
9c	++	++	++	++	++	+-	++	--	++
9d	--	--	--	--	-+	--	+-	--	++
9e	--	--	--	--	+-	-+	++	--	++
10a	++	++	++	+-	++	+-	++	--	++
10b	++	++	++	+-	++	+-	++	--	++

^a Key: ++, soluble at room temperature; +-, soluble on heating; -+, partially soluble on heating; --, insoluble

Abbreviations: CH₂Cl₂, methylene chloride; CHCl₃, chloroform; Py, pyridine; THF, tetrahydrofuran; DMF, N,N-dimethylformamide; NMP, N-methyl 2-pyrrolidinone; DMSO, dimethyl sulfoxide

Table 3 Physical and thermal properties of aromatic polyimides containing 1,1'-binaphthyl-2,2'-diyl units

Polymers	T_g^a (°C)	T_m^b (°C)	T.g.a. ^c (air/N ₂) (°C)	η_{intr}^d (dl g ⁻¹)	M_w^e × 10 ⁻⁴	M_w/M_n	Elemental analysis ^f		
							C	H	N
9a	272		537/540	0.50	4.94	1.52	77.60 (77.62)	3.84 (3.54)	4.01 (3.77)
9b	255		535/538	0.39	2.07	1.55	77.79 (77.68)	3.95 (3.63)	3.21 (3.35)
9c	262		473/502	0.36	1.68	1.42	79.37 (79.44)	4.13 (3.82)	4.01 (3.78)
9d	294	338	536/541				73.67 (73.46)	3.51 (3.24)	4.40 (4.08)
9e	273		528/536	0.30			73.58 (73.46)	3.47 (3.24)	4.51 (4.08)
10a	269		513/520	0.30			78.03 (77.62)	3.93 (3.54)	3.79 (3.77)
10b	265		512/524	0.35			77.82 (77.62)	3.72 (3.54)	3.85 (3.79)

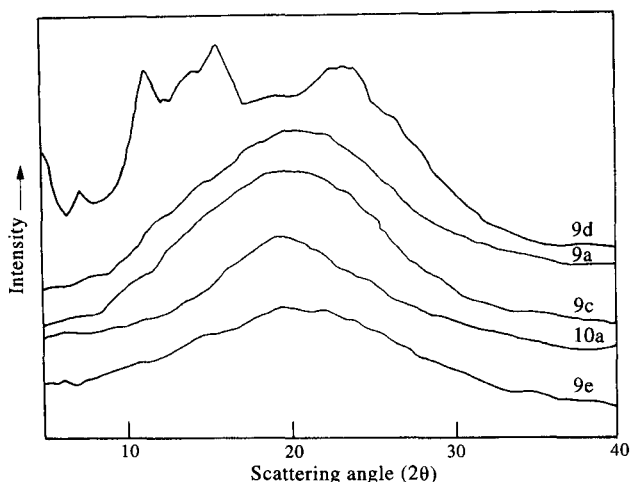
^a T_g and ^b T_m were determined by d.s.c. at heating rate 20°C min⁻¹ under nitrogen

^c Temperature at which 5% weight loss was determined by t.g.a. at heating rate 10°C min⁻¹ under nitrogen or air

^d Intrinsic viscosity was measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C

^e Molecular weight was determined by g.p.c. in THF based on polystyrene standards

^f Data in parentheses are calculated values


Figure 1 Wide-angle X-ray diffractograms of aromatic polyimides

and crystallinity. The good solubility of polyimides 9a–c can be attributed to the incorporation of flexible aryl ether groups and noncoplanarity in 2,2'-substituted 1,1'-binaphthyl units. All of the polyimides were insoluble in acetone but soluble in conc. H₂SO₄.

The crystallinity of the polyimides was examined by WAXD patterns with 2θ ranging from 5–40° as shown in Figure 1. Polyimide 9d showed partial crystallinity due to the more efficient packing of polymer chain containing the rigid structure of *p*-phenylene units, whereas the other polyimides showed amorphous patterns.

The thermal behaviours of the polymers were evaluated by d.s.c. and t.g.a. Table 3 summarizes the thermal transition data of polyimides 9a–e and 10a–b. The thermogravimetric curves for these polymers indicate that all the polymers were stable until 400°C either in nitrogen or air (Figure 2). Temperatures at 5% weight loss were recorded for these polyimides in the range of 502–541°C in nitrogen and 473–537°C in air.

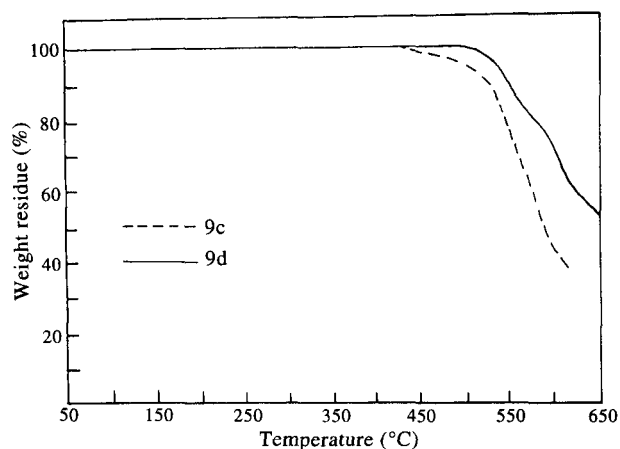


Figure 2 T.g.a. thermogram (weight loss vs temperature) for aromatic polyimides 9c and 9d under air

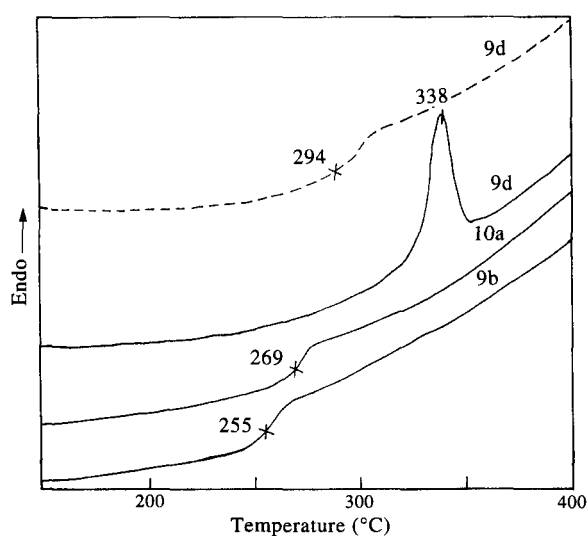


Figure 3 D.s.c. traces (at a heating rate of 20°C min⁻¹) of aromatic polyimides 9b, 9d and 10a: (—) first heating; (---) second heating

Glass transition temperatures of the polymers were determined by d.s.c. at a heating rate of 20°C min⁻¹ under nitrogen. The obtained polyimides (9a–e, 10a–b) showed T_g 's in the range of 255–294°C. Figure 3 showed the typical d.s.c. traces of polyimides 9b, 9d and 10a. A well defined melting point could be obtained in the first heating of 9d, however, disappeared in the second heating. Moreover, the copolymer 10a was obviously amorphous and the T_g of 10a appeared at the temperature between these of the corresponding homopolymers 9b and 9d (Figure 3).

The molecular weights of the polyimides 9a–c were determined by g.p.c. in THF using polystyrene as the standard. These polymers have weight average molecular

weight in the range of 16 800–49 400 and polydispersities (M_w/M_n) of 1.42–1.55. The film cast from polyimides except 9b, were brittle.

CONCLUSIONS

We have successfully synthesized 2,2'-bis(3,4-dicarboxyphenoxy)-1,1'-binaphthyl dianhydride in high yield from 1,1'-bi-2-naphthol and 4-nitrophthalonitrile. A series of aromatic polyimides were prepared from the dianhydride and a variety of diamines. Most of the obtained polyimides possessed good solubility in common solvents, high T_g 's, high thermal stability and excellent transparent to visible light and showed no evidence of any crystallinity, except that from *p*-phenylene diamine.

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