

## Syntheses and Properties of New Aromatic Polyamides Based on 1,4-Bis(4-aminophenoxy)naphthalene and Comparison with Its Related Isomers

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**ABSTRACT:** New polyamides (PAs, **III-A<sub>n-n</sub>**) were synthesized by the direct polycondensation of 1,4-bis(4-aminophenoxy)naphthalene (**I-A**) with various aromatic dicarboxylic acids. These polymers were obtained in quantitative yields with inherent viscosities of 0.84—1.26 dL g<sup>-1</sup>. Except for **III-A<sub>n-n</sub>**, most of the polymers were soluble in aprotic polar solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP), and could be solution cast into transparent, flexible and tough films. The glass transition temperatures of these polyamides ranged from 250—288°C. Thermogravimetric analyses confirmed that these polymers were fairly stable up to 430°C, and 10% weight loss temperatures were recorded in the range of 493-523°C under nitrogen and 483-500°C under air atmosphere. Compared to polyamides with similar structures like 1,5-bis(4-aminophenoxy)naphthalene (series **III-B**) and 1,4-bis(4-aminophenoxy)benzene (series **III-C**) or the isomeric 1,4-bis(4-carboxylphenoxy)naphthalene (series **IV**), the solubility of **III-A<sub>d</sub>** was higher than **III-B<sub>d</sub>** and **III-C<sub>d</sub>** in DMAc and NMP, while other polymers **III-A** showed higher solubility than those of **III-C** in pyridine and *m*-cresol. The crystallinity of series **III-A** was lower than **III-B**, **III-C**, and **IV**. Polymers of **III-A** also exhibited better thermal stability than those of series **IV**.

**KEY WORDS** 1,4-Bis(4-aminophenoxy)naphthalene / Aromatic Polyamide / Direct Polycondensation /

Wholly aromatic polyamides (PAs) belong to the class of high-performance materials which exhibit useful properties such as high thermal stability, chemical resistance, and low flammability, and have excellent mechanical properties.<sup>1,2</sup> Due to high melting and/or softening temperature and/or poor solubility in common organic solvent, difficulties are encountered on casting these polymers into articles.<sup>3,4</sup> A commonly successful approach to increase the processability of these PAs is the introduction of flexible links,<sup>5,6</sup> asymmetric units<sup>7,8</sup> or bulky substituents<sup>9,10</sup> into backbones of the PAs. Ether linkages are the most popularly flexible linkages introduced into the polymer backbones. They can be introduced by inserting either diamine or to dicarboxylic acid monomers, and the former is more economical.<sup>11,12</sup> The naphthalene segment exhibits higher thermal stability than benzene. In recent publications,<sup>13-16</sup> the diamine or diacid monomers containing bis(phenoxy)naphthalene moieties were synthesized and used to prepare organosoluble PAs which retain high thermal stability. 1,4-Bis(phenoxy)naphthalene has a structure similar to 1,4-bis(phenoxy)benzene but with another phenyl ring in the 2,3-position. The introduction of the 1,4-bis(phenoxy)naphthalene moieties into polymer chains is possible by the route shown in Scheme 1.

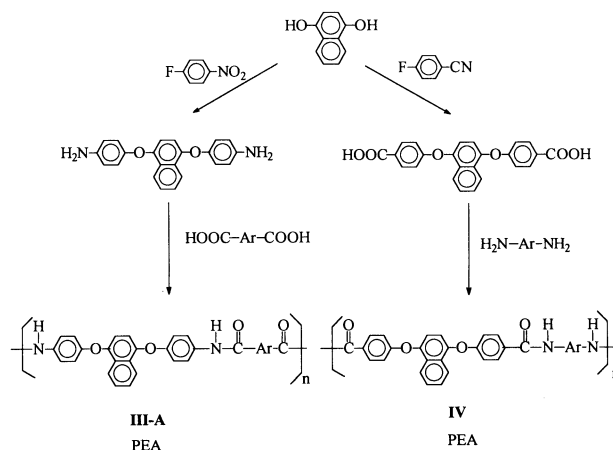
By the displacement reaction of 1,4-dihydroxynaphthalene with *p*-floronitrobenzene or *p*-florobenzonitile, 1,4-bis(4-aminophenoxy)naphthalene or 1,4-bis(4-carboxylphenoxy)naphthalene were synthesized, followed by polymerization with suitable diacids or diamines to the polyamides. Although the PAs derived from the 1,4-bis(4-carboxylphenoxy)naphthalene have been reported,<sup>15</sup> the synthesis of 1,4-bis(4-aminophenoxy)naphthalene is more difficult than that of other bis-

(4-aminophenoxy)naphthalenes,<sup>17</sup> so the properties of PAs containing 1,4-bis(4-aminophenoxy)naphthalene are not known. We describe here the polycondensation properties of 1,4-bis(4-aminophenoxy)naphthalene and basic characterizations of its PAs. The physical properties of these new PAs are compared with the PAs containing similar structures.

### EXPERIMENTAL

#### Materials

1,4-Dihydroxynaphthalene (from Tokyo Chemical Industry Co., Ltd.; TCI), *p*-fluoronitrobenzene (from Janssen), 10% palladium on activated carbon (Pd/C) (from Fluka) and 1,4-bis(4-aminophenoxy)benzene (**I-C**, from TCI) were used as received. According to the method in the preceding paper, 1,4-bis(4-aminophenoxy)naphthalene (**I-A**, mp 113—115°C) was synthesized starting from nucleophilic displacement of 1,4-dihydro-



Scheme 1.

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xynaphthalene and *p*-fluoronitrobenzene, followed by catalytic reduction with hydrazine. 1,5-Bis(4-aminophenoxy)naphthalene (**I-B**, mp 170–171°C) was prepared as in the preceding paper.<sup>14</sup> 1,4-Bis(4-carboxylphenoxy)naphthalene (mp 354–355°C) was prepared according to the literature.<sup>15</sup>

Terephthalic acid (**II<sub>a</sub>**, from TCI), isophthalic acid (**II<sub>b</sub>**, from Wako, Osaka), 5-*t*-butylisophthalic acid (**II<sub>c</sub>**, from Wako), 2,6-naphthalenedicarboxylic acid (**II<sub>d</sub>**, from TCI), biphenyldicarboxylic acid (**II<sub>e</sub>**, from TCI), 4,4'-oxydibenzoic acid (**II<sub>f</sub>**, from TCI), 4,4'-sulfonyldibenzoic acid (**II<sub>g</sub>**, from New Japan Chemical Co., Osaka) and 4,4'-hexafluoroisopropylidenedibenzoic acid (**II<sub>h</sub>**, from Chriskev, U.S.A.) were used as received. Reagent-grade calcium chloride and lithium chloride were dried under vacuum at 180°C before use. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

### Polymerization

The polyamides (series **III-A**) were prepared by direct polycondensation using the following general procedure. Taking **III-A<sub>a</sub>** as example, a mixture of 0.320 g (1.0 mmol) of diamine (**I-A**), 0.166 g (1.0 mmol) of terephthalic acid (**II<sub>a</sub>**), 0.2 g of calcium chloride, 0.1 g of lithium chloride, 3.0 mL of NMP, 0.8 mL of pyridine and 0.6 mL of triphenyl phosphite was heated with stirring at 100°C. The polymer solution was too viscous to stir after 1 h and was diluted gradually with an additional 1 mL of NMP to maintain smooth stirring. After dilution, the reaction mixture was heated at 100°C for 2 h. The high viscous polymer solution was trickled into 400 mL of stirred methanol. The stringy precipitated polymer was washed thoroughly with methanol and hot water, collected by filtration and dried at 100°C under vacuum. The yield was quantitative. The inherent viscosity of the polymer, measured at a concentration of 0.5 g dL<sup>-1</sup> in DMAc at 30°C, was 1.26 dL g<sup>-1</sup>.

Other polyamides (**III-A<sub>b-h</sub>**) were synthesized analogously. The synthetic conditions and inherent viscosities of the obtained polymers are summarized in Table I.

A typical example of polycondensation of **III-C** is described as follows. A mixture of 0.268 g (1.0 mmol) of diamine (**I-C**), 0.222 g (1.0 mmol) of 5-*t*-butylisophthalic acid (**II<sub>c</sub>**), 0.2 g of calcium chloride, 0.1 g of lithium chloride, 3.5 mL of NMP, 1.0 mL of pyridine, and 0.8 mL of triphenyl phosphite was heated with stirring at 100°C under nitrogen. The obtained polymer solution was trickled into 500 mL of stirred methanol. The precipitated fibrous polymer was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100°C under vacuum. The yield was 0.47 g (99%). The inherent viscosity of **III-C<sub>c</sub>** in DMAc was 1.15 dL g<sup>-1</sup>, measured at a concentration of 0.5 g dL<sup>-1</sup> at 30°C.

Other PAs of **III-C** (**III-C<sub>a-h</sub>**) were prepared similarly as. PAs **III-B<sub>a-h</sub>**<sup>14</sup> and **IV<sub>a,b,e,f</sub>**<sup>15</sup> were prepared according to the literature.

### Measurements

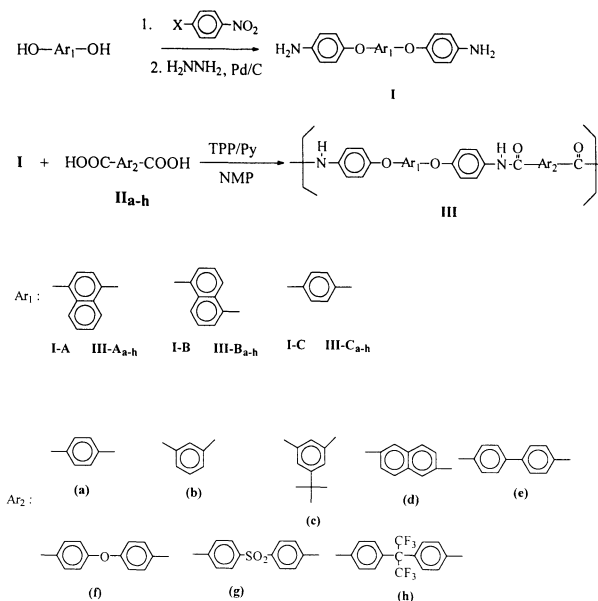
Melting points were measured in capillaries on a Yamato mp apparatus (Model MP-21) without correction. Elemental analyses were run in a Perkin-Elmer

model 2400 C, H, N analyzer. The inherent viscosities of all PAs were measured at 0.5 g dL<sup>-1</sup> concentration with a Cannon-Fenske viscometer at 30°C. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate of 20°C min<sup>-1</sup>. Differential scanning calorimetry (DSC) traces were performed on a Sinku-Riko DSC-7000 differential scanning calorimeter coupled to a TA 7000 thermal analyzer in flowing nitrogen (30 cm<sup>3</sup> min<sup>-1</sup>) at a heating rate of 20°C min<sup>-1</sup>. Wide-angle X-ray diffraction patterns were obtained on a Rigaku Geiger D-Max IIIa X-ray diffractometer, using Ni-filtered Cu-K<sub>α</sub> radiation (40 kV, 15 mA) with film specimens of about 0.1 mm in thickness. The scanning rate was 2° min<sup>-1</sup>. An Instron universal test Model 1130 with a load cell of 5 kg was used to study stress-strain of the samples. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and 0.1 mm thick). The average of at least six individual determinations was used.

## RESULTS AND DISCUSSION

### Polymer Synthesis

Novel polyamides (PAs, **III-A<sub>a-h</sub>**) were synthesized by the direct polycondensation of 1,4-bis(4-aminophenoxy)naphthalene (**I-A**) with various aromatic dicarboxylic acids (**II<sub>a-h</sub>**) in the TPP/Py activation system as shown in Scheme 2. As reported recently,<sup>17</sup> the diamine monomer (**I-A**) was prepared from the displacement reaction between 1,4-dihydroxynaphthalene and *p*-fluoronitrobenzene, followed by catalytic reduction. To obtain polyamides of high molecular weight in the direct polycondensation reaction, the solubility of polymers seems important; though optimum conditions may be different according to the monomer. Generally, under homogenous conditions higher polymer concentrations and sufficient amounts of salts (CaCl<sub>2</sub>, LiCl or both in concert) were favorable for polymerization.



Scheme 2.

Synthesis conditions and inherent viscosities of the polyamides are presented in Table I. The inherent viscosities of polyamides were 0.84 to 1.26 dL g<sup>-1</sup>. Different results were obtained under different reaction conditions for the reactions of I-A with terephthalic acid. Polymers were obtained with lower degree of polymerization either without addition of salt or adding in excess amount. When the suitable amounts of salts were added, the promotion effect of CaCl<sub>2</sub> was similar to LiCl for PAs like III-A<sub>a(1,2)</sub>, while a combination of both salts

gave the best results. Large amounts of solvent and salts were needed to prevent precipitation from reaction solution and kept the direct polycondensation to proceed smoothly for PAs derived from rigid diacid moieties (such as: II<sub>a</sub>, II<sub>d</sub>, II<sub>e</sub>). To the polymers (III<sub>b,c,g,h</sub>) containing flexible diacid moieties, solvent and salts could be reduced to less than those of III<sub>a,d,e</sub>.

The results of elemental analyses of all the PAs are listed in Table II, carbon values were lower than calculated values for the proposed structures in all cases. This is attributed to the hygroscopic nature of amide groups of these PAs. The intake of water was 2.04–3.75%, as calculated from the weight change of the vacuum-dried polymer samples after exposure to air at room temperature. When the values were corrected by eliminating water absorbed, the values were in good agreement with those calculated.

Table I. Reaction conditions on preparation of polyamides<sup>a</sup>

Polymer	Amount of reagents <sup>b</sup>				Polymer	
	NMP	CaCl <sub>2</sub>	LiCl	Py	$\eta_{inh}^c$	Remark <sup>e</sup>
	mL	g	g	mL	dL g <sup>-1</sup>	
III-A <sub>a(3)</sub>	3+1	0.2	0.1	0.8	1.26 <sup>d</sup>	S
III-A <sub>b</sub>	2.5	0.2	—	0.5	0.84	S
III-A <sub>c</sub>	2.5	0.2	—	0.5	0.84	S
III-A <sub>d</sub>	3	0.3	—	0.8	0.85	S
III-A <sub>e</sub>	4	0.3	0.1	1.0	0.93 <sup>d</sup>	S
III-A <sub>f</sub>	2.5	0.2	—	0.6	1.06	S
III-A <sub>g</sub>	2.5	0.25	—	0.6	0.97	S
III-A <sub>h</sub>	2.5+1	0.25	—	0.6	1.03	S
III-A <sub>a(1)</sub>	2.5	0.3	—	0.8	1.15 <sup>d</sup>	S
III-A <sub>a(2)</sub>	2.5	—	0.3	0.8	1.14 <sup>d</sup>	S
III-A <sub>a(4)</sub>	4.0	0.3	0.3	1.0	0.73 <sup>d</sup>	S
III-A <sub>a(5)</sub>	3.5	—	—	0.8	0.32 <sup>d</sup>	P

<sup>a</sup> In each polymerization, 1.0 mmol monomer and 0.6 mL triphenyl phosphite were used. Reaction temperature = 100°C; reaction time = 3 h. <sup>b</sup> Py, pyridine; NMP, *N*-methyl-2-pyrrolidone. <sup>c</sup> Measured at a polymer concentration of 0.5 g dL<sup>-1</sup> in DMAc at 30°C. <sup>d</sup> Measured at a polymer concentration of 0.5 g dL<sup>-1</sup> in DMAc + 0.5 wt% LiCl at 30°C. <sup>e</sup> Appearance of polymerization mixture: S, solution throughout the reaction; P, precipitation during reaction.

### Properties of Polymers

The qualitative solubility (Table III) of PAs was examined in various solvents at room temperature with a concentration of 1% (w/v). All PAs of III-A, except III-A<sub>a,e</sub>, were readily soluble in polar solvents like *N,N*-dimethylacetamide (DMAc) and NMP. Polymers III-A<sub>a</sub> and III-A<sub>e</sub> showed the least solubility due to the presence of the rigid *para* phenylene and 4,4'-biphenyl units. When compared with related polymers, III-A<sub>a,e</sub> showed partial solubility in NMP but other polymers such as III-B<sub>a,e</sub> and III-C<sub>a,e</sub> could not dissolve in organic solvents. For PAs with 2,6-naphthalene units in diacid moieties, III-A<sub>d</sub> was soluble in NMP and DMAc while III-B<sub>d</sub> and III-C<sub>d</sub> were insoluble. From these results, the incorporation of diamine moieties with 1,4-bis(phenoxy)naphthalene increases solubility in organic solvents

Table II. Elemental analysis of polyamides

Polymer	Formula (Molecular weight)	Elemental analysis <sup>a</sup> /%			Moisture intake <sup>b</sup> /%	
		C	H	N		
III-A <sub>a</sub>	(C <sub>30</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> (472.50) <sub>n</sub>	Calcd	76.26	4.26	5.93	3.57
		Found	73.30	4.44	5.66	
		Corrected	76.09	4.28	5.87	
III-A <sub>b</sub>	(C <sub>30</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> (472.50) <sub>n</sub>	Calcd	76.26	4.26	5.93	3.75
		Found	73.50	4.48	5.75	
		Corrected	76.36	4.31	5.97	
III-A <sub>c</sub>	(C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> (528.61) <sub>n</sub>	Calcd	70.58	3.95	4.75	3.01
		Found	68.07	3.92	4.47	
		Corrected	70.21	4.03	4.59	
III-A <sub>d</sub>	(C <sub>34</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> (522.56) <sub>n</sub>	Calcd	78.16	4.21	5.36	3.71
		Found	75.26	4.23	5.27	
		Corrected	78.05	4.07	5.46	
III-A <sub>e</sub>	(C <sub>36</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> (548.60) <sub>n</sub>	Calcd	78.83	4.38	5.11	3.18
		Found	76.35	4.60	4.50	
		Corrected	78.85	4.46	4.61	
III-A <sub>f</sub>	(C <sub>36</sub> H <sub>24</sub> N <sub>2</sub> O <sub>5</sub> ) <sub>n</sub> (564.64) <sub>n</sub>	Calcd	76.59	4.26	4.96	3.48
		Found	73.89	4.52	4.66	
		Corrected	76.46	4.34	4.82	
III-A <sub>g</sub>	(C <sub>36</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> S) <sub>n</sub> (612.66) <sub>n</sub>	Calcd	70.58	3.92	4.57	2.78
		Found	67.92	4.26	4.23	
		Corrected	70.01	4.14	4.36	
III-A <sub>h</sub>	(C <sub>39</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> F <sub>6</sub> ) <sub>n</sub> (690.62) <sub>n</sub>	Calcd	67.05	3.46	4.01	2.04
		Found	65.75	3.35	3.72	
		Corrected	67.07	3.28	3.79	

<sup>a</sup> For C and N: corrected value = found value × (100% + moisture intake %). For H: corrected value = found value × (100% - moisture intake %). <sup>b</sup> Moisture intake (%) = (W - W<sub>0</sub>)/W<sub>0</sub> × 100%; W = weight of polymer sample after standing at room temperature for 3 days; W<sub>0</sub> = weight of polymer sample after being dried in vacuum at 100°C for 12 h.

Table III. Solubility of polymers<sup>a</sup>

Polymer <sup>c</sup>	Solvent <sup>b</sup>						
	DMAc	NMP	DMF	DMAc+5%LiCl	DMSO	Py	<i>m</i> -Cresol
III-A <sub>a</sub>	+ -	+ -	-	+	-	-	-
III-A <sub>b</sub>	+	+	+	+	+	+	+ -
III-A <sub>c</sub>	+	+	+	+	+	+	+
III-A <sub>d</sub>	+	+	+ -	+	-	-	-
III-A <sub>e</sub>	-	+ -	-	+	-	-	-
III-A <sub>f</sub>	+	+	+	+	+	+ -	+
III-A <sub>g</sub>	+	+	+	+	+	+	+
III-A <sub>h</sub>	+	+	+	+	+	+	+
III-B <sub>a</sub>	-	-	-	+	-	-	-
III-B <sub>b</sub>	+	+	+	+	+	-	+
III-B <sub>c</sub>	-	-	-	+	+	-	-
III-B <sub>d</sub>	-	-	-	+ -	-	-	-
III-B <sub>e</sub>	-	-	-	+ -	-	-	-
III-C <sub>a</sub>	-	-	-	+	-	-	-
III-C <sub>b</sub>	+	+	+ -	+	+ -	-	-
III-C <sub>c</sub>	+	+	+	+	+ -	+ -	+ -
III-C <sub>d</sub>	-	-	-	+	-	-	-
III-C <sub>e</sub>	-	-	-	+	-	-	-
III-C <sub>f</sub>	+ -	+	-	+	-	-	-
IV <sub>a</sub>	-	-	-	+	-	-	-
IV <sub>b</sub>	+	+	+	+	+	+	+
IV <sub>c</sub>	-	-	-	+ -	-	-	-
IV <sub>f</sub>	+ -	+	+ -	+	+ -	+ -	+

<sup>a</sup> Solubility: (+) Soluble at room temperature, (+ -) partially soluble or swelling and (-) insoluble. <sup>b</sup> DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; Py, pyridine. <sup>c</sup> Data of III-B and IV were obtained from ref 14 and 15.

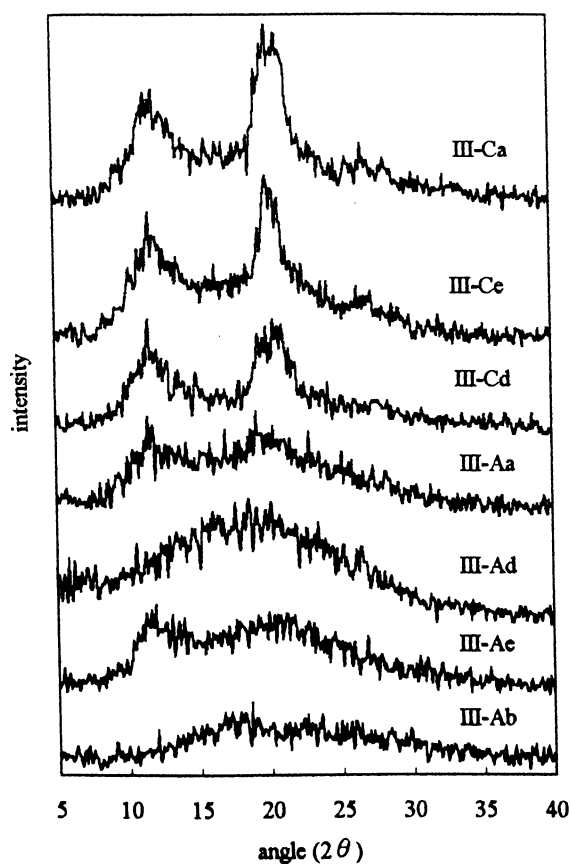


Figure 1. Wide-angle X-ray diffractograms of polymers.

more than those from 1,5-bis(phenoxy)naphthalene and 1,4-bis(phenoxy)benzene. When compared with isomeric IV, taking III-A<sub>f</sub> and IV<sub>f</sub> as examples, the former showed better solubility than the latter in the amide type

solvents. This implies that the introduction of the 1,4-bis(phenoxy)naphthalene into the diamine moiety is better than the alternative introduction into diacid moiety for the solubility improvement.

The crystallinity of polymers was evaluated by X-ray diffraction measurement at scattering angles  $2\theta$  from  $5^\circ$ – $40^\circ$ , as shown in Figure 1. Polyamides III-A<sub>a,e</sub> showed semicrystalline characteristic and exhibited weak reflection peak around  $10^\circ$ – $15^\circ$ . This might be caused by the *para*-linkage of polymer chain and presence of rigid biphenyl unit. The patterns of other PAs (III-A) were interpreted due to amorphous nature. Among III-C, III-C<sub>a,d,e</sub> showed crystalline characteristic and stronger reflection peaks. Polymers III-B<sub>a,e</sub> and IV<sub>a,e</sub> also showed crystalline characteristic similar to III-C<sub>a,e</sub>. From these results, the lower crystallinity of series III-A is confirmed.

Table IV summarizes the tensile properties of the polymers. Most polymers afforded transparent, tough and flexible films by being cast from DMAc solutions. The numbers of PAs, which could be cast into tensile films of III-A, were more than others, revealing that the incorporation of 1,4-bis(4-aminophenoxy)naphthalene unit into the polymer chains for processability improvement is better than other related units. The polyamide films had tensile strength of 67–88 MPa, elongation at a break of 7–10% and initial moduli of 1.7–2.4 GPa. Film III-A<sub>d</sub> was toughest and possessed the highest tensile strength and initial modulus.

The thermal stability and glass transition temperatures ( $T_g$ s) of polyamides were evaluated by TGA and DSC, respectively. 10% decomposition temperatures ( $T_d$ ) in air or in nitrogen atmosphere and char yields at  $800^\circ\text{C}$  in nitrogen are summarized in Table V.  $T_g$ s of the polyamides were recorded at 493–523 $^\circ\text{C}$  in nitrogen and

Table IV. Tensile properties of polymers

Polymer <sup>a</sup>	Strength at break	Elongation at break	Initial modulus
	MPa	%	GPa
III-A <sub>b</sub>	67	9	1.7
III-A <sub>c</sub>	75	8	2.0
III-A <sub>d</sub>	88	10	2.0
III-A <sub>f</sub>	78	7	2.4
III-A <sub>g</sub>	87	9	1.9
III-A <sub>h</sub>	85	8	2.1
III-B <sub>b</sub>	82	9	2.0
III-B <sub>c</sub>	88	10	1.9
III-B <sub>g</sub>	78	9	2.2
III-B <sub>h</sub>	82	9	2.1
III-C <sub>b</sub>	72	7	2.1
III-C <sub>c</sub>	79	9	1.9
III-C <sub>g</sub>	65	10	1.7
III-C <sub>h</sub>	86	7	2.2
IV <sub>b</sub>	84	10	1.9

<sup>a</sup> Films were cast from polymer solutions of DMAc; data of III-B and IV were obtained from ref 14 and 15.

Table V. Thermal properties of polymers

Polymer <sup>c</sup>	TGA			wt% Residue at 800°C in N <sub>2</sub>
	DSC	Decomposition temperature <sup>b</sup> /°C		
		T <sub>g</sub> <sup>a</sup> /°C	In N <sub>2</sub>	
III-A <sub>a</sub>	288	512	496	69.8
III-A <sub>b</sub>	260	494	483	64.0
III-A <sub>c</sub>	265	493	488	56.4
III-A <sub>d</sub>	263	512	500	63.0
III-A <sub>e</sub>	—	523	498	66.7
III-A <sub>f</sub>	250	504	495	65.3
III-A <sub>g</sub>	282	500	487	61.2
III-A <sub>h</sub>	255	505	497	62.3
III-B <sub>a</sub>	350	516	470	65.6
III-B <sub>e</sub>	—	540	489	69.8
III-C <sub>a</sub>	—	507	486	57.9
III-C <sub>b</sub>	267	497	483	61.2
III-C <sub>e</sub>	—	516	500	54.4
IV <sub>a</sub>	—	475	469	64.3
IV <sub>e</sub>	—	504	484	60.3

<sup>a</sup> From second heating DSC traces conducted at a heating of 20°C min<sup>-1</sup> in nitrogen. <sup>b</sup> Temperature at which a 10% weight loss was recorded by TG at a heating rate of 20°C min<sup>-1</sup>. <sup>c</sup> Data of III-B and IV were obtained from ref 14 and 15.

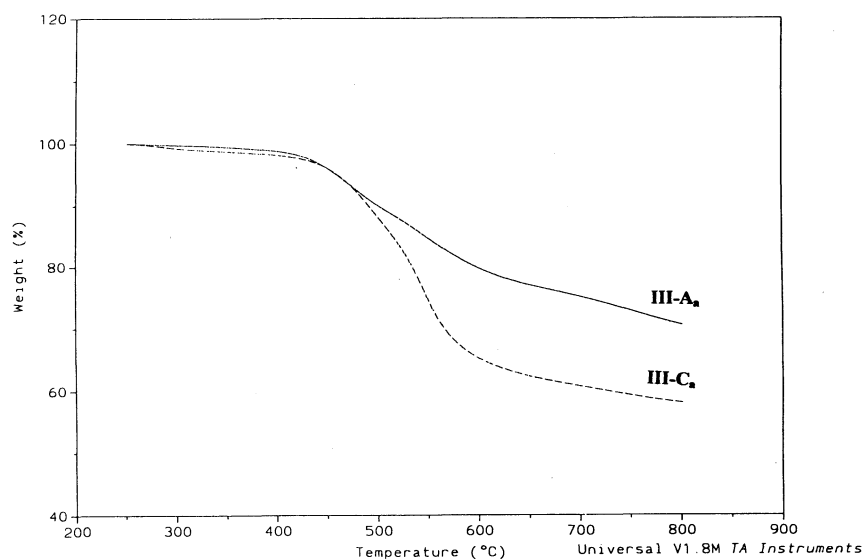


Figure 2. TGA curves of III-A<sub>a</sub> and III-C<sub>a</sub> at a heating rate of 20°C min<sup>-1</sup> under nitrogen.

483—500°C in air. The char yields of the PAs at 800°C in nitrogen were higher than 56% and went up to 69%. Polyamide III-A<sub>a</sub> higher thermal stability than III-A<sub>b</sub> is reasonable, for it is a wholly *para* linkage polymer. PAs III-A<sub>d</sub> and III-A<sub>e</sub> showed higher thermal stability and residues might be caused by higher aromaticity. Comparisons of thermal properties with the related polymers are also shown in Table V and Figure 2. TGA curves of PAs III-A<sub>a</sub> and III-C<sub>a</sub> under nitrogen are shown in Figure 2. Both showed high thermal stability below 430°C, and III-A<sub>a</sub> showed higher residue than III-C<sub>a</sub>. When compared with the related PAs, the following relative order of the thermal stability was observed: III-B > III-A, III-C > IV. 1,4-Bis(phenoxy)naphthalene unit introduced into the diamine moiety seemed to better retain thermal stability than that introduced into dicarboxylic moiety. T<sub>g</sub>s of PAs were recorded at 250—

288°C. However, no discernible T<sub>g</sub> of the polymer III-A<sub>d</sub> was detected from DSC traces in the test range, which might be caused by the rigid biphenyl unit in the polymer chain. III-A<sub>a</sub> derived from the rigid *para* phenylene showed the highest T<sub>g</sub> in series III-A. The lowest polymer III-A<sub>f</sub> T<sub>g</sub> is reasonable because its diacid moiety had a flexible ether linkage.

## CONCLUSIONS

Novel aromatic PAs containing 1,4-bis(phenoxy)naphthalene units were prepared by direct polycondensation of 1,4-bis(4-aminophenoxy)naphthalene and various dicarboxylic acids. Most of the PAs obtained were characterized by good solubility in organic solvents, excellent mechanical properties, and high thermal stability. When compared with relative isomers, these new

polymers exhibited advantages such as lower crystallinity, better solubility and maintained high thermal stability.

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