

Polyimides Based on "Multiring" Flexible Diamines

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Abstract: The five benzene rings-containing (hereafter for convenience, referred to as "five-ring") diamines α,α' -bis[4-(4-aminophenoxy)phenyl]-1,4 (or 1,3)-diisopropylbenzene (*p*- or *m*-**3**) were prepared by a nucleophilic substitution of α,α' -bis(4-hydroxyphenyl)-1,4 (or 1,3)-diisopropylbenzene (*p*- or *m*-**1**) with *p*-chloronitrobenzene in the presence of K_2CO_3 and then hydro-reduced. The polyimides were synthesized from diamine **3** and various aromatic dianhydrides via the two-stage procedure that include ring-opening polyaddition in DMAc to give poly(amic acid)s, followed by thermal conversion to polyimides. The poly(amic acid)s had inherent viscosities of 0.63-1.54 dL/g depending on the dianhydrides used. Almost all the poly(amic acid)s could be solution-cast and thermally converted into transparent, flexible, and tough polyimide films. These polyimides have glass transition temperatures in the range of 186-290 °C and almost no weight loss up to 500 °C in air or nitrogen atmosphere. The polyimide obtained from pyromellitic dianhydride and diamine *m*-**3** showed two endothermic peaks of 270 and 300 °C on the diagram of differential scanning calorimetry (DSC), and the other polyimides showed no endotherms on their DSC traces.

Keywords: "Multiring" diamines, Aromatic dianhydrides, Poly(amic acid)s, Polyimides.

Introduction

Polyimides are gaining wide acceptance by industry because of their outstanding thermal behavior combined with their excellent mechanical and electrical properties [1-5]. Their versatile applications, however, have been restricted owing to their high melting points and insolubility in organic solvents. Considerable efforts to polyimide structural modification are devoted continuously to improve the processability with limited reduction in thermal stability. For example, the incorporation of flexibilizing or angular linkages such as arylene ether (-O-), methylene (-CH₂-), ketone (-CO-), sulfone (-SO₂-), isopropylidene [-C(CH₃)₂-], perfluoroisopropylidene [-C(CF₃)₂-] etc. and/or bulky substituents such as fluorene, tetraphenylthiophene, indane etc. [6-12] into polymer backbone are common strategies. Solubility, glass transition temperature, and crystallinity can be adjusted by varying the nature of aromatic ring systems and the number of ether-, ketone-, and sulfone linkages within the diamine monomer. Ultem (General Electric), XU 218 (Ciba Geigy), and LARC-TPI (NASA) are some examples.

Introduction of aryl ether linkages into polymer backbone is known to impart solubility and processability to the polymer without greatly sacrificing thermal stability. This kind of polyimide structural modification was usually employed by the insertion of arylene ether segments to the diamine monomer. The approach to synthesize the bis(*p*-aminophenoxy) compound by a nucleophilic substitution of a bisphenol with *p*-chloronitrobenzene followed by reduction of the resulting dinitro compound was very popular in the literature [11-17].

In this study, two bisphenol compounds α,α' -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (*p*-**1**) and α,α' -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (*m*-**1**) are condensed with *p*-chloronitrobenzene to yield α,α' -bis[4-(4-nitrophenoxy)phenyl]-1,4 (or 1,3)-diisopropylbenzene (*p*-**2** or *m*-**2**), and subsequently reduced to α,α' -[4-(4-aminophenoxy)phenyl]-1,4 (or 1,3)-diisopropylbenzene (*p*-**3** or *m*-**3**). These two long-chain diamines have five phenylene rings, linked by two ether and two isopropylidene groups between the rings, between the amino groups. Although the syntheses of the diamines and some of their derived polyimides have been reported in the patent

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literature [18], only a little information is available about this kind of polyimides. The preparation and characterization of a series of polyimides derived from the five-ring diamines will be described in the present article. The introduction of the five-ring diamine leads not only to the incorporation of flexible aryl ether and isopropylidene groups coupling the aromatic portions of the polymer chains but also to a dilution of the phthalimide groups in the polymer chains. Therefore, the beneficial effects on polyimide processability such as enhanced solubility and thermostability are expected.

Experimental

1. Materials

α,α' -Bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (**p-1**) and α,α' -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (**m-1**) were used as received from Mitsui Petrochemical Ind. (Japan). Hydrazine monohydrate (from Wako), *p*-chloronitrobenzene (from TCI), 10 % palladium on activated charcoal (Pd/C) (from Fluka) were used without further purification.

Pyromellitic dianhydride (PMDA; **4a**, from Aldrich) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA; **4d**, from Aldrich) were recrystallized from acetic anhydride before use. 3,3',4,4'-Biphenyl tetracarboxylic dianhydride (BPDA; **4b**, from Oxychem), 4,4'-oxydiphthalic anhydride (ODPA; **4c**, from Oxychem), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA; **4e**, from New Japan Chemical Co.), and 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA; **4f**, from Chriskev) were used without further purification. *N,N*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2. α,α' -Bis[4-(4-nitrophenoxy)phenyl]-1,4-diisopropylbenzene (**p-2**)

In a 500 mL round-bottomed flask, 69.3 g (0.2 mol) of bisphenol **p-1** and 66.3 g (0.42 mol) of *p*-chloronitrobenzene were dissolved in 200 mL of dried DMF. Then, 72.2 g (0.52 mol) of anhydrous potassium carbonate was added and the reaction mixture which appeared in a form of suspension solution was refluxed at 160 °C for 8 hrs. The mixture was allowed to cool and subsequently poured into 600 mL of 1:1 methanol-water to precipitate a yellow solid which was collected by filtration and dried. Yield: 115.4 g (98 %). The crude product was recrystallized from DMF. Yield: 111.8 g (95 %); mp 195-197 °C.

IR (KBr): 1568 and 1342 cm^{-1} ($-\text{NO}_2$), 1296

cm^{-1} ($-\text{O}-$). Anal. calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_6$: C, 73.45; H, 5.48; N, 4.76 %. Found: C, 73.39; H, 5.71; N, 4.92 %.

3. α,α' -Bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**p-3**)

The dinitro compound **p-2** (100 g; 0.17 mol), 0.4 g of Pd/C, 1000 mL of ethanol and 700 mL of tetrahydrofuran (THF) were placed into a 2000 mL flask to which 200 mL of hydrazine monohydrate were added dropwise over a period of 1 hr at 85 °C. After the addition was complete, the reaction was continued at reflux temperature for another 10 hrs. The mixture was then filtered to remove Pd/C. After cooling, the precipitated white crystals were isolated by filtration and dried in vacuum; mp 187-189 °C. Yield: 85.4 g (95 %).

IR (KBr): 3412, 3344 cm^{-1} ($-\text{NH}_2$), and 1236 cm^{-1} ($-\text{O}-$). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.10 (t, 8H), 6.73 (d, 8H), 6.57 (d, 4H), 4.95 (s, 4H, $-\text{NH}_2$), and 1.57 ppm (s, 12H, $-\text{CH}_3$). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$): δ 156.69, 147.34, 145.59, 145.35, 143.49, 127.61, 125.97, 120.86, 115.80, 114.83 (aromatic carbons), 41.42 (quaternary carbon), and 30.48 ppm (methyl carbon). Anal. calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_6$: C, 81.79; H, 6.86; N, 5.36 %. Found: C, 81.78; H, 7.15; N, 5.37 %.

4. α,α' -Bis[4-(4-nitrophenoxy)phenyl]-1,3-diisopropylbenzene (**m-2**)

The dinitro compound **m-2** was prepared by a similar procedure of **p-2** synthesis. Yield: 94 %; mp 155-156 °C.

IR (KBr): 1589 and 1348 cm^{-1} ($-\text{NO}_2$), 1270 cm^{-1} ($-\text{O}-$). Anal. calcd for $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_6$: C, 73.45; H, 5.48; N, 4.76 %. Found: C, 73.43; H, 5.69; N, 4.93 %.

5. α,α' -Bis[4-(4-aminophenoxy)phenyl]-1,3-diisopropylbenzene (**m-3**)

The dinitro compound **m-2** (100 g; 0.17 mol), 0.3 g of Pd/C, and 500 mL of ethanol were placed into a 1000 mL flask to which 130 mL of hydrazine monohydrate were added dropwise over a period of 1 hr at 85 °C. After the addition was complete, the reaction was continued at reflux temperature for another 8 hrs. The mixture was then filtered to remove Pd/C and 700 mL of H_2O were added after cooling. Subsequently, the product gradually solidified and lumped. After the lumped product was ground, the white powders were collected by filtration, and dried in vacuum. Yield: 83.6 g (93 %); mp 101-103 °C.

IR (KBr): 3456, 3300 cm^{-1} ($-\text{NH}_2$), and 1236 cm^{-1} ($-\text{O}-$). $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.07 (m, 8H), 6.60 (d, 8H), 6.58 (d, 4H), 4.90 (s, 4H, $-\text{NH}_2$), and 1.56 ppm (s, 12H, $-\text{CH}_3$). $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$): δ 156.53, 149.67, 145.81, 145.10, 143.52, 127.49, 124.54, 123.65, 120.61, 115.78, 114.81 (aromatic carbons), 41.92 (quaternary carbon), and 30.54 (methyl

carbon). Anal. calcd for $C_{36}H_{36}N_2O_2$: C, 81.79; H, 6.86; N, 5.30 %. Found: C, 81.80; H, 7.18; N, 5.40 %.

6. Polymer Synthesis

6.1 Preparation of poly(amic acid) (*p*-5a)

0.2921 g (1.34 mmol) of pyromellitic dianhydride was slowly added to a stirred solution of 0.7079 g (1.34 mmol) of diamine *p*-3 in 9.5 mL of DMAc under a nitrogen atmosphere at room temperature. Polymerization solution was continuously stirred for 1 hr after the complete addition of the dianhydride, and a highly viscous poly(amic acid) solution of 10 wt % solid was obtained. The inherent viscosity of the poly(amic acid) in DMAc was 1.39 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): 2970-3308 cm^{-1} (carboxylic acid O-H and amide N-H), 1719 cm^{-1} (carboxylic C=O), and 1660 cm^{-1} (amide, C=O).

6.2 Polyimide *p*-6a prepared by thermal conversion method

The obtained poly(amic acid) solution of *p*-5a was poured into a $\phi = 9$ cm glass culture dish. Then, the culture dish was placed in a 80 °C oven for 4 hrs to remove the solvent. The obtained semi-dried poly(amic acid) film was further dried and transformed into polyimide by sequential heating at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 200 °C for 10 min, 220 °C for 10 min, and 250 °C for 30 min. On cooling, a flexible and tough polyimide film of about 0.1 mm thickness was obtained. IR (film): 1779 and 1727 cm^{-1} (imide ring, symmetrical and asymmetrical C=O stretching), and 725 cm^{-1} (imide ring deformation).

All other poly(amic acid)s and polyimides were prepared by an analogous procedure as above.

7. Measurements

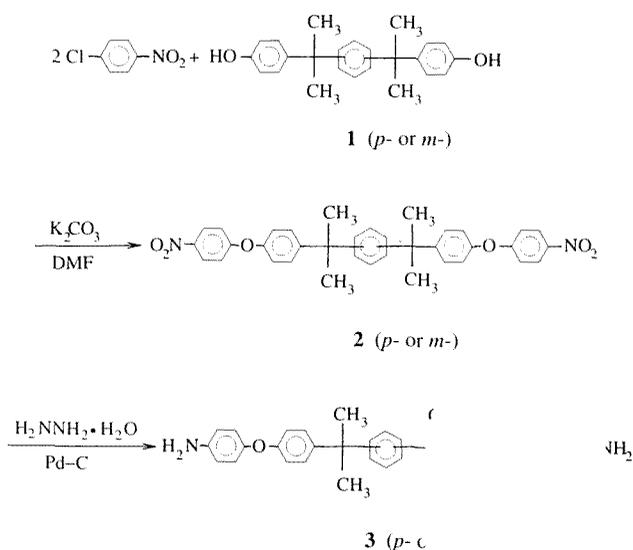
The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30 °C. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were performed using a Perkin-Elmer C, H, N 2400 elemental analyzer. 1H NMR and ^{13}C NMR spectra were determined at 30 °C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide ($DMSO-d_6$) as an external reference, working at 400 and 100 MHz, respectively. The DSC traces were measured on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller at the heating rate of 20 °C/min in flowing nitrogen (30 cm^3/min). Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or

air (50 cm^3/min) at a heating rate of 20 °C/min. The measurements were taken after an initial 250 °C/5min drying step. The wide-angle X-ray scattering measurements were performed at room temperature (about 25 °C) with film specimens of about 0.1 mm thick with a Rigaku Geiger Flex D-Max III_a X-ray diffractometer, using Ni-filtered $CuK\alpha$ radiation (operating at 40 kV and 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5-40^\circ$. Tensile properties were determined from stress-strain curves obtained by an Instron universal tester Model 1130 with a load cell of 5 kg. A gauge of 2 cm and an elongation rate of 5 cm/min were used for this study. The measurements were performed at room temperature using solution-cast film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick) and an average of at least five individual determinations was used.

Results and Discussion

1. Monomer Synthesis

The five-ring diamines *p*-3 and *m*-3 were synthesized in two steps starting from their bisphenol precursors and *p*-chloronitrobenzene (Scheme 1). In the first step, α, α' -bis(4-hydroxyphenyl)-1,4 (or 1,3)-diisopropylbenzene (*p*- or *m*-1) and *p*-chloro nitrobenzene were condensed in the presence of a base such as K_2CO_3 in an aprotic polar solvent like DMF, giving rise to the corresponding bis(4-nitrophenoxy) compound 2. The intermediate dinitro compounds 2 were then catalytically reduced to the desired di-



Scheme 1

amines *m*- and *p*-**3** using hydrazine as the reducing agent and palladium as the catalyst. The yield was high (93-95 %), and the purity was also high enough for the preparation of polymers with high molecular weights. The structures of intermediate dinitro compounds **2** and diamines **3** were confirmed by elemental analysis, FTIR, ¹H NMR and ¹³C NMR spectroscopy, and the results were in good agreement with proposed structures.

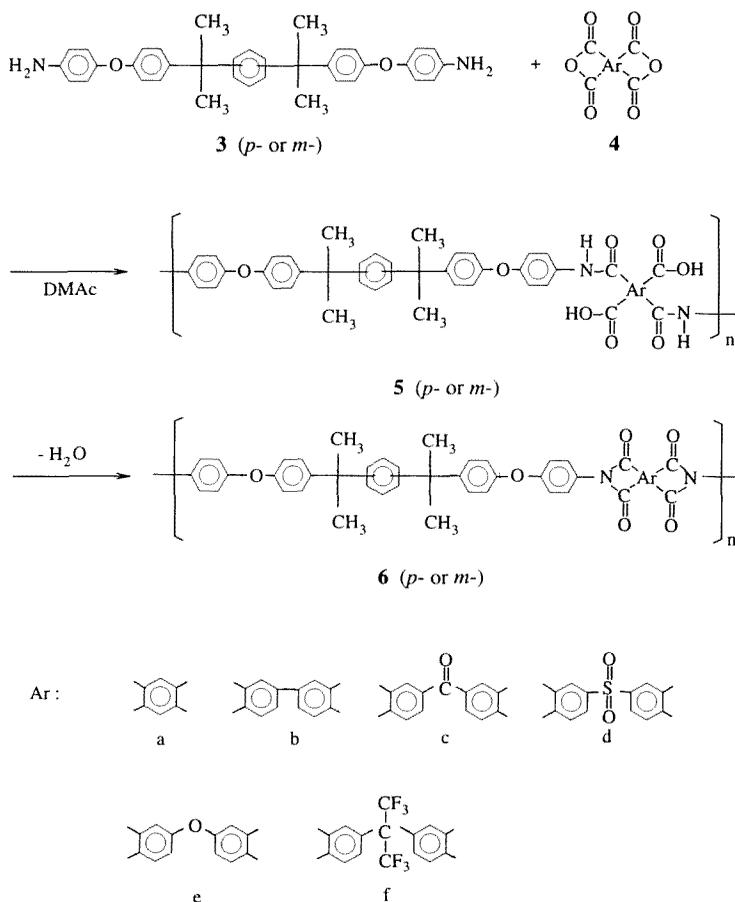
2. Polymer Synthesis

The synthesis of polyimide was carried out by the classic two-step method. As shown in Scheme 2, a series of poly(amic acid)s were produced by reacting the diamine *p*-**3** or *m*-**3** with various aromatic dianhydrides via ring-opening polyaddition in dried DMAc at room temperature. The generated poly(amic acid)s were then cyclodehydrated to the corresponding polyimides by extended heating at elevated temperature. The inherent viscosities of the poly(amic acid)s were in the range of 0.63-1.54 dL/g, measured

at 30 °C on a concentration of 0.5 g/dL in DMAc (Table I). All the poly(amic acid)s were of sufficiently high molecular weights to permit casting flexible and tough poly(amic acid) films. The poly(amic acid)s *m*-**5a-f**, which have meta catenation of the central benzene in the diamine moiety, had less rigid polymer backbone and, hence, exhibited relatively lower viscosities compared with their corresponding *p*-isomers. Except for poly(amic acid) *m*-**5a**, all the poly(amic acid)s could be converted into tough and flexible polyimide films by heat treatment. The formation of poly(amic acid)s and polyimides was confirmed by means of IR spectroscopy. The elemental analysis values were in good agreement with the proposed structures of the polyimides.

3. Properties of Polymers

The solubility of polyimides were tested qualitatively in various solvents. As shown in Table II, the polyimides derived from ODA (**4c**), DSDA (**4e**), and 6FDA (**4f**), the dianhydrides with flexible ether link-



Scheme 2

Table I. Inherent Viscosities of Poly(amic acid)s **5a-f** and Elemental Analyses of Polyimides **6a-f**.

Poly(amic acid)		Polyimide					
Code	$\eta_{inh}^{(a)}$ (dL/g)	Code	Formula (M.W.)	Elemental analysis			
				C %	H %	N %	
<i>p</i> -5a	1.39	<i>p</i> -6a	(C ₄₆ H ₃₄ N ₂ O ₆) _n (710.79) _n	Calc.	77.73	4.82	3.94
				Found	76.83	4.70	4.07
<i>p</i> -5b	1.16	<i>p</i> -6b	(C ₅₂ H ₃₈ N ₂ O ₆) _n (786.89) _n	Calc.	79.37	4.87	3.56
				Found	78.61	4.93	3.61
<i>p</i> -5c	0.92	<i>p</i> -6c	(C ₅₂ H ₃₈ N ₂ O ₇) _n (802.89) _n	Calc.	77.7	4.77	3.49
				Found	77.32	4.73	3.43
<i>p</i> -5d	1.40	<i>p</i> -6d	(C ₅₃ H ₃₈ N ₂ O ₇) _n (814.90) _n	Calc.	78.12	4.70	3.44
				Found	77.46	4.70	3.54
<i>p</i> -5e	1.43	<i>p</i> -6e	(C ₅₂ H ₃₈ N ₂ SO ₈) _n (850.95) _n	Calc.	73.40	4.50	3.29
				Found	72.61	4.52	3.36
<i>p</i> -5f	1.54	<i>p</i> -6f	(C ₅₅ H ₃₈ N ₂ F ₆ O ₆) _n (936.92) _n	Calc.	70.51	4.09	2.99
				Found	70.18	4.08	3.10
<i>m</i> -5a	1.01	<i>m</i> -6a	(C ₄₆ H ₃₄ N ₂ O ₆) _n (710.79) _n	Calc.	77.73	4.82	3.94
				Found	77.46	4.75	4.04
<i>m</i> -5b	0.98	<i>m</i> -6b	(C ₅₂ H ₃₈ N ₂ O ₆) _n (786.89) _n	Calc.	79.37	4.87	3.56
				Found	79.03	4.76	3.55
<i>m</i> -5c	0.63	<i>m</i> -6c	(C ₅₂ H ₃₈ N ₂ O ₇) _n (802.89) _n	Calc.	77.79	4.77	3.49
				Found	77.65	4.77	3.54
<i>m</i> -5d	1.20	<i>m</i> -6d	(C ₅₃ H ₃₈ N ₂ O ₇) _n (814.90) _n	Calc.	78.12	4.70	3.44
				Found	77.73	4.65	3.52
<i>m</i> -5e	1.01	<i>m</i> -6e	(C ₅₂ H ₃₈ N ₂ SO ₈) _n (850.95) _n	Calc.	73.40	4.50	3.29
				Found	73.07	4.46	3.32
<i>m</i> -5f	0.87	<i>m</i> -6f	(C ₅₅ H ₃₈ N ₂ F ₆ O ₆) _n (936.92) _n	Calc.	70.51	4.09	2.99
				Found	70.37	3.96	3.01

(a) Measured on 0.5 g/dL in DMAc, at 30 °C.

Table II. Solubilities of Polyimides^(a).

Polymer	Solvents ^(b)						
	conc. H ₂ SO ₄	NMP	DMI	DMAc	DMF	DMSO	Py
<i>p</i> -6a	-	-	-	-	-	-	-
<i>p</i> -6b	-	-	-	-	-	-	-
<i>p</i> -6c	+	+	-	-	+	-	+
<i>p</i> -6d	+	-	-	-	-	-	-
<i>p</i> -6e	+	+	+	+	+	-	+
<i>p</i> -6f	+	+	+	+	+	-	+
<i>m</i> -6a	-	-	-	-	-	-	-
<i>m</i> -6b	+	-	-	-	-	-	-
<i>m</i> -6c	+	+	+	+	+	-	+
<i>m</i> -6d	+	-	+	-	-	-	-
<i>m</i> -6e	+	+	+	+	+	+	+
<i>m</i> -6f	+	+	+	+	+	+	+

(a) +: soluble, -: insoluble.

(b) NMP: *N*-methyl-2-pyrrolidone; DMI: 1,3-dimethyl-2-imidazolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine.

age or polar -SO₂- and -C(CF₃)₂- groups between the phthalic anhydride units, were quite soluble in most of the tested solvents. In contrast, the polyimides prepared from the dianhydrides PMDA (**4a**), BPDA (**4b**), and BTDA (**4d**) were sparingly soluble in common organic solvents. This solubility behavior may be explicable in terms of the polymer chain rigidity. Polymers containing ODPA, DSDA, and 6FDA will have a flexible linking moiety that can also participate in solvation. Whereas, the polyimides from the dianhydrides PMDA and BPDA will lack functional groups that can participate in solvation, thereby diminishing their solubility in the usual organic solvents. However, the poor solubility of polyimides from BTDA may be associated with strong interpolymer interactions caused by the highly dipolar carbonyl bridge. Polyimide *m*-6c obtained from ODPA showed slightly higher solubility than its *p*-isomer *p*-6c due to the less symmetrical polymer backbone. From these results, it may be concluded that the incorporation of the five-ring diamine moieties into the polyimide backbone seems not to give significant improvement in solubility; however,

soluble polyimides can be obtained by the combination of these five-ring diamines with the dianhydrides containing flexibilizing bridge such as ODPa, DSDA, and 6FDA.

The wide-angle X-ray scattering patterns of some polyimides with a more rigid backbone were taken on films. The results are shown in Figure 1, and all the samples do not show apparent crystallinity. However, beyond expectation, polyimide *m-6a* showed some degree of crystallinity, with a reflection peak around $2\theta = 20^\circ$. This corresponded to the brittle nature of the polyimide film of *m-6a*. All other polymers showed amorphous nature and afforded flexible and tough polyimide films.

The tensile properties of the polyimide films are summarized in Table III. These films had tensile strength of 64-90 MPa, elongation to break of 6-21 %, and initial modulus of 1.04-1.69 GPa. The films of polyimides *p-6d* and *p-6e* possessed a yield point in their stress-strain curves, and exhibited higher elongation to break than the others. This indicates that they are more ductile than the other polyimides.

The thermal properties of these polyimides were evaluated by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). The thermal behavior data are listed in Table IV. DSC measure-

ments were conducted with a heating rate of 20 °C/min in nitrogen. Rapid cooling from elevated temperatures (about 400 °C) to room temperatures yield more amorphous samples so that in all cases clear base line shifts were observed in the subsequent second heating traces of DSC. The mid-point of the base line shift was defined as T_g of the polymer. The T_g values of polyimides *p-6a-f* were recorded in the range of 225-290 °C, and their *m*-isomers, *m-6a-f*, showed relatively lower T_g values between 186-248 °C. This is quite reasonable because the meta catenation increased the overall chain flexibility. Comparison of T_g 's of the polyimides obtained from different

Table III. Tensile Properties of Polyimide Films.

Polymer	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
<i>p-6a</i>	—	85	9	1.40
<i>p-6b</i>	—	66	7	1.04
<i>p-6c</i>	80	76	21	1.46
<i>p-6d</i>	70	64	15	1.31
<i>p-6e</i>	—	73	8	1.34
<i>p-6f</i>	—	86	11	1.48
<i>m-6a</i>	—	—	—	—
<i>m-6b</i>	—	68	7	1.50
<i>m-6c</i>	—	72	7	1.42
<i>m-6d</i>	—	85	8	1.33
<i>m-6e</i>	—	90	7	1.69
<i>m-6f</i>	—	61	6	1.28

Table IV. Thermal Properties of Polyimides.

Polymer	T_g (°C) ^(a)	T_d (°C) ^(b)		Char residual (%)
		in air	in N ₂	
<i>p-6a</i>	290	540	535	47.0
<i>p-6b</i>	228	550	535	65.9
<i>p-6c</i>	225	539	533	49.0
<i>p-6d</i>	235	542	534	53.9
<i>p-6e</i>	251	501	500	30.3
<i>p-6f</i>	241	531	539	57.3
<i>m-6a</i>	248 ^(c)	535	535	47.0
<i>m-6b</i>	195	535	536	52.0
<i>m-6c</i>	186	532	529	45.0
<i>m-6d</i>	197	520	518	54.7
<i>m-6e</i>	209	509	495	31.1
<i>m-6f</i>	204	541	536	50.4

(a) From the second heating DSC trace after quenched from 400 °C to room temperature. Heating rate: 20 °C/min.

(b) Temperatures at which 10 % weight loss was recorded by TG at a heating rate of 20 °C/min.

(c) With two endothermic peaks around 270 and 300 °C in the first heating trace of DSC.

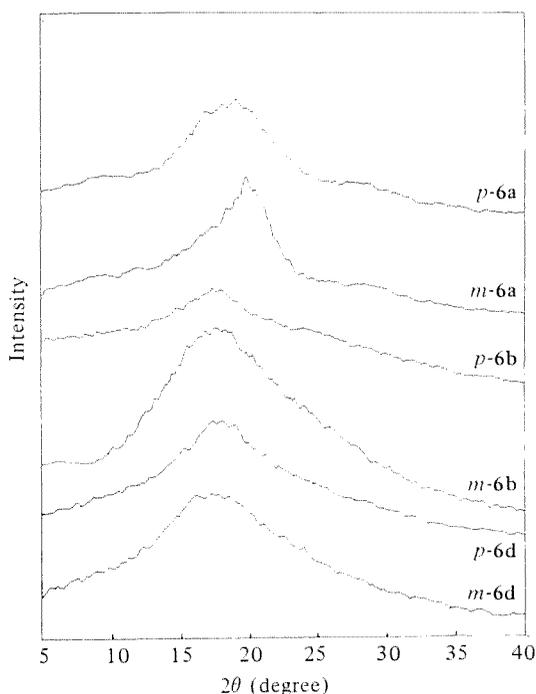


Figure 1. X-ray diffraction patterns of some representative polyimides.

dianhydrides showed that the polyimides derived from rigid PMDA had the highest T_g 's, and, on the contrary, those derived from ODPDA showed the lowest T_g 's because of the presence of flexible ether bridge between the phthalimide groups. Only polyimide *m-6a* revealed endothermic peaks on the DSC heating traces; the other polyimides, however, showed no endotherms. Figure 2 shows the DSC thermograms of polyimide *m-6a*. This polyimide shows two endothermic peaks of 270 and 300 °C. It has been proved to be a liquid crystalline polyimide, reported in a recent publication [19]. Although the reasons that the molecular structure of polyimide *m-6a* exhibits a liquid crystalline phase is unclear, the hard pyromellitimide unit and the flexible *m*-diisopropylbenzene unit are probably important for showing thermotropic liquid crystal polyimide.

Figure 3 illustrates typical TG thermograms for the representative polyimide *p-6a* in both air and nitrogen atmosphere at a heating rate of 20 °C/min. From these TG curves it is deduced that the polymer is highly resistant to heat, since no significant weight loss occurred before 500 °C. In nitrogen atmosphere, the initial decomposition temperature is slightly higher than in air, and about 47 % weight residue were obtained even at 800 °C, in contrast to the almost weight loss of the polymer when decomposed in air well below this temperature. However, presumably due to some oxidative crosslinking, the rate of thermal decomposition in air was slightly lower than in nitrogen before 600 °C. All other polyimides showed a similar thermal behavior, and almost all the polymers lost 10 % weight above 500 °C, with 30.3-65.9 % char residue remaining at 800 °C in a nitrogen atmosphere (Table IV). The relatively lower char residues for the polyimides obtained from DSDA may be associated with the degradation of the sulfonyl bridging groups.

Conclusion

Two five-ring diamines were successfully prepared in high purity and high yields in this study, and moderate to high molecular weight poly(amic acid)s were synthesized by reacting these diamines with aromatic tetracarboxylic dianhydrides in DMAc. Almost all the poly(amic acid)s could be thermally converted into transparent, tough, and flexible polyimide films with excellent tensile properties. The results of thermal analyses and solubility test of these polymers proved that the introduction of this kind of diamine structure could impart processability to the polymer while with limited reduction in thermal stability. Thus, the present polyimides are considered as new candidates for processable high-performance polymeric materials.

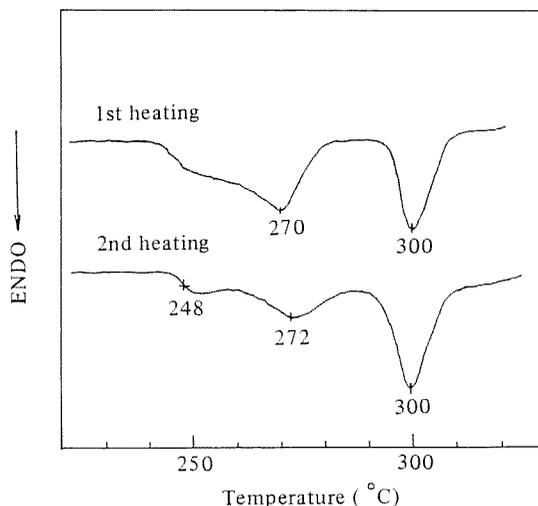


Figure 2. DSC thermograms of polyimide *m-6a*, with a heating rate of 20 °C/min in N_2 .

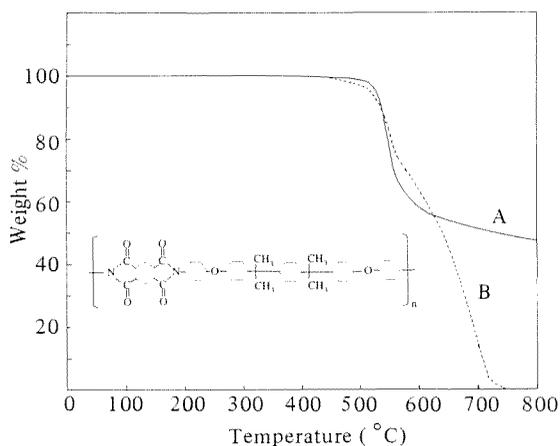


Figure 3. TG curves of polyimide *p-6a* (A) in N_2 and (B) in air, with a heating rate of 20 °C.

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