

# Syntheses and Properties of Polyimides based on Bis(*p*-aminophenoxy)biphenyls

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**Abstract:** Three biphenyl unit-containing diamines, 4,4'-bis(*p*-aminophenoxy)biphenyl (III<sub>a</sub>), 2,2'-bis(*p*-aminophenoxy)biphenyl (III<sub>b</sub>), and 3,3',5,5'-tetramethyl-4,4'-bis(*p*-aminophenoxy)biphenyl (III<sub>c</sub>), were prepared by the chlorodisplacement of *p*-chloronitrobenzene with 4,4'-biphenol (I<sub>a</sub>), 2,2'-biphenol (I<sub>b</sub>), and 3,3',5,5'-tetramethyl-4,4'-biphenol (I<sub>c</sub>), respectively, giving the corresponding bis(nitrophenoxy) compounds II<sub>a-c</sub>, followed by catalytic reduction with palladium (Pd) and hydrazine. Three series of polyimides *p*-PI, *o*-PI, and Me-PI were prepared from diamines III<sub>a-c</sub> and aromatic tetracarboxylic dianhydrides via a two-stage procedure that included ring-opening polyaddition to give poly(amic acid)s followed by thermal cyclodehydration to polyimides. The resultant three series of poly(amic acid)s had inherent viscosities of 1.09-2.83, 0.78-1.93, and 1.55-3.09 dL/g, respectively. Almost all the poly(amic acid)s could be solution-cast and thermally converted into transparent, flexible, and tough polyimide films. All the polyimides were characterized by solubility, tensile test, wide-angle X-ray scattering measurements, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Effects of the structures of aromatic diamines and dianhydrides on the properties of polyimides were investigated.

**Keywords:** Bis(*p*-aminophenoxy)biphenyl, Polyimides.

## Introduction

Because of the unique combination of mechanical and electrical properties, chemical inertness, and elevated temperature performance, aromatic polyimides are a class of thermally stable representative polymers and are becoming more and more important [1-5]. Polyimides are primarily used in the aerospace and electronic industries in the forms of films and moldings. Other uses for these polymers such as adhesives, composite matrices, coatings and foams are rapidly increasing. However, aromatic polyimides are difficult to process because of the poor flow characteristics below their decomposition temperatures and insolubility in commercially available solvents. In fact, they are usually processed via the form of their poly(amic acid) precursors.

Films of aromatic polyimide represent the largest end-use area for the polyimides. DuPont's Kapton (ODA-PMDA)\*\* dominated the polyimide market until expiration of patent protection some years ago. The competitive products came on the market included Ube's Upilex-R (ODA-BPDA) and Upilex-S (PPD-BPDA), Mitsubishi's Novax [ODA/3,3'-

dimethylben-zidine (50/50)-PMDA] and Kaneguchi's Apical (ODA-PMDA). Despite the numerous polymeric structures studied over the past several decades, the search for new ones continues unabated because emerging applications demand even better performance not met by current commercial products. For instance, advancing technology has placed more stringent demands on polyimides including higher mechanical stiffness and strength; lower dielectric constant, moisture absorption, and coefficient of thermal expansion (CTE); and ease of processing. Many polyimides derived from biphenylene unit-containing diamines such as 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) [6], 2,2'-bis(fluoroalkoxy) benzidines [7], and 2,2',3,3',5,5'-hexamethyl-4,4'-bis(*p*-aminophenoxy)biphenyl [8], were reported to have low dielectric constant and thermal expansion coefficient.

In this work, three biphenyl unit-containing diamines 4,4'-bis(*p*-aminophenoxy)biphenyl (III<sub>a</sub>), 2,2'-bis(*p*-aminophenoxy)biphenyl (III<sub>b</sub>), and 3,3',5,5'-tetramethyl-4,4'-bis(*p*-aminophenoxy)biphenyl (III<sub>c</sub>) are synthesized starting from their corresponding biphenols I<sub>a-c</sub> and *p*-chloronitrobenzene. The poly-

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\*\* ODA = 4,4'-oxydianiline, PPD = *p*-phenylenediamine, PMDA = pyromellitic dianhydride, BPDA = 3,3', 4,4'-biphenyltetracarboxylic dianhydride

imides are prepared via a conventional two-step procedure from these resultant diamines and aromatic tetracarboxylic dianhydride. Some properties such as solubility, crystallinity, tensile properties, and thermal properties of the obtained polyimides are also investigated. Although some polyimides prepared from diamines III<sub>a</sub> and III<sub>c</sub> have been reported in the patent literature [8-10], only limited information is available about this kind of polyimides. More detailed and systematic studies on these polyimides are carried out in the present work. For comparison, the polyimides of diamine III<sub>b</sub> are also synthesized and characterized though they have been described in a recent publication [11].

## Experimental

### 1. Materials

Three kinds of biphenol such as 4,4'-biphenol (I<sub>a</sub>) (from Fluka), 2,2'-biphenol (I<sub>b</sub>) (from Aldrich), and 3,3',5,5'-tetramethyl-4,4'-biphenol (I<sub>c</sub>) (from Mitsubishi Petrochemical Co.) were used as received. *p*-Chloronitrobenzene (from TCI), hydrazine monohydrate (from Wako), potassium carbonate (from Wako), 10% palladium on activated charcoal (Pd/C) (from Fluka) were used without purification. *N,N*-Dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Reagent grade aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (PMDA; IV<sub>a</sub>, from Aldrich) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA; IV<sub>d</sub>, from Aldrich) were recrystallized from acetic anhydride before use. 3,3',4,4'-Biphenyl tetracarboxylic dianhydride (BPDA; IV<sub>b</sub>, from Oxychem), 4,4'-oxydiphthalic anhydride (ODPA; IV<sub>c</sub>, from Oxychem), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA; IV<sub>e</sub>, from New Japan Chemical Co.), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; IV<sub>f</sub>, from Chriskev) were used as received.

### 2. Syntheses of dinitro compounds II<sub>a-c</sub>

The dinitro compounds II<sub>a-c</sub> were prepared by a nucleophilic aromatic substitution of *p*-chloronitrobenzene with the corresponding biphenols I<sub>a-c</sub> in the presence of a base, such as potassium carbonate, in a polar aprotic solvent like DMF. A typical preparative procedure for 4,4'-bis(*p*-nitrophenoxy)biphenyl (II<sub>a</sub>) is described as follows. In a 500-mL round-bottom flask, 40 g (0.161 mol) of 4,4'-biphenol (I<sub>a</sub>) and 50 g (0.323 mol) of *p*-chloronitrobenzene were dissolved in 150 ml of dry DMF. Then, 48 g (0.347 mol) of anhydrous potassium carbonate were added

into the above stirred solution, and the suspension was refluxed at 160°C for about 10 hrs. After cooling to room temperature, the reaction mixture was poured into 300 mL of a 1:1 volume mixture of water and methanol. The yellow precipitates were collected by filtration and recrystallized from DMF to afford 58 g (85% yield) of orange-yellow crystals; mp. 199-200°C. IR (KBr): 1586 (asym. NO<sub>2</sub> str.), 1340 (sym. NO<sub>2</sub> str.), 1245 cm<sup>-1</sup> (C-O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 8.29 (d, 4H), 7.82 (d, 4H), 7.30 (d, 4H), 7.21 ppm (d, 4H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 162.67, 153.97, 142.39, 136.34, 128.69, 126.69, 120.86, 117.59 ppm. Anal. calcd for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub> (428.40): C, 67.29; H, 3.76; N, 6.54%. Found: C, 67.20; H, 3.76; N, 6.41%.

The other two dinitro compounds, 2,2'-bis(*p*-nitrophenoxy)biphenyl (II<sub>b</sub>) and 3,3',5,5'-tetramethyl-4,4'-bis(*p*-nitrophenoxy)biphenyl (II<sub>c</sub>), were synthesized in an analogous procedure.

II<sub>b</sub>: mp. 158-159°C (lit. [11] 159-160°C), yield 88.7%. IR (KBr): 1587 (asym. NO<sub>2</sub> str.), 1350 (sym. NO<sub>2</sub> str.), 1234 cm<sup>-1</sup> (C-O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 8.09 (d, 4H), 7.43 (m, 4H), 7.30 (m, 2H), 7.14 (d, 2H), 6.09 ppm (d, 4H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): 162.45, 151.55, 141.99, 132.13, 130.12, 129.62, 125.91, 125.28, 120.68, 117.10 ppm. Anal. calcd for C<sub>24</sub>H<sub>16</sub>N<sub>2</sub>O<sub>6</sub> (428.40): C, 67.29; H, 3.76; N, 6.54%. Found: C, 67.39; H, 3.89; N, 6.41%.

II<sub>c</sub>: mp. 249-250°C, yield 74%. IR (KBr): 1591, 1340 (NO<sub>2</sub>), 1238 cm<sup>-1</sup> (C-O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 8.26 (d, 4H), 7.56 (s, 4H), 7.00 (d, 4H), 2.14 ppm (s, 12H, -CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 162.30, 149.37, 141.89, 137.18, 130.83, 127.72, 126.53, 115.16 (aromatic carbons), 15.94 ppm (methyl carbon). Anal. calcd for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub> (484.51): C, 69.41; H, 4.99; N, 5.78%. Found: C, 69.78; H, 5.07; N, 5.81%.

### 3. Syntheses of diamines III<sub>a-c</sub>

A typical synthetic example for 4,4'-bis(*p*-aminophenoxy)biphenyl (III<sub>a</sub>) is described as follows. Twenty grams (0.0467 mol) of the dinitro compound II<sub>a</sub>, 0.15 g of 10% Pd/C, and 600 mL of ethanol were placed into a 1500-mL flask. The suspension was heated to reflux temperature at about 85°C, and then 70 mL of hydrazine monohydrate were added dropwise over a period of 1 hr. After complete addition, the reaction was continued at reflux temperature for another 20 hrs. Since some products precipitated in the reaction medium, additional 400 mL of ethanol were added to redissolve the precipitates. The hot solution was filtered to remove Pd/C, and the product precipitated on cooling as shiny white platelets. After cooling, the white crystals were isolated by filtration, washed thoroughly with water, and then dried; mp. 198-199°C. Yield: 12.3 g (72%). IR (KBr): 1456, 3372 (N-H), 1228 cm<sup>-1</sup> (C-O). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.52 (d, 4H), 6.90 (d, 4H), 6.80 (d, 4H), 6.61 (d, 4H),

5.00 ppm (s, 4H, -NH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ 158.21, 145.53, 145.42, 133.35, 127.54, 120.94, 116.73, 114.85 ppm. Anal. calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (368.43): C, 78.24; H, 5.47; N, 7.60%. Found: C, 78.18; H, 5.55; N, 7.59%.

2,2'-Bis(*p*-aminophenoxy)biphenyl (III<sub>b</sub>) and 3,3',5,5'-tetramethyl-4,4'-bis(*p*-aminophenoxy)biphenyl (III<sub>c</sub>) were prepared in a similar manner.

Diamine III<sub>b</sub> was obtained in 96% yield; mp 157-158 °C (lit. [11] 158-159 °C). IR (KBr): 3460, 3370 (N-H), 1230 cm<sup>-1</sup> (C-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 7.36 (m, 2H), 7.22 (m, 2H), 7.06 (m, 2H), 6.73 (d, 6H), 6.62 (s, 4H), 4.95 ppm (s, 4H, -NH<sub>2</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ 156.53, 146.36, 145.08, 131.62, 128.73, 128.27, 121.72, 120.81, 115.96, 115.01 ppm. Anal. calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> (368.43): C, 78.24; H, 5.47; N, 7.60%. Found: C, 78.22; H, 5.58; N, 7.42%.

Diamine III<sub>c</sub> was obtained in 72 % yield; mp. 227-228 °C. IR (KBr): 3428, 3380 (N-H), 1205 cm<sup>-1</sup> (C-O). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 7.39 (s, 2H), 6.51 (d, 2H), 6.47 (d, 2H), 4.68 (s, 4H, -NH<sub>2</sub>), 2.11 ppm (s, 12H, -CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>): δ 150.87, 148.64, 143.05, 136.15, 131.21, 127.12, 115.14, 114.85 (aromatic carbons), 16.26 ppm (methyl carbon). Anal. calcd for C<sub>28</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub> (424.54): C, 79.22; H, 6.65; N, 6.60%. Found: C, 79.54; H, 6.71; N, 6.58%.

#### 4. Polymer synthesis

A typical polymerization procedure for the synthesis of poly(amic acid) *p*-PAA is as follows. To a stirred solution of 0.6281 g (1.7 mmol) of III<sub>a</sub> in 9.5 mL of dry *N,N*-dimethylacetamide (DMAc), 0.3719 g (1.7 mmol) of PMDA was added portionwise within 30 min at room temperature. After the addition of the dianhydride was complete, the reaction was continued for another 1 hr, 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 2.83 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): 3300-3000 (O-H and N-H), 1717 (C = O of carboxylic acid), 1657 (C = O of amide), 1241 cm<sup>-1</sup> (C-O-C).

All other poly(amic acid)s were prepared by a similar method.

#### 5. Polyimide film preparation

The poly(amic acid) solution was diluted with about 10 ml of DMAc and poured into a φ = 9-cm glass culture dish. The culture dish was placed in a 80 °C oven overnight to remove the solvent. The semi-dried poly(amic acid) film thus obtained was further dried and transformed into polyimide by sequential heating at 120 °C for 20 min, 150 °C for 20 min, 180 °C for 20 min, 200 °C for 20 min, 220 °C for 20 min, and 250 °C for 30 min. On cooling, a flexible and tough polyimide film of about 0.1 mm thickness self-

stripped from the glass surface.

#### 6. Measurements

The inherent viscosities were measured with a Cannon-Fenske viscosimeter 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. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were determined at 30 °C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-d<sub>6</sub>) 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<sup>3</sup>/min). Thermogravimetric analysis (TGA) 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<sup>3</sup>/min) at a heating rate of 20 °C/min. The measurements were taken after an initial 250 °C/5min drying step. Thermo-mechanical analysis (TMA) was performed by penetration method using a Rigaku TMA 8140 coupled to a Rigaku TAS-100 with a constant load of 10 g at a heating rate of 10 °C/min. 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<sub>g</sub> X-ray diffractometer, using Ni-filtered CuK<sub>α</sub> radiation (operating at 40 kV and 15 mA). The scanning rate was 2°/min over a range of 2θ = 5-40°. 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

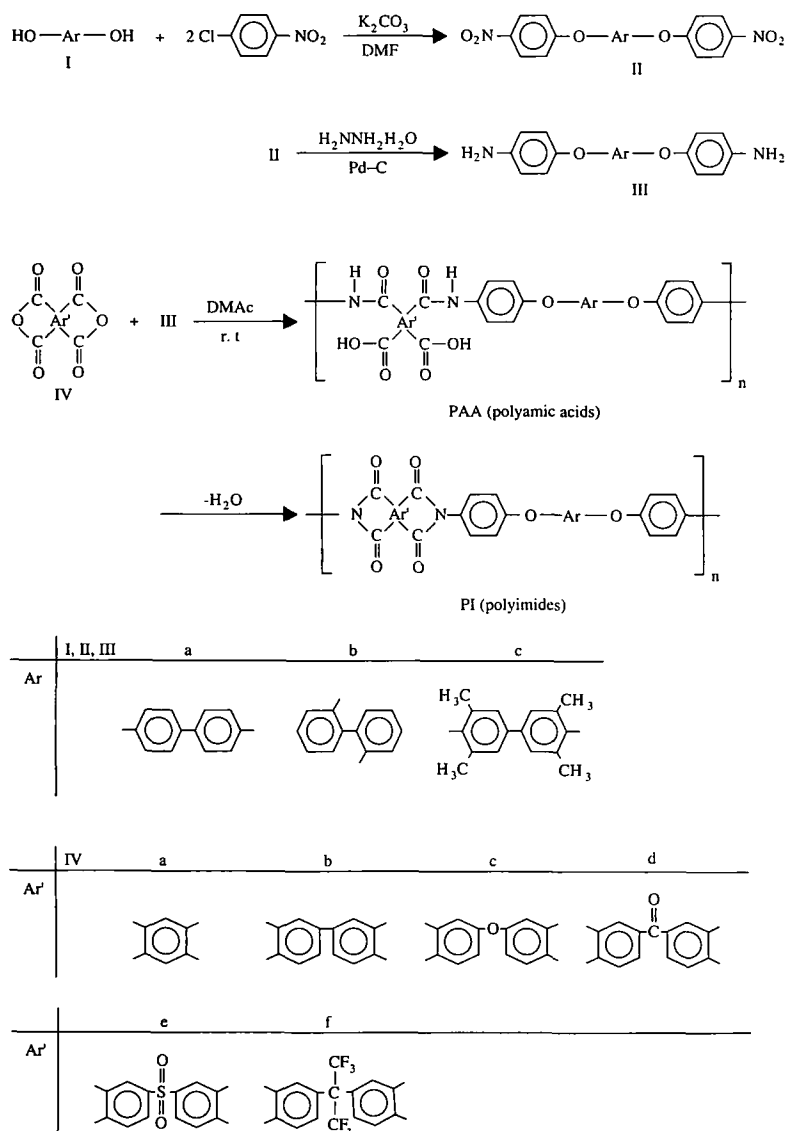
The diamines III<sub>a-c</sub> containing aryl ether and biphenyl groups were prepared by the aromatic nucleophilic substitution reaction of the corresponding biphenols and *p*-chloronitrobenzene, giving bis(*p*-nitrophenoxy) compounds II<sub>a-c</sub> and subsequent reduction of the dinitro compounds. The synthetic procedure is outlined in Scheme 1. Reduction of the nitro group was carried out by using hydrazine as the reducing agent and Pd-C as the catalyst [12-18]. The

structures of intermediate dinitro compounds  $\text{II}_{a-c}$  and diamines  $\text{III}_{a-c}$  were confirmed through IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, and elemental analysis. Figures 1 and 2 show the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of diamines  $\text{III}_{a-c}$ , and the assignments of all protons and carbons. All expected absorptions are observed. Protons off-resonance decoupling and comparison of the spectra of starting materials and intermediates were used as additional aids in signal assignment.

## 2. Polymer synthesis

The synthetic route of the polyimides from diamines  $\text{III}_{a-c}$  and various tetracarboxylic acid

dianhydrides is also depicted in Scheme 1. Three series of poly(amic acid)s described as *p*-PAA, *o*-PAA, and Me-PAA were prepared by reacting 4,4'-bis(*p*-aminophenoxy)biphenyl ( $\text{III}_a$ ), 2,2'-bis(*p*-aminophenoxy)biphenyl ( $\text{III}_b$ ), and 3,3',5,5'-tetramethyl-4,4'-bis(*p*-aminophenoxy)biphenyl ( $\text{III}_c$ ), respectively, with dianhydrides  $\text{IV}_{a-f}$  in dried DMAc. The above procedure yields a 10% solution which can be stirred without difficulty. In some cases the mixture becomes extremely viscous, and dilution to 5-7% solids may be required for efficient stirring. Poly(amic acid)s so prepared exhibited inherent viscosities of 1.09-2.83 dL/g for the *p*-PAA series, 0.78-1.93 dL/g



Scheme 1

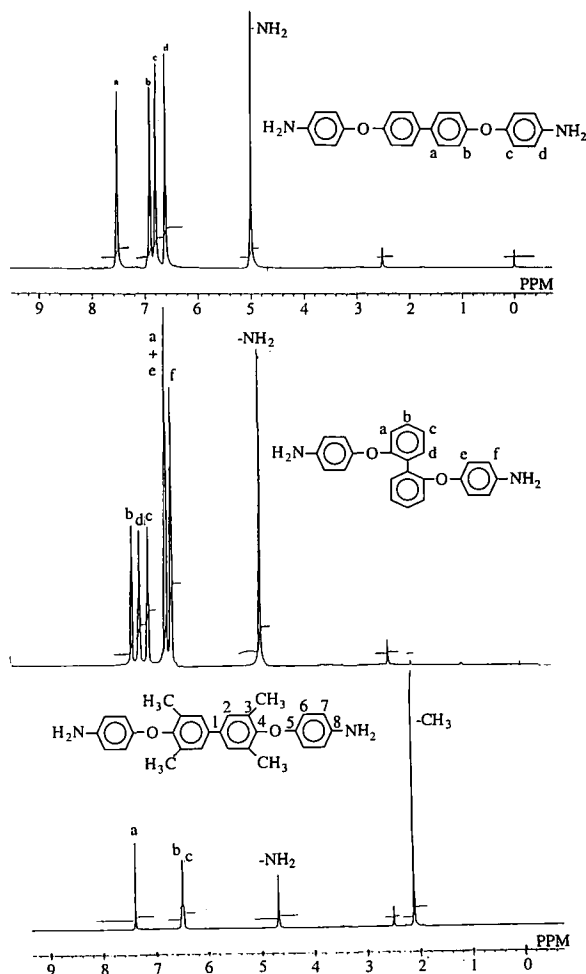


Figure 1.  $^1\text{H}$  NMR spectra of diamines III<sub>a-c</sub> in  $\text{DMSO-d}_6$ .

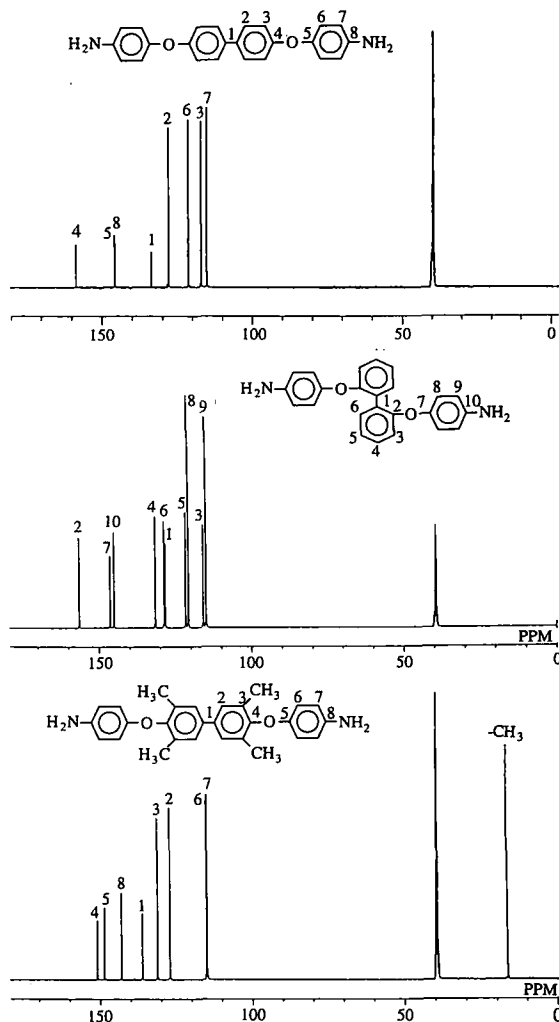


Figure 2.  $^{13}\text{C}$  NMR spectra of diamines III<sub>a-c</sub> in  $\text{DMSO-d}_6$ .

for the *o*-PAA series, and 1.55-3.09 dL/g for the Me-PAA series, measured at 0.5 g/dL in DMAc at 30 °C (Table I). The relatively higher inherent viscosity of the Me-PAA series can be attributable to two possible factors. The one may be associated with enhanced basicity of diamine III<sub>c</sub> caused by the methyl substituents leading to an increased degree of polymerization when reacting with the dianhydrides. The other may be ascribed to the hindrance effect of the chain rotation caused by the methyl groups which results in an increased viscosity. The 2,2'-biphenylene-containing *o*-PAA series poly(amic acid)s had a less rigid polymer backbone and, hence, revealed a relatively lower inherent viscosity. In any series of poly(amic acid)s, those obtained from ODPA (IV<sub>c</sub>) and DSDA (IV<sub>e</sub>) exhibited lower  $\eta_{\text{inh}}$  values than the others. PMDA (IV<sub>a</sub>)-based poly(amic acid)s *p*- and *o*-PAA<sub>a</sub> and 6FDA (IV<sub>f</sub>)-based poly(amic acid) Me-PAA<sub>f</sub> were

obtained with the highest  $\eta_{\text{inh}}$  values of 2.83, 1.93, and 3.09 dL/g, respectively, in each poly(amic acid) series.

The molecular weights of all the poly(amic acid)s are sufficiently high to permit casting flexible and tough poly(amic acid) films. However, the poly(amic acid) is easily degraded owing to hydrolysis in ambient atmosphere. Therefore, the prepared poly(amic acid)s are subsequently converted into polyimides as soon as possible by extended heating at elevated temperature or by treatment with chemical dehydrating agents. In this study, the thermal cyclodehydration method was employed, and the film properties were summarized in Table I. For the unsubstituted polyimides, *p*-PI<sub>a</sub>, *p*-PI<sub>d</sub>, *o*-PI<sub>a</sub>, and *o*-PI<sub>d</sub> derived from PMDA and BTDA (IV<sub>d</sub>) embrittled during the thermal imidization process. This may be due to a high degree of crystallinity of these polyimides, as

Table I. Inherent viscosities of polyamic acids and film property of polyimides.

Monomers		Polyamic acid		Polyimide	
Tetracarboxylic dianhydride	Diamine	Code	$\eta_{inh}^{(a)}$ (dL/g)	Code	Film property
IV <sub>a</sub>	III <sub>a</sub>	<i>p</i> -PAA <sub>a</sub>	2.83	<i>p</i> -PI <sub>a</sub>	Slightly brittle
IV <sub>b</sub>	III <sub>a</sub>	<i>p</i> -PAA <sub>b</sub>	1.98	<i>p</i> -PI <sub>b</sub>	Flexible
IV <sub>c</sub>	III <sub>a</sub>	<i>p</i> -PAA <sub>c</sub>	1.12	<i>p</i> -PI <sub>c</sub>	Flexible
IV <sub>d</sub>	III <sub>a</sub>	<i>p</i> -PAA <sub>d</sub>	1.88	<i>p</i> -PI <sub>d</sub>	Brittle
IV <sub>e</sub>	III <sub>a</sub>	<i>p</i> -PAA <sub>e</sub>	1.09	<i>p</i> -PI <sub>e</sub>	Flexible
IV <sub>f</sub>	III <sub>a</sub>	<i>p</i> -PAA <sub>f</sub>	2.24	<i>p</i> -PI <sub>f</sub>	Flexible
IV <sub>a</sub>	III <sub>b</sub>	<i>o</i> -PAA <sub>a</sub>	1.93	<i>o</i> -PI <sub>a</sub>	Brittle
IV <sub>b</sub>	III <sub>b</sub>	<i>o</i> -PAA <sub>b</sub>	1.25	<i>o</i> -PI <sub>b</sub>	Flexible
IV <sub>c</sub>	III <sub>b</sub>	<i>o</i> -PAA <sub>c</sub>	0.80	<i>o</i> -PI <sub>c</sub>	Flexible
IV <sub>d</sub>	III <sub>b</sub>	<i>o</i> -PAA <sub>d</sub>	1.26	<i>o</i> -PI <sub>d</sub>	Brittle
IV <sub>e</sub>	III <sub>b</sub>	<i>o</i> -PAA <sub>e</sub>	0.78	<i>o</i> -PI <sub>e</sub>	Flexible
IV <sub>f</sub>	III <sub>b</sub>	<i>o</i> -PAA <sub>f</sub>	1.41	<i>o</i> -PI <sub>f</sub>	Flexible
IV <sub>a</sub>	III <sub>c</sub>	Me-PAA <sub>a</sub>	2.29	Me-PI <sub>a</sub>	Flexible
IV <sub>b</sub>	III <sub>c</sub>	Me-PAA <sub>b</sub>	2.30	Me-PI <sub>b</sub>	Flexible
IV <sub>c</sub>	III <sub>c</sub>	Me-PAA <sub>c</sub>	1.55	Me-PI <sub>c</sub>	Flexible
IV <sub>d</sub>	III <sub>c</sub>	Me-PAA <sub>d</sub>	1.92	Me-PI <sub>d</sub>	Flexible
IV <sub>e</sub>	III <sub>c</sub>	Me-PAA <sub>e</sub>	1.61	Me-PI <sub>e</sub>	Flexible
IV <sub>f</sub>	III <sub>c</sub>	Me-PAA <sub>f</sub>	3.09	Me-PI <sub>f</sub>	Flexible

(a) Inherent viscosity measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

evidenced from the X-ray diffractograms shown later. All other unsubstituted polyimides and all the methyl-substituted polyimides (Me-PI<sub>a-f</sub>) afforded flexible and tough films.

The formation of poly(amic acid)s and polyimides was confirmed by means of IR spectroscopy and elemental analysis. In the IR spectra, the poly(amic acid)s showed a broad absorption band in the range of 3000-3500 cm<sup>-1</sup> due to the N-H and O-H stretching vibration, and strong absorptions at 1720 and 1660 cm<sup>-1</sup> assigned to carbonyl stretching of carboxylic acid and amide. An absorption band for the N-H bending vibration appeared at 1545 cm<sup>-1</sup>. The IR spectra of polyimides showed the characteristic absorptions at 1780, 1730, 1380, 1100, and 725 cm<sup>-1</sup>. The bands around 1780 and 1730 cm<sup>-1</sup> were attributed to the asymmetrical and symmetrical stretching vibration of carbonyl groups of imide ring, and those around 1380 and 1100 cm<sup>-1</sup> were peculiar to the C-N stretching. Band of ring bending vibration appeared at approximately 725 cm<sup>-1</sup>. Table II lists the results of elemental analyses of all the polyimides. The values found were in good agreement with the calculated ones of the proposed structures.

### 3. Properties of polyimides

The solubility of polyimides was studied qualitatively, and the results are shown in Table III. Obviously, the *o*-PI series containing the kinked 2,2'-biphenylene units showed better solubility than the other two series. Due to the existence of flexible ether

linkage and polar -SO<sub>2</sub>- and -C(CF<sub>3</sub>)<sub>2</sub>- groups, the polyimides *o*-PI<sub>c</sub>, *o*-PI<sub>e</sub>, and *o*-PI<sub>f</sub> obtained from diamine III<sub>b</sub> with ODP, DSDA, and 6FDA, respectively, were readily soluble in polar organic solvents such as DMAc, DMF, NMP, DMI, and DMSO. However, polyimides *o*-PI<sub>a</sub>, *o*-PI<sub>b</sub>, and *o*-PI<sub>d</sub> containing a more rigid dianhydride moiety were insoluble in all the tested solvents. In the other two series of polyimides, *p*-PI<sub>a-f</sub> and Me-PI<sub>a-f</sub>, only the polyimides (*p*-PI<sub>f</sub> and Me-PI<sub>f</sub>) obtained from dianhydride 6FDA were soluble at room temperature or on heating. From the results of solubility test, it may be concluded that the introduction of bulky and kinked 2,2'-biphenylene unit into the polyimide backbone leads to an enhanced solubility. On the other hand, methyl substitution on the 4,4'-biphenylene unit gives a very limited improvement in solubility.

X-ray diffractograms of all the polyimides are shown in Figure 3. Polyimide *o*-PI<sub>a</sub> was measured in a powder form due to the fact that it could not be cast into a polymer film with enough self-supporting strength. All other polyimides were determined with films. The scattering curve for polyimide *o*-PI<sub>a</sub> showed the highest degree of crystallinity and exhibited three medium to strong reflection peaks around  $2\theta = 13, 20,$  and  $26^\circ$ . The polyimides *o*-PI<sub>d</sub>, *p*-PI<sub>a</sub> and *p*-PI<sub>d</sub> also showed crystalline diffraction patterns. These results implied that the polyimides composed of the more rigid dianhydride moiety of PMDA or BTDA and the rigid 4,4'-biphenyl unit-containing diamine III<sub>a</sub> or kinked 2,2'-biphenyl unit-containing diamine III<sub>b</sub> pos-

**Table II.** Elemental analyses of polyimides.

Polymer	Formula (Formula weight)	Elemental analysis (%)			
		C	H	N	
<i>p</i> -PI <sub>a</sub>	(C <sub>34</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub> (550.53) <sub>n</sub>	Calcd	74.18	3.30	5.09
		Found	73.19	3.30	5.20
<i>p</i> -PI <sub>b</sub>	(C <sub>40</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub> (626.62) <sub>n</sub>	Calcd	76.67	3.54	4.47
		Found	75.92	3.48	4.73
<i>p</i> -PI <sub>c</sub>	(C <sub>40</sub> H <sub>22</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (642.62) <sub>n</sub>	Calcd	74.76	3.45	4.36
		Found	74.11	3.31	4.47
<i>p</i> -PI <sub>d</sub>	(C <sub>41</sub> H <sub>22</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (654.63) <sub>n</sub>	Calcd	75.23	3.39	4.28
		Found	74.34	3.33	4.48
<i>p</i> -PI <sub>e</sub>	(C <sub>40</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub> S) <sub>n</sub> (690.69) <sub>n</sub>	Calcd	69.56	3.21	4.06
		Found	68.77	3.18	4.27
<i>p</i> -PI <sub>f</sub>	(C <sub>43</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub> (776.64) <sub>n</sub>	Calcd	66.50	2.86	3.61
		Found	66.25	2.76	3.73
<i>o</i> -PI <sub>a</sub>	(C <sub>34</sub> H <sub>18</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub> (550.53) <sub>n</sub>	Calcd	74.18	3.30	5.09
		Found	74.11	3.45	5.08
<i>o</i> -PI <sub>b</sub>	(C <sub>40</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub> (626.62) <sub>n</sub>	Calcd	76.67	3.54	4.47
		Found	76.30	3.63	4.66
<i>o</i> -PI <sub>c</sub>	(C <sub>40</sub> H <sub>22</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (642.62) <sub>n</sub>	Calcd	74.76	3.45	4.36
		Found	74.58	3.55	4.40
<i>o</i> -PI <sub>d</sub>	(C <sub>41</sub> H <sub>22</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (654.63) <sub>n</sub>	Calcd	75.23	3.39	4.28
		Found	74.87	3.67	4.46
<i>o</i> -PI <sub>e</sub>	(C <sub>40</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub> S) <sub>n</sub> (690.69) <sub>n</sub>	Calcd	69.56	3.21	4.06
		Found	69.30	3.36	4.07
<i>o</i> -PI <sub>f</sub>	(C <sub>43</sub> H <sub>22</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub> (776.64) <sub>n</sub>	Calcd	66.50	2.86	3.61
		Found	66.48	2.76	3.56
Me-PI <sub>a</sub>	(C <sub>38</sub> H <sub>26</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub> (606.62) <sub>n</sub>	Calcd	75.24	4.32	4.62
		Found	74.24	4.49	4.67
Me-PI <sub>b</sub>	(C <sub>44</sub> H <sub>30</sub> N <sub>2</sub> O <sub>6</sub> ) <sub>n</sub> (682.73) <sub>n</sub>	Calcd	77.41	4.43	4.10
		Found	76.32	4.51	4.15
Me-PI <sub>c</sub>	(C <sub>44</sub> H <sub>30</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (698.73) <sub>n</sub>	Calcd	75.63	4.33	4.01
		Found	74.55	4.41	3.99
Me-PI <sub>d</sub>	(C <sub>45</sub> H <sub>30</sub> N <sub>2</sub> O <sub>7</sub> ) <sub>n</sub> (710.74) <sub>n</sub>	Calcd	76.05	4.25	3.94
		Found	74.59	4.48	4.27
Me-PI <sub>e</sub>	(C <sub>44</sub> H <sub>30</sub> N <sub>2</sub> O <sub>8</sub> S) <sub>n</sub> (746.80) <sub>n</sub>	Calcd	70.77	4.05	3.75
		Found	70.17	4.15	3.85
Me-PI <sub>f</sub>	(C <sub>47</sub> H <sub>30</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub> (832.75) <sub>n</sub>	Calcd	67.79	3.63	3.36
		Found	67.74	3.83	3.56

sessed better packing of polymer chains. The crystalline nature of these polyimides resulted into their poor solubility and brittleness of their casting films. All the polyimides of Me-PI series showed amorphous diffraction patterns. This can be explained by the substitution of methyl groups on the aromatic rings which inhibits close packing of the polymer chains.

The polyimide films of *p*-PI<sub>a</sub>, *p*-PI<sub>d</sub>, *o*-PI<sub>a</sub>, and *o*-PI<sub>d</sub> were too brittle to be subjected to tensile test. The other polyimides afforded flexible and tough films and could be creased without cracking. The tensile properties of these polyimides are summarized in Table IV. All the polyimide films showed no yield points in their stress-strain curves, and they had tensile strength of 68-111 MPa, elongation at break of 4.1-20.4%, and tensile modulus of 1.34-1.82 GPa. These results indicate that they belong to strong and hard materials.

The thermal properties of the polyimides were evaluated by TGA and DSC. The TGA and DSC data of these polyimides are listed in Table V. Some polyimides such as *p*-PI<sub>a</sub>, *p*-PI<sub>b</sub>, *p*-PI<sub>d</sub>, and *o*-PI<sub>a</sub> had a more rigid structure, and no discernible glass transitions could be observed on their DSC thermograms. With these exceptions, all other polyimides could be rapidly quenched from the elevated temperatures at approximately 400 °C to room temperature to form more amorphous materials. Thus, they displayed clear glass transitions on the subsequent heating DSC traces. It is quite reasonable that the methyl-substituted polyimides Me-PI exhibited higher T<sub>g</sub>s compared with the corresponding unsubstituted polyimides *p*-PI because of the hindrance effect of the chain rotation in the methyl-substituted polymers. The introduction of bulky, kinked, and cranked 2,2'-biphenylene unit reduced rigidity and symmetry of the polymer backbone. Thus, the *o*-PI series polyimides showed relatively lower T<sub>g</sub>s in comparison with the other two series. For the polyimides from the same diamine component, those composed of ODPA had the lowest T<sub>g</sub>s because the ether bridge between the phthalimide groups increased the flexibility of polymer chain. The polyimides derived from PMDA (IV<sub>a</sub>) were expected to have the highest T<sub>g</sub>s, for example Me-PI<sub>a</sub> had T<sub>g</sub> up to 387 °C. The polyimides obtained from BPDA (IV<sub>b</sub>) or DSDA (IV<sub>c</sub>), the dianhydride with direct bonding or the polar sulfonyl bridging group between the phthalic anhydride unit, also revealed high T<sub>g</sub>s.

As a representative example, the TGA curves of poly(amic acid) Me-PAA<sub>a</sub> and polyimide Me-PI<sub>a</sub> obtained from PMDA and diamine III<sub>a</sub> are shown in Figure 4, and the thermal behavior data of all the polyimides are given in Table V. In the TGA profile, the initial decomposition temperature (T<sub>i</sub>) is noted as the point where the TGA curve intersects the bisected line drawn through the intersection of the extrapolation of the two slopes in the TGA curve. The poly(amic acid) showed two-step weight losses corresponding to the imidization process and thermal degradation. In the range 200-350 °C, the poly(amic acid) showed a weight loss of about 13 % corresponding to the loss of water during imidization. The second step on the TGA curve of poly(amic acid) starts at temperatures above 460 °C (10% weight loss around 532 °C) and corresponds to the thermal degradation of the polyimides. All the polyimides were stable up to 405 °C in both air and nitrogen atmospheres. The *p*-PI series polyimides derived from the 4,4'-biphenyl group-containing diamine showed higher T<sub>g</sub>s. As expected, the methyl-substituted polyimides (Me-PI series) began to decompose at lower temperatures compared with the corresponding unsubstituted polymers. The 10 % weight loss temperatures of three series of polyimides *p*-PI, *o*-PI, Me-PI were recorded respectively in the

Table III. Solubility of polyimides<sup>(a)</sup>

Polymer	Solvent <sup>(b)</sup>							conc. H <sub>2</sub> SO <sub>4</sub>
	DMAc	DMF	NMP	DMI	DMSO	Py	<i>m</i> -Cresol	
<i>p</i> -PI <sub>a</sub>	-	-	-	-	-	-	-	-
<i>p</i> -PI <sub>b</sub>	-	-	-	-	-	-	-	+
<i>p</i> -PI <sub>c</sub>	-	-	-	-	-	-	-	+h
<i>p</i> -PI <sub>d</sub>	-	-	-	-	-	-	-	+h
<i>p</i> -PI <sub>e</sub>	-	-	-	-	-	-	-	+
<i>p</i> -PI <sub>f</sub>	+h	+	+h	+h	+h	+h	+h	+h
<i>o</i> -PI <sub>a</sub>	-	-	-	-	-	-	-	+h
<i>o</i> -PI <sub>b</sub>	-	-	-	-	-	-	-	+h
<i>o</i> -PI <sub>c</sub>	+	+	+	+	+h	+	+	+
<i>o</i> -PI <sub>d</sub>	-	-	-	-	-	-	-	-
<i>o</i> -PI <sub>e</sub>	+	+	+	+	+h	+h	-	+
<i>o</i> -PI <sub>f</sub>	+	+	+	+	+	+	+h	+
Me-PI <sub>a</sub>	-	-	-	-	-	-	-	+h
Me-PI <sub>b</sub>	-	-	-	-	-	-	-	+h
Me-PI <sub>c</sub>	-	-	-	-	-	-	-	+h
Me-PI <sub>d</sub>	-	-	-	-	-	-	-	+h
Me-PI <sub>e</sub>	-	-	-	-	-	-	-	+h
Me-PI <sub>f</sub>	+	+	+h	+h	-	+	+h	+

(a) Solubility: +, soluble at room temperature; +h, soluble on heating; -, insoluble.

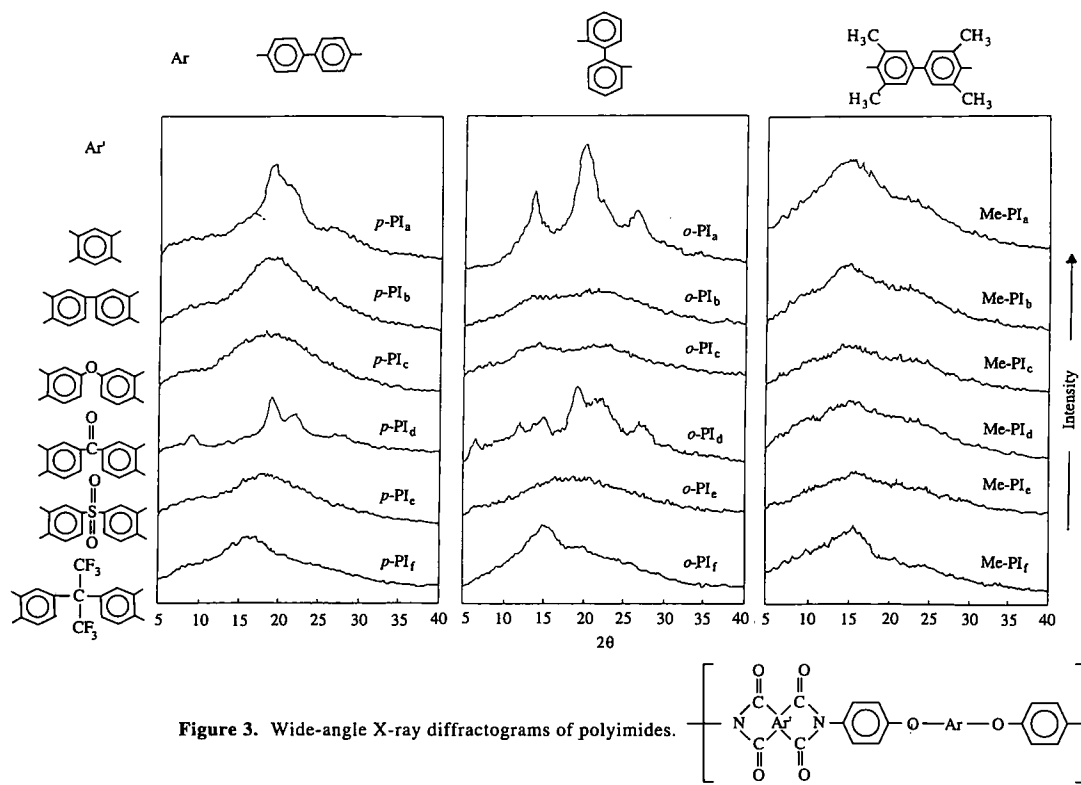
(b) DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethylsulfoxide; DMI, 1,3-dimethyl-2-imidazolidone.

Figure 3. Wide-angle X-ray diffractograms of polyimides.

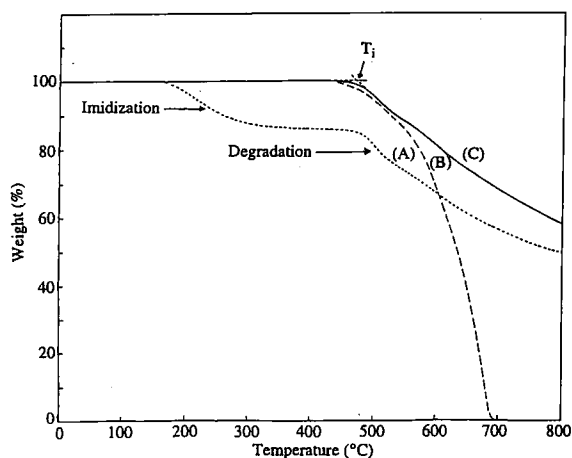


**Table IV.** Tensile properties of polyimide films.

Polymer <sup>(a)</sup>	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
<i>p</i> -PI <sub>a</sub>	—	—	—
<i>p</i> -PI <sub>b</sub>	111	15.9	1.82
<i>p</i> -PI <sub>c</sub>	92	20.4	1.62
<i>p</i> -PI <sub>d</sub>	—	—	—
<i>p</i> -PI <sub>e</sub>	97	15.9	1.46
<i>p</i> -PI <sub>f</sub>	95	12.0	1.43
<i>o</i> -PI <sub>a</sub>	—	—	—
<i>o</i> -PI <sub>b</sub>	72	5.1	1.82
<i>o</i> -PI <sub>c</sub>	89	5.7	1.81
<i>o</i> -PI <sub>d</sub>	—	—	—
<i>o</i> -PI <sub>e</sub>	68	4.1	1.74
<i>o</i> -PI <sub>f</sub>	80	5.2	1.72
Me-PI <sub>a</sub>	74	10.6	1.34
Me-PI <sub>b</sub>	96	13.1	1.52
Me-PI <sub>c</sub>	94	17.5	1.40
Me-PI <sub>d</sub>	100	14.6	1.51
Me-PI <sub>e</sub>	71	6.6	1.56
Me-PI <sub>f</sub>	91	9.6	1.40

(a) Films were cast from polymer solutions in DMAc.

range of 553-586 °C, 549-578 °C, and 481-540 °C in air and 534-592 °C, 546-581 °C, and 469-545 °C in nitrogen. Almost all the polyimides underwent exten-



**Figure 4.** TGA curves of poly(amic acid) Me-PAA<sub>a</sub> in nitrogen (A) and polyimide Me-PI<sub>a</sub> in air (B) and in nitrogen (C), with a heating rate of 20 °C/min.

sive carbonization upon non-oxidative degradation with more than 50% residue remaining at 800 °C in nitrogen. It is worth noting that the polyimides of Me-PI series left a similar char residue compared with the analogues of *p*-PI series. This implied that there are some possibilities of crosslinking between the polymer chains during the degradation process, such as the

**Table V.** Thermal properties of polyimides

Polymer	DSC		TG			
	$T_g^{(a)}$ (°C)	$T_i^{(c)}$ (°C)		$T_{10}^{(c)}$ (°C)		Residue at 800 °C (wt%)
		In air	In nitrogen	In air	In nitrogen	
<i>p</i> -PI <sub>a</sub>	—	554	567	585	592	60.4
<i>p</i> -PI <sub>b</sub>	—	542	558	586	591	63.7
<i>p</i> -PI <sub>c</sub>	258	525	548	580	584	63.2
<i>p</i> -PI <sub>d</sub>	—	535	530	584	576	60.0
<i>p</i> -PI <sub>e</sub>	303	478	486	553	534	54.7
<i>p</i> -PI <sub>f</sub>	288	496	504	554	558	57.9
<i>o</i> -PI <sub>a</sub>	—	512	525	554	566	49.8
<i>o</i> -PI <sub>b</sub>	240 (262) <sup>(b)</sup>	517	538	578	581	53.2
<i>o</i> -PI <sub>c</sub>	214	502	515	560	559	50.3
<i>o</i> -PI <sub>d</sub>	235 (335)	512	524	559	566	50.7
<i>o</i> -PI <sub>e</sub>	250 (284)	503	508	549	546	57.7
<i>o</i> -PI <sub>f</sub>	235	498	513	543	555	55.0
Me-PI <sub>a</sub>	387	465	480	525	532	58.1
Me-PI <sub>b</sub>	335	475	492	540	545	61.8
Me-PI <sub>c</sub>	307	470	483	531	537	61.2
Me-PI <sub>d</sub>	315	458	470	530	540	63.9
Me-PI <sub>e</sub>	329	405	420	481	469	54.3
Me-PI <sub>f</sub>	317	483	492	526	524	54.2

(a) From the second heating trace of DSC measurements conducted at a heating rate of 20 °C/min in nitrogen.

(b) Values in parentheses were the endotherm peak temperatures observed on the first DSC heating trace, with a heating rate of 20 °C/min.

(c) Initial decomposition temperatures ( $T_i$ ) and temperatures at 10% weight ( $T_{10}$ ) were determined by TG at a heating rate of 20 °C/min.

dimerization of benzyl radicals [19]. This could be clearly observed from Figure 5. Figure 5 compares the TGA thermograms of polyimides  $p$ -PI<sub>a</sub>,  $o$ -PI<sub>a</sub>, and Me-PI<sub>a</sub> in nitrogen. The initial decomposition temperatures of the polymers decreased in the order:  $p$ -PI<sub>a</sub> >  $o$ -PI<sub>a</sub> > Me-PI<sub>a</sub>. The polymer Me-PI<sub>a</sub> began to degrade around 450 °C, but the rate of polymer degradation slowed down when the temperature was over 500 °C. The occurring of crosslinking reactions should be a reasonable explanation.

Figure 6 shows the isothermal TGA thermograms of polyimides  $p$ -PI<sub>a</sub>,  $o$ -PI<sub>a</sub>, and Me-PI<sub>a</sub> at 400 °C. These polymers were very thermally stable at 400 °C in nitrogen and showed isothermal weight loss of only less than 5 % after 10 hrs at 400 °C. However, they revealed marked differences in isothermal thermal stability at 400 °C in air. It was worth to note that polymer  $o$ -PI<sub>a</sub> showed higher thermooxidative stability at 400 °C than the more symmetrical structure-containing polymer  $p$ -PI<sub>a</sub>. The polymer Me-PI<sub>a</sub> containing methyl substituents showed the fastest degradation rate in the air atmosphere. Almost one-half of the original weight was lost after 10 hrs at 400 °C.

Table VI summarizes the thermal properties and water absorption rates of some polyimides synthesized in this work, including three commercialized polyimide products with similar structures. Among the polyimides tested, those derived from biphenylene-containing diamines revealed the relatively higher softening temperature ( $T_s$ ) than the corresponding 4,4'-oxydianiline-derived polyimides such as Kapton (Du Pont), Upilex-R, and Skybond 700. The polyimides  $p$ -PI<sub>a,b,d</sub> obtained from 4,4'-bis( $p$ -aminophenoxy)biphenyl exhibited comparable thermal stability to Kapton, Upilex-R, and Skybond 700.

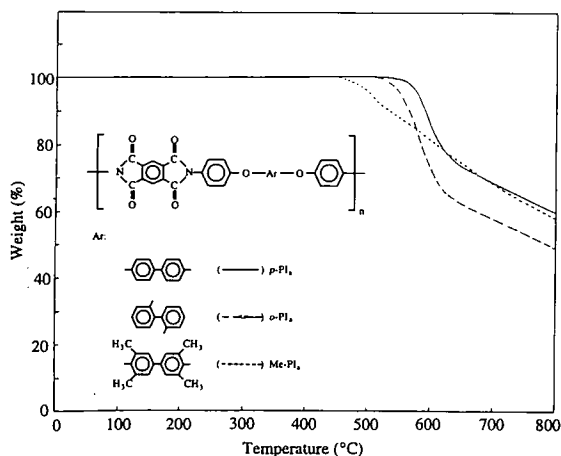


Figure 5. TGA curves for polyimides  $p$ -PI<sub>a</sub>,  $o$ -PI<sub>a</sub>, and Me-PI<sub>a</sub> at a heating rate of 20 °C/min in nitrogen.

However, in comparison with these commercialized products, the polyimides obtained from 2,2'-bis( $p$ -aminophenoxy)biphenyl and 3,3',5,5'-tetramethyl-4,4'-bis( $p$ -aminophenoxy)biphenyl showed lower thermal stability. It was interesting to note that the water absorption of all the biphenylene-containing polyimides were less than 2.0%, lower than the commercially available polyimides.

## Conclusions

The biphenylene-containing diamines 4,4'-bis( $p$ -aminophenoxy)biphenyl (III<sub>a</sub>), 2,2'-bis( $p$ -aminophenoxy)biphenyl (III<sub>b</sub>), and 3,3',5,5'-tetramethyl-4,4'-bis( $p$ -aminophenoxy)biphenyl (III<sub>c</sub>) were prepared in high purity and high yield by the two-step reaction starting from the corresponding biphenols and  $p$ -chloronitrobenzene. High molecular weight poly(amic acids) were synthesized by reacting these diamines and aromatic tetracarboxylic dianhydrides in the aprotic polar solvent DMAc. Most of the poly(amic acids) could be thermally converted into flexible polyimide films with excellent tensile properties. Combinations of PMDA or BTDA with diamine III<sub>a</sub> or III<sub>b</sub> produced polyimides with moderate to high degree of crystallinity, which could not be formed into flexible and tough polyimide films. The polyimides possessing 2,2'-biphenylene groups exhibited better

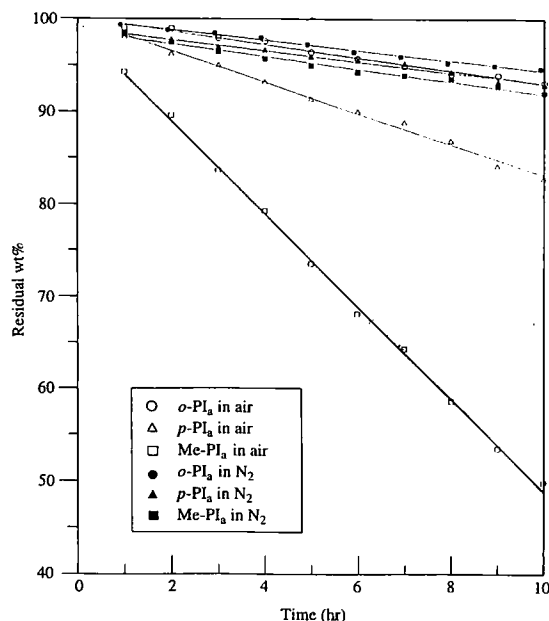


Figure 6. Isothermal TGA curves of polyimides  $p$ -PI<sub>a</sub>,  $o$ -PI<sub>a</sub>, and Me-PI<sub>a</sub> under air and nitrogen at 400 °C.

Table VI. Structures and properties of polyimides prepared in this work and some commercialized ones.

Polymer Code	Structure	$\eta_{inh}^{(a)}$ (dL/g)	$T_s^{(b)}$ (°C)	$T_{10}^{(c)}$		Equilibrium Moisture Pickup (%) <sup>(d)</sup>
				In Air	In Nitrogen	
<i>p</i> -PI <sub>a</sub>		2.83	256	585	592	1.7
<i>o</i> -PI <sub>a</sub>		1.93	254	554	566	—
Me-PI <sub>a</sub>		2.29	259 (387) <sup>(e)</sup>	525	532	1.4
Kapton		2.90	232	587	590	2.8
<i>p</i> -PI <sub>b</sub>		1.98	230	586	591	1.3
<i>o</i> -PI <sub>b</sub>		1.25	221 (240)	578	581	1.6
Me-PI <sub>b</sub>		2.30	255 (335)	540	545	1.9
Upilex-R		1.58	210 (270)	595	594	1.6
<i>p</i> -PI <sub>d</sub>		1.88	232	584	576	1.3
<i>o</i> -PI <sub>d</sub>		1.26	253 (235)	559	566	1.4
Me-PI <sub>d</sub>		1.92	239 (315)	530	540	1.4
Skybond 700		1.70	231	579	579	2.0

(a) Inherent viscosities of poly(amic acid)s, measured in DMAc on 0.5 g/dL at 30 °C.  
 (b) Softening temperatures measured by TMA with a load of 10 g at a heating rate of 10 °C/min.  
 (c) 10% weight loss temperatures measured by TG with a heating rate of 20 °C/min.  
 (d) Determined according to ASTM D 570-81.  
 (e) Values in parentheses are  $T_g$ s measured by DSC with a heating rate of 20 °C/min.

solubility. Among the 4,4'-biphenylene or 3,3',5,5'-tetramethyl-4,4'-biphenylene unit-containing polyimides, only those derived from the trifluoromethyl groups-containing dianhydride 6FDA were soluble in a few polar organic solvents. These polyimides showed good thermal properties—high  $T_g$  and excellent thermal and thermooxidative stability. The methyl-substituted polyimides had higher  $T_g$  than the corresponding unsubstituted polymers, but showed lower initial decomposition temperatures.

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