

Synthesis and properties of new polyamides and polyimides derived from 2,2'-dimethyl-4,4'-bis(4-aminophenoxy)biphenyl

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(Received 7 January 1997; revised 26 February 1997)

In this work, we synthesised a new diamine containing noncoplanar 2,2'-dimethyl-biphenylene and flexible aryl ether units, 2,2'-dimethyl-4,4'-bis(4-aminophenoxy)biphenyl (DBAPB), by nucleophilic substitution of 2,2'-dimethylbiphenyl-4,4'-diol with *p*-chloronitrobenzene in the presence of K_2CO_3 , followed by catalytic reduction with hydrazine/Pd–C system. A series of aromatic polyamides having inherent viscosities of 1.03–1.48 dl g⁻¹ were prepared by direct polycondensation with aromatic dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents. Nearly all of the polymers revealed an amorphous nature and were readily soluble in a variety of organic solvents. These polymer films had a tensile strength ranging from 22 to 65 MPa. The glass transition and melting temperature of these polyamides could be determined by d.s.c. and ranged from 226 to 273°C and 392–438°C, respectively. These polyamides remained fairly stable up to a temperature around or below 400°C. Moreover, 10% mass losses were recorded in the range 467–496°C in nitrogen atmosphere. The new polyimides were synthesised from DBAPB and various aromatic tetracarboxylic dianhydrides by the conventional two-step method which involved ring-opening polyaddition to form poly(amic acid)s and subsequently thermal or chemical cyclodehydration to polyimides. The inherent viscosities of poly(amic acid)s and polyimides were in the range 1.32–2.01 and 0.82–1.10 dl g⁻¹, respectively. These polyimide films had a tensile strength range of 83–139 MPa. These polyimides had glass transition temperatures between 239 and 303°C. Thermogravimetric analyses demonstrated that almost all polymers were stable up to 450°C, and the 10% mass loss temperatures were recorded in the range 488–534°C in nitrogen. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: 2,2'-dimethyl-4,4'-bis(4-aminophenoxy)biphenyl (DBAPB); noncoplanar; polyamides)

INTRODUCTION

The synthesis of rigid, rod-like polyamides and polyimides has been an important target in polymer science for many years, as these polymers exhibit good mechanical properties combined with an excellent thermal resistance^{1–4}. However, in many cases they are insoluble and do not melt below their decomposition temperature. The infusibility and limited solubility of unsubstituted rod-like aromatic polyamides and polyimides are characteristic properties which restrict synthesis, characterisation, processing, and applications, particularly for a high molecular weight material. Thus, a variety of concepts for structural modifications such as bulky lateral substituents^{5–7}, flexible alkyl side chains^{8,9}, noncoplanar biphenylene moieties^{10–12}, as well as flexible alkyl or aryl ether spacers^{13–15} have been used to enhance the solubility and lower the phase transition temperatures. To develop high performance materials, modifications increasing the solubility and lowering the transition temperatures while maintaining the rod-like characteristic and thermal stability are of particular interest.

Incorporating 2,2'-disubstituted biphenylene in a para-linked polymer chain does not initially change the polymer backbone's rod-like structure, but reduces the interchain interactions. The phenyl rings are forced by the 2,2'-disubstitution into a noncoplanar conformation, decreasing

the intermolecular forces between the polymer chains. The crystallisation tendency and transition temperatures are markedly lowered and the solubilities are significantly enhanced^{12,16–18}. In addition, aryl ether linkages inserted in aromatic main chains provide a significantly lower energy of internal rotation which leads to a lower glass transition temperature and crystalline melting temperature, as well as to significantly improving solubility and other process characteristics of the polymers without greatly sacrificing thermal stability. Therefore, the introduction of both noncoplanar 2,2'-disubstituted biphenylene and flexible aryl ether units into polymer backbone would be expected to be potential structural modifications to the rod-like polymer.

This article describes the synthesis of a new diamine, DBAPB, containing both 2,2'-dimethylbiphenylene and aryl ether units. It is used to prepare a series of polyamides and polyimides by polycondensating with various aromatic dicarboxylic acids and aromatic tetracarboxylic dianhydrides, respectively. The synthesis and characterisation of these polymers are also investigated and discussed. In addition, the effect of the methyl substitution to the aromatic condensation polymer is discussed.

EXPERIMENTAL

Materials

2,2'-Dimethyl-4,4'-diaminobiphenyl dihydrochloride

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(Wakayama Seika Co.), *p*-chloronitrobenzene (Merck), anhydrous potassium carbonate (Janssen), hydrazine monohydrate (Janssen), and 10% palladium on activated carbon (Merck) were used as received. Reagent-grade aromatic dicarboxylic acids such as terephthalic acid (**I_a**), isophthalic acid (**I_b**), 5-*tert*-butylisophthalic acid (**I_c**), 2,6-naphthalenedicarboxylic acid (**I_d**), 4,4'-biphenyldicarboxylic acid (**I_e**), 4,4'-sulfonyldibenzoic acid (**I_f**), and 4,4'-hexafluoroisopropylidenedibenzoic acid (**I_g**); and aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydiphthalic anhydride (ODPA), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA), 4,4'-sulfonyldiphthalic anhydride (SDPA), and 4,4'-hexafluoroisopropylidenediphthalic anhydride (6FDA) were used without purification. Reagent-grade calcium chloride was dried under vacuum at 180°C before use. *N*-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and pyridine were purified on distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å).

Monomer synthesis

2,2'-Dimethylbiphenyl-4,4'-diol. This compound was synthesised and purified according to a procedure by Schmidt *et al.*¹⁶; m.p. 121–123°C (Lit.¹⁶: m.p. 122–124°C); i.r. (KBr): 3280 cm⁻¹ (O–H); ¹H n.m.r. (DMSO-*d*₆) δ (ppm) = 1.88 (s, 6H, CH₃), 6.62–6.79 (m, 6H, aromatic), 9.20 (s, 2H, OH). ¹³C n.m.r. (DMSO-*d*₆) δ (ppm) = 19.92, 112.63, 116.46, 130.65, 132.05, 136.87, 156.19.

ANAL. calcd. for C₁₄H₁₄O₂: C, 78.50%; H, 6.54%; found: C, 79.10%; H, 6.78%.

2,2'-Dimethyl-4,4'-bis(4-nitrophenoxy)biphenyl (DBNPB). This compound was synthesised by the reaction of 2,2'-dimethylbiphenyl-4,4'-diol 30 g (0.14 mol) and *p*-chloronitrobenzene 47.2 g (0.3 mol) in the presence of potassium carbonate 48.7 g (0.35 mol) and DMF 250 ml at 160°C for 8 h. The mixture was then cooled and poured into methanol/water (1:1 by volume). The crude product was recrystallised from glacial acetic acid to provide brown needle (m.p. 142–144°C) in 83% yield. The i.r. spectrum (KBr) exhibited absorptions at 1580 and 1339 cm⁻¹ (NO₂), 1238 cm⁻¹ (C–O–C). ¹H n.m.r. (CDCl₃): δ (ppm) = 2.09 (s, 6H), 6.96 (d, 4H), 7.01 (s, 2H), 7.07 (d, 2H), 7.17 (d, 2H), 8.22 (d, 4H). ¹³C n.m.r. (CDCl₃): δ (ppm) = 19.98, 117.24, 117.53, 121.61, 125.91, 131.15, 137.68, 138.62; 142.72, 154.00, 163.27.

ANAL. calcd. for C₂₆H₂₀O₄N₂: C, 68.42%; H, 4.39%; N, 6.14%; found: C, 67.98%; H, 4.59%; N, 6.22%.

2,2'-Dimethyl-4,4'-bis(4-aminophenoxy)biphenyl (DBAPB). The obtained dinitro compound 45.6 g (0.1 mol), 0.3 g of 10% Pd–C, and 300 ml ethanol were introduced into a three-necked flask to which hydrazine monohydrate (100 ml) was added dropwise over a period of 0.5 h at 85°C. After the addition was complete, the reaction was continued at reflux temperature for another 24 h. The mixture was then filtered to remove Pd–C. After cooling, the precipitated crystals were isolated by filtration and recrystallised from ethanol and dried *in vacuo*. The yield was 80%; m.p. 138–139°C. The i.r. spectrum (KBr) exhibited absorptions at 3324 and 3406 cm⁻¹ (N–H), 1226 cm⁻¹ (C–O–C).

ANAL. calcd. for C₂₆H₂₄O₂N₂: C, 78.79%; H, 6.06%; N, 7.07%; found: C, 78.41%; H, 6.34%; N, 7.10%.

Polymerisation

Polyamide II_a from DBAPB and diacid **I_a**. A mixture of 0.495 g (1.25 mmol) of diamine DBAPB, 0.207 g (1.25 mmol) of diacid **I_a**, 0.45 g of calcium chloride, 0.9 ml of triphenyl phosphite, 0.9 ml of pyridine, and 4.5 ml of NMP was heated with stirring at 100°C for 3 h. After cooling, the reaction mixture was poured into large amount methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100°C under vacuum. All other polyamides were prepared using a similar procedure.

Polyimide VI_a from DBAPB and PMDA. To a stirred solution of 0.496 g (1.25 mmol) of DBAPB in 8 ml of DMAc, was gradually added 0.273 g (1.25 mmol) of dianhydride PMDA. The mixture was stirred at room temperature for 2–4 h under argon atmosphere to form the poly(amic acid). From this solution a film was cast onto a glass plate and heated (8 h at 80°C, 1 h at 120°C, 1 h at 150°C, 2 h at 200°C, 1 h at 250°C) to convert the poly(amic acid) into polyimide film.

Chemical cyclodehydration was also carried out by adding DMAc, and an equimolar mixture of acetic anhydride and pyridine into the above-mentioned poly(amic acid) solution with stirring at room temperature for 1 h, and then heating at 100°C for 3 h. The polymer solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100°C under vacuum.

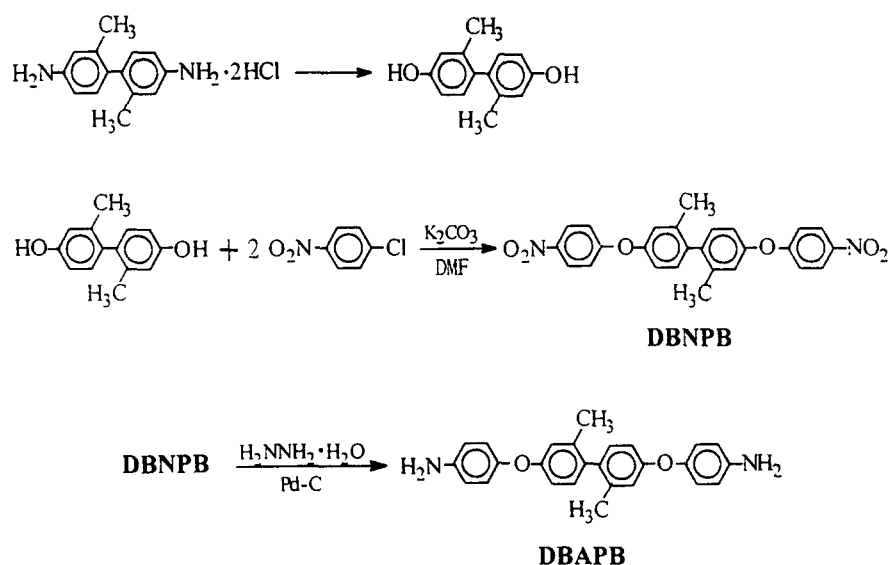
Measurements

Melting point were measured in capillaries on a BÜCHI apparatus (model BÜCHI 535). I.r. spectra were recorded in the range 4000–400 cm⁻¹ for the synthesised monomers and polymers in KBr discs (JASCO IR-700 spectrometer). The inherent viscosities of all polyamides were measured using Ubbelohde viscometer. Elemental analysis was made (Perkin–Elmer 2400 instrument). Wide-angle x-ray diffraction patterns were performed at room temperature with film specimens on an x-ray diffractometer (Philips model PW 1710) using Ni filtered Cu–Kα radiation (40 Kv, 30 mA). The scanning rate was 3° min⁻¹. N.m.r. spectra were recorded using a Varian VXR400S (¹H at 399.96 MHz and ¹³C at 100.58 MHz). Thermogravimetric data were obtained on a Du Pont 2200 in flowing nitrogen (60 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. Differential scanning calorimetry (d.s.c.) was performed on a differential scanning calorimeter (Du Pont 2000) at a heating rate of 20°C min⁻¹. Tensile properties were determined from stress–strain curves obtained with a Orientec Tensilon with a load cell of 10 kg. A gauge of 3 cm and a strain rate of 2 cm min⁻¹ were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ≈ 0.5 mm thick).

RESULTS AND DISCUSSION

Monomer synthesis

Scheme 1 shows the synthetic route of 2,2'-dimethyl-4,4'-bis(4-aminophenoxy) biphenyl (DBAPB). 2,2'-Dimethylbiphenyl-4,4'-diol was synthesised from 2,2'-dimethyl-4,4'-diaminobiphenyl dihydrochloride according to a procedure by Schmidt *et al.*¹⁶ The aromatic nucleophilic substitution reaction of 2,2'-dimethylbiphenyl-4,4'-diol and



Scheme 1

p-chloronitrobenzene in the presence of K_2CO_3 yielded a dinitro compound (DBNPB). Reducing of the dinitro derivative in ethanol in the presence of hydrazine and a catalytic amount of palladium on activated carbon at 80°C produced diamine DBAPB. The structures of these compounds were confirmed by elemental analysis, i.r. and n.m.r. spectroscopy. As indicated in the Experimental section, the elemental analysis values of the dinitro and diamine compounds correspond to the calculated values of their structures. Figure 1 compares the i.r. spectra of the dinitro DBNPB [Figure 1(A)] and diamine DBAPB (Figure 1B). DBNPB reveals absorption bands appearing around 1339 and 1580 cm^{-1} due to symmetric and asymmetric stretching of $-\text{NO}_2$ group. After reduction, the characteristic absorption of nitro groups disappeared and the characteristic bands of the amino groups at 3406 and 3324 cm^{-1} (N–H stretching) and 1598 cm^{-1} (N–H bending) appeared. The ^1H and ^{13}C n.m.r. spectra of diamine DBAPB in $\text{DMSO}-d_6$ are shown in Figure 2A and B. The signal appearing at 4.99 ppm in ^1H n.m.r. spectrum is peculiar to the amino group. The ^{13}C n.m.r. spectrum of DBAPB exhibited 11 features in the range 19.76 – 157.01 ppm for each carbon atom in the sample. Figure 2C displays the 2D ^1H – ^{13}C COSY spectrum of DBAPB. With the assistance of the proton spectrum assignments, protonated carbons were readily identified. The carbon resonances at 117.36 and 121.11 ppm correlate with the proton doublet centred at 6.79 and 6.81 ppm , respectively. Those results clearly confirm that the diamine prepared herein is consistent with the proposed structure.

Preparation of polyamides

The polyamides were prepared by the direct polycondensation of diamine DBAPB with seven aromatic dicarboxylic acids I_{a-g} in NMP using triphenyl phosphite and pyridine as condensing agents (Scheme 2). The conditions and results of the preparation of polyamides are summarised in Table 1. All the polycondensation readily proceeded within a homogeneous solution. Tough, stringy precipitates formed when the viscous polyamide solutions were trickled into stirring methanol. Because the solubilities of polyamides II_c , II_f , and II_g are better, the quantities of CaCl_2 and solvents do not need to be high during the reaction. In

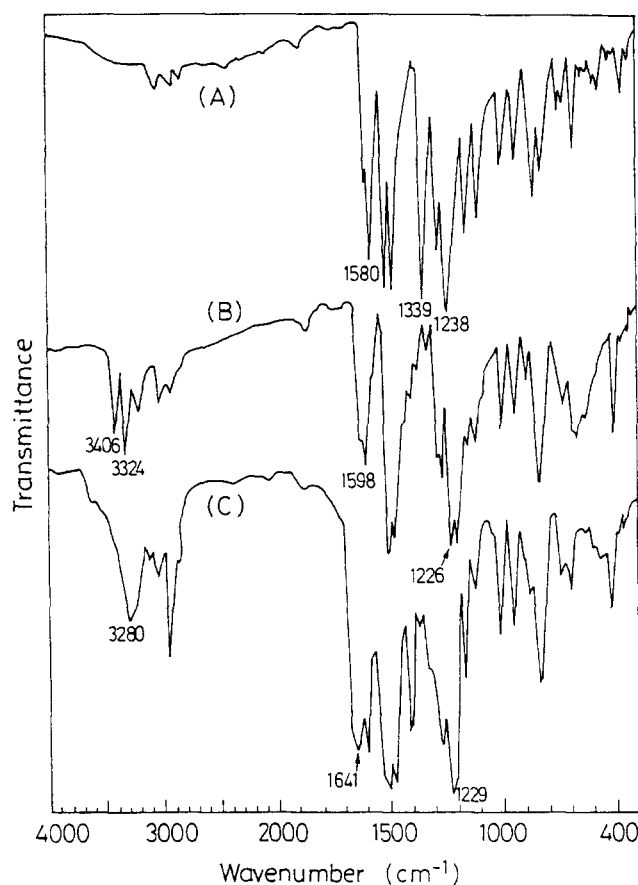


Figure 1 I.r. spectra of dinitro DBNPB (A), diamine DBAPB, and polyamide II_a (C)

some cases of the reaction, additional amounts of NMP had to be supplemented to maintain a degree of agitation because the polymer solutions were too viscous to stir. All the polymers were obtained in quantitative yields with moderate to high inherent viscosities of 1.03 – 1.48 dl g^{-1} .

In this study polyamide III and copolyamides IV_{a-c} were designed to examine the influence of the dimethyl substituent on polymer properties. Aromatic copolyamides were synthesised by using DBAPB and

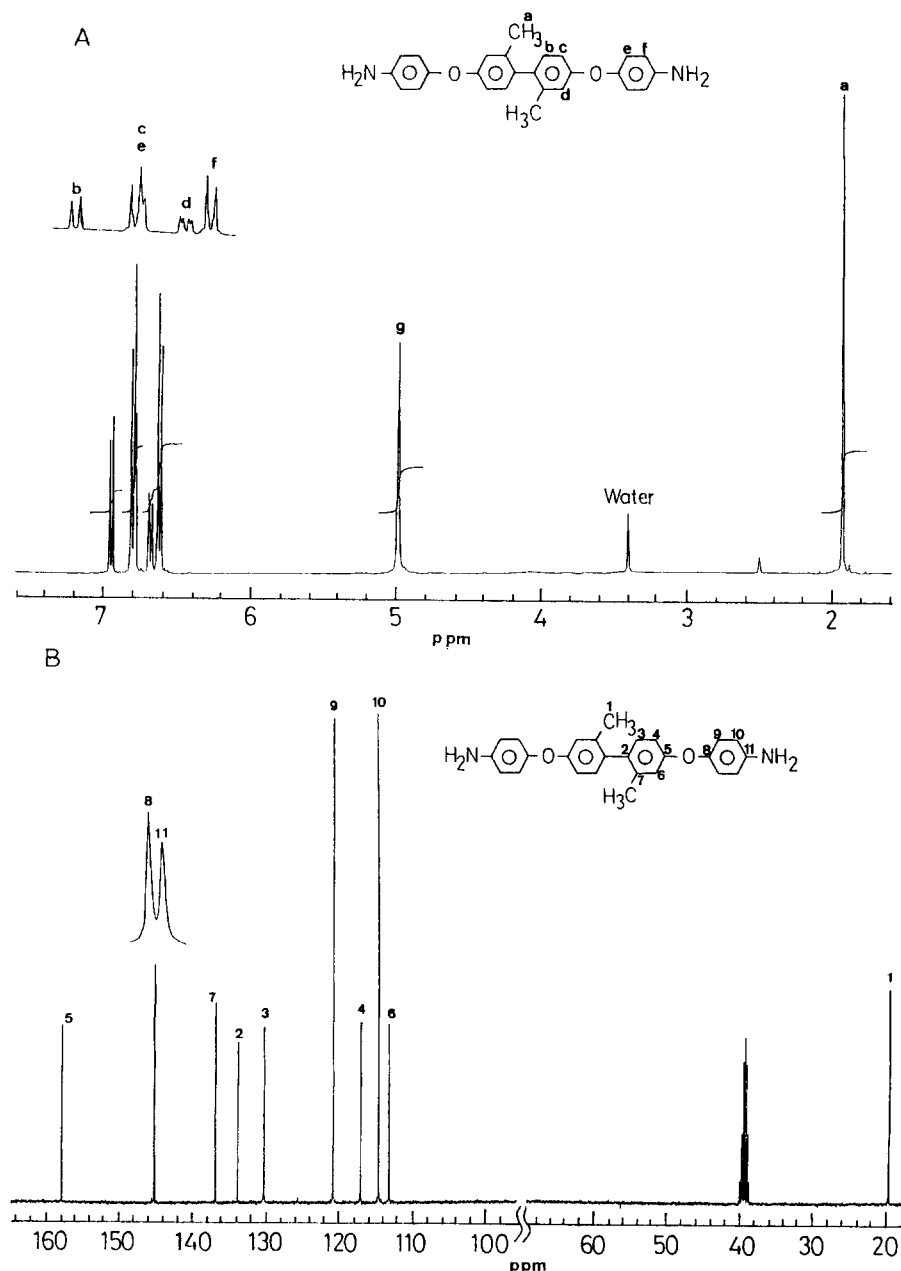
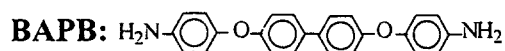


Figure 2 N.m.r. spectra of diamine DBAPB. Use $\text{DMSO}-d_6$ as solvent: (A) ^1H n.m.r., (B) ^{13}C n.m.r., (C) $2\text{D } ^1\text{H}-^{13}\text{C}$ n.m.r.

4,4'-bis(4-aminophenoxy)biphenyl (BAPB)



having no substituent on biphenylene as the diamine component, and I_d as the diacid component. These copolyamides had inherent viscosities of $0.32\text{--}1.23 \text{ dl g}^{-1}$. Interestingly, polyamide III , derived from unsubstituted diamine BAPB, exhibited the lowest inherent viscosity owing to the fact that the polyamide III generally precipitated in the reaction media, causing low molar mass products due to its poor solubility. The inherent viscosity of these copolymers tended to increase with an increasing content of diamine DBAPB. In addition, DBAPB-based polyamide films II_a and II_e could be obtained by casting from their NMP solutions and the other films could be obtained from DMAc solutions. All the polymer films, except II_e , showed a transparent and flexible nature.

The formation of polyamides could be confirmed by i.r. spectroscopy and elemental analysis. *Figure 1C* presents the i.r. spectrum of representative polyamide II_a . The characteristic absorptions of amide groups occurred around 3280 and 1641 cm^{-1} , peculiar to N-H stretching and carbonyl stretching, respectively. *Table 2* lists the elemental analysis values of these polymers. As this table reveals, carbon values were lower than the calculated values for the proposed structures. Such a difference may be attributed to the amide group's hygroscopic characteristics. The amount of absorbed water of these polyamides and copolyamides ranged from 2.86 to 4.72% . The corrected values correlated well with the calculated ones after the found values had been corrected.

Preparation of polyimides

Polyimides VI_{a-f} were synthesised by the conventional two-step procedure, as shown in *Scheme 3*. Poly(amic acid)s V_{a-f} were prepared by the ring-opening polyaddition of diamine DBAPB with aromatic tetracarboxylic dianhydrides,

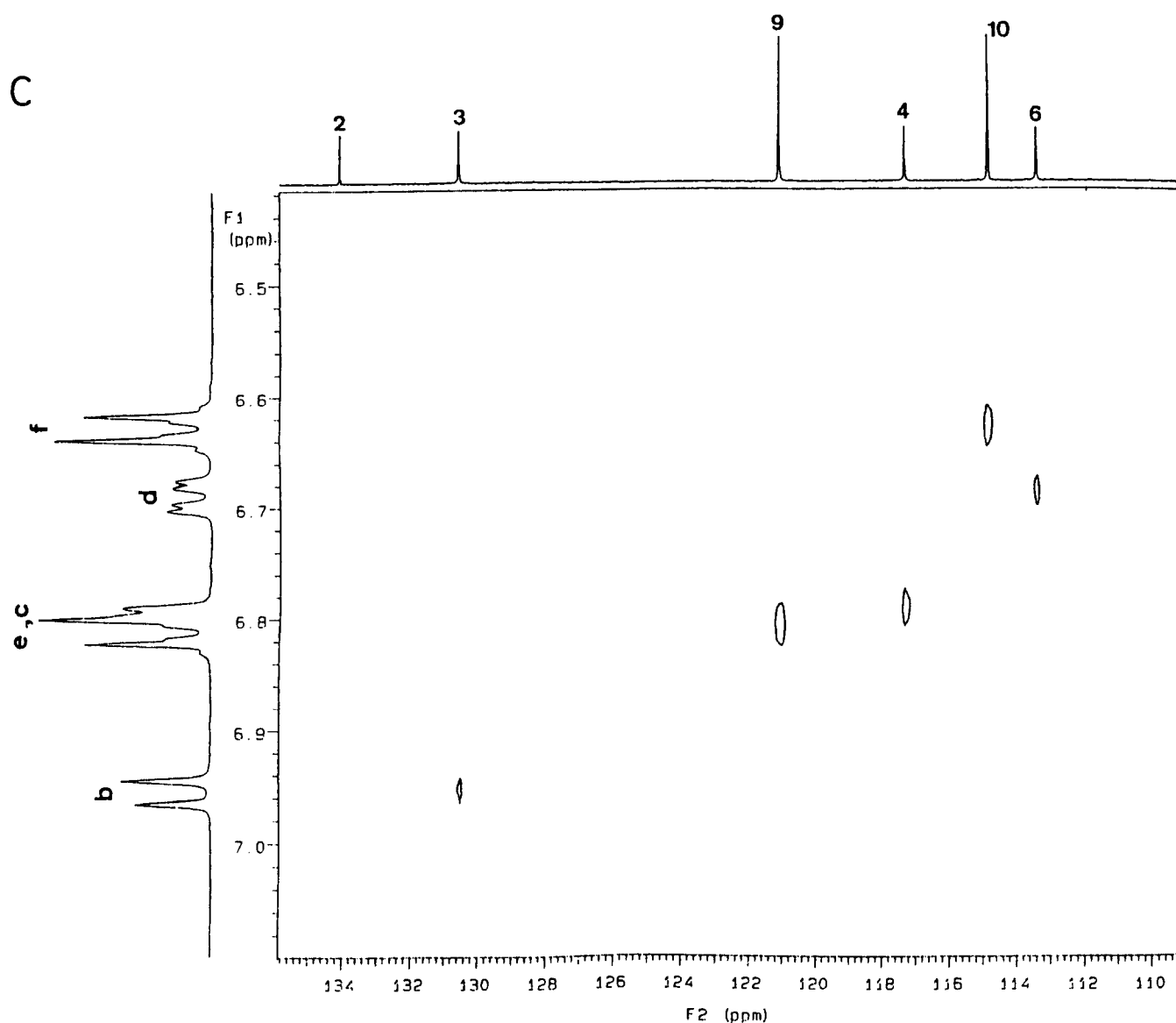


Figure 2 Continued

Table 1 Preparation of polyamides and copolyamides from diamine and various diacids^a

Diamine component		Polymer						
Diacid	Code	NMP (ml)	CaCl ₂ (g)	Yield (%)	η_{inh}^b (dl g ⁻¹)	Aspect	Film quality	
DBAPB	I _a	II _a	4.5	0.45	91	1.29 ^c	String	Flexible
DBAPB	I _b	II _b	3	0.30	99	1.12	String	Flexible
DBAPB	I _c	II _c	2.5	0.25	97	1.04	String	Flexible
DBAPB	I _d	II _d	4 + 5	0.40	99	1.48	String	Flexible
DBAPB	I _e	II _e	4 + 2	0.40	99	1.22 ^c	String	Brittle
DBAPB	I _f	II _f	2.5 + 2	0.25	99	1.07	String	Flexible
DBAPB	I _g	II _g	2.5 + 1	0.25	99	1.03	String	Flexible
DBAPB/BAPB								
(0/100)	I _d	III	5	0.50	88	0.32 ^d	Powder	- ^c
(30/70)	I _d	IV _a	5	0.50	94	0.53 ^d	Powder	-
(50/50)	I _d	IV _b	5	0.50	99	1.11 ^d	String	-
(70/30)	I _d	IV _c	5	0.5	99	1.23 ^d	String	-

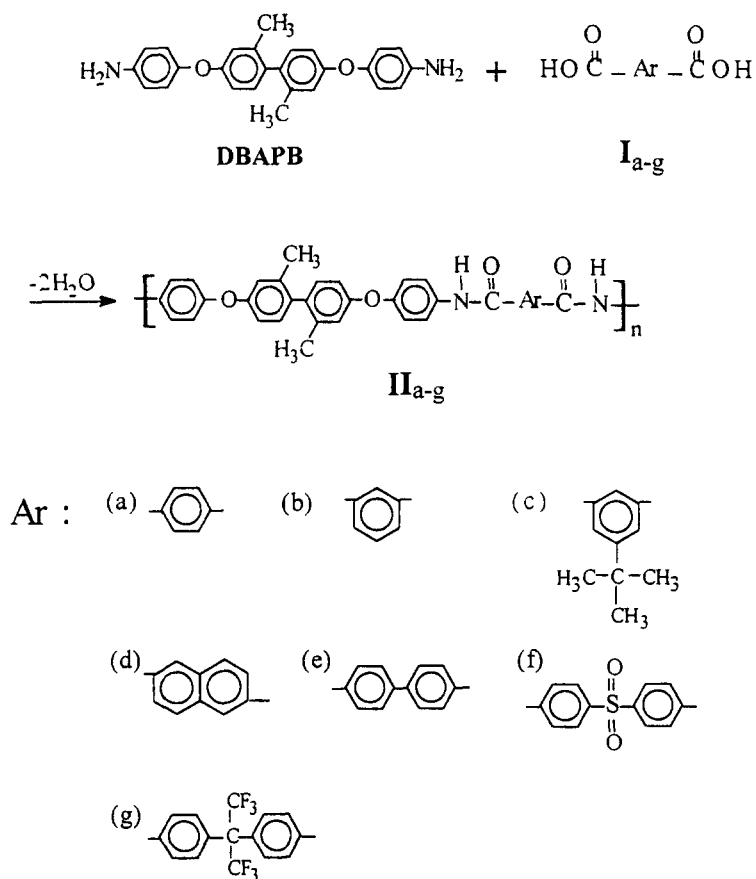
^aPolymerisation was carried out using 1.25 mmol of diamine and 1.25 mmol of diacids with 0.9 ml of triphenyl phosphite and 0.9 ml of pyridine at 100°C for 3 h

^bInherent viscosity measured at a concentration of 0.5 g dl⁻¹ DMAC at 30°C

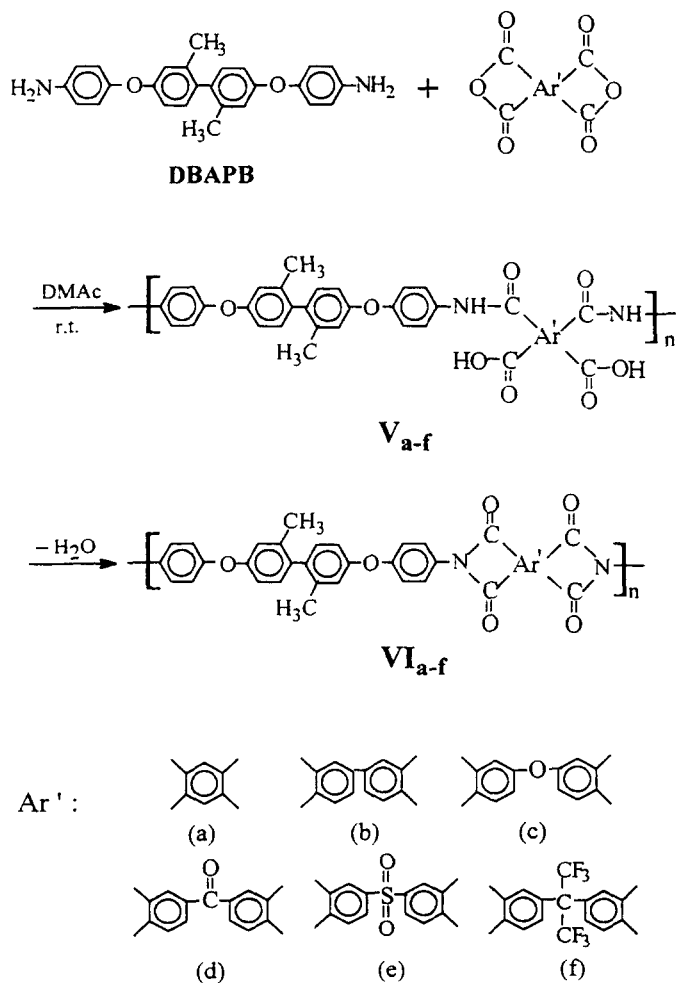
^cInherent viscosity measured at a concentration of 0.5 g dl⁻¹ NMP at 30°C

^dInherent viscosity measured at a concentration of 0.5 g dl⁻¹ conc. H₂SO₄ at 30°C

^ePolymer was insoluble in DMAC or NMP



Scheme 2



Scheme 3

Table 2 Elemental analysis of polyamides and copolyamides

Polymer		Elemental analysis (%)			Fraction of absorbed water ^a (%)
		C	H	N	
II _a	Calcd	77.55	4.98	5.32	3.06
	Found	74.73	5.15	5.10	
	Corrtd ^b	77.09	4.99	5.26	
II _b	Calcd	77.55	4.98	5.32	4.72
	Found	73.76	5.03	5.03	
	Corrtd	77.41	4.80	5.28	
II _c	Calcd	78.33	5.88	4.81	2.86
	Found	76.06	5.95	4.68	
	Corrtd	78.30	5.78	4.82	
II _d	Calcd	79.15	4.89	4.86	3.56
	Found	76.10	5.18	4.73	
	Corrtd	78.91	5.00	4.90	
II _e	Calcd	79.72	5.02	4.65	3.73
	Found	76.37	5.31	4.49	
	Corrtd	79.33	5.12	4.66	
II _f	Calcd	72.06	4.54	4.20	3.97
	Found	68.99	4.67	4.05	
	Corrtd	71.84	4.49	4.22	
II _g	Calcd	68.62	4.02	3.72	2.90
	Found	66.40	4.14	3.61	
	Corrtd	68.38	4.02	3.72	
III	Calcd	78.81	4.41	5.11	4.34
	Found	75.21	4.69	4.80	
	Corrtd	78.62	4.49	5.02	
IV _a	Calcd	78.92	4.56	5.03	3.63
	Found	75.73	4.74	4.73	
	Corrtd	78.58	4.57	4.91	
IV _b	Calcd	78.99	4.66	4.98	3.91
	Found	75.63	4.82	4.74	
	Corrtd	78.71	4.64	4.93	
IV _c	Calcd	79.05	4.75	4.93	3.14
	Found	76.41	4.87	4.79	
	Corrtd	78.89	4.72	4.95	

^aAmount of absorbed water (%) = (Sample mass at room temperature - Sample mass after drying under vacuum at 100°C)/Sample mass at room temperature

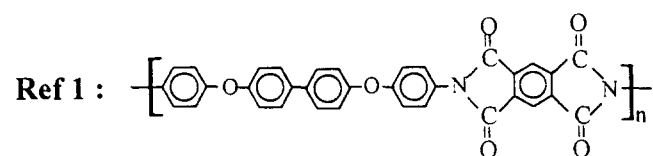
$$^b\text{Corrected value} = \frac{\text{Found value}}{(1 \pm \text{Fraction of absorbed water})}$$

where + for H, - for C and N

followed by thermal or chemical cyclodehydration. The inherent viscosities of all the poly(amic acid)s together with those of the corresponding polyimides are summarised in *Table 3*. The inherent viscosities of the poly(amic acid)s indicated high values; they were found in the range of 1.32–2.01 dl g⁻¹. The polyimide films could be obtained by thermal cyclodehydration. Almost all the polyimide films are tough and creasible, except polyimide VI_d derived from BTDA. Alternatively, chemical conversion of poly(amic acid)s with a mixture of acetic anhydride and pyridine is also effective in obtaining polyimides. By the chemical procedure the resulting polyimides had inherent viscosities of 0.82–1.10 dl g⁻¹ in concentrated sulfuric acid or DMAc.

The polymers were characterised by elemental analysis and i.r. spectroscopy. The elemental analysis values of these polyimides listed in *Table 3* were in agreement with their respective structures. The i.r. spectra of poly(amic acid) V_b and the corresponding polyimide VI_b are shown in *Figure 3*. The i.r. spectrum of poly(amic acid) V_b [*Figure 3(A)*] showed major absorption peaks at 1649, 1535, and 1713 cm⁻¹, assigned to amide I, amide II, and acid carbonyl group (C=O), respectively, and characteristic absorptions around 3270 cm⁻¹ for N–H and O–H group. In the spectrum of the polyimide VI_b (*Figure 3(B)*) obtained by thermal treatment, the characteristic bands at 1767 and 1716 cm⁻¹ are commonly attributed to the asymmetric and symmetric stretches of carbonyl group of imide, respectively. The C–N band at 1371 cm⁻¹ verified the formation of the imide structure. Furthermore, the bands of 1649 cm⁻¹ (amide I) and 1535 cm⁻¹ (amide II) disappeared which indicated good imidisation.

For comparison, polyimides Ref. 1 and Ref. 2 containing unsubstituted biphenylene were prepared by condensation of 4,4'-bis(4-aminophenoxy)biphenyl with PMDA and SDPA, respectively.

**Table 3** Results of the preparations of poly(amic acid)s and polyimides

Poly(amic acid)	Polyimide ^b			Elemental analysis			
	Code	Code	Code	C%	H%	N%	
V _a	1.61	VI _a	0.89	Found	72.95	4.07	5.21
				Calc.	(74.67)	(3.80)	(4.84)
V _b	1.43	VI _b	0.91	Found	75.06	3.93	4.09
				Calc.	(77.01)	(3.97)	(4.28)
V _c	1.69	VI _c	0.82	Found	72.95	3.65	4.00
				Calc.	(75.17)	(3.88)	(4.18)
V _d	2.01	VI _d	1.08	Found	74.14	3.90	4.02
				Calc.	(75.60)	(3.81)	(4.10)
V _e	1.32	VI _e	0.97 ^a	Found	73.28	3.89	4.06
				Calc.	(70.14)	(3.62)	(3.90)
V _f	1.75	VI _f	1.10 ^a	Found	64.98	3.00	3.35
				Calc.	(67.12)	(3.23)	(3.48)

^aMeasured in DMAc at a concentration of 0.5 g dl⁻¹ at 30°C

^bObtained by chemical cyclisation from the corresponding poly(amic acid)s

^cMeasured in concentrated sulfuric acid at a concentration of 0.5 g dl⁻¹ at 30°C

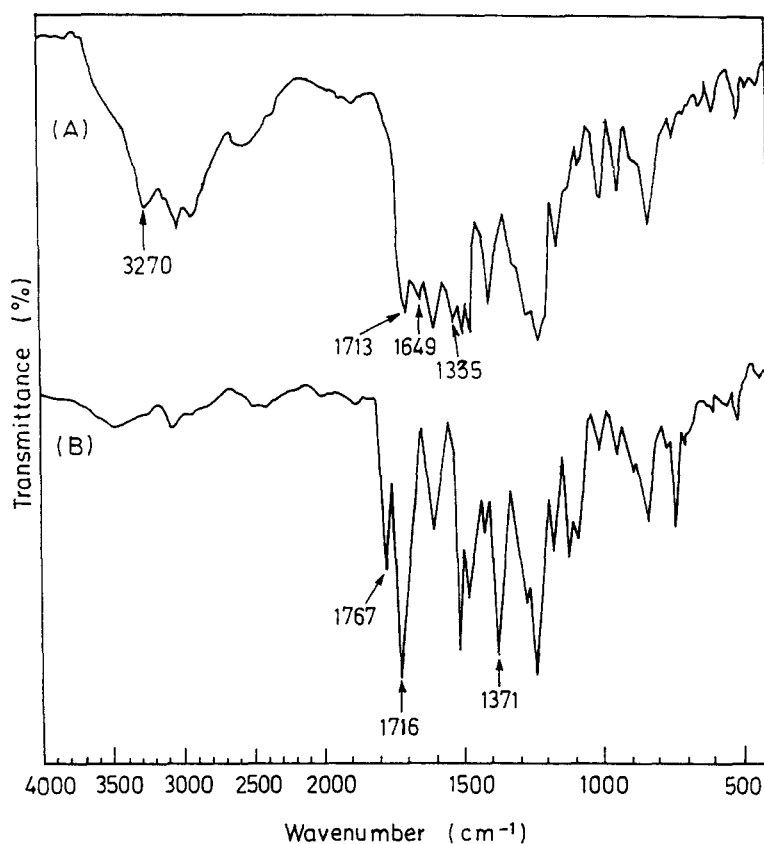
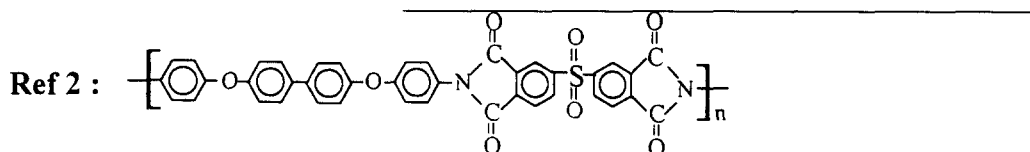


Figure 3 I.r. spectra of poly(amic acid) V_b (A) and the corresponding polyimide VI_b (B)



Properties of polyamides

Typical x-ray diffractograms of some polyamides are shown in Figure 4. Nearly all of the DBAPB-based polyamides and copolyamides IV , except II_e , exhibited amorphous patterns similar to those of polyamide II_b . This observation is quite reasonable because the presence of noncoplanar conformation decreases the intermolecular forces between the polymer chain, subsequently causing a decrease in crystallinity. The polyamide II_e revealed higher crystalline patterns than the other DBAPB-based polyamides possibly due to the presence of rigid biphenyl structures. The relatively higher crystalline nature of polyamide film (II_e) reflects in its brittle nature. In contrast, the polyamide III derived from rigid unsubstituted biphenylene diamine BAPB exhibited highly crystalline patterns due to a better packing of the polymer backbone.

The solubility of these polyamides and copolyamides was tested qualitatively in various solvents. Table 4 summarises these results. All the DBAPB-based polyamides, except for II_a and II_e exhibit good solubility in a variety of solvents such as NMP, DMSO, DMAc, DMF and even in *m*-cresol and pyridine. Polyamide II_g containing hexafluoroisopropylidene group exhibited the best solubility and was soluble even in common organic solvent such as THF. Polyamides II_a and II_e revealed less solubility, possibly due to the more rigid nature of their diacid moieties, terephthalic acid (I_a) and 4,4'-biphenylenedicarboxylic acid (I_c). However, they

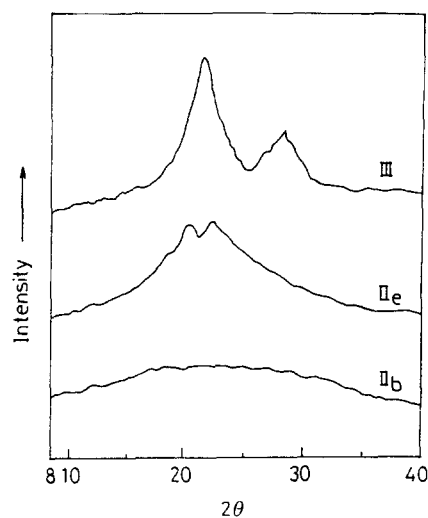


Figure 4 Wide-angle x-ray diffractograms of some representative polyamides

were entirely soluble in NMP; thus, all polyamides derived from DBAPB can be readily processed from solutions. The excellent solubility of DBAPB-based polyamides is attributed to the presence of noncoplanar biphenylene and flexible aryl ether moieties. In contrast, the unsubstituted polyamide III was entirely insoluble in the test solvent

Table 4 Solubility of polyamides and copolyamides^a

Polymer	Solvent ^b							
	NMP	DMSO	DMAc	DMF	<i>m</i> -Cresol	Py	THF	Conc. H ₂ SO ₄
II _a	+	+ -	+ -	-	-	-	-	+
II _b	+	+	+	+	+	+	+ -	+
II _c	+	+	+	+	+	+	+ -	+
II _d	+	+	+	+	+	+	+ -	+
II _e	+	-	-	-	-	-	-	+
II _f	+	+	+	+	+	+	+ -	+
II _g	+	+	+	+	+	+	+	+
III	-	-	-	-	-	-	-	+
IV _a	+ -	-	-	-	-	-	-	+
IV _b	+ -	-	+ -	-	-	-	-	+
IV _c	+ -	-	+ -	+ -	+ -	+ -	-	+

^aSolubility: +, soluble at room temperature; + -, partial soluble; -, insoluble

^bAbbreviations: DMSO, dimethylsulfoxide; DMAc, *N,N*-dimethylacetamide; Py, pyridine

except for conc. H₂SO₄. In series IV, the solubility of these copolyamides increase with an increasing content of noncoplanar diamine DBAPB. Obviously, 2,2'-dimethyl substituted biphenylene unit effectively reduces the rod-like nature of the polyamide backbone and enhances polymer solubility.

Table 5 summarises the tensile properties of the DBAPB-based polyamide films, except II_e. The films had a tensile strength ranging from 22 to 65 MPa, elongation at break of 2–4%, and initial modulus of 1.12–2.61 GPa.

The thermal properties of these polyamides were assessed by d.s.c. and thermogravimetry (TG). The thermal

behaviour data of polyamides and copolyamides are summarised in Table 6. Rapid cooling from elevated temperature of approximately 400°C to room temperature was done to form more amorphous materials. Thus, some polyamides displayed distinct glass transitions on subsequent heating d.s.c. traces. These DBAPB-based polyamides had glass transition temperatures (*T*_gs) in the range 226–273°C, depending on the diacid component's structure. However, some DBAPB-based polyamides like II_a, II_d, and II_e that possess rigid diacid moieties display no discernible glass transition in their d.s.c. traces but exhibit endotherm peaks around 392–438°C in the first heating. It was found that rigid polyamide III not only displayed no distinct glass transitions but endotherm peak in the d.s.c. trace up to 500°C. Restated, polyamide III could not be moulded below its decomposition temperature. Compared with copolyamides IV, the melting temperature could be lowered by incorporating noncoplanar diamine into the copolymer backbone, i.e. an increase of noncoplanar diamine content in the copolymer's backbone shifts melting temperature to a lower temperature.

TGA traces reveal that all the DBAPB-based polyamides do not decompose around or below 400°C in nitrogen atmosphere. Their decomposition temperatures of 10%

Table 5 Mechanical properties of polyamides

Polymer	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
II _a	60	3	2.61
II _b	31	2	1.12
II _c	65	4	1.93
II _d	40	3	1.42
II _f	22	2	1.16
II _g	57	3	1.88

Table 6 Thermal properties of polyamides and copolyamides

Polymer	<i>T</i> _g ^a (°C)	<i>T</i> _m ^a (°C)	IDT ^c (°C)	PDT ^c (°C)	PDT _{max} ^c (°C)	Char yield (%)
II _a	- ^b	410	422	476	481	61
II _b	226	- ^b	391	480	507	56
II _c	255	-	401	467	518	54
II _d	-	392	396	496	519	61
II _e	-	438	442	494	498	69
II _f	273	-	390	470	482	60
II _g	243	-	385	493	551	55
III	-	-	411	505	687	45
IV _a	-	473	424	478	486	69
IV _b	-	462	420	491	488	63
IV _c	-	437	419	492	515	66

^aFrom d.s.c. measurements conducted at a heating rate of 20°C min⁻¹

^bNo *T*_g or *T*_m was observed in d.s.c. trace

^cInitial decomposition temperature (IDT), temperature at 10% mass loss (PDT), and maximum decomposition temperature (PDT_{max}) were determined by TG in nitrogen at a heating rate of 20°C min⁻¹

^dChar yield at 800°C in nitrogen

mass loss were in the range of 467–496°C in nitrogen and the char yields at 800°C in nitrogen atmosphere exceed 54%. Experimental results indicate that unsubstituted polyamide III exhibits the lowest initial decomposition temperature and char yield, possibly due to its low molar mass. Considering these three copolymers, there is no significant difference between their decomposition temperatures. Thus, the above result demonstrates that the methyl substituent in polymer backbone only slightly influences the polymer's thermal stability.

Properties of polyimides

The wide angle x-ray diffractograms of polyimides VI and polyimide Ref. 1 are given in Figure 5. Polyimide VI_d containing benzophenone moiety showed a little crystallinity, whereas all the other DBAPB-based polyimides showed amorphous patterns. In contrast, the polyimide Ref. 1 containing unsubstituted biphenylene unit exhibited relatively higher crystalline patterns than polyimide VI_a. This may be due to a better packing of its polymer backbone than polyimide VI_a containing 2,2'-dimethyl substituted biphenylene. This is quite reasonable because the presence of noncoplanar conformation decreases the intermolecular forces between the polymer chains, subsequently causing a decrease in crystallinity.

The solubility behaviour of polyimides VI and polyimide

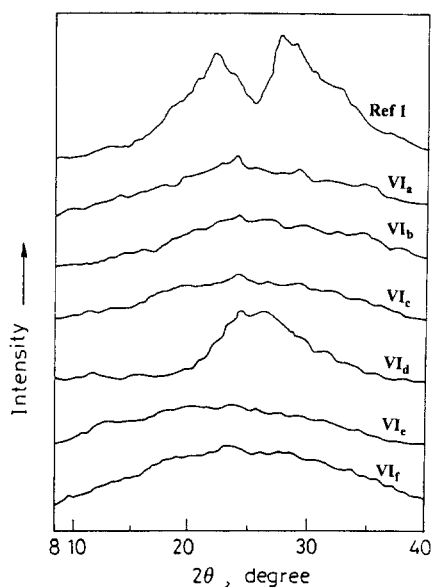


Figure 5 Wide-angle x-ray diffractograms of polyimides VI_{a-f} and Ref. 1

Ref. 2 is shown in Table 7. Polyimides VI_{a-d} and Ref. 2 were almost insoluble in the tested solvents but dissolved in concentrated sulfuric acid. However, polyimides (VI_e and VI_f) derived from dianhydrides SDPA and 6FDA were highly soluble in organic solvents such as NMP, DMAc, DMF and *m*-cresol. This result revealed that the solubility of polyimide VI_e is greatly superior to that of polyimide Ref. 2 in all organic solvents, indicating the solubility of polyimide was improved by the noncoplanar conformation of 2,2'-dimethyl substituted biphenylene in the polymer backbone.

The mechanical properties of the polyimide films prepared by the thermal imidisation are summarised in Table 8. The polyimide films had tensile strength of 83–139 MPa, elongation at break of 5–9%, and initial modulus of 1.81–2.68 GPa. Most of the polymer films exhibited high tensile strength, high modulus and low elongation; thus, they could be considered as hard and strong materials.

Table 9 presents the thermal properties of the polyimides. Polyimide VI_d which exhibits crystalline nature showed a melt endothermic peak around 336°C in the first heating trace of d.s.c. measurements. The polyimides had T_gs in the range 239–303°C. As expected oxy-bridge containing polyimide VI_c had the lowest T_g, while pyromellitimide containing polyimide VI_a had the highest. The high T_g of VI_e can be attributed to the presence of polar group of sulfonyl unit¹⁹. The T_g order was comparable to the decreasing order of stiffness and polarity of the polymer backbones. It was found that polyimide Ref. 1 showed no discernible transition in the d.s.c. traces. This indicates that its transition temperature is above the decomposition temperature, and is not mouldable. In contrast, polyimide VI_a containing noncoplanar conformation of 2,2'-dimethyl-biphenylene unit had lower transition temperature than polyimide Ref. 1 containing unsubstituted-biphenylene. Thus, incorporation of the noncoplanar 2,2'-dimethyl substituted biphenylene into the polymer backbone markedly lowers the polymer transition temperature.

Table 8 Mechanical properties of polyimides

Polymer	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
VI _a	92	7	2.25
VI _b	83	6	2.68
VI _c	138	9	2.19
VI _d	139	8	1.81
VI _e	89	5	2.23
VI _f	98	8	2.53

Table 7 Solubility of polyimides^a

Polymer	Solvent ^b						
	NMP	DMSO	DMAc	DMF	<i>m</i> -Cresol	Py	Conc. H ₂ SO ₄
VI _a	–	–	–	–	–	–	++
VI _b	–	–	–	–	+	–	++
VI _c	+ –	–	–	–	+	–	++
VI _d	–	–	–	–	–	–	++
VI _e	++	+ –	++	++	++	+ –	++
VI _f	++	+	++	++	++	++	++
Ref. 2	–	–	–	–	–	–	++

^aSolubility: ++, soluble at room temperature; +, soluble on heating; + –, partial soluble; –, insoluble

^bAbbreviations: NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethylsulfoxide; DMF, *N,N*-dimethylformamide; Py, pyridine

Table 9 Thermal properties of polyimides

Polymer	T_g (°C) ^a	T_m (°C) ^a	T_i (°C) ^c	T_{10} (°C) ^c	Char yield ^d (%)
VI _a	303	— ^b	462	511	55.1
VI _b	253	—	451	506	45.9
VI _c	239	—	474	529	59.0
VI _d	256	336	457	527	64.1
VI _e	275	—	411	488	59.5
VI _f	258	—	475	534	59.2

^aFrom d.s.c. measurements conducted at a heating rate of 20°C min⁻¹^bNo T_m was observed in d.s.c. trace^cInitial decomposition temperature (T_i) and temperature at 10% mass loss determined by TG in nitrogen at a heating rate of 20°C min⁻¹^dChar yield at 800°C in nitrogen

These polyimides were stable up to a temperature around or below 450°C. Their decomposition temperatures of 10% mass loss were in the range 488–534°C in nitrogen. The amount of carbonised residue of all polyimides at 800°C in nitrogen atmosphere was higher than 45.9%, and the polyimide VI_d had the highest char yield up to 64.1%. Among the polyimides, VI_e derived from dianhydride SDPA had the lowest initial decomposition temperature and 10% mass loss temperature; thus showing less thermal stability.

CONCLUSIONS

This study successfully prepared the new diamine containing noncoplanar 2,2'-dimethyl-biphenylene and flexible aryl ether units. In addition, moderate to high inherent viscosities of polyamides and polyimides were obtained. These polyamides and polyimides derived from the new diamine DBAPB exhibit good mechanical properties, thermal stability and processability. Thus, these DBAPB-based polyamides and polyimides are promising soluble high-temperature polymeric materials. Results presented herein also clearly demonstrate that incorporating 2,2'-dimethyl substituted biphenylene into polymer backbone markedly lowers the transition temperatures and enhances the rod-like polymer's solubilities.

ACKNOWLEDGEMENTS

The authors thank the National Science Council of the Republic of China for support of this work, under grant NSC 87-2216-E011-015.

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