

# New Poly(amide-imide) Syntheses. XXI. Synthesis and Properties of Aromatic Poly(amide-imide)s Based on 2,6-Bis(4-trimellitimidophenoxy)naphthalene and Aromatic Diamines

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**ABSTRACT:** A novel polymer-forming diimide-diacid, 2,6-bis(4-trimellitimidophenoxy)-naphthalene, was prepared by the condensation reaction of 2,6-bis(4-aminophenoxy)-naphthalene with trimellitic anhydride (TMA). A series of novel aromatic poly(amide-imide)s containing 2,6-bis(phenoxy)naphthalene units were prepared by the direct polycondensation of the diimide-diacid with various aromatic diamines using triphenyl phosphite (TPP) in *N*-methyl-2-pyrrolidone (NMP)/pyridine solution containing dissolved calcium chloride. Thirteen of the obtained polymers had inherent viscosities above 1.01 dL/g and up to 2.30 dL/g. Most of polymers were soluble in polar solvents such as DMAc and could be cast from their DMAc solutions into transparent, flexible, and tough films. These films had tensile strengths of 79–117 MPa, elongation-at-break of 7–61%, and initial moduli of 2.2–3.0 GPa. The wide-angle X-ray diffraction revealed that some polymers are partially crystalline. The glass transition temperatures of some polymers could be determined with the help of differential scanning calorimetry (DSC) traces, which were recorded in the range 232–300°C. All the poly(amide-imide)s exhibited no appreciable decomposition below 450°C, and their 10% weight loss temperatures were recorded in the range 511–577°C in nitrogen and 497–601°C in air. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 919–927, 1998

**Keywords:** poly(amide-imide)s; direct polycondensation; 2,6-bis(4-aminophenoxy)-naphthalene; 2,6-bis(4-trimellitimidophenoxy)naphthalene

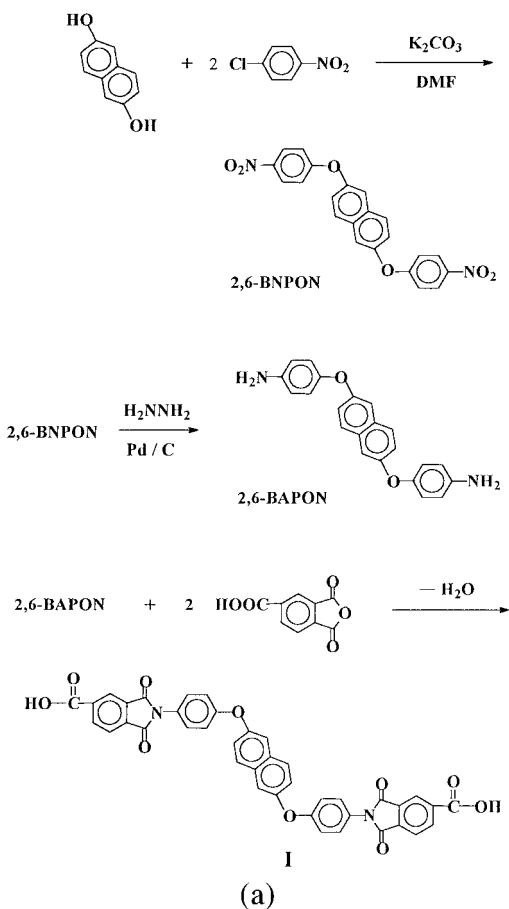
## INTRODUCTION

Polyimides are important thermally stable and high-performance polymers, but the major limitations of aromatic polyimides for the versatile applications are their high melting points and insolubility in organic solvents.<sup>1,2</sup> To overcome these problems, some copolymers have been proposed, especially for poly(amide-imide)s. This class of polymers seems to be a good compromise between thermostability and processability.

The triphenyl phosphite activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides has been reported by Yamazaki et al.<sup>3</sup> and has been extended to the synthesis of poly(amide-imide)s at our laboratory. In our earlier studies,<sup>4–11</sup> many series of poly(amide-imide)s were successfully synthesized from the direct polycondensation of imide ring-containing diacids and aromatic diamines by using the phosphorylation reaction. In the previous articles, we demonstrated that the incorporation of a diphenoxynaphthalene moiety into the poly(amide-imide) backbone is one effective means of enhancing the solubility with retention of good thermal properties.<sup>15–18</sup> In continuation of

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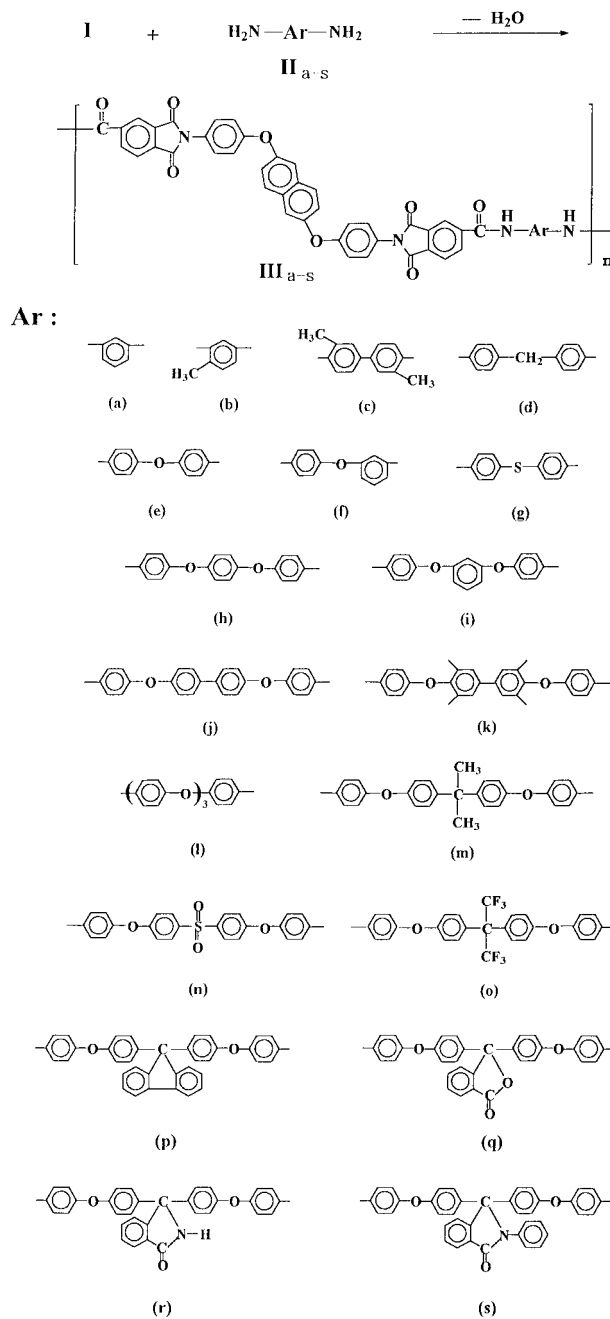
Scheme 1a.

these studies, the present work deals with the synthesis and basic characterization of a novel series of poly(amide-imide)s on the basis of the imide ring-preformed dicarboxylic acid 2,6-bis(4-trimellitimidophenoxy)naphthalene.

## EXPERIMENTAL

### Materials

According to the method reported in preceding papers,<sup>18-20</sup> 2,6-bis(4-aminophenoxy)naphthalene (2,6-BAPON) (mp 202–203°C) was synthesized starting from the nucleophilic chloro displacement of 2,6-dihydroxynaphthalene and *p*-chloronitrobenzene in the presence of potassium carbonate, giving 2,6-bis(4-nitrophenenoxy)naphthalene (2,6-BNPON), and followed by reduction with the hydrazine/Pd-C system (Scheme 1). Trimellitic anhydride (TMA) (from Wako) and triphenyl phosphite (TPP) (from TCI) were used without previous purification. Commercially ob-



Scheme 1b.

tained anhydrous calcium chloride was dried under vacuum at 150°C for 6 h. *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. *m*-Phenylenediamine (**IIa**; from TCI) was vacuum-distilled before use. The diamines such as 2,4-diaminotoluene (**IIb**),

*o*-tolidine (**IIc**), 4,4'-methylenedianiline (**IIId**), 4,4'-oxydianiline (**IIe**), 3,4'-oxydianiline (**IIIf**), 4,4'-thiodianiline (**IIg**), and 1,4-bis(4-aminophenoxy)benzene (**IIh**) were used directly as received from TCI. 1,3-Bis(4-aminophenoxy)benzene (**IIi**), 4,4'-bis(4-aminophenoxy)biphenyl (**IIj**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**IIm**), 2,2-bis[4-(4-aminophenoxy)phenyl] sulfone (**IIIn**), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IIo**) were obtained from Chriskev and used without further purification. 3,3',5,5'-Tetramethyl-4,4'-bis(4-aminophenoxy)biphenyl (**IIk**) and bis[4-(aminophenoxy)phenyl] ether (**IIl**) were prepared from the condensation of 3,3',5,5'-tetramethyl-4,4'-biphenol and 4,4'-oxydiphenol, respectively, with *p*-chloronitrobenzene and followed by reduction of the intermediate dinitro compounds with hydrazine/Pd-C.<sup>21,22</sup> The cardo bis(ether amine)s such as 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene (**IIp**), 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide (**IIq**), 3,3-bis[4-(4-aminophenoxy)phenyl]phthalimidine (**IIr**), and *N*-phenyl-3,3-bis[4-(4-aminophenoxy)phenyl]phthalimidine (**IIs**) were prepared according to the method reported in the preceding papers.<sup>24-27</sup>

## Monomer Synthesis

### Synthesis of 2,6-Bis(4-trimellitimidophenoxy)-naphthalene (I)

A mixture of 8.08 g (42 mmol) of trimellitic anhydride and 6.83 g (20 mmol) of diamine (2,6-BAPON) were dissolved in 100 mL of dry DMF at 60°C and stirred for 1 h. About 60 mL of toluene was then added, and the mixture was heated with reflux for 3 h until about 1.1 mL of water was azeotropically distilled off under a Dean-Stark trap. Heating was continued to distill off the residual toluene. After cooling, the yellow precipitate of diimide-diacid (**I**) was separated by filtration and washed with methanol. It was purified by recrystallization from DMF. The purified product was dried in vacuum, and the mass of the solid thus obtained was 13.18 g (95% yield); mp 340–341°C. Anal. Calcd. for C<sub>40</sub>H<sub>22</sub>N<sub>2</sub>O<sub>10</sub> (690.62): C, 69.57%; H, 3.20%; N, 4.07%. Found: C, 69.11%; H, 3.30%; N, 4.07%.

### Polymerization

A typical example of polycondensation is described as follows. A mixture of 0.43 g (0.625 mmol) of diimide-diacid **I**, 0.0675 g (0.625 mmol)

of *m*-phenylenediamine (**IIa**), 0.35 g of calcium chloride, 4 mL of NMP, 0.8 mL of pyridine, and 0.4 mL of triphenyl phosphite was heated with stirring at 100°C for 3 h. An additional volume of 4.5 mL of NMP was added to the reaction mixture after about 1 h because the solution was too viscous to stir. The obtained highly viscous polymer solution was trickled on 400 mL of stirred methanol. The precipitated stringy 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 was 1.44 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C.

Other poly(amide-imide)s were synthesized analogously. The synthesis conditions and the inherent viscosity of the obtained polymers are summarized in Table I.

### Measurements

Melting points were measured in capillaries on a Yamato melting point apparatus (Model MP-21) without correction. 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 TG 8110 thermoflex coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 2 mg of samples heated in flowing air or nitrogen (50 cm<sup>3</sup>/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 TA-7000 thermal analyzer in flowing nitrogen (30 cm<sup>3</sup>/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 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 Model 1130 universal tester 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.

**Table I.** Synthesis of Poly(amide–imide)s

Polymer	Amount of Reagents Used <sup>a</sup>				$\eta_{inh}^b$ (dL/g)	Remark <sup>e</sup>
	NMP (mL)	Additional NMP (mL)	CaCl <sub>2</sub> (g)	Pyridine (mL)		
<b>IIIa</b>	4.0	4.5	0.35	0.8	1.44	S
<b>IIIb</b>	3.0	0.5	0.30	0.7	1.01	S
<b>IIIc</b>	4.0	0	0.35	0.8	0.87 <sup>d</sup>	P
<b>IIId</b>	4.0	0	0.40	0.8	1.24 <sup>c</sup>	S
<b>IIIe</b>	4.0	0	0.40	1.0	0.88 <sup>d</sup>	P
<b>IIIf</b>	4.0	8.0	0.40	0.8	1.37 <sup>c</sup>	S
<b>IIIg</b>	4.0	4.0	0.40	0.8	1.80 <sup>c</sup>	S
<b>IIIh</b>	4.0	0	0.40	0.8	0.50 <sup>d</sup>	P
<b>IIIi</b>	4.0	0	0.40	0.8	0.34 <sup>d</sup>	P
<b>IIIj</b>	4.5	0	0.45	0.9	0.49 <sup>d</sup>	P
<b>IIIk</b>	5.0	5.0	0.48	1.0	1.28	S
<b>IIIl</b>	4.0	0	0.40	0.8	0.68 <sup>d</sup>	P
<b>IIIm</b>	4.0	5.0	0.32	0.8	1.36	S
<b>III n</b>	4.0	3.0	0.40	0.8	1.27	S
<b>IIIo</b>	4.0	6.0	0.30	0.8	1.47	S
<b>IIIp</b>	5.0	6.0	0.4	1.0	1.46	S
<b>IIIq</b>	5.0	10.0	0.42	0.8	2.30	S
<b>IIIr</b>	5.0	3.0	0.4	0.8	1.23	S
<b>III s</b>	5.0	3.5	0.4	1.0	1.07	S

<sup>a</sup> Polymerization was carried out using 0.625 mmol of each monomer and 1.25 mmol (about 0.4 mL) of triphenyl phosphite.

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

<sup>c</sup> Measured in DMAc + 5 wt % LiCl.

<sup>d</sup> Measured in concentrated sulfuric acid.

<sup>e</sup> S, soluble throughout the reaction; P, precipitation occurs during the reaction.

## RESULTS AND DISCUSSION

### Monomer Synthesis

2,6-Bis(4-trimellitimidophenoxy)naphthalene (**I**) was synthesized from the condensation of 2,6-bis(4-aminophenoxy)naphthalene with trimellitic anhydride. The complete cyclization of the intermediate amic acid was achieved by toluene–water azeotropic distillation (Scheme 1a). The IR spectrum of diimide–diacid **I** exhibited characteristic absorptions at 3442 cm<sup>-1</sup>, due to carboxylic acid —OH, and at 1785 and 1721 cm<sup>-1</sup>, peculiar to the coupled carbonyl stretching vibrations of imide rings. The elemental analysis result was in good agreement with the proposed structure.

### Polymer Syntheses

A series of novel poly(amide–imide)s **IIIa–s** containing a 2,6-bis(phenoxy)naphthalene unit were synthesized from diimide–diacid **I** and various aromatic diamines **IIa–s** by the direct polycondensation using triphenyl phosphite as promoter in

NMP in the presence of pyridine and calcium chloride at 100°C (Scheme 1b). All of the poly(imide–amide)s were isolated as yellowish materials with almost quantitative yield; the conditions of the preparation of poly(amide–imide)s are summarized in Table I. Most of the reactions, except for polymers **IIIc,e,h–IIIc,e,h–j,l**, proceeded readily in homogeneous solution. If the solution was too viscous to stir during the reaction, additional NMP was added to reduce the viscosity of the polymer solution and to promote smooth stirring. For example, in the reactions of diimide–diacid **I** with diamines **IIa,b,f,g,k,m–s**, an additional volume of 0.5–10 mL of NMP was added to the reaction mixture after about 1–1.5 h. The solubility of the polymer and the state of stirring affected the inherent viscosity of the resulting poly(amide–imide)s significantly. Generally, the molecular weight of the polymers obtained from the phosphorylation reaction is highly dependent on the reactant concentration. Higher molecular weights of these polymers could be obtained by using a higher initial reactant concentration and

**Table II.** Elemental Analysis of Poly(amide-imide)s

Polymer	Formula (FW)	Elemental Analysis <sup>a</sup> (%)			Moisture Intake <sup>b</sup> (%)	
			C	H		N
<b>IIIa</b>	$(C_{46}H_{26}N_4O_8)_n$ (762.73) <sub>n</sub>	Calcd	72.44	3.44	7.35	4.90
		Found	68.88	3.90	6.24	
		Corr <sup>c</sup>	72.25	3.71	6.56	
<b>IIIb</b>	$(C_{47}H_{28}N_4O_8)_n$ (776.76) <sub>n</sub>	Calcd	72.68	3.63	7.21	4.31
		Found	69.55	3.97	6.50	
		Corr	72.54	3.79	6.79	
<b>IIIc</b>	$(C_{54}H_{34}N_4O_8)_n$ (866.89) <sub>n</sub>	Calcd	74.82	3.95	6.46	3.04
		Found	72.54	4.13	5.98	
		Corr	74.74	4.01	6.16	
<b>IIId</b>	$(C_{53}H_{32}N_4O_8)_n$ (852.86) <sub>n</sub>	Calcd	74.64	3.78	6.57	4.89
		Found	70.89	4.04	6.0	
		Corr	74.35	3.84	6.29	
<b>IIIe</b>	$(C_{52}H_{30}N_4O_9)_n$ (854.83) <sub>n</sub>	Calcd	73.06	3.54	6.55	2.58
		Found	71.16	3.80	6.25	
		Corr	72.99	3.70	6.41	
<b>IIIf</b>	$(C_{52}H_{30}N_4O_9)_n$ (854.83) <sub>n</sub>	Calcd	73.06	3.54	6.55	3.27
		Found	70.67	3.85	5.84	
		Corr	72.98	3.72	6.03	
<b>IIIg</b>	$(C_{52}H_{30}N_4O_8S)_n$ (870.89) <sub>n</sub>	Calcd	71.72	3.47	6.43	3.81
		Found	68.98	3.79	6.85	
		Corr	71.61	3.64	7.11	
<b>IIIh</b>	$(C_{58}H_{34}N_4O_{10})_n$ (946.93) <sub>n</sub>	Calcd	73.57	3.62	5.92	2.65
		Found	71.61	3.76	5.46	
		Corr	73.51	3.66	5.61	
<b>IIIi</b>	$(C_{58}H_{34}N_4O_{10})_n$ (946.93) <sub>n</sub>	Calcd	73.57	3.62	5.92	2.48
		Found	71.74	3.89	6.20	
		Corr	73.52	3.78	6.35	
<b>IIIj</b>	$(C_{64}H_{38}N_4O_{10})_n$ (1023.03) <sub>n</sub>	Calcd	75.14	3.74	5.48	2.51
		Found	73.25	3.96	4.86	
		Corr	75.08	3.86	4.79	
<b>IIIk</b>	$(C_{68}H_{46}N_4O_{10})_n$ (1079.13) <sub>n</sub>	Calcd	75.69	4.30	5.19	3.79
		Found	72.82	4.34	4.99	
		Corr	75.58	4.17	5.18	
<b>IIIl</b>	$(C_{64}H_{38}N_4O_{11})_n$ (1039.03) <sub>n</sub>	Calcd	73.98	3.69	5.39	3.24
		Found	71.58	3.86	4.85	
		Corr	73.89	3.73	5.01	
<b>IIIm</b>	$(C_{67}H_{44}N_4O_{10})_n$ (1065.11) <sub>n</sub>	Calcd	75.55	4.16	5.26	2.82
		Found	73.47	4.27	5.06	
		Corr	75.54	4.15	5.20	
<b>III n</b>	$(C_{64}H_{38}N_4O_{12}S)_n$ (1087.09) <sub>n</sub>	Calcd	70.71	3.52	5.15	3.31
		Found	68.37	3.70	4.91	
		Corr	70.63	3.58	5.07	
<b>IIIo</b>	$(C_{67}H_{38}N_4O_{10}F_6)_n$ (1173.05) <sub>n</sub>	Calcd	68.60	3.27	4.78	2.52
		Found	66.87	3.42	4.66	
		Corr	68.55	3.33	4.77	
<b>IIIp</b>	$(C_{77}H_{46}N_4O_{10})_n$ (1039.03) <sub>n</sub>	Calcd	77.90	3.91	4.72	3.25
		Found	75.37	4.08	4.58	
		Corr	77.82	3.78	4.73	
<b>IIIq</b>	$(C_{72}H_{42}N_4O_{12})_n$ (1039.03) <sub>n</sub>	Calcd	74.86	3.66	4.85	3.88
		Found	71.95	3.84	4.72	
		Corr	74.36	3.69	4.89	

**Table II.** Continued

Polymer	Formula (FW)	Elemental Analysis <sup>a</sup> (%)			Moisture Intake <sup>b</sup> (%)	
			C	H		N
<b>IIIr</b>	(C <sub>72</sub> H <sub>43</sub> N <sub>5</sub> O <sub>11</sub> ) <sub>n</sub> (1039.03) <sub>n</sub>	Calcd	74.39	3.76	6.07	4.11
		Found	71.85	3.95	5.82	
		Corr	74.80	3.78	6.05	
<b>IIIs</b>	(C <sub>78</sub> H <sub>47</sub> N <sub>5</sub> O <sub>11</sub> ) <sub>n</sub> (1039.03) <sub>n</sub>	Calcd	76.15	3.85	5.69	3.88
		Found	73.19	4.05	5.40	
		Corr	76.03	3.89	5.61	

<sup>a</sup> For C and N, corrected value = found value × (100% + moisture uptake %). For H, corrected value = found value × (100% - moisture uptake %).

<sup>b</sup> Moisture uptake (%) = (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 dried in vacuum at 100°C for 10 h.

<sup>c</sup> Corr = corrected.

adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of swollen gel. Stringy precipitates were obtained when most of the polymer solutions were trickled into stirred methanol. However, a powder product was obtained from the polymer solutions of **IIIc, e, h–j, l**. All the polymers were obtained in almost quantitative yields. As shown in Table I,

the six poly(amide–imide)s which precipitated out from the reaction system during the polymerization exhibited a relatively lower inherent viscosity between 0.34 and 0.88 dL/g. The other 13 soluble poly(amide–imide)s were produced with a higher inherent viscosity ranging from 1.01 to 2.30 dL/g and could be easily solution cast into flexible and tough films.

**Table III.** Solubility<sup>a</sup> of Poly(amide–imide)s

Polymer	Solvent <sup>b</sup>								
	DMAc	DMAc + 5% LiCl	NMP	DMF	DMSO	<i>m</i> -Cresol	Py	THF	Conc. H <sub>2</sub> SO <sub>4</sub>
<b>IIIa</b>	+	+	+	+	+	+	–	–	+
<b>IIIb</b>	+	+	+	+–	+	+	+–	–	+
<b>IIIc</b>	–	–	–	–	–	–	–	–	+
<b>III d</b>	+–	+	+	–	–	–	–	–	+
<b>IIIe</b>	–	+–	–	–	–	–	–	–	+
<b>III f</b>	+–	+	+	+–	+	–	–	–	+
<b>III g</b>	+–	+	+	–	+–	–	–	–	+
<b>III h</b>	–	–	–	–	–	–	–	–	+
<b>III i</b>	–	+–	–	–	–	–	–	–	+
<b>III j</b>	–	–	–	–	–	+–	–	–	+
<b>III k</b>	+	+	+	+	+–	+	+–	–	+
<b>III l</b>	–	–	–	–	–	–	–	–	+
<b>III m</b>	+	+	+	+–	+–	+	–	–	+
<b>III n</b>	+	+	+	+	+	+–	+–	–	+
<b>III o</b>	+	+	+	+	+	+–	+–	–	+
<b>III p</b>	+	+	+	+	+	+	+–	–	+
<b>III q</b>	+	+	+	+	+–	+–	+–	–	+
<b>III r</b>	+	+	+	+	+	+	+	–	+
<b>III s</b>	+	+	+	+	+	+	+	–	+

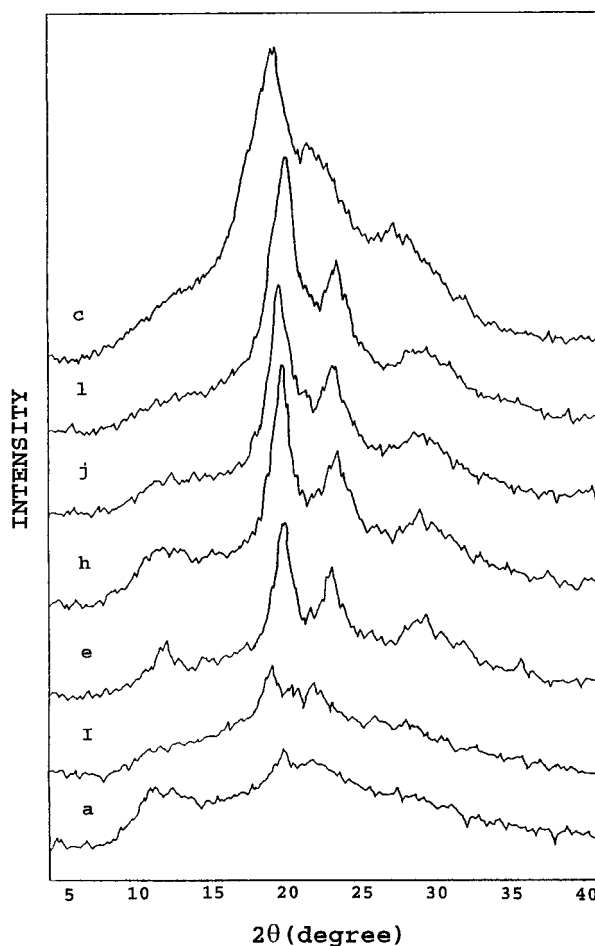
<sup>a</sup> Solubility: +, soluble at room temperature; +–, partially soluble; –, insoluble even on heating.

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

The IR spectrum of the poly(amide-imide) exhibited characteristic absorptions for the imide ring at 1785 and 1720  $\text{cm}^{-1}$ , indicative of the asymmetrical and symmetrical C=O stretching vibrations, and at 945 and 721  $\text{cm}^{-1}$ , due to ring deformation. Bands of amide groups appeared at approximate 3300 and 1650  $\text{cm}^{-1}$ . The results of elemental analyses of all the poly(amide-imide)s are listed in Table II. In all cases, however, the carbon values were found to be lower than the calculated ones for the proposed structures. This can possibly be attributed to the hygroscopic nature of amide groups of these poly(amide-imide)s. The uptakes of water were in the range 2.48–4.90%, which were calculated from the weight change of the vacuum-dried polymer samples after they were exposed in air at room temperature. When the found values were corrected by eliminating the amount of absorbed water, the correction values agreed well with the calculated ones.

### Properties of Polymers

The qualitative solubilities of the poly(amide-imide)s are listed in Table III. Among the 19 poly(amide-imide)s obtained, with the exception of polymers **IIIc,e,g-i,l** which are insoluble in NMP and DMAc, the others are soluble in these two polar solvents and most of them are also soluble in DMF and DMSO. The solubility behavior of this series of poly(amide-imide)s is very similar to that of their corresponding counterparts from the diimide-diacids of 1,5-, 2,7-, and 1,7-bis-(4-aminophenoxy)naphthalenes.<sup>15,16,18</sup> Obviously the solubility of these naphthalenediylidioxo units-containing poly(amide-imide)s highly depended on the diamine component. Those polymers containing *p*-phenylene, 4,4'-biphenylene, or 4,4'-oxydiphenylene units in the diamine residue such as **IIIe,h-j,l** are insoluble in nearly all the solvents tested. This may be attributed to a higher crystalline tendency of their polymer chains, which was evidenced by the X-ray diffraction patterns. Incorporation of methyl substituents on the benzene rings led to an increased solubility (such as **III d,k**). Insertion of flexibilizing groups such as isopropylidene (**III m**), sulfone (**III n**), and hexafluoroisopropylidene (**III o**) and bulky cardo groups (**III p-s**) between phenylene units resulted in a significant enhancement in solubility. Polymers **III m-s** are even soluble in less polar solvents like *m*-cresol and pyridine. All the polymers are insoluble in common organic sol-



**Figure 1.** Wide-angle X-ray diffractograms of poly(amide-imide)s.

vents such as chloroform, acetone, and benzene; however, they are all soluble in concentrated sulfuric acid.

To confirm the crystallinity of these poly(amide-imide)s, they were subjected to wide-angle X-ray diffraction measurements using nickel-filtered Cu  $K\alpha$  radiation. As shown in Figure 1, most of polymers that showed limited solubility exhibit moderate to high level of crystallinity. The strongest reflection occurred at  $2\theta \approx 20^\circ$ . The highly soluble poly(amide-imide)s displayed an amorphous diffraction pattern similar to that of **III a**.

Most of the poly(amide-imide)s were cast into films from polymer solutions of DMAc or NMP. The tensile properties of the polymer films were determined by an Instron machine. The results are summarized in Table IV. These films had tensile strengths of 79–117 MPa, elongations-to-break of 7–61%, and initial moduli of 2.2–3.0 GPa. Several poly(amide-imide)s in this series in-

**Table IV.** Tensile Properties of Poly(amide-imide) Films

Polymer <sup>a</sup>	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
<b>IIIa</b>	—	109	7	2.9
<b>IIIb</b>	—	98	11	2.4
<b>IIIf<sup>b</sup></b>	—	110	15	2.2
<b>IIIg<sup>b</sup></b>	—	117	7	2.7
<b>IIIk</b>	—	79	12	2.2
<b>III<sub>m</sub></b>	84	95	61	2.4
<b>III<sub>n</sub></b>	88	79	22	2.3
<b>III<sub>o</sub></b>	86	82	30	2.4
<b>III<sub>p</sub></b>	92	101	18	3.0
<b>III<sub>q</sub></b>	94	107	25	2.1
<b>III<sub>r</sub></b>	104	101	13	2.7
<b>III<sub>s</sub></b>	83	87	11	2.6

<sup>a</sup> Films were cast from polymer solutions in DMAc unless otherwise indicated.

<sup>b</sup> Films were cast from NMP.

cluding **III<sub>m</sub>–s** necked under tension and exhibited moderate elongation-to-break, indicating a ductile nature. Among these polymers, **III<sub>m</sub>** showed the highest elongation-to-break, and **III<sub>p</sub>** revealed the highest initial modulus up to 3.0 GPa.

The thermal properties of the polymers were evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The thermogravimetric traces indicate that all the poly(amide-imide)s possess high thermal stability with no significant weight loss up to temperatures of approximately 450°C in a nitrogen or an air atmosphere. The thermal behavior data of all poly(amide-imide)s are summarized in Table V. The 10% weight loss temperatures were recorded in the range 511–577°C in nitrogen and 497–601°C in air. The char yields at 800°C in nitrogen of all polymers were above 58%. Table V also summarizes the thermal transition data of poly(amide-imide)s. DSC measurements were conducted with a heating rate of 20°C/min. Quenching from the elevated temperatures (about 400°C) to room temperature yields more amorphous samples so that in some cases the glass transition temperatures ( $T_g$ s) could be easily observed in the second heating traces of DSC. The glass transition temperatures of some polymers could be discerned on their DSC traces and were read in the range 232–300°C.

## CONCLUSIONS

A series of bis(phenoxy)naphthalene-containing poly(amide-imide)s with moderate to high mo-

lecular weights could be easily obtained by the direct polycondensation reaction of 2,6-bis(4-trimellitimidophenoxy)naphthalene and aromatic diamines by means of triphenyl phosphite and pyridine. Depending on the diamines used, these

**Table V.** Thermal Properties of Poly(amide-imide)s

Polymer	$T_g^a$ (°C)	$T_d^b$ (°C)		Char Yield <sup>c</sup> (%)
		In Air	In N <sub>2</sub>	
<b>IIIa</b>		523	554	61
<b>IIIb</b>	265	536	533	60
<b>IIIc</b>		511	531	58
<b>III<sub>d</sub></b>		497	558	65
<b>III<sub>e</sub></b>	232	566	552	61
<b>III<sub>f</sub></b>		601	577	63
<b>III<sub>g</sub></b>	265	525	566	65
<b>III<sub>h</sub></b>	241	529	558	62
<b>III<sub>i</sub></b>		538	565	62
<b>III<sub>j</sub></b>		551	561	61
<b>III<sub>k</sub></b>	260	520	511	66
<b>III<sub>l</sub></b>		513	535	59
<b>III<sub>m</sub></b>	247	535	533	63
<b>III<sub>n</sub></b>		525	552	60
<b>III<sub>o</sub></b>	300	539	550	58
<b>III<sub>p</sub></b>	288	550	565	65
<b>III<sub>q</sub></b>	276	520	536	62
<b>III<sub>r</sub></b>		506	532	59
<b>III<sub>s</sub></b>	283	540	550	66

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

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

<sup>c</sup> Residual weight % at 800°C in nitrogen.



poly(amide-imide)s may be made with high crystallinity or an amorphous nature. Most of the resulting poly(amide-imide)s showed good solubility, high  $T_g$ , and excellent thermal stability. Thus, they are considered to be new promising processable high-temperature polymeric materials.

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## REFERENCES AND NOTES

1. C. E. Sroog, *Encyclopedia of Polymer Science and Technology*, H. F. Mark, Ed., Wiley, New York, 1969, Vol. II.
2. K. L. Mittal, Ed., *Polyimides: Synthesis, Characterization, and Applications*, Plenum, New York, 1984.
3. N. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci., Polym. Chem.*, **13**, 1373 (1975).
4. C. P. Yang and S. H. Hsiao, *Makromol. Chem.*, **190**, 2119 (1989).
5. S. H. Hsiao and C. P. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 2169 (1990).
6. S. H. Hsiao and C. P. Yang, *Makromol. Chem.*, **191**, 155 (1990).
7. S. H. Hsiao and C. P. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 1149 (1990).
8. C. P. Yang, J. H. Lin, and S. H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 1175 (1991).
9. S. H. Hsiao and C. P. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, **29**, 447 (1991).
10. C. P. Yang and Y. Y. Yen, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1855 (1992).
11. C. P. Yang, S. H. Hsiao, and J. H. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, **30**, 1865 (1992).
12. C. P. Yang, J. M. Cheng, and S. H. Hsiao, *Makromol. Chem.*, **193**, 445 (1992).
13. C. P. Yang, S. H. Hsiao, and J. H. Lin, *Makromol. Chem.*, **193**, 1299 (1992).
14. C. P. Yang, S. H. Hsiao, and J. H. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2995 (1993).
15. C. P. Yang and W. T. Chen, *Makromol. Chem.*, **194**, 3071 (1993).
16. C. P. Yang and W. T. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 3081 (1993).
17. C. P. Yang and W. T. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 435 (1994).
18. C. P. Yang and J. H. Lin, *J. Polym. Res.*, **3**, 193 (1996).
19. C. P. Yang and W. T. Chen, *Makromol. Chem.*, **193**, 2323 (1992).
20. C. P. Yang and W. T. Chen, *J. Polym. Sci., Polym. Part A: Polym. Chem.*, **31**, 1571 (1993).
21. C. P. Yang and W. T. Chen, *Makromol. Chem.*, **194**, 1596 (1993).
22. R. W. Stackman and A. B. Conciatori, U.S. Pat. 4,064,107 (1977); *Chem. Abstr.*, **88**, 122122d (1978).
23. S. H. Hsiao, C. P. Yang, and C. K. Lin, *J. Polym. Res.*, **2**, 1 (1995); *Chem. Abstr.*, **123**, 287811 g (1995).
24. C. P. Yang and J. H. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 2153 (1993).
25. C. P. Yang and J. H. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 423 (1994).
26. C. P. Yang and J. H. Lin, *Polymer*, **36**, 2607 (1995).
27. C. P. Yang and J. H. Lin, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 369 (1994).