

# Synthesis and Properties of Aromatic Polyamides Derived from 1,6-Bis(4-aminophenoxy)naphthalene and Aromatic Dicarboxylic Acids

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## SYNOPSIS

A new bis(phenoxy)naphthalene-containing diamine, 1,6-bis(4-aminophenoxy)naphthalene, was synthesized in two steps from the condensation of 1,6-dihydroxynaphthalene with *p*-chloronitrobenzene in the presence of potassium carbonate, giving 1,6-bis(4-nitrophenoxy)naphthalene, followed by hydrazine hydrate/Pd—C reduction. A series of polyamides were synthesized by the direct polycondensation of the diamine with various aromatic dicarboxylic acids in the *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved metal salts such as CaCl<sub>2</sub> or LiBr using triphenyl phosphite and pyridine as condensing agents. The polymers were obtained in quantitative yield with inherent viscosities of 0.78–3.72 dL/g. Most of the polymers were soluble in aprotic solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), NMP, and they could be solution-cast into transparent, flexible and tough films. The casting films had tensile strength of 102–175 MPa, elongation at break of 8–42%, and tensile modulus of 2.4–3.8 GPa. The polymers derived from rigid dicarboxylic acids such as terephthalic acid and 4,4'-biphenyldicarboxylic acid exhibited some crystalline characteristics. The glass transition temperatures of the polyamides were in the range of 238–337°C, and their 10% weight loss temperatures were above 487°C in nitrogen and above 438°C in air. © 1995 John Wiley & Sons, Inc.

**Keywords:** 1,6-bis(4-aminophenoxy)naphthalene • direct polycondensation • polyamides

## INTRODUCTION

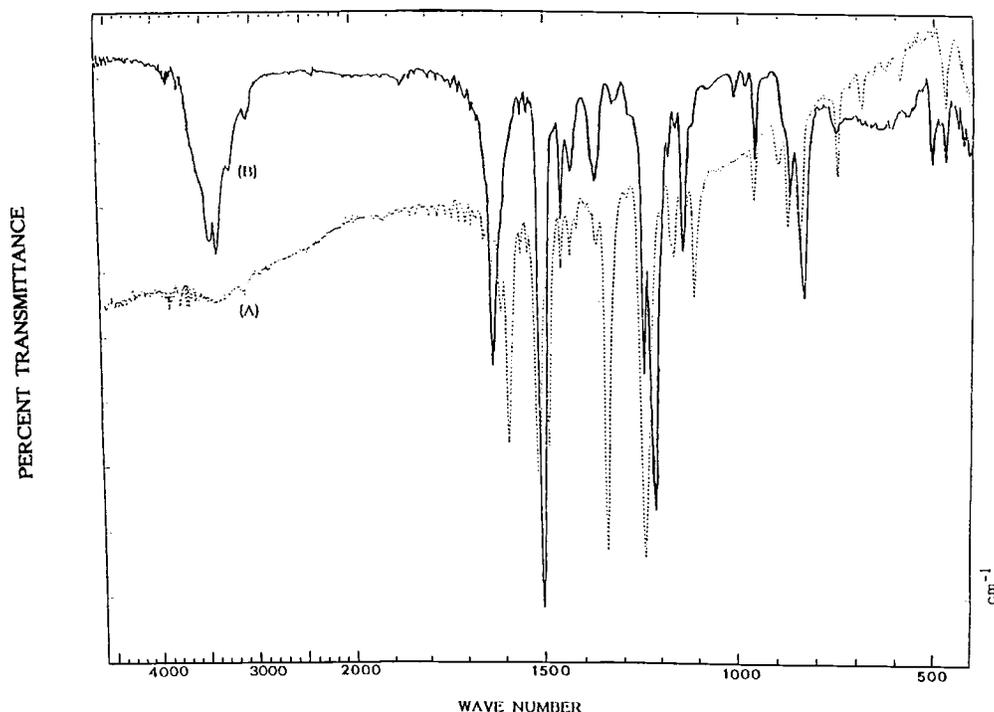
Historically and commercially, polyamides,<sup>1,2</sup> occupy an important place in the world of polymers. Early work dealt with polyamides, with emphasis on the commercial development of synthetic fiber and plastic, known commonly as nylons.

Wholly aromatic polyamides (aramids) belong to the class of high-performance heat-resistant materials.<sup>3,4</sup> For example, Kevlar® (poly-*p*-phenylene-terephthalamide) and Nomex® (poly-*m*-phenylene-isophthalamide), commercially known, are composed of phenylene units linked via an amide group and

exhibit high crystallinity. Thus, they are useful as ultrahigh-strength/high-modulus fibers. These polyamides exhibit a number of excellent properties such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties as fibers. However, the applications of these aramids have generally been hampered by the high crystallinity and limited solubility.

One of the approaches to increase the solubility of aramids without extreme loss of their high thermal stability is the introduction of flexible groups such as aryl ether, aryl sulfide, or sulfone group into the polymer chain.<sup>5,6</sup> Another approach is replacement of symmetrical aromatic rings by the unsymmetrical ones, which would decrease the crystallinity. Either symmetric or asymmetric bulky substitution on the aromatic rings can be employed to

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**Figure 1.** FTIR spectra of (A) 1,6-bis(4-nitrophenoxy)naphthalene and (B) 1,6-bis(4-aminophenoxy)naphthalene.

disrupt crystallinity to obtain amorphous aromatic polyamides.<sup>7-9</sup>

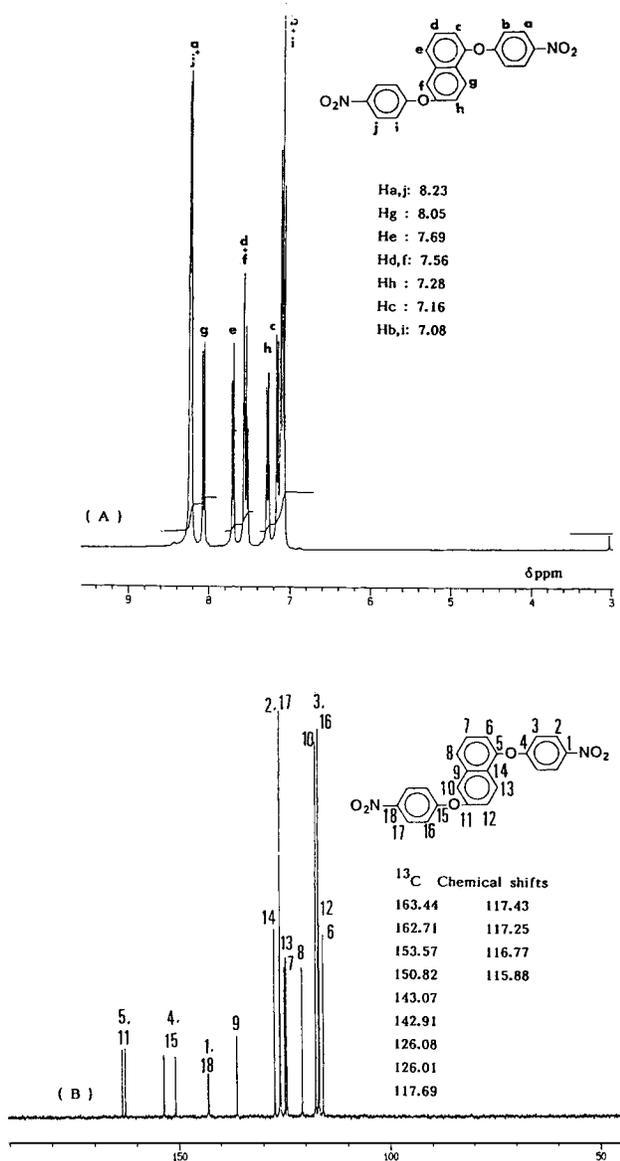
Conventionally, it is more convenient to synthesize the modified aramids via the incorporation of flexible moiety into the diamine monomers followed by the polycondensation reaction with dicarboxylic acids or their derivatives. Popular ether linkage-containing diamines include 4,4'-oxydianiline and 3,4'-oxydianiline; however, there are also many aromatic diamine monomers which contain more ether linkages, such as 1,4-bis(4-aminophenoxy)benzene and 1,3-bis(4-aminophenoxy)benzene, which have been employed in the aramid synthesis.<sup>10-12</sup> Like the benzene ring, the naphthalene ring is also unusually stable. Several studies on the preparation of naphthalene ring-containing polyamides have appeared in the literature.<sup>13-20</sup> Introduction of a naphthalene ring into the polymer main chain is expected to increase the thermal stability in comparison with the benzene ring because of the contribution from the more rigid structure of the former. Thus, polyamides incorporating the bis(phenoxy)naphthalene bonding in the polymer backbone have been proposed as new candidates for increasing the solubility without extreme loss of the high thermal stability. It has been reported in our earlier articles that polyamides containing 2,7-, 1,5-, and 2,3-substituted

bis(phenoxy)naphthalene units could be dissolved in various solvents and maintain their thermal stability,<sup>20-22</sup> which suggests that the bis(phenoxy)naphthalene unit would be a potential segment for the preparation of soluble aromatic polyamides. In continuing this study, the present article describes a successful synthesis of another novel substituted bis(phenoxy)naphthalene diamine, 1,6-bis(4-aminophenoxy)naphthalene, and use for the preparation of polyamides by the direct polycondensation<sup>26-29</sup> of the diamine with various aromatic dicarboxylic acids. The solubility, mechanical properties, x-ray diffraction, and thermal behavior of the polyamides are also discussed.

## EXPERIMENTAL

### Materials

1,6-Dihydroxynaphthalene (from TCI), *p*-chloronitrobenzene (from Hanawa), 10% palladium on activated carbon (from Fluka), and triphenyl phosphite (from Wako) were used as received. Isophthalic acid (**IIIb**, from Wako) was purified by recrystallization from ethanol. The other reagent-grade aromatic dicarboxylic acids, such as terephthalic acid



**Figure 2.** (A) <sup>1</sup>H- and (B) <sup>13</sup>C-NMR spectra of 1,6-bis(4-nitrophenoxy)naphthalene (1,6-BNPON).

(IIIa, from Fluka), 4,4'-biphenyldicarboxylic acid (IIIc, from TCI), 2,6-naphthalenedicarboxylic acid (III d, from TCI), 4,4'-sulfonyldibenzoic acid (III e, from New Japan Chemical Co.), 5-*tert*-butylisophthalic acid (III f, from Amoco), 4,4'-oxydibenzoic acid (III g, from TCI), and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (III h, from Chriskev) were used without purification.

Reagent-grade calcium chloride and lithium chloride were dried under vacuum at 180°C before use. NMP, DMAc, *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under re-

duced pressure over calcium hydride and stored over 4 Å molecular sieves.

## Monomer Synthesis

### 1,6-Bis(4-nitrophenoxy)naphthalene (1,6-BNPON) (I)

A mixture of 30 g (0.187 mol) of 1,6-dihydroxynaphthalene, 60 g (0.438 mol) of *p*-chloronitrobenzene, 31 g (0.224 mol) of anhydrous K<sub>2</sub>CO<sub>3</sub>, and 250 mL of dry DMAc was refluxed at 160°C on an oil bath for 8 h and cooled. The mixture was then poured into 300 mL of an ethanol–water mixture (vol. ratio 1:1). The precipitate was collected by filtration and recrystallized from glacial acetic acid to give yellow crystals; mp 188–189°C. The yield was 72.3 g (96%). The infrared (IR) spectrum (KBr) exhibited absorptions at 1344 and 1578 cm<sup>-1</sup> (NO<sub>2</sub>).

ANAL. Calcd for C<sub>22</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub> (402.29): C, 65.63%; H, 3.48%; N, 6.96%. Found: C, 65.64%; H, 3.57%; N, 6.79%.

### 1,6-Bis(4-Aminophenoxy)naphthalene (1,6-BAPON) (II)

The dinitro compound I 20 g (0.050 mol), 0.2 g of 10% Pd—C, and 100 mL of ethanol were introduced into a 300 mL three-necked flask, into which 15 mL of hydrazine monohydrate were added dropwise over a period of 1 h at 85°C. After the addition was completed, the reaction was allowed to continue refluxing for another 4 h. The mixture was filtered to remove the Pd—C and afford the product. The product was crystallized from ethanol to give white crystals; mp 163–164°C. The yield was 13.1 g (76%). The IR spectra (KBr) exhibited the pair of N—H stretching bands at 3428 and 3380 cm<sup>-1</sup>.

ANAL. Calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub> (342.29): C, 77.19%; H, 5.26%; N, 8.18%. Found: C, 77.08%; H, 5.63%; N, 8.11%.

## Polymerization

### Polyamide IVa from Diamine II and Diacid IIIa

A mixture of 0.428 g (1.25 mmol) of diamine II, 0.208 g (1.25 mmol) of diacid IIIa, 0.40 g of calcium chloride, 5.0 mL of NMP, 0.8 mL of pyridine, and 0.8 mL of triphenyl phosphite was heated with stirring at 100°C for 3 h. The obtained polymer solution was precipitated into 250 mL of stirring methanol giving rise to a stringy product which was washed thoroughly with methanol and hot water, collected by

filtration, and dried under vacuum. The yield was quantitative. The inherent viscosity of the polymer in DMAc was 1.20 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The IR spectra (film) exhibited absorptions at 3300  $\text{cm}^{-1}$  (N—H) and 1650  $\text{cm}^{-1}$  (C=O).

Other polyamides were synthesized by an analogous procedure.

### Measurements

Melting points were measured in capillaries on a MEL-TEMP II mp apparatus without correction.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were operated at 30°C on

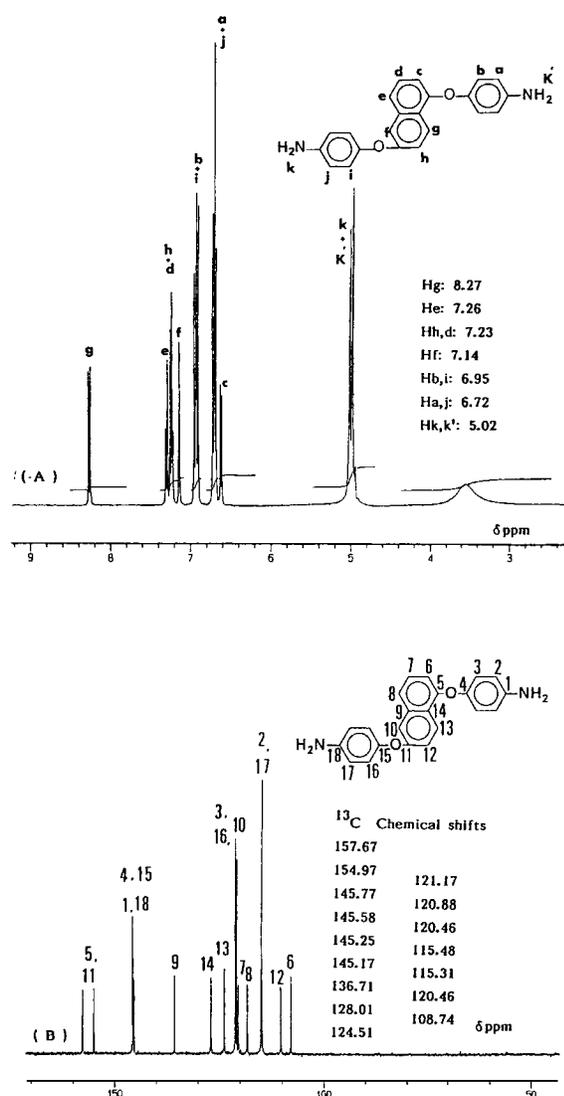


Figure 3. (A)  $^1\text{H}$ - and (B)  $^{13}\text{C}$ -NMR spectra of 1,6-bis(4-aminophenoxy)naphthalene (1,6-BAPON).

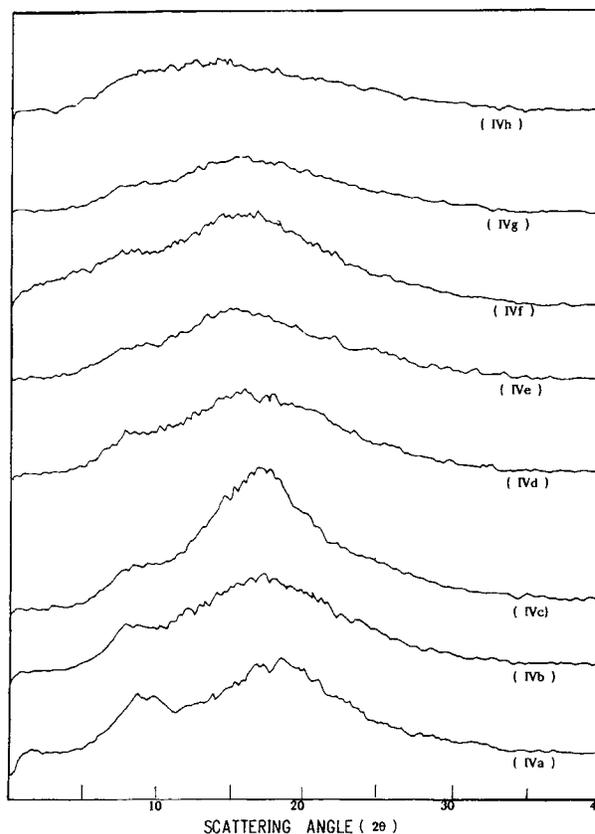


Figure 4. Wide-angle x-ray diffractograms of polyamides.

a Jeol EX-400 NMR spectrometer with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were run in a Perkin-Elmer model 240 C,H,N analyzer. The inherent viscosities of all the polymers were measured at 0.5 g/dL concentration with a Cannon-Fenske viscosimeter 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 LiBr). Thermogravimetric analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku thermal analysis station TAS-100. Experiments were carried out on  $10 \pm 2$  mg samples heated in flowing nitrogen ( $50 \text{ cm}^3/\text{min}$ ) at a heating rate of  $20^\circ\text{C}/\text{min}$ . The differential scanning calorimetry (DSC) traces were performed on a Sinku-Riko 7000 Differential Scanning Calorimeter coupled to a TA 7000 Thermal Analyzer in flowing nitrogen ( $30 \text{ cm}^3/\text{min}$ ) at a heating rate of  $20^\circ\text{C}/\text{min}$ .

**Table I.** Synthesis of Polyamides with Different Polymerization Conditions<sup>a</sup>

| Polymer          | Diacid | NMP (mL) | LiCl (g) | LiBr (g) | CaCl <sub>2</sub> (g) | $\eta_{inh}^b$ (dL/g) | $\bar{M}_n$ ( $\times 10^4$ ) | $\bar{M}_w$ ( $\times 10^4$ ) |
|------------------|--------|----------|----------|----------|-----------------------|-----------------------|-------------------------------|-------------------------------|
| IVa              | IIIa   | 5        | 0        | 0        | 0.40                  | 1.26                  | —                             | —                             |
| IVb              | IIIb   | 3        | 0        | 0        | 0.30                  | 0.79                  | 10.89                         | 24.62                         |
| IVc              | IIIc   | 4 + 2    | 0        | 0        | 0.40                  | 1.77 <sup>c</sup>     | —                             | —                             |
| IVd              | IIIc   | 4        | 0        | 0        | 0.35                  | 1.81                  | 16.74                         | 34.16                         |
| IVe              | IIIe   | 3 + 1    | 0        | 0        | 0.30                  | 0.91                  | 12.31                         | 26.60                         |
| IVf              | IIIc   | 2.5      | 0        | 0        | 0.18                  | 1.82                  | 17.54                         | 35.44                         |
| IVg              | IIIg   | 3        | 0        | 0        | 0.30                  | 0.78                  | 10.14                         | 24.87                         |
| IVh              | IIIh   | 2.5      | 0        | 0        | 0.18                  | 0.96                  | 9.56                          | 22.29                         |
| IVd <sub>1</sub> | IIIc   | 6        | 0        | 0        | 0.35                  | 1.18                  | 5.14                          | 12.50                         |
| IVd <sub>2</sub> | IIIc   | 4        | 0.35     | 0        | 0                     | 0.29                  | 2.68                          | 4.66                          |
| IVd <sub>3</sub> | IIIc   | 4        | 0.20     | 0        | 0.20                  | 1.27                  | 5.30                          | 9.15                          |
| IVd <sub>4</sub> | IIIc   | 4        | 0        | 0.35     | 0                     | 2.41                  | 8.32                          | 39.48                         |
| IVd <sub>5</sub> | IIIc   | 4        | 0        | 0.20     | 0.20                  | 3.63                  | 9.87                          | 49.88                         |
| IVd <sub>6</sub> | IIIc   | 4        | 0.20     | 0.20     | 0                     | 0.31                  | 3.11                          | 4.07                          |
| IVd <sub>7</sub> | IIIc   | 4        | 0        | 0.20     | 0.40                  | 3.72                  | 9.98                          | 53.28                         |
| IVd <sub>8</sub> | IIIc   | 4        | 0        | 0.40     | 0.20                  | 2.93                  | 9.47                          | 47.79                         |

<sup>a</sup> Polymerization was carried out with 1.25 mmol each monomer, 0.8 mL of TPP, 0.8 mL of pyridine at 100°C for 3 h under nitrogen.

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

<sup>c</sup> Measured at a concentration of 0.5 g/dL in NMP at 30°C.

The wide-angle x-ray diffraction patterns were obtained on a Rigaku Geiger D-Max IIIa x-ray diffractometer, using Ni-filtered CuK $\alpha$  radiation (40 kV, 15 mA) with film specimens of about 0.1 mm in thickness. The scanning rate was 2°/min. An Instron universal tester Model 1130 with a load cell of 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 ca. 0.1 mm thick); an average of at least six individual determinations was used.

## RESULTS AND DISCUSSION

### Monomer Synthesis

1,6-Bis(4-aminophenoxy)naphthalene (1,6-BAPON) was prepared in a two-step process. First, 1,6-dihydroxynaphthalene was reacted with *p*-chloronitrobenzene in DMAc in the presence of potassium carbonate at 160°C for about 8 h to give the desired dinitro compound. Reduction of the dinitro derivative in ethanol in the presence of hydrazine and a catalytic amount of palladium on activated carbon at 80°C for about 4 h gave 1,6-BAPON. The structures of the intermediate dinitro compound 1,6-

BNPON and diamine 1,6-BAPON were confirmed by means of elemental analysis and IR and NMR spectroscopy. As shown in the Experimental section, the elemental analysis values of the dinitro and diamine compounds agreed well with the calculated values of their structures. Figure 1 compares the FTIR spectra of the dinitro compound **I** and diamine **II**. 1,6-BNPON showed absorption bands around 1344 and 1578 cm<sup>-1</sup> due to symmetric and asymmetric stretching of —NO<sub>2</sub> group. After reduction, the characteristic absorption of nitro groups disappeared and the amino groups showed the pair of N—H stretching bands around 3430 and 3380 cm<sup>-1</sup>. Figures 2 and 3 show the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of dinitro compound **I** and diamine **II**, respectively, and assignments of protons and carbons. Almost all the expected absorptions are observed.

### Preparation of Polymers

Traditionally, most aramids were synthesized by low temperature solution polycondensation of aromatic diacid chlorides with aromatic diamines in polar aprotic solvents. The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids using triphenyl phosphite (TPP) and pyridine as condensing agents has been known to be another convenient method for the preparation of aromatic

**Table II.** Elemental Analysis of Polyamides Based on 1,6-Bis(4-aminophenoxy)naphthalene

| Polymer    | Formula<br>(Molecular<br>Weight)   |                   | Elemental Analysis |       |       | Amount of Absorbed<br>Water <sup>a</sup><br>(%) |
|------------|--|-------------------|--------------------|-------|-------|---|
|            |  |                   | C (%)              | H (%) | N (%) |   |
| <b>IVa</b> | (C <sub>30</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>                | Calcd             | 76.26              | 4.26  | 5.93  | 2.98  |
|            |  | Found             | 73.98              | 4.42  | 5.54  |   |
|            |  | Corr <sup>b</sup> | 76.23              | 4.28  | 5.70  |   |
| <b>IVb</b> | (C <sub>30</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>                | Calcd             | 76.26              | 4.26  | 5.93  | 3.56  |
|            |  | Found             | 73.54              | 4.37  | 5.57  |   |
|            |  | Corr              | 76.18              | 4.21  | 5.77  |   |
| <b>IVc</b> | (C <sub>36</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>                | Calcd             | 78.81              | 4.41  | 5.11  | 2.88  |
|            |  | Found             | 76.60              | 4.52  | 4.81  |   |
|            |  | Corr              | 78.80              | 4.39  | 4.95  |   |
| <b>IVd</b> | (C <sub>34</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>                | Calcd             | 78.15              | 4.24  | 5.36  | 3.66  |
|            |  | Found             | 75.29              | 4.30  | 4.90  |   |
|            |  | Corr              | 78.80              | 4.41  | 5.08  |   |
| <b>IVe</b> | (C <sub>36</sub> H <sub>24</sub> N <sub>2</sub> SO <sub>6</sub> ) <sub>n</sub>               | Calcd             | 70.58              | 3.95  | 4.57  | 2.96  |
|            |  | Found             | 68.49              | 4.08  | 4.34  |   |
|            |  | Corr              | 70.49              | 3.96  | 4.46  |   |
| <b>IVf</b> | (C <sub>34</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>                | Calcd             | 77.25              | 5.34  | 5.30  | 2.89  |
|            |  | Found             | 75.01              | 5.40  | 5.11  |   |
|            |  | Corr              | 77.17              | 5.24  | 5.26  |   |
| <b>IVg</b> | (C <sub>36</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub>                | Calcd             | 78.81              | 4.41  | 5.11  | 5.38  |
|            |  | Found             | 74.57              | 4.66  | 4.68  |   |
|            |  | Corr              | 78.73              | 4.40  | 4.93  |   |
| <b>IVh</b> | (C <sub>39</sub> H <sub>24</sub> F <sub>6</sub> N <sub>2</sub> O <sub>4</sub> ) <sub>n</sub> | Calcd             | 67.05              | 3.46  | 4.01  | 1.74  |
|            |  | Found             | 65.88              | 3.54  | 3.86  |   |
|            |  | Corr              | 67.01              | 3.47  | 3.92  |   |

<sup>a</sup> Amount of absorbed water (%)

$$= \frac{\text{Sample weight at room temperature} - \text{Sample weight after dried under vacuum at } 100^{\circ}\text{C}}{\text{Sample weight after dried under vacuum at } 100^{\circ}\text{C}} \times 100\%$$

$$\text{<sup>b</sup> Corrected value} = \frac{\text{Found value}}{(1 \pm \text{Amount of absorbed water})}$$

where: + for H, - for C and N.

polyamides<sup>20-29</sup> or poly(amide-imide)s<sup>30-35</sup> on laboratory scale. This method was adopted here to prepare the bis(phenoxy)naphthalene-containing aramids (**IVa-h**) based on 1,6-BAPON (Scheme 1).

Table I summarizes the results of the polymerization. By using the conditions listed in Table I, most of the polymerization reaction could be carried out homogeneously throughout the reaction. In the cases of polyamides **IVc** and **IVe** from 4,4'-biphenyldicarboxylic acid (**IIIc**) and 4,4'-sulfonyldibenzoic acid (**IIIe**), respectively, an additional amount of NMP must be supplemented to maintain a degree of agitation because the polymer solutions were too viscous to stir. Tough, stringy precipitates were produced when the resultant viscous polyamide solutions were precipitated into methanol. All the poly-

mers were obtained in quantitative yields with inherent viscosities of 0.78-1.82 dL/g. The GPC curves indicated that the  $\bar{M}_w$  values of these polyamides were in the range of 220,000-350,000 relative to standard polystyrene. The homogeneity of reaction medium plays an important role in order to acquire high-molecular-weight polymers in the polycondensation of aromatic diamines and dicarboxylic acids by means of the Yamazaki phosphorylation reaction.<sup>23,24</sup> Thus, a proper choice of the solvent system and reactant concentration is very important. The NMP solution containing the dissolved metal salts such as LiCl and CaCl<sub>2</sub> is the commonly used solvent system for this kind of reaction.<sup>23</sup> Here we report some interesting findings concerning the addition of LiBr into the reaction medium of 1,6-BAPON

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

| Polymer    | Solvent <sup>b</sup> |     |      |                  |     |                 |  |
|------------|----------------------|-----|------|------------------|-----|-----------------|--|
|            | DMAcDMF              | NMP | DMSO | <i>m</i> -Cresol | Py  | <i>o</i> -Clpol |  |
| <b>IVa</b> | +                    | -   | +    | + -              | -   | -               |  |
| <b>IVb</b> | +                    | +   | +    | +                | +   | +               |  |
| <b>IVc</b> | + -                  | -   | +    | -                | -   | -               |  |
| <b>IVd</b> | +                    | +   | +    | +                | -   | -               |  |
| <b>IVe</b> | +                    | +   | +    | +                | +   | +               |  |
| <b>IVf</b> | +                    | +   | +    | -                | + - | +               |  |
| <b>IVg</b> | +                    | +   | +    | -                | + - | +               |  |
| <b>IVh</b> | +                    | +   | +    | +                | +   | +               |  |

<sup>a</sup> Solubility: (+) soluble at room temperature, (+-) partially soluble, (-) insoluble.

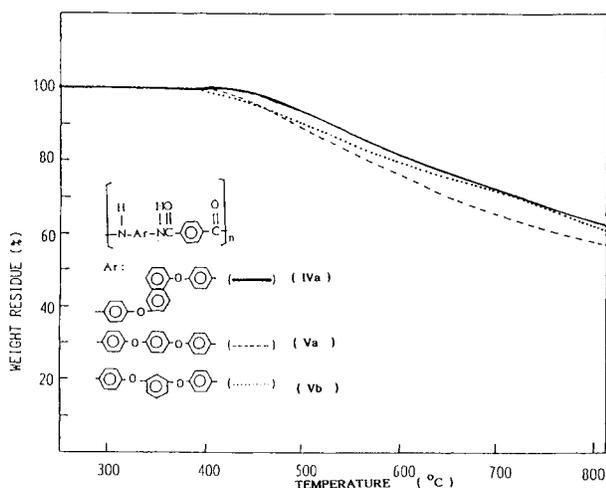
<sup>b</sup> DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethyl sulfoxide; Py, pyridine; *o*-Clpol, *o*-chlorophenol.

All the polymers were soluble in concentrated H<sub>2</sub>SO<sub>4</sub> and DMAc + 5 wt % LiCl; all the polymers were insoluble in common organic solvents such as benzene, acetone, chloroform, etc.

and 2,6-naphthalene dicarboxylic acid (**IIIId**). As shown in the lower half of Table I, polyamide **IVd** was prepared in various reaction media, and the products were coded with **IVd**<sub>1-8</sub>. First, if more solvent was used at the initial period, e.g., 6 mL, (i.e., a lower initial reactant concentration) the  $\eta_{inh}$  of the resulting polyamide (**IVd**<sub>1</sub>) decreased from 1.81 to 1.18 dL/g. When CaCl<sub>2</sub> was replaced with LiCl, the  $\eta_{inh}$  value decreased significantly to 0.29 dL/g (see **IVd**<sub>2</sub>). However, if CaCl<sub>2</sub> was replaced with LiBr, the  $\eta_{inh}$  value increased to 2.41 dL/g (**IVd**<sub>4</sub>). Simultaneous addition of LiBr and CaCl<sub>2</sub> gave markedly increased molecular weight ( $\eta_{inh}$  up to 3.72 dL/g and  $\bar{M}_w$  up to 530,000) such as in the cases of **IVd**<sub>5</sub>, **IVd**<sub>7</sub>, and **IVd**<sub>8</sub>. In contrast, the result was

not satisfactory when adding LiCl and LiBr simultaneously, e.g., when adding 0.2 g of LiCl and 0.2 g of LiBr, the polymer (**IVd**<sub>6</sub>) was obtained with  $\eta_{inh}$  of only 0.31 dL/g. Moderate molecular weight also could be obtained when adding LiCl and CaCl<sub>2</sub> simultaneously (see **IVd**<sub>3</sub>).

The formation of polyamides could be confirmed by IR spectroscopy and elemental analysis. The IR spectra of these polymers showed characteristic absorptions around 3300 cm<sup>-1</sup> peculiar to N—H stretching and 1650 cm<sup>-1</sup> due to carbonyl stretching. The elemental analysis values of these polymers are listed in Table II. In all cases, however, the found values of carbon were lower than the calculated values for the proposed structures. This may be attributed to the hygroscopic characteristics of amide group. The amount of absorbed water for bis(phenoxy)naphthalene-containing polyamides was in the range of 2.89–5.38%. The corrected values were in good agreement with the calculated ones after the found values had been corrected.



**Figure 5.** TGA curves of polyamides **IVa**, **Va**, and **Vb**, with a heating rate of 20°C/min in nitrogen.

### Properties of Polymers

The solubility of polyamides was studied qualitatively, and the results are shown in Table III. Almost all the polyamides were soluble in the amide-type solvents such as DMAc, DMF, and NMP. The polyamides derived from terephthalic acid (**IIIa**) and 4,4-biphenyldicarboxylic acid (**IIIc**) showed less solubility, possibly due to their more rigid backbones. If the aromatic dicarboxylic acids for the polycondensation reaction with diamine 1,6-BAPON were of asymmetrical structures, e.g., *m*-phen-

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

| Polymer    | Yield Strength (MPa) | Tensile Strength (MPa) | Elongation at Break (%) | Initial Modulus (GPa) |
|------------|----------------------|------------------------|-------------------------|-----------------------|
| <b>IVa</b> | —                    | 131                    | 12                      | 2.54                  |
| <b>IVb</b> | 160                  | 140                    | 8                       | 3.12                  |
| <b>IVc</b> | 179                  | 172                    | 43                      | 2.45                  |
| <b>IVd</b> | 164                  | 159                    | 19                      | 3.53                  |
| <b>IVe</b> | 107                  | 102                    | 11                      | 3.04                  |
| <b>IVf</b> | 125                  | 115                    | 12                      | 2.67                  |
| <b>IVg</b> | 119                  | 115                    | 26                      | 2.45                  |
| <b>IVh</b> | 145                  | 120                    | 15                      | 3.81                  |

<sup>a</sup> Films were cast from polymer solutions of DMAc.

ylene (**IIIb**), 5-*tert*-butyl-1,3-phenylene (**IIIc**), or contained the sulfonyl (**IIIe**), ether (**IIIg**), or hexafluoroisopropylidene (**IIIh**) group, the resultant polyamides showed better solubility and were soluble even in less polar solvents such as *m*-cresol, *o*-chlorophenol, and pyridine. All the polymers were practically insoluble in common organic solvents like benzene, acetone, chloroform, etc. The high solubility of these polyamides may be attributed in part to the introduction of bulky, asymmetrical 1,6-bis(phenoxy)naphthalene units along the polymer backbone.

Crystallinity of the polyamide films was examined by the wide-angle x-ray diffraction diagrams. As shown in Figure 4, the polyamides **IVa** and **IVc** exhibited some crystalline characteristics possibly due to a better packing of their polymer chains induced by terephthalamide and 4,4'-biphthalamide units. All

other polyamides showed amorphous diffraction patterns.

Transparent, tough, and flexible films of polymers could be cast from DMAc solutions. Table IV summarizes the tensile properties of all the polymer films. These films had tensile strength of 102–175 MPa, yield strength of 107–178 MPa, elongation at break of 8–43%, and initial modulus of 2.4–3.8 GPa. Those polyamides showed much higher strength and modulus than their analogues from bis(*p*-aminophenoxy)naphthalene with different substituted positions on the naphthalene ring which were reported in the previous publications.<sup>21,22,25</sup>

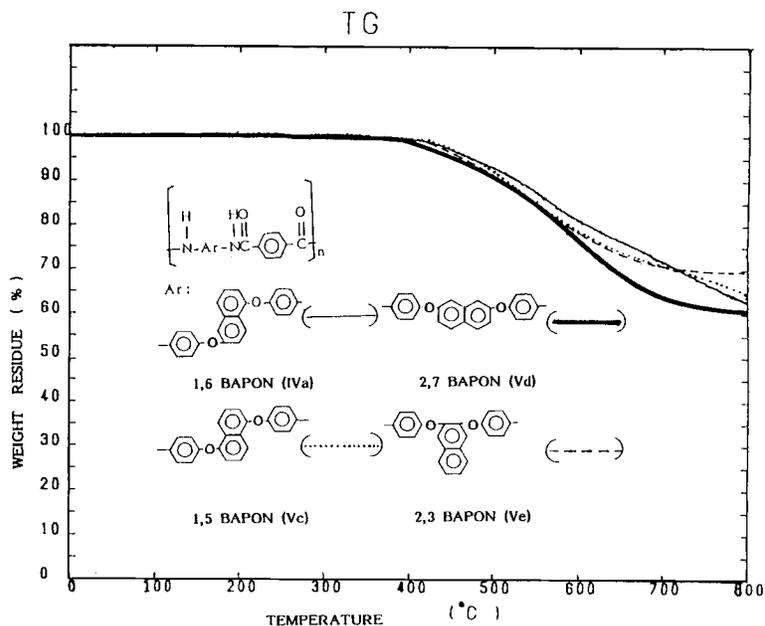
The thermal behavior of polymers was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The  $T_g$  values, the temperatures at 10% weight loss, and char yields at 800°C in nitrogen of all polymers are summarized

**Table V.** Thermal Properties of Polyamides

| Polymer    | TGA |   |                   |   |
|------------|-----|---|-------------------|---|
|            | DSC | Decomposition Temperature <sup>b</sup> (°C) |                   | Wt % Residue at 800°C in N <sub>2</sub> |
|            |     | $T_g^a$ (°C)                                | In N <sub>2</sub> |   |
| <b>IVa</b> | 287 | 529   | 479               | 62.7                                    |
| <b>IVb</b> | 238 | 500   | 470               | 60.6                                    |
| <b>IVc</b> | 252 | 538   | 482               | 65.1                                    |
| <b>IVd</b> | 337 | 529   | 487               | 65.5                                    |
| <b>IVe</b> | 272 | 489   | 484               | 58.2                                    |
| <b>IVf</b> | 277 | 493   | 438               | 58.0                                    |
| <b>IVg</b> | 277 | 500   | 503               | 57.7                                    |
| <b>IVh</b> | 278 | 487   | 477               | 46.5                                    |

<sup>a</sup> From the second heating DSC traces conducted at a heating of 20°C/min in nitrogen.

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



**Figure 6.** TGA curves of polyamides **IVa**, **Vc**, **Vd**, and **Ve**, with a heating rate of 20°C/min in nitrogen.

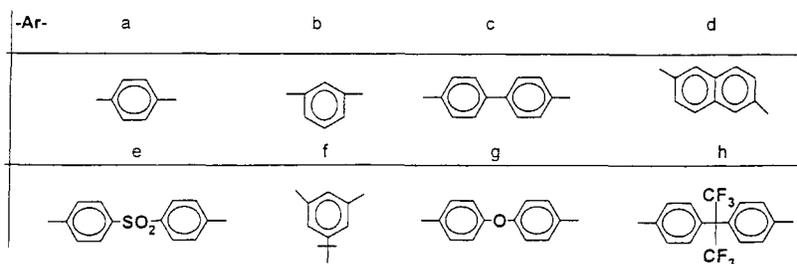
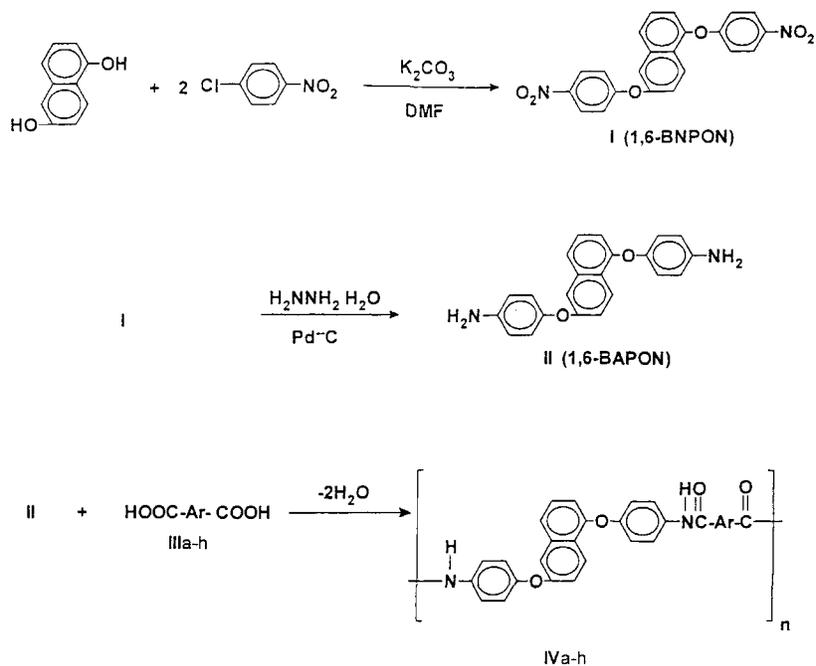
in Table V. The decomposition temperatures (10% weight loss) were recorded in the range of 487–538°C in nitrogen and 438–503°C in air. The amount of carbonized residue of polyamides when heated to 800°C in nitrogen was above 46.5%, and up to 65.5% for polymer **IVd**. DSC measurements were conducted with a heating rate of 20°C/min. Quenching from the elevated temperatures to room temperature in air gave more amorphous samples so that the glass transition temperatures ( $T_g$ s) could be easily measured in the second heating trace of DSC. The glass transition temperatures of polyamides were in the range of 238–337°C. Polymer **IVd** derived from 2,6-naphthalene dicarboxylic acid (**IIIId**) showed the highest  $T_g$ , and the isophthalic acid (**IIIb**)-derived polyamide (**IVb**) had the lowest one. The use of 5-*t*-butylisophthalamide (polymer **IVf**) group in place of isophthalamide (polymer **IVb**) increased the  $T_g$  of the resulting polymer. The phenomenon can be explained by the presence of bulky *tert*-butyl side group hindering the movement of polymer segments.

For comparison, polymers **Va** and **Vb** were prepared from 1,4-bis(*p*-aminophenoxy)benzene and 1,3-bis(*p*-aminophenoxy)benzene with terephthalic acid by means of TPP and pyridine. The comparison of the TGA curves of polyamides **IVa**, **Va** and **Vb** is shown in Figure 5. Naphthalene ring-containing polyamide **IVa** showed slightly higher stability than its homologues containing the phenylene ring only.

Moreover, the thermal stability of polyamide **IVa** was compared with that of its isomeric polyamides **Vc**, **Vd**, and **Ve** which exhibited 1,5-, 2,7-, and 2,3-substituted bis(phenoxy)naphthalene units in their polymer backbones. The syntheses of these three isomeric polymers have been described previously.<sup>21,22,25</sup> The comparative TGA curves shown in Figure 6 indicated that polymer **IVa** had better or comparable stability than polymer **Vc**, **Vd**, or **Ve**.

## CONCLUSIONS

1,6-Bis(4-aminophenoxy)naphthalene (1,6-BAPON) was prepared in high purity and high yield in two steps starting from 1,6-dihydroxynaphthalene and *p*-chloronitrobenzene. High molecular weight aromatic polyamides could be directly synthesized from diamine 1,6-BAPON and various aromatic dicarboxylic acids by means of triphenyl phosphite and pyridine. Almost all the resultant polyamides showed an amorphous nature and good solubility, and they could be solution-cast into transparent, flexible, and tough films. The polymer films had excellent tensile properties and high  $T_g$ s and thermal stability. Thus, the present polyamides are considered to be new, promising, soluble, high-temperature materials.



Scheme 1.

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