

# New Poly(amide-imide)s Syntheses. XXIII. Synthesis and Properties of Poly(amide-imide)s Derived from 4,4'-[1,4-Phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline and Various Bis(trimellitamide)s

CHIN-PING YANG, SHENG-HUEI HSIAO, HSIU-CHUN HSIAO

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., Sec. 3, Taipei 104, Taiwan, Republic of China

Received 4 March 1998; accepted 30 May 1998

**ABSTRACT:** A series of poly(amide-imide)s **III**<sub>a-m</sub> containing flexible isopropylidene and ether groups in the backbone were synthesized by the direct polycondensation of 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (PIDA) with various bis(trimellitamide)s **II**<sub>a-m</sub> in *N*-methyl-2-pyrrolidone (NMP) using triphenyl phosphite and pyridine as condensing agents. The resulting poly(amide-imide)s had inherent viscosities in the range of 0.80–1.36 dL/g. Except for those from the bis(trimellitamide)s of *p*-phenylenediamine and benzidine, all the polymers could be cast from DMAc into transparent and tough films. They exhibited excellent solubility in polar solvents. The 10% weight loss temperatures of the polymers in air and in nitrogen were all above 495°C, and their  $T_g$  values were in the range of 201–252°C. Some properties of poly(amide-imide)s **III** were compared with those of the corresponding poly(amide-imide)s **V** prepared from the bis(trimellitamide) of diamine PIDA and various aromatic diamines. © 1999 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 37: 69–76, 1999

**Keywords:** isopropylidene; poly(amide-imide)s

## INTRODUCTION

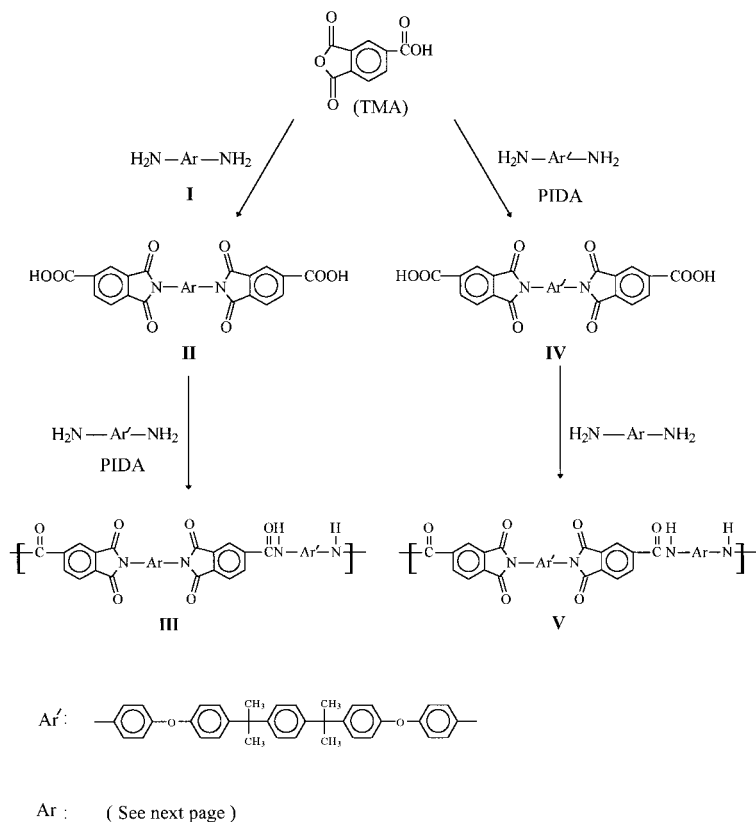
Aromatic poly(amide-imide)s possess desirable characteristics between polyamides and polyimides such as high thermal stability and good mechanical properties together with easy processability. Conventionally, aromatic poly(amide-imide)s can be prepared in several ways starting from trimellitic anhydride (TMA), such as two-step polycondensation from the acid chloride of TMA with aromatic diamines involving polyaddition and subsequent cyclodehydration,<sup>1</sup> low-temperature solution polycondensation of TMA-derived imide ring-preformed diacid chloride and aromatic diamines,<sup>2</sup> polycondensation of TMA or

TMA-derived imide ring-containing dicarboxylic acids with diisocyanates,<sup>3</sup> and phosphorylation polyamidation between TMA-derived imide ring-preformed dicarboxylic acids and aromatic diamines.<sup>4</sup>

Since we successfully applied the phosphorylation reaction<sup>5</sup> to the direct synthesis of high-molecular-weight poly(amide-imide)s from the TMA-derived imide ring-bearing dicarboxylic acids and aromatic diamines using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents,<sup>6</sup> this route has proved to exhibit significant advantages in preparing operations in comparison with conventional acid chloride or isocyanate methods. Thus, several series of novel poly(amide-imide)s have been readily prepared by this convenient technique in our laboratory.<sup>7</sup> In addition, this synthetic procedure can offer us the option of the incorporation of specific functional-

Correspondence to: C.-P. Yang

*Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 37, 69–76 (1999)  
© 1999 John Wiley & Sons, Inc. CCC 0887-624X/99/010069-08



Scheme 1.

ities between amide or imide groups in the poly-(amide-imide) backbone. The incorporation of such functional groups may provide a method of controlling certain physical properties of the resulting poly(amide-imide)s. In one of our previous publications,<sup>7r</sup> a diimide ring-containing dicarboxylic acid, or a bis(trimellitimide) (IV), was prepared via condensation of 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (PIDA) and TMA, and a series of poly(amide-imide)s **V<sub>a-m</sub>** were synthesized by the TPP-Py direct polycondensation reaction of this diimide-diacid with various aromatic diamines (see Scheme 1). The results of thermal analyses and solubility test of these polymers proved that incorporation of isopropylidene and aryl ether groups could impart processability to the polymer, with only limited reduction of thermal stability. The residue of diamine PIDA has also been incorporated in other polymer systems, such as polyimides, polyamides, and bis(maleimide) resins, to enhance the processing characteristics and toughness of the resulting polymers.<sup>8-15</sup> As a continuation of our efforts on screening new poly-(amide-imide)s, the present study deals with the

preparation and characterization of a novel series of poly(amide-imide)s based on the diamine PIDA and the bis(trimellitimide)s (**II<sub>a-m</sub>**) condensed from TMA and many other aromatic diamines. A comparative study on the properties of the two analogous series of poly(amide-imide)s, **III<sub>a-m</sub>** and **V<sub>a-m</sub>**, is also presented.

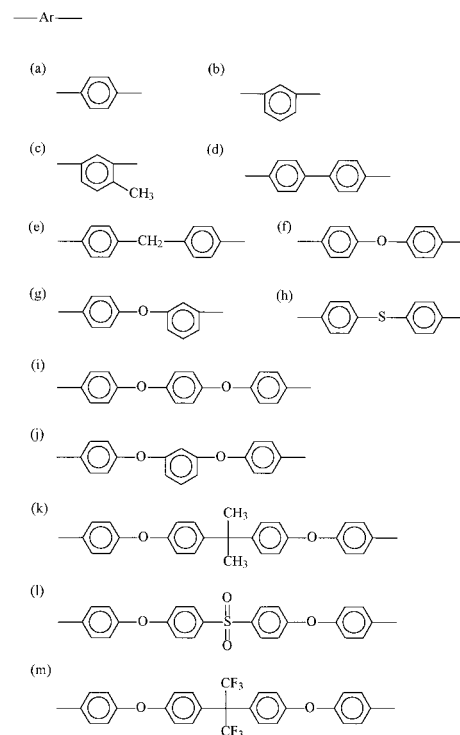
## EXPERIMENTAL

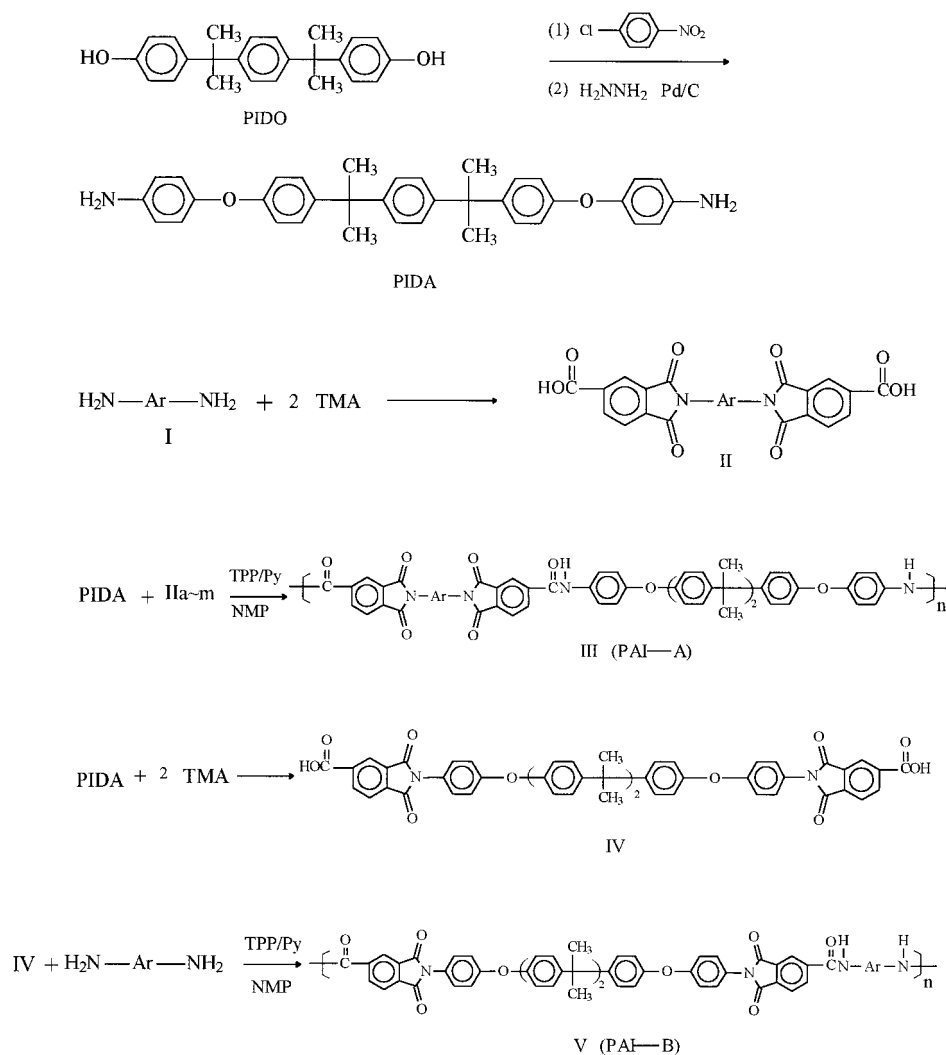
### Materials

*p*-Chloronitrobenzene (TCI), 10% palladium on activated charcoal (Pd/C, Fluka), hydrazine monohydrate (Wako), triphenyl phosphite (TPP; TCI), and trimellitic anhydride (TMA; Wako) were used without previous purification. 4,4'-[1,4-Phenylenediisopropylidene]diphenol (PIDO) was also used directly as they were received from Mitsui Petrochemical Ind. (Tokyo, Japan).

As described previously,<sup>10,11</sup> 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (PIDA) (mp 187–189°C) was prepared by the nucleophilic chloro-displacement reaction of *p*-chloro-

Scheme 1 continued





Scheme 2.

ronitrobenzene and bisphenol PIDO followed by Pd-catalyzed hydrazine reduction. Diimide-diacarboxylic acids **II<sub>a-m</sub>** and **IV** were obtained as described in previous reports<sup>7,17</sup> by the condensation from TMA with the corresponding diamine in 1 : 2 molar ratio. Commercially obtained anhydrous calcium chloride was dried under vacuum at 180°C for 10 h. *N*-Methyl-2-pyrrolidone (NMP; Fluka) and pyridine (Py; Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

### Polymerization

A typical example for the preparation of poly(amide-imide) **III<sub>b</sub>** is as follows: A mixture of

0.528 g (1 mmol) of diamine PIDA, 0.456 g (1 mmol) of diimide-diacid **II<sub>b</sub>**, 0.4 g of calcium chloride, 5 mL of NMP, 1 mL of pyridine, and 0.6 mL of triphenyl phosphite was heated with stirring at approximately 110°C for 3 h. The polymer solution thus obtained was slowly poured into 400 mL of stirring methanol, and a yellow fiberlike precipitate was obtained. The product 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 poly(amide-imide) was 0.97 dL/g, measured at a concentration of 0.5 g/dL in *N,N*-dimethylacetamide (DMAc)-5% LiCl at 30°C.

The other poly(amide-imide)s were synthesized in an analogous procedure.

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

Polymer	Initial NMP (mL)	Additional NMP (mL)	CaCl <sub>2</sub> (g)	$\eta_{inh}^b$ (dL/g)	Remark <sup>d</sup>
<b>III<sub>a</sub></b>	6.5	0	0.5	0.11 <sup>c</sup>	Powder
<b>III<sub>b</sub></b>	5	0	0.4	0.97	String
<b>III<sub>c</sub></b>	4.5	0	0.3	0.90	String
<b>III<sub>d</sub></b>	6.5	0	0.8	0.13 <sup>c</sup>	Powder
<b>III<sub>e</sub></b>	5	0	0.4	0.80	String
<b>III<sub>f</sub></b>	5	2	0.4	1.36	String
<b>III<sub>g</sub></b>	5	0	0.3	0.87	String
<b>III<sub>h</sub></b>	4.5	5	0.3	1.20	String
<b>III<sub>i</sub></b>	4	1.5	0.4	1.10	String
<b>III<sub>j</sub></b>	5	2	0.3	1.21	String
<b>III<sub>k</sub></b>	4.5	6.5	0.3	1.36	String
<b>III<sub>l</sub></b>	6	0	0.3	0.96	String
<b>III<sub>m</sub></b>	4.5	4	0.5	0.86	String

<sup>a</sup> Polymerization was carried out with 1 mmol of each monomer, 0.6 mL of triphenyl phosphite, and 1 mL of pyridine at 110°C for 3 h.

<sup>b</sup> Measured at a concentration of 0.5 g/dL in DMAc-5% LiCl at 30°C, unless otherwise indicated.

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

<sup>d</sup> Appearance of the polymer when precipitated in stirred methanol.

## Measurements

Infrared 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. Inherent viscosities of all polymers were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer. Thermogravimetric data were obtained on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyzer. Measurements were performed with  $10 \pm 2$  mg samples heated in following nitrogen or air (50 cm<sup>3</sup>/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 following nitrogen (30 cm<sup>3</sup>/min) at a heating rate of 10°C/min. Glass transition temperatures were taken as the midpoint of the change in slope of the baseline on the second DSC heating trace after quick cooling prior to the scan. Wide-angle X-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered Cu K $\alpha$  radiation (40 kV, 20 mA), and the scanning rate was 4°/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 per-

formed at room temperature (about 25°C) with film specimens (0.5 cm wide, 6 cm long, and about 0.1 mm thick), and an average of at least five individual determinations was used.

## RESULTS AND DISCUSSION

### Polymer Synthesis

Poly(amide-imide)s with alternating (amide-imide)-(imide-imide) sequence could be tailored from two diamines and TMA. A specific molecular skeleton of diamine could be inserted in the amide or imide segments by different ways. In our previous report<sup>7r</sup> the diamine PIDA served as a specific diamine and was first condensed with TMA to give a PIDA-bis(trimellitimide) (**IV**), which was directly polycondensated with various aromatic diamines to prepare poly(amide-imide)s **V<sub>a-m</sub>** having PIDA residues in the imide segments. Here, another series of poly(amide-imide)s **III<sub>a-m</sub>** bearing PIDA residues in the amide segments were synthesized from PIDA with various aromatic diamines-derived bis(trimellitimide)s **II<sub>a-m</sub>** (Scheme 1). These polymers were synthesized by the triphenyl phosphite-activated method, the same as used in the synthesis of poly(amide-imide)s **V<sub>a-m</sub>**.

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

Polymer	Formula (Molecular Weight)		Elemental Anal. (%)			Moisture <sup>a</sup> Intake (%)
			C	H	N	
<b>III<sub>a</sub></b>	(C <sub>60</sub> H <sub>44</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (948) <sub>n</sub>	Calcd.	75.93	4.67	5.91	4.0
		Found	72.99	4.92	5.55	
<b>III<sub>b</sub></b>	(C <sub>60</sub> H <sub>44</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (948) <sub>n</sub>	Calcd.	75.93	4.67	5.91	2.9
		Found	73.74	4.96	5.67	
<b>III<sub>c</sub></b>	(C <sub>61</sub> H <sub>46</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (962) <sub>n</sub>	Calcd.	76.07	4.81	5.82	3.0
		Found	73.80	4.98	5.42	
<b>III<sub>d</sub></b>	(C <sub>66</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (1022) <sub>n</sub>	Calcd.	77.33	4.72	5.47	2.4
		Found	75.45	9.98	5.23	
<b>III<sub>e</sub></b>	(C <sub>67</sub> H <sub>50</sub> N <sub>4</sub> O <sub>8</sub> ) <sub>n</sub> (1038) <sub>n</sub>	Calcd.	77.44	4.85	5.39	2.7
		Found	75.28	5.12	4.96	
<b>III<sub>f</sub></b>	(C <sub>66</sub> H <sub>48</sub> N <sub>4</sub> O <sub>9</sub> ) <sub>n</sub> (1040) <sub>n</sub>	Calcd.	76.15	4.65	5.38	3.3
		Found	73.59	5.00	5.46	
<b>III<sub>g</sub></b>	(C <sub>66</sub> H <sub>48</sub> N <sub>4</sub> O <sub>9</sub> ) <sub>n</sub> (1040) <sub>n</sub>	Calcd.	76.15	4.64	5.38	1.4
		Found	74.11	4.76	4.72	
<b>III<sub>h</sub></b>	(C <sub>66</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub> S) <sub>n</sub> (1056) <sub>n</sub>	Calcd.	74.98	4.58	5.30	2.1
		Found	73.40	4.70	5.00	
<b>III<sub>i</sub></b>	(C <sub>72</sub> H <sub>52</sub> N <sub>4</sub> O <sub>10</sub> ) <sub>n</sub> (1132) <sub>n</sub>	Calcd.	76.31	4.63	4.95	2.2
		Found	74.59	4.82	4.66	
<b>III<sub>j</sub></b>	(C <sub>72</sub> H <sub>52</sub> N <sub>4</sub> O <sub>10</sub> ) <sub>n</sub> (1132) <sub>n</sub>	Calcd.	76.31	4.63	4.95	1.9
		Found	74.80	4.77	4.77	
<b>III<sub>k</sub></b>	(C <sub>81</sub> H <sub>62</sub> N <sub>4</sub> O <sub>10</sub> ) <sub>n</sub> (1250) <sub>n</sub>	Calcd.	77.74	4.99	4.48	1.9
		Found	76.27	5.00	4.32	
<b>III<sub>l</sub></b>	(C <sub>78</sub> H <sub>56</sub> N <sub>4</sub> O <sub>12</sub> S <sub>2</sub> ) <sub>n</sub> (1304) <sub>n</sub>	Calcd.	73.57	4.43	3.73	2.1
		Found	72.00	4.55	4.15	
<b>III<sub>m</sub></b>	(C <sub>88</sub> H <sub>56</sub> O <sub>10</sub> N <sub>4</sub> F <sub>6</sub> ) <sub>n</sub> (1442) <sub>n</sub>	Calcd.	71.57	4.15	4.12	1.9
		Found	70.16	4.26	3.89	

<sup>a</sup> Moisture intake (%) =  $(W - W_0/W_0) \times 100\%$ .  $W$  = weight of polymer sample after standing at room temperature for 3 days.  $W_0$  = weight of polymer sample after dried in vacuum at 100°C for 10 h.

Synthesis conditions and inherent viscosities of the produced polymers are summarized in Table I. With the exception of **III<sub>a</sub>** and **III<sub>d</sub>**, all the reaction solutions were homogeneously transparent. The solubility of the polymer in the reaction medium and the state of stirring affected the inherent viscosity of the resulting poly(amide-imide) significantly. In general, the molecular weight of the polymer obtained from the phosphorylation reaction is highly dependent on the reactant concentration. According to earlier papers, it was repeatedly observed that the higher the concentration of monomers, the higher the final inherent viscosity if no precipitation or gelation of the product from the reaction medium took place. It was anticipated that the isopropylidene and ether groups-containing polymers **III** would have an increased solubility in organic solvents and a higher monomer concentration could be tolerated during polymerization. In some cases

such as the reaction of PIDA with bis(trimellitimide)s **II<sub>f,h-k,m</sub>**, additional 1.5–6.5 mL of NMP was added to the reaction mixture after about 40–60 min to avoid the formation of a swollen gel. A high molecular weight for these polymers could be obtained by the use of a higher reactant concentration and adding a proper amount of supplemental solvent into the viscous reaction medium before formation of a swollen gel. However, in the cases of **III<sub>a</sub>** and **III<sub>d</sub>**, an early precipitation occurred during polymerization, and increasing the amount of CaCl<sub>2</sub> or NMP in order to carry out the reaction in a homogeneous phase has met with failure in obtaining clear, viscous polymer solutions. A powder precipitate was obtained when pouring the resulting polymer solutions into methanol. The unsatisfactory results may be attributed to their poor solubility, due to the presence of rigid planar 1,4-bis(phthalimido)phenylene or 4,4'-bis(phthalimido)biphenylene segments in their polymer back-

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

Polymer	Solvents <sup>b</sup>							
	DMAc	DMAc-5% LiCl	NMP	DMF	DMSO	THF	<i>m</i> -Cresol	H <sub>2</sub> SO <sub>4</sub>
<b>III<sub>a</sub></b>	–	+–	+	–	–	–	–	+
<b>III<sub>b</sub></b>	+	+	+	+	+	+	+	+
<b>III<sub>c</sub></b>	+	+	+	+	+	+	+	+
<b>III<sub>d</sub></b>	–	–	–	–	–	–	–	+
<b>III<sub>e</sub></b>	+	+	+	+	+	+	+	+
<b>III<sub>f</sub></b>	+	+	+	+	+h	+–	+	+
<b>III<sub>g</sub></b>	+	+	+	+	+	+	+	+
<b>III<sub>h</sub></b>	+	+	+	+	–	+–	+	+
<b>III<sub>i</sub></b>	+	+	+	+	+h	–	+h	+
<b>III<sub>j</sub></b>	+	+	+	+	+h	–	+h	+
<b>III<sub>k</sub></b>	+	+	+	+	–	+	+	+
<b>III<sub>l</sub></b>	+	+	+	+	–	+–	+	+
<b>III<sub>m</sub></b>	+	+	+	+	+	+	+	+

<sup>a</sup> Solubility: (+) soluble at room temperature, (+–) partially soluble or swelling, (+h) soluble on heating, (–) insoluble even on heating.

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

bones, leading to a better packing of polymer chains. Polymer **III<sub>a</sub>** and **III<sub>d</sub>** were insoluble in all the available organic solvents. Sulfuric acid dissolved but simultaneously degraded them, as shown by a relatively lower  $\eta_{inh}$  value. The degradation of these polymers is likely to be related to the presence of acid-sensitive isopropylidene linkage along the macromolecular backbone. In the other cases, clear and highly viscous polymer solutions could be obtained, which were poured slowly and stirred into methanol to produce stringy fiberlike polymer precipitates. Inherent viscosities of these polymers varied between 0.80 and 1.36 dL/g, indicative of moderate to high molecular weight.

The structural characterization was carried out by means of FTIR spectroscopy and elemental analysis. Absorption bands around 1780 and 1720  $\text{cm}^{-1}$ , due to the asymmetric and symmetric C=O stretching vibrations, were assigned to the imide ring. Characteristic bands of amide groups appeared around 3350 (N–H) and 1650  $\text{cm}^{-1}$  (C=O). The results of elemental analyses of all the poly(amide-imide)s **III<sub>a-m</sub>** are listed in Table II. In all cases, however, the carbon values were found to be lower and the hydrogen values were found to be slightly higher than the calculated ones for the proposed structures. This can probably be explained by the hygroscopic nature of the samples caused by the amide groups of poly(amide-imide)s. The water uptake was in the range

of 1.4–4.0%, calculated from the weight change of the vacuum-dried polymer samples after they were exposed in air at room temperature. When the experimental values were corrected by eliminating the amount of absorbed water, the corrected values agreed well with the calculated values.

### Properties of Polymers

The solubility of polymers **III** was tested qualitatively in various solvents, and the results are summarized in Table III. All polymers, except for **III<sub>a</sub>** and **III<sub>d</sub>**, show excellent solubility in aprotic dipolar solvents, such as NMP, DMAc, DMF, and DMSO, and even in less polar *m*-cresol. The poor solubility of **III<sub>a</sub>** and **III<sub>d</sub>** may be due to their semicrystalline nature, as evidenced by X-ray diffractograms. In a comparison of the solubilities of the polymers **III** with the corresponding polymers **V** that differ only by incorporation of the PIDA moiety in the amide or imide segment, their solubility behaviors are similar.

With the exception of **III<sub>a</sub>** and **III<sub>d</sub>**, this series of poly(amide-imide)s were all soluble in DMAc and could be cast into flexible films. Table IV presents the results of tensile tests of these flexible films. They showed tensile strengths in the range of 68–92 MPa, elongations at break of 9–25%, and initial moduli of 1.45–2.14 GPa. Some polymers necked during tensile test and

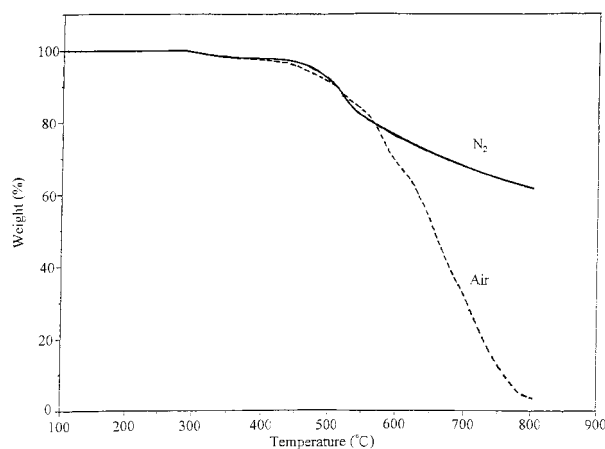
**Table IV.** Tensile Properties of Poly(amide-imide)s<sup>a</sup>

Polymer	Yield Strength (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
<b>III<sub>b</sub></b>		80	10	1.96
<b>III<sub>c</sub></b>		92	13	1.72
<b>III<sub>e</sub></b>		89	11	2.13
<b>III<sub>f</sub></b>	79	73	25	1.85
<b>III<sub>g</sub></b>	88	86	21	1.96
<b>III<sub>h</sub></b>		71	9	1.66
<b>III<sub>i</sub></b>	79	74	11	1.63
<b>III<sub>j</sub></b>	76	72	14	1.73
<b>III<sub>k</sub></b>	76	68	15	1.48
<b>III<sub>l</sub></b>	89	80	11	2.14
<b>III<sub>m</sub></b>	75	68	15	1.45

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

exhibited yield strengths in the range of 75–89 MPa. In comparison with the films made from **V** polymers, these polymers revealed higher strengths and toughness. This may be attributable to the fact that the **III** series polymers exhibited higher average molecular weights than the corresponding **V** series polymers.

The thermal stability and transition temperatures of the poly(amide-imide)s were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). Typical TG curves are shown in Figure 1. The results show that the polymers are stable up to 450°C and start degrading thereafter. The thermal stability data of poly(amide-imide)s **III** are summarized in Table V. The temperatures of 10% weight loss of the present polymers were recorded in the range of



**Figure 1.** TG curves of poly(amide-imide) **III<sub>b</sub>**, with a heating rate of 20°C/min.

495–520°C in nitrogen and 498–523°C in air, respectively. There is no significant difference in thermal stability as compared to the corresponding poly(amide-imide)s of the **V** series.

The glass transition temperatures ( $T_g$ s) of the poly(amide-imide)s **III<sub>a-m</sub>** ranged from 201 to 252°C. This order is quite comparable to the increasing order of rigidity and polarity of the polymer chains. As can be seen from Table V, the  $T_g$  values of all the poly(amide-imide)s **III** contain-

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

Polymer	$T_g^a$ (°C)	Decomposition Temp. <sup>b</sup> (°C)		Residual wt % at 800°C in N <sub>2</sub>
		in N <sub>2</sub>	in Air	
<b>III<sub>a</sub></b>	250 (255) <sup>c</sup>	503	511	54.3
<b>III<sub>b</sub></b>	216 (267)	511	511	63.0
<b>III<sub>c</sub></b>	246 (255)	506	506	64.3
<b>III<sub>d</sub></b>		503	501	64.4
<b>III<sub>e</sub></b>	231 (255)	495	498	61.9
<b>III<sub>f</sub></b>	234 (253)	497	506	60.0
<b>III<sub>g</sub></b>	219 (260)	503	515	62.9
<b>III<sub>h</sub></b>	234 (256)	511	516	60.0
<b>III<sub>i</sub></b>	226 (246)	516	506	60.0
<b>III<sub>j</sub></b>	201 (225)	513	523	61.4
<b>III<sub>k</sub></b>	233 (236)	520	514	55.7
<b>III<sub>l</sub></b>	252 (264)	500	516	54.3
<b>III<sub>m</sub></b>	236 (242)	517	509	57.0

<sup>a</sup> Baseline shifts in the second heating DSC traces at a heating rate of 10°C/min in nitrogen.

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

<sup>c</sup> Data in all the parentheses are those of the corresponding poly(amide-imide)s of the **V** series.

ing PIDA residues in the amide segment are slightly lower than those of the corresponding polymers **V** with PIDA residues in the imide segment of the polymer backbone. The difference in  $T_g$  between these two series of isomeric polymers may be a reflection of the deviation of interchain hydrogen bonding caused by the different lengths and structures of the amide segment.

## CONCLUSIONS

Poly(amide-imide)s **III** having moderate to high molecular weights were successfully prepared by the direct polycondensation of 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]dianiline (PIDA) with various aromatic bis(trimellitimide)s using triphenyl phosphite and pyridine as condensing agents. These polymers generally show good thermal stability and excellent solubility, and the cast films exhibit good tensile properties. The isomeric effect was observed between polymers **III** and **V** bearing the PIDA moiety in the amide and imide segment, respectively. The solubility behavior and thermal stability of polymers **III** were similar to the corresponding polymers **V**. Polymers **III** showed lower  $T_g$ s than the corresponding polymers **V**.

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

- Imai, Y.; Maldar, N.; Kakimoto, M. *J Polym Sci Part A: Polym Chem* 1985, 23, 2077.
- Wrasidlo, W.; Augl, J. M. *J Polym Sci Part A: Polym Chem* 1969, 7, 321.
- Kakimoto, M.; Akiyama, R.; Negi, Y. S.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1988, 26, 99.
- Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. U.S. Pat. 5,414,070, 1995, assigned to the National Science Council of the Republic of China.
- Yamazaki, N.; Matsumoto, M.; Higashi, F. *J Polym Sci Part A: Polym Chem* 1975, 13, 1373.
- (a) Yang, C.-P.; Hsiao, S.-H. *Makromol Chem* 1989, 190, 2219; (b) Hsiao, S.-H.; Yang, C.-P. *J Polym Sci Part A: Polym Chem* 1990, 28, 1149; (c) Hsiao, S.-H.; Yang, C.-P. *Makromol Chem* 1990, 191, 155; (d) Hsiao, S.-H.; Yang, C.-P. *J Polym Sci Part A: Polym Chem* 1990, 28, 2169; (e) Hsiao, S.-H.; Yang, C.-P. *J Polym Sci Part A: Polym Chem* 1991, 29, 449.
- (a) Yang, C.-P.; Yen, Y.-Y. *J Polym Sci Part A: Polym Chem* 1992, 30, 1855; (b) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. *J Polym Sci Part A: Polym Chem* 1992, 30, 1865; (c) Yang, C.-P.; Cheng, J.-M.; Hsiao, S.-H. *Makromol Chem* 1992, 193, 445; (d) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. *Makromol Chem* 1992, 193, 1299; (e) Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. *J Polym Sci Part A: Polym Chem* 1993, 31, 2995; (f) Yang, C.-P.; Chen, W.-T. *Makromol Chem* 1993, 194, 3071; (g) Yang, C.-P.; Chen, W.-T. *J Polym Sci Part A: Polym Chem* 1993, 31, 3081; (h) Yang, C.-P.; Chen, W.-T. *J Polym Sci Part A: Polym Chem* 1994, 32, 435; (i) Yang, C.-P.; Chen, W.-T. *J Polym Sci Part A: Polym Chem* 1994, 32, 1101; (j) Hsiao, S.-H.; Yang, C.-P.; Wu, F.-Y. *J Polym Sci Part A: Polym Chem* 1994, 32, 1481; (k) Yang, C.-P.; Lin, J.-H. *Polym Sci Part A: Polym Chem* 1994, 32, 2653; (l) Hsiao, S.-H.; Yang, C.-P.; Wu, F.-Y. *Macromol Chem Phys* 1994, 195, 2531; (m) Yang, C.-P.; Hsiao, S.-H.; Chen, C.-D. *J Polym Res* 1994, 1, 43; (n) Yang, C.-P.; Lin, J.-H. *Macromol Chem Phys* 1995, 196, 2979; (o) Yang, C.-P.; Lin, J.-H. *Macromol Chem Phys* 1995, 196, 3929; (p) Yang, C.-P.; Lin, J.-H. *Polym Int* 1995, 38, 335; (q) Yang, C.-P.; Hsiao, S.-H.; Chou, W.-L. *J Polym Res* 1995, 2, 179; (r) Hsiao, S.-H.; Yang, C.-P.; Fan, J.-C. *Macromol Chem Phys* 1995, 196, 3053; (s) Yang, C.-P.; Hsiao, S.-H.; Tsai, M.-R. *J Polym Res* 1998, 5, 23.
- Kataoka, T.; Tamai, M.; Oikawa, H.; Yamaguchi, T. (Mitsui Toatsu Chemical Inc.) *Jpn. Kokai Yokkyo Koho JP 04,183,722*, 1992.
- Hsiao, S.-H.; Chang, C.-F. *J Polym Res* 1996, 3, 31.
- Hsiao, S.-H.; Yang, C.-P.; Fan, J.-C. *Macromol Chem Phys* 1995, 196, 3041.
- Hsiao, S.-H.; Yang, C.-P.; Fan, J.-C. *J Polym Res* 1996, 1, 345.
- Kataoka, T.; Ohta, M.; Yamaguchi, T. (Mitsui Toatsu Chemicals Inc.), *Jpn. Kokai Tokkyo Koho JP 03,185,023*, 1992.
- Asanuma, T.; Oikawa, H.; Oikawa, Y.; Yamasita, W.; Matsuo, M.; Yamaguchi, A. *J Polym Sci Part A: Polym Chem* 1994, 32, 2111.
- Tamai, M.; Oikawa, J.; Yamashita, W.; Yamaguchi, T. (Mitsui Toatsu Chemicals Inc.), *Jpn. Kokai Tokkyo Koho JP 08,106,096*, 1996.
- Okawa, Y.; Koga, N.; Oikawa, H.; Asanuma, T.; Yamaguchi, A. (Mitsui Toatsu Chemicals Inc.), *Eur. Pat. Appl. EP 564,299*, 1994.
- Kataoka, T.; Tamai, M.; Oikawa, H.; Yamaguchi, T. (Mitsui Toatsu Chemicals Inc.), *Jpn. Kokai Tokkyo Koho JP 04,183,722*, 1993.
- Yang, C.-P.; Hsiao, S.-H.; Lin, J.-H. U.S. Pat. 5,268,487, 1993, assigned to the National Science Council of the Republic of China.