Polyimides Derived from Novel Asymmetric Ether Diamine

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ABSTRACT: A new aromatic asymmetrical ether diamine, 5-(4-aminophenoxy)-1-naphthylamine, was synthesized through the nucleophilic displacement of 4-chloronitrobenzene with the potassium phenolate of 5-amino-1-naphthol in dimethylformamide, followed by hydrazine palladium-catalyzed reduction. A series of novel aromatic polyimides containing asymmetrical diaryl ether segments were prepared from the diamine with various aromatic dianhydrides via a conventional two-step thermal or chemical imidization method. The poly(amic acid) precursors had inherent viscosities of 1.21–1.99 dL/g, and all of them could be cast and thermally converted into transparent, flexible, and tough polyimide films. The polyimides derived from less stiff dianhydrides generally displayed higher solubility. The glass-transition temperatures of these polyimides were recorded between 307 and 336 °C by differential scanning calorimetry, and the softening temperatures of the polymer films were 299–344 °C according to thermomechanical analysis. The polyimides showed insignificant decomposition before 520 °C in air or nitrogen. For a comparative study, two series of analogous polyimides based on symmetrical diamines such as 1,5-diaminonaphthalene and 1,5-bis(4-aminophenoxy)naphthalene were also prepared and characterized. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 331–341, 2005

Keywords: asymmetric ether diamine; polyimides; solubility; structure-property relations; thermal properties

INTRODUCTION

Aromatic polyimides are a class of advanced materials because of their high-temperature stability, excellent mechanical and electrical properties, and good chemical resistance.[1–3] Despite their outstanding properties, most of them have high melting temperatures or softening temperatures (T_s's) and limited solubility in most solvents because of their rigid backbones and strong between-chain interactions, which may restrict their application in some fields. Therefore, several modifications of the chemical structure have been made to enhance their processability and solubility while other advantageous polymer properties are retained.[4,5] Typical approaches include the introduction of flexible or kinked linkages,[6–10] bulky lateral or cardo groups,[11–16] noncoplanar structures,[17–20] and spiro-skeletons[21–26] into the polymer backbone.

Ether linkages are the most popular, flexible linkages introduced into polyimide backbones. It is generally recognized that an aryl–ether linkage imparts properties such as better solubility and melt-processing characteristics and improved toughness in comparison with those of polymers without an aryl–ether linkage. Recently, one attractive method for improved processability has been to incorporate geometrically or molecularly asymmetric dianhydride components into the

polyimide main chain.[27–33] These structural modifications for dianhydride monomers have led to new polyimides with improved solubility and melt processability and other desirable properties.

Recently, there have been many reports on naphthalene-based polyimides.[34–37] 1,5-Diaminonaphthalene (1,5-DAN) has a symmetric and rigid molecular structure, and its derived polyimides generally exhibit low solubility and high melting temperatures and T_s's, together with a highly brittle character. Previous investigations have shown that polyimides derived from 1,5-bis(4-aminophenoxy)naphthalene (1,5-BAPON) display many desirable properties, except for relatively poor solubility.[38] Inserting one phenoxy unit into 1,5-DAN produces a new asymmetric ether diamine, 5-(4-aminophenoxy)-1-naphthylamine (**2**), which to our knowledge has not been reported in the literature. Because the new monomer is molecularly asymmetric, the resulting polyimides should possess three possible dyads in the main chain, which may lead to better solubility than that of 1,5-DAN- and 1,5-BAPON-based polyimides and retain other desirable properties such as high thermal stability.

EXPERIMENTAL

Reagents and Solvents

5-Amino-1-naphthol (TCI), 1,5-DAN (TCI), potassium carbonate (K_2CO_3; Fluka), 4-chloronitrobenzene (Acros), 10% palladium on charcoal (Pd/C; Fluka), and hydrazine monohydrate (Wako) were used as received. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves. Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (**3a** or PMDA; Aldrich) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**3c** or BTDA; Aldrich) were purified by recrystallization from acetic anhydride. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (**3b** or BPDA; Oxychem), 4,4′-oxydiphthalic dianhydride (**3d** or ODPA; Oxychem), 3,3′4,4′-diphenylsulfonetetracarboxylic dianhydride (**3e** or DSDA; New Japan Chemical Co.), and 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (**3f** or 6FDA; Hoechst Celanese) were heated at 250 °C *in vacuo* for 3 h before use. According to a reported method,[38] the bis(ether amine) 1,5-BAPON (mp = 170–171 °C) was prepared from the aromatic chloro-displacement reaction of *p*-chloronitrobenzene with 1,5-dihydroxynaphthalene in the presence of K_2CO_3 in *N,N*-dimethylformamide (DMF) and the subsequent Pd/C-catalyzed hydrazine reduction of the intermediate dinitro compound.

Synthesis of 5-(4-Nitrophenoxy)-1-naphthylamine (1)

In a 250-mL flask, a reaction solution of 5-amino-1-naphthol (10.03 g, 0.063 mol), *p*-chloronitrobenzene (10 g, 0.063 mol), and K_2CO_3 (8.7 g, 0.063 mol) in 100 mL of DMF was heated at the reflux temperature for 10 h. After cooling, the mixture was poured into 400 mL of a saturated aqueous sodium chloride solution. The precipitated brown solid was washed repeatedly with water and dried to give a dark brown product [16.4 g, 93%; mp = 115–117 °C (onset to the peak top temperature) according to differential scanning calorimetry (DSC) at a scanning rate of 5 °C/min].

ELEM. ANAL. Calcd. for $C_{16}H_{12}N_2O_3$ (280.28): C, 68.57%; H, 4.32%; N, 9.99%. Found: C, 68.95%; H, 4.12%; N, 9.96%. IR (KBr; Fig. 1): 1512, 1342 (—NO_2), 1250 cm^{-1} (C—O). ^{1}H NMR [deuterated dimethyl sulfoxide (DMSO-d_6), δ, ppm; for the assignment of peaks, see Fig. 2(a)]: 8.15 (d, J = 8.6 Hz, 2H, H_h), 7.90 (d, J = 8.3 Hz, 1H, H_d), 7.42 (t, J = 7.7 Hz, 1H, H_e), 7.22 (d, J = 6.6 Hz, 2H, H_b, H_c), 7.15 (d, J = 7.1 Hz, 1H, H_f), 6.99 (d, J = 8.6 Hz, 2H, H_g), 6.81 (d, J = 5.8 Hz, 1H, H_a), 4.99 (2H, —NH_2). ^{13}C NMR [DMSO-d_6, δ, ppm; for the assignment of peaks, see Fig. 3(a)]: 164.1 (C^{11}), 150.2 (C^5), 143.9 (C^1), 142.2 (C^{14}), 127.7 (C^{10}), 127.4 (C^3), 125.9 (C^{13}), 125.0 (C^9), 123.9 (C^7), 119.7 (C^8), 116.7 (C^4), 116.4 (C^{12}), 110.5 (C^2), 109.7 (C^6).

Synthesis of 5-(4-Aminophenoxy)-1-naphthylamine (2)

A mixture of nitro compound **1** (16 g, 0.057 mol), 10% Pd/C (0.2 g), ethanol (150 mL), and hydrazine monohydrate (10 mL) was heated at the reflux temperature for about 4 h. The reaction solution was filtered while hot to remove Pd/C, and the filtrate was poured into a saturated aqueous sodium chloride solution to give a light brown precipitate that was isolated by filtration and dried *in vacuo* (10.2 g, 71%; mp = 109–110 °C according to DSC at 5 °C/min).

ELEM. ANAL. Calcd. for $C_{16}H_{14}N_2O$ (250.30): C, 76.78%; H, 5.64%; N, 11.19%. Found: C, 76.22%;
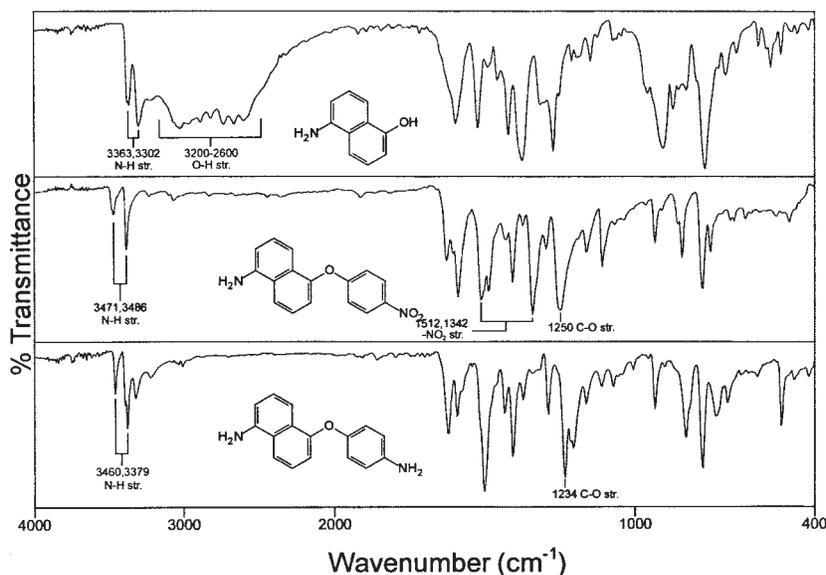
Figure 1. FTIR spectra of 5-amino-1-naphthol (top), **1** (middle), and **2** (bottom).

H, 5.68%; N, 11.24%. IR (KBr; Fig. 1): 3460, 3379 (—NH$_2$), 1234 cm^{-1} (C—O). ^{1}H NMR [DMSO-d_6, δ, ppm; for the assignment of peaks, see Fig. 2(b)]: 7.66 (d, J = 8.4 Hz, 1H, H$_d$), 7.53 (d, J = 8.4 Hz, 1H, H$_c$), 7.25 (t, J = 7.8 Hz, 1H, H$_e$), 7.22 (t, J = 7.7 Hz, 1H, H$_b$), 6.84 (d, J = 8.7 Hz, 2H, H$_g$), 6.79 (d, J = 7.3 Hz, 1H, H$_a$), 6.70 (d, J = 7.6 Hz, 1H, H$_f$), 6.66 (d, J = 8.7 Hz, 2H, H$_h$), 4.57 (2H, —NH$_2$), 3.15 (2H, —NH$_2$). ^{13}C NMR [DMSO-d_6, δ, ppm; for the assignment of peaks, see Fig. 3(b)]: 155.0 (C^5), 148.2 (C^{11}), 143.5 (C^1), 142.9 (C^{14}), 127.0 (C^{10}), 126.1 (C^3), 124.6 (C^9), 124.1 (C^7), 120.6 (C^{12}), 115.9 (C^{13}), 115.3 (C^4), 111.5 (C^8), 110.5 (C^2), 109.7 (C^6).

Polymer Synthesis

The polyimides were synthesized from various dianhydrides and diamine **2** via a two-step method. The synthesis of polyimide **5a** is used as an example to illustrate the general synthetic route used to produce the polyimides. To a solution of 0.8015 g (2.79 mmol) of diamine **2** in 14.2 mL of CaH$_2$-dried DMAc, 0.6985 g (2.79 mmol) of PMDA was added in one portion. The mixture was stirred at the ambient temperature for about 24 h to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) (**4a**) was 1.99 dL/g, as measured in DMAc at a concentration of 0.5 g/dL at 30 °C. The poly(amic acid) was converted into polyimide

with either a thermal or chemical imidization process.

For the thermal imidization method, about 7 g of the poly(amic acid) solution was spread into a Petri culture dish 7 cm in diameter and baked at 90 °C overnight (ca. 12 h) for the removal of the casting solvent. The semidried poly(amic acid) film was further dried and converted into the polyimide by sequential heating at 150 °C for 30 min, at 200 °C for 30 min, and at 250 °C for 1 h. For the elemental analysis, tensile testing, X-ray crystallography, and thermal analysis, the polyimide films were further heated at 350 °C for another 1 h to ensure the complete imidization.

For the chemical imidization method, 5 mL of acetic anhydride and 2 mL of pyridine were added to the remaining poly(amic acid) solution, and the mixture was heated at 100 °C for 1 h to effect a complete imidization. The resultant solution of the polymer was poured slowly into 250 mL of methanol, and the precipitate was washed thoroughly with methanol and hot water, collected by filtration, and dried in air at 150 °C for 4 h.

Characterization Methods

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analysis was performed on a Heraeus
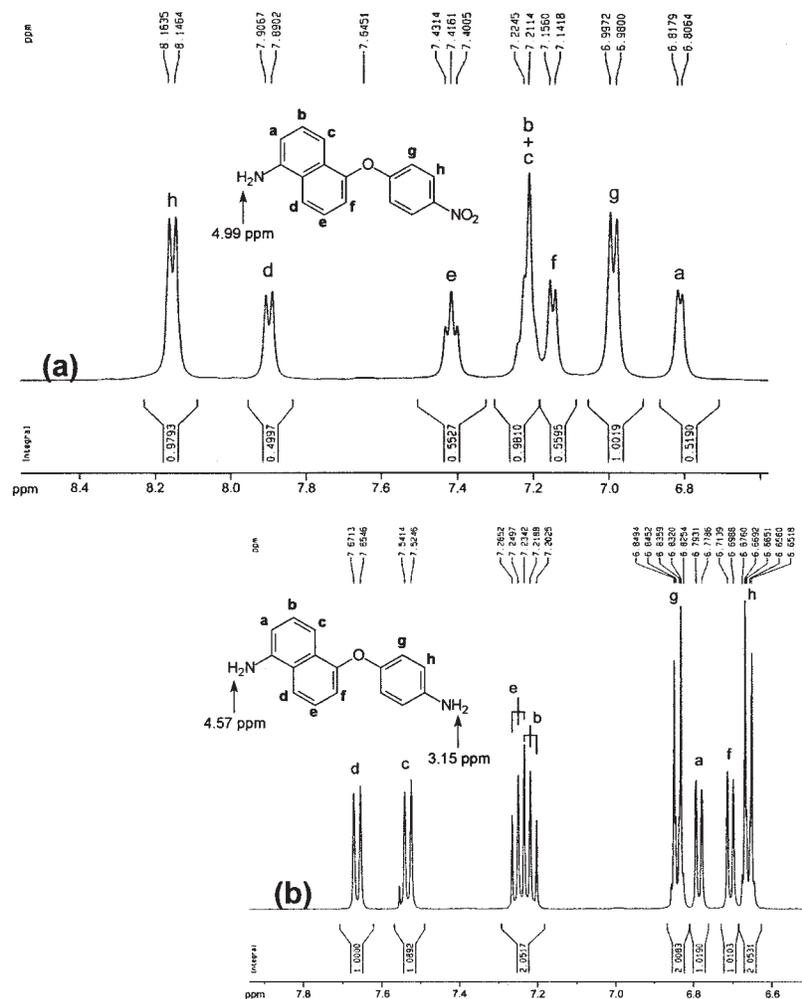
Figure 2. ^{1}H NMR spectra of (a) **1** and (b) **2** in DMSO-d_6.

Vario EL-III CHN analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT NMR spectrometer. The inherent viscosities of the poly(amic acid)s were determined with an Ubbelohde viscometer at 30 °C. A Lloyd LRX universal tester with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. The measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 0.08 mm thick), and an average of at least five individual determinations was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a graphite monochromator (operating at 40 kV and 30 mA) with nickel-filtered Cu Kα radiation (λ = 1.5418 Å).

The scanning rate was 2°/min over a range of 2θ = 10–40°. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA instrument. The experiments were carried out on approximately 4–6-mg samples in flowing nitrogen (flow rate = 30 cm^3/min) at a heating rate of 20 °C/min. The DSC analyses were performed on a PerkinElmer Pyris 1 DSC instrument at a heating rate of 20 °C/min under nitrogen. Glass-transition temperatures (T_g's) were read at the middle of the transition in the heat capacity. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 50 to 400 °C at a scanning rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. T_s's were taken as the onset temperature of the probe displacement on the TMA traces.

RESULTS AND DISCUSSION

Monomer Synthesis

The new asymmetrical aromatic ether diamine **2** was prepared in two steps, starting from the nucleophilic etherification of 5-amino-1-naphthol and 4-chloronitrobenzene in the presence of K_2CO_3 in DMF, which was followed by subsequent hydrazine Pd/C-catalyzed reduction of intermediate nitro-amine compound **1** (Scheme 1). The molecular structure of diamine **2** was confirmed with elemental, IR, and NMR analysis.

Figure 1 shows the FTIR spectra of 5-amino-1-naphthol, nitro-amine compound **1**, and diamine
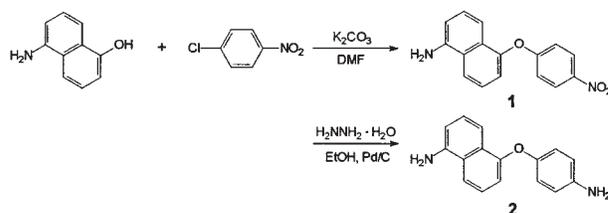
Scheme 1. Synthesis of **2**.

2. After 5-amino-1-naphthol reacted with 4-chloronitrobenzene into intermediate compound **1**, the broad hydrogen-bonded O—H stretching band in the region of 2600–3200 cm^{-1} disappeared, and the bands representative of the nitro functionality appeared near 1510 (asymmetric stretch) and 1340 cm^{-1} (symmetric stretch). After reduction, the aromatic primary amine absorption at 3460 and 3379 cm^{-1} were identified, and the bands for the nitro group vanished.

The structures of **1** and **2** were also corroborated by high-resolution NMR spectra. In Figure 2, the ^1H NMR spectra demonstrated that the nitro group was completely converted into the amino group by the high-field shift of the aromatic protons and by the signal at 3.15 ppm peculiar to the amino protons. In the ^{13}C NMR spectra (Fig. 3), upfield shifts of the phenylene carbon resonances, especially for the carbons ortho (C^{13}) and para (C^{11}) to the amino group, were observed in diamine **2** because of the resonance effect caused by the electron-donating amino group. All the spectroscopic data obtained were in good agreement with the expected structures.
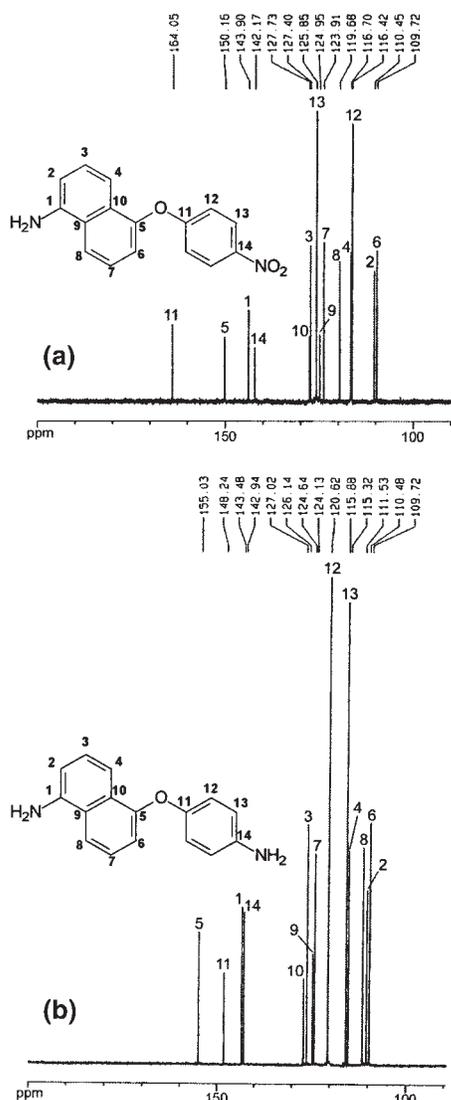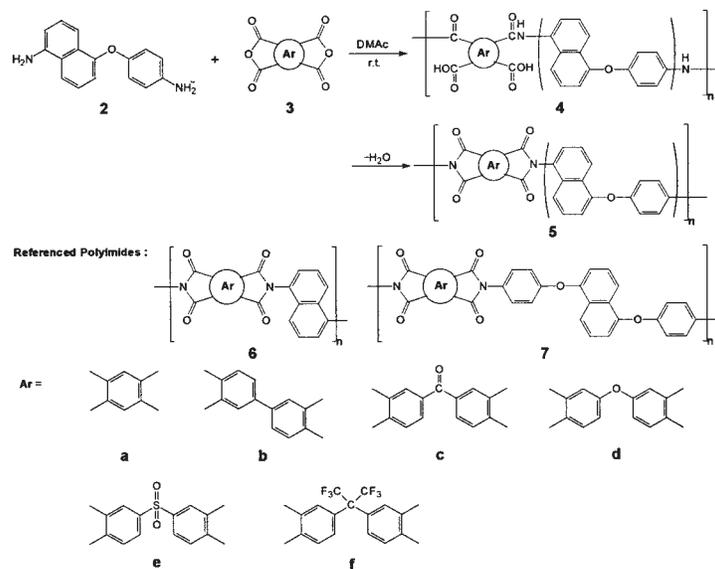
Polymer Synthesis

Novel polyimides **5a–5f** were prepared by the reaction of ether diamine **2** with various commercially available dianhydrides (**3a–3f**) to form poly(amic acid)s (**4a–4f**), followed by thermal or chemical imidization. The structures and codes of the prepared polymers are shown in Scheme 2. The parentheses in the formulas of polymers **4** and **5** indicate that the asymmetric moieties may appear in the polymer chain as shown or in the reverse orientation. As shown in Table 1, the inherent viscosities of the poly(amic acid) precursors (**4a–4f**) were 1.21–1.99 dL/g. For comparison, two series of referenced polyimides (**6a–6f** and **7a–7f**) were synthesized from 1,5-DAN and 1,5-BAPON, respectively, with dianhydrides **3a–3f**.

Figure 3. ^{13}C NMR spectra of (a) **1** and (b) **2** in DMSO-d_6.

Scheme 2. Synthesis of the polyimides.

The inherent viscosities of the poly(amic acid) precursors of **6a–6f** and **7a–7f** were 0.79–1.26 and 1.08–1.95 dL/g, respectively, indicating the formation of high-molecular-weight polymers.

All the poly(amic acid)s of the **5** and **7** series polyimides could be cast into flexible and tough poly(amic acid) films, which could be subsequently converted into tough polyimide films by

Table 1.   Inherent Viscosity (η_{inh}), Film Properties, and Solubility Behavior of the Polyimides

Polymer	η_{inh} (dL/g)[a]	Film Quality[b]	Solubility[c]					
			NMP	DMAc	DMF	DMSO	m-Cresol	THF
5a	1.99	Flexible	−	−	−	−	−	−
5b	1.35	Flexible	−	−	−	−	−	−
5c	1.40	Flexible	−	−	−	−	−	−
5d	1.60	Flexible	+	+	+	+	+h	−
5e	1.64	Flexible	+	+	+	+h	+h	−
5f	1.21	Flexible	+	+	+	+	+	+
6a	1.15	Brittle	−	−	−	−	−	−
6b	1.26	Brittle	−	−	−	−	−	−
6c	0.88	Brittle	−	−	−	−	−	−
6d	1.08	Brittle	−	−	−	−	−	−
6e	0.79	Brittle	+	+	+	+	−	−
6f	0.87	Brittle[d]	+	+	+	+	−	+
7a	1.95	Flexible	−	−	−	−	−	−
7b	1.87	Flexible	−	−	−	−	−	−
7c	1.20	Flexible	−	−	−	−	−	−
7d	1.08	Flexible	−	−	−	−	−	−
7e	1.58	Flexible	−	−	−	−	−	−
7f	1.43	Flexible	+h	+h	−	−	−	−

[a] Inherent viscosity of the poly(amic acid) precursor measured at a concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Imidization was achieved thermally by a stepwise increase of the temperature, with a maximum of 250 °C for 1 h.
[c] Qualitative solubility was tested with 10 mg of a sample (chemically imidized) in 1 mL of the solvent. + = soluble at room temperature; +h = soluble on heating; − = insoluble; NMP = N-methyl-2-pyrrolidone; THF = tetrahydrofuran.
[d] A flexible film was obtained from a chemically imidized sample of **6f** via solution casting.
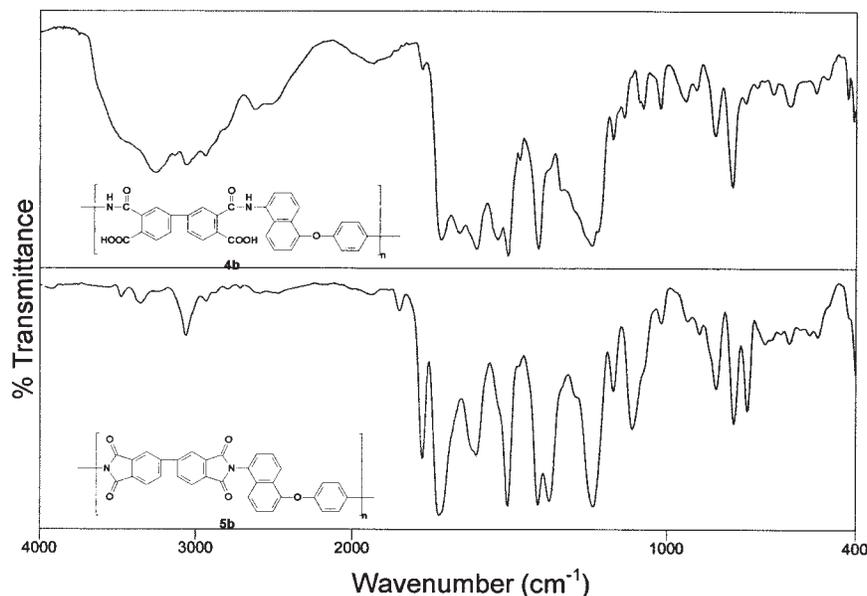
Figure 4. Thin-film IR spectra for poly(amic acid) **4b** and polyimide **5b**.

extended heating at elevated temperatures. However, almost all the **6** series polyimides afforded highly brittle films because of the rigid nature of the polymer backbone caused by 1,5-DAN moieties.

The formation of polyimides was confirmed with FTIR and ^{1}H NMR spectroscopy and elemental analysis. As shown in Figure 4, all the poly-

imides exhibited characteristic imide group absorptions around 1780 (asymmetrical C=O stretch) and 1725 cm^{-1} (symmetrical C=O stretch), 1380 cm^{-1} (C—N stretch), and 1100 and 720 cm^{-1} (imide ring deformation), together with some strong absorption bands in the region of 1300–1100 cm^{-1} due to C—O stretching. The disappearance of amide and carboxyl bands at 1700–
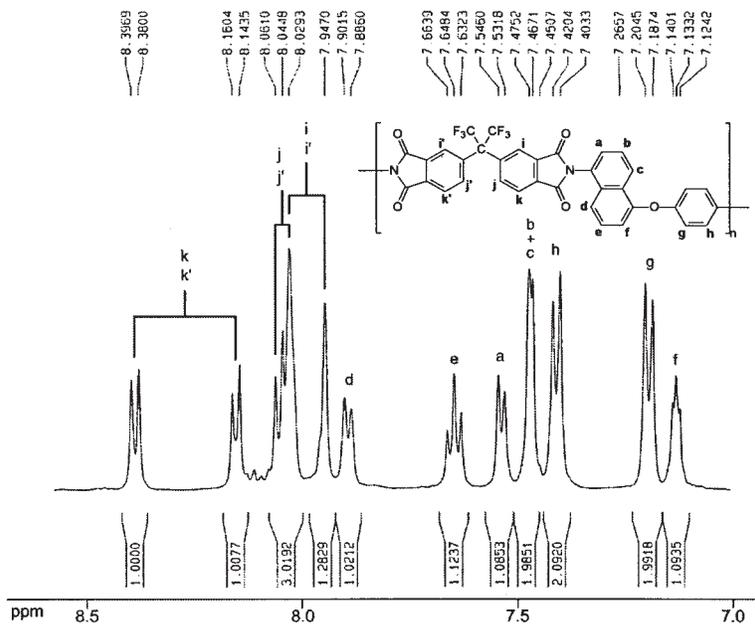

Figure 5. ^{1}H NMR spectra of polyimide **5f** in DMSO-d_6.

Table 2. Elemental Analysis of Polyimides **5a–5f**[a]

Polymer	Formula (Formula weight)	Calculated (%)			Found (%)		
		C	H	N	C	H	N
5a	$C_{26}H_{12}O_5N_2$ (432.39)	72.22	2.80	6.48	70.60	2.86	6.38
5b	$C_{32}H_{16}O_5N_2$ (508.49)	75.59	3.17	5.51	74.32	3.18	5.49
5c	$C_{33}H_{16}O_6N_2$ (536.50)	73.88	3.01	5.22	72.03	3.08	5.27
5d	$C_{32}H_{16}O_6N_2$ (524.49)	73.28	3.07	5.34	72.28	3.04	5.19
5e	$C_{32}H_{16}O_7N_2S$ (572.55)	67.13	2.82	4.89	65.97	2.85	4.56
5f	$C_{35}H_{16}O_5N_2F_6$ (658.51)	63.84	2.45	4.25	63.83	2.18	4.20

[a] Sample prepared via thermal imidization.

1650 and 3500–2800 cm^{-1} indicated a virtually complete conversion of the poly(amic acid) precursor into the polyimide. Figure 5 shows a typical ^{1}H NMR spectrum of polyimide **5f** in DMSO-d_6; all the peaks were readily assigned to the hydrogen atoms of the recurring units. The results of the elemental analysis of all the thermally cured polyimides are listed in Table 2. The values are generally in good agreement with the calculated values of the proposed structures.

Properties of the Polyimides

Organosolubility

The solubility behavior of the polyimides prepared by chemical imidization was tested qualitatively in various organic solvents, and the results are also reported in Table 1. The or-ganosolubility behavior of the polyimides generally depended on their chain packing density and intermolecular interactions, which were affected by the rigidity, symmetry, and regularity of the molecular backbone. Thus, the polyimides derived from more flexible dianhydrides such as ODPA, DSDA, and 6FDA generally displayed a higher solubility than those obtained from more rigid components such as PMDA, BPDA, and BTDA. As shown in Table 1, the asymmetric diamine-based polyimides **5d–5f** revealed an enhanced solubility in comparison with that of the corresponding analogues of the **6** series and **7** series. This can be attributed to the resulting three possible dyad microstructures within the polyimide backbone and the molecular chain nonlinearity caused by the specific ether diamine **2**.
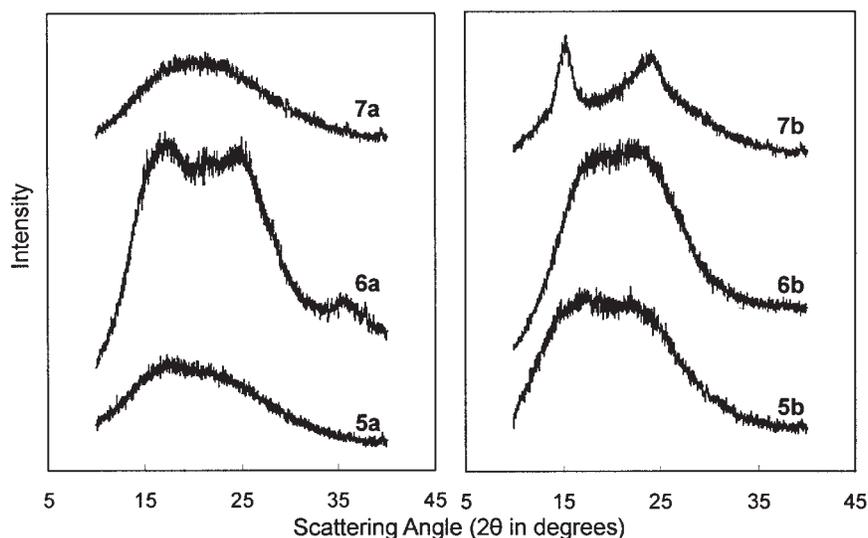

Figure 6. WAXD patterns of some thermally cured polyimide films.

Table 3. Tensile Properties of the Polyimide Films[a]

Polymer	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
5a	138	14	2.18
5b	154	13	2.26
5c	169	14	2.38
5d	144	15	2.08
5e	177	12	2.71
5f	131	9	2.41

[a] The samples were prepared via thermal imidization.

Crystallinity

The crystallinity of the prepared polyimides was evaluated by WAXD scans. The representative WAXD patterns of some thermally cured polyimide films are presented in Figure 6. As expected, all the **5** series polyimides showed almost completely amorphous diffraction patterns because of the asymmetric diamine moieties. As mentioned earlier, polyimides **6a** and **6b**, which became brittle during film casting, revealed a stronger reflection hump around $2\theta = 15$–30°. This indicated that the **6** series polyimides had a higher packing density. All the **7** series polyimides except **7b** also showed an amorphous diffraction pattern because of the incorporation of flexible phenoxy units into the polymer backbone. Polyimide **7b** exhibited two strong peak reflections at 2θ values of about 15 and 25°, which were indicative of a slightly higher crystallinity.

Tensile Properties

The tensile properties of the **5a**–**5f** polyimide films prepared by thermal curing are summarized in Table 3. These films had tensile strengths of 131–177 MPa, elongations to break of 9–15%, and tensile moduli of 2.08–2.71 GPa, which indicated strong and tough materials.

Table 4. Thermal Properties of the Polyimides

Polymer	T_g (°C)[a]	T_s (°C)[c]	T_d (°C)[c] at 5% Weight Loss In Air	In N$_2$	T_d (°C)[c] at 10% Weight Loss In Air	In N$_2$	Char Yield (%)[f]
5a	—[b]	344	574	593	594	614	66
5b	336	330	588	593	608	612	69
5c	315	299	566	574	589	596	66
5d	307	300	571	583	592	598	65
5e	331	330	528	533	556	557	60
5f	323	314	541	558	559	578	58
6a	—	ND[d]	547	563	581	597	62
6b	—	330	575	592	613	623	69
6c	—	340	548	558	578	589	67
6d	—	336	560	587	583	609	65
6e	—	356	477	488	517	519	57
6f	—	348	536	554	561	578	58
7a	319	317	555	579	580	593	61
7b	—	302	578	590	600	604	65
7c	283	269	559	577	587	596	65
7d	263	258	554	563	584	580	64
7e	301	298	526	514	557	542	58
7f	287	280	534	558	557	579	61

[a] The samples were heated from 50 to 400 °C at a scan rate of 20 °C /min; this was followed by rapid cooling to 50 °C at -200 °C /min in N$_2$. The midpoint temperature of the heat capacity jump on the subsequent DSC heating trace (from 50 to 400 °C at 20 °C /min) was defined as T_g.
[b] No discernible transitions.
[c] Taken as the onset temperature of the probe displacement on the TMA trace. The films samples were heated at 350 °C for 1 h before the TMA experiment.
[d] Not detected (no available specimens).
[e] Decomposition temperature recorded via TGA at a heating rate of 20 °C /min and a gas-flow rate of 35 cm^3/min.
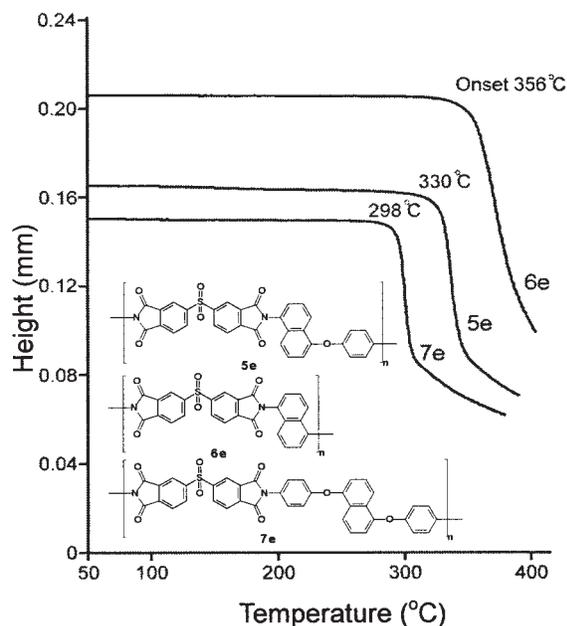[f] Residual weight percentages at 800 °C under a nitrogen flow.

Figure 7. TMA curves of polyimides **5e**, **6e**, and **7e** at a heating rate of 10 °C/min.

Thermal Properties

DSC, TMA, and TGA were used to investigate the thermal properties of the polyimide films, and some of the thermal behavior data are reported in Table 4. The **6** series polyimides and polyimides **5a** and **7a** did not show discernible glass transitions on the DSC thermograms, possibly because of their high level of crystallinity or the rigid nature of their backbones. All the **5** series polyimides exhibited a T_g value higher than 300 °C. As expected, polyimide **5d** revealed the lowest T_g of 307 °C in the **5** series polymers because of the flexible dianhydride (ODPA) moieties. T_s's of all the polyimide films except **6a** were determined by the TMA method with a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. As representative examples, the TMA curves of polyimides **5e**, **6e**, and **7e** are illustrated in Figure 7. The trend of T_s variation generally followed the chain stiffness: **6e** > **5e** > **7e**. The thermal stability of the polyimides was evaluated by TGA measurements in both air and nitrogen atmospheres. Typical TGA curves for polyimide **5a** are shown in Figure 8. The decomposition temperature at a 10% weight loss of the **5** series polyimides in nitrogen and air stayed in the ranges of 557–614 °C and 554–608 °C, respectively. They left more than a 57% char yield at 800 °C in nitrogen. The

high char yield of these polyimides can be explained by their high aromatic content. The TGA data indicated that these polyimides had fairly high thermal stability, and the incorporation of phenoxy units and molecular asymmetry did not seem to affect their thermal stability significantly.

CONCLUSIONS

A novel asymmetrical aromatic ether diamine (**2**) was synthesized via a high-yielding two-step procedure. A series of novel aromatic polyimides with high molecular weights were obtained successfully from **2** with various aromatic dianhydrides by a conventional two-step technique with thermal or chemical imidization of the intermediate poly(amic acid)s. The obtained polyimides displayed enhanced solubility, were noncrystalline, and could afford transparent, flexible, and tough films with good tensile properties. These polyimides were also characterized by excellent thermal stability and high T_g's (>300 °C). Thus, this series of polyimides has a good combination of properties required for high-performance materials and demonstrates promising potential for future applications.
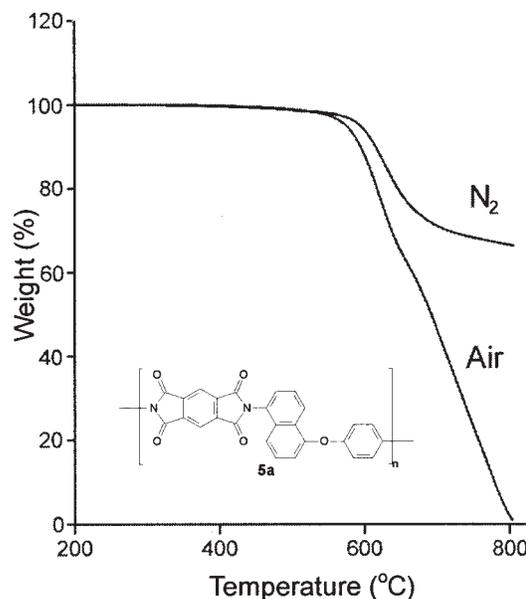

Figure 8. TGA curves of polyimide **5a** at a heating rate of 20 °C/min.

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