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Synthesis and Properties of Novel Aromatic Polyimides of 2,3-Bis(4-aminophenoxy)naphthalene

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ABSTRACT: Novel aromatic polyimides containing bis(phenoxy)naphthalene units were synthesized from 2,3-bis(4-aminophenoxy)naphthalene (BAPON) and various aromatic tetracarboxylic dianhydrides by the usual two-step procedure that included ring-opening polyaddition to give poly(amic acid)s, followed by cyclodehydration to polyimides. The poly(amic acid)s had inherent viscosities between 0.61 and 2.13 dL/g depending on the tetracarboxylic dianhydrides used. All the polyimides afforded transparent and flexible films. Almost all of the polyimides were soluble in a wide range of organic solvents such as *N*-methyl-2-pyrrolidone, *m*-cresol, and *o*-chlorophenol. The polyimide prepared from pyromellitic dianhydride was semicrystalline, whereas the other polyimides showed amorphous patterns in X-ray diffraction studies. Tensile strength and elongation at break of the BAPON-based polyimide films ranged from 75 to 96 MPa and 3 to 6%, respectively. These polyimides had glass transition temperatures between 226 and 316 °C. Thermal analysis indicated that these polymers were fairly stable. The 10% weight loss temperatures were recorded in the range 523–578 °C in nitrogen and 518–569 °C in air atmosphere.

Introduction

Wholly aromatic polyimides have long been known for their outstanding physical properties and are widely used, especially in aerospace and electrical/electronic applications.[1–5] Unless carefully designed, however, polyimides have high softening temperatures and are often insoluble in most organic solvents in their fully imidized form, making them extremely difficult to fabricate. Therefore, several approaches such as incorporation of flexible bridging units,[6–12] bulky pendant groups,[13–16] or asymmetric meta catenation[8] into the rigid polymer backbone have been made to obtain processable or soluble polyimides. One successful approach to increase solubility and processability of polyimides without sacrificing their thermal stability is the introduction of flexible bridging units into the polymer backbone.

Generally, aromatic diamines with ether linkages should lower polymer chain rigidity; naphthyl groups should preserve the thermal stability of the polymer. Many bis(phenoxy)-containing diamines could be prepared by the reaction of aromatic bisphenols and *p*-chloronitrophenol in the presence of potassium carbonate.[17–21] Commercial aryl–ether diamines such as 4,4′-oxydianiline, 3,4′-oxydianiline, 1,4-bis(4-aminophenoxy)benzene, and 1,3-bis(4-aminophenoxy)benzene have been used in the synthesis of polyimides. In recent years, soluble polyimides have been very important and needed as coating materials on specific space components such as solar cells and thermal control systems.[22] Many reports have investigated the synthesis and characterization of fluorinated polyimides for application to electrical and optical components.[23–25] Polymers derived from diaminonaphthalene, such as 1,5-diaminonaphthalene, showed less favorable properties and their applications were limited.[26–29] Hence, aromatic diamines containing bis(phenoxy)naphthalene units are proposed as a new choice to prepare soluble polymers while maintaining reasonably high temperature characteristics. However, little is known about the synthesis of polyimides starting from bis(phenoxy)naphthalenediamines to date.[30] It is of interest to synthesize bis(phenoxy)naphthalenediamines with the ortho catenation on the outer rings and to prepare soluble polyimides.

Our recent studies revealed that bis(phenoxy)naphthalenediamines are useful in the preparation of soluble high temperature aromatic polyamides and polyimides.[31–34] In continuing our studies, the present article describes the synthesis and characterization of new soluble polyimides derived from 2,3-bis(4-aminophenoxy)naphthalene (BAPON) and various aromatic tetracarboxylic dianhydrides.

Experimental Section

Materials. 2,3-Dihydroxynaphthalene (from Janssen), *p*-chloronitrobenzene (from Hanawa), and 10% palladium on activated carbon (from Fluka) were used as received. Reagent grade aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA, **2a**; from TCI), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, **2b**; from CHRISKEV), 4,4′-oxydiphthalic anhydride (ODPA, **2c**; from CHRISKEV), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, **2d**; from TCI), and 4,4′-sulfonyldiphthalic anhydride (SDPA, **2e**; from New Japan Chemical Co.) were recrystallized from acetic anhydride before use. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

2,3-Bis(4-nitrophenoxy)naphthalene. This compound was synthesized by the reaction of 2,3-dihydroxynaphthalene (40 g, 0.25 mol) and *p*-chloronitrobenzene (82.6 g, 0.52 mol) in the presence of potassium carbonate (79.4 g, 0.57 mol) and *N,N*-dimethylformamide (300 mL) at 160 °C for 8 h. The mixture was then cooled and poured into 500 mL of methanol–water (1:1 by volume). The crude product was recrystallized from glacial acetic acid to provide yellow needles in 82% yield (mp 199–200 °C). ^{1}H NMR (DMSO-d_6): δ 8.18 (d, 4H, phenylene), 7.98 (s, 2H and d, 2H, naphthalene), 7.60 (d, 2H, naphthalene), 7.10 ppm (d, 4H, phenylene). ^{13}C NMR (DMSO-d_6): δ 162.17, 144.40, 142.59, 131.43, 127.42, 126.66, 126.05, 120.37, 117.00 ppm. Anal. Calcd for $C_{22}H_{14}N_2O_6$: C, 65.63; H, 3.48; N, 6.96. Found: C, 65.64; H, 3.57; N, 6.79.

2,3-Bis(4-aminophenoxy)naphthalene (1). To a dispersion of 2,3-bis(4-nitrophenoxy)naphthalene (56 g, 0.139 mol) in ethanol (400 mL) was added palladium charcoal (0.3 g); hydrazine hydrate (138 mL) was added to the stirred mixture dropwise at 85 °C within 1 h. After complete addition, the mixture was heated at 85 °C for another 4 h. The reaction solution was then filtered to remove Pd–C. The crude product was recrystallized from ethanol to give white needles in 84% yield (mp 176–177 °C). ^{1}H NMR (DMSO-d_6): δ 7.66 (d, 2H, naphthalene), 7.30 (d, 2H, naphthalene), 7.15 (s, 2H, naphthalene), 6.83 (d, 4H, phenylene), 6.63 (d, 4H, phenylene), 4.97 ppm (s, 4H, amino). ^{13}C NMR (DMSO-d_6): δ 149.03, 145.94, 145.35, 129.42, 126.42, 124.70,

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Table I. Effect of the Monomer Addition Mode on the Preparation of Poly(amic acid)s

run	process[a]	η_{inh}[b] (dL/g) of poly(amic acid)
1	The total amount of **BAPON** and PMDA was added into DMAc in one portion.	1.28
2	**BAPON** was first dissolved in DMAc, then the total amount of PMDA was added at once.	1.41
3	**BAPON** was first dissolved in DMAc, and then a 50% stiochiometric quantity of PMDA was added with the remaining 50% PMDA added 10 min later.	1.67
4	**BAPON** was first dissolved in DMAc, and then 90% PMDA was added, with the final 10% PMDA added 10 min later.	1.83
5	**BAPON** was first dissolved in DMAc, and then PMDA was added in four portions of 90, 5, 3, and 2% within 30 min.	2.13
6	PMDA was first dissolved in DMAc, and then the total amount of **BAPON** was added at once.	0.98

[a] 0.342 g of **BAPON**, 0.218 g of PMDA, and 5.4 mL of DMAc were used in each process. [b] Measured in a concentration of 0.5 g/dL in DMAc at 30 °C.

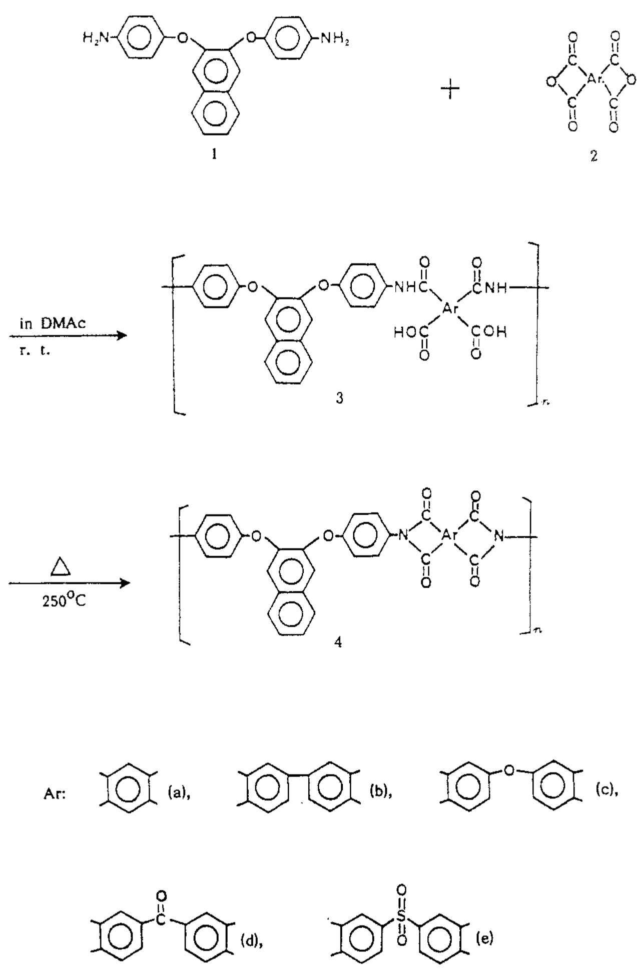
120.22, 114.96, 113.11 ppm. Anal. Calcd for $C_{22}H_{18}N_2O_2$: C, 77.19; H, 5.26; N, 8.18. Found: C, 77.06; H, 5.46; N, 8.08.

Polymerization. A typical example of polymerization was as follows. To a solution of 0.856 g (2.5 mmol) of BAPON in 13.5 mL of DMAc, was added gradually 0.545 g (2.5 mmol) of PMDA. The mixture was stirred at room temperature for 2 h under nitrogen. The inherent viscosity of the poly(amic acid) in the DMAc solution was 2.13 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The poly(amic acid) solution thus obtained was spread on a glass plate and the solvent was removed at 80 °C. Imidization was carried out by thermal cyclodehydration of the poly(amic acid) film by sequential heating at 110, 150, 180, 210, and 250 °C for 15 min each, respectively. The film was stripped from the plate by soaking in hot water. The inherent viscosity of the polyimide thus obtained was 0.80 dL/g in concentrated sulfuric acid, measured at a concentration of 0.5 g/dL at 30 °C.

Chemical cyclodehydration was also carried out by adding a mixture of acetic anhydride and pyridine (volume ratio 2:1) to the aforementioned poly(amic acid) solution, while being stirred at room temperature for 1 h, and then heating at 80 °C for 3 h. In all cases, polymer precipitated during the heating period. The polymer solution was poured into methanol. The yellow precipitate was collected by filtration, washed thoroughly with methanol and hot water, and dried at 100 °C under vacuum.

All other polyimides **4b–e** were prepared by the same procedure as above from BAPON and the tetracarboxylic dianhydrides **2b–e**.

Scheme I



Measurements. Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform spectrometer. Elemental analyses were run in a Perkin-Elmer Model 240 C, H, N analyzer. Inherent viscosities of all polymers were determined at 0.5 g/dL in concentrated sulfuric acid (thermal imidization) and in *N*-methyl-2-pyrrolidone (chemical imidization) using a Cannon-Fenske viscometer. Thermogravimetric data were obtained using a Rigaku TAS-100 thermal analysis station. Measurements were performed on 10 ± 2 mg samples heated in flowing nitrogen (50 cm^3/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analysis was performed with a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller at a rate of 20 °C/min in flowing nitrogen (30 cm^3/min). Thermomechanical analysis (TMA) was performed at a heating rate of 10 °C/min with a

Table II. Synthesis of Polymers III and IV from BAPON and Various Aromatic Tetracarboxylic Dianhydrides

	poly(amic acid)[a]		polyimide[b]				
					elemental analysis[e]		
tetracarboxylic dianhydride	code	η_{inh}[c] (dL/g)	code	η_{inh}[d] (dL/g)	C	H	N
2a	3a	2.13	4a	0.80 (–)	73.25 (73.28)	3.35 (3.07)	5.70 (5.34)
2b	3b	1.02	4b	0.74 (0.94)	74.12 (74.02)	3.56 (3.27)	4.81 (4.54)
2c	3c	0.72	4c	0.50 (0.65)	72.07 (72.15)	3.40 (3.19)	4.63 (4.43)
2d	3d	0.75	4d	0.77 (–)	72.77 (72.67)	3.14 (3.13)	4.58 (4.34)
2e	3e	0.61	4e	0.50 (0.60)	67.33 (67.05)	3.02 (2.96)	4.18 (4.11)

[a] Polymerization was carried out with equimolar quantities of **BAPON** and aromatic dianhydrides to obtain 10 wt % poly(amic acid) solutions. [b] Obtained by thermal cyclization from the corresponding poly(amic acid)s. [c] Measured in DMAc at a concentration of 0.5 g/dL at 30 °C. [d] Measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30 °C. Data in parentheses are the inherent viscosities obtained from chemically imidized polymers, measured in NMP solution at a concentration of 0.5 g/dL at 30 °C. [e] Data in parentheses are calculated values.

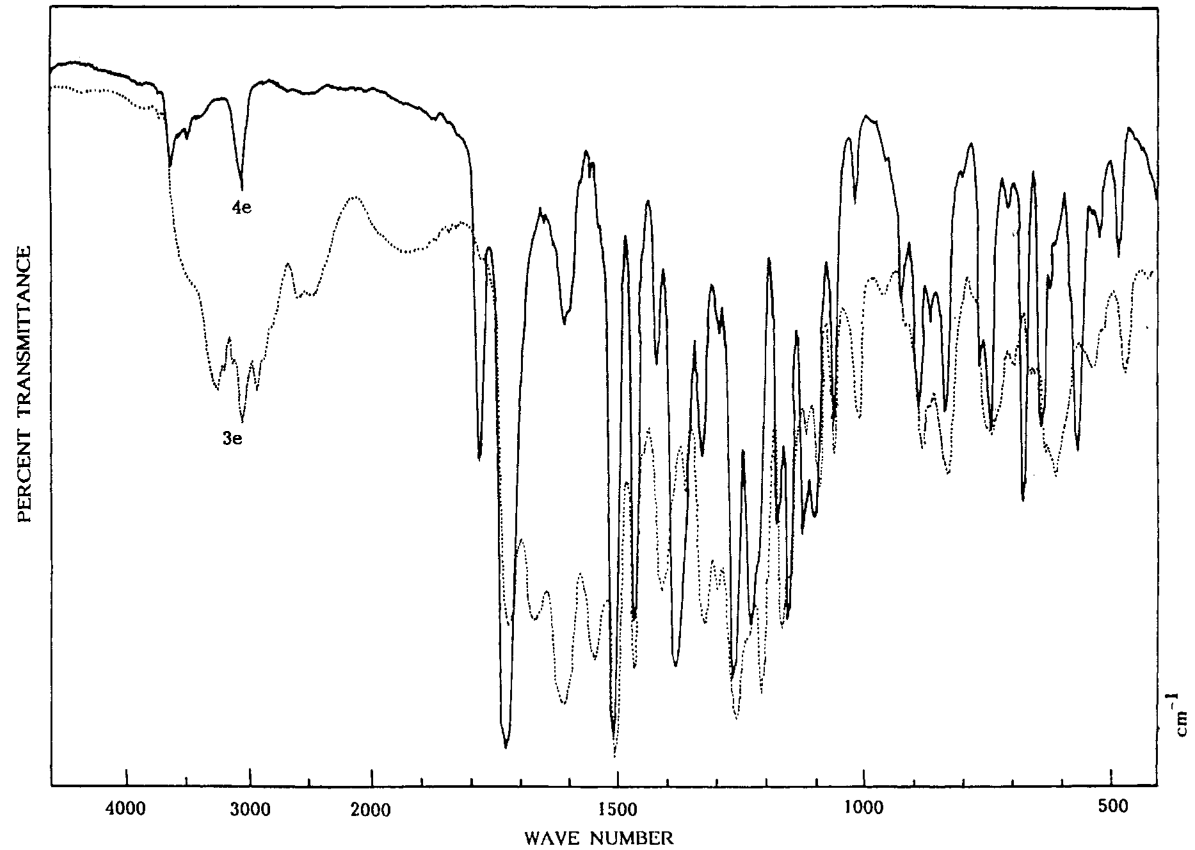


Figure 1. IR spectra of the poly(amic acid) **3e** and the corresponding polyimide **4e**.

DuPont 2000. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger D-max IIIa, using Ni-filtered Cu Kα radiation (40 kV, 15 mA). The scanning rate was 4°/min. An Instron universal tester Model 1130 with a load cell of 5 kg was used to study the stress–strain behavior of the samples at a drawing speed of 5 cm/min. Measurements were performed at room temperature with film specimens (5 mm wide, 6 cm long, and about 0.1 mm thick). An average of at least six individual measurements was used.

Results and Discussion

Synthesis of Monomer. 2,3-Bis(4-aminophenoxy)-naphthalene (**1**), a new polymer-forming diamine, was synthesized in two steps by the aromatic nucleophilic displacement reaction of 2,3-dihydroxynaphthalene and *p*-chloronitrobenzene, giving the dinitro compound, followed by reduction with hydrazine hydrate/Pd–C. The structures of the dinitro and diamine compounds were confirmed by elemental analysis and ^{1}H NMR and ^{13}C NMR spectroscopy. The results were in good agreement with the proposed structures.

Preparation of Polymers. Removal of moisture from the reaction system was necessary to obtain high-molecular-weight poly(amic acid)s. In the preparation of poly(amic acid) from aromatic diamines and dianhydrides in a polar solvent, the process of monomer addition plays an important role for successful polymerization.[1,35] The effect of the monomer addition mode on the viscosity of the poly(amic acid) based on BAPON and PMDA (**2a**) was first investigated. The results are summarized in Table I. It was found that the addition of PMDA to the solution of BAPON yielded poly(amic acid)s with higher molecular weights than obtained by the reverse addition or by mixing both reactants. Higher viscosities were obtained if PMDA was added in multiple portions; for instance, the highest inherent viscosity of 2.13 dL/g was obtained by the multistep addition of PMDA to the diamine solution (see run 5). These results correspond with those observed for the polyaddition of PMDA and 4,4′-oxydianiline as described in previous work.[35]

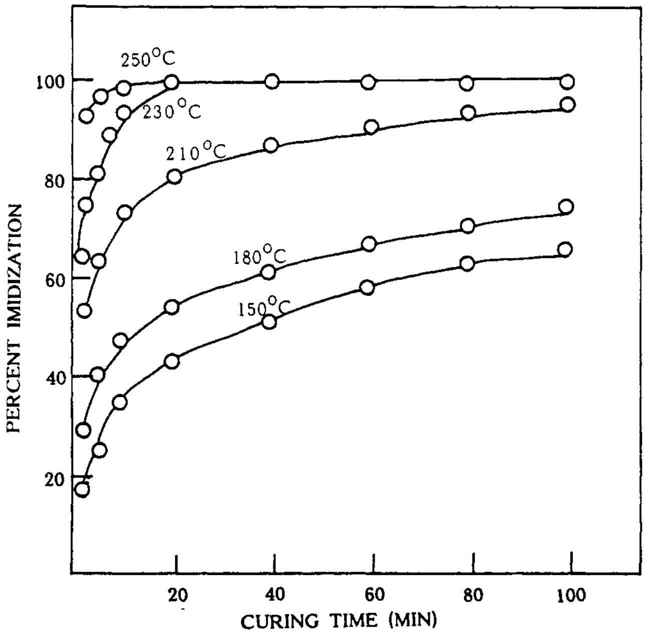


Figure 2. Change in percent imidization of poly(amic acid) **3a**. Heated for various time intervals at various temperatures.

The poly(amic acid)s **3b–e** were prepared by a similar process as run 5 in Table I (see Scheme I). The inherent viscosities of all poly(amic acid)s together with those of the corresponding polyimides are summarized in Table II. In the first step, the ring-opening polyaddition of BAPON with the aromatic tetracarboxylic dianhydrides in DMAc at room temperature formed the poly(amic acid)s (**3**) with inherent viscosities in the range 0.61–2.13 dL/g, suggesting the formation of high-molecular-weight poly-

Table III. Solubility of DAPON-Based Polyimides[a]

polymer	solvent[b] DMAc	NMP	DMF	DMSO	*m*-cresol	*o*-chlorophenol	conc H_2SO_4
4a	–	–	–	–	–	–	++
4b	–	++	–	–	++	++	++
4c	++	++	+	+	++	++	++
4d	+–	+	+–	–	+	++	++
4e	++	++	+	–	++	++	++

[a] Obtained by chemical cyclodehydration from poly(amic acid)s. [b] Key: ++, soluble at room temperature; +, soluble on heating; +–, partial soluble on heating; –, insoluble. Abbreviations: DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide.

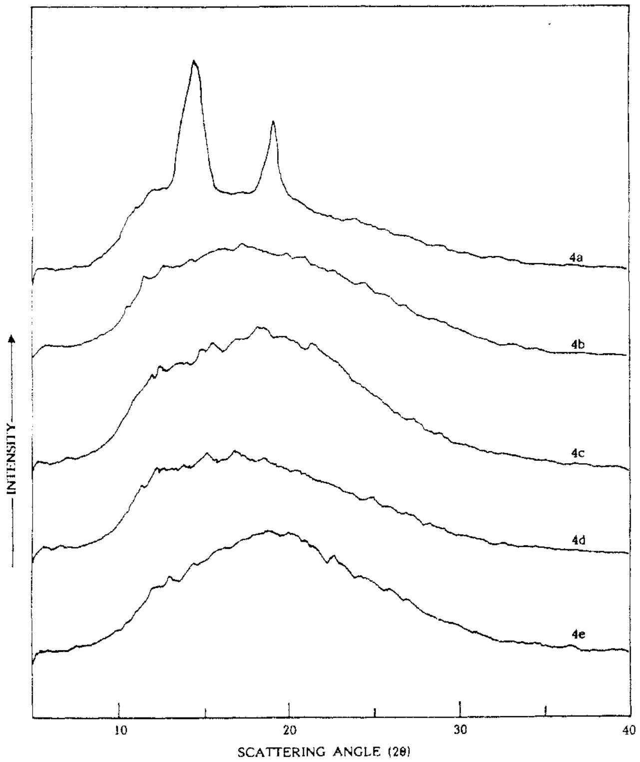


Figure 3. Wide-angle X-ray diffractograms of the polyimides 4a–4e.

Table IV. Mechanical Properties of Polyimides

polymer	tensile strength (MPa)	elongation at break (%)	initial modulus (GPa)	thermal expansion coefficient[a] ($°C^{-1} \times 10^5$)
4a	77	3	1.41	5.62
4b	96	5	1.76	6.35
4c	87	6	1.65	9.17
4d	92	5	1.82	7.14
4e	75	4	1.76	7.63

[a] Measured by thermomechanical analysis (TMA) at a heating rate of 10 °C/min in nitrogen from 20 to 350 °C.

mers. Among them, the poly(amic acid) **3a** derived from PMDA exhibited the highest inherent viscosity. Because the poly(amic acid)s are sensitive to hydrolysis by water, the obtained poly(amic acid) solutions were cast into films as soon as possible.

Most of the films adhered tenaciously to the glass plate by stepwise heating poly(amic acid) films to 250 °C and could only be removed by immersion in hot water. The polyimide films were pale yellow, transparent, and flexible. The pale yellow color of the films is probably attributable to the formation of charge transfer complexes between the electron donating bis(phenoxy)naphthalene unit and the strongly electron accepting pyromellitimide or phthalimide unit. The inherent viscosities of the polyimides measured in concentrated sulfuric acid ranged from 0.50 to 0.80 dL/g. Alternatively, the poly(amic acid)s were chemically converted to the polyimides, yielding inherent viscosities measured in NMP solution in the range 0.60–0.94 dL/g. Table II also lists the results of elemental analysis of the polyimides, which agree well with the calculated values based on the polymer repeat units.

Thermal Cyclodehydration of Poly(amic acid). The thermal conversion of poly(amic acid) to polyimide was monitored by infrared. The IR films were prepared by casting 2–3 wt % poly(amic acid) solutions in DMAc onto glass substrate and heating at 80 °C in a hot air oven for about 1 h. The poly(amic acid) films were further dried and imidized by thermal treatment. Figure 1 shows the IR spectra of the representative poly(amic acid) **3e** and the corresponding polyimide **4e**. The poly(amic acid) revealed characteristic absorptions at around 3300 and 1550–1650 cm^{-1}. These bands disappeared entirely after cyclodehydration and the absorptions of the imide ring appeared at 1780 cm^{-1} (asymmetrical C═O stretching) and 1100 and 720 cm^{-1} (ring deformation).

The degree of poly(amic acid) to polyimide conversion was analyzed by the band ratio method.[36] The absorbance of the asymmetric carbonyl stretch at 1780 cm^{-1} was ratioed with a reference aromatic stretch at 1500 cm^{-1}. The percent imidization of poly(amic acid) was calculated by using the following equation:[36]

$$\text{percent imidization} = \frac{[A(1)/A(2)]_t - [A(1)/A(2)]_{t=0}}{[A(1)/A(2)]_{t=\infty} - [A(1)/A(2)]_{t=0}} \times 100$$

where $A(1)$ = absorbance of the imide peak at 1780 cm^{-1}, $A(2)$ = absorbance of the standard reference at 1500 cm^{-1}, and $t = \infty$ was taken as the time beyond which no further changes in the imide peak were observe at 250 °C.

Figure 2 shows the percent imidization versus time at various temperatures. Almost all the amic acids were cyclized to imide rings within 10 min at 250 °C and within 20 min at 230 °C. When the sample was heated at 180 °C for 100 min, the imide peak grew to approximately 75% of its final size. The sample was then cured at 210 °C for up to 100 min. The degree of imidization increased, indicating that the imidization reaction was not completed by curing at 180 °C. The degree of imidization of polyimides **4a** seemed to show slightly lower at 150 °C for 40 min, compared with those other polyimides derived from 4,4′-oxydianiline/PMDA,[37–39] *p*-phenylenediamine/PMDA,[37] and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl/2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanoic dianhydride.[23]

Properties of Polyimides. The solubility of the 2,3-substituted bis(phenoxy)naphthalene polyimides obtained by the various methods of imidization were studied qualitatively. The results are shown in Table III. Polyimides treated thermally are soluble only in concentrated sulfuric acid; this indicates the presence of intermolecular interaction between the polymer chain.[40,41] However,

Table V. Thermal Properties of Polyimides

polyimide	T_g (°C)[a] DSC	TMA	T_m[c] (°C)	dec temp[b] (°C) in N_2	in Air	R_{800}[d] (%)
4a	316	316	380	574	568	55.4
4b	252	255		578	569	66.0
4c	226	241		563	554	58.8
4d	245	247		561	554	57.2
4e	255	295		523	518	50.2

[a] Glass transition temperature (T_g) measured by DSC and TMA at a heating rate of 20 and 10 °C/min, respectively. [b] Temperature at 10% weight loss recorded by TG at a heating rate of 20 °C/min. [c] Melting temperature measured by DSC at a heating rate of 20 °C/min. [d] Residual weight % at 800 °C in nitrogen.

polyimides obtained by chemical imidization show better solubility compared to the ones imidized thermally. The polyimides **4c–e** which possess ether, ketone, or sulfone units between two phthalimide units were readily soluble in organic solvents such as DMAC, NMP, *m*-cresol, and *o*-chlorophenol. The insolubility of polyimide **4a** may be due to its rigid structure. The high solubility of polyimides **4b–e** can be attributed to the incorporation of aryl ether groups and the 2,3-substituted naphthalene ring in the polymer backbone. The 2,3-substituted naphthalene units look like pendant bulky groups along the polyimide backbone. In conclusion, the 2,3-bis(phenoxy(naphthalene-containing polyimides show better solubility than the 2,7- or the 1,5-substituted bis(phenoxy)naphthalene polyimides reported in previous studies.[33,34] The present polyimides 4 showed the better solubility as compared to the other similar polyimides derived from oxydianiline or bis(aminophenoxy)benzene[24,42] and exhibited similar solubility as compared to the polyimides based on highly phenylated and bulky pendant diamines.[13-16]

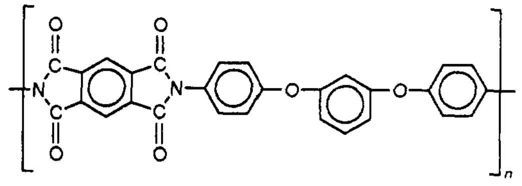
The crystallinity of the polyimide films, prepared by thermal imidization, was evaluated by X-ray diffraction analysis with 2θ ranging from 5 to 40°. As shown in Figure 3, polyimide **4a** showed crystalline character and exhibited two strong peaks around 15 and 20°, which may be due to the more efficient packing of polymer chains containing polypyromellitimide. All the other polyimides **4b–4e** showed amorphous patterns.

Table IV summarizes the tensile properties of the aromatic polyimide films prepared by the thermal treatment. The films had tensile strengths of 75–96 MPa, elongations at break of 3–6%, and initial moduli of 1.41–1.82 GPa. Although poly(amic acid) **3a** showed the highest inherent viscosity, polyimide **4a** exhibited the lowest tensile strength compared with the other polyimides. This is probably due to the semicrystallinity of polymer **4a**. Most of the polymer films exhibited high tensile strength and modulus and low elongation. The tensile properties of polyimides 4 are similar with the analogous polyimides in the literature.[43,44] The thermal expansion coefficients determined by thermomechanical analysis (TMA) are also listed in Table IV. The thermal expansion coefficients (TEC) were in the range (5.62–9.17) $\times 10^{-5}$ °C^{-1}. Conventional polyimides have a TEC in the range (3–6.5) $\times 10^{-5}$ °C^{-1}. Visually, the polyimides based on the 2,3-bis(4-aminophenoxy)naphthalene showed slightly higher TEC compared to analogous polyimides.[45] The polyimides **4a** and **4b** which were composed of only benzenes fused at the para position had lower thermal expansion coefficients. The lowest expansion found in polyimide **4a** may be caused by its crystalline and rigid natures. Polyimide **4c** derived from ODPA had the highest thermal expansion coefficient.

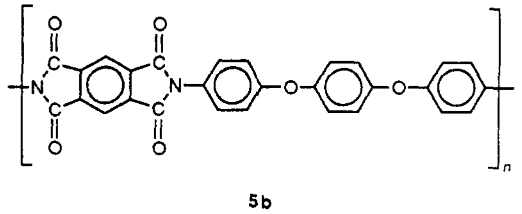
The thermal behavior of the polymers was evaluated by differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and thermogravimetric (TG) analysis. Table V summarizes the thermal transition data of polyimides **4a–4e**. All polyimides show a similar decomposition behavior characterized by no weight loss below 450 °C in air or nitrogen. The temperatures at which 10% weight loss was observed for these polyimides were in the range 523–578 °C in nitrogen and 518–569 °C in air, depending on the dianhydrides used. Polyimides **4a** and **4b** exhibit higher thermal stability. The 10% weight loss temperature in air atmosphere is by a value of about 4–9 deg lower than that in nitrogen, indicating polyimides based on BAPON showed thermooxidative stability in air. Although the lowest stability, in both air and nitrogen, was observed for polyimide **4e** containing a sulfone linkage, polyimide **4e** showed a higher 10% weight loss temperature compared to analogous polyimides.[44] The SDPA-based polyimides seemed to show lower thermal stability, as reported in the literature.[13-16,46] The amount of carbonized residue of all polyimides at 800 °C in nitrogen atmosphere was higher than 50%; the polyimide **4b** had the highest char yield of up to 66%.

DSC measurements were conducted with a heating rate of 20 °C/min. In all cases the samples were quenched from elevated temperature to room temperature to produce an easier detectable glass transition step. Figure 4 shows the typical DSC traces of polyimide **4a** and **4b**. A well-defined melting point could be obtained in the first heating of **4a**. However, it displayed only one broad peak in the second heating, indicating a slow rate of crystallization. The polymers **4a–e** have glass transition temperatures of 226–316 °C by DSC and 241–316 °C by TMA. The T_g's tend to decrease in the order **4a** > **4e** > **4b** > **4d** > **4c**. This order is consistent with the decreasing order of stiffness and polarity of the polymer backbone. The T_g values of polyimides 4 were slightly higher when compared to analogous polyimides derived from 1,4-bis(4-aminophenoxy)benzene and 1,3-bis(4-aminophenoxy)benzene.[42]

For comparison, the polyimides **5a** and **5b** containing the bis(phenoxy)benzene unit were prepared from 1,4-bis(4-aminophenoxy)benzene or 1,3-bis(4-aminophenoxy)benzene with PMDA by the two-step procedure.



5a



5b

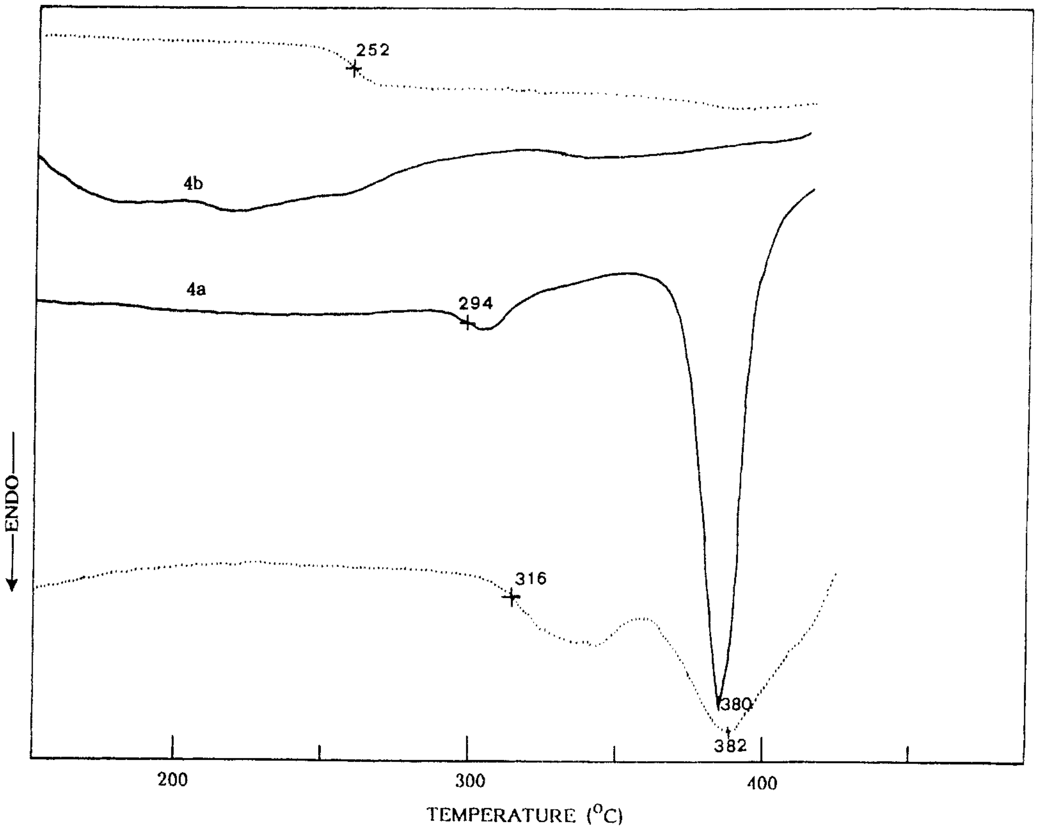


Figure 4. DSC traces (at a heating rate of 20 °C/min) of polyimides **4a** and **4b**: (—) first heating; (···) second heating.

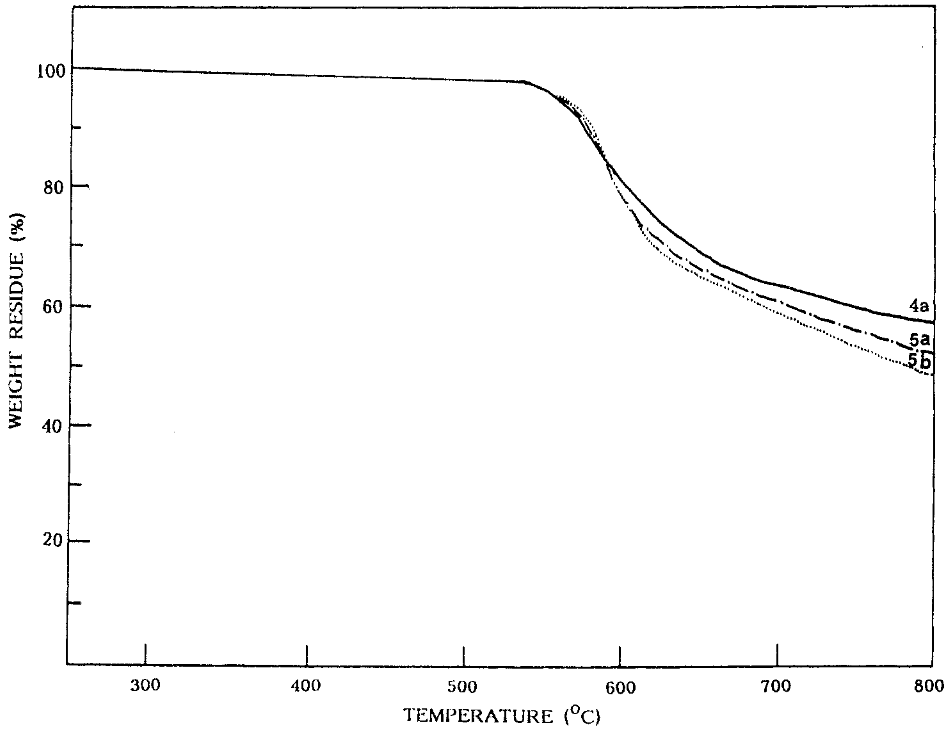


Figure 5. TG curves for polyimides **4a**, **5a**, and **5b** at a heating rate of 20 °C/min under nitrogen.

Figure 5 shows TG curves of polyimides **4a**, **5a**, and **5b** with a heating rate of 20 °C/min under flowing nitrogen. They show a similar TG behavior for the initial 20% weight loss. However, polyimide **4a** exhibits a higher thermal stability above 600 °C and undergoes extensive carbonization upon nonoxidative degradation, leaving a higher char yield at 800 °C. This indicates that the bis(phenoxy)-naphthalene-containing polyimides have higher thermal stability compared to their analogs.

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References and Notes

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