

# Preparation and Characterization of Aromatic Polyamides Based on a Bis(ether-carboxylic acid) or a Dietheramine Extended from 1,1-Bis(4-hydroxyphenyl)-1-Phenylethane

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**ABSTRACT:** Thermoplastic and organic-soluble aromatic polyamides containing both bulky triphenylethane units and flexible ether linkages were prepared directly from 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane (**III**) with various aromatic diamines or from 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**V**) with various aromatic dicarboxylic diacids via triphenyl phosphite and pyridine. These polyamides had inherent viscosities ranging from 0.71 to 1.77 dL/g. All the polymers easily were dissolved in aprotic polar solvents such as *N*-methyl-2-pyrrolidone and *N,N*-dimethylacetamide, and some even could be dissolved in less polar solvents such as tetrahydrofuran. The flexible and tough films cast from the polymer solutions possessed tensile strengths of 89 to 104 MPa. The polyamides were thermally stable up to 460°C in air or nitrogen. Glass-transition temperatures of these polyamides were observed in a range of 179 to 268°C via differential scanning calorimetry or thermomechanical analysis. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 247–260, 2000

**Keywords:** polyamides; triphenylethane; ether linkage; triphenyl phosphite

## INTRODUCTION

Wholly aromatic polyamides such as poly(1,4-phenyleneterephthalamide) and poly(1,4-benzamide) are well accepted as heat-resistant materials with a high mechanical strength, easily giving lyotropic solutions.<sup>1–4</sup> Fibers obtained from anisotropic solutions of these materials have been used in applications where high thermal stability and mechanical strength are required. However, infusibility and limited solubility are characteristic properties of wholly aromatic polyamides that restrict their synthesis, characterization, and applications, especially in high molecular weight materials. There are several routes to reducing the transition temperatures and increasing the

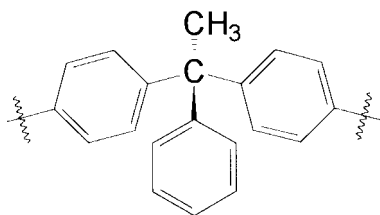
solubility of these polymers. The most common method to achieve this goal is the incorporation of bulky pendent groups, flexible linking groups, or both along the backbone.<sup>5–12</sup> Soluble or thermoplastic aromatic polyamides may open applications in films, coatings, polymer blends, and composites.

In connection with our interest in preparing easily processable high-temperature polymers, this study deals with the synthesis and basic characterization of novel aromatic polyamides based on 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane (**III**) and 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**V**). The “multiring” diacid and diamine monomers **III** and **V** have been prepared readily from the chain extension of 1,1-bis(4-hydroxyphenyl)-1-phenylethane (**I**) via well-known synthetic procedures.<sup>5,10–12</sup> The starting bisphenol **I** has been synthesized easily via a common bisphenol synthesis from the condensation of acetophenone with excess phenol

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in the presence of an acidic condensing agent.<sup>13–16</sup> The diamine and diacid moieties have the following propeller-shaped triphenylethane structure:



The three benzene rings can not be all into the same plane because of steric hindrance. Thus, it was expected that the incorporation of these hindered moieties would interrupt the intermolecular hydrogen bonding of the polyamides and generally disturb the coplanarity of the aromatic unit to reduce packing efficiency and crystallinity. This should enhance solubility while maintaining a high glass-transition temperature ( $T_g$ ) through controlled segmental mobility.

## EXPERIMENTAL

### Materials

1,1-Bis(4-hydroxyphenyl)-1-phenylethane (**I**; Mitsui Petrochemical Ind., Tokyo, Japan) was used without previous purification. *p*-Fluorobenzonitrile (Wako, Osaka, Japan), *p*-chloronitrobenzene [Tokyo Chemical Industry (TCI)], and hydrazine monohydrate (Acros, Geel, Belgium) were used as received. *p*-Phenylenediamine (**VI<sub>a</sub>**) and benzidine (**VI<sub>c</sub>**) were purified by vacuum sublimation. *m*-Phenylenediamine (**VI<sub>b</sub>**) was purified by vacuum distillation. 4,4'-Oxydianiline (**VI<sub>d</sub>**; TCI), 3,4'-oxydianiline (**VI<sub>e</sub>**; Mitsui Petrochemical Ind.), 4,4'-methylenedianiline (**VI<sub>f</sub>**; TCI), 1,4-bis(4-aminophenoxy)benzene (**VI<sub>g</sub>**; TCI),  $\alpha,\alpha'$ -bis(4-aminophenyl)-1,4-diisopropylbenzene (**VI<sub>h</sub>**; Mitsui Petrochemical Ind.), and  $\alpha,\alpha'$ -bis(4-aminophenyl)-1,3-diisopropylbenzene (**VI<sub>i</sub>**; Mitsui Petrochemical Ind.) were used without further purification. According to a well-developed method,<sup>17,18</sup> 4,4'-bis(4-aminophenoxy)biphenyl (**VI<sub>j</sub>**; mp = 198–199°C), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**VI<sub>k</sub>**; mp = 125–126°C), 2,2-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (**VI<sub>l</sub>**; mp = 162–163°C), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**V** or **VI<sub>m</sub>**; mp = 68°C), bis[4-(4-aminophenoxy)phenyl] sulfone (**VI<sub>n</sub>**; mp = 228–230°C), and  $\alpha,\alpha'$ -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropyl-

benzene (**VI<sub>o</sub>**; mp = 187–189°C) were prepared by the chlorodisplacement reaction of *p*-chloronitrobenzene with its corresponding bisphenol precursors in the presence of potassium carbonate followed by a catalytic hydrazine reduction. A more detailed synthetic procedure for the synthesis of diamine **V** is described later. Aromatic dicarboxylic acids such as terephthalic acid (**VIII<sub>a</sub>**; Wako), isophthalic acid (**VIII<sub>b</sub>**; Wako), 4,4'-biphenyldicarboxylic acid (**VIII<sub>c</sub>**; TCI), 4,4'-oxydibenzoic acid (**VIII<sub>d</sub>**; TCI), 5-*tert*-butylisophthalic acid (**VIII<sub>e</sub>**; Aldrich), 4,4'-sulfonyldibenzoic acid (**VIII<sub>f</sub>**; New Japan Chemical Co.), 4,4'-hexafluoroisopropylidenedibenzoic acid (**VIII<sub>g</sub>**; Chriskev), 2,6-naphthalenedicarboxylic acid (**VIII<sub>h</sub>**; TCI), and 1,4-naphthalene-dicarboxylic acid (**VIII<sub>i</sub>**; Wako) were used as received. Commercially obtained anhydrous calcium chloride (CaCl<sub>2</sub>) was dried under vacuum at 200°C for 10 h. Pyridine was purified by distillation after being refluxed with KOH. *N*-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure and stored over 4-Å molecular sieves. Similarly, triphenyl phosphite (TPP; Fluka) was purified by distillation under reduced pressure.

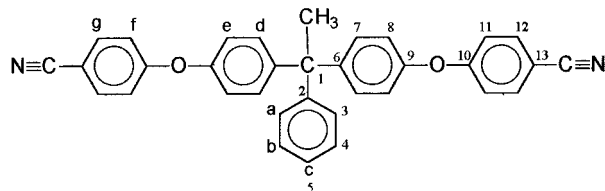
### Monomer Synthesis

#### 1,1-Bis[4-(4-cyanophenoxy)phenyl]-1-Phenylethane (**II**)

1,1-Bis(4-hydroxyphenyl)-1-phenylethane (**I**) (29 g, 0.1 mol) and K<sub>2</sub>CO<sub>3</sub> (27.6 g, 0.2 mol) were suspended in a mixture of 80 mL of *N,N*-dimethylformamide (DMF) and 50 mL of toluene and heated with stirring at the reflux temperature with a Dean–Stark trap to remove the water azeotropically. After most of the toluene had been removed, the reaction mixture was cooled to about 60°C, and *p*-fluorobenzonitrile (24.3 g, 0.2 mol) was added. The reaction mixture was reheated to reflux and held for 10 h. The reaction mixture then was allowed to cool and was poured into 500 mL of water; a glutinous product aggregated in the bottom of the beaker. After being washed repeatedly with water, the product was used directly for the synthesis of diacid **III**.

IR (KBr): 2228 (C≡N stretch), 1249 cm<sup>-1</sup> (C—O—C stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 2.16 (—CH<sub>3</sub>), 6.92 (d, 4H, H<sub>e</sub>), 6.98 (d, 4H, H<sub>f</sub>), 7.10 (s, 6H, H<sub>a</sub> + H<sub>d</sub>), 7.19 (d, 1H, H<sub>c</sub>), 7.25 (d, 2H, H<sub>b</sub>), 7.54 (d, 4H, H<sub>g</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ , ppm): 30.30 (—CH<sub>3</sub>), 51.43 (C<sup>1</sup>), 106.14 (C<sup>13</sup>), 118.44 (C<sup>8</sup>), 119.23 (—CN), 120.04 (C<sup>11</sup>), 126.89 (C<sup>5</sup>), 128.68

(C<sup>3</sup>), 129.04 (C<sup>4</sup>), 130.97 (C<sup>7</sup>), 134.75 (C<sup>12</sup>), 146.43 (C<sup>6</sup>), 149.22 (C<sup>2</sup>), 153.86 (C<sup>9</sup>), 162.40 (C<sup>10</sup>).

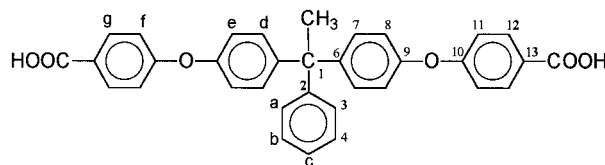


ELEM. ANAL. Calcd. for C<sub>34</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub> (492.57): C, 82.91%; H, 4.91%; N, 5.69%. Found: C, 81.18%; H, 5.74%; N, 5.91%.

### 1,1-Bis[4-(4-carboxyphenoxy)phenyl]-1-Phenylethane (III)

Dicarboxylic acid **III** was synthesized by the hydrolysis of dinitrile compound **II**. A mixture of potassium hydroxide (100 g), the lump of dinitrile compound **II** prepared previously, ethanol (300 mL), and distilled water (200 mL) was stirred at a reflux temperature until no further ammonia was generated. The resulting hot solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and was acidified by concentrated HCl to pH 2–3, and the white precipitate was collected by filtration, washed with water, and dried in vacuum.

Yield: 47.6 g (89.7%). mp: 269°C [peak temperature of melting endotherm on the differential scanning calorimetry (DSC) trace]. IR (KBr): 2500–3500 (carboxyl O—H stretch), 1688 cm<sup>-1</sup> (C=O stretch). <sup>1</sup>H NMR [dimethyl sulfoxide (DMSO)-d<sub>6</sub>, δ, ppm]: 2.16 (—CH<sub>3</sub>), 7.04 (two overlapped AB doublets, 8H, H<sub>e</sub> + H<sub>f</sub>), 7.13 (s, 6H, H<sub>a</sub> + H<sub>d</sub>), 7.24 (d, 1H, H<sub>c</sub>), 7.23 (d, 2H, H<sub>b</sub>), 7.98 (d, 4H, H<sub>g</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ, ppm): 30.37 (—CH<sub>3</sub>), 51.53 (C<sup>1</sup>), 117.39 (C<sup>8</sup>), 119.05 (C<sup>11</sup>), 126.26 (C<sup>13</sup>), 127.76 (C<sup>5</sup>), 128.19 (C<sup>3</sup>), 128.36 (C<sup>4</sup>), 130.19 (C<sup>7</sup>), 131.65 (C<sup>12</sup>), 144.73 (C<sup>6</sup>), 148.79 (C<sup>2</sup>), 153.74 (C<sup>9</sup>), 160.10 (C<sup>10</sup>), 167.55 (C=O).

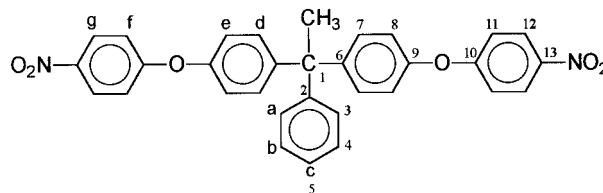


ELEM. ANAL. Calcd. for C<sub>34</sub>H<sub>26</sub>O<sub>6</sub> (530.57): C, 76.97%; H, 4.94%. Found: C, 76.60%; H, 4.50%.

### 1,1-Bis[4-(4-nitrophenoxy)phenyl]-1-Phenylethane (IV)

1,1-Bis(4-hydroxyphenyl)-1-phenylethane (29 g, 0.1 mol) and *p*-chloronitrobenzene (35 g, 0.22 mol) were dissolved in 100 mL of DMF in a 250-mL round-bottomed flask connected to a reflux condenser. Anhydrous potassium carbonate (35 g, 0.25 mol) was added to this solution, and the mixture then was heated to reflux and stirred for 8 h. After cooling to room temperature, the product was poured into 600 mL of water/methanol (1 : 1 volume ratio) to give a yellow powder, washed thoroughly by methanol, and collected by filtration.

Yield: 50 g (94%). mp: 177°C (by DSC). IR (KBr): 1503, 1340 (NO<sub>2</sub> stretch), 1164 cm<sup>-1</sup> (C—O—C stretch). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ, ppm): 2.17 (—CH<sub>3</sub>), 7.03–7.21 (H<sub>a</sub>, H<sub>c,e-f</sub>), 7.29 (d, 2H, H<sub>b</sub>), 8.20 (d, 4H, H<sub>g</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ, ppm): 30.04 (—CH<sub>3</sub>), 51.57 (C<sup>1</sup>), 118.14 (C<sup>8</sup>), 120.52 (C<sup>11</sup>), 126.92 (C<sup>5</sup>), 127.10 (C<sup>12</sup>), 128.99 (C<sup>3</sup>), 129.20 (C<sup>4</sup>), 131.29 (C<sup>7</sup>), 143.45 (C<sup>6</sup>), 146.81 (C<sup>13</sup>), 149.51 (C<sup>2</sup>), 153.77 (C<sup>9</sup>), 164.19 (C<sup>10</sup>).

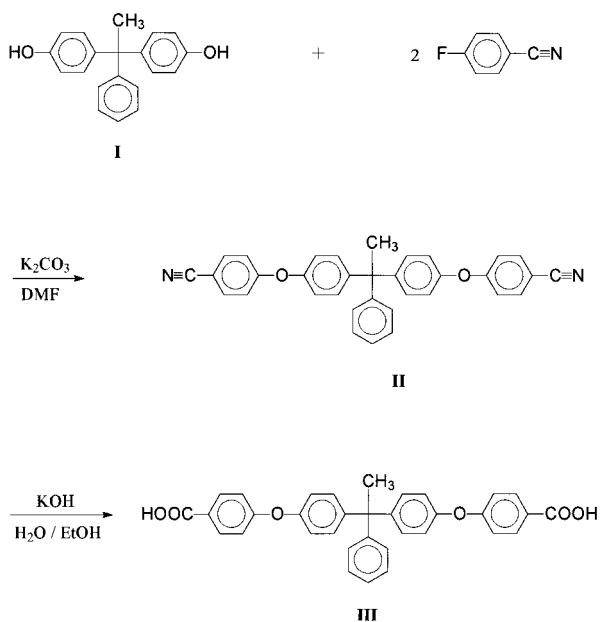


ELEM. ANAL. Calcd. for C<sub>32</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub> (532.55): C, 72.17%; H, 4.54%; N, 5.26%. Found: C, 72.08%; H, 4.57%; N, 5.24%.

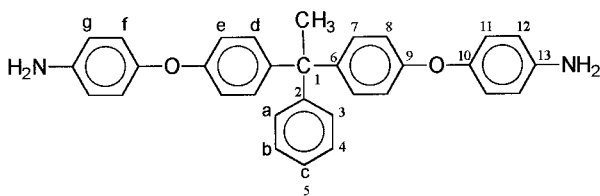
### 1,1-Bis[4-(4-aminophenoxy)phenyl]-1-Phenylethane (V)

The dinitro compound **IV** (45 g, 0.084 mol) and 10% palladium on charcoal (Pd/C) (0.1 g) were suspended in 300 mL of ethanol in a 500-mL flask equipped with a dropping funnel and condenser. The suspension solution was heated to reflux, and hydrazine hydrate (100 mL) was added dropwise to the mixture over a period of 1 h. After a further 4-h reflux, the catalyst was removed by hot filtration. Upon cooling, light-brown crystals precipitated that were isolated by filtration and dried *in vacuo* at 100°C overnight.

Yield: 34.3 g (86%). mp: 68°C (by DSC). IR (KBr): 3368, 3442 (N—H stretch), 1174 cm<sup>-1</sup> (C—O—C stretch). <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ, ppm): 2.09 (—CH<sub>3</sub>), 3.43 (—NH<sub>2</sub>), 6.57 (d, 4H, H<sub>g</sub>), 6.78 (d,

**Scheme 1.**

4H, H<sub>e</sub>), 6.83 (d, 4H, H<sub>f</sub>), 6.97 (d, 4H, H<sub>d</sub>), 7.08 (d, 2H, H<sub>a</sub>), 7.15 (d, 1H, H<sub>c</sub>), 7.21 (d, 2H, H<sub>b</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ, ppm): 29.92 (—CH<sub>3</sub>), 50.89 (C<sup>1</sup>), 116.50 (C<sup>12</sup>), 116.80 (C<sup>8</sup>), 121.58 (C<sup>11</sup>), 126.39 (C<sup>5</sup>), 128.35 (C<sup>3</sup>), 129.08 (C<sup>4</sup>), 130.27 (C<sup>7</sup>), 143.44 (C<sup>6</sup>, C<sup>13</sup>), 149.03 (C<sup>10</sup>), 157.82 (C<sup>9</sup>).



ELEM. ANAL. Calcd. for C<sub>32</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub> (472.58): C, 81.33%; H, 5.97%; N, 5.93%. Found: C, 81.18%; H, 6.01%; N, 5.88%.

### Polymer Synthesis

A typical example of polycondensation is as follows. A mixture of 0.7958 g (1.5 mmol) of 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane (**III**), 0.2303 g (1.5 mmol) of benzidine (**VI<sub>c</sub>**), 0.3 g of CaCl<sub>2</sub>, 0.9 mL of TPP, 0.8 mL of pyridine, and 3 mL of NMP was heated with stirring at 120°C for 3 h. As polycondensation proceeded, the solution became viscous gradually. The resulting highly viscous polymer solution was poured slowly into 300 mL of methanol with stirring, giving a fibrous white precipitate that was washed thoroughly

with methanol and hot water, collected by filtration, and dried. The yield was quantitative, and the inherent viscosity of the polymer (**VII<sub>c</sub>**) in *N,N*-dimethylacetamide (DMAc) and 5 wt % LiCl was 1.23 dL/g.

IR (film): 3312 (N—H stretch), 2982 (aliphatic C—H stretch), 1655 (C=O stretch), 1230 cm<sup>-1</sup> (C—O—C stretch).

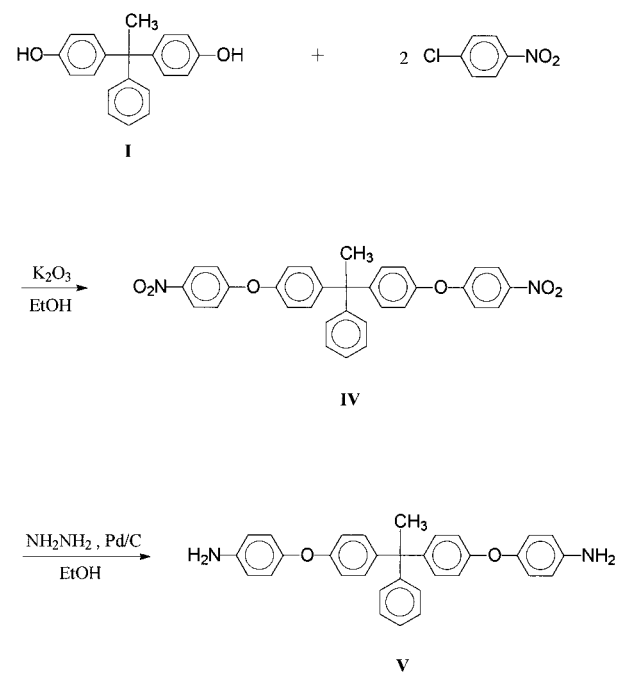
All other polyamides were synthesized by a similar procedure.

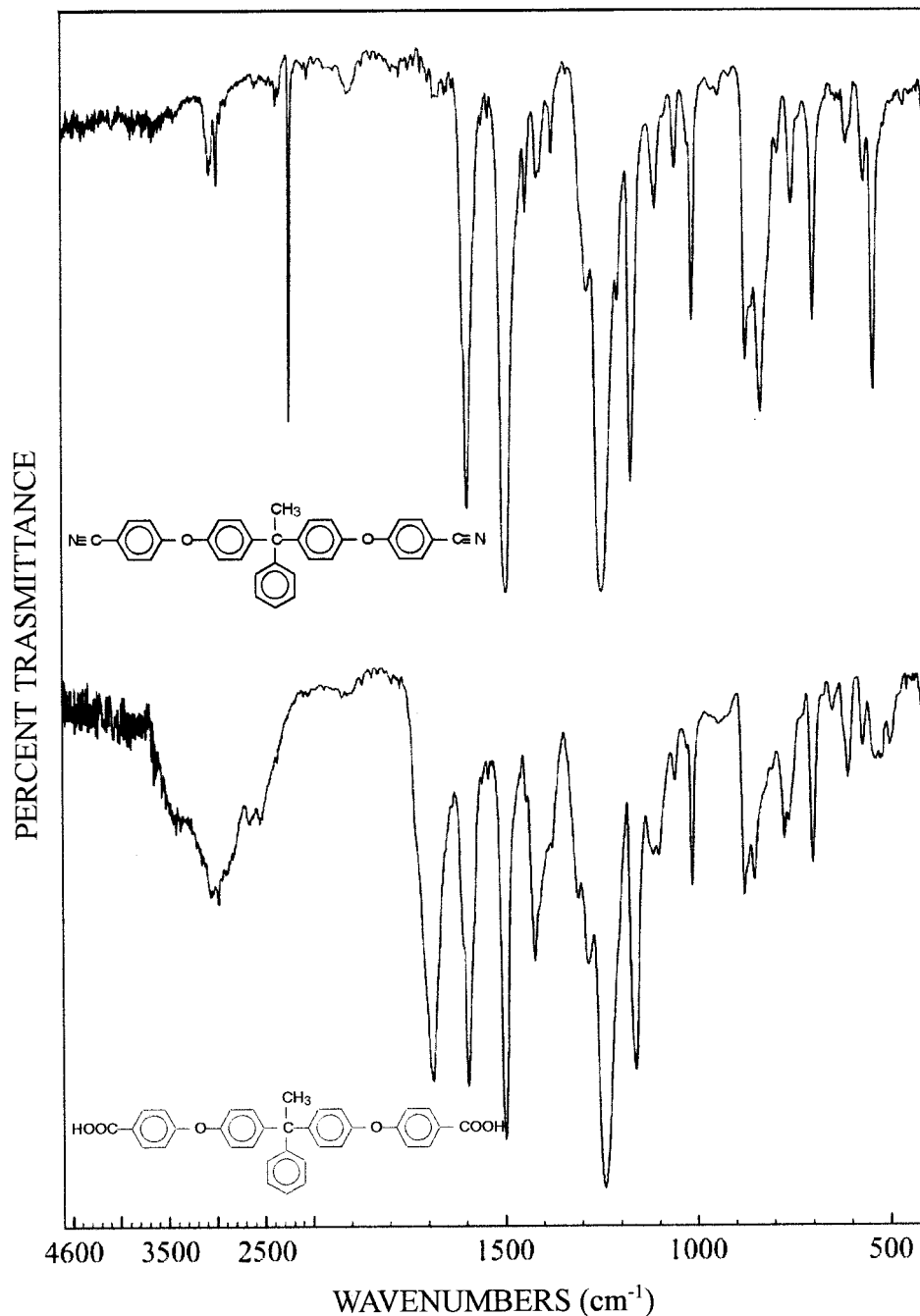
### Preparation of the Polyamide Films

A polymer solution of approximately 10% was made by the dissolving of polyamide in hot DMAc. The solution was poured into a glass culture dish 9 cm in diameter that was placed in a 90°C oven overnight to remove the solvent. Then, the obtained semidried polymer film was stripped from the glass substrate and further dried in vacuum at 160°C for 6 h. The obtained films were about 0.06 mm thick.

### Measurements

Infrared spectra were recorded on a Jasco (Japan) FT/IR-7000 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run in a Perkin-Elmer Model 2400 C—H—N analyzer. <sup>1</sup>H

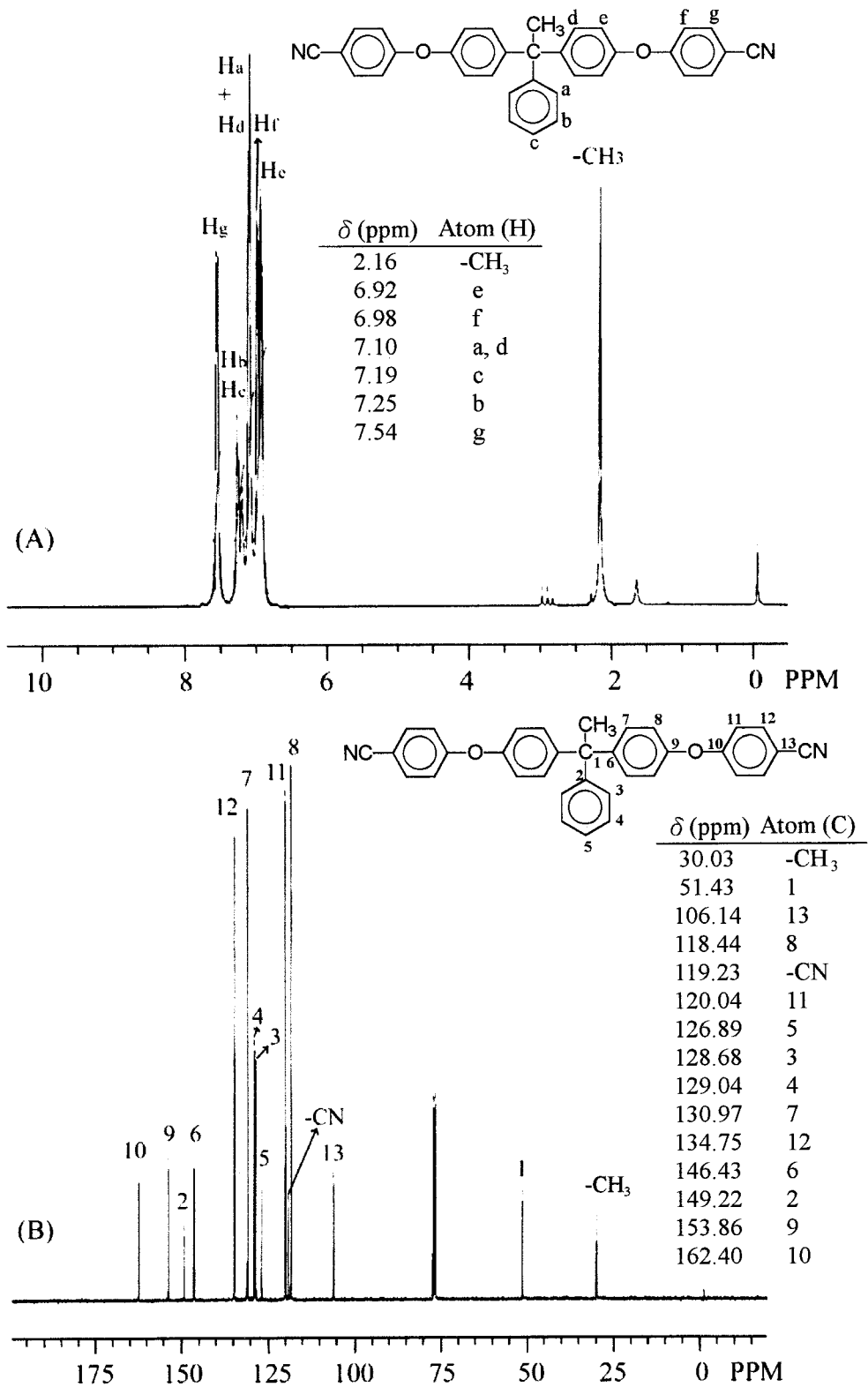
**Scheme 2.**



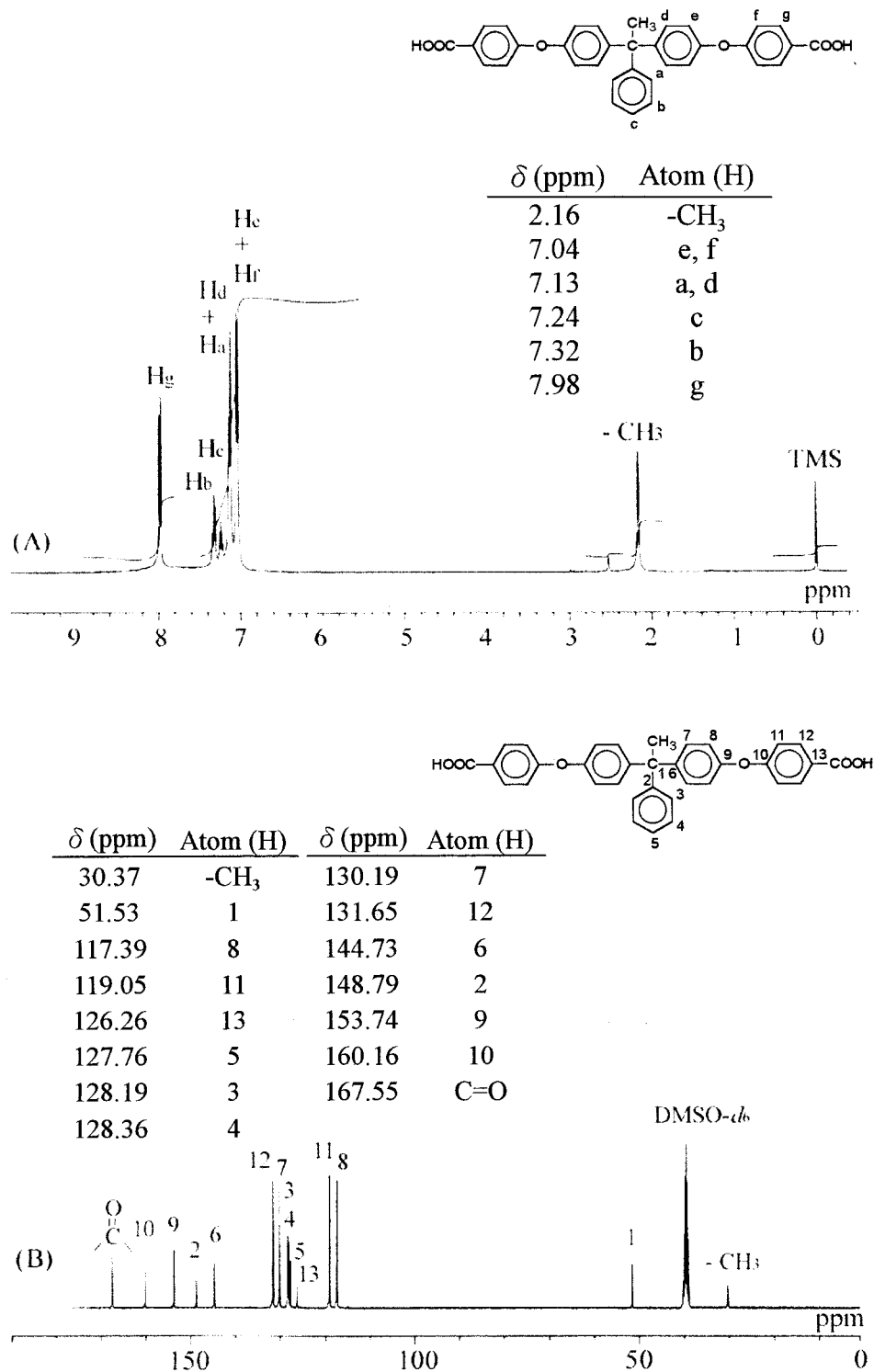
**Figure 1.** IR spectra of 1,1-bis[4-(4-cyanophenoxy)phenyl]-1-phenylethane and 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane.

NMR and  $^{13}\text{C}$  NMR spectra were measured on a Jeol (Japan) EX-400 spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration with a Cannon–Fenske viscometer. Thermogravimetric analysis (TG) was conducted with a Du Pont 951 or a Rigaku (Japan) TG8110 thermogravimetric analyzer. Measurements were car-

ried out on 9–11-mg film samples heated in flowing nitrogen or air ( $50\text{ cm}^3/\text{min}$ ) at a heating rate of  $20^\circ\text{C}/\text{min}$ . DSC analyses were performed on a Perkin–Elmer DSC 7 in flowing nitrogen with a heating rate of  $20^\circ\text{C}/\text{min}$ .  $T_g$ 's were read as the midpoint of the heat capacity jump and were taken from the second heating scan after a quick



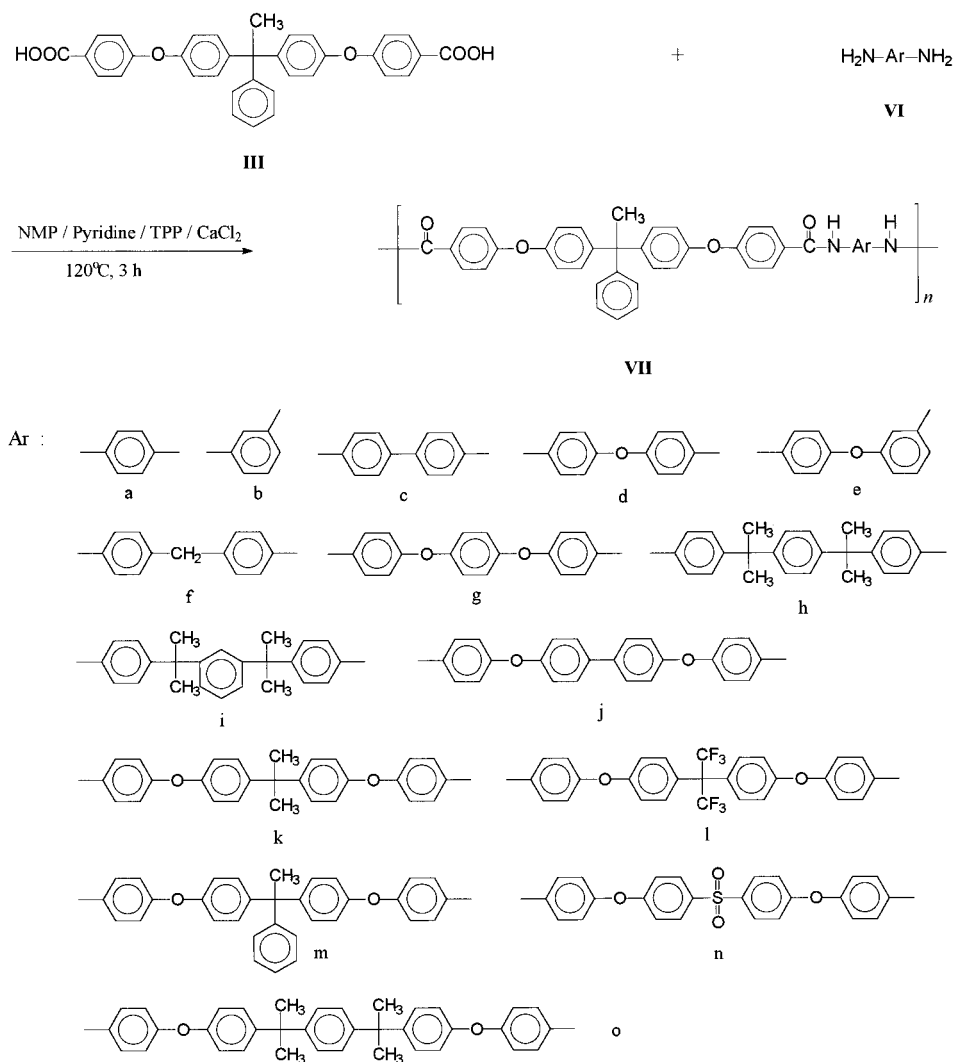
**Figure 2.** (A) <sup>1</sup>H NMR and (B) <sup>13</sup>C NMR spectra of 1,1-bis[4-(4-cyanophenoxy)phenyl]-1-phenylethane in CDCl<sub>3</sub>.



**Figure 3.** (A)  $^1\text{H}$  NMR and (B)  $^{13}\text{C}$  NMR spectra of 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane in  $\text{DMSO}-d_6$ .

cooling down from  $400^\circ\text{C}$ . Thermomechanical analysis (TMA) was conducted with a Perkin-Elmer TMA 7 instrument with a penetration

probe 1.0 mm in diameter and with an applied constant load of 30 mN (stress = 0.038 MPa). The TMA experiments were conducted in duplicate



Scheme 3.

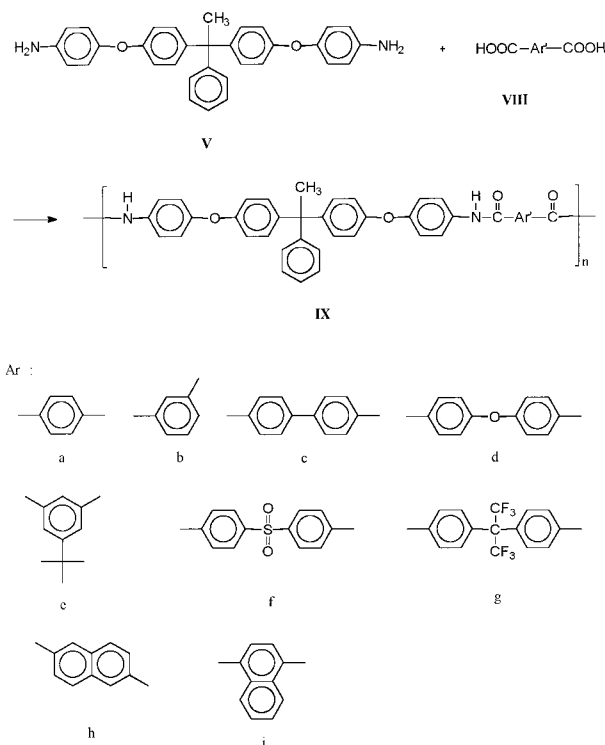
from 30 to 300°C at a scan rate of 10°C/min. Apparent  $T_g$ 's were taken as the onset temperature of probe displacement on the second TMA traces. Wide-angle X-ray diffractograms were obtained on a Siemens (Germany) Kristalloflex D5000 X-ray diffractometer with Ni-filtered Cu  $K_\alpha$  radiation (40 kV, 15 mA) at a scanning rate of 2°/min. Measurements were performed with film specimens about 0.06 mm thick. 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 crosshead speed of 5 cm/min. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, ca. 0.06 mm thick), and an average of at least five individual determinations was used.

## RESULTS AND DISCUSSION

### Monomer Synthesis

According to Schemes 1 and 2, 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane (**III**) and 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**V**) were prepared with a two-stage procedure starting from 1,1-bis(4-hydroxyphenyl)-1-phenylethane (**I**). The intermediate compounds, 1,1-bis[4-(4-cyanophenoxy)phenyl]-1-phenylethane (**II**) and 1,1-bis[4-(4-nitrophenoxy)phenyl]-1-phenylethane (**IV**), were synthesized by nucleophilic aromatic halogen displacement of *p*-fluorobenzonitrile or *p*-chloronitrobenzene with bisphenol **I** in the presence of potassium carbon-





ate in DMF. The dinitrile **II** then was converted readily into dicarboxylic acid **III** by alkaline hydrolysis. The diamine **V** was obtained by the catalytic hydrogenation of dinitro compound **IV** with hydrazine hydrate and Pd/C catalyst in refluxing ethanol.

All the structures of the intermediates and monomers were verified by FTIR, solution NMR, and microanalysis. Figure 1 shows the IR spectra of intermediate **II** and dicarboxylic acid **III**. Dinitrile compound **II** displayed a characteristic absorption band corresponding to C≡N stretching at 2228 cm<sup>-1</sup> that disappeared after hydrolysis. The diacid compound **III** showed typical C=O stretching at 1711 cm<sup>-1</sup> and hydrogen-bonded O—H stretching bands in the region of 2500 to 3500 cm<sup>-1</sup>. Both the dinitrile and diacid compounds showed the —C—O—C— stretching band around 1245 cm<sup>-1</sup>, confirming the presence of the aromatic ether linkage. Figures 2 and 3 illustrate the <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of dinitrile **II** and diacid **III**. Assignments of each carbon and proton also are given in the figures. These spectra were in good agreement with the proposed structures. In the <sup>1</sup>H NMR spectra, downfield shifts of the proton resonance, especially for H<sub>g</sub>, were observed for diacid **III** because of the stronger in-

ductive effect of the carboxyl group. The most obvious features of the <sup>13</sup>C NMR spectra are the shifts of the resonance peaks for the carbon of the C≡N group and its adjacent carbon C<sup>13</sup>. The C<sup>13</sup> of dinitrile **II** resonated at a higher field than the other aromatic carbons because of the anisotropic shielding by the π electrons of C≡N. After hydrolysis, the resonance peak of C<sup>13</sup> shifted to a lower field (from 106.14 to 126.26 ppm) because of the lack of an anisotropic field, the original signal at 119.23 peculiar to cyano carbon vanished, and the resonance of the carboxyl carbon was observed at the farthest downfield (167.55 ppm).

Concerning the synthesis of diamine compound **V**, the transformation of functional groups could

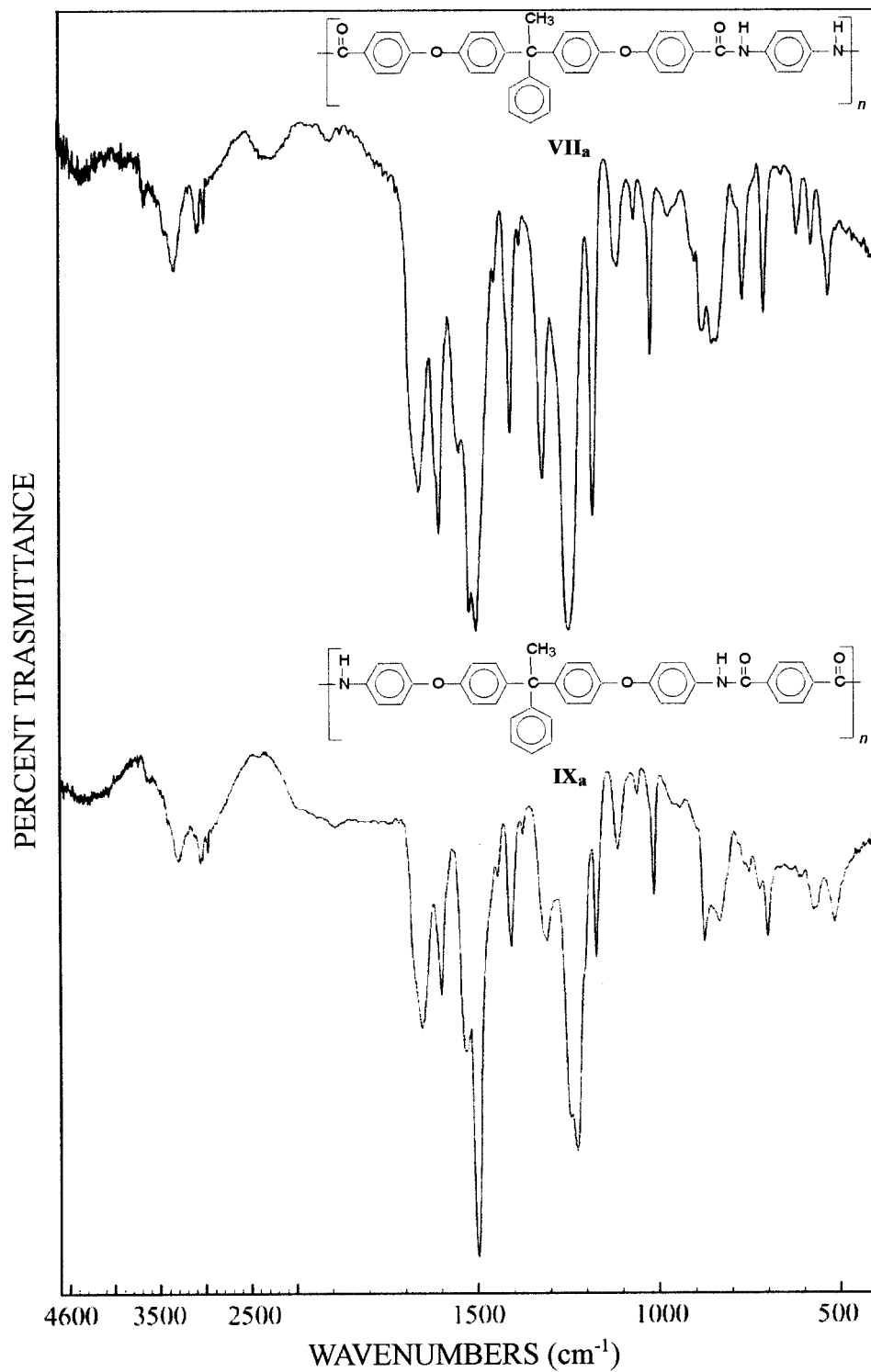
**Table I.** Synthesis Conditions and Inherent Viscosities of Polyamides

Polymer	Amounts of Reagents Used <sup>a</sup>				
	NMP (mL)	Py (mL)	TPP (mL)	CaCl <sub>2</sub> (g)	η <sub>inh</sub> (dL/g) <sup>b</sup>
<b>VII<sub>a</sub></b>	3	0.8	0.9	0.3	1.13
<b>VII<sub>b</sub></b>	2	0.5	0.9	0.2	0.81
<b>VII<sub>c</sub></b>	3	0.8	0.9	0.3	1.23
<b>VII<sub>d</sub></b>	3 + 1 <sup>c</sup>	0.8	0.9	0.3	1.07
<b>VII<sub>e</sub></b>	2	0.5	0.9	0.3	0.79
<b>VII<sub>f</sub></b>	3	0.8	0.9	0.3	0.97
<b>VII<sub>g</sub></b>	2 + 2	0.5	0.9	0.2	1.26
<b>VII<sub>h</sub></b>	3	0.8	0.9	0.3	0.95
<b>VII<sub>i</sub></b>	3	0.8	0.9	0.3	0.71
<b>VII<sub>j</sub></b>	4	1.0	0.9	0.4	1.77
<b>VII<sub>k</sub></b>	4 + 1	1.0	0.9	0.4	1.00
<b>VII<sub>l</sub></b>	4 + 2	1.0	0.9	0.4	1.23
<b>VII<sub>m</sub></b>	4 + 1	1.0	0.9	0.4	0.99
<b>VII<sub>n</sub></b>	4 + 1	1.0	0.9	0.4	1.09
<b>VII<sub>o</sub></b>	4 + 5	1.0	0.9	0.4	1.17
<b>IX<sub>a</sub></b>	4	1.0	1.6	0.4	1.49
<b>IX<sub>b</sub></b>	3	0.8	1.6	0.4	0.84
<b>IX<sub>c</sub></b>	4	1.0	1.6	0.4	1.53
<b>IX<sub>d</sub></b>	4	1.0	1.6	0.4	1.49
<b>IX<sub>e</sub></b>	3	0.8	1.6	0.3	0.87
<b>IX<sub>f</sub></b>	3	0.8	1.6	0.3	1.10
<b>IX<sub>g</sub></b>	3	0.8	1.6	0.3	1.17
<b>IX<sub>h</sub></b>	4	1.0	1.6	0.4	1.68
<b>IX<sub>i</sub></b>	3	0.8	1.6	0.4	1.09

<sup>a</sup> 1.25 mmol (for **VII**) or 1.5 mmol (for **IX**) each of the diacid and diamine monomer were used. Reaction temperature = 120 °C; time = 3 h; NMP = *N*-methyl-2-pyrrolidone; Py = pyridine; TPP = triphenyl phosphite.

<sup>b</sup> Measured in *N,N*-dimethylacetamide containing 5 wt % LiCl at 30 °C on 0.5 g/dL.

<sup>c</sup> "3 + 1" means that an initial amount of 3 mL of NMP was used and an additional 1 mL of NMP was added when the reaction solution was too viscous to stir.



**Figure 4.** IR spectra of isomeric polyamides VII<sub>a</sub> and IX<sub>a</sub>.

be monitored by IR and NMR spectroscopy. After reduction, the characteristic bands at 1340 and 1586 cm<sup>-1</sup> due to the N=O stretching of dinitro

compound IV disappeared, and the pair of N—H stretching bands appeared in the region of 3300 to 3500 cm<sup>-1</sup>. The NMR data shown in the Experi-

**Table II.** Solubility Behavior of Polyamides<sup>a</sup>

Polymer	Solvent <sup>b</sup>						
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	THF/H <sub>2</sub> O (90/10)
VII <sub>a</sub>	+	+	+	+	+	-	+
VII <sub>b</sub>	+	+	+	+	+	-	+
VII <sub>c</sub>	+	+	+	+	-	-	-
VII <sub>d</sub>	+	+	+	+	+	-	+
VII <sub>e</sub>	+	+	+	+	+	-	+
VII <sub>f</sub>	+	+	+	+	+	-	+
VII <sub>g</sub>	+	+	+	+	+	-	+
VII <sub>h</sub>	+	+	+	+h	+	+	+
VII <sub>i</sub>	+	+	+	+	+	+	+
VII <sub>j</sub>	+	+	+	+	+	-	+h
VII <sub>k</sub>	+	+	+	+h	+	-	+
VII <sub>l</sub>	+	+	+	+	+	+	+
VII <sub>m</sub>	+	+	+	+	+	+	+
VII <sub>n</sub>	+	+	+	+	+	-	+
VII <sub>o</sub>	+	+	+	-	+	+	+
IX <sub>a</sub>	+	+	+	+	+	-	+
IX <sub>b</sub>	+	+	+	+	+	-	+
IX <sub>c</sub>	+	+	+	+	-	-	-
IX <sub>d</sub>	+	+	+	+	+	-	+
IX <sub>e</sub>	+	+	+	+	+	-	+
IX <sub>f</sub>	+	+	+	+	+	-	+
IX <sub>g</sub>	+	+	+	+	+	+	+
IX <sub>h</sub>	+	+	+	+	+	-	+
IX <sub>i</sub>	+	+	+	+	+	-	+

<sup>a</sup> + = soluble at room temperature; +h = soluble on heating at 100 °C; - = insoluble even on heating; polymer concentration = 10 mg/mL.

<sup>b</sup> NMP = *N*-methyl-2-pyrrolidone; DMAc = *N,N*-dimethylacetamide; DMF = *N,N*-dimethylformamide; DMSO = dimethyl sulfoxide; THF = tetrahydrofuran.

mental section were consistent with the structures of dinitro compound **IV** and diamine monomer **V**.

### Polymer Synthesis

The phosphorylation technique developed by Yamazaki and coworkers<sup>19</sup> was used to prepare polyamides **VII<sub>a-o</sub>** and **IX<sub>a-i</sub>** from diacid **III** with various aromatic diamines (**VI<sub>a-o</sub>**) and from diamine **V** with various aromatic dicarboxylic acids (**VIII<sub>a-i</sub>**), respectively. Structures and codes of the polymers prepared are shown in Schemes 3 and 4. No attempts were made to maximize molecular weights. Using the reaction conditions listed in Table I, we generally obtained high molecular weight polymers. Viscosities of the polymerization mixtures were normally very high, and the

nature of the precipitated polymers implied high molecular weight products. As shown in Table I, the resulting polymers had inherent viscosities higher than 0.71 dL/g and up to 1.77 dL/g. All of the polyamides prepared could be solvent-cast into creasable, high-strength films. Key structural features were verified by FTIR on the basis of characteristic absorption bands observed around 3300 (N—H stretch) and 1650 to 1670 cm<sup>-1</sup> (C=O stretch). Figure 4 illustrates the IR spectra of polyamides **VII<sub>a</sub>** and **IX<sub>a</sub>**, which had isomeric repeat units.

### Polymer Characterization

#### Solubility

The solubility behavior of the aromatic polyamides was tested qualitatively in various sol-

**Table III.** Tensile Properties of Polyamide Films<sup>a</sup>

Polymer	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation To Break (%)	Tensile Modulus (GPa)
VII <sub>a</sub>	104	101	30	2.32
VII <sub>b</sub>	105	104	9	2.43
VII <sub>c</sub>	102	99	65	2.17
VII <sub>d</sub>	100	95	20	2.10
VII <sub>e</sub>	108	102	11	2.26
VII <sub>f</sub>	94	89	55	2.03
VII <sub>g</sub>	96	92	37	1.94
VII <sub>h</sub>	106	102	13	2.08
VII <sub>i</sub>	99	99	7	2.20
VII <sub>j</sub>	95	94	41	2.15
VII <sub>k</sub>	104	95	33	2.03
VII <sub>l</sub>	101	94	31	1.98
VII <sub>m</sub>	107	103	13	2.15
VII <sub>n</sub>	101	95	17	2.11
VII <sub>o</sub>	100	91	21	2.19
IX <sub>a</sub>	79	69	21	1.79
IX <sub>b</sub>	84	66	12	1.67
IX <sub>c</sub>	84	71	20	1.60
IX <sub>d</sub>	77	64	28	1.52
IX <sub>e</sub>	84	83	7	1.76
IX <sub>f</sub>	75	66	13	2.29
IX <sub>g</sub>	79	73	14	1.72
IX <sub>h</sub>	86	83	12	1.57
IX <sub>i</sub>	91	90	7	1.55

<sup>a</sup> Films were cast from slow evaporation of the polymer solutions in *N,N*-dimethylacetamide. The cast films were dried under vacuum at 150 °C for 6 h prior to the tensile test.

vents. The results are listed in Table II. All the polyamides were readily soluble in amide-type polar aprotic solvents (e.g., NMP, DMAc, and DMF). Almost all of the polymers were also soluble in DMSO and *m*-cresol. In addition, polyamides obtained from flexible group-linked multi-ring diamines, such as VI<sub>l</sub> and VI<sub>m</sub>, dissolved even in less polar solvents such as tetrahydrofuran (THF). According to a Du Pont patent,<sup>20</sup> we also tested the solubility of these polyamides in 90 : 10 (by volume) THF/H<sub>2</sub>O and found all of the polyamides except VII<sub>c</sub> and IX<sub>c</sub> were soluble in this solvent pair. Polymers VII<sub>c</sub> and IX<sub>c</sub> showed a slightly lower solubility because of their symmetrical and rigid biphenylene segments. Similar to the results reported in our preceding articles,<sup>21–23</sup> the two set analogous polyamides VII<sub>a–d</sub> and IX<sub>a–d</sub> showed a similar solubility behavior. The high solubility of these polyamides was apparently due in part to the presence of the packing-

disruptive triphenylethane unit in the polymer backbone, which resulted in increased chain packing distances and decreased intermolecular interactions. One of the factors contributing to the enhanced solubility was the characteristic amorphous nature caused by the introduction of a triphenylethane structure and flexible ether linkage.

### Crystallinity and Tensile Properties

X-ray diffraction patterns confirmed that all the polyamides were amorphous. Transparent, tough, and flexible films of all of the polyamides could be obtained by casting their DMAc solutions. The

**Table IV.** Thermal Properties of Polyamides

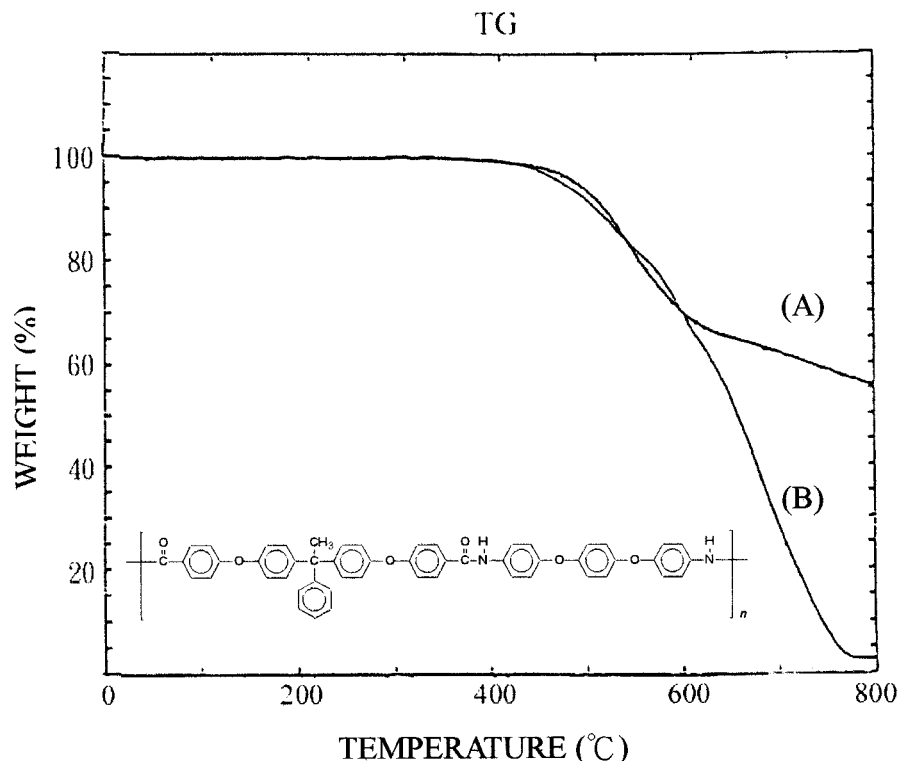
Polymer	<i>T<sub>g</sub></i> (°C) <sup>a</sup>	<i>T<sub>d</sub></i> (°C) <sup>b</sup>		Char Yield (%) <sup>c</sup>
		In N <sub>2</sub>	In Air	
VII <sub>a</sub>	212	510	509	64
VII <sub>b</sub>	197	513	494	71
VII <sub>c</sub>	260	504	511	67
VII <sub>d</sub>	194	508	511	58
VII <sub>e</sub>	181	514	518	66
VII <sub>f</sub>	194	498	507	61
VII <sub>g</sub>	201	511	502	56
VII <sub>h</sub>	185	494	498	56
VII <sub>i</sub>	179	498	503	50
VII <sub>j</sub>	218	527	498	70
VII <sub>k</sub>	188	507	514	55
VII <sub>l</sub>	193	520	515	58
VII <sub>m</sub>	194	513	509	55
VII <sub>n</sub>	204	514	520	61
VII <sub>o</sub>	184	514	516	56
IX <sub>a</sub>	216	496	475	67
IX <sub>b</sub>	201	516	487	66
IX <sub>c</sub>	(268) <sup>d</sup>	475	496	67
IX <sub>d</sub>	210	504	475	63
IX <sub>e</sub>	224	502	489	60
IX <sub>f</sub>	224	489	491	62
IX <sub>g</sub>	219	516	504	61
IX <sub>h</sub>	218	504	493	68
IX <sub>i</sub>	220	467	473	62

<sup>a</sup> Baseline shifts in the second heating DSC traces with a heating rate of 20 °C/min.

<sup>b</sup> Decomposition temperatures at which a 10% weight loss was recorded by TG at a heating rate of 20 °C/min.

<sup>c</sup> Residual weight (%) when heated to 800 °C at a scan rate of 20 °C/min in nitrogen.

<sup>d</sup> Difficult to judge on the DSC curve. The value shown in parentheses is that measured by TMA (penetration method) with an applied stress of 0.038 MPa at a heating rate of 10 °C/min.



**Figure 5.** TG curves for polyamide **VII<sub>g</sub>** in (A) nitrogen and (B) air with a heating rate of 20°C/min.

tensile properties of the polyamide films are summarized in Table III. Most of these polymer films necked during tensile testing and had moderate elongations to break, indicative of high toughness.

#### Thermal Properties

The thermal behavior data of all the polymers are given in Table IV. Polyamides **VII<sub>a-o</sub>** and **IX<sub>a-i</sub>** showed  $T_g$  values in the range of 179 to 260°C and 201 to 224°C, respectively, by DSC. No discernible  $T_g$ 's were observed for the polyamide **IX<sub>c</sub>** from 4,4'-biphenylenedicarboxylic acid by DSC. Thus, the TMA method was used to determine its  $T_g$ , which was recorded at 268°C. In general, the  $T_g$  values depended on the structures of the diamine and diacid moieties and decreased with decreasing rigidity and symmetry of the polymer backbone. This trend was similar to that found in previous papers.<sup>21-23</sup>

The thermal stability of the polyamides was studied by TG. Typical TG curves in air and nitrogen atmospheres of the representative polymer **VII<sub>g</sub>** are shown in Figure 5. The temperatures at the 10% weight loss in nitrogen and air atmo-

spheres were determined from the original thermograms and are included in Table IV. All the polymers exhibited good thermal stability with no significant weight loss up to approximately 400°C in both air and nitrogen atmospheres, and the temperatures at the 10% weight loss were above 460°C. The anaerobic char yield at 800°C for all the polymers was in the range of 50 to 75 wt %, showing a high intrinsic fire resistance.

#### CONCLUSIONS

Extended diacid **III** and diamine **V**, 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane and 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane, were synthesized successfully with a high purity and in high yields from readily available reagents. Two series of high molecular weight polyamides were prepared in high yields from various combinations of **III** with aromatic diamines or **V** with aromatic diacids via the Yamazaki-Higashi phosphorylation technique. Because of the presence of bulky, propeller-shaped triphenylethane cores in the main chain, no crystallinity was ob-

served for any of these polymers. Good solubility, moderate  $T_g$  values suitable for molding, and reasonable thermal stability make these aromatic polyamides promising high-performance polymeric materials.

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