

# Synthesis and Characterization of New Rigid-Rod and Organosoluble Poly(amide-imide)s Based on 1,4-Bis(trimellitimido)-2,3,5,6-tetramethylbenzene

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**ABSTRACT:** A series of new aromatic poly(amide-imide)s (PAIs) was synthesized by triphenyl phosphite-activated polycondensation of the diimide-diacid, 1,4-bis(trimellitimido)-2,3,5,6-tetramethylbenzene (**I**), with various aromatic diamines in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), pyridine, and calcium chloride. The PAIs had inherent viscosities of 0.82–2.43 dL/g. The diimide-diacid monomer (**I**) was prepared from 2,3,5,6-tetramethyl-*p*-phenylenediamine with trimellitic anhydride (TMA). Most of the resulting polymers showed an amorphous nature and were readily soluble in a variety of organic solvents including NMP, *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylformamide (DMF). Transparent, flexible, and tough films of these polymers could be cast from DMAc solutions. Their cast films had tensile strengths ranging from 80 to 95 MPa, elongation at break from 10 to 45%, and initial modulus from 2.01 to 2.50 GPa. The 10% weight loss temperatures of these polymers were above 510°C in nitrogen. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1162–1170, 2000

**Key words:** aromatic poly(amide-imide)s; 1,4-bis(trimellitimido)-2,3,5,6-tetramethylbenzene; solubility; thermal behavior

## INTRODUCTION

The major limitations of aromatic polyimides for the versatile applications are their high melting or glass transition temperatures and limited solubility in organic solvents. To overcome these drawbacks, some copolymers have been proposed, in particular, for poly(amide-imide)s (PAIs) and poly(ether-imide)s. This class of polymers seems to be a good compromise between thermostability

and processability.<sup>1–4</sup> Conventionally, trimellitic anhydride (TMA)-based PAIs could be prepared in several ways such as two-step polycondensation from the acid chloride of TMA with aromatic diamines involving polyaddition and subsequent cyclodehydration,<sup>5</sup> low-temperature solution polycondensation of TMA-derived imide-ring-preformed diacid chlorides and aromatic diamines,<sup>6–9</sup> and polycondensation of TMA or TMA-derived imide-ring-containing dicarboxylic acids with diisocyanates.<sup>10–12</sup> Other synthetic routes of PAIs included the polymerization of *N,N'*-bis(trimethylsilyl)-substituted aromatic diamines with 4-chloroformylphthalic anhydride,<sup>13</sup> the palladium-catalyzed carbonylation and coupling of aromatic diamines and diimide-containing diiodides,<sup>14</sup> as well

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as the simultaneous catalytic amidation and imidization of TMA derived *o*-ester acids.<sup>15</sup>

Recently, we successfully applied a phosphorylation reaction<sup>16</sup> to the synthesis of high-molecular-weight PAIs by the direct polycondensation of imide-containing dicarboxylic acids with aromatic diamines using triphenyl phosphite (TPP) and pyridine (Py) as condensing agents.<sup>17–25</sup> The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in the laboratory preparation of aramids. Very recently, in a continuation of this study, we were interested in the potential usefulness of a substituent-containing *p*-phenylene structure as a simultaneously bulky and symmetrical unit in the polymer main chain. We reported that the PAIs containing monomethyl-substituted *p*-phenylene units show improved solubility with retention of a high thermal stability.<sup>26</sup> To obtain more insight into the effect of different substituted numbers on properties of PAIs, 1,4-bis(trimellitimidido)-2,3,5,6-tetramethylbenzene was synthesized in the present study. The novel PAIs were prepared by direct polycondensation of the diimide–diacid with various aromatic diamines. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers were also investigated.

To make a comparison of the effect of the introduction of a bulky group on the solubility behavior with above-mentioned corresponding PAIs derived from 1,4-bis(trimellitimidido)-2,3,5,6-tetramethylbenzene, PAIs derived from 1,4-bis(trimellitimidido)benzene without a methyl substituent were also synthesized in present study.

## EXPERIMENTAL

### Materials

2,3,5,6-Tetramethyl-*p*-phenylenediamine (from TCI), TMA (from Wako), and TPP (from TCI, Tokyo, Japan) were used without further purification. Commercially obtained anhydrous calcium chloride was dried under a vacuum at 150°C for 6 h. *N*-Methyl-2-pyrrolidone (NMP) and Py were purified by distillation under reduced pressure over calcium hydride and stored over a 4 Å molecular sieve. *p*-Phenylenediamine (**IIa**, from Wako) and *m*-phenylenediamine (**IIb**, from TCI) were distilled under a vacuum before use. All other diamines such as 2,4-diaminotoluene (**IIc**, from TCI), 4,4'-methylenedianiline (**IIId**, from TCI), 4,4'-oxydianiline (**IIe**, from TCI), 3,4'-oxy-

dianiline (**IIf**, from Teijin Ltd., Tokyo), 4,4'-thio-dianiline (**IIg**, from TCI), 1,4-bis(4-aminophenoxy)benzene (**IIh**, from TCI), and diamines including 1,3-bis(4-aminophenoxy)benzene (**IIi**), bis[4-(4-aminophenoxy)phenyl]sulfone (**IIj**), 2,2-bis-[4-(4-aminophenoxy)phenyl]propane (**IIk**), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**IIl**) were obtained from the Chriskev Corp. and used without further purification.

### Monomer Synthesis: 1,4-Bis(trimellitimidido)-2,3,5,6-tetramethylbenzene (**I**)

A mixture of 4.92 g (30 mmol) of 2,3,5,6-tetramethyl-*p*-phenylenediamine and 11.55 g (60 mmol) of TMA were dissolved in 80 mL of dry NMP 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 1.1 mL of the water was distilled off azeotropically under a Dean–Stark trap. Heating was continued to distill off the residual toluene. After cooling, the white precipitate of diimide–diacid (**I**) was isolated by filtration and washed with methanol. The product obtained was dried under a vacuum, affording 14.6 g (95% yield) of white powders; mp 461–462°C (by DSC).

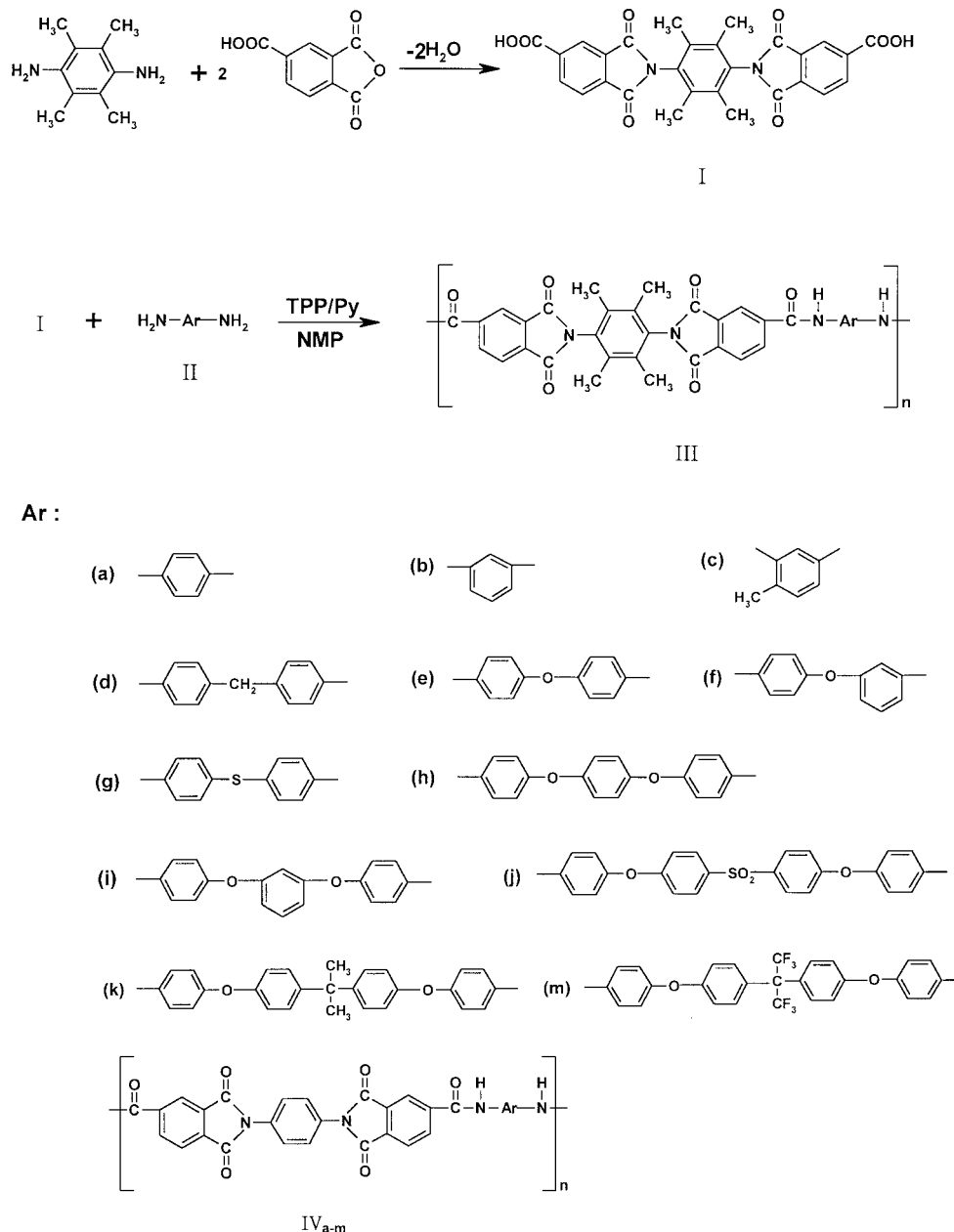
ANAL. Calcd for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>O<sub>8</sub>: C, 65.62%; H, 3.93%; N, 5.47%. Found: C, 64.95%; H, 4.15%; N, 5.11%.

### Polymerization

A typical example of polycondensation is as follows: A mixture of 0.200 g (1.0 mmol) of diamine **IIe**, 0.512 g (1.0 mmol) of diimide–diacid **I**, 0.30 g of calcium chloride, 5 mL of NMP, 1.0 mL of Py, and 0.6 mL of TPP was heated at 100°C for 3 h. The obtained polymer solution was trickled into 300 mL of methanol. The stringy polymer was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100°C under a vacuum. The yield was 0.69 g (99%). The inherent viscosity of the polymer was 1.37 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C. Other PAIs were synthesized analogously.

### Characterization

Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analysis was run in a Perkin–Elmer Model 240 C,H,N analyzer. Inherent viscosities of all the polymers were determined at a 0.5 g/dL concentration using a Cannon–Fenske viscosimeter. Thermogravimetric analysis was conducted



Scheme 1

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  $20^\circ\text{C}/\text{min}$ . 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  $20^\circ\text{C}/\text{min}$ . Thermomechanical analysis (TMA) was performed at a heating rate of  $10^\circ\text{C}/\text{min}$  with a DuPont 2000 device. Wide-angle X-ray diffractograms were ob-

tained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 15 mA), and the scanning rate was  $4^\circ/\text{min}$ . Measurements were performed with film specimens of about 0.1 mm in thickness. An Instron Universal Tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples at a drawing speed of 5 cm/min. Measurements were performed at room temperature (ca.  $20^\circ\text{C}$ ) with the 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.

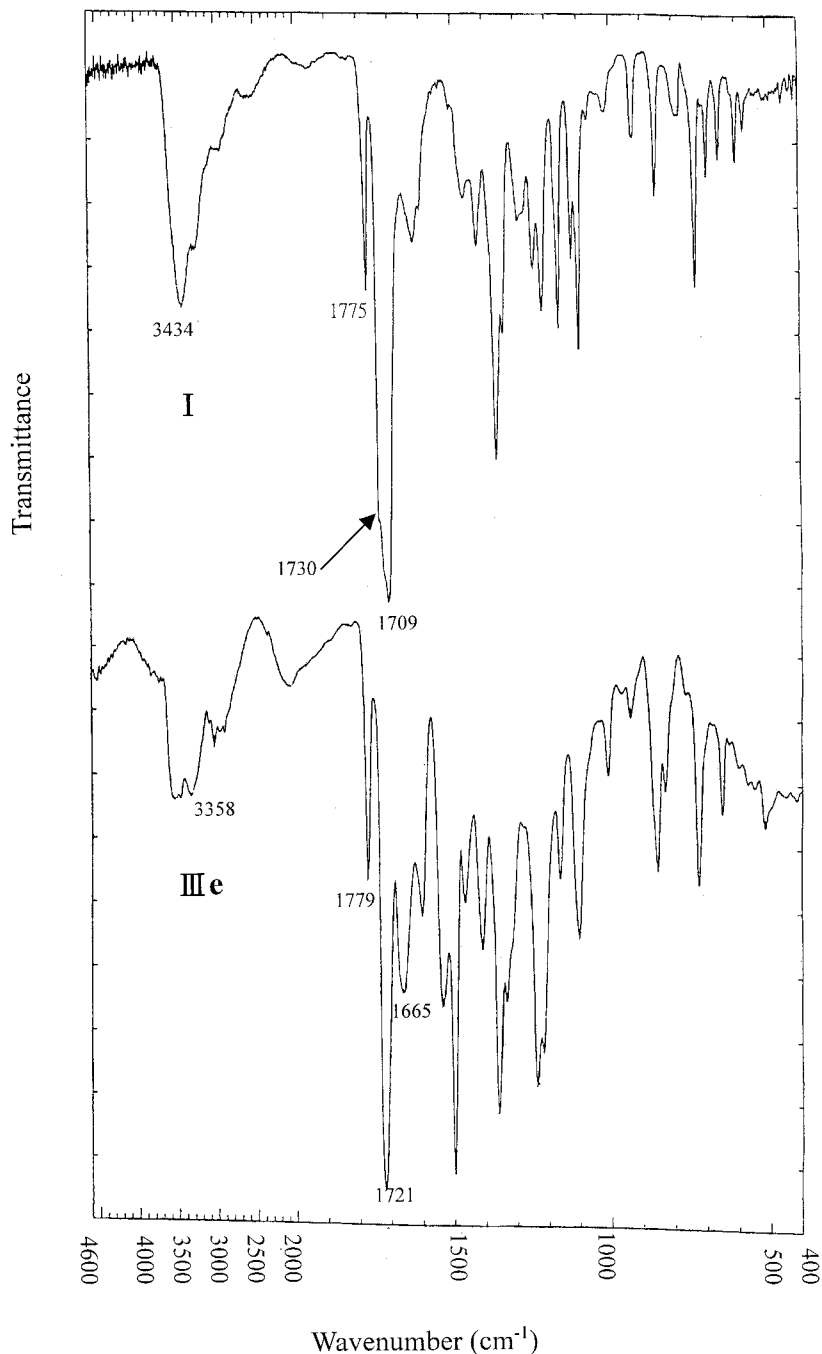


Figure 1 IR spectra of diimide-diacid (I) and PAI (IIIe).

## RESULTS AND DISCUSSION

### Synthesis

1,4-Bis(trimellitimido)-2,3,5,6-tetramethylbenzene (I), the novel PAI-forming diimide-diacid with preformed imide rings, was synthesized via a two-stage procedure that included ring-opening addition of 2,3,5,6-tetramethyl-*p*-phenylenediamine with two

equivalents of TMA, followed by cyclodehydration to the imidodicarboxylic acid by toluene-water azeotropic distillation (Scheme 1). The FTIR spectrum (KBr) of the dicarboxylic acid (I) showed absorption bands at 3450–3200  $\text{cm}^{-1}$  (acid —OH), 1775  $\text{cm}^{-1}$  (imide, symmetric C=O stretching), 1730  $\text{cm}^{-1}$  (asymmetric imide C=O stretching), and 1709  $\text{cm}^{-1}$  (acid C=O stretching) (Fig. 1).

**Table I** Preparation of PAIs from Diimide–Diacid I and Various Aromatic Diamines

Polymer	Amount of Reagents Used					Polymer Appearance
	NMP (mL)	CaCl <sub>2</sub> (g)	Py (mL)	TPP (mL)	$\eta_{inh}^a$ (dL/g)	
<b>IIIa</b>	6	0.5	1.2	0.6	2.43 <sup>b</sup>	Stringy
<b>IIIb</b>	5	0.34	1.1	0.6	1.17	Stringy
<b>IIIc</b>	4.5	0.3	1.0	0.6	0.82	Stringy
<b>IIId</b>	4.5 + 1	0.3	1.0	0.6	1.14	Stringy
<b>IIIe</b>	5	0.3	1.0	0.6	1.37	Stringy
<b>IIIf</b>	4.2	0.3	1.0	0.6	1.09	Stringy
<b>IIIg</b>	5	0.3	1.0	0.6	1.19	Stringy
<b>IIIh</b>	5 + 1	0.32	1.0	0.6	1.15	Stringy
<b>IIIi</b>	5	0.3	1.0	0.6	1.57	Stringy
<b>IIIj</b>	5 + 1	0.3	1.0	0.6	1.01	Stringy
<b>IIIk</b>	5	0.3	1.0	0.6	2.15	Stringy
<b>IIIl</b>	5	0.3	1.0	0.6	1.07	Stringy

Polymerization was carried out with 1.0 mmol of each monomer at 100°C for 3 h.

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

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

A series of new PAIs (**IIIa–m**) containing the 2,3,5,6-tetramethyl-*p*-phenylene unit was prepared from diimide–diacid **I** and various aromatic diamines **IIa–m** by the direct polycondensation reaction using TPP and Py as condensing agents (Scheme 1). The reaction conditions and results of the polycondensation are summarized in Table I. These polymers were obtained in almost a quantitative yield with inherent viscosities of 0.82–2.43 dL/g. The solubility of the polymer solution and the state of stirring affected the inherent viscosity of the resulting PAIs 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 adding a proper amount of supplementary NMP into the viscous reaction medium before the formation of a swollen gel. All the molecular weights of these polymers are sufficiently high to permit casting tough and flexible films.

The formation of PAIs was confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these polymers are listed in Table II. In all cases, however, the found values of carbon were lower than the calculated values for the proposed structures. This may be attributed to the hygroscopic characteristics of the amide group. The moisture intake for PAIs **IIIa–m** was in the range of 3.33–6.78% at room temperature

and normal pressure in our laboratory. The corrected values were in good agreement with the calculated ones after deducting the amount of moisture intake. The IR spectra of the polymers exhibited characteristic absorptions for the imide ring at 1779 and 1721 cm<sup>-1</sup>, peculiar to the symmetrical and asymmetrical carbonyl stretching vibration. Bands of amide groups appeared at 3358 cm<sup>-1</sup> (N–H) and 1665 cm<sup>-1</sup> (C=O) (Fig. 1).

#### Properties of Polymers

Table III shows the qualitative solubility of the PAIs in various solvents. Most polymers were soluble in aprotic polar solvents such as DMAc, NMP, and DMF and even in less polar solvents like Py and *m*-cresol. However, polymer **IIIa** with a rigid and symmetrical *p*-phenylene structure showed somewhat limited solubility. This may be due to the semicrystalline nature of polymer **IIIa**, as evidenced by an X-ray diffractogram discussed later. All the polymers were insoluble in common organic solvents such as tetrahydrofuran, chloroform, acetone, and toluene. The solubility behavior of the new PAIs derived from the diimide–diacid (**I**) and aromatic diamines was compared with that of the corresponding PAIs derived from 1,4-bis(trimellitimidio)benzene without a methyl-substituent and is also summarized in Table III. Thus, the solubility of PAIs was found to be greatly improved by the introduction of a bulky 2,3,5,6-tetramethyl-substituent into the *p*-phenylene unit along the polymer backbone.

**Table II** Elemental Analysis of PAIs

Polymers	Formula (Molecular Weight)	Elemental Analysis <sup>a</sup> (%)			Moisture Intake (%) <sup>b</sup>	
			C	H		N
<b>IIIa</b>	$(C_{34}H_{24}N_4O_6)_n$ (584.59) <i>n</i>	Calcd	69.86	4.14	9.58	6.07
		Found	65.62	4.51	8.61	
		Corrected	69.60	4.24	9.13	
<b>IIIb</b>	$(C_{34}H_{24}N_4O_6)_n$ (584.59) <i>n</i>	Calcd	69.86	4.14	9.58	6.23
		Found	65.51	4.70	8.43	
		Corrected	69.59	4.41	8.96	
<b>IIIc</b>	$(C_{35}H_{86}N_4O_6)_n$ (598.61) <i>n</i>	Calcd	70.23	4.38	9.36	6.78
		Found	65.47	4.70	8.43	
		Corrected	69.91	4.38	9.00	
<b>III d</b>	$(C_{41}H_{30}N_4O_6)_n$ (674.71) <i>n</i>	Calcd	72.99	4.48	8.30	5.86
		Found	68.71	4.87	7.30	
		Corrected	72.74	4.58	7.73	
<b>IIIe</b>	$(C_{40}H_{28}N_4O_7)_n$ (676.68) <i>n</i>	Calcd	71.00	4.17	8.28	6.04
		Found	66.71	4.57	7.44	
		Corrected	70.74	4.29	7.89	
<b>III f</b>	$(C_{40}H_{28}N_4O_7)_n$ (676.68) <i>n</i>	Calcd	71.00	4.17	8.28	5.07
		Found	67.40	4.56	7.59	
		Corrected	70.82	4.33	7.97	
<b>III g</b>	$(C_{40}H_{28}N_4O_6S)_n$ (692.75) <i>n</i>	Calcd	69.35	4.07	8.09	5.38
		Found	65.62	4.50	7.23	
		Corrected	69.15	4.26	7.62	
<b>III h</b>	$(C_{46}H_{32}N_4O_8)_n$ (768.78) <i>n</i>	Calcd	71.87	4.20	7.29	4.88
		Found	68.36	4.55	6.74	
		Corrected	71.70	4.33	7.07	
<b>III i</b>	$(C_{46}H_{32}N_4O_8)_n$ (768.78) <i>n</i>	Calcd	71.87	4.20	7.29	4.72
		Found	68.48	4.68	6.59	
		Corrected	71.71	4.46	6.90	
<b>III j</b>	$(C_{52}H_{36}N_4O_{10}S)_n$ (908.95) <i>n</i>	Calcd	68.71	3.99	6.16	4.09
		Found	65.90	4.39	5.50	
		Corrected	68.60	4.21	5.72	
<b>III k</b>	$(C_{55}H_{42}N_4O_8)_n$ (886.96) <i>n</i>	Calcd	74.48	4.77	6.32	3.49
		Found	71.88	5.05	5.68	
		Corrected	74.39	4.87	5.88	
<b>III m</b>	$(C_{55}H_{36}N_4O_8F_6)_n$ (994.90) <i>n</i>	Calcd	66.40	3.65	5.63	3.33
		Found	64.19	4.09	4.96	
		Corrected	66.33	3.95	5.13	

<sup>a</sup> For C and N: corrected value = found value  $\times$  (100% + moisture intake %). For H: corrected value = found value  $\times$  (100% - moisture intake %)

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

The crystallinity of the prepared PAIs was measured by wide-angle X-ray diffraction studies. Typical diffraction patterns for some representative polymers are presented in Figure 2. Polymer **IIIa** revealed a fair degree of crystallinity. This can be attributed to the existence of symmetrical *p*-phenylene segments and rigid planar imide rings in the polymer backbones that led to a better packing of the polymer chains, whereas all the other polymers showed a completely amorphous

pattern. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, which is in agreement with the general rule that the solubility decreased with increasing crystallinity. In addition, the solubility behavior of the new PAIs (**IIIa–m**) derived from 1,4-bis(trimellitimido)-2,3,5,6-tetramethylbenzene (**I**) with aromatic diamines was compared with those of the corresponding PAIs<sup>26</sup> prepared from 2,5-bis(trimellitimido)toluene. The solubility of the

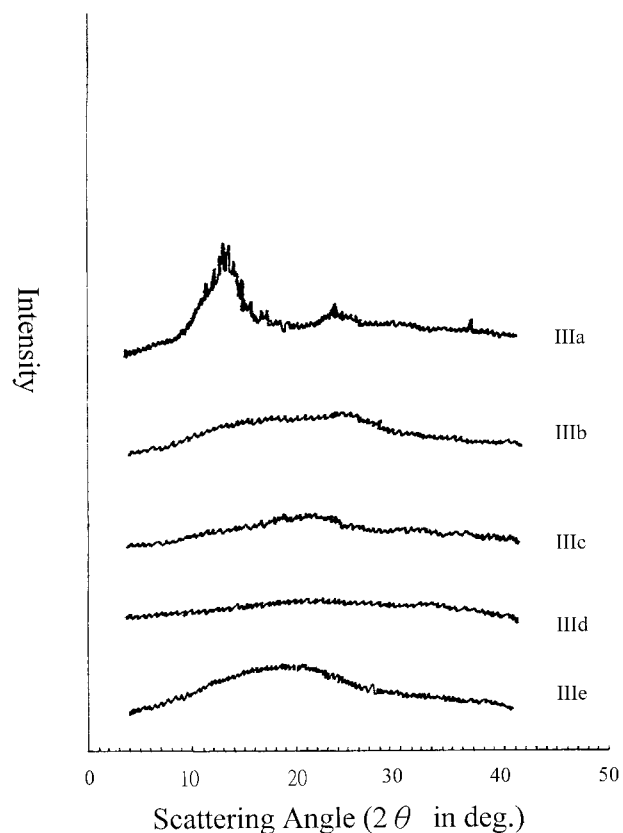
**Table III Solubility of PAIs**

Polymer	Solvent <sup>a</sup>						
	DMAc	DMAc +5 wt % LiCl	NMP	DMF	DMSO	Py	<i>m</i> -Cresol
<b>IIIa</b>	–	+	–	–	–	–	–
<b>IIIb–f</b>	+	+	+	+	+	+	–
<b>IIIg</b>	+	+	+	–	–	–	–
<b>IIIh,i</b>	+	+	+	+	–	+	–
<b>IIIj–m</b>	+	+	+	+	+	+	+
<b>IVa,k</b>	–	–	–	–	–	–	–
<b>IVb,c</b>	–	+	–	–	–	–	–
<b>IVd–i</b>	–	–	–	–	–	–	–
<b>IVj,m</b>	–	+	–	–	–	–	–

<sup>a</sup> Solubility: (+) soluble at room temperature; (–) insoluble.

<sup>b</sup> DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide.

above-mentioned tetramethyl-substituent *p*-phenylene-containing PAIs (**IIIa–m**) was found to have better solubility than that of the 2-methyl-*p*-phenylene-containing PAIs.<sup>26</sup> This phenomenon is because the former should be able to further lower the interchain interactions or prevent the polymer chains from close packing.



**Figure 2** Wide-angle X-ray diffractograms of PAIs **IIIa–e**.

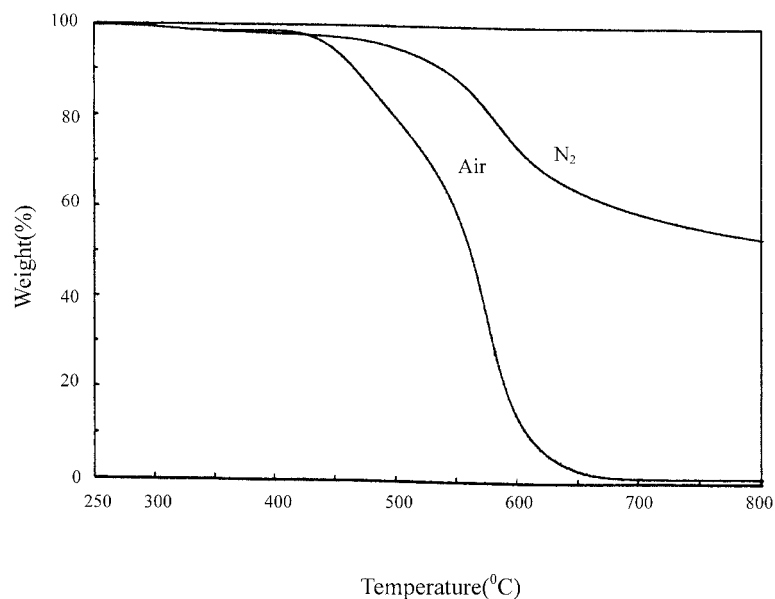
Transparent, flexible, and yellowish films could be cast from the DMAc or NMP solutions of most PAIs and were subjected to a tensile test. The tensile properties of these polymers are summarized in Table IV. These films had tensile strengths of 80–95 MPa, elongation to break of 10–45%, and an initial modulus of 2.01–2.50 GPa. Some of the polymers yielded during tensile testing and had a fairly high elongation to break, indicative of high toughness.

The thermal stability of the PAIs was studied by thermogravimetric analysis (TGA). Typical TGA curves in both air and nitrogen atmospheres of representative PAI **IIIe** are shown in Figure 3. The temperatures of 10% weight loss in nitrogen

**Table IV Tensile Properties of PAI Films**

Polymer	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
<b>IIIa</b>	—	—	—
<b>IIIb</b>	88	39	2.30
<b>IIIc</b>	93	26	2.50
<b>III d</b>	90	13	2.38
<b>IIIe</b>	80	20	2.18
<b>III f</b>	84	45	2.36
<b>III g</b>	83	12	2.26
<b>III h</b>	80	43	2.01
<b>III i</b>	95	14	2.48
<b>III j</b>	82	28	2.14
<b>III k</b>	83	10	2.28
<b>III m</b>	90	21	2.11

Polymer films were prepared by slow evaporation of their DMAc solutions at 90°C for 12 h, followed by vacuum drying at 150°C for 10 h.



**Figure 3** TGA curves for PAI **IIIe** with a heating rate of 20°C/min.

and air atmospheres were determined from original thermograms and are tabulated in Table V. In general, all the polymers exhibited a high thermal stability with no significant weight loss up to temperatures of approximately 450°C in nitrogen, and their 10% weight loss temperatures were recorded in the range of 510–540°C in nitrogen and

445–480°C in air. The amount of carbonized residue (char yield) of PAIs in the nitrogen atmosphere was in the range of 51–60% weight even at 800°C, showing high intrinsic fire-retardant characteristics. Thermal properties of these PAIs **IIIa–m** measured by TMA are shown in Table V. The observed softening transition temperatures

**Table V** Thermal Behavior of PAIs

Polymer	TGA				
	TMA <sup>a</sup> $T_s$ (°C)	DSC <sup>b</sup> $T_g$ (°C)	Decomposition Temperature (°C) <sup>c</sup>		Wt % Residue <sup>d</sup> at 800°C in N <sub>2</sub>
			In Air	In Nitrogen	
<b>IIIa</b>	343	— <sup>e</sup>	480	540	55
<b>IIIb</b>	338	—	465	520	56
<b>IIIc</b>	351	—	465	520	56
<b>III d</b>	303	—	460	525	56
<b>IIIe</b>	325	—	450	520	53
<b>III f</b>	329	—	460	535	58
<b>III g</b>	320	—	460	510	51
<b>III h</b>	292	—	445	530	56
<b>III i</b>	313	—	450	540	60
<b>III j</b>	325	—	460	510	54
<b>III k</b>	308	—	445	530	56
<b>III m</b>	283	—	465	520	54

<sup>a</sup> Softening temperature measured by TMA at a heating rate of 10°C/min.

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

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

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

<sup>e</sup> No  $T_g$  was observed in DSC traces.



( $T_g$ ) were in the range of 283–351°C, depending on the structure of the diamine component, and decreased with decreasing rigidity of the polymer backbone or with introduction of flexible linkages in the polymer main chain. In addition, the glass transition temperatures ( $T_g$ 's) of these PAIs were measured in the second heating traces of the DSC. Although these polymers revealed a completely amorphous pattern by X-ray diffractograms, no  $T_g$  was observed in the second heating run of the DSC. This may be due to the restricted rotation about the bond joining the 2,3,5,6-tetramethyl-*p*-phenylene aromatic ring systems, resulting in a more rigid-rod-like conformation. Thus, the 2,3,5,6-tetramethyl-*p*-phenylene-based PAIs should have higher  $T_g$ 's than those of the 2-methyl-*p*-phenylene-based analogs, which were in the range of 253–328°C.<sup>26</sup>

## CONCLUSIONS

A series of new high molecular weight aromatic PAIs based on the diimide–diacid 1,4-bis(trimellitimidio)-2,3,5,6-tetramethylbenzene was successfully prepared by direct polycondensation with various aromatic diamines using TPP and Py as condensing agents. Typical PAIs were non-crystalline. The introduction of the bulky and symmetrical 2,3,5,6-tetramethyl-*p*-phenylene unit into the polymer backbone led to significantly improved solubility of the polymer in various organic solvents. Most of these polymers exhibited a desired combination of properties required for high-performance materials that include excellent mechanical properties, high thermal stability, and excellent solubility in organic solvents for fabrication.

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