

# Synthesis and Properties of Novel Aromatic Polyamides Based on "Multi-Ring" Flexible Dicarboxylic Acids

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## SYNOPSIS

The five benzene rings-containing (hereafter referred to as "five-ring") dicarboxylic acids  $\alpha,\alpha'$ -bis[4-(4-carboxyphenoxy)phenyl]-1,4-diisopropylbenzene (*p*-III) and  $\alpha,\alpha'$ -bis[4-(4-carboxyphenoxy)phenyl]-1,3-diisopropylbenzene (*m*-III) were prepared by the fluoro-displacement of  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene and  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene with *p*-fluorobenzonitrile, and subsequent alkaline hydrolysis of the intermediate dinitriles. A number of high-molecular-weight polyamides based on these two "five-ring" dicarboxylic acids (*p*-III and *m*-III) and various aromatic diamines were directly synthesized in *N*-methyl-2-pyrrolidone (NMP) containing lithium chloride (LiCl) or calcium chloride (CaCl<sub>2</sub>) using triphenyl phosphite and pyridine as condensing agents. These polyamides were obtained with inherent viscosities above 0.51 and up to 0.91 dL/g. The weight-average molecular weight were in the range of 51,000–211,000. Most of these polyamides were amorphous and readily soluble in polar solvents such as NMP, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and afforded tough, flexible, and transparent films by solution-casting. The films had tensile strength of 50–83 MPa, elongation to break of 4–8%, and tensile modulus of 1.3–2.0 GPa. Most polyamides showed distinct glass transitions on the differential scanning calorimetry (DSC) curves ranging from 147 to 177°C. In nitrogen or air, all the polymers showed no significant weight loss up to 490°C, as indicated by thermogravimetric analysis (TG). © 1996 John Wiley & Sons, Inc.

**Keywords:** polyamides • "five-ring" • dicarboxylic acids • fluoro-displacement • triphenyl phosphite

## INTRODUCTION

Aromatic polyamides (aramids), typical of which are poly-*p*-phenyleneterephthalamide (well-known as Kevlar) and poly-*m*-phenyleneisophthalamide (Nomex), possess high thermal stabilities and good mechanical properties, and find use in high strength/high modulus fibers and high-performance engineering resins.<sup>1,2</sup> Drawbacks of these polymers are their insolubility and intractability, which cause difficulties in both synthesis and processing. Therefore, numerous attempts have been tried to improve their processability. The introduction of either flexible

spacer groups or kinks in the polymer backbone and the incorporation of thermally stable bulky pendant groups have been general approaches to make aromatic polyamides more tractable.<sup>3–20</sup> A useful approach to improve the processability without extreme loss of their outstanding properties is to introduce groups such as —O—, —SO<sub>2</sub>—, —C(CH<sub>3</sub>)<sub>2</sub>—, —C(CF<sub>3</sub>)<sub>2</sub>—, —S— into the backbone so as to increase the overall flexibility.<sup>3–11</sup> The present study is concerned with the synthesis and characterization of two new series of polyamides based on two isomeric multiring dicarboxylic acids bearing —O— and —C(CH<sub>3</sub>)<sub>2</sub>— bridges between the phenylene units. The incorporation of these flexibilizing linkages into the aramid backbone is expected to enhance the solubility and melt-moldability of aramids.

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## EXPERIMENTAL

## Materials

Both of the isomeric bisphenols,  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (*p*-I) and  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (*m*-I), were used as received from Mitsui Petrochemical Ind. (Japan). *p*-Fluorobenzonitrile (TCI) was used without purification.

*p*-Phenylenediamine (**IV<sub>a</sub>**, from TCI) was purified by vacuum distillation. *m*-Phenylenediamine (**IV<sub>b</sub>**, from Janssen), 4,4'-oxydianiline (**IV<sub>c</sub>**, from TCI), 3,4'-oxydianiline (**IV<sub>d</sub>**, from Mitsui Petrochemical Ind.), 4,4'-diaminodiphenylmethane (**IV<sub>e</sub>**, from TCI), and 1,4-bis(4-aminophenoxy)benzene (**IV<sub>f</sub>**, from TCI) were obtained in high purity from the manufacturers. According to a literature procedure,<sup>21</sup> the other diamines such as 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IV<sub>g</sub>**), 4,4'-bis(4-aminophenoxy)biphenyl (**IV<sub>h</sub>**), bis[4-(4-aminophenoxy)phenyl]sulfone (**IV<sub>i</sub>**), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IV<sub>j</sub>**) were synthesized by the aromatic nucleophilic substitution reaction of the corresponding precursor bisphenols and *p*-chloronitrobenzene in the presence of potassium carbonate, giving the bis(*p*-nitrophenoxy) compounds, and subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst.

Commercially obtained anhydrous lithium chloride and calcium chloride were dried under vacuum at 150°C for 6 h and at 180°C for 10 h, respectively. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TCI) was purified by distillation under reduced pressure.

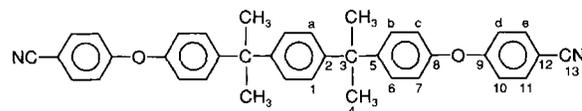
## Monomer Synthesis

**Syntheses of  $\alpha,\alpha'$ -Bis[4-(4-cyanophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-II) and  $\alpha,\alpha'$ -Bis[4-(4-cyanophenoxy)phenyl]-1,3-diisopropylbenzene (*m*-II)**

$\alpha,\alpha'$ -Bis[4-(4-cyanophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-II) was prepared by a nucleophilic fluoro-displacement of *p*-fluorobenzonitrile with  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene, and the synthetic procedure is as follows:  $\alpha,\alpha'$ -bis(4-

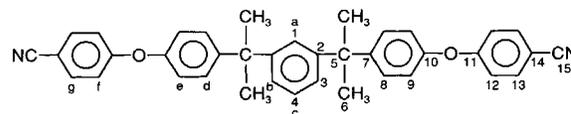
hydroxyphenyl)-1,4-diisopropylbenzene (17.32 g, 0.05 mol) and  $K_2CO_3$  (13.82 g, 0.1 mol) were suspended in a mixture of 100 mL of DMF and 70 mL of toluene, and heated with stirring at reflux temperature using a Dean-Stark trap to remove the water azeotropically. After removal of the residual toluene, *p*-fluorobenzonitrile (12.11 g, 0.1 mol) was added, and heating was continued at 150°C for 6 h. Then, the reaction mixture was cooled and poured into 600 mL of water. The precipitated product was filtered off and dried (98% yield), and recrystallized from methanol to afford colorless needles of  $\alpha,\alpha'$ -bis[4-(4-cyanophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-II), mp 185–186°C. IR (KBr): 2230  $cm^{-1}$  [C≡N str.], 1499–1597  $cm^{-1}$  [arom. C=C str.], 1247  $cm^{-1}$  [C—O—C str.]. <sup>1</sup>H-NMR ( $\delta$  ppm, in  $CDCl_3$ ): 7.58 (d, 4H, H<sub>e</sub>), 7.27 (d, 4H, H<sub>b</sub>), 7.15 (s, 4H, H<sub>a</sub>), 7.00 (d, 4H, H<sub>c</sub>), 6.95 (d, 4H, H<sub>d</sub>), 1.67 (s, 12H, —CH<sub>3</sub>). <sup>13</sup>C-NMR ( $\delta$  ppm, in  $CDCl_3$ ): 161.71 (C<sub>8</sub>), 152.47 (C<sub>9</sub>), 147.65 (C<sub>2</sub>), 147.52 (C<sub>5</sub>), 134.04 (C<sub>11</sub>), 128.54 (C<sub>6</sub>), 126.32 (C<sub>1</sub>), 119.70 (C<sub>7</sub>), 117.82 (C<sub>10</sub>), 105.62 (C<sub>12</sub>) (aromatic carbons), 118.83 (cyano carbon, C<sub>13</sub>), 42.27 (quaternary carbon, C<sub>3</sub>), 30.84 (methyl carbon, C<sub>4</sub>).

ANAL. Calcd for  $C_{38}H_{32}N_2O_2$  (548.68): C, 83.18%; H, 5.88%; N, 5.11%. Found: C, 83.27%; H, 6.00%; N, 5.22%.



The other dinitrile,  $\alpha,\alpha'$ -bis[4-(4-cyanophenoxy)phenyl]-1,3-diisopropylbenzene (*m*-II), was prepared in an analogous procedure; yield 98%, mp 120°C. IR (KBr): 2228  $cm^{-1}$  [C≡N str.], 1497–1597  $cm^{-1}$  [arom. C=C str.], 1253  $cm^{-1}$  [C—O—C str.]. <sup>1</sup>H-NMR ( $\delta$  ppm, in  $CDCl_3$ ): 7.58 (d, 4H, H<sub>e</sub>), 7.23 (d, 4H, H<sub>d</sub>), 7.11 (d, 2H, H<sub>b</sub>), 6.96 (m, 10H, H<sub>a,c,e,f</sub>), 1.66 (s, 12H, —CH<sub>3</sub>). <sup>13</sup>C-NMR ( $\delta$  ppm, in  $CDCl_3$ ): 161.67 (C<sub>10</sub>), 152.27 (C<sub>11</sub>), 149.77 (C<sub>2</sub>), 147.68 (C<sub>7</sub>), 133.97 (C<sub>13</sub>), 128.41 (C<sub>8</sub>), 127.66 (C<sub>4</sub>), 125.48 (C<sub>1</sub>), 124.00 (C<sub>3</sub>), 119.65 (C<sub>9</sub>), 117.60 (C<sub>12</sub>), 105.51 (C<sub>14</sub>) (aromatic carbons), 118.73 (cyano carbon, C<sub>15</sub>), 42.71 (quaternary carbon, C<sub>5</sub>), 30.75 (methyl carbon, C<sub>6</sub>).

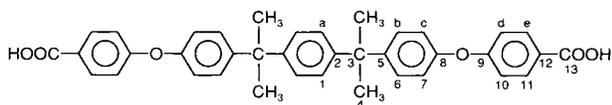
ANAL. Calcd for  $C_{38}H_{32}N_2O_2$  (548.68): C, 83.18%; H, 5.88%; N, 5.11%. Found: C, 83.77%; H, 6.39%; N, 5.07%.



**Syntheses of  $\alpha,\alpha'$ -Bis[4-(4-carboxyphenoxy)phenyl]-1,4-diisopropylbenzene (*p*-III) and  $\alpha,\alpha'$ -Bis[4-(4-carboxyphenoxy)phenyl]-1,3-diisopropylbenzene (*m*-III)**

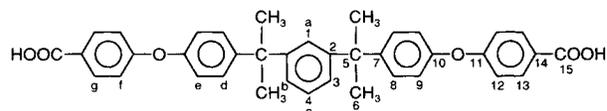
A suspension of dinitrile *p*-II (21.3 g, 38.8 mmol) in 600 mL of a water/ethanol mixture (1 : 1 by vol.) containing 43.5 g (0.776 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after 3 days. Reflux was continued for about 1 day until the evolution of ammonia ceased. The resulting hot, transparent solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and acidified by conc. HCl to pH = 3. The white precipitate formed was collected by filtration and dried in vacuum, to give 27 g of diacid *p*-III (98% yield); mp 294–295°C. IR (KBr): 2556–3444  $\text{cm}^{-1}$  [O—H str.], 1686  $\text{cm}^{-1}$  [C=O str.], 1431–1599  $\text{cm}^{-1}$  [arom. C=C str.], 1243  $\text{cm}^{-1}$  [C—O—C str.].  $^1\text{H-NMR}$  ( $\delta$  ppm, in DMSO- $d_6$ ): 7.94 (d, 4H, H<sub>e</sub>), 7.28 (d, 4H, H<sub>b</sub>), 7.16 (s, 4H, H<sub>a</sub>), 7.00 (d, 8H, H<sub>c,d</sub>), 1.67 (s, 12H, CH<sub>3</sub>).  $^{13}\text{C-NMR}$  ( $\delta$  ppm, in DMSO- $d_6$ ): 160.90 (C<sub>8</sub>), 152.74 (C<sub>9</sub>), 147.13 (C<sub>2</sub>), 146.38 (C<sub>5</sub>), 131.55 (C<sub>11</sub>), 128.20 (C<sub>6</sub>), 126.04 (C<sub>1</sub>), 125.16 (C<sub>12</sub>), 119.22 (C<sub>7</sub>), 116.99 (C<sub>10</sub>) (aromatic carbons), 166.70 (carbonyl carbon, C<sub>13</sub>), 41.66 (quaternary carbon, C<sub>3</sub>), 30.40 (methyl carbon, C<sub>4</sub>).

ANAL. Calcd for C<sub>36</sub>H<sub>34</sub>O<sub>6</sub> (586.68): C, 77.79%; H, 5.84%. Found: C, 77.74%; H, 5.48%.



$\alpha,\alpha'$ -Bis[4-(4-carboxyphenoxy)phenyl]-1,3-diisopropylbenzene (*m*-III) was prepared in a similar method; yield 98%, mp 218°C. IR (KBr): 2554–3418  $\text{cm}^{-1}$  [O—H str.], 1688  $\text{cm}^{-1}$  [C=O str.], 1427–1599  $\text{cm}^{-1}$  [arom. C=C str.], 1251  $\text{cm}^{-1}$  [C—O—C str.].  $^1\text{H-NMR}$  ( $\delta$  ppm, in DMSO- $d_6$ ): 7.93 (d, 4H, H<sub>g</sub>), 7.20 (d, 4H, H<sub>d</sub>), 7.06 (d, 2H, H<sub>b</sub>), 6.96 (m, 10H, H<sub>a,c,e,f</sub>), 1.60 (s, 12H, —CH<sub>3</sub>).  $^{13}\text{C-NMR}$  ( $\delta$  ppm, in DMSO- $d_6$ ): 161.12 (C<sub>10</sub>), 152.68 (C<sub>11</sub>), 149.61 (C<sub>2</sub>), 146.63 (C<sub>7</sub>), 131.60 (C<sub>13</sub>), 128.27 (C<sub>8</sub>), 127.76 (C<sub>4</sub>), 125.14 (C<sub>1</sub>), 125.07 (C<sub>14</sub>), 123.68 (C<sub>3</sub>), 119.33 (C<sub>9</sub>), 116.88 (C<sub>12</sub>) (aromatic carbons), 166.73 (carbonyl carbon, C<sub>15</sub>), 42.26 (quaternary carbon, C<sub>5</sub>), 30.47 (methyl carbon, C<sub>6</sub>).

ANAL. Calcd for C<sub>38</sub>H<sub>34</sub>O<sub>6</sub> (586.68): C, 77.79%; H, 5.84%. Found: C, 77.08%; H, 6.09%.



### Polymer Synthesis

A typical example (*m*-V<sub>c</sub>) of polymerization is as follows: a mixture of 0.7333 g (1.25 mmol) of *m*-III, 0.2503 g (1.25 mmol) of 4,4'-oxydianiline, 0.2 g of calcium chloride, 0.9 mL of triphenyl phosphite, 0.8 mL of pyridine, and 1 mL of NMP was heated with stirring at 120°C for 3 h. The viscous polymer solution obtained was trickled into 200 mL of methanol, giving a stringy precipitate that was washed thoroughly with methanol and hot water, collected by filtration, and dried: Yield 99%. Inherent viscosity of the polymer (*m*-V<sub>c</sub>) in DMAc + 5 wt % LiCl was 0.65 dL/g.

All other polymers were synthesized by a similar procedure.

### Measurements

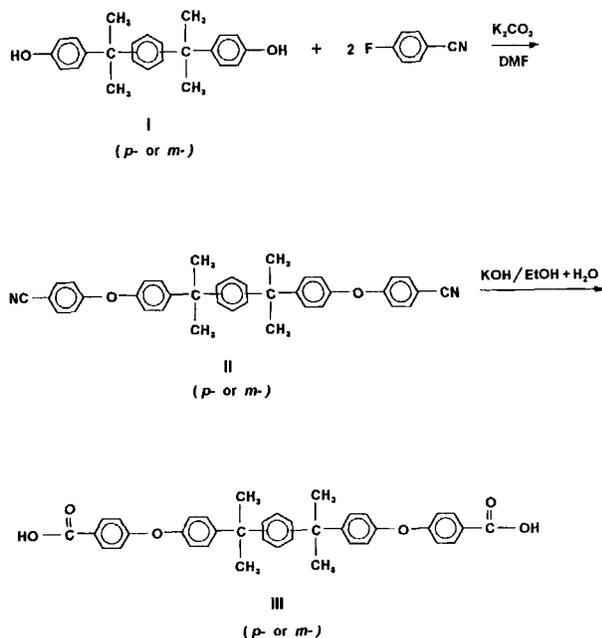
Melting points were measured in capillaries on a MEL-TEMP II apparatus. Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform spectrometer.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured at 30°C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO- $d_6$ ) as an external reference, working at 400 and 100 MHz, respectively. Elemental analyses were run in a Perkin-Elmer model 240 C, H, N analyzer. The inherent viscosities of all polymers were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer thermostated at 30°C. Weight- ( $\bar{M}_w$ ) and number-average molecular weight ( $\bar{M}_n$ ) were determined by gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0.01 mol/L of lithium bromide; pumping rate: 1 mL/min; detector: a refractive index detector; temperature: 40°C). Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko 7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analyzer at the heating rate of 10°C/min in flowing nitrogen (30  $\text{cm}^3/\text{min}$ ). Thermogravimetric data were obtained on a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with  $10 \pm 2$  mg samples heated in flowing nitrogen or air (50  $\text{cm}^3/\text{min}$ ) at a heating rate of 20°C/min. The wide-angle x-ray diffraction measurements were performed at room temperature (ca. 25°C) with film (or powder) spec-

imens of about 0.1 mm thick on a Rigaku Geiger-Flex D-Max III<sub>a</sub> x-ray diffractometer, using Ni-filtered CuK<sub>α</sub> radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of 2θ = 5–40°. An Instron universal tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick) and an average of at least five individual determinations was used.

## RESULTS AND DISCUSSION

### Monomer Synthesis

The dicarboxylic acids comprised of five benzene rings connected by two ether and two isopropylidene linkages, i.e., α,α'-bis[4-(4-carboxyphenoxy)phenyl]-1,4-diisopropylbenzene (*p*-III) and α,α'-bis[4-(4-carboxyphenoxy)phenyl]-1,3-diisopropylbenzene (*m*-III), were prepared by a reported two-step synthetic route<sup>7,11</sup> outlined in Scheme 1. In the first step, α,α'-bis[4-(4-cyanophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-II) and α,α'-bis[4-(4-cyanophenoxy)phenyl]-1,3-diisopropylbenzene (*m*-II) were obtained from the nucleophilic fluoro-displacement of *p*-fluorobenzonitrile with the potassium phenolates of bisphenols *p*-I and *m*-I in DMF.



Scheme 1.

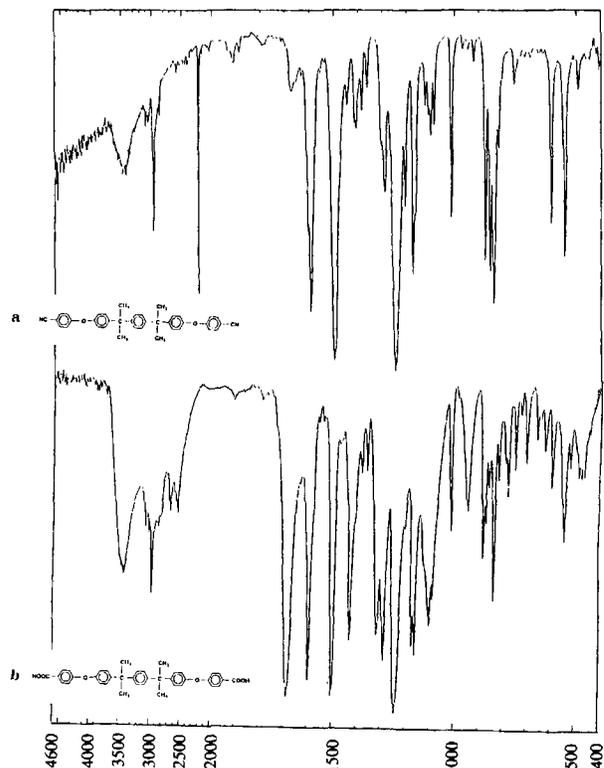
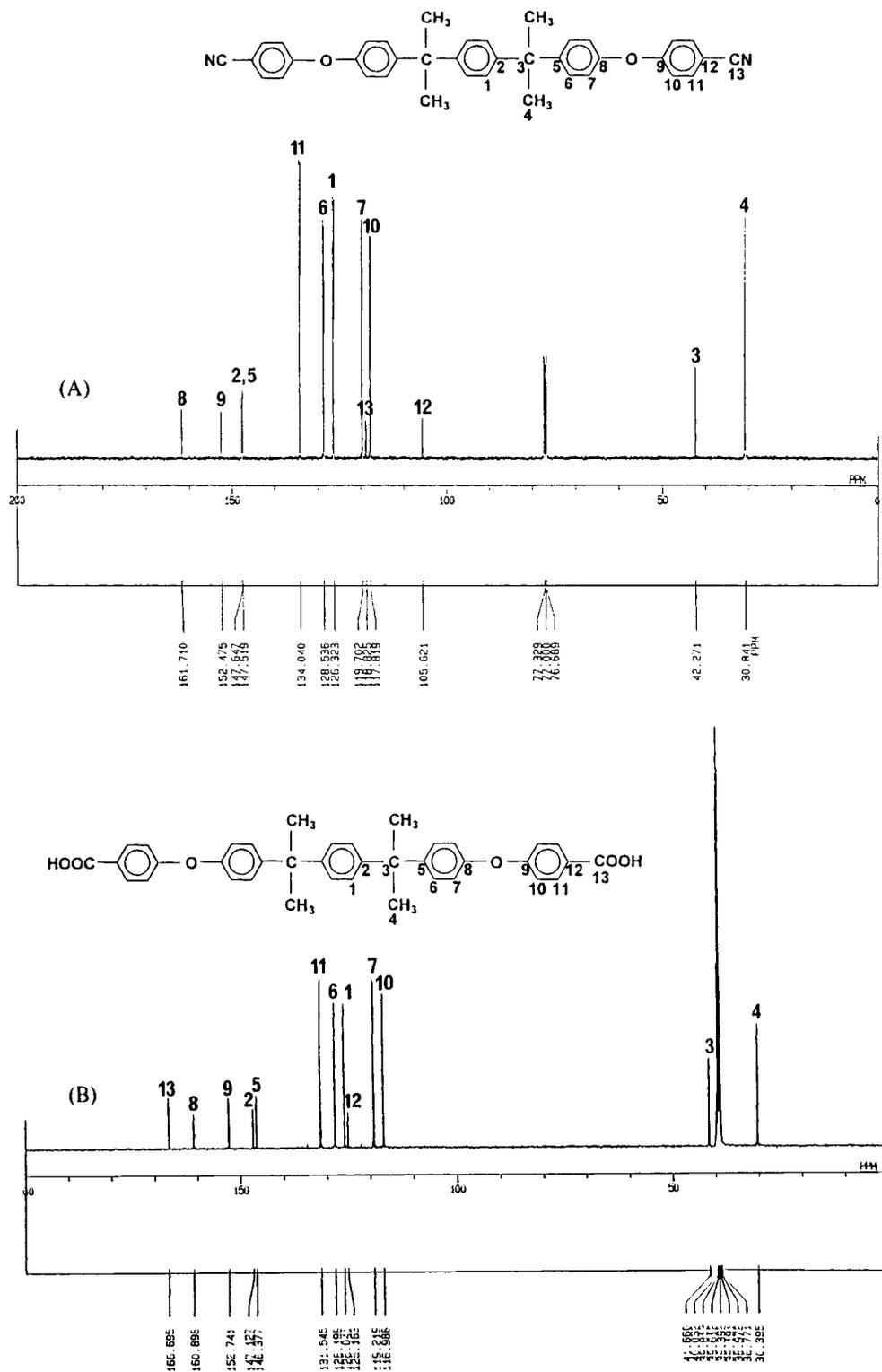


Figure 1. IR spectra of (a) α,α'-bis[4-(4-cyanophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-II) and (b) α,α'-bis[4-(4-carboxyphenoxy)phenyl]-1,4-diisopropylbenzene (*p*-III).

The dinitriles were then readily converted into the corresponding dicarboxylic acids by alkaline hydrolysis. The yield was high (98%), and the purity was high enough for the preparation of high-molecular-weight polymers.

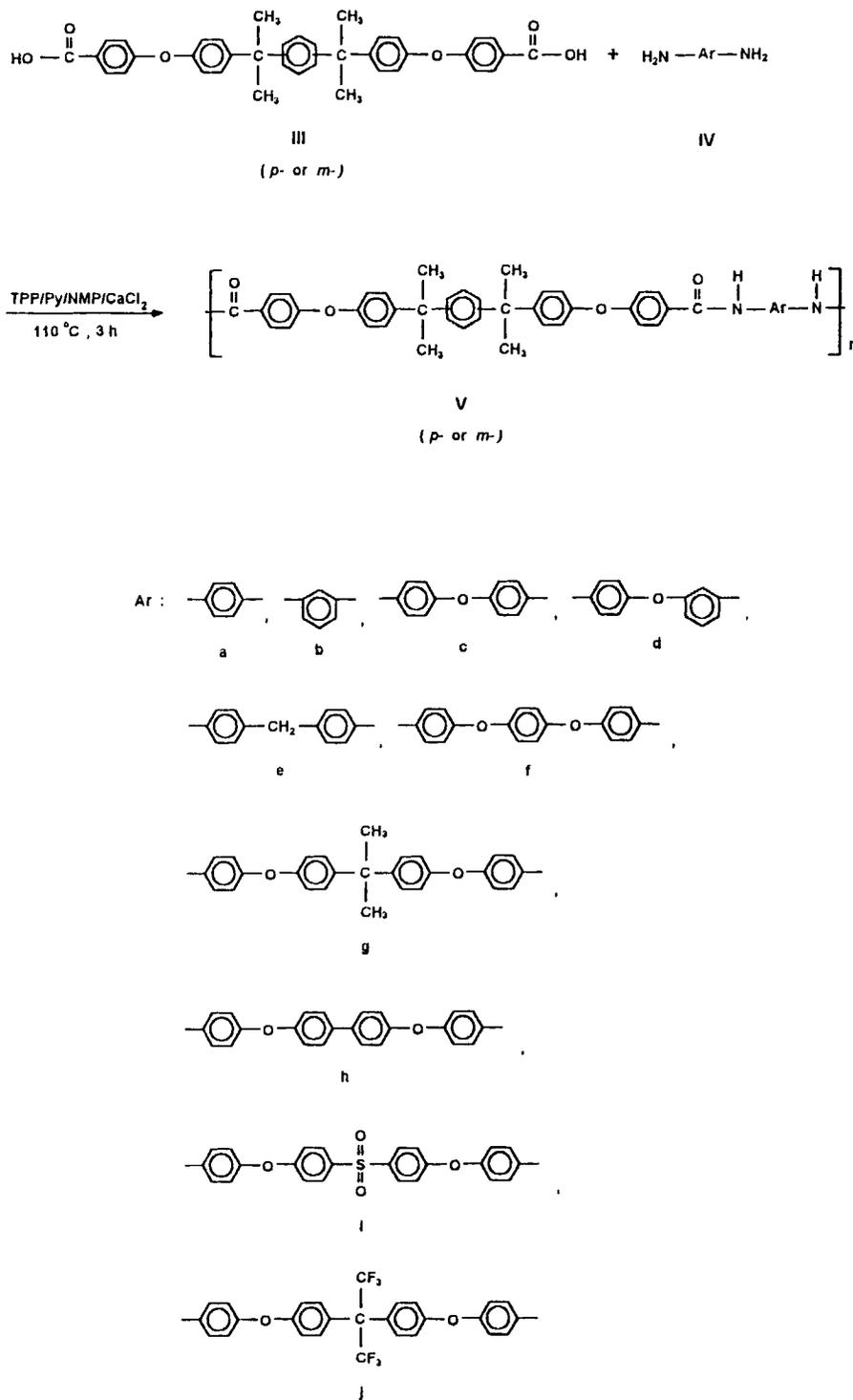
The structures of intermediate dinitriles *p*-II and *m*-II and dicarboxylic acids *p*-III and *m*-III were confirmed by elemental analysis and FTIR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. Obvious changes in the IR and <sup>13</sup>C-NMR spectra could be observed if the nitriles were converted into the carboxylic acids. Figures 1(a) and (b) show the FTIR spectra for dinitrile *p*-II and diacid *p*-III, respectively. After *p*-II was hydrolyzed to *p*-III, a sharp absorption near 2230 cm<sup>-1</sup> peculiar to the C≡N group in *p*-II disappeared, and the carbonyl (C=O) stretching absorption around 1690 cm<sup>-1</sup> and the broad O—H absorption in the region between 2550–3400 cm<sup>-1</sup> appeared in the spectrum of *p*-III. The comparative <sup>13</sup>C-NMR spectra of dinitrile *p*-II and diacid *p*-III are shown in Figure 2, and all carbon atoms give separate and assignable resonances. The most obvious features of the spectra are the shifts of the resonance signals



**Figure 2.**  $^{13}\text{C}$ -NMR spectra of (A)  $\alpha,\alpha'$ -bis[4-(4-cyanophenoxy)phenyl]-1,4-diisopropylbenzene (*p*-II) in  $\text{CDCl}_3$  and (B)  $\alpha,\alpha'$ -bis[4-(4-carboxyphenoxy)phenyl]-1,4-diisopropylbenzene (*p*-III) in  $\text{DMSO}-d_6$ .

for the carbon of  $C\equiv N$  group and its adjacent carbon  $C_{12}$ . The  $C_{12}$  of *p*-II is shielded by the anisotropic field induced by the  $\pi$  electrons of  $C\equiv N$ , and thus  $C_{12}$  has resonance at higher field than the other aromatic carbons. After the cyano group was converted

into carboxyl group, the resonance peak of  $C_{12}$  moved to lower field (from 105.62 to 125.16 ppm) due to the lack of anisotropic shielding, the original signal at 118.83 ppm assigned to  $C\equiv N$  carbon disappeared, and the resonance of carbonyl carbon occurred at



Scheme 2.

the farthest downfield (166.70 ppm). The IR,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR spectra of dinitrile *m*-II and diacid *m*-III are also in good agreement with their proposed structures.

### Polymer Synthesis

Serial polyamides *p*-V<sub>a-j</sub> and *m*-V<sub>a-j</sub> having ether and isopropylidene groups in the polymer backbone were prepared by the direct polycondensation technique,<sup>22</sup> which was carried out under 120°C for 3 h by reacting diacid *p*-III and *m*-III, respectively, with various aromatic diamines in NMP containing dissolved CaCl<sub>2</sub> using triphenyl phosphite and pyridine as condensing agents (Scheme 2). All the reactions proceeded readily in homogeneous solutions and resulted in viscous polymer solutions. The resulting reaction solutions of polyamides *m*-V<sub>a-j</sub> were transparent; however, most of the solutions of *p*-isomeric polymers were semi-transparent probably due to less solubility. Tough, stringy precipitates were produced when the viscous polyamide solutions were trickled into stirring methanol. The results of polycondensation

are given in Table I. All the polymers were obtained in quantitative yields with inherent viscosities of 0.51–0.91 dL/g. The GPC curves indicated that  $\bar{M}_w$  values of the polyamides were in the range of 51,000–211,000, relative to standard polystyrene, and the polydispersity index  $\bar{M}_w/\bar{M}_n$  ranged from 1.3 to 1.9. Owing to lack of solubility in the GPC eluent, the molecular weights of polyamides *p*-V<sub>a</sub>, *p*-V<sub>b</sub>, and *m*-V<sub>h</sub> were not determined. The molecular weights of these polyamides are sufficiently high to permit casting flexible and tough films. However, the polyamide *p*-V<sub>a</sub> obtained from diacid *p*-III and *p*-phenylenediamine afforded a brittle film by solvent casting, possibly due to higher crystallinity caused by the rigid and symmetric polymer backbone.

The structure of these polyamides was checked by IR spectroscopy. Figure 3 shows the typical IR spectrum of representative polyamide *m*-V<sub>c</sub>. Some characteristic absorptions appeared in the IR spectra, such as N—H stretching near 3300 cm<sup>-1</sup>, C=O stretching near 1650 cm<sup>-1</sup>, and aromatic ether group stretching near 1250 cm<sup>-1</sup>.

Table I. Preparation of Polyamides<sup>a</sup>

Polymer	$\eta_{inh}^b$ (dL/g)	$\bar{M}_w^c$ $\times 10^{-4}$	$\bar{M}_n^c$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Film Quality <sup>d</sup>
<i>p</i> -V <sub>a</sub>	0.59	—	—	—	Brittle
<i>p</i> -V <sub>b</sub>	0.59	—	—	—	Flexible
<i>p</i> -V <sub>c</sub>	0.77	7.9	4.1	1.9	Flexible
<i>p</i> -V <sub>d</sub>	0.51	5.1	3.3	1.5	Flexible
<i>p</i> -V <sub>e</sub>	0.55	6.7	4.2	1.8	Flexible
<i>p</i> -V <sub>f</sub>	0.60	6.9	4.4	1.6	Flexible
<i>p</i> -V <sub>g</sub>	0.60	7.1	4.1	1.7	Flexible
<i>p</i> -V <sub>h</sub>	0.67	7.4	4.4	1.7	Flexible
<i>p</i> -V <sub>i</sub>	0.63	7.3	4.1	1.6	Flexible
<i>p</i> -V <sub>j</sub>	0.54	6.0	3.8	1.6	Flexible
<i>m</i> -V <sub>a</sub>	0.82	16.3	8.2	1.5	Flexible
<i>m</i> -V <sub>b</sub>	0.61	8.9	6.5	1.5	Flexible
<i>m</i> -V <sub>c</sub>	0.65	9.2	5.5	1.8	Flexible
<i>m</i> -V <sub>d</sub>	0.67	16.3	6.4	1.5	Flexible
<i>m</i> -V <sub>e</sub>	0.63	10.7	5.8	1.3	Flexible
<i>m</i> -V <sub>f</sub>	0.63	12.0	6.1	1.8	Flexible
<i>m</i> -V <sub>g</sub>	0.69	12.2	7.1	1.5	Flexible
<i>m</i> -V <sub>h</sub>	0.79	—	—	—	Flexible
<i>m</i> -V <sub>i</sub>	0.91	21.1	8.4	1.3	Flexible
<i>m</i> -V <sub>j</sub>	0.71	12.6	8.1	1.8	Flexible

<sup>a</sup> Polymerization was carried out with 1.25 mmol of diamines and 1.25 mmol of diacid and about 1.5 mL NMP, 0.8 mL pyridine, 0.9 mL triphenyl phosphite, and 0.2 g calcium chloride at 120°C for 3 h.

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

<sup>c</sup> Determined by GPC, using DMF/0.01 mol % of LiBr as the eluent and polystyrene as the standard.

<sup>d</sup> Films were cast from polymer solutions in DMAc.

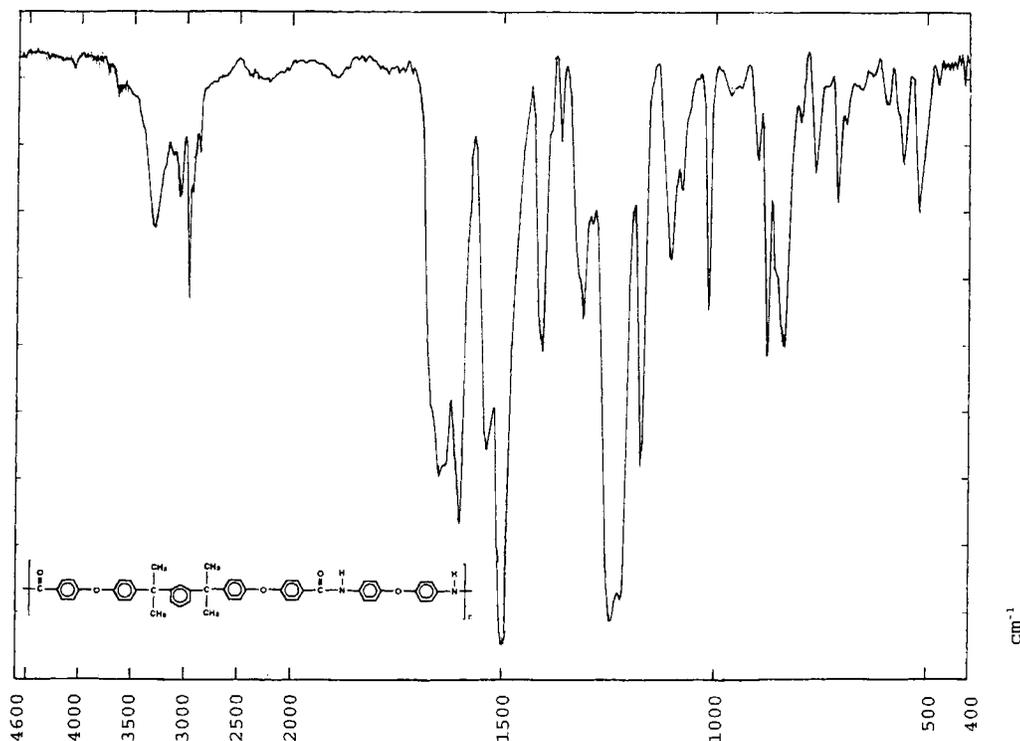


Figure 3. The IR spectrum of polyamide *m-V<sub>c</sub>*.

## Properties of Polymers

### Solubility

The qualitative solubility behavior of all the polyamides is shown in Table II. The solubility is related to the nature of the dicarboxylic acid and the diamine. The *m-III*-derived polyamides show higher solubility than the corresponding *p-III*-derived ones. This is reasonable because *m*-phenylene unit gives increased overall chain flexibility. For *m-V<sub>a-j</sub>* series, *m-V<sub>b-e</sub>* and *m-V<sub>i</sub>* are readily soluble at room temperature in all the six solvents tested; except for *m-V<sub>h</sub>* which is soluble in hot DMF, all other polyamides of this series are soluble in amide-type polar aprotic solvents such as NMP, DMAc, and DMF; and most polymers in this series are also soluble in DMSO and less polar *m*-cresol and THF. For *p-V<sub>a-j</sub>* series, except for the polymers containing rigid structure and high aromaticity like *p-V<sub>a</sub>* and *p-V<sub>b</sub>* revealing less solubility, they have high solubility in NMP, DMAc, and DMF. However, the *p*-series polyamides show less solubility in DMSO, *m*-cresol, and THF. Most of them are soluble in these solvents only on heating. In general, the introduction of flexible ether, isopropylidene and hexafluoroisopropylidene linkages, polar sulfonyl group, or asymmetrical *m*-phenylene unit into the polymer backbone leads to improved solubility.

### Crystallinity and Tensile Properties

The crystallinity of the polymers was examined by wide-angle x-ray diffraction. Polyamide *p-V<sub>a</sub>* revealed one stronger and rough peak reflection between  $2\theta = 15\text{--}25^\circ$ , and it implied that polyamide *p-V<sub>a</sub>* had a higher degree of crystallinity corresponding with its poor solubility and the brittleness of its casting film as previously mentioned. All other polyamides showed amorphous patterns and could afford flexible films by solution-casting from DMAc. The tensile properties of these flexible films are given in Table III. The films had a tensile strength of 50–83 MPa, elongation at break of 4–8%, and initial modulus of 1.3–2.0 GPa. They behave as strong and rigid materials.

### Thermal Properties

Thermal properties of all the polyamides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The values of glass transition temperature ( $T_g$ ), 10% weight loss temperature in nitrogen or air, and char yield at 800°C in nitrogen of all polymers are summarized in Table IV. Rapid cooling from the elevated temperatures (about 350°C) to room temperature in air yields more amorphous samples so that in all cases the  $T_g$ s could be easily measured in the second heat-

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

Polymer	Solvent <sup>b</sup>					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
<i>p</i> -V <sub>a</sub>	+h	+h	—	—	—	—
<i>p</i> -V <sub>b</sub>	+h	+h	s	+h	+h	s
<i>p</i> -V <sub>c</sub>	+	+	+	+h	+h	—
<i>p</i> -V <sub>d</sub>	+	+	+	+	+h	+
<i>p</i> -V <sub>e</sub>	+	+	+	+h	+h	+h
<i>p</i> -V <sub>f</sub>	+	+	+h	+h	+h	—
<i>p</i> -V <sub>g</sub>	+	+	+	+h	+h	+
<i>p</i> -V <sub>h</sub>	+	+	+	+h	+h	+h
<i>p</i> -V <sub>i</sub>	+	+	+	+	+h	+h
<i>p</i> -V <sub>j</sub>	+	+	+	+	+h	+
<i>m</i> -V <sub>a</sub>	+	+	+	+	+h	—
<i>m</i> -V <sub>b</sub>	+	+	+	+	+	+
<i>m</i> -V <sub>c</sub>	+	+	+	+	+	+
<i>m</i> -V <sub>d</sub>	+	+	+	+	+	+
<i>m</i> -V <sub>e</sub>	+	+	+	+	+	+
<i>m</i> -V <sub>f</sub>	+	+	+	+	+	s
<i>m</i> -V <sub>g</sub>	+	+	+	+h	+	+
<i>m</i> -V <sub>h</sub>	+	+	+h	+h	—	—
<i>m</i> -V <sub>i</sub>	+	+	+	+	+	+
<i>m</i> -V <sub>j</sub>	+	+	+	+h	+	+

<sup>a</sup> +: soluble at room temperature; +h: soluble on heating; s: swelling; —: insoluble.

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

**Table III.** Tensile Properties of Polyamide Films

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
<i>p</i> -V <sub>b</sub>	81	6	2.0
<i>p</i> -V <sub>c</sub>	80	8	1.6
<i>p</i> -V <sub>d</sub>	72	5	1.8
<i>p</i> -V <sub>e</sub>	70	6	1.6
<i>p</i> -V <sub>f</sub>	71	7	1.6
<i>p</i> -V <sub>g</sub>	83	7	1.7
<i>p</i> -V <sub>h</sub>	71	7	1.5
<i>p</i> -V <sub>i</sub>	81	6	1.8
<i>p</i> -V <sub>j</sub>	73	7	1.6
<i>m</i> -V <sub>a</sub>	58	4	1.9
<i>m</i> -V <sub>b</sub>	51	4	1.7
<i>m</i> -V <sub>c</sub>	61	6	1.5
<i>m</i> -V <sub>d</sub>	50	5	1.3
<i>m</i> -V <sub>e</sub>	50	6	1.3
<i>m</i> -V <sub>f</sub>	53	5	1.4
<i>m</i> -V <sub>g</sub>	60	6	1.4
<i>m</i> -V <sub>h</sub>	64	5	1.5
<i>m</i> -V <sub>i</sub>	67	7	1.5
<i>m</i> -V <sub>j</sub>	66	6	1.5

ing traces of DSC. The base-line shift on the second DSC heating trace was judged as  $T_g$ . Polyamides *m*-V<sub>a-j</sub> revealed lower  $T_g$ s than the corresponding polyamides *p*-V<sub>a-j</sub> by about 10–30°C due to the presence of more flexible *m*-phenylenediisopropylidene structure. The  $T_g$  values of *p*- and *m*-V<sub>a-j</sub> are in the range of 162–177 and 147–167°C, respectively. The introduction of rigid biphenyl structure and polar sulfonyl group led to increase  $T_g$ , e.g., polyamides V<sub>h</sub> and V<sub>i</sub> exhibited relatively higher  $T_g$ s in both two serial polyamides.

The representative TG diagrams of polyamide *m*-V<sub>i</sub> in air and nitrogen are shown in Figure 4. Polyamide *m*-V<sub>i</sub> did not show significant weight loss up to 490°C in nitrogen, whereas it decomposed rapidly between 500 and 540°C. The rate of weight loss was slowed down above 550°C, and about 49% residual char were left at 800°C in nitrogen. The initial decomposition temperature in air is lower than in nitrogen. In air, the oxidative degradation continued above 600°C, and there was no residue remaining at 800°C. All other polyamides showed a similar thermal behavior. Their TG data are listed in Table IV.

**Table IV.** Thermal Properties of Polyamides

Polymer	$T_g^a$ (°C)	$T_d^b$ (°C)		Residue <sup>c</sup> (wt %)
		In N <sub>2</sub>	In Air	
<i>p</i> -V <sub>a</sub>	163	492	492	57.0
<i>p</i> -V <sub>b</sub>	173	497	489	59.0
<i>p</i> -V <sub>c</sub>	174	516	520	59.4
<i>p</i> -V <sub>d</sub>	168	498	513	52.6
<i>p</i> -V <sub>e</sub>	162	491	506	60.2
<i>p</i> -V <sub>f</sub>	165	519	523	58.3
<i>p</i> -V <sub>g</sub>	163	502	516	52.9
<i>p</i> -V <sub>h</sub>	177	521	530	59.7
<i>p</i> -V <sub>i</sub>	177	506	504	54.0
<i>p</i> -V <sub>j</sub>	169	510	502	54.2
<i>m</i> -V <sub>a</sub>	154	516	516	60.4
<i>m</i> -V <sub>b</sub>	155	501	515	46.7
<i>m</i> -V <sub>c</sub>	155	504	499	59.2
<i>m</i> -V <sub>d</sub>	147	506	517	58.1
<i>m</i> -V <sub>e</sub>	149	504	508	54.2
<i>m</i> -V <sub>f</sub>	147	509	509	54.3
<i>m</i> -V <sub>g</sub>	147	514	520	50.7
<i>m</i> -V <sub>h</sub>	167	525	537	57.4
<i>m</i> -V <sub>i</sub>	167	514	495	49.3
<i>m</i> -V <sub>j</sub>	154	514	517	50.8

<sup>a</sup> From the second DSC heating traces with a heating rate of 10°C/min in nitrogen.

<sup>b</sup> Decomposition temperatures at which 10% weight loss were recorded by TG.

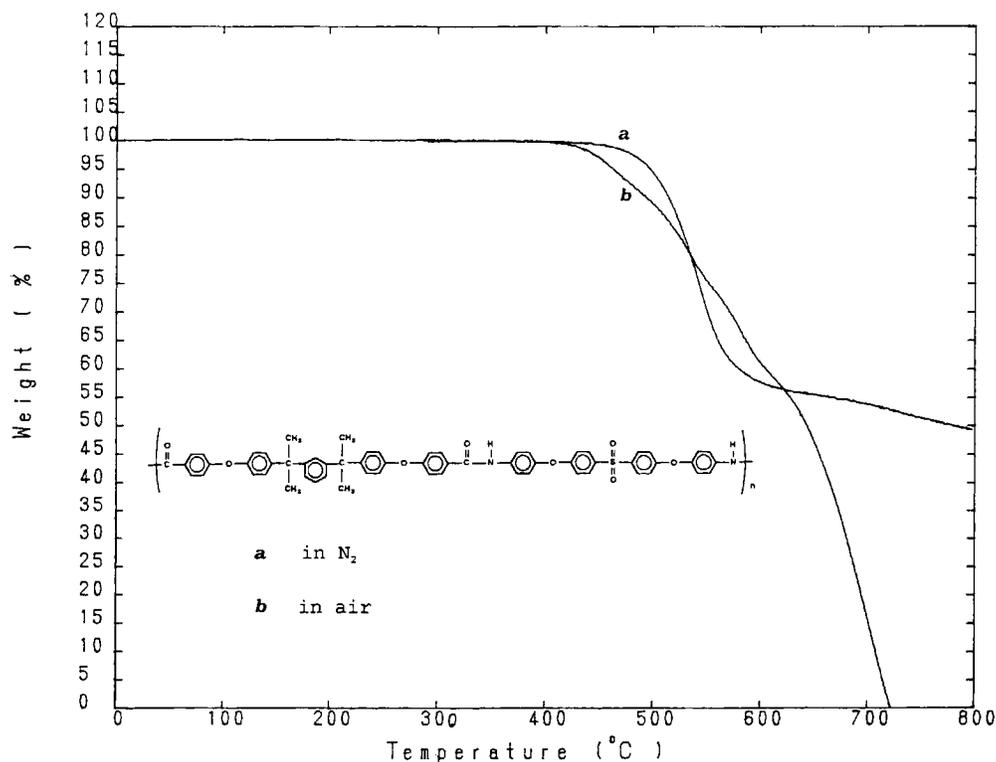
<sup>c</sup> At 800°C in nitrogen.

## CONCLUSION

We have obtained two "five-ring" dicarboxylic acids,  $\alpha,\alpha'$ -bis[4-(4-carboxyphenoxy)phenyl]-1,4-diisopropylbenzene (*p*-III) and  $\alpha,\alpha'$ -bis[4-(4-carboxyphenoxy)phenyl]-1,3-diisopropylbenzene (*m*-III), in high yields and of high purity that were derived via the nucleophilic aromatic displacement of fluoride of *p*-fluorobenzonitrile by the potassium phenolates of  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene and  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene, followed by alkaline hydrolysis of the intermediate dinitriles. The structures of diacids *p*-III and *m*-III were confirmed by FT-IR and <sup>1</sup>H- and <sup>13</sup>C-NMR analysis.

The solution direct polycondensation of diacids *p*-III or *m*-III with aromatic diamines, using triphenyl phosphite and pyridine as the condensing agents, to generate high molecular weight polyamides was successful. The polyamides obtained had inherent viscosities above 0.51 and up to 0.91 dL/g in DMAc-5 wt % LiCl. Polymer structure was confirmed by FTIR spectroscopy.

With the exception of polyamide *p*-V<sub>a</sub> derived from diacid *p*-III and *p*-phenylenediamine, all the polyamides were amorphous in nature and generally soluble in various organic solvents including NMP, DMAc, DMF, DMSO, *m*-cresol, and THF, and af-



**Figure 4.** TG curves of polyamide *m*-V<sub>i</sub> in N<sub>2</sub> and in air.

forded transparent, tough, and flexible films by casting from the DMAc solutions. The glass transition temperatures of these polyamides were recorded in the range of 147–177°C by DSC. TGA confirmed the thermooxidative stability of the polyamides, showing 10% weight loss temperatures higher than 490°C and a char yield of greater than 46.7% at 800°C under nitrogen.

High solubility and not too high  $T_g$ s indicate that the polyamides are readily processable from solution or melt even at high molecular weight. Thus, the improved processability of these polyamides with respect to conventional, stiff-chain aramids, combined with the retention of a good thermal resistance, makes these polymers an attractive thermo-plastic high-performance material.

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