

Synthesis and Properties of Polyimides Derived from 1,6-Bis(4-aminophenoxy)naphthalene and Aromatic Tetracarboxylic Dianhydrides

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SYNOPSIS

1,6-Bis(4-aminophenoxy)naphthalene (I) was used as a monomer with various aromatic tetracarboxylic dianhydrides to synthesize polyimides via a conventional two-stage procedure that included ring-opening polyaddition in a polar solvent such as *N,N*-dimethylacetamide (DMAc) to give poly(amic acid)s, followed by thermal cyclodehydration to polyimides. The diamine (I) was prepared through the nucleophilic displacement of 1,6-dihydroxynaphthalene with *p*-chloronitrobenzene in the presence of K_2CO_3 , followed by catalytic reduction. Depending on the dianhydrides used, the poly(amic acid)s obtained had inherent viscosities of 0.73–2.31 dL/g. All the poly(amic acid)s could be solution cast and thermally converted into transparent, flexible, and tough polyimide films. The polyimide films had a tensile modulus range of 1.53–1.84 GPa, a tensile strength range of 95–126 MPa, and an elongation range at break of 9–16%. The polyimide derived from 4,4'-sulfonyldiphthalic anhydride (SDPA) had a better solubility than the other polyimides. These polyimides had glass transition temperatures between 248–286°C (DSC). Thermogravimetric analyses established that these polymers were fairly stable up to 500°C, and the 10% weight loss temperatures were recorded in the range of 549–595°C in nitrogen and 539–590°C in air atmosphere.

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INTRODUCTION

Because of the unique combination of mechanical and physical properties, chemical inertness, and elevated temperature performance, polyimides are a class of representative thermally stable polymers and are becoming more and more important.^{1–5} Polyimides are primarily used in the aerospace and electronics industries in the form of films and moldings. Other uses for these polymers such as adhesives, composite matrices, coatings, and foams are rapidly increasing. Polyimides consist of two types, linear condensation polymers and addition polyimides. The most widespread route for the preparation of linear condensation polyimides is the two-stage

polyaddition and polycondensation of a dianhydride with a diamine in an aprotic solvent, such as *N,N*-dimethylacetamide (DMAc). A soluble poly(amic acid) is obtained as polyimide prepolymer in the first stage, then cyclodehydration of this intermediate polymer, either by heat or by chemical reagents, yields the polyimide. Unless carefully designed, however, polyimides are often insoluble and intractable in their fully imidized form, presenting serious processing difficulties. Therefore, preparation of soluble or thermoplastic polyimides has been a major research interest. Approaches such as the incorporation of flexible bridging linkages^{6–10} or meta-oriented or ortho-oriented phenylene rings^{11,12} into polymer backbone and the introduction of bulky substituents^{13–17} along polymer backbone led to considerable success.

It has been generally recognized that aromatic ether linkages inserted in aromatic main chains

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Table I. Synthesis of Polyimides from **1,6-BAPON** and Various Aromatic Tetracarboxylic Dianhydrides

Poly-(amic acid) ^a		Polyimide ^b				
Code	η_{inh}^c (dL/g)	Code	η_{inh}^d (dL/g)	Elemental Analysis ^e (%)		
				C	H	N
IIIa	2.31	IVa	1.02	73.79 (73.28)	3.04 (3.07)	5.48 (5.34)
IIIb	1.49	IVb	0.96	74.19 (74.02)	3.21 (3.27)	4.65 (4.54)
IIIc	0.94	IVc	0.92	72.12 (72.15)	3.23 (3.19)	4.73 (4.43)
IIId	1.30	IVd	0.97	72.75 (72.67)	3.18 (3.13)	4.38 (4.34)
IIIe	0.73	IVe	0.69	67.13 (67.05)	2.96 (2.96)	4.20 (4.11)

^a Polymerization was carried out with equimolar quantities of **1,6-BAPON** and aromatic dianhydrides to obtain a 10 wt % poly(amic acid) solution.

^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.

^e Data in parentheses are the calculated values.

properties, and thermal properties of the polyimides were investigated.

EXPERIMENTAL

Materials

1,6-Bis(4-aminophenoxy)naphthalene (**1,6-BAPON**) (**I**) was synthesized by the method as described in the accompanying article. Reagent grade aromatic tetracarboxylic dianhydrides such as 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA, **IIb**, from

Chriskev), 4,4'-oxydiphthalic anhydride (ODPA, **IIc**, from Chriskev), and 4,4'-sulfonyldiphthalic anhydride (SDPA, **IIe**, from New Japan Chemical Co.) were used as received, and pyromellitic dianhydride (PMDA, **IIa**, from TCI), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, **IIId**, from TCI) 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.

Polymerization

A typical example of polymerization is as follows. To a solution of 0.4280 g (1.25 mmol) of **1,6-BAPON** in 6.75 mL of DMAc, 0.2725 g (1.25 mmol) of PMDA was gradually added in small portions. The solution was stirred at room temperature for 2 h under a nitrogen atmosphere. The inherent viscosity of the resultant poly(amic acid) in DMAc was 2.31 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The weight-average molecular weight (\bar{M}_w) of the obtained poly(amic acid) was 21.32×10^4 g/mol, determined by GPC. The poly(amic acid) solution was spread on a glass plate and baked at 80°C for 1 h to obtain a semidried poly(amic acid) film. The imidization of the poly(amic acid) film was carried out by sequential heating at 120, 150, 180, 210, and 250° for 15 min each. The resulting polyimide film was stripped from the glass plate by soaking in hot water. The inherent viscosity of the polyimide was 1.02 dL/g in concentrated sulfuric acid (0.5 g/dL, 30°C).

Chemical cyclodehydration was also carried out by adding the mixture of acetic anhydride and pyridine (vol. ratio 2:1) into the poly(amic acid) solution with stirring at room temperature for 1 h, and then heating at 80°C for 3 h. The solution of the polymer was poured into methanol and the yellow precipitate was collected by filtration, washed thoroughly with

Table II. Average Molecular Weights of Poly(amic acid)s^a

Polymer	\bar{M}_n^b ($\times 10^4$ g/mol)	\bar{M}_w^b ($\times 10^4$ g/mol)	\bar{M}_w/\bar{M}_n Polydispersity Index
IIIa	8.32	21.32	2.56
IIIb	6.34	14.67	2.31
IIIc	4.32	8.69	2.01
IIId	5.80	12.89	2.22
IIIe	7.24	16.58	2.29

^a Polymerization was carried out with equimolar quantities of **1,6-BAPON** and aromatic dianhydrides to obtain 10 wt % poly(amic acid) solution.

^b Determined by GPC in DMF + 0.01 mol/L LiBr solution.

Table III. Solubility of 1,6-BAPON-Based Polyimides^a

Polymer ^c	Solvent ^b							
	DMAc	DMF	NMP	DMSO	<i>m</i> -Cresol	Py	<i>o</i> -Clpol	DMAc + 5 wt % LiCl
IVa	—	—	—	—	—	—	—	—
IVb	—	—	—	—	—	—	+	—
IVc	—	—	+—	—	+	—	+	—
IVd	—	—	—	—	—	—	+—	—
IVe	+	+	+	—	—	—	+	+

^a Solubility: +, soluble at room temperature; +—, partially soluble at room temperature; —, insoluble at room temperature.

^b DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide; Py, pyridine; *o*-Clpol, *o*-chlorophenol. All the polyimides were soluble in concentrated sulfuric acid.

^c Polyimides were obtained by the chemical conversion technique.

methanol and hot water, and dried at 100°C under vacuum.

The other polyimides (IVb–IVe) were prepared in a similar manner from 1,6-BAPON and other tetracarboxylic dianhydrides (IIb–IIe).

Measurements

Melting points were measured on a MEL-TEMP II capillary melting point apparatus (Laboratory Devices) without correction. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were run in a Perkin–Elmer model 240 C,H,N analyzer. The inherent viscosities of all the polymers were measured at 0.5 g/dL concentration with a Cannon–Fenske viscosimeter thermostated at 30°C. Weight- (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0.01 mol/L of LiBr).

Table IV. Mechanical Properties of 1,6-BAPON-Based Polyimides

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)	Thermal Expansion
				Coefficient ^a ($\mu\text{m}/\text{m}^\circ\text{C}$)
IVa	— ^b	—	—	58.2
IVb	126	16	1.53	46.6
IVc	104	10	1.84	65.7
IVd	95	11	1.59	54.0
IVe	100	9	1.80	46.6

^a Measured by thermomechanical analysis (TMA) at a heating rate of 10°C/min in nitrogen from room temperature to 350°C.

^b Could not be determined due to brittleness of cast film.

The thermal expansion coefficient was measured with a TMA V5.1A (Du Pont 2000) heated in flowing nitrogen (50 cm³/min) at a heating rate 20°C/min with film specimens of about 12 mm thick. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku thermal analysis station TAS-100. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm³/min) at a heating rate of 20°C/min. The differential scanning calorimetry (DSC) traces were performed on a SINKU-RIKO 7000 Differential Scanning Calorimeter coupled to a TA 7000 Thermal Analyzer in flowing nitrogen (30 cm³/min) at a heating rate of 20°C/min. The wide-angle x-ray diffraction patterns were obtained on a Rigaku Geiger D-Max IIIa x-ray diffractometer, using Ni-filtered CuK_α radiation (40 kV, 15 mA) with film specimens of about 0.1 mm in thickness. The scanning rate was 2°/min. An Instron universal

Table V. Thermal Properties of Polyimides Based on 1,6-BAPON

Polyimide	T_g (°C) ^a		Decomposition ^b Temperature (°C)		Residual ^c at 800°C (%)
	DSC	TMA	In N ₂	In Air	
	IVa	—	267	578	
IVb	273	269	595	590	65.0
IVc	248	271	578	550	64.9
IVd	268	232	574	571	60.9
IVe	286	266	549	539	53.8

^a Glass transition temperature (T_g) measured on DSC and TMA at a heating rate of 20°C/min and 10°C/min, respectively.

^b Temperature at 10% weight loss recorded on TGA at a heating rate of 20°C/min.

^c Residual wt % when heated to 800°C in nitrogen.

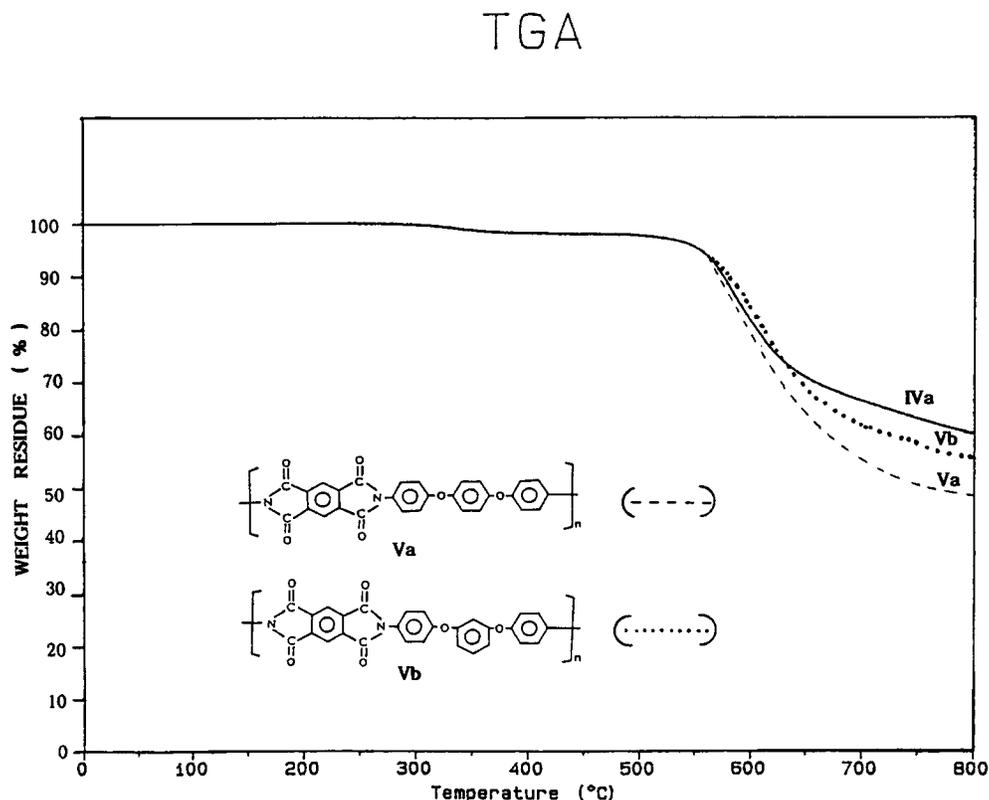


Figure 1. TGA thermograms of polyimides **IVa**, **Va**, and **Vb**, at a heating rate of 20°C/min in nitrogen.

tester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 0.1 mm thick); an average of at least six individual determinations was used.

RESULTS AND DISCUSSION

Preparation of Polyimides

New bis(phenoxy)naphthalene-containing aromatic polyimides were prepared by the conventional two-step procedure as shown in Scheme I. In the preparation of poly(amic acid)s from aromatic diamines and dianhydrides in a polar solvent, the process of monomer addition plays an important role for successful polymerization. As described in the previous study,¹⁹ the addition mode of adding solid PMDA to the solution of diamine produced poly(amic acid)s of higher molecular weight than the reverse addition mode or mixing the reactants together before po-

lymerization. The poly(amic acid)s **IIIa–e** were prepared by adding the dianhydride to the diamine as described previously (see Scheme 1).¹⁹

The inherent viscosities of all the poly(amic acid)s and the polyimides are summarized in Table I. The inherent viscosities of the poly(amic acid)s were in the range of 0.73–2.31 dL/g. The GPC curves indicated that \bar{M}_w values of poly(amic acid)s were in the range of 86,900–213,200 g/mol relative to standard polystyrene, and \bar{M}_w/\bar{M}_n values, a measure of molecular weight distribution, were not broad (2.01–2.56) (Table II). Except for the polymer from PMDA (dianhydride **IIIa**), all the poly(amic acid)s could be thermally converted into flexible and transparent polyimide films. By the thermal cyclodehydration procedure, the resulting polyimides had 0.69–1.02 dL/g in concentrated sulfuric acid. The elemental analysis values of these polyimides were in good agreement with the calculated values for the proposed structures (Table I). The IR spectrum showed characteristic absorptions for the imide ring around 1780 (asymmetrical C=O stretching), 1120 and 740 cm^{-1} (ring deformation). The poly(amic acid) appeared characteristic absorptions around 3300 and 1550–1650 cm^{-1} .

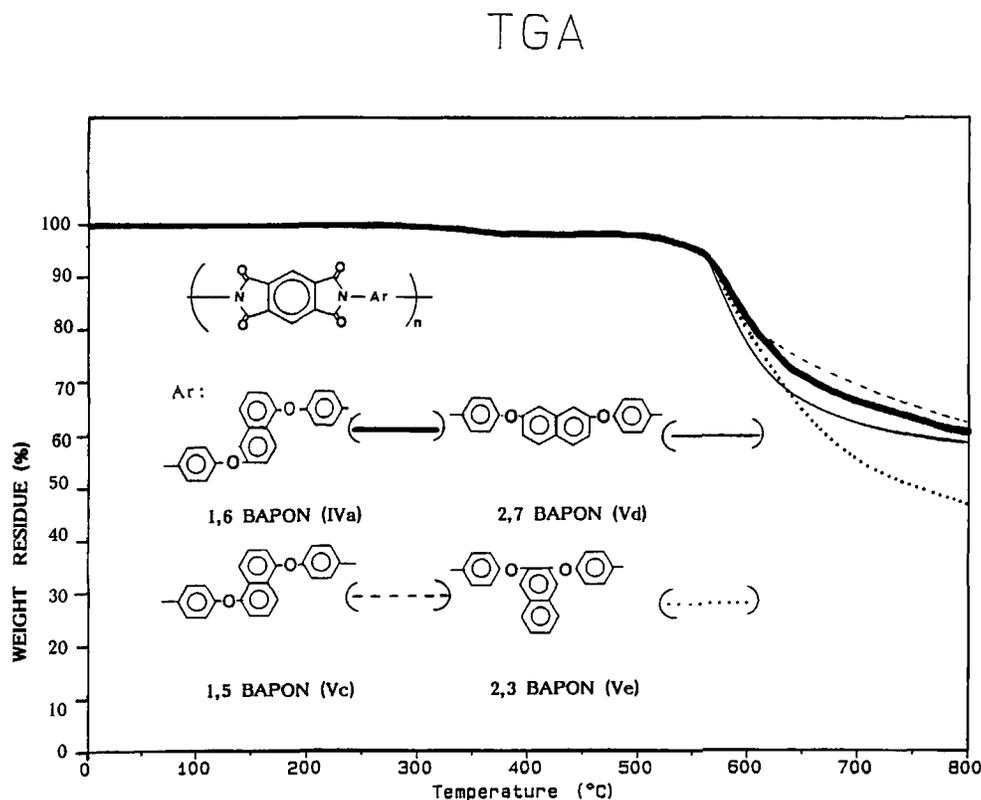


Figure 2. TGA thermograms of isomeric polyimides IVa, Vc, Vd, and Ve, with a heating rate of 20°C/min in nitrogen.

Properties of Polyimides

The solubility of the 1,6-substituted bis(phenoxy)naphthalene polyimides obtained by thermal or chemical imidization method was tested qualitatively in various solvents. The results are shown in Table III. Most of the polyimides prepared from thermal process are insoluble in the tested solvents, possibly due to the presence of partial intermolecular crosslinking. However, the polyimides obtained by chemical imidization showed slightly better solubility compared with those obtained by thermal imidization. Chemically cyclized polyimides IVc and IVe, possessing ether and sulfone linkages between phthalimide units, were soluble in organic solvents such as NMP and *o*-chlorophenol. Owing to the rigid structure of pyromellitimide, the polyimide IVa had the least solubility. All the polyimides imidized by thermal treatment or by chemical treatment are soluble in concentrated sulfuric acid.

Crystallinity of the polymers was examined by wide-angle x-ray diffraction diagrams. The polyimide films obtained by thermal imidization were employed as the samples. Except for polyimide IVa, which revealed slightly crystalline pattern, all the

polyimide films showed amorphous patterns. The tensile properties of the aromatic polyimide films prepared by the thermally imidization were summarized in Table IV. Polyimide IVa could not be cast into flexible film due to its rigid property. The films of the other polyimides had tensile strength of 95–126 MPa, elongation to break of 9–16%, and initial modulus of 1.53–1.84 GPa. Most of the polymer films exhibited a high tensile strength, high modulus, and a low elongation; thus, they could be considered as hard and strong materials.

The thermal behavior of the polymers was evaluated by differential scanning calorimetry (DSC), thermomechanical analyses (TMA), and thermogravimetric (TG) analyses. Table V summarizes the thermal transition data of all the polyimides. The TG curves for these polymers indicated that all polymers did not lose weight below 450°C, both in air and nitrogen atmospheres. The decomposition temperatures at which 10% weight loss were observed in the range of 549–595°C in nitrogen and 539–590°C in air, depending on the dianhydride. The amount of carbonized residue of polyimides at 800°C in nitrogen was above 53%, and polyimide IVb had the highest char yield up to 65%.

The thermal expansion coefficients determined by TMA were recorded in the range of $46.6\text{--}65.7 \times 10^{-6}/^\circ\text{C}$, as shown in Table IV. The polyimide (IVb), which derived from BPDA, had the lowest thermal expansion coefficient.

DSC measurements were conducted with a heating rate of $20^\circ\text{C}/\text{min}$. Quenching from the elevated temperature to room temperature in air shows more amorphous samples so that the glass transition temperatures (T_g) could be easily measured in the second heating traces of DSC. The glass transition temperatures of the polyimides were in the range of $248\text{--}286^\circ\text{C}$ by DSC and of $224\text{--}271^\circ\text{C}$ by TMA. Polymer IVa showed no discernible transition in the DSC traces. The high T_g of IVe can be attributed to the presence of polar sulfonyl group.

For comparison, the analogous polyimides Va and Vb, having phenylene rings only, were achieved from the polycondensation of 1,4-bis(*p*-aminophenoxy) benzene and 1,3-bis(*p*-aminophenoxy)benzene with PMDA. The comparative TG curves of polyimides IVa, Va, and Vb are indicated in Figure 1. They showed similar behavior before 550°C , whereas the naphthalene unit-containing polyimide IVa had a relatively higher char yield due to higher aromaticity. Moreover, the thermal stability of polyimide IVa was compared with that of its isomeric polyimides Vc, Vd, and Ve which exhibited 1,5-, 2,7-, and 2,3-substituted bis(phenoxy)naphthalene units in their polymer backbones. The syntheses of these three isomeric polymers have been described previously.¹⁸⁻²⁰ The comparative TGA curves shown in Figure 2 indicated that the 1,6-bis(phenoxy)naphthalene-containing polyimide IVa had slightly less stability than the 1,5-substituted isomeric polyimide Vc and higher stability than the 2,7- and 2,3-substituted isomeric polyimides Vd and Ve.

CONCLUSIONS

The 1,6-bis(phenoxy)naphthalene-containing aromatic polyimides having high molecular weight were successfully prepared from 1,6-bis(4-aminophenoxy)naphthalene. The polyimides have T_g s in the range $248\text{--}286^\circ\text{C}$ and lose 10% weight in the range $539\text{--}590^\circ\text{C}$ in nitrogen as determined by TGA. Furthermore, the films of the present polyimides possessed excellent tensile properties. Accordingly, the present polyimides may be considered as new promising high-temperature polymeric materials.

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