

Aromatic Polyimides from *m*-Phenylene Diamines Containing Pendant Groups: Synthesis and Characterization

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ABSTRACT: Two diamine monomers, 4-[4-(1-methyl-1-phenylethyl)phenoxy]-1,3-diamino benzene and 4-[4-[(4-methylphenyl)sulfonyl]phenoxy]-1,3-diamino benzene, were synthesized, and both diamines were polycondensed with three commercial dianhydrides to obtain aromatic polyimides containing pendant groups. The polyimides were characterized by solubility tests, viscosity measurements, IR, ¹H-NMR, and ¹³C-NMR spectroscopy, X-ray diffraction studies, and thermogravimetric analysis. The polyimides had inherent viscosities of 0.33–0.58 dL/g in *m*-cresol at 30 ± 0.1°C. All the polyimides

were amorphous and were soluble in solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, and *m*-cresol. Thermogravimetric analysis of the polyimides indicated no weight loss below 410°C under a nitrogen atmosphere. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1377–1384, 2005

Key words: heteroatom-containing polymers; high performance polymers; polyimides

INTRODUCTION

Aromatic polyimides possess high glass-transition and melting temperatures, which lead to their limited solubility and hence limit their usefulness for many applications.^{1–3} The chemistry of aromatic polyimides has undergone outstanding development in the last few years.

Many novel species have been prepared by the polycondensation of dianhydrides and diamines specially designed to overcome the traditional processing problems caused by the limited solubility and tractability of polyimides. Some approaches, such as the incorporation of flexible or bridging functional groups,^{4–7} bulky pendant groups,^{8–11} or cardo groups,^{12–14} copolymerization,¹⁵ and meta or ortho catenation of less symmetric aromatic units,^{16–20} have shown success in the preparation of organosoluble polyimides.

This investigation reports the synthesis of aromatic polyimides with two diamine monomers, 4-[4-(1-methyl-1-phenylethyl)phenoxy]-1,3-diamino benzene

(**3a** or CDA) and 4-[4-[(4-methylphenyl)sulfonyl]phenoxy]-1,3-diamino benzene (**3b** or SDA), and commercial dianhydrides by a one-step polymerization method.

EXPERIMENTAL

Materials

1-Chloro-2,4-dinitrobenzene (S.D. Fine, India) and 10% palladium on activated carbon (Pd/C; Aldrich) were used as received. 4-(2-Phenylisopropyl)phenol (PCP; Ms. Herdillia Chemicals, Ltd., India) was used after recrystallization from petroleum ether. 4-Hydroxy-4'-methylidiphenylsulfone (MSP) was synthesized by the reported procedure.²¹ Pyromellitic dianhydride (PMDA; Aldrich), 3,3', 4,4'-biphenyltetracarboxylic dianhydride (BPDA; Aldrich), and 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA; Aldrich) were used after sublimation. *m*-Cresol (S.D. Fine) was purified by distillation, and *N,N*-dimethylacetamide (DMAc; S.D. Fine) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

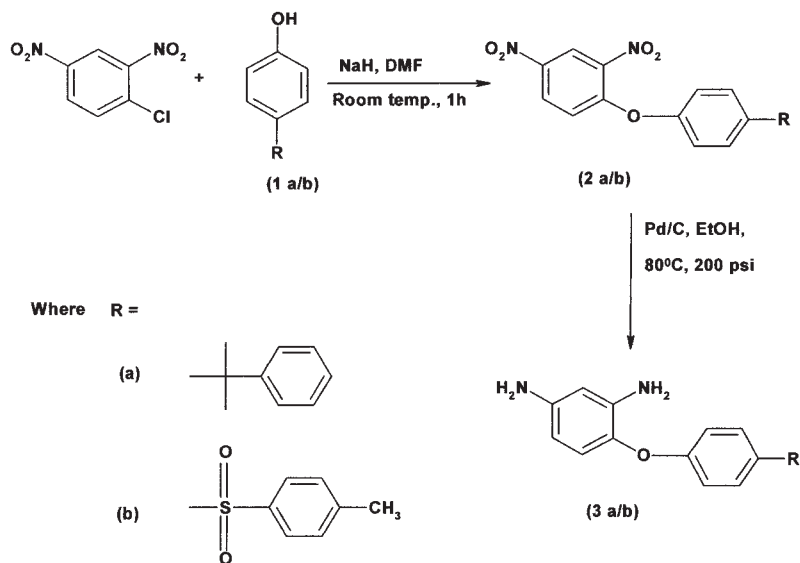
Monomer synthesis

3a and **3b** were prepared in two steps by the aromatic nucleophilic displacement of 1-chloro-2,4-dinitrobenzene with sodium salts of PCP or MSP, respectively, to

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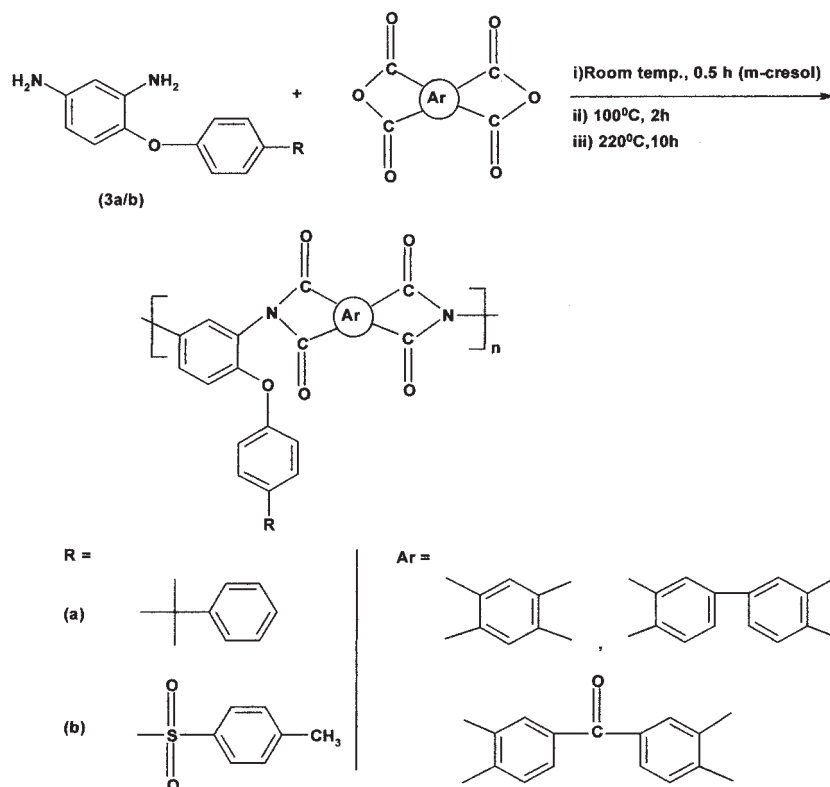


Scheme 1

produce the corresponding dinitro compounds, 4-[4-(1-methyl-1-phenylethyl)phenoxy]-1,3-dinitrobenzene (2a) and 4-[4-[(4-methylphenyl)sulfonyl]phenoxy]-1,3-dinitrobenzene (2b); this was followed by their reduction under hydrogen pressure with 10% Pd/C as the catalyst. The detailed procedure for the preparation of the diamines is as follows.

2a

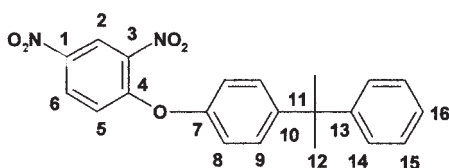
Into a 250-mL, round-bottom flask containing PCP (10.6 g, 0.05 mol) and *N,N*-dimethylformamide (DMF; 100 mL), sodium hydride (1.2 g, 0.05 mol) was added under cooling. The solution was stirred for 10 min, and then 1-chloro-2,4-dinitrobenzene (10.1 g, 0.05 mol)



Scheme 2

was added slowly to this reaction mixture. After the addition, the solution was stirred for 1 h at room temperature. Then, the reaction mixture was poured into ice. The crude product was filtered and washed well with water. The product was purified from pet ether/CHCl₃ (80:20 v/v) to give pure **2a**.

Yield: 17.50 g (93%). mp: 124°C. IR (KBr, cm⁻¹): 1530 (asymmetric NO₂ stretching), 1350 (symmetric NO₂ stretching), 1250 and 1060 (C—O—C stretching). ¹H-NMR (500 MHz, CDCl₃, δ): 8.84 (1H, d, H-2), 8.3 (1H, dd, H-6), 7.29–7.34 (4H, m, H-9 and H-14), 7.19–7.25 (3H, m, H-5 and H-8), 7.02–7.06 (3H, m, H-15 and H-16), 1.72 (6H, s, H-12). ¹³C-NMR (500 MHz, CDCl₃, δ, ppm): 156.3 (C₇), 151.2.9 (C₄), 149.8 (C₁), 149.4 (C₃), 141.2 (C₁₀), 139.4 (C₁₃), 129.0 (C₁₄), 128.6 (C₉), 128.1 (C₆), 126.6 (C₁₅), 125.9 (C₁₆), 122.0 (C₅), 119.9 (C₈), 118.2 (C₂), 42.8 (C₁₁), 30.7 (C₁₂). Mass [*m/e* (relative intensity)]: M⁺ 378 (50%), 363 (100%), 196 (55%), 181 (25%), 91 (20%).



2b

Into a 250-mL, round-bottom flask containing MSP (12.4 g, 0.05 mol) and DMF (100 mL), sodium hydride (1.2 g, 0.05 mol) was added under cooling. The solution was stirred for 10 min, and then 1-chloro-2,4-dinitrobenzene (10.1 g, 0.05 mol) was added slowly to this reaction mixture. After the addition, the solution was stirred for 1 h at room temperature. Then, the reaction mixture was poured into ice. The crude product was filtered and washed well with water. The crude product was purified by column chromatography with pet ether/CHCl₃ (80:20 v/v) as the eluent.

Yield: 19.6 g (95%). mp: 164°C. IR (KBr, cm⁻¹): 1530 (asymmetric NO₂ stretching), 1350 (symmetric NO₂ stretching), 1330, 1140 (—SO₂ stretching), 1250 and 1060 (C—O—C stretching). ¹H-NMR (500 Hz, CDCl₃, δ): 8.9 (1H, d, H-2), 8.4 (1H, dd, H-6), 8.0 (2H, d, H-12), 7.9 (2H, d, H-9), 7.3 (2H, d, H-13), 7.2 (2H, d, H-8), 7.1 (1H, d, H-5), 2.3 (3H, s, H-15). ¹³C-NMR (500 MHz, CDCl₃, δ, ppm): 157.8 (C₇), 153.9 (C₄), 144.6 (C₁), 142.8 (C₃), 140.5 (C₁₁), 139.4 (C₁₀), 138 (C₁₄), 130.3 (C₉), 130.1 (C₁₂), 129.0 (C₆), 127.7 (C₁₃), 122.1 (C₅), 120.6 (C₂), 120.1 (C₈), 21.5 (C₁₅). Mass [*m/e* (relative intensity)]: M⁺ 414 (50%), 167 (55%), 139 (100%), 91 (40%), 65 (20%).

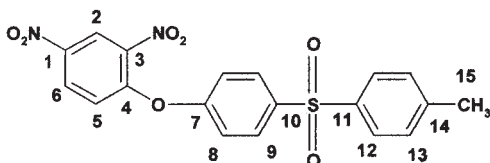


TABLE I
Synthesis of Polyimides Containing Pendant Groups

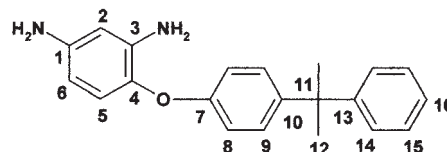
Polyimide	Diamine	Dianhydride	Yield (%)	η_{inh} (dL/g) ^a
PI-1	CDA	PMDA	97	0.33
PI-2	CDA	BPDA	98	0.45
PI-3	CDA	BTDA	99	0.53
PI-4	SDA	PMDA	99	0.35
PI-5	SDA	BPDA	98	0.50
PI-6	SDA	BTDA	99	0.58

^a Measured at a concentration of 0.5 g/dL at 30 ± 0.1°C in *m*-cresol.

3a

The dinitro compound (**2a**; 18.90 g, 0.05 mol) and 10% Pd/C (1.65 g, 8 wt %) catalyst were added to ethanol (80 mL), and the mixture was placed in a Parr hydrogenation apparatus. After 2 h at 80°C and 200 psi of hydrogen pressure, the solution was filtered. The solution was concentrated, and the crude diamine was isolated. The diamine was crystallized from a hexane-ethanol mixture (80:20 v/v).

Yield: 15.0 g (95%). mp: 98°C. IR (KBr, cm⁻¹): 3366 (—N—H stretching), 1618 (—N—H bending), 1222, 1060 (—C—O—C stretching).



¹H-NMR (500 MHz, CDCl₃, δ): 7.2–7.3 (4H, m, H-9, 14), 7.1–7.2 (3H, m, H-15 and H-16), 6.85 (2H, d, H-8), 6.75 (1H, d, H-5), 6.25 (1H, s, H-2), 6.1 (1H, d, H-6), 3.7 (4H, s, —NH₂), 1.65 (6H, s, H-12). ¹³C-NMR (500 MHz, CDCl₃, δ, ppm): 156.3 (C₇), 150.7 (C₄), 144.2 (C₁), 143.6 (C₃), 139.7 (C₁₃), 135.4 (C₁₀), 127.97 (C₁₄), 127.91 (C₉), 126.7 (C₁₆), 125.5 (C₁₅), 122.3 (C₅), 115.3 (C₈), 105.9 (C₆), 103.3 (C₂), 42.3 (C₁₁), 30.8 (C₁₂). Mass [*m/e* (relative intensity)]: M⁺ 318 (100%), 303 (50%), 123 (65%), 95 (25%).

3b

The dinitro compound (**2b**; 20.70 g, 0.05 mol) and 10% Pd/C (1.65 g, 8 wt %) catalyst were added to ethanol (80 mL), and the mixture was placed in a Parr hydrogenation apparatus. After 2.5 h at 80°C and 200 psi of hydrogen pressure, the solution was filtered. The solution was concentrated, and the crude diamine was isolated. The diamine was purified by a neutral alumina column with chloroform and ethanol (99:1 v/v) as a solvent system.

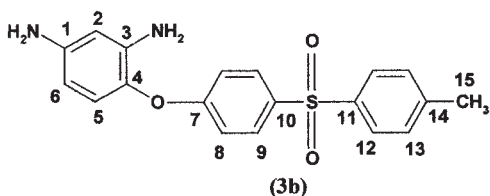
Yield: 15.05 g (85%). mp: 184°C. IR (KBr, cm⁻¹): 3366 (—N—H stretching), 1618 (—N—H bending), 1330,

TABLE II
Spectral Assignments for the Protons and Carbons of Polyimides Containing Pendant Groups

$^1\text{H-NMR}$ of PI-6		$^{13}\text{C-NMR}$ of PI-6					
δ (ppm)	P	δ (ppm)	C	δ (ppm)	C	δ (ppm)	C
8.24–8.05	i, j, and k	194.0	24	136.4	10	129.4	19
7.89–7.68	e, e', f, and f'	166.0	16	135.8	21	128.3	6
7.57–7.35	a, b, c, d, and d'	165.4	17	134.6	18	127.2	13
7.16	g and g'	159.8	7	134.3	23	123.9	5
2.25	h	150.9	4	131.8	22	121.0	2
		144.2	1	131.5	20	118.7	8
		141.6	3	130.1	9	20.9	15
		138.8	11	129.7	12		

P = proton.

1140 ($-\text{SO}_2$ stretching), 1250 and 1060 ($\text{C}-\text{O}-\text{C}$ stretching).



$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ): 7.8 (4H, m, H-9, 12), 7.3 (2H, d, H-8), 6.9–7.0 (2H, d, H-13), 6.7 (1H, d, H-5), 6.2–6.1 (1H, d, H-2), 6.1 (1H, dd, H-6), 3.6 (4H, s, $-\text{N}-\text{H}$), 2.4 (3H, s, H-15). $^{13}\text{C-NMR}$ (500 MHz,

CDCl_3 , δ , ppm, δ): 162.40 (C_7), 145.0 (C_4), 143.72 (C_{11}), 139.61 (C_1), 139.23 (C_3), 134.70 (C_{10}), 133.51 (C_{14}), 129.80 (C_9), 129.74 (C_{12}), 127.41 (C_{13}), 122.50 (C_5), 116.0 (C_8), 105.81 (C_6), 103.0 (C_2), 21.51 (C_{15}). Mass [m/e (relative intensity)]: M^+ 354 (100%), 123 (50%).

Polymer synthesis

A typical polymerization procedure was as follows. To a three-necked, round-bottom flask fitted with an N_2 inlet, a reflux condenser with a guard tube, a thermowell, and a magnetic stirring bar, the diamine (3a; 0.318 g, 1 mmol) and *m*-cresol (5 mL) were added, and the solution was stirred at room temperature.

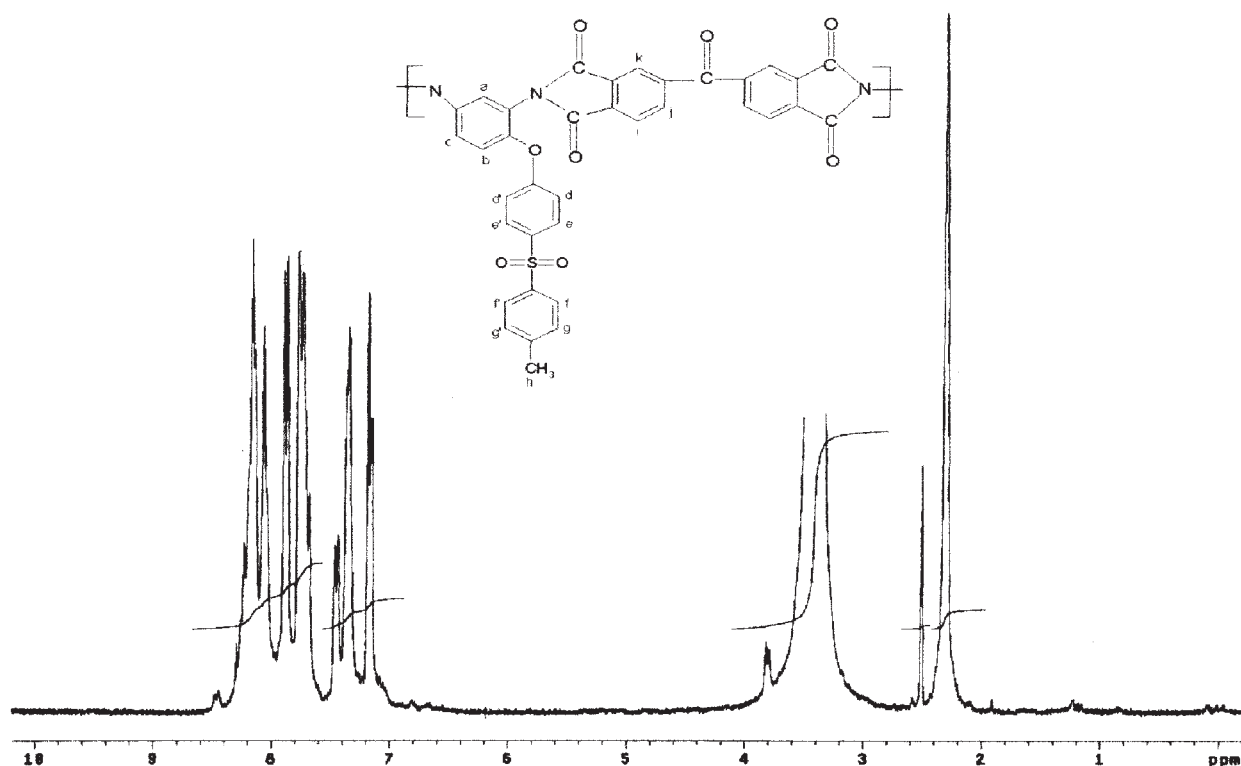


Figure 1 $^1\text{H-NMR}$ spectrum of PI-6.

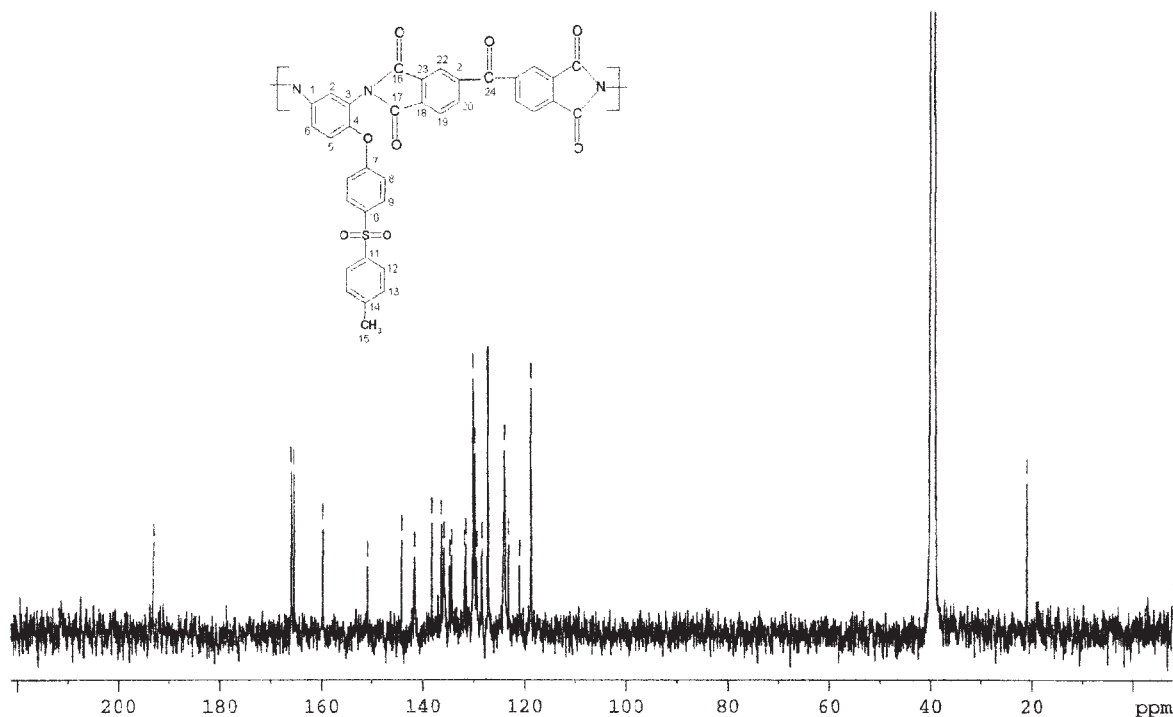


Figure 2 ^{13}C -NMR spectrum of PI-6.

PMDA (0.218 g, 1 mmol) was added, and the solution was stirred at room temperature for 0.5 h and then heated at 100°C for 2 h. After that, the reaction temperature was slowly raised to 220°C and heated at that temperature for 10 h. The viscous solution was cooled and poured into methanol. The polymer was filtered and washed with methanol. The polymer was dried at 150°C for 12 h and was further baked at 250°C for 30 min to ensure complete imidization. All the other polyimides were synthesized by a similar procedure.

Measurements

The inherent viscosity (η_{inh}) measurements were performed with a 0.5% (w/v) solution of polyimides in *m*-cresol at $30 \pm 0.1^\circ\text{C}$ with an Ubbelohde suspended level viscometer. The IR spectra of the polyimides were recorded on a PerkinElmer 1600 Fourier trans-

form infrared (FTIR) spectrometer with a KBr pellet technique. ^1H - and ^{13}C -NMR spectra of the monomers (in CDCl_3) and polymers [in dimethyl sulfoxide- d_6 ($\text{DMSO}-d_6$)] were recorded on a Bruker AMX 500-MHz spectrophotometer. The mass spectra of the monomers were taken on a Hewlett-Packard G 1800A GCD system. The thermogravimetric analysis (TGA) was performed with a Netzsch 409 thermal analyzer. The measurements were recorded under an N_2 atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The differential scanning calorimetry (DSC) was performed on a DSCQ100V instrument at a heating rate of $10^\circ\text{C}/\text{min}$. Wide-angle X-ray diffraction (WAXD) measurements were made with the powder form of polyimide at room temperature on a Joel JDX-8030 X-ray diffractometer (operating at 30 kV and 30 mV) with nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The scanning rate was $1.0^\circ/\text{min}$ over the range of $2\theta = 10\text{--}50^\circ$.

TABLE III
Solubility Behavior Data of the Polyimides Containing Pendant Groups

Polyimide	DMF	DMAc	NMP	DMSO	<i>m</i> -Cresol	CHCl_3	THF	1,4-Dioxane	Pyridine	H_2SO_4
PI-1	+	+	+	\pm	+	\pm	–	–	–	+
PI-2	+	+	+	\pm	+	\pm	\pm	\pm	–	+
PI-3	+	+	+	+	+	+	+	+	++	+
PI-4	+	+	+	\pm	+	\pm	–	–	–	+
PI-5	+	+	+	++	+	+	\pm	–	–	+
PI-6	+	+	+	+	+	+	+	+	++	+

+ = soluble at room temperature; ++ = soluble after heating; \pm = partially soluble after heating; – = insoluble.

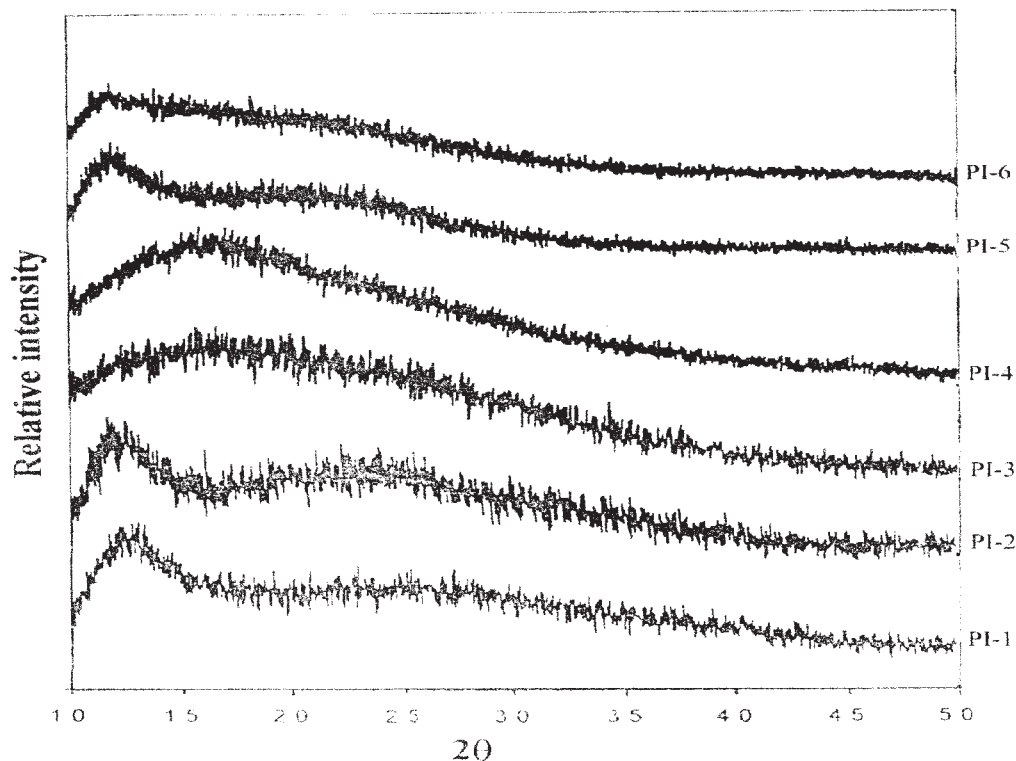


Figure 3 X-ray diffractograms of polyimides.

RESULTS AND DISCUSSION

Monomer synthesis

The synthesis of two diamine monomers, **3a** and **3b**, was achieved in two steps according to Scheme 1. The intermediate dinitro compounds, **2a** and **2b**, were synthesized by the aromatic nucleophilic displacement

reaction of 1-chloro-2,4-dinitrobenzene with PCP and MSP in the presence of NaH in DMF at room temperature. The diamine monomers **3a** and **3b** were obtained by the catalytic hydrogenation of the dinitro compounds (**2a** and **2b**) with 10% Pd/C in a Parr hydrogenation apparatus. Of the two diamine monomers, CDA is reported in the patent literature, but

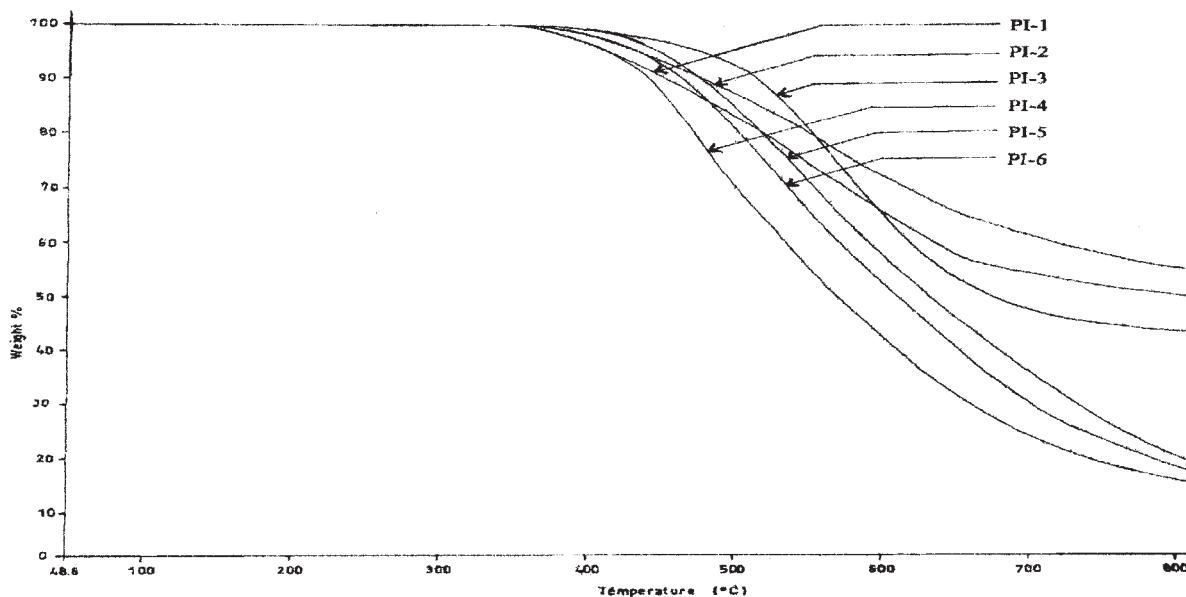


Figure 4 TG curves of polyimides.

TABLE IV
Thermal Behavior Data of Polyimides Containing
Pendant Groups

Polymer	T_g (°C) ^a	IDT (°C)	Temperature (°C) at various weight loss percentages			
			T_{10}	T_{20}	T_{30}	T_{40}
PI-1	340	420	500	575	575	625
PI-2	275	435	470	550	610	700
PI-3	267	470	490	555	580	615
PI-4	320	410	450	482	580	625
PI-5	281	420	480	555	620	695
PI-6	293	415	465	525	580	665

IDT = initial decomposition temperature.

^a Measured by DSC at a heating rate of 10°C/min.

there are no physical data available for this diamine,²² whereas the other diamine, SDA, is a new compound. The structures of the diamine monomers (**3a** and **3b**) and dinitro compounds (**2a** and **2b**) were ascertained by IR, ¹H-NMR, ¹³C-NMR, and mass spectroscopy. All the spectral data are given in the Experimental section.

Polyimide synthesis

Aromatic polyimides were prepared by a one-step procedure from diamines **3a** and **3b** with three different commercially available aromatic dianhydrides with *m*-cresol as a solvent²³ (Scheme 2). The viscosity of the polyimides was recorded in the *m*-cresol solvent (Table I). These polyimides had reasonably high molecular weights, and tough, transparent, and flexible films could be cast from *m*-cresol solutions of the polyimides.

Polymer characterization

FTIR spectroscopy studies of all the polyimides exhibited characteristic absorption bands for the imide ring at 1776 and 1723 cm⁻¹ (asymmetrical and symmetrical C=O stretching vibrations). The polyimides also showed peaks at 1398 (C—N stretching), 1222 and 1060 (C—O—C stretching), and 1100 and 737 cm⁻¹ (imide-ring deformation). Strong absorption bands at 1330 and 1140 cm⁻¹ were observed for polyimides containing a sulfone group.

¹H- and ¹³C-NMR spectra of all the polyimides were consistent with their structure. As an example, ¹H- and ¹³C-NMR spectra of polyimide PI-6 along with their proton or carbon assignments (Table II) are presented in Figures 1 and 2, respectively.

The solubility characteristics of the polyimides are shown in Table III. A 3% (w/v) solution was taken as a criterion for the solubility. All the polyimides dissolved readily at room temperature in dipolar solvents such as *N*-methyl-2-pyrrolidone (NMP), DMAc, and DMF. Polyimides were also soluble in *m*-cresol and concentrated H₂SO₄. Polyimides PI-3 and PI-6 were also soluble in some other solvents such as chloroform and tetrahydrofuran. The bulky pendant groups of the aromatic diamine reduced the interactions among the polyimide chains and thus improved the solubility.

The WAXD patterns of all the polyimides are presented in Figure 3. The results revealed that all the polyimides were amorphous in nature. The amorphous nature of the polyimides could be attributed to their asymmetric structural units because of the incorporation of bulky pendant groups.

The thermal properties of these polymers were assessed by DSC and TGA. The thermal stability of the

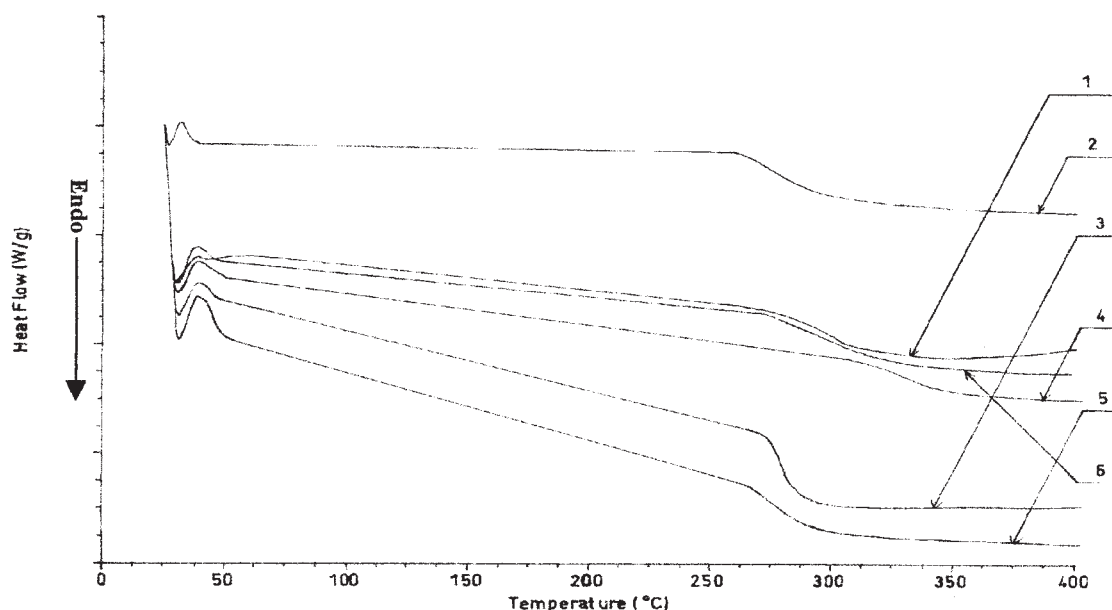


Figure 5 DSC curves of polyimides.

polyimides containing bulky pendant groups were determined by TGA under a nitrogen atmosphere at a heating rate 10°C/min. Thermogravimetric (TG) curves (Fig. 4) of all the polyimides showed more or less similar patterns of decomposition. The temperature characteristics, such as the initial decomposition temperature, temperature for 10% weight loss, and glass-transition temperature (T_g), are given in Table IV. These polyimides displayed distinct T_g 's in the second-heating DSC traces (Fig. 5). These polyimides had T_g 's in the range of 267–340°C, depending on the structure of the diamine and dianhydride. As expected, the polymer containing the most rigid dianhydride PMDA exhibited the highest T_g value. The results showed that the heat-resistance temperature of the polyimides varied from 410 to 470°C (the sharp drop in the TG curve was taken as the onset of decomposition), thus indicating good thermal stability.

CONCLUSIONS

The aromatic polyimides were synthesized from *m*-phenylene diamines containing pendant groups with aromatic dianhydrides. The solubility of these polyimides in organic solvents was significantly improved with the incorporation of pendant groups, and good thermal stability was maintained.

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