

Synthesis and Properties of Aromatic Polyamides Derived from 2,6-Bis(4-aminophenoxy)naphthalene and Various Aromatic Dicarboxylic Acids

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Received 15 August 1996; accepted 19 December 1996

ABSTRACT: 2,6-Bis(4-aminophenoxy)naphthalene (2,6-BAPON) was synthesized in two steps from the condensation of 2,6-dihydroxynaphthalene with *p*-chloronitrobenzene in the presence of potassium carbonate, giving 2,6-bis(4-nitrophenoxy)naphthalene, followed by hydrazine hydrate/Pd-C reduction. A series of new polyamides were synthesized by the direct polycondensation of 2,6-BAPON with various aromatic dicarboxylic acids in the *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved metal salts such as CaCl₂ or LiCl using triphenyl phosphite and pyridine as condensing agents. The polymers were obtained in quantitative yields with inherent viscosities of 0.62–2.50 dL/g. Most of the polymers were soluble in aprotic dipolar solvents such as *N,N*-dimethylacetamide (DMAc) and NMP, and they could be solution cast into transparent, flexible, and tough films. The casting films had yield strengths of 84–105 MPa, tensile strengths of 68–95 MPa, elongations at break of 8–36%, and tensile moduli of 1.4–2.1 GPa. The glass transition temperatures of the polyamides were in the range 155–225°C, and their 10% weight loss temperatures were above 505°C in nitrogen and above 474°C in air. © 1997 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* **35**: 2147–2156, 1997

Keywords: 2,6-bis(4-aminophenoxy)naphthalene; polyamides

INTRODUCTION

Wholly aromatic polyamides (aramids) belong to the class of high-performance heat-resistant materials.^{1,2} For example, poly(*p*-phenyleneterephthalamide) and poly(*m*-phenyleneisophthalamide), commercially known as Kevlar and Nomex aramid fiber, respectively, are composed of phenylene units linked via an amide group and exhibit high crystallinity. Thus, they are useful as ultra-high-strength/high-modulus fibers. These aramids exhibit a number of useful properties

such as high thermal stability, chemical resistance, and low flammability, and they have excellent mechanical properties as fibers. However, the poor solubility and high softening or melting temperature caused by the high crystallinity and high stiffness of the polymer backbones lead to difficult processability of these aramids. The need for engineering plastics circumventing these problems recently increased. A successful approach commonly used to increase the processability of aramids is the introduction of flexible links^{3,4} or asymmetric units^{5–7} into the aramid backbone.

Conventionally, the modified aramids are prepared using diamine monomers incorporating a flexible group. Useful diamines are the well-known 4,4'- and 3,4'-oxydianiline (one ether linkage), and 1,4- and 1,3-bis(4-aminophenoxy)benzene (two ether linkages)^{8–10}; recently, diamine

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Contract grant sponsor: National Science Council of the Republic of China; contract grant number: NSC 85-2216-E-036-008

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monomers containing both ether and naphthalene moieties have been used in our laboratory.^{11–15} In our earlier publications,^{11–15} 1,5-, 1,6-, 1,7-, 2,3-, and 2,7-bis(4-aminophenoxy)naphthalene were synthesized and used to prepare organosoluble aramids while retaining high thermal stability. These efforts suggest that the introduction of a bis(phenoxy)naphthalene segment into the polymer backbone is another successful route to improve the solubility of aramids. In our continuing effort to develop easily processable high-performance polymers, the present work describes a successful synthesis of another substituted bis(aminophenoxy)naphthalene diamine, 2,6-bis(4-aminophenoxy)naphthalene (2,6-BAPON), and its use to prepare aramids by the polycondensation of this diamine with different aromatic dicarboxylic acids. Although 2,6-BAPON has been documented in a Japanese patent,¹⁶ little is known concerning its derived polymers. We describe here the preparation and basic characterization of aramids based on 2,6-BAPON.

EXPERIMENTAL

Materials

2,6-Dihydroxynaphthalene (from Tokyo Chemical Industry Co., Ltd; TCI), *p*-chloronitrobenzene (from Hanawa), 10% palladium on activated carbon (Pd/C) (from Fluka), and triphenyl phosphite (from Wako) were used as received.

Isophthalic acid (**Ib**) (from Wako) was purified by recrystallization from ethanol. The other reagent-grade aromatic dicarboxylic acids, such as terephthalic acid (**Ia**) (from Fluka), 5-*tert*-butylisophthalic acid (**Ic**) (from Amoco), 2,6-naphthalenedicarboxylic acid (**Id**) (from TCI), 4,4'-biphenyldicarboxylic acid (**Ie**) (from TCI), 4,4'-oxydibenzoic acid (**If**) (from TCI), 4,4'-sulfonyldibenzoic acid (**Ig**) (from New Japan Chem.), and 4,4'-hexafluoroisopropylidenedibenzoic acid (**Ih**) (from Central Glass), were used as received.

According to a reported method,^{17–20} bis(ether carboxylic acid)s **Ii–m** were prepared in high purity and high yields by condensing the corresponding bisphenol precursors with *p*-fluorobenzonitrile, followed by hydrolysis.

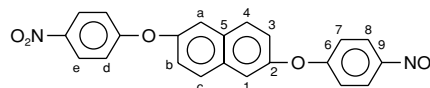
Reagent-grade calcium chloride and lithium chloride were dried under vacuum at 180°C before use. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and pyridine were pu-

rified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Monomer Synthesis

2,6-Bis(4-nitrophenoxy)naphthalene (2,6-BNPON)

A mixture of 16 g (0.10 mol) of 2,6-dihydroxynaphthalene, 33 g (0.21 mol) of *p*-chloronitrobenzene, 16 g (0.12 mol) of anhydrous K₂CO₃, and 160 mL of dry DMAc was refluxed at 150°C on an oil bath for 8 h. The mixture was then cooled and poured into 300 mL of methanol. The precipitate was collected by filtration, washed thoroughly with water and methanol, and dried. The crude product (40 g) was washed with glacial acetic acid and then recrystallized from dimethyl sulfoxide to give 32 g (80%) of pure 2,6-BNPON as light yellow crystals; mp 264–266°C. The infrared (IR) spectrum (KBr) exhibited absorptions at 1342 and 1582 cm⁻¹ (—NO₂), and 1250 cm⁻¹ (C—O—C). ¹H-NMR (δ, ppm, in DMSO-*d*₆): 8.28 (d, H_e, 4H), 8.07 (d, H_c, 2H), 7.80 (s, H_a, 2H), 7.44 (d, H_b, 2H), 7.22 (d, H_d, 4H). ¹³C-NMR (δ, ppm, in DMSO-*d*₆): 162.83 (C²), 151.91 (C⁶), 142.46 (C⁹), 131.62 (C⁵), 130.28 (C⁴), 126.26 (C⁸), 121.39 (C¹), 117.70 (C⁷), 116.95 (C³).

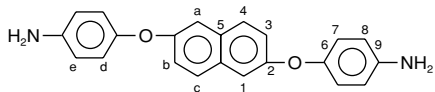


Anal. Calcd for C₂₂H₁₄N₂O₆: C, 65.67%; H, 3.48%; N, 6.96%. Found: C, 65.48%; H, 3.49%; N, 6.80%.

2,6-Bis(4-aminophenoxy)naphthalene (2,6-BAPON)

The dinitro compound (2,6-BNPON) 10 g (0.025 mol), 0.1 g of 10% Pd/C, and 80 mL of ethanol were introduced into a 400-mL three-necked flask to which 10 mL of hydrazine monohydrate was added dropwise over a period of 1 h at 85°C. After the addition was complete, the reaction was kept refluxing for 4 h. To the suspension, 100 mL of tetrahydrofuran was added to redissolve the precipitated product, and refluxing was continued for another 1 h. The mixture was filtered to remove the Pd/C and afforded colorless crystal product on cooling (mp 202–203°C). The filtrate was concentrated under reduced pressure. Thus, the total yield was 7.8 g (91%). The IR spectrum (KBr)

exhibited absorptions at 3406 and 3314 cm^{-1} ($-\text{NH}_2$) and 1250 cm^{-1} ($\text{C}-\text{O}-\text{C}$). $^1\text{H-NMR}$ (δ , ppm, in $\text{DMSO-}d_6$): 7.70 (d, H_c , 2H), 7.15 (d, H_b , 2H), 7.11 (s, H_a , 2H), 6.81 (d, H_d , 4H), 6.63 (d, H_e , 4H), 4.99 (s, $-\text{NH}_2$, 4H). $^{13}\text{C-NMR}$ (δ , ppm, in $\text{DMSO-}d_6$): 155.61 (C^2), 148.77 (C^6), 145.44 (C^9), 129.82 (C^5), 128.63 (C^4), 120.82 (C^7), 119.92 (C^1), 114.78 (C^8), 110.93 (C^3).



Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2$: C, 77.19%; H, 5.26%; N, 8.18%. Found: C, 77.04%; H, 5.20%; N, 8.11%.

Polymerization

The polyamides were prepared by direct polycondensation using the following general procedure. Take aramid **IId**, as an example. A mixture of 0.428 g (1.25 mmol) of diamine 2,6-BAPON, 0.27 g (1.25 mmol) of 2,6-naphthalenedicarboxylic acid (**Id**), 0.5 g of calcium chloride, 0.15 g of lithium chloride, 6 mL of NMP, 1.6 mL of pyridine, and 0.8 mL of triphenyl phosphite was heated with stirring at 100°C under nitrogen. The polymer solution was too viscous to stir after 1 h and was diluted gradually with an additional 4 mL of NMP to maintain smooth stirring. After dilution, the reaction mixture was continuously heated at 100°C for a further 2 h. 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 1.08 g (100%). The inherent viscosity of the aramid **IId** in DMAc + 5 wt % LiCl was 2.50 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

The other polyamides were prepared in a process similar to that as above. The preparation conditions of all polyamides are collected on Table II; the results of their elemental analyses are listed in Table III.

Measurements

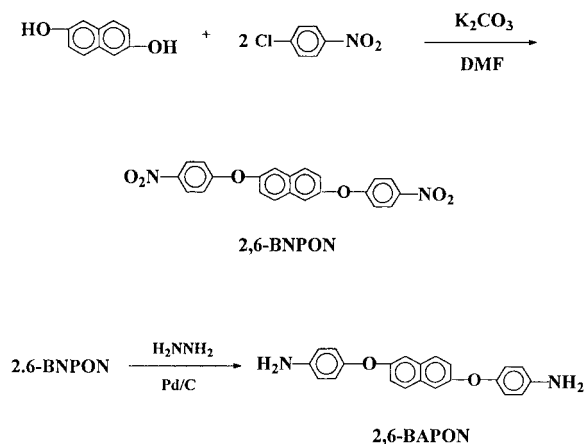
Melting points were measured in capillaries on a Yamato melting point apparatus (Model MP-21) without correction. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Jeol EX-400 NMR spec-

trometer operated at 30°C with tetramethylsilane (TMS) as an internal standard and perdeuteriodimethyl sulfoxide ($\text{DMSO-}d_6$) as an external standard, respectively. IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer. The inherent viscosities of all the polymers were measured at 0.5 g/dL concentration with a Cannon-Fenske viscometer thermostated at 30°C. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20°C/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 cm^3/min) at a heating rate of 20°C/min. The wide-angle X-ray diffraction patterns were obtained on a Rigaku Geiger D-Max IIIa X-ray diffractometer, using Ni-filtered Cu $\text{K}\alpha$ radiation (40 kV, 15 mA) with powder or film specimens of about 0.1 mm in thickness. The scanning rate was 2°/min. An Instron universal test 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 0.1 mm thick); an average of at least six individual determinations was used.

RESULTS AND DISCUSSION

Monomers Synthesis

The diamine monomer, 2,6-BAPON, was prepared from 2,6-dihydroxynaphthalene (2,6-DHON) by a two-step process as shown in Scheme 1. In the first step, 2,6-DHON was condensed with *p*-chloronitrobenzene in *N,N*-dimethylformamide in the presence of anhydrous potassium carbonate to 2,6-BNPON. In the second step, the dinitro compound 2,6-BNPON was catalytically reduced to bis(ether amine) 2,6-BAPON by using hydrazine as the reducing agent and Pd-C as the catalyst. The yield of diamine 2,6-BNPON is high, and its purity is good enough for the preparation of high molecular weight polyamides. The structure of the intermediate dinitro compound 2,6-BNPON and the diamine 2,6-BAPON were confirmed by



Scheme 1.

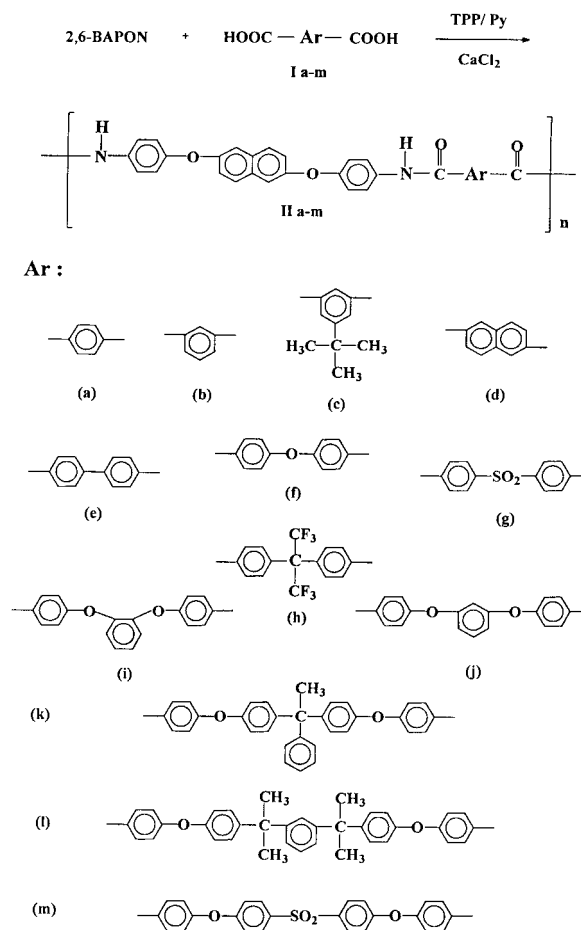
means of elemental analysis, IR spectroscopy, and $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy.

Preparation of Polymers

The polyamides were synthesized by the direct polycondensation reaction of diamine 2,6-BAPON with various aromatic dicarboxylic acids (**IIa–m**) as shown in Scheme 2. Since 1975, the direct polycondensation technique reported by Yamazaki et al.²¹ was popularly used in the laboratory for the polyamide synthesis. To obtain polyamides of high molecular weight in the Yamazaki phosphorylation reaction, although the reaction conditions required may be different due to the different kinds of monomers used, the optimum polymerization conditions seem to depend upon two main factors: The first is the amount of solvent (i.e., the monomer concentration) during the initial period of reaction; the second is the amount of metal salts such as calcium chloride or lithium chloride. Take the reaction of 2,6-BAPON with 2,6-naphthalenedicarboxylic acid (**Id**) as an example. The reaction conditions and results are summarized in Table I. The polymerization could proceed without addition of salts as Run 10 or with less amount of solvent in the initial period as Runs 1–3, and the inherent viscosities of the resulting polyamides only stayed in the range of 0.55–0.91 dL/g. In the course of reaction, the reaction monomers dissolved first and formed a clear solution, and then a faint turbidity occurred after about 20–50 min and enhanced gradually with time because the resulting polymer was insoluble in the reaction medium. The powdery polymer precipitates could only be obtained under this state when the solution of the products was trickled into methanol;

on the contrary, the reaction mixture might persist in a transparent and viscous state when a sufficient amount of solvent and salts (CaCl_2 , LiCl , or both in concert) was added at first, and a stringy, fiberlike polymer precipitate could be obtained upon precipitation in methanol. The inherent viscosities of these polymers might achieve in the range 1.87–2.47 dL/g (Runs 4–8). The results indicate that the solubility of formed polymer is concerned with the molecular weight of polyamides. However, earlier in the reaction too low reactant concentration would cause a decrease in inherent viscosity as shown by Run 9.

Synthesis conditions and inherent viscosities of the other polyamides are presented in Table II. With the exception of polyamide **IIe**, which was derived from rigid 4,4'-biphenyldicarboxylic acid, all the other polymers remained in the reaction solutions throughout the reaction and were produced with inherent viscosities ranging from 0.87 to 2.50 dL/g. These polyamides except for **IIe** could be solution-cast into transparent, flexible,



Scheme 2.

Table I. Effect of Reaction Conditions on the Preparation of Polyamide **II**d from 2,6-BAPON and 2,6-Naphthalenedicarboxylic Acid (**Id**)^a

Run	Amount of Reagents ^b						Polymer	
	Initial NMP (mL)	CaCl ₂ (g)	LiCl (g)	Py (mL)	TPP (mL)	Additional NMP (mL)	η_{inh}^c (dL/g)	Remark ^d
1	1.5	0.10	0.03	0.4	0.4		0.55	P
2	2.0	0.15		0.4	0.4	1.0	0.57	P
3	2.0	0.20	0.15	0.6	0.4	2.0	0.91	P
4	3.0	0.25	0.07	0.8	0.4	2.0	2.47	S
5	3.0	0.20	0.10	0.8	0.4		1.87	S
6	3.0	0.35		0.8	0.4	1.0	2.00	S
7	3.0		0.30	0.8	0.4	1.2	1.93	S
8	4.0	0.25	0.07	0.9	0.4		1.89	S
9	6.0	0.25	0.07	1.2	0.4		0.93	S
10	4.0			0.8	0.4		0.69	P

^a In each polymerization, 0.625 mmol of monomers was used, i.e., 0.2137 g of 2,6-BAPON and 0.135 g of **Id**. Reaction temperature = 100°C; reaction time = 3 h.

^b Py, pyridine; TPP, triphenyl phosphite.

^c Measured at a polymer concentration of 0.5 g/dL in DMAc + 0.5 wt % LiCl at 30°C.

^d Appearance of the reaction mixtures: S, homogeneous solution throughout the reaction; P, precipitation occurred during the reaction.

and tough films, indicating the formation of high molecular weights.

The polymers thus obtained were identified by elemental analyses and IR spectroscopy. The elemental analyses values of these polymers are

listed in Table III. In all cases, however, the values of carbon obtained were found to be lower than the calculated values for the proposed structure. These results may be attributed to the spectroscopic characteristics of the amide group.

Table II. Preparation of Polyamides from 2,6-BAPON and Various Aromatic Dicarboxylic Acids **Ia–m**

Polymer	Reaction Condition ^a						Polymer	
	Initial NMP (mL)	CaCl ₂ (g)	LiCl (g)	Py (mL)	TPP (mL)	Additional NMP (mL)	η_{inh}^b (dL/g)	Remark
IIa	6		0.64	1.6	0.8		2.10	S
IIb	4	0.24		1.2	0.8		1.88	S
IIc	4	0.2		1.2	0.8		1.20	S
IIId	6	0.5	0.15	1.6	0.8	4	2.50	S
IIe	6	0.5	0.2	1.6	0.8		0.62	P
IIIf	5	0.44	0.1	1.4	0.8		1.53	S
IIg	4	0.22		1.4	0.8	2	1.73	S
IIh	4	0.20		1.2	0.8		1.43	S
IIi	4	0.25		1.2	0.8		1.12	S
IIj	6	0.4		1.4	0.8		1.65	S
IIk	4	0.3		1.0	0.8		0.87	S
III	4		0.2	1.2	0.8	4	1.35	S
IIIm	6	0.2		1.0	0.8		0.94	S

^a In each polymerization, 1.25 mmol of monomers was used, i.e., 0.428 g of 2,6-BAPON and the equivalent quantities of dicarboxylic acids. Reaction temperature = 100°C; time = 3 h.

^b Measured at a polymer concentration of 0.5 g/dL in DMAc + 5 wt % LiCl at 30°C.

^c Appearance of the reaction mixture: S, homogeneous solution throughout the reaction; P, precipitation occurred during the reaction.

Table III. Elemental Analysis of Polyamides Based on 2,6-BAPON

Polymer	Formula (MW)		Anal. ^a (%)			Moisture Intake (%)
			C	H	N	
IIa	(C ₃₀ H ₂₀ N ₂ O ₄) _n (472) _n	Calcd	76.27	4.23	5.93	2.81
		Found	74.13	4.28	5.60	
		Corr	76.21	4.16	5.76	
IIb	(C ₃₀ H ₂₀ N ₂ O ₄) _n (472) _n	Calcd	76.27	4.23	5.93	3.99
		Found	73.23	4.22	5.62	
		Corr	76.15	4.05	5.84	
IIc	(C ₃₄ H ₂₈ N ₂ O ₄) _n (528) _n	Calcd	77.27	5.30	5.30	3.07
		Found	74.90	5.30	4.91	
		Corr	77.20	5.14	5.46	
IId	(C ₃₄ H ₂₂ N ₂ O ₄) _n (522) _n	Calcd	78.16	4.21	5.36	3.71
		Found	75.26	4.23	5.27	
		Corr	78.05	4.07	5.46	
IIe	(C ₃₆ H ₂₄ N ₂ O ₄) _n (548) _n	Calcd	78.83	4.38	5.11	3.53
		Found	76.05	4.62	4.83	
		Corr	78.73	4.46	5.00	
IIf	(C ₃₆ H ₂₄ N ₂ O ₅) _n (564) _n	Calcd	76.59	4.26	4.96	3.48
		Found	73.89	4.50	4.66	
		Corr	76.46	4.34	4.82	
IIg	(C ₃₆ H ₂₄ N ₂ O ₆ S) _n (612) _n	Calcd	70.58	3.92	4.57	3.44
		Found	68.15	3.94	4.31	
		Corr	70.50	3.81	4.46	
IIh	(C ₃₉ H ₂₄ N ₂ O ₄ F ₆) _n (690) _n	Calcd	67.05	3.46	4.01	2.01
		Found	65.70	3.35	3.72	
		Corr	67.02	3.28	3.79	
IIi	(C ₄₂ H ₂₈ N ₂ O ₆) _n (656) _n	Calcd	76.83	4.27	4.25	2.89
		Found	74.61	4.21	4.07	
		Corr	76.76	4.09	4.19	
IIj	(C ₄₂ H ₂₈ N ₂ O ₆) _n (656) _n	Calcd	76.83	4.27	4.25	5.23
		Found	72.81	4.49	4.03	
		Corr	76.62	4.26	4.24	
IIk	(C ₅₆ H ₄₀ N ₂ O ₆) _n (836) _n	Calcd	80.36	4.78	3.35	4.05
		Found	77.10	4.67	3.34	
		Corr	80.22	4.48	3.52	
III	(C ₆₀ H ₄₈ N ₂ O ₆) _n (892) _n	Calcd	80.71	5.38	3.14	4.56
		Found	77.03	5.20	3.16	
		Corr	80.54	4.96	3.31	
IIm	(C ₄₈ H ₃₂ N ₂ O ₈ S) _n (796) _n	Calcd	72.36	4.02	3.51	2.43
		Found	70.60	4.01	3.31	
		Corr	72.32	3.91	3.39	

^a For C and N: corrected value = found value × (100% + moisture intake %). For H: corrected value = found value × (100% - moisture intake %).

^b Moisture intake (%) = (W - W₀)/W₀ × 100%. W = weight of polymer sample after standing at room temperature for 3 days. W₀ = weight of polymer sample after dried in vacuum at 100°C.

The amounts of absorbed water for these bis(phenoxy)naphthalene-containing polyamides were in the 2.01–5.23% range. The corrected values were in good agreement with the calculated ones after the moisture intake were deducted. The IR spectra of these polyamides showed absorptions near 3300 cm⁻¹ (N—H stretching) and 1650

cm⁻¹ (C=O stretching), characteristic of the amide group. The characteristic absorption of aryl ether stretching appeared around 1250 cm⁻¹.

Properties of Polymers

The qualitative solubility of the obtained polyamides was tested in various solvents at room tem-

Table IV. Solubility of Polyamides Based on 2,6-BAPON^a

Polymer	Solvent ^b							
	DMAc	DMAc + 1% LiCl	DMAc + 5% LiCl	NMP	DMF	DMSO	Py	THF
IIa	–	+	+	–	–	–	–	–
IIb	+	+	+	+	+	+–	–	–
IIc	+	+	+	+	+	+–	+	–
IId	–	+	+	–	–	–	–	–
IIe	–	–	+	–	–	–	–	–
IIf	–	+	+	+	–	–	–	–
IIg	+	+	+	+	+	+–	–	–
IIh	+	+	+	+	+	+	+	+
IIi	+	+	+	+	+	+	+	–
IIj	–	+	+	+	–	–	–	–
IIk	+	+	+	+	+	+	+	–
III	+	+	+	+	+	+	+	–
IIIm	+	+	+	+	+	+	+	–

^a Solubility: (+) soluble at room temperature, (+–) partially soluble, (–) insoluble.

^b DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran. All the polymers were soluble in concentrated H₂SO₄.



perature with a concentration of approximately 1% (w/v). The results are shown in Table IV. Among these polyamides, polymer **IIe** revealed the least solubility due to the presence of a rigid

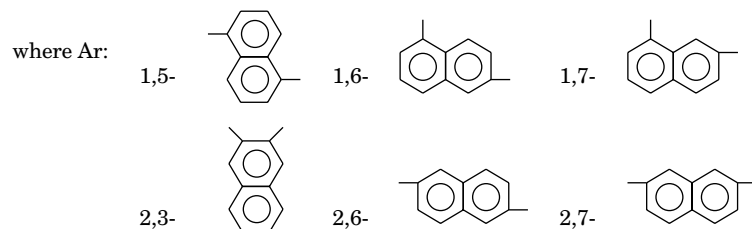
4,4'-biphenyl unit. It just could be dissolved in DMAc containing 5 wt % LiCl or in concentrated sulfuric acid. Polyamides **IIa**, **d**, **f**, **j** also showed relatively less solubility, possibly due to their

Table V. Solubility^a in DMAc of Aromatic Polyamides Based on Various Dicarboxylic Acids and BAPON Isomers^b

Diamine BAPON	Diacid ^c					
	Ia	Ib	Id	Ie	If	Ij
2,6-	–	+	–	–	–	–
1,5-	–	+	–	–	No ^d	No
2,3-	+	+	+	+	+	+
1,7-	–	+	–	–	+	+
2,7-	–	+	+	–	No	No
1,6-	+	+	+	+–	+	No

^a Solubility: (+) soluble at room temperature, (+–) partially soluble, (–) insoluble.

^b BAPON isomer: general formula H₂N––O–Ar–O––NH₂



^c The structures of diacids were as shown in Scheme 2.

^d The polymer has not been prepared.

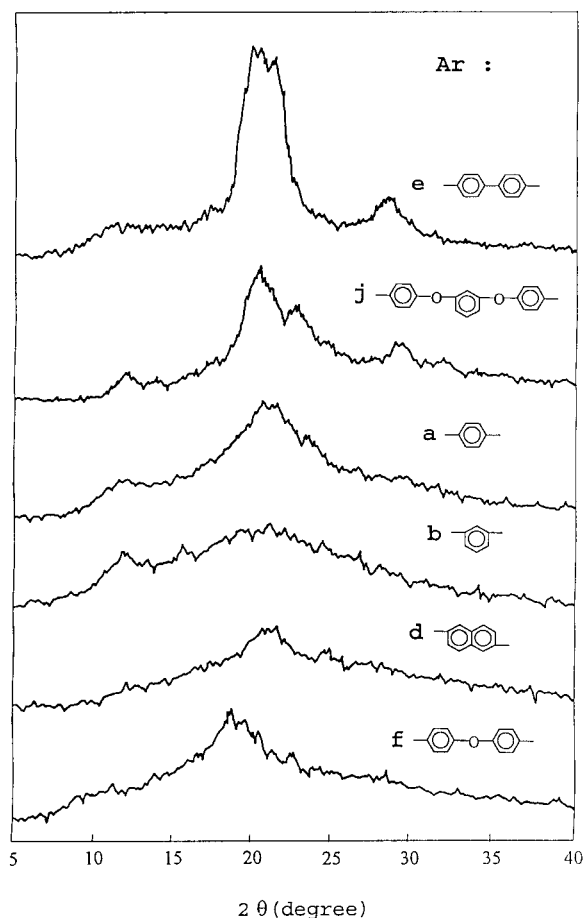


Figure 1. Wide-angle X-ray diffractograms of polyamides shown in Scheme 2.

some crystalline characteristics as shown by their X-ray diffraction patterns. They cannot easily dissolve in the polar solvents without a metal salt also dissolved. Into the polymer chain incorpora-

tion of the diacid moieties with asymmetrical aromatic units (such as polyamides **IIb**, **c**, **i** and **III**) or with flexibilizing linkages like $-\text{O}-$, $-\text{SO}_2-$, $-\text{C}(\text{CF}_3)_2-$, and $-\text{C}(\text{CH}_3)_2-$ between aromatic units leads to an enhanced solubility. These polyamides were readily soluble in polar solvents like DMF, DMSO, DMAc, and NMP. The introduction of hexafluoroisopropylidene [$-\text{C}(\text{CF}_3)_2-$] significantly enhances the solubility of polymers; therefore, polyamide **IIIh** seems to exhibit the highest solubility among the series of polyamides. Polymer **IIIh** was readily soluble even in pyridine and THF.

The comparison of the solubility of 2,6-BAPON aramids with its various isomeric aramids from BAPON isomers in the pure DMAc solvent is shown in Table V. The 2,6-series of aramids showed a comparative solubility with that of the 1,5-series ones. These two series aramids exhibited relatively lower solubility among these isomeric series, probably due to the fact that the symmetric 1,5- and 2,6-BAPON moieties led to a better packing of their polymer chains. The other isomeric series of aramids, especially for the 2,3- and 1,6-series, exhibited an increased solubility due to the less symmetry of substitution on the naphthalene unit.

The crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams obtained by the powder (for polymers **IIa**, **b**, **d-f**, **j**) or film (for the other polymers) method with the use of nickel-filtered $\text{CuK}\alpha$ radiation. As shown in Figure 1, polyamides **IIa**, **e**, **f**, **j** exhibited somewhat or moderately crystalline patterns due to a better packing of the symmetrical polymer backbones. The aramids showing crystalline patterns

Table VI. Mechanical Properties of Polyamide Films^a

Polymer	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
IIb	105	93	13	1.9
IIc	84	82	33	1.5
IId	88	95	19	2.1
IIg		88	36	1.6
IIIh		75	14	1.4
IIIi	84	72	34	1.6
IIIk		81	9	1.5
III		79	8	1.7
IIIm		68	10	1.4

^a Films were cast from slow evaporation of polymer solutions in DMAc.

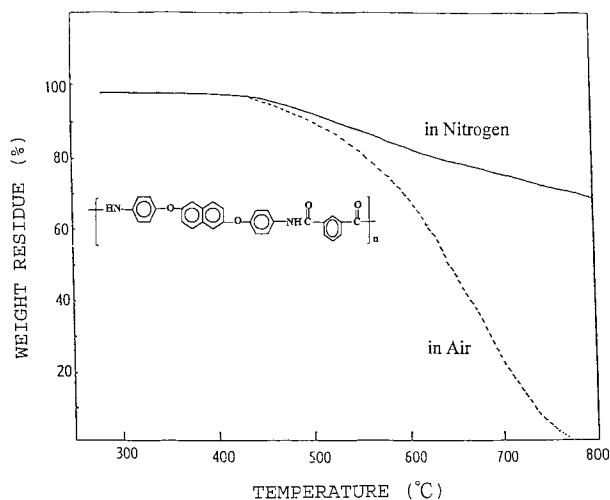


Figure 2. TGA curves for polyamide **IIb** at a heating rate of 20°C/min.

are insoluble in pure polar solvents (such as DMAc), which is in agreement with the general rule that the solubility decreases with increasing crystallinity. The other aramids showed amorphous diffraction patterns.

Most polymers could afford transparent, tough, and flexible films by casting from their DMAc solutions. Table VI summarizes the tensile properties of the polymers. The films had tensile strengths of 68–95 MPa, yield strengths of 84–105 MPa, elongations at break of 8–36%, and ini-

tial moduli of 1.4–2.1 GPa. Among them, aramids **IIc**, **IIg**, **IIi** behaved as ductile materials with high strength and moderate elongation at break.

The thermal stability and glass transition temperatures (T_g s) of polyamides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. As a representative example, the TGA thermograms of polyamide **IIb** measured in air and nitrogen were reproduced in Figure 2. The TGA curves for these polymers indicated that all polymers did not lose weight below 400°C in air or nitrogen. The 10% decomposition temperatures (T_{10}) both in air or nitrogen atmosphere and the char yields at 800°C in nitrogen are summarized in Table VII. The T_{10} values of these polyamides were recorded in the range 505–546°C in nitrogen and 474–526°C in air. The char yields of the aramids at 800°C in nitrogen were higher than 52% and up to 70%. The highly carbonized residues may be accounted for by their high aromaticity.

DSC measurements were conducted with a heating rate of 20°C/min in nitrogen. Quenching from the elevated temperatures to room temperature in air gave more amorphous samples so that the glass transition temperatures (T_g s) of some aramids could be easily measured in the second heating traces of DSC. The T_g s of some polyamides were recorded in the range 155–226°C. However, no discernible T_g of the polymers **IIa**, **b** and

Table VII. Thermal Properties of Polyamides on 2,6-BAPON

Polymer	DSC ^a T_g (°C)	TGA		Residual Wt % at 800°C in N ₂
		T_{10} ^b (°C)		
		In N ₂	In Air	
IIa		531	492	52
IIb		545	474	70
IIc	225	505	484	62
IId		546	490	59
IIe		542	482	68
IIf		508	495	62
IIg		517	503	62
IIh	226	527	515	59
IIi	170	532	503	67
IIj	205	517	486	61
IIk	176	524	508	66
III	155	523	526	67
IIIm	193	524	520	62

^a Conducted at a heating of 20°C/min in nitrogen.

^b Temperature at which a 10% weight loss was recorded by TGA at a heating of 20°C/min.

IId-g was detected from DSC traces. In general, the T_g of these polymers is decreasing with the flexibility of the polymer chain. For example, polyamide **III** revealed the lowest T_g (155°C), which is due to the highest amount of flexible groups, isopropylidene and ether linkages, per repeated unit of the polymer chain.

CONCLUSIONS

2,6-Bis(4-aminophenoxy)naphthalene (2,6-BAPON) was successfully synthesized in high purity and high yield in two steps from the condensation of 2,6-dihydroxynaphthalene and *p*-chloronitrobenzene followed by reduction of the intermediate dinitro compound with hydrazine/Pd-C system. A series of novel high molecular weight aramids containing 2,6-bis(phenoxy)naphthalene units were prepared by the direct polycondensation of 2,6-BAPON and various dicarboxylic acids by means of triphenyl phosphite and pyridine. Most of the polyamides obtained are characterized by high solubility in organic solvents, excellent mechanical properties, and high thermal stability. Thus, they may be considered to be promising for use as high-temperature plastic materials.

The authors are grateful to the National Science Council of the Republic of China for the support of this work (Grant NSC 85-2216-E-036-008).

REFERENCES AND NOTES

1. P. W. Morgan, *Chemtech*, **9**, 316 (1979).
2. P. E. Cassidy, *Thermally Stable Polymers*, Dekker, New York, 1980.
3. R. S. Lenk, J. L. White, and J. F. Feller, *Polym. Sci. Eng. Rep.*, **56** and **58**, (1975).
4. B. F. Malichenko, V. V. Sherikova, L. C. Chervgatsova, A. A. Kachan, and G. I. Motryuk, *Vysokomol. Soedin., Ser. B*, **14**, 423 (1972).
5. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1797 (1985).
6. H. J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Polym. Chem.*, **28**, 3293 (1990).
7. H. J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Polym. Chem. Ed.*, **29**, 767 (1991).
8. A. G. Farbenfabriken Bayer, Fr. Pat. 1,537,387 (1968); *Chem. Abstr.*, **71**, 13559e (1969).
9. F. Heroed, G. Keil, W. Bruckner, J. Cardinal, and C. Bennet, Ger. Offen. DE 3,727,097 (1987).
10. A. M. Dubnova, M. M. Koton, and E. M. Nekrasova, *Vysokomol. Soedin. Ser. B*, **19**, 39 (1977).
11. C.-P. Yang and W.-T. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 1571 (1993).
12. C.-P. Yang, S.-H. Hsiao, and C.-C. Jang, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 1095 (1995).
13. C.-P. Yang and W.-T. Chen, *Makromol. Chem.*, **193**, 2323 (1992).
14. C.-P. Yang and W.-T. Chen, *Makromol. Chem.*, **194**, 1595 (1993).
15. C.-P. Yang and J.-H. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 341 (1996).
16. Y. Imai, T. Niwa, M. Kato, Y. Taguchi, C. Imai, and Y. Imai, Jpn. Kokai Tokkyo Koho JP 01 29,431 (1989); *Chem. Abstr.*, **111**, 155395s (1989).
17. N. Avella, G. Maglio, R. Palumbo, F. Russo, and M. C. Vignola, *Makromol. Chem. Rapid Commun.*, **14**, 545 (1993).
18. G. Maglio, R. Palumbo, and M. C. Vignola, *Macromol. Chem. Phys.*, **196**, 2775 (1995).
19. S.-H. Hsiao and C.-F. Chang, *Macromol. Chem. Phys.*, **197**, 1255 (1996).
20. S.-H. Hsiao and H.-Y. Chang, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 1421 (1996).
21. N. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1373 (1975).