

# Synthesis and Properties of Aromatic Polyamides Based on a Benzonorbornane Bis(ether carboxylic acid)

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**ABSTRACT:** A set of new aromatic polyamides containing ether and benzonorbornane units were synthesized by the direct phosphorylation polycondensation of 3,6-bis(4-carboxyphenoxy)benzonorbornane with various aromatic diamines. The polymers were produced in high yields and moderate to high inherent viscosities (0.64–1.70 dL/g). The polyamides derived from rigid diamines such as *p*-phenylenediamine and benzidine were semicrystalline and insoluble in organic solvents. The other polyamides were amorphous and organosoluble and afforded flexible and tough films via solution casting. These films exhibited good mechanical properties, with tensile strengths of 95–101 MPa, elongations at break of 13–25%, and initial moduli of 1.97–2.33 GPa. The amorphous polyamides showed glass-transition temperatures between 176 and 212 °C (by differential scanning calorimetry) and softening temperatures between 194 and 213 °C (by thermomechanical analysis). Most of the polymers did not show significant weight loss before 450 °C in nitrogen or in air. Some properties of these polyamides were also compared with those of homologous counterparts without the pendent norbornane groups. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 947–957, 2002

**Keywords:** benzonorbornane; polyamides; solubility; thermal properties; structure-property relations

## INTRODUCTION

Rigid-rod aromatic polyamides (aramids), such as poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide), have already been reported for their high-temperature resistance and excellent mechanical strength, easily giving lyotropic solutions.<sup>1–5</sup> Fibers obtained from anisotropic solutions of these materials have been used in applications for which high thermal stability and mechanical strength are required.<sup>6</sup> However, infusibility and limited solubility in organic solvents are the characteristic properties of aramids

that restrict synthesis and applications, especially of high molecular weight materials.

Therefore, many efforts have been made with the aim of designing the chemical structure of the rigid aromatic backbone to obtain aramids that are processable by conventional techniques.<sup>7–16</sup> Attempts in this area include introducing flexible linkages into the polymer chain; replacing symmetrical aromatic rings with unsymmetrical ones, which leads to a reduction in crystallinity; incorporating bulky pendent groups to minimize crystallization; and forming a noncoplanar structure, thereby making crystallization impossible. These modifications lower the melting temperature and lead to soluble and amorphous polymers. In general, amorphous polyamides have a lower softening temperature ( $T_g$ ) and improved solubility with respect to crystalline analogues, and so they may open applications in the areas of films,

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gas-separation membranes, coatings, engineering plastics, polymer blends, and composites.

During recent years, many studies<sup>17–21</sup> have focused on introducing both ether and bulky pendent groups along the aramid backbone to minimize the tradeoff between the processability and positive/useful properties of aramids. The introduction of ether linkages is known to enhance the processability and toughness of aromatic polymers without a significant reduction in thermal stability. Furthermore, the incorporation of bulky pendent groups can decrease hydrogen bonding and interchain interactions in polyamides and generally disturb the coplanarity of aromatic units to reduce packing density and crystallinity. This should enhance solubility and maintain a high glass-transition temperature ( $T_g$ ) through controlled segmental mobility.

In this study, we dealt with the synthesis of new polyamides with the pendent norbornane group fused on the aromatic unit by the polycondensation of 3,6-bis(4-carboxyphenoxy)benzonorbornane with various aromatic diamines. The effect of the fused norbornane side group on the properties of the polymers was evaluated.

## EXPERIMENTAL

### Materials

3,6-Dihydroxybenzonorbornane (Acros), *p*-fluorobenzonitrile (TCI), and potassium carbonate ( $K_2CO_3$ ; Wako) were used as received. *p*-Phenylenediamine (**VI-a**; TCI) and benzidine (**VI-c**; TCI) were purified by vacuum sublimation. *m*-Phenylenediamine (**VI-b**; Janssen) was purified by vacuum distillation. 4,4'-Oxydianiline (**VI-d**; TCI), 1,4-bis(4-aminophenoxy)benzene (**VI-e**; TCI), and 1,3-bis(4-aminophenoxy)benzene (**VI-f**; TCI) were used as received. As described previously,<sup>22,23</sup> 4,4'-bis(*p*-aminophenoxy)phenyl (**VI-g**; mp = 198–199 °C) and bis[4-(4-aminophenoxy)phenyl] ether (**VI-h**; mp = 128–129 °C) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenol precursors and *p*-chloronitrobenzene in the presence of  $K_2CO_3$  and by the subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compounds with hydrazine monohydrate as the reducing reagent and Pd/C as the catalyst.

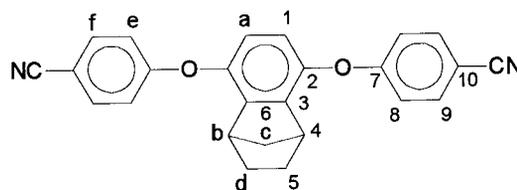
### Monomer Synthesis

#### 3,6-Bis(4-cyanophenoxy)benzonorbornane (I)

In a 300-mL, round-bottom flask, 3,6-dihydroxybenzonorbornane (25.8 g, 0.15 mol) and anhy-

drous  $K_2CO_3$  (41.4 g, 0.3 mol) were suspended in a mixture of 100 mL of dry *N,N*-dimethylformamide (DMF) and 60 mL of toluene. Then, the mixture was refluxed at 140 °C with a Dean–Stark trap for the azeotropic removal of water. After most of the toluene had been removed, *p*-fluorobenzonitrile (36.9 g, 0.3 mol + 0.1 g) was added to the mixture, and heating was continued at reflux for 12 h. The resulting solution was allowed to cool to room temperature and was then poured into 600 mL of methanol/water (1/1 v/v) to give white precipitates. After being washed repeatedly with water, the product was collected by filtration and was recrystallized from a mixture of ethanol and acetonitrile (800 mL/200 mL) to afford 47 g (85% yield) of pure white needles [mp = 179–181 °C by differential scanning calorimetry (DSC)].

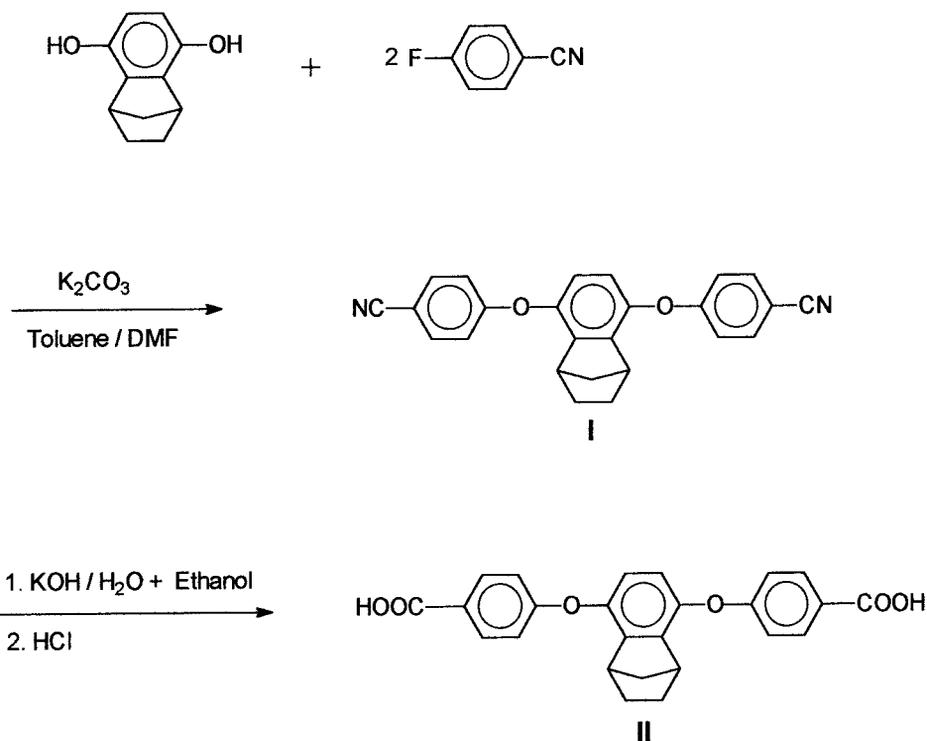
IR (KBr): 2965, 2875 (aliphatic C—H stretching), 2225 (C≡N stretching), 1240  $cm^{-1}$  (C—O—C stretching). <sup>1</sup>H NMR [400 MHz, dimethyl sulfoxide (DMSO)-*d*<sub>6</sub>, δ, ppm]: 7.85 (d, H<sub>f</sub>, 4H), 7.11 (d, H<sub>e</sub>, 4H), 6.96 (d, H<sub>a</sub>, 2H), 3.18 (s, H<sub>b</sub>, 2H), 1.79, 1.08 (d, H<sub>d</sub>, 4H), 1.68, 1.44 (d, H<sub>c</sub>, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 163.57 (C<sup>7</sup>), 145.94 (C<sup>2</sup>), 143.22 (C<sup>3</sup>), 136.25 (C<sup>9</sup>), 121.84 (C<sup>1</sup>), 120.20 (—CN), 118.45 (C<sup>8</sup>), 105.91 (C<sup>10</sup>), 49.28 (C<sup>4</sup>), 40.50 (C<sup>6</sup>), 25.73 (C<sup>5</sup>).



ELEM. ANAL. Calcd. for  $C_{25}H_{18}N_2O_2$  (378.43): C, 79.35%; H, 4.79%; N, 7.40%. Found: C, 79.40%; H, 4.81%; N, 7.24%.

#### 3,6-Bis(4-carboxyphenoxy)benzonorbornane (II)

A suspension of the intermediate dinitrile **I** (26 g, 0.069 mol) in a mixture of water (200 mL) and ethanol (500 mL) containing dissolved potassium hydroxide (38.5 g, 0.69 mol) was heated at reflux for 48 h until ammonia evolution ceased. The resulting clear solution was filtered hot for the removal of any insoluble impurities, cooled, and acidified to pH 2–3 by concentrated HCl; a white solid precipitated. The solid was filtered off, washed thoroughly with water, and dried to give 27.1 g (yield 95%) of diacid **II** (mp = 293–298 °C by DSC).



**Scheme 1.** Synthesis of 3,6-bis(4-carboxyphenoxy)benzonorbornane (**II**).

IR (KBr): 2500–3500 (O—H stretching), 1683 (C=O stretching),  $1234 \text{ cm}^{-1}$  (C—O—C stretching).  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 12.84 (s, —COOH, 2H), 7.97 (d, 4H), 7.02 (d, 4H), 6.93 (s, 2H), 3.19 (s, 2H), 1.77, 1.10 (d, 4H), 1.69, 1.43 (d, 2H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 168.85 (C=O), 163.67, 146.31, 142.99, 133.06, 126.26, 121.52, 117.46, 49.25, 40.55, 25.81. ELEM. ANAL. Calcd. for  $\text{C}_{25}\text{H}_{20}\text{O}_6$  (416.43): C, 72.11%; H, 4.84%. Found: C, 72.04%; H, 4.59%.

### Polymer Synthesis

A typical phosphorylation polycondensation for the preparation of polyamide **IV-a** is given. A flask was charged with 0.6246 g (1.5 mmol) of diacid **II**, 0.1622 g (1.5 mmol) of *p*-phenylenediamine (**III-a**), 0.4 g of  $\text{CaCl}_2$ , 1.5 mL of triphenyl phosphite (TPP), 1 mL of pyridine (Py), and 4 mL of *N*-methyl-2-pyrrolidone (NMP). This mixture was heated with stirring at 120 °C for 3 h. As polycondensation proceeded, the solution gradually became viscous. The viscous polymer solution was subsequently poured slowly into 300 mL of stirred methanol. The resultant white and fibrous solid was filtered off, washed thoroughly with methanol and hot water, and dried. The inherent

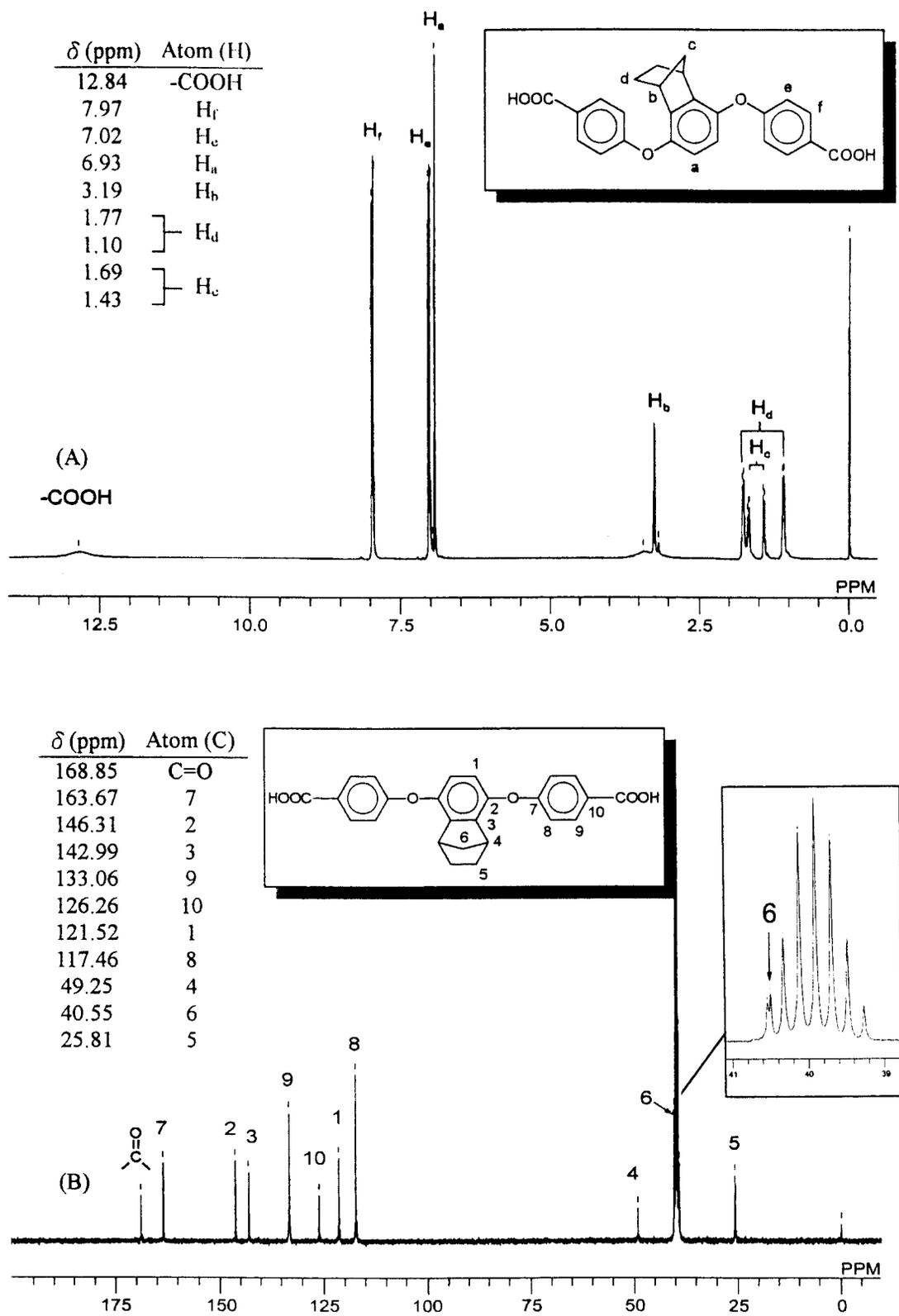
viscosity of the polymer (**IV-a**) was 1.03 dL/g, as measured at a concentration of 0.5 g/dL in dimethylacetamide (DMAc) containing 5 wt % LiCl at 30 °C.

### Preparation of the Polyamide Films

A solution of polymer was made by the dissolution of about 0.8 g of the polyamide in 8 mL of hot DMAc to afford an approximately 10 wt % solution. The clear solution was poured into a 9-cm-diameter glass culture dish, which was placed in a 90 °C oven for 12 h for evaporation of the solvent. The semidried polyamide film was stripped off from the glass substrate and further dried in a vacuum oven at about 160 °C for 6 h. The obtained films were about 0.08 mm thick and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

### Measurements

Elemental analysis was performed on a PerkinElmer 2400 CHN analyzer. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a JEOL EX 400



spectrometer with DMSO- $d_6$  as the solvent and tetramethylsilane as the internal reference. The inherent viscosities of the poly(amic acid)s were measured with a Cannon-Fenske viscometer at 30 °C. An Instron model 1130 universal tester with a load cell of 5 kg was used to study the stress-strain behavior of the polyamide film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens 0.5 cm wide, 6 cm long, and about 0.08 mm thick, and an average of at least five individual determinations was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer (operating at 40 kV and 20 mA) with nickel-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The scanning rate was 3°/min over a range of 2 $\theta = 5$ –45°. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 3–5-mg samples in flowing nitrogen or air (flow rate = 40 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen.  $T_g$ 's were read at the middle of the transition in the heat capacity. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 40 to 300 °C at a scanning rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN.  $T_s$  values were taken as the onset temperatures of probe displacement on the TMA traces.

## RESULTS AND DISCUSSION

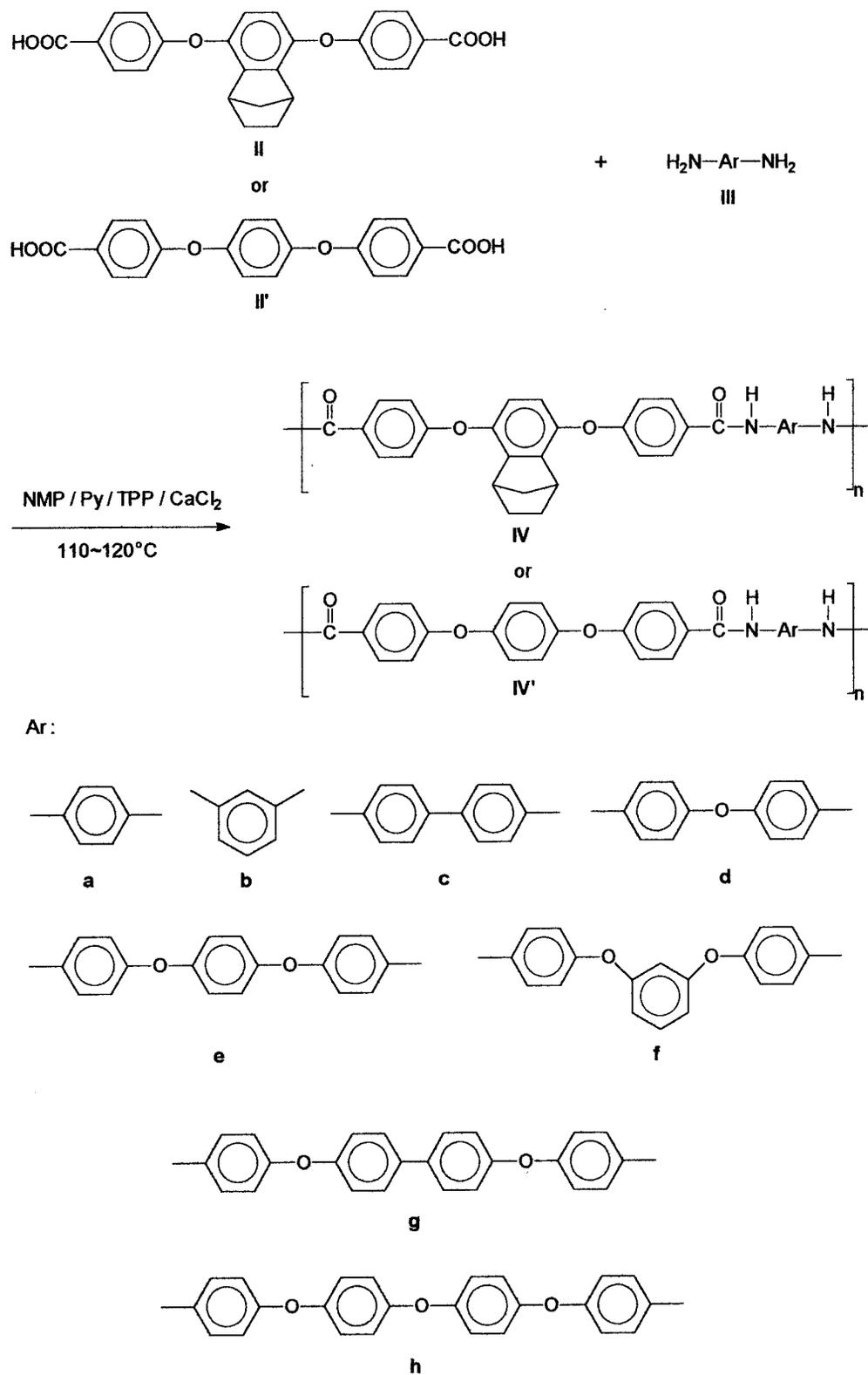
### Monomer Synthesis

The two-step route outlined in Scheme 1 shows the method applied for the synthesis of 3,6-bis(4-carboxyphenoxy)benzonorbornane (**II**). The first step was an aromatic nucleophilic substitution reaction of 4-fluorobenzonitrile with potassium phenolate of 3,6-dihydroxybenzonorbornane, producing the bis(ether nitrile) **I**. In the second step, the dinitrile was readily converted into dicarboxylic acid **II** in high purity and high yield by alkaline hydrolysis. IR, NMR, and elemental analysis confirmed the structures of the intermediate dinitrile and the diacid monomer. Dinitrile compound **I** showed a characteristic sharp absorption

band corresponding to  $\text{—C}\equiv\text{N}$  stretching at 2225  $\text{cm}^{-1}$  that disappeared after hydrolysis. The dicarboxylic acid **II** displayed strong absorption bands of  $\text{—COOH}$  at 2500–3500 ( $\text{—O—H}$  stretching) and 1683  $\text{cm}^{-1}$  ( $\text{C=O}$  stretching). Figure 1 provides  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of dicarboxylic acid **II**. Assignments of each carbon and proton are also given in the figure. These spectra are in good agreement with the proposed structures. In the  $^{13}\text{C}$  NMR spectra, the most relevant change on passing from the dinitrile to the dicarboxylic acid monomer was the disappearance of the resonance peak for the cyano carbon at 120.20 ppm and the appearance of the carbonyl peak at 168.85 ppm. Other important evidence of this change is the shifting of the carbon resonance signals of  $\text{C}^{10}$  adjacent to the cyano or carboxyl group. The  $\text{C}^{10}$  of dinitrile **I** resonated at a higher field than the other aromatic carbons because of the anisotropic shielding by the  $\pi$  electrons of  $\text{—C}\equiv\text{N}$ . After hydrolysis, the resonance peak of  $\text{C}^{10}$  shifted to a lower field, from 105.91 to 126.26 ppm, because of the lack of an anisotropic field.

### Polymer Synthesis

Aromatic polyamides **IV-a** to **IV-h** were prepared by the synthetic route shown in Scheme 2. The phosphorylation polyamidation method first described by Yamazaki and coworkers<sup>24,25</sup> was used as a general approach for all the polymers with TPP-Py-CaCl<sub>2</sub>. For comparison, some polyamides (**IV'**) without the fused pendent norbornane group that have been reported previously<sup>8</sup> are used as a reference. With the reaction conditions listed in Table 1, all the polycondensations proceeded readily in homogeneous solutions, except for polyamide **IV-c**, which precipitated from the reaction medium when the system became viscous. Furthermore, for polymer **IV-b**, gelation usually occurred when the reaction solution became viscous. Therefore, a lower initial reactant concentration was employed to avoid the formation of a swollen gel. In some cases, using a higher initial reaction concentration and adding more solvent to the highly viscous reaction medium before the formation of the swollen gel could yield higher molecular weights of the polymers. The polyamide series **IV-a** to **IV-h**, with inherent viscosities of 0.64–1.70 dL/g, was obtained in almost quantitative yields. Except for **IV-c**, all the other polyamides could be solution-cast into free-standing films. The films of **IV-a** and **IV-b** cracked upon creaking, possibly because of a high level of



Scheme 2. Preparation of the polyamides.

**Table 1.** Reaction Conditions, Inherent Viscosities ( $\eta_{inh}$ ), and Film Quality of the Polyamides

Polymer Code	Amounts of Reagents <sup>a</sup>				$\eta_{inh}$ (dL/g) <sup>b</sup>	Film Quality <sup>c</sup>
	NMP (mL)	Py (mL)	TPP (mL)	CaCl <sub>2</sub> (g)		
<b>IV-a</b>	4 + 1	1	1.5	0.4	1.03 (0.52) <sup>d</sup>	B (—)
<b>IV-b</b>	7.5	2	1.5	0.7	1.70 (0.69)	B (B)
<b>IV-c</b>	5 + 5	1.25	1.5	0.5 + 0.3	0.64	— <sup>e</sup>
<b>IV-d</b>	3 + 6	0.8	1.5	0.3	1.40 (0.76)	F (—)
<b>IV-e</b>	5 + 1.5	1.25	1.5	0.5	1.27 (0.81)	F (—)
<b>IV-f</b>	5	1.25	1.5	0.5	0.86 (0.39)	F (—)
<b>IV-g</b>	5 + 1	1.25	1.5	0.5	1.16	F (—)
<b>IV-h</b>	4	1	1.5	0.4	0.89 (0.52)	F

<sup>a</sup> The polymerization was carried out at 120 °C for 3 h with 1.5 mmol of each diacid and diamine monomer and the amounts of the other reagents as indicated.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30 °C.

<sup>c</sup> Films were cast from slow evaporation of the polymer solutions in DMAc. B - brittle and cracked upon creasing; F - flexible.

<sup>d</sup> Values shown in parentheses are those of the reference polyamides **IV'** reported in a previous article (see ref. 8).

<sup>e</sup> Insoluble in any available organic solvents.

crystallinity or structural rigidity. The other films were flexible and creasable, indicative of high molecular weights. As described previously,<sup>8</sup> most of the reference **IV'** polyamides precipitated from the reaction media and did not dissolve in available organic solvents for film casting. This implies that the incorporation of the pendent norbornane group enhances the solubility and film formability of polyamides.

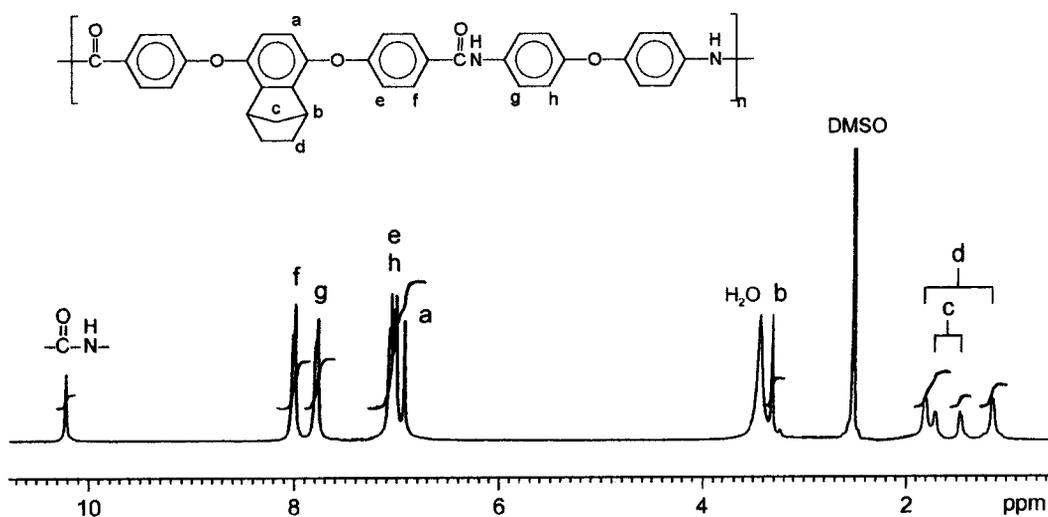
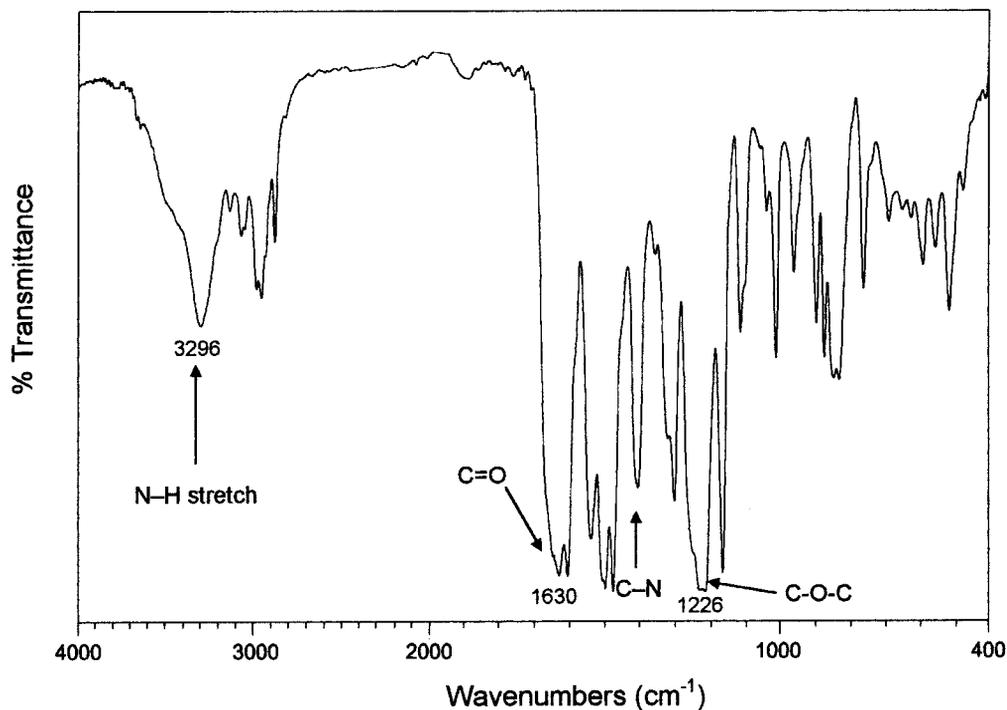
Structural features of these polyamides were confirmed with FTIR and NMR spectroscopy. They exhibited characteristic absorptions of the amide group around 3300 (N—H stretching) and 1620–1660 cm<sup>-1</sup> (C=O stretching). The strong absorption of aryl ether stretching appeared in the region of 1200–1250 cm<sup>-1</sup>. In addition to the characteristic absorption bands of the aromatic units, these polyamides also showed aliphatic C—H stretching absorptions ranging from 2800 to 3000 cm<sup>-1</sup> due to the norbornane moieties. Figure 2 shows a typical set of FTIR and <sup>1</sup>H NMR spectra for polyamide **IV-d**. As can be seen, the spectra are in good agreement with the proposed structure.

### Properties of the Polymers

The solubility behavior of all aramids was qualitatively tested in a number of organic solvents, and the results are summarized in Table 2. All the benzonorbornane-based aramids, except for **IV-a** and **IV-c**, showed excellent solubility in aprotic dipolar solvents, such as NMP, DMAc,

DMF, and DMSO. Some of them even were soluble in less polar *m*-cresol and tetrahydrofuran (THF), especially for those containing the *m*-phenylene units, such as **IV-b** and **IV-f**. The poor solubility of **IV-a** and **IV-c** may be attributed to their semicrystalline nature, as evidence by X-ray diffractograms. The aramids (**IV-d** to **IV-h**) bearing the pendent norbornane group exhibited much better solubility than the corresponding ones (**IV'-d** to **IV'-g**) without the norbornane group and could afford flexible and tough films by solvent casting. Table 3 presents the results of tensile tests of these flexible films. They showed tensile strengths of 95–101 MPa, elongations at break of 13–25%, and initial moduli of 1.97–2.33 GPa. Most of these films necked during tensile tests and showed a moderate extension to break, indicating strong and ductile materials.

The WAXD patterns are illustrated in Figure 3. The results revealed that aramids **IV-a** and **IV-c** had a fair degree of crystallinity, whereas all of the others of the **IV** series showed amorphous patterns. Therefore, the amorphous nature of most aramids was reflected in their excellent solubility, and the crystalline aramids **IV-a** and **IV-c** were less soluble. It also can be seen from Figure 3 that all the **IV'** aramids except **IV'-b** exhibited high levels of crystallinity. From a comparison of the diffraction patterns of aramids **IV-d** to **IV-h** with those of analogous **IV'-d** to **IV'-g**, an obvious effect of the introduction of the norbornane group on the crystallinity of these aramids can be confirmed. Apparently, the introduction of the bulky



**Figure 2.** Typical IR and <sup>1</sup>H NMR spectra of the representative polyamide IV-d in DMSO-d<sub>6</sub>.

pendent norbornane groups decreases the inter-chain interactions between amide groups and increases the free volume, which interferes with the close packing of polymer chains, thereby leading to an enhancement in organosolubility and a decrease in crystallinity.

The thermal properties of the polymers evaluated by DSC, TMA, and TGA are summarized in

Table 4. To avoid the effects of the water absorbed by the samples and the residual solvent in the film samples, we heated the samples, sealed in an aluminum pan, in the DSC sample holder at a heating rate of 20 °C/min up to 400 °C and then quenched them at a programmed cooling rate of -200 °C/min to 40 °C. This quenching procedure led to predominantly amorphous samples in most

**Table 2.** Solubility Behavior of the Polyamides<sup>a</sup>

Polymer Code	Solvent					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
<b>IV-a</b>	-	-	-	-	-	-
<b>IV-b</b>	+	+	+	+	+	+
<b>IV-c</b>	-	-	-	-	-	-
<b>IV-d</b>	+	+	+	+	+	-
<b>IV-e</b>	+	+	+	+	+h	-
<b>IV-f</b>	+	+	+	+	+	+
<b>IV-g</b>	+	+	+	+h	+h	-
<b>IV-h</b>	+	+	+	+	+	+h
<b>IV'-a</b>	-	-	-	-	-	-
<b>IV'-b</b>	+	+	+	+	+	+
<b>IV'-d</b>	-	-	-	-	-	-
<b>IV'-e</b>	-	-	-	-	-	-
<b>IV'-f</b>	-	-	-	-	-	-
<b>IV'-g</b>	-	-	-	-	-	-

<sup>a</sup> + soluble at room temperature; +h soluble on heating at 100 °C; - insoluble even on heating.

of the **IV** series aramids. Reheating produced neat DSC thermograms in a second run from 40 to 400 °C, and within this range, a clear heat capacity jump attributable to a glass transition could be observed in every case with the exception of semicrystalline **IV-a** and **IV-c**. The amorphous benzonorbornane-based polyamides had  $T_g$ 's of 173–212 °C by DSC, following the decreasing order of chain flexibility. The lowest  $T_g$  of 173 °C was observed for polyamide **IV-h**, which was derived from the multiring flexible diamine **III-h**. The  $T_s$  values of these aramids were determined by TMA experiments and were observed in the range 194–231 °C. The  $T_s$  values measured by TMA experiments are slightly higher than the  $T_g$  values observed by DSC. Different thermal histories and the distinctive natures of the testing techniques may cause the difference.

Because of the high degree of crystallinity, most of the unmodified aramids (**IV'**) did not show discernible  $T_g$ 's by DSC. Although polymer **IV'-a** exhibited a crystalline WAXD pattern, well-defined endotherms were not observed on the DSC trace before decomposition, possibly because of high melting temperatures. The incorporation of ether linkages decreased the structural rigidity; therefore, polyamides **IV'-d** to **IV'-g** showed a clear melting endotherm around 371–438 °C. By contrast, none of the benzonorbornane-based analogous polyamides **IV-a** to **IV-f** showed any well-defined melting endotherms on the DSC

traces because of their low crystallinity or amorphous characteristics.

The thermal stabilities of these polyamides were evaluated under both nitrogen and air atmospheres with 10% weight-loss values for comparison. Decomposition temperatures at 10% weight losses for the **IV** series aramids, except for **IV-b**, were recorded in the ranges 475–548 °C in nitrogen and 483–542 °C in air, which are reasonable values if we consider the aliphatic contents of these aramids. In comparison with unmodified **IV'** aramids, these aramids showed less thermal resistance due to the presence of the norbornane side group. Moreover, the aramids (**IV-b** and **IV'-b**) obtained from *m*-phenylenediamine seemed to reveal a relatively lower stability than that of the other analogues. However, to the best of our knowledge, the reason is not known.

## CONCLUSIONS

A novel benzonorbornane-based bis(ether carboxylic acid), 3,6-bis(4-carboxyphenoxy)benzonorbornane (**II**), was synthesized successfully from 3,6-dihydroxybenzonorbornane and *p*-fluorobenzonitrile with nucleophilic aromatic substitution and alkaline hydrolysis. A series of high molecular weight polyamides were prepared from **II** with various aromatic diamines in high yields. Except for those obtained from rigid diamines such as *p*-phenylenediamine and benzidine, the obtained polyamides were noncrystalline, displayed good solubility, and gave flexible and tough films. In comparison with analogous polyamides without the norbornane side group, these polyamides showed apparently decreased crystallinity and enhanced solubility.

**Table 3.** Tensile Properties of Some Polyamide Films<sup>a</sup>

Polymer Code	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
<b>IV-d</b>	101	23	2.33
<b>IV-e</b>	97	21	2.08
<b>IV-f</b>	95	13	2.27
<b>IV-g</b>	100	25	1.97
<b>IV-h</b>	95	18	2.01

<sup>a</sup> The cast films were dried *in-vacu.* at 160 °C for 6 h before the tensile test.

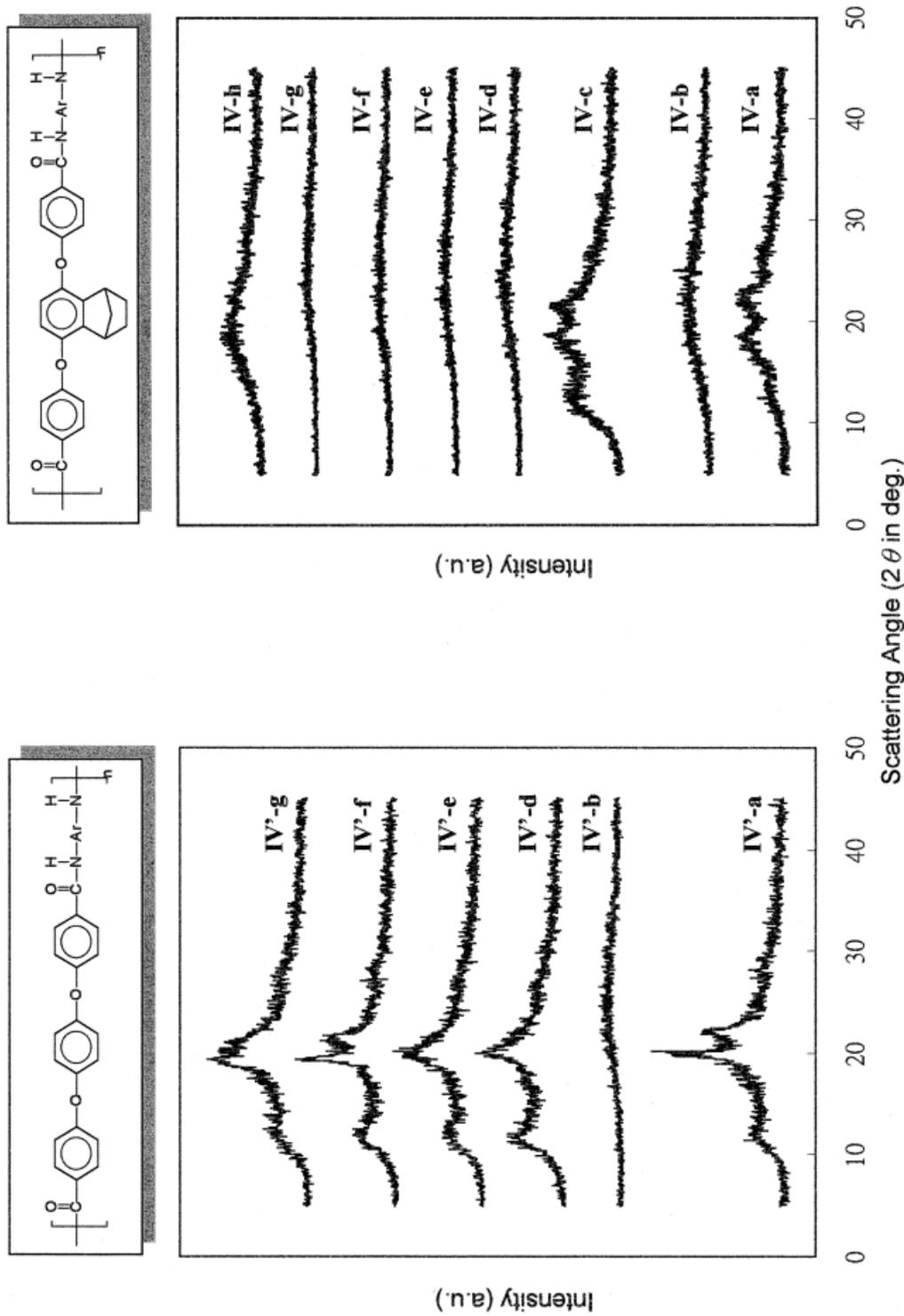


Figure 3. Wide-angle X-ray diffractograms of polyamides IV'-a to IV'-g and IV-a to IV-j.

**Table 4.** Thermal Properties of the Polyamides

Polymer Code	$T_g$ (°C) <sup>a</sup>	$T_s$ (°C) <sup>b</sup>	$T_d$ (°C) <sup>c</sup>		Char Yield (wt %) <sup>d</sup>
			In N <sub>2</sub>	In Air	
<b>IV-a</b>	— <sup>e</sup>	— <sup>g</sup>	475	487	63
<b>IV-b</b>	202	208	434	440	57
<b>IV-c</b>	—	—	511	483	66
<b>IV-d</b>	212	231	504	540	69
<b>IV-e</b>	191	221	516	513	64
<b>IV-f</b>	176	194	511	508	68
<b>IV-g</b>	195	214	548	517	68
<b>IV-h</b>	173	196	511	542	60
<b>IV'-a</b>	—	—	535	520	66
<b>IV'-b</b>	212	—	394	419	42
<b>IV'-d</b>	— (432) <sup>f</sup>	—	531	549	66
<b>IV'-e</b>	— (419)	—	545	539	64
<b>IV'-f</b>	186 (317)	—	551	530	66
<b>IV'-g</b>	— (438)	—	556	492	64

<sup>a</sup> Midpoint temperature of the baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C.

<sup>b</sup> Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min. The film samples were heated at 300 °C for 30 min before the TMA experiments.

<sup>c</sup> Decomposition temperature at which a 10% weight loss was recorded by TGA conducted at a heating rate of 20 °C/min.

<sup>d</sup> Residual weight percentage at 800 °C in nitrogen.

<sup>e</sup> No discernible transition was detectable by DSC.

<sup>f</sup> Values in parentheses are the peak top temperatures of the medium-intensity melting endotherms on the first DSC heating trace.

<sup>g</sup> Not detected.

## REFERENCES AND NOTES

- Bair, T. I.; Morgan, P. W.; Killian, F. L. *Macromolecules* 1997, 10, 1396.
- Panar, M.; Beste, L. F. *Macromolecules* 1997, 10, 1401.
- Morgan, P. W. *CHEMTECH* 1979, 9, 316.
- Thermally Stable Polymers; Cassidy, P. E., Ed.; Marcel Dekker: New York, 1980.
- Aromatic High-Strength Fibers; Yang, H. H., Ed.; Wiley: New York, 1989.
- Kevlar Aramid; Product Bulletin; DuPont.
- Maglio, G.; Palumbo, R.; Vignola, M. C. *Macromol Chem Phys* 1995, 196, 775.
- Hsiao, S.-H.; Chang, C.-F. *Macromol Chem Phys* 1996, 197, 1255.
- Hsiao, S.-H.; Chang, H.-Y. *J Polym Sci Part A: Polym Chem* 1996, 34, 1421.
- Eastmond, G. C.; Paprotny, J.; Irwin, R. S. *Polymer* 1999, 40, 469.
- Hsiao, S.-H.; Yang, C.-P.; Chen, S.-H. *Polymer* 2000, 41, 6537.
- Imai, Y.; Malder, N. N.; Kakimoto, M. *J Polym Sci Polym Chem Ed* 1985, 22, 2189.
- Liou, G.-S.; Maruyama, M.; Kakimoto, M.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1993, 31, 2499.
- Chern, Y.-T.; Wang, W.-L. *J Polym Sci Part A: Polym Chem* 1998, 36, 2185.
- Hsiao, S.-H.; Yang, C.-P.; Yang, C.-Y. *J Polym Sci Part A: Polym Chem* 1997, 35, 1487.
- Liaw, D.-J.; Liaw, B.-Y.; Jeng, M.-Q. *Polymer* 1998, 39, 1597.
- Espeso, J. F.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. *J Polym Sci Part A: Polym Chem* 2000, 38, 1014.
- Espeso, J. F.; Ferrero, E.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. *J Polym Sci Part A: Polym Chem* 2001, 39, 475.
- Hsiao, S.-H.; Chang, C.-F. *J Polym Sci Part A: Polym Chem* 1996, 34, 1433.
- Yang, C.-P.; Hsiao, S.-H.; Yang, H.-W. *Macromol Chem Phys* 1999, 200, 1528.
- Yagci, H.; Mathias, L. J. *Polymer* 1998, 39, 3779.
- Hsiao, S.-H.; Yang, C.-P.; Lin, C.-K. *J Polym Res* 1995, 2, 1.
- Hsiao, S.-H.; Chen, Y.-J. *J Polym Res* 2000, 7, 205.
- Yamazaki, N.; Higashi, F.; Kawabata, J. *J Polym Sci Polym Chem Ed* 1974, 12, 2149.
- Yamazaki, N.; Matsumoto, M.; Higashi, F. *J Polym Sci Polym Chem Ed* 1975, 13, 1373.