

# Synthesis and Properties of New Organo-Soluble and Strictly Alternating Aromatic Poly(ester-imide)s from 3,3-Bis[4-(trimellitimidophenoxy)phenyl]phthalide and Bisphenols

CHIN-PING YANG,<sup>1</sup> GUEY-SHENG LIOU,<sup>2</sup> RUEI-SHIN CHEN,<sup>1</sup> CHING-YNE YANG<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Sec., Taipei, Taiwan, Republic of China

<sup>2</sup> Department of Chemical Engineering, I-Shou University, 1 Hsuen-Cheng Road 1st Sec., Ta-Hsu Hsiang, Kaohsiung, 84008, Taiwan, Republic of China

Received 30 August 1999; accepted 14 January 2000

**ABSTRACT:** A series of new strictly alternating aromatic poly(ester-imide)s having inherent viscosities of 0.20–0.98 dL/g was synthesized by the diphenylchlorophosphate (DPCP) activated direct polycondensation of the preformed imide ring-containing diacid, 3,3-bis[4-(trimellitimidophenoxy)phenyl]phthalide (**I**), with various bisphenols in a medium consisting of pyridine and lithium chloride. The diimide–diacid **I** was prepared from the condensation of 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide and trimellitic anhydride. Most of the resulting polymers showed an amorphous nature and were readily soluble in a variety of organic solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc). Transparent and flexible films of these polymers could be cast from their DMAc solutions. The cast films had tensile strengths ranging 66–105 MPa, elongations at break from 7–10%, and initial moduli from 1.9–2.4 GPa. The glass-transition temperatures of these polymers were recorded between 208–275 °C. All polymers showed no significant weight loss below 400 °C in the air or in nitrogen, and the decomposition temperatures at 10% weight loss all occurred above 460 °C. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 1090–1099, 2000

**Keywords:** poly(ester-imide); organo-soluble; 3,3-bis[4-(trimellitimido-phenoxy)phenyl]phthalide; 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide

## INTRODUCTION

Wholly aromatic polyimides are widely used in the semiconductor and electronic packaging industry because of their outstanding thermal stability, high mechanical strength, good insulation properties with low dielectric constant, good adhesion to commonly used substrates, and superior chemical stability.<sup>1,2</sup> However, these polymers

are generally intractable and lack the properties essential for successful fabrication into useful forms because of their high melting or glass-transition temperatures and limited solubility in organic solvents. In most applications where polyimides are utilized, a precursor polymer (polyamic acid) is used instead of directly using the polyimide resin. The storage of polyamic acid prior to process often causes a significant problem in the polyimide processing industry. This problem is aggravated by the strong corrosiveness of the polyamic acid. Furthermore, the water evolved from imidization can also form voids in

Correspondence to: C.-P. Yang

*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 38, 1090–1099 (2000)  
© 2000 John Wiley & Sons, Inc.

bulk materials. Therefore, copolyimides such as poly(amide-imide)s and poly(ester-imide)s have been developed.

The general methods used in the synthesis of the poly(ester-imide)s are (a) polycondensation between trimellitic acid or its derivative with a diamine and a diol,<sup>3–5</sup> (b) reaction between a dicarboxylic acid containing an imide ring with diol,<sup>5–7</sup> (c) polycondensation of a dianhydride containing ester group with a diamine,<sup>8–11</sup> (d) reaction from *N*-(4-carboxyphenyl)-4-acetoxypthalimide and 4-acetoxybenzoic acid,<sup>12,13</sup> (e) pyrolytic polymerization of monomers containing preformed ester linkages,<sup>14,15</sup> (f) direct polycondensation between a 4-carboxy-*N*-(*p*- or *m*-hydroxyphenyl)phthalimide, diacid, and bisphenol A in the presence of a direct condensation agent.<sup>16–18</sup> The unsatisfactory result obtained from this direct polycondensation<sup>16</sup> was caused by the poor solubility of monomers resulting in its early precipitation within the reaction medium retarding further polymerization. These poly(ester-imide)s had relatively low inherent viscosities and formed brittle films. Also, poly(ester-imide)s<sup>5–7</sup> synthesized from dicarboxylic acid containing an imide group with diol had low inherent viscosities ranging from 0.09 to 0.37 dL/g. All these indicate that it is difficult to synthesize a high molecular weight aromatic poly(ester-imide) from imide–diacid and bisphenol. Recently, we have successfully applied phosphorylation reaction<sup>19</sup> to the synthesis of high molecular weight poly(amide-imide)s by the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents.<sup>20–24</sup>

The direct polycondensation route avoids using moisture-sensitive acid chlorides and provides significant advantages in manufacturing operations compared with conventional methods. We have reported that the cyclic side cardo phthalide group-containing polyamides and polyimides derived from 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide with various aromatic dicarboxylic acids and dianhydrides.<sup>25</sup> Solubility of poly(amide-imide)s derived from diimide–diacid, 3,3-bis[4-(4-trimellitimidophenoxy)phenyl]phthalide, and various aromatic diamines<sup>26</sup> can be improved in various organic solvents with retention of moderately high thermal stability. In this article, we describe a successful synthesis of high molecular weight organo-soluble poly(ester-imide)s from diimide–diacid, 3,3-bis[4-(trimellitimidophenoxy)phenyl]phthalide, and various biphenols by using

the direct polycondensation method in the presence of diphenylchlorophosphate (DPCP) and pyridine (Py) as condensing agent. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers will also be investigated.

## EXPERIMENTAL

### Materials

Trimellitic anhydride, pyridine (Py; from Wako), and diphenylchlorophosphate (DPCP; from Merck) were used without further purification. Commercially obtained anhydrous lithium chloride was dried under vacuum at 150 °C for 10 h. The bisphenol monomers that included hydroquinone (**IIa**; from TCI), resorcinol (**IIb**; from TCI), methylhydroquinone (**IIc**; from TCI), chlorohydroquinone (**IId**; from Fluka), phenylhydroquinone (**IIe**; from Aldrich), 4,4'-biphenol (**IIf**; from TCI), 2,2',6,6'-tetramethylbiphenol (**IIg**; from Mitsubishi), 4,4'-dihydroxybenzophenone (**IIh**; from TCI), bis(4-hydroxyphenyl)sulfone (**IIi**; from TCI), 2,2'-bis(4-hydroxyphenyl)propane (**IIj**; from Wako), 2,2'-bis(4-hydroxyphenyl)hexafluoropropane (**IIk**; from Asahi Glass Co.), 1,1-bis(4-hydroxyphenyl)-1-phenylethane (**IIl**; from Honshu Chem. Co.), 4,4'-[1,4-phenylenebis(1-methylethylidene)]biphenol (**IIm**; from Mitsui), and phenolphthalein (**IIn**; from Wako) were used without further purification.

### Monomer Synthesis

#### 3,3-Bis[4-(4-aminophenoxy)phenyl]phthalide (PPDA)

According to the previously reported procedure, 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide (PPDA) and its intermediate compound, 3,3-bis[4-(4-nitrophenoxy)phenyl]phthalide, were prepared by the condensation of *p*-chloronitrobenzene with phenolphthalein, followed by the catalytic reduction of dinitrocompound in ethanol. The yield of the diamine PPDA was 84%; mp: 98–100 °C (lit.<sup>26</sup> 98–101 °C). The IR spectrum (KBr) exhibited absorptions at 3368 (N—H), 1238 (C—O—C), and 1760 cm<sup>-1</sup> (C=O, lactone).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, δ): 7.64–7.90 (m, 4H, phthalide aromatic), 7.20 (d, 4H, Ar—O), 6.83 (d, 4H, Ar—O), 6.72 (d, 4H, Ar—NH<sub>2</sub> aromatic), 6.59 (d, 4H, Ar—NH<sub>2</sub> aromatic), and 5.00 ppm (s, 4H, amino). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, δ): 90.9, 115.2,

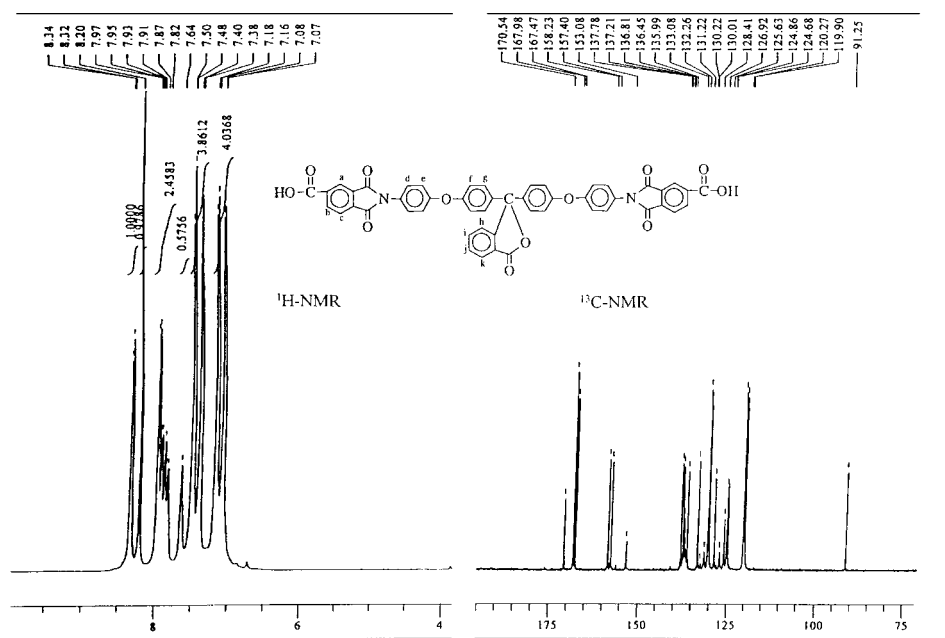


Figure 1. NMR spectra of diimide-diacid I.

116.4, 121.3, 124.5, 124.6, 125.7, 128.5, 130.1, 134.0, 135.3, 145.2, 145.9, 152.0, 159.3, 169.2 ppm.

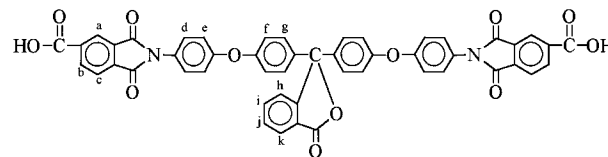
ELEM. ANAL. Calcd. for  $C_{32}H_{24}N_2O_4$ : C, 76.79%; H, 4.83%; N, 5.60%. Found: C, 76.48%; H, 4.88%; N, 5.66%.

### 3,3-Bis[4-(trimellitimidophenoxy)phenyl]-phthalide (I)

A mixture of 10.0 g (20 mmol) of PPDA and 7.69 g (40 mmol) of trimellitic anhydride was dissolved in 50 mL of dry DMF at 60 °C and stirred for 1 h. About 30 mL of toluene was then added, and the mixture was heated with reflux for 3 h until about 0.8 mL of water was distilled off azeotropically under a Dean–Stark trap. Heating was continued to distill off the residue toluene. After cooling, 30 mL of methanol was added and the yellow precipitate of diimide-diacid I was isolated by filtration and washed with methanol, collected by filtration and dried under vacuum. The product obtained was 16.14 g (95% yield); mp: 278–279 °C (lit.<sup>26</sup> 278–279 °C). The FTIR spectrum (KBr) showed absorption bands at 3465 (acid —OH), 1774 (imide, symmetric C=O stretching), 1724 (acid C=O stretching and asymmetric imide C=O stretching), 1381 (imide, imide ring vibration, axial), 1117 (imide, imide ring vibration, transverse), and 729  $\text{cm}^{-1}$  (imide, imide ring vibration, out of plane).

$^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ ): 8.33 (d, 2H,  $H_b$ ), 8.20 (s, 2H,  $H_a$ ), 7.96 (d, 2H,  $H_c$ ), 7.93–7.82 (m, 3H,  $H_i$  +  $H_j$  +  $H_k$ ), 7.64 (m, 1H,  $H_h$ ), 7.49 (d, 4H,  $H_d$ ), 7.39 (d, 4H,  $H_g$ ), 7.17 (d, 4H,  $H_e$ ), and 7.07 ppm (d, 4H,  $H_f$ ).  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ ): 91.25, 119.90, 120.27, 124.68, 124.86, 125.63, 126.92, 128.41, 130.01, 130.22, 131.22, 132.26, 133.09, 135.99, 136.45, 136.81, 137.21, 137.78, 153.08, 157.40, 158.23, 167.47, 167.98, 170.54 ppm (Fig. 1).

ELEM. ANAL. Calcd. for  $C_{50}H_{28}N_2O_{12}$ : C, 70.75%; H, 3.33%; N, 3.30%. Found: C, 69.86%; H, 3.81%; N, 3.62%.



### Polymerization

A typical example of polycondensation is described as follows: A solution of diphenylchlorophosphate (DPCP) (0.86 g), LiCl (0.1 g), and pyridine (5.0 mL) was stirred at room temperature for 30 min and then added dropwise for 20 min to a hot solution (preheated at 120 °C for 5 min) containing 1.060 g (1.25 mmol) of diimide-diacid I and 0.433 g (1.25 mmol) of bisphenol (II $m$ ) in pyridine (2.5 mL). The final solution was heated

at 120 °C for 3 h under stirring. The obtained polymer solution was trickled into 200 mL of methanol, giving rise to a stringy precipitate, which 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 0.98 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

Other poly(ester-imide)s were synthesized in an analogous manner. Representative IR spectra and elemental analysis are shown in Figure 2, Table I, and Table II.

### Measurements

Infrared spectra were recorded on a Jasco FTIR-7000 Fourier transform infrared spectrometer. Elemental analysis was run in a Perkin-Elmer model 2400 C,H,N analyzer. Inherent viscosities were determined using Cannon-Fenske viscosimeter at 30 °C. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermal analysis station TAS-100. Measurements were performed with  $10 \pm 2$  mg samples heated in flowing nitrogen ( $50 \text{ cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller in flowing nitrogen ( $30 \text{ cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 15 mA), and the scanning rate was 2°/min. Measurements were performed with film specimens of about 0.1 mm in thickness. Instron Universal Tester Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the sample. A strain rate of 5 cm/min was used for this study. Measurements were performed at room temperature (ca. 20 °C) with film specimens (0.5-cm wide, 4-cm long, and about 0.05-mm thick), and an average of at least five individual determinations was used.

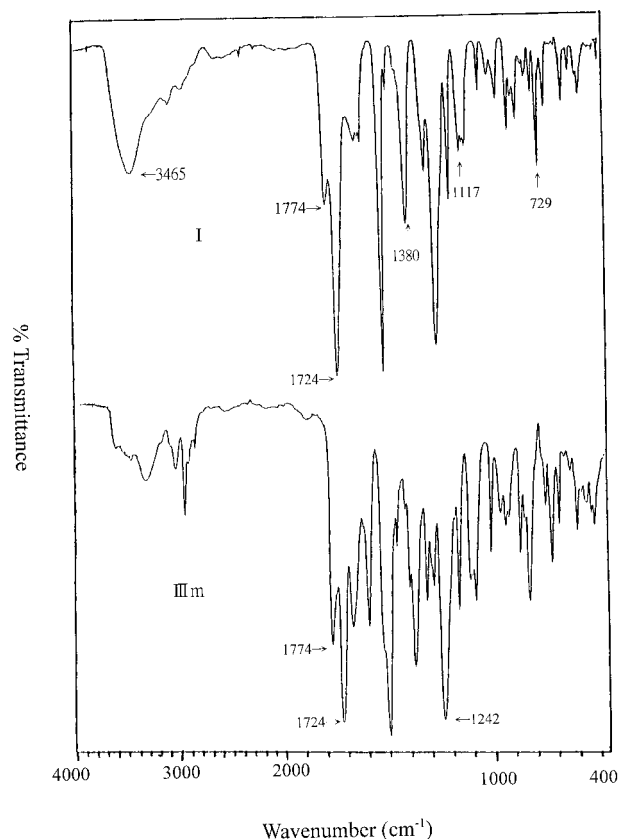
## RESULTS AND DISCUSSION

### Synthesis

A series of novel strictly alternating aromatic poly(ester-imide)s (**IIIa-n**) containing a phthalide group was synthesized starting from diol monomer of phenolphthalein (PP). By incorporating

ether groups, diether-diamine 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide (PPDA) was prepared from PP, followed by condensation of PPDA with trimellitic anhydride (TMA) to form diimide-diacid, 3,3-bis[4-(trimellitimidophenoxy)phenyl]phthalide (**I**). Final, poly(ester-imide)s were synthesized from diimide-diacid **I** and various bisphenols using diphenylchlorophosphate (DPCP) as condensing agents, as shown in Scheme 1.

For preparation of PPDA, PP and *p*-chloronitrobenzene were condensed in the presence of potassium carbonate in DMF, and subsequent reduction of dinitrocompound was occurred with a Pd/C catalyst and hydrazine hydrate (or  $\text{H}_2$ ). The diimide-diacid **I** was synthesized via the two-stage procedure that included ring-opening addition of PPDA with two equivalent amount of TMA in amide-type solvent, followed by cyclodehydration to the imidodicarboxylic acid by toluene-water azeotropic distillation. Resulting compounds PPDA and **I** were confirmed by IR spectra,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy, and elemental analysis (see Experimental). The results were in



**Figure 2.** IR spectra of diimide-diacid **I** and poly(ester-imide) **III.m**.

**Table I.** Synthesis of Poly(ester-imide)s<sup>a</sup>

Polymer	Additional Amount of Pyridine (mL)	$\eta_{inh}^b$	Polymer Appearance	Remark <sup>c</sup>
IIIa	4	–	Powder	P
IIIb	0	0.39	String	S
IIIc	1.5	0.60	String	S
IIId	4	0.20	String	S
IIIe	8	0.83	String	S
IIIf	1	–	Powder	P
IIIg	0	0.74	String	S
IIIh	4	–	Powder	P
IIIi	3	0.24	String	S
IIIj	3	0.71	String	S
IIIk	0	0.35	String	S
IIIl	0	0.39	String	S
IIIm	0	0.98	String	S
III n	0	0.48	String	S

<sup>a</sup> Polymerization was carried out using 1.25 mmol of diacid and bisphenols with 1 mL DPCP, 0.1 g LiCl in 7.5 mL of pyridine at 120 °C for 3 h.

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

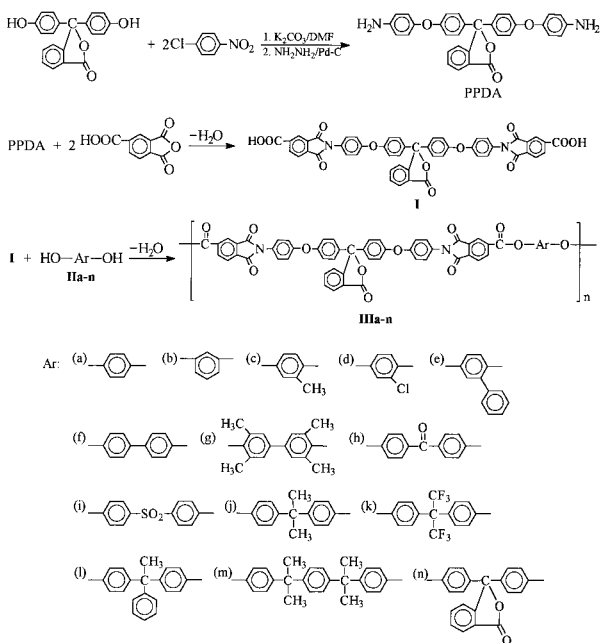
<sup>c</sup> S, solution through the reaction; P, precipitation during the reaction.

good agreement with the expected characteristics. According to the basis of the shielding effect of carbon, the positions of chemical shifts for car-

bons were readily assigned from <sup>13</sup>C NMR experiments of compounds PPDA and I. Because of symmetry of PPDA and I, their <sup>13</sup>C NMR

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

Polymer	Formula		Elemental Analysis (%)		
	$M_w$		C	H	N
IIIa	(C <sub>56</sub> H <sub>30</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	72.88	3.28	3.04
	(922.86) <sub>n</sub>	found	71.46	3.13	3.14
IIIb	(C <sub>56</sub> H <sub>30</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	72.88	3.28	3.04
	(922.86) <sub>n</sub>	found	71.75	3.15	3.08
IIIc	(C <sub>57</sub> H <sub>32</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	73.07	3.44	2.99
	(936.89) <sub>n</sub>	found	72.14	3.92	2.99
IIId	(C <sub>56</sub> H <sub>29</sub> N <sub>2</sub> ClO <sub>12</sub> ) <sub>n</sub>	calcd	70.26	3.05	2.93
	(957.31) <sub>n</sub>	found	68.96	3.28	2.84
IIIe	(C <sub>62</sub> H <sub>34</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	74.55	3.43	2.80
	(998.96) <sub>n</sub>	found	73.12	3.59	2.72
IIIg	(C <sub>66</sub> H <sub>42</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	75.14	4.01	2.66
	(1055.07) <sub>n</sub>	found	73.79	4.07	2.60
IIIj	(C <sub>65</sub> H <sub>40</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	74.99	3.87	2.69
	(1041.04) <sub>n</sub>	found	73.73	3.99	2.62
IIIk	(C <sub>65</sub> H <sub>34</sub> N <sub>2</sub> F <sub>6</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	67.95	2.98	2.44
	(1148.98) <sub>n</sub>	found	67.43	3.20	2.45
IIIl	(C <sub>70</sub> H <sub>42</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	76.22	3.84	2.54
	(1103.11) <sub>n</sub>	found	75.20	3.96	2.55
III m	(C <sub>74</sub> H <sub>50</sub> N <sub>2</sub> O <sub>12</sub> ) <sub>n</sub>	calcd	76.66	4.35	2.42
	(1158.40) <sub>n</sub>	found	74.78	4.51	2.36
III n	(C <sub>70</sub> H <sub>38</sub> N <sub>2</sub> O <sub>14</sub> ) <sub>n</sub>	calcd	74.33	3.39	2.48
	(1131.08) <sub>n</sub>	found	73.10	3.65	2.40



Scheme 1

spectra exhibited exactly 16 and 24 peaks, respectively, and were consistent with the calculated values.

The direct polycondensation conditions and results are summarized in Table I. These polymers were obtained in almost quantitative yield with inherent viscosities of 0.20–0.98 dL/g. The solu-

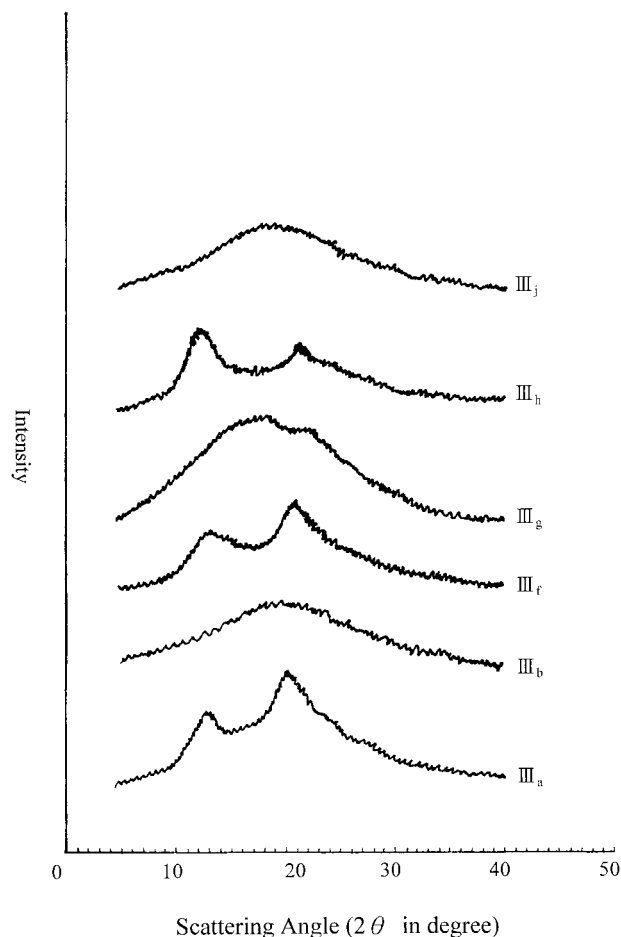
bility of the polymer solution affected the inherent viscosity of the resulting poly(ester-imide)s significantly. The molecular weight of the polymers **III**d and **III**i obtained from chlorohydroquinone (**II**d) and bis(4-hydroxyphenyl)sulfone (**II**i) were low. This might be attributed to their lower nucleophilicity because of the presence of the electron-withdrawing chloro and sulfonyl groups. The unsatisfactory results obtained from more rigid monomers such as hydroquinone (**II**a), 4,4'-biphenol (**II**f), and 4,4'-dihydroxybenzophenone (**II**h) were probably due to the fact that the poor solubility of these polymers resulted in an early precipitation during the course of reaction, which retarded further polymerization. The formation of poly(ester-imide)s was confirmed by elemental analysis and IR spectroscopy. The elemental analysis data of the poly(ester-imide)s listed in Table II were generally in good agreement with the respective structures for hydrogen and nitrogen, while the carbon analysis data were slightly lower than the theoretical values, a phenomenon common to high-temperature polyimides. The IR spectra of the polymers exhibited characteristic absorptions for the imide ring at 1774 and 1724  $\text{cm}^{-1}$ , peculiar to the symmetrical and asymmetrical carbonyl stretching vibration. Bands of ester groups appeared at 1242 (C—O—C) and 1724  $\text{cm}^{-1}$  (C=O), which was overlapped with one of the absorptions of imide ring (Fig. 2).

Table III. Solubility<sup>a</sup> of Poly(ester-imide)s

Polymer	Solvent <sup>b</sup>						
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	THF
IIIa	+–	–	–	–	–	–	–
IIIb	+	+	+	+	+	+	+
IIIc	+	+	+	–	+	+	+
IIId	+	+	+	+	+	+	+
IIIe	+	+	+	+	+	+	+
IIIf	–	–	–	–	–	–	–
IIIg	+	+	+	–	–	+	+
IIIh	+	–	–	–	–	–	–
IIIi	+	+	+	+	+	+	+
IIIj	+	+	+	–	+	+	+
IIIk	+	+	+	+	+	+	+
IIIl	+	+	+	+–	+	+	+
IIIm	+	+	+	–	+	+	+
IIIn	+	+	+	+	+	+	+

<sup>a</sup> + = Soluble; – = insoluble; +– = partially soluble or swollen.

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



**Figure 3.** Wide-angle X-ray diffractograms of some poly(ester-imide)s.

### Properties of Polymers

Table III shows the qualitative solubility of the poly(ester-imide)s in various solvents. Most polymers were soluble in aprotic polar solvents such as NMP, DMAc, and DMF. In addition to highly polar solvents, they were also soluble in less polar solvents like *m*-cresol, pyridine, and even in tetrahydrofuran (THF). This may be due to the existence of the bulky phthalide groups to prevent close chain-packing and allow solvent molecules to diffuse into the polymer chains. The solubility behavior of the new poly(ester-imide)s derived from **I** and various bisphenols were compared with those of the corresponding poly(ester-imide)s without bulky phthalide groups, and it also revealed that the new poly(ester-imide)s had much better solubility than other poly(ester-imide)s in many organic solvents. Thus, the solubility of poly(ester-imide)s was greatly improved by the introduction of bulky phthalide group into the

polymer backbone. However, polymers **IIIa**, **IIIf**, and **IIIh** with *p*-phenylene, 4,4'-biphenylene, and 4,4'-benzophenone *para*-aromatic ring structures, respectively, were quite insoluble in any organic solvents. X-ray diffraction results, as discussed below, revealed that polymers **IIIa**, **IIIf**, and **IIIh** had higher crystallization tendency among all the polymers. The solubility behavior was consistent with the results of X-ray diffraction studies.

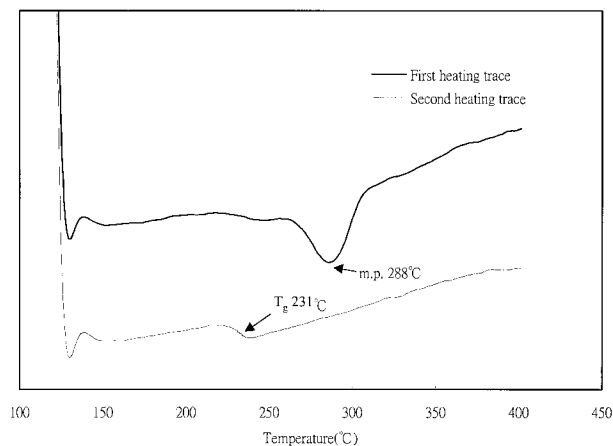
The structural characterization was made by X-ray methods with the as-prepared powders or films. Polymers **IIIa**, **IIIf**, and **IIIh** showed diffraction peaks, which indicate the presence of a fair degree of crystallinity, as shown in Figure 3. Because the diffraction patterns of **IIIa** and **IIIf** are rather similar in the positions of their peaks angles, similarity in lattice parameters for both polymers are expected, whereas all of the other polymers were completely amorphous. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, which is in agreement with the general rule that the solubility decreases with increasing crystallinity, and this could be attributed to the incorporation of bulky phthalide groups along the poly(ester-imide) backbone. The semicrystalline behavior of the polymers **IIIa**, **IIIf**, and **IIIh** was speculated because of the introduction of rigid-rod *p*-phenylene structure (**IIIa**) and symmetrical biphenyl catenation with lower rotation energy ketone linkage (**IIIf** and **IIIh**) in the main chain.

All the poly(ester-imide)s except polymers **IIIa**, **IIIf**, and **IIIh** were highly soluble in DMAc, and films could be cast from the DMAc solutions. Among them, the films of polymers **IIIb**, **IIIc**, **IIIe**, **IIIg**, **IIIi**, and **IIIk** were too brittle to be measured.

**Table IV.** Tensile Properties of Poly(ester-imide) Films<sup>a</sup>

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
IIIb	40	2	1.8
IIIc	87	8	2.1
IIIe	105	8	2.4
IIIg	66	9	2.0
IIIj	86	7	1.9
IIIk	90	8	2.1
IIIl	66	8	1.9
IIIm	94	10	2.1

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



**Figure 4.** DSC curves of poly(ester-imide) **IIIa** with a heating rate of 20 °C/min.

This may be due to their lower viscosity, whereas the other films of poly(ester-imide)s **III** having higher viscosity or more flexible structure were flexible with good quality and were subjected to tensile test. Tensile properties of these polymers are summarized in Table IV. All specimens except **IIIb** showed high tensile strength up to 105 MPa with moderate elongations at break and tensile

moduli in the range of 8–10% and 1.9–2.4 GPa, respectively.

The thermal behavior of the poly(ester-imide)s was evaluated by means of DSC and TGA. Figure 4 shows typical DSC curves of a representative polymer **IIIa**. The influence of residual water or solvent and history of thermal annealing are sometimes observed in the first scanning of DSC. Quenching from the elevated temperatures to room temperature yields predominantly amorphous samples so that discernible baseline shifts could be easily measured in the DSC charts of the second heating trace. The glass-transition temperatures ( $T_g$ ), defined by the midpoint of the baseline shift, of polymer **IIIa–n** were observed in the range of 210–275 °C, depending on the structure of bisphenol component, and decreased with decreasing rigidity and symmetry of the polymer backbone (Table V). In addition, polymer **IIIi** containing a bulky phthalide group in bisphenol had the highest  $T_g$  value, and the tetramethyl-substituted biphenylene containing polymer **IIIg** also had higher  $T_g$  by about 30 °C than the corresponding polymer **IIIf** without methyl-substituent. This phenomenon can be attributed to the restricted rotation about the bond joining the ar-

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

Polymer	DSC		TGA		Residual <sup>d</sup> wt % at 800 °C
	$T_m^a$ (°C)	$T_g^b$ (°C)	Decomposition Temperature <sup>c</sup> (°C)		
			In Air	In Nitrogen	
IIIa	288	231	495	503	47
IIIb	–	228	480	490	49
IIIc	–	230	480	480	48
IIId	–	208	485	490	45
IIIe	–	223	490	495	44
IIIf	287	235	500	500	47
IIIg	–	268	491	496	58
IIIh	272	215	470	475	39
IIIi	–	210	455	460	51
IIIj	–	244	480	475	45
IIIk	–	232	490	495	47
IIIl	–	252	490	490	45
IIIm	–	248	470	436	45
IIIn	–	275	480	480	53

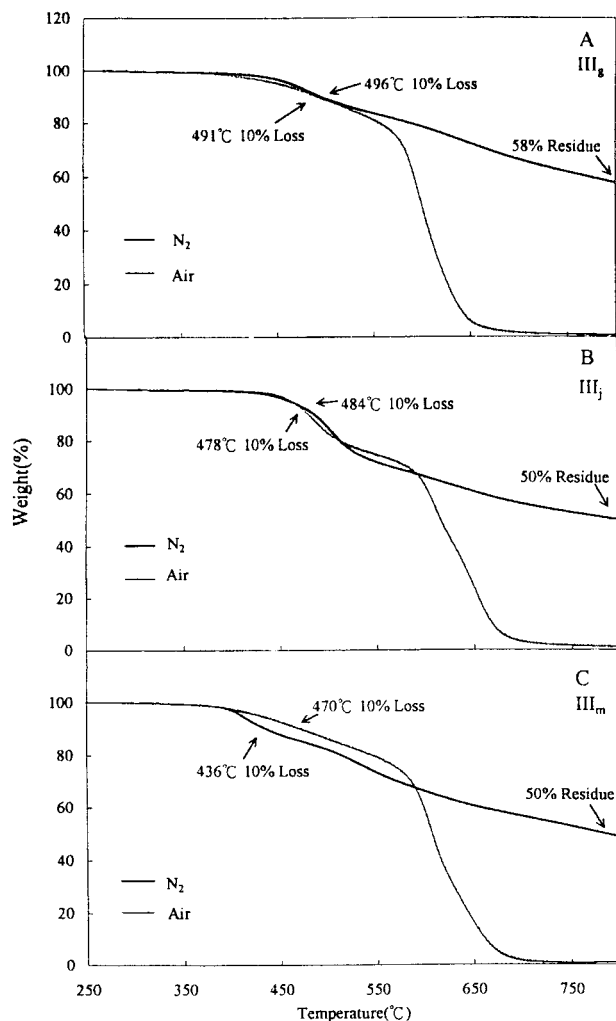
<sup>a</sup> From the first heating trace of DSC measurement conducted at a heating rate of 20 °C/min in nitrogen.

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

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

<sup>d</sup> Char yield was recorded by TGA at 800 °C under nitrogen atmosphere.





**Figure 5.** Typical TGA curves for poly(ester-imide)s **IIIg**, **IIIj** and **IIIm** with a heating rate of 20 °C/min.

omatic ring systems. Some of the poly(ester-imide)s (**IIIa**, **IIIf**, and **IIIh**) having a fair degree of crystallinity, as evidenced by X-ray diffraction studies (Fig. 3), showed a medium broad endothermic peak in their first DSC heating traces. However, in all cases rapid cooling and reheating showed a strong  $T_g$  and disappearance of the melting transition. Thus, it appears that the initial endothermic peak results were due to the presence of crystallinity.

The thermal stability of the poly(ester-imide)s **III** was studied by TGA. Typical TGA curves in both air and nitrogen atmospheres of representative polymer **IIIg**, **IIIj**, and **IIIm** are illustrated in Figure 5. The temperatures of 10% weight loss ( $T_d$ ) in nitrogen and air atmospheres were determined from original thermograms and tabulated in Table V. In general, all the polymers except

**III** exhibited good thermal stability with no significant weight loss up to temperatures of approximately 450 °C, and their  $T_d$ 's were recorded in the range of 455–500 °C both in nitrogen and air. In addition, the  $T_d$  values are higher for the more aromatic rings and fluorine-containing systems, such as **IIIa**, **IIIe**, **IIIg**, **IIIk**, **IIIl**, and **IIIo**, but decreased in the order of **IIIa** > **IIIe** > **III** > **IIId** > **IIIc** with different substituent (phenyl, chlorine, and methyl) attracted to the aromatic ring units. Generally speaking, the introduction of more bulky substituents into aromatic rings leads to significantly improved solubility of the polymer in various organic solvents, but stability decreases relatively, especially for the methyl substituent.

## CONCLUSIONS

New organo-soluble and strictly alternating aromatic poly(ester-imide)s containing a phthalide unit were successfully prepared by direct polycondensation of the diimide–diacid with various bisphenols by diphenylchlorophosphate (DPCP) and pyridine. The poly(ester-imide)s having moderate-to-high molecular weight were obtained. Most of these polymers showed good thermal stability, excellent solubility in organic solvents, and could be cast into transparent and flexible films. Thus, the present aromatic poly(ester-imide)s are considered as new candidates for processable high-performance polymeric materials.

The authors are grateful to the National Science Council of the Republic of China for financial support of this work (Grant NSC 87-2216-E-036-014).

## REFERENCES AND NOTES

1. Ghosh, M. K.; Mittal, K. L. *Polyimide: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
2. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M. *Polyimide*; Chapman & Hall: New York, 1990.
3. Schmidt, K.; Wille, D. U.S. Patent 3,562,219, 1971.
4. Shen, D. C. U.S. Patent 4,362,861, 1982.
5. Dolui, S. K.; Pal, D.; Maiti, S. *J Appl Polym Sci* 1985, 30, 3867.
6. Maiti, S.; Das, S. *J Appl Polym Sci* 1981, 26, 957.

7. Maiti, S.; Das, S. *Angew Makromol Chem* 1980, 86, 181.
8. Loncrini, D. F. *J Polym Sci* 1966, 4, 1531.
9. Koton, M. M. *Vysokomol Soedin, Ser A* 1973, A15, 310.
10. Malvaney, J. G. *J Polym Sci Part A: Polym Chem* 1986, 24, 613.
11. Tanaka, H.; Saiaguchi, M. *Polyimide: Material, Chemistry and Characterization*; Elsevier: Amsterdam, 1989.
12. Kricheldorf, H. R.; Schwarz, G.; Nowatzky, W. *Polymer* 1989, 30, 936.
13. Kricheldorf, H. R.; Pakull, R. *J Polym Sci Part A: Polym Lett Ed* 1985, 23, 413.
14. Kurita, K.; Mikawa, N.; Koyama, Y.; Kaneda, K.; Murakoshi, H. *J Polym Sci Part A: Polym Lett Ed* 1989, 27, 115.
15. Kurita, K.; Mikawa, N.; Koyama, Y.; Nishimura, S. *Macromolecules* 1990, 23, 2605.
16. Li, C. H.; Chen, C. C.; Chen, K. M. *J Appl Polym Sci* 1994, 52, 1751.
17. Li, C. H.; Chen, C. C.; Chen, K. M.; Chang T. C. *J Appl Polym Sci* 1995, 55, 747.
18. Li, C. H.; Jung, A.; Liang, A. L.; Chang T. C. *J Appl Polym Sci* 1995, 56, 1661.
19. Yamazaki, N.; Matsumoto, M.; Higashi, F. *J Polym Sci Part A: Polym Chem Ed* 1975, 13, 1373.
20. Yang, C. P.; Hsiao, S. H. *Makromol Chem* 1992, 193, 1299.
21. Yang, C. P.; Hsiao, S. H.; Lin, J. H. *J Polym Sci Part A: Polym Chem* 1993, 31, 2995.
22. Yang, C. P.; Chen, W. T. *Makromol Chem* 1993, 194, 3071.
23. Yang, C. P.; Lin, J. H. *J Polym Sci Part A: Polym Chem* 1994, 32, 2653.
24. Yang, C. P.; Jeng, S. H.; Liou, G. S. *J Polym Sci Part A: Polym Chem* 1998, 36, 1169.
25. Yang, C. P.; Lin, J. H. *J Polym Sci Part A: Polym Chem* 1994, 32, 423.
26. Yang, C. P.; Lin, J. H. *Polymer* 1995, 36, 2835.