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Synthesis and properties of new poly(amide-imide)s based on 2,5-bis(trimellitimido)toluene

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Summary

A series of new aromatic poly(amide-imide)s were synthesized by the triphenyl phosphite activated polycondensation of the diimide-diacid, 2,5-bis(trimellitimido)toluene (**I**) with various aromatic diamines. The poly(amide-imide)s had inherent viscosities of 0.69-1.89 dL/g. Most of the resulting polymers showed an amorphous nature and were readily soluble in a variety of organic solvents. Transparent, flexible, and tough films of these polymers could be cast from DMAc or NMP solutions. Their cast films had tensile strengths ranging from 76 to 112 MPa, elongations at break from 8 to 31%, and initial moduli from 2.20 to 2.99 GPa. The glass transition temperatures of these polymers were in the range of 253-328°C.

Introduction

Wholly aromatic poly(amide-imide)s (PAIs) are an important class of materials having excellent resistant to high temperatures and favorable balance of other physical and chemical properties (1,2). However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms due to their high melting or glass transition temperatures and limited solubility in organic solvents. Conventionally, 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(3), low-temperature solution polycondensation of TMA-derived imide ring-preformed diacid chlorides and aromatic diamines(4-7), polycondensation of TMA or TMA-derived imide ring-containing dicarboxylic acids with diisocyanates(8-10). Recently, we have successfully applied phosphorylation reaction(11) 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(12-16). The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in manufacturing operations compared with conventional methods.

Recently, in a continuation of these studies, we are interested in the potential usefulness of substituent-containing p-phenylene structure as simultaneously bulky and symmetrical unit in the polymer main chain. However, only a limited number of poly(ester-imide)s derived from the diimide-diacid, 2,5-bis(trimellitimido)toluene, with bisphenols had been reported earlier(17) and have not been investigated in detail. The

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present article describes the synthesis of a series of novel poly(amide-imide)s from 2,5-bis(trimellitimido)toluene and various aromatic diamines. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers will also be investigated.

In order to get more insight into the effect of the introduction of bulky group on properties of poly(amide-imide)s, 1,4-bis(trimellitimido) benzene was also synthesized in present study and the diimide-diacid was used to prepare poly(amide-imide)s to make a comparison of the solubility behavior with above mentioned corresponding poly(amide-imide)s derived from 2,5-bis(trimellitimido)toluene.

Experimental

Materials

2-Methyl-p-phenylenediamine dihydrochloride (from TCI), trimellitic anhydride (from Wako) and triphenyl phosphite (from TCI) were used without further purification. Commercially obtained anhydrous calcium chloride was dried under vacuum at 150°C for 6 h. N-methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride. p-Phenylenediamine (**IIa**) and m-phenylenediamine (**IIb**) were distillated under vacuum befored use. All other reagent-grade diamines were used without further purification.

Monomer Synthesis

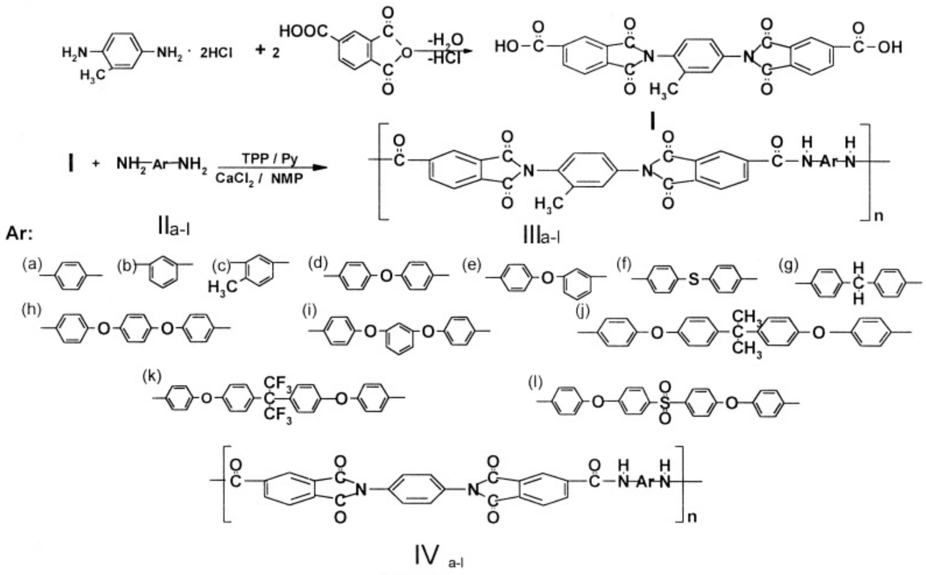
2,5-Bis(trimellitimido)toluene **(I)**

A mixture of 5.85g (30 mmol) of 2-methyl-p-phenylenediamine dihydrochloride and 11.55g (60 mmol) of trimellitic anhydride 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 water was distillated off azeotropically under a Dean-Stark trap. Heating was continued to distill off the residue toluene. After cooling, the white precipitate of diimide-diacid (**I**) was isolated by filtration and washed with methanol. The product obtained was dried under vacuum affording 12.4g (87% yield) of white powders; mp 369-370°C.

ANAL. Calcd for $\mathbf{C_{25}H_{14}N_2O_8}$: C, 63.77%; H, 3.19%; N, 5.93%. Found: C, 63.37%, H, 3.16%; N, 5.82%.

Polymerization

A typical example of polycondensation follows: A mixture of 0. 112 g (1.0 mmol) of diamine **IIc**, 0.470 g (1.0 mmol) of diimide-diacid **I**, 0.30 g of calcium chloride, 4.5 mL of NMP, 1.0 mL of pyridine, and 0.6 mL of triphenyl phosphite was heated at 100°C for 3 h. The obtained polymer solution was trickled into 200 mL of methanol. The 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 1.10 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C. Other Poly(amide-imide)s were synthesized analogously.



Scheme 1

Characterization
Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analysis were run in a Perkin-Elmer model 240 C,H,N, analyzer. Inherent viscosities of all polymers were determined at 0.5 g/dL concentration using Cannon-Fenske viscosimeter. Thermogravimetric analysis was conducted with a Rigaku thermal analysis station TAS-100. Measurements were performed with 10 ± 2 mg samples heated in flowing nitrogen (50 cm^3/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 cm^3/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 CuK_α radiation (40 kV, 15 mA), and the scanning rate was 4°/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 were used for this study. Measurements were performed at room temperature (ca. 20°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

Synthesis
2,5-Bis(trimellitimido)toluene (**I**), the novel poly(amide-imide)s-forming diimide-diacid with preformed imide rings, was synthesized via the two-stage procedure that included ring-opening addition of 2-methyl-p-phenylenediamine dihydrochloride with two equivalent amount of trimellitic anhydride, followed by cyclodehydration to the imidodicarboxylic acid by toluene-water azeotropic distillation (Scheme 1). The FT-IR spectrum (KBr) of the dicarboxylic acid (**I**) showed absorption bands at 3320 cm^{-1} (acid -OH), 1780 cm^{-1} (imide, symmetric C=O stretching), 1724 cm^{-1} (acid C=O stretching and asymmetric imide C=O stretching).

A series of new poly(amide-imide)s (**III**$_{a-l}$) containing 2-methyl-p-phenylene unit were prepared from diimide-diacid **I** and various aromatic diamines **II**$_{a-l}$ by the direct polycondensation reaction using triphenyl phosphite and pyridine as condensing agents (Scheme 1). The reaction condition and results of the polycondensation are summarized in Table 1. These polymers were obtained in almost quantitative yield with inherent viscosities of 0.69-1.89 dL/g. The solubility of the polymer solution 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 adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of swollen gel. Most of the molecular weights of these polymers are sufficiently high to permit casting tough and flexible films.

The formation of poly(amide-imide)s was confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these polymers are listed in Table 2. In all cases, however, the found values of carbon were lower than the calculated values for the proposed structures. These may be attributed to the hygroscopic characteristics of amide group. The moisture intake for poly(amide-imide)s **IIIa-l** was in the range of 0.89-3.32% 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 1780 and 1720 cm^{-1}, peculiar to the symmetrical and asymmetrical carbonyl stretching vibration. Bands of amide groups appeared at 3358 cm^{-1} (N-H) and 1654 cm^{-1} (C=O).

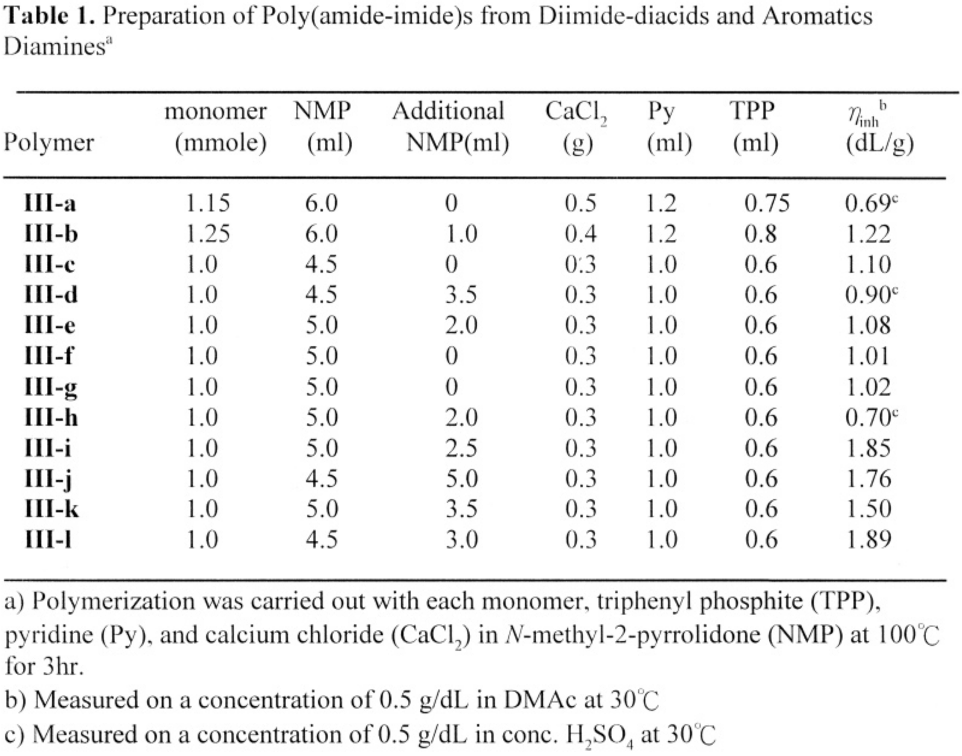


Table 1. Preparation of Poly(amide-imide)s from Diimide-diacids and Aromatics Diamines[a]

Polymer	monomer (mmole)	NMP (ml)	Additional NMP(ml)	$CaCl_2$ (g)	Py (ml)	TPP (ml)	η_{inh}[b] (dL/g)
III-a	1.15	6.0	0	0.5	1.2	0.75	0.69[c]
III-b	1.25	6.0	1.0	0.4	1.2	0.8	1.22
III-c	1.0	4.5	0	0.3	1.0	0.6	1.10
III-d	1.0	4.5	3.5	0.3	1.0	0.6	0.90[c]
III-e	1.0	5.0	2.0	0.3	1.0	0.6	1.08
III-f	1.0	5.0	0	0.3	1.0	0.6	1.01
III-g	1.0	5.0	0	0.3	1.0	0.6	1.02
III-h	1.0	5.0	2.0	0.3	1.0	0.6	0.70[c]
III-i	1.0	5.0	2.5	0.3	1.0	0.6	1.85
III-j	1.0	4.5	5.0	0.3	1.0	0.6	1.76
III-k	1.0	5.0	3.5	0.3	1.0	0.6	1.50
III-l	1.0	4.5	3.0	0.3	1.0	0.6	1.89

a) Polymerization was carried out with each monomer, triphenyl phosphite (TPP), pyridine (Py), and calcium chloride ($CaCl_2$) in *N*-methyl-2-pyrrolidone (NMP) at 100℃ for 3hr.

b) Measured on a concentration of 0.5 g/dL in DMAc at 30℃

c) Measured on a concentration of 0.5 g/dL in conc. H_2SO_4 at 30℃

Table 2. Elemental Analysis of Poly(amide-imide)s

Polymers	Formula (Molecular Weight)	Elemental Analysis[a](%)				Moisture Intake(%)[b]
			C	H	N	
IIIa	$(C_{30}H_{14}N_4O_6Cl_2)n$	Calcd	60.33	2.37	9.38	4.33
	(597.24)n	Found	57.18	3.15	8.32	
		Corrected	59.66	3.01	8.68	
IIIb	$(C_{30}H_{14}N_4O_6Cl_2)n$	Calcd	60.33	2.37	9.38	4.49
	(597.24)n	Found	57.08	2.98	8.38	
		Corrected	59.88	2.84	8.79	
IIIc	$(C_{36}H_{18}N_4O_7Cl_2)n$	Calcd	62.71	2.63	8.13	3.42
	(689.30)n	Found	60.25	3.11	7.79	
		Corrected	62.31	3.00	8.06	
IIId	$(C_{36}H_{18}N_4O_7Cl_2)n$	Calcd	62.71	2.63	8.13	2.68
	(689.30)n	Found	60.40	3.06	7.46	
		Corrected	62.62	2.88	7.73	
IIIe	$(C_{37}H_{20}N_4O_6Cl_2)n$	Calcd	64.64	2.93	8.15	4.41
	(687.31)n	Found	61.79	3.26	7.52	
		Corrected	64.51	3.11	7.85	
IIIf	$(C_{36}H_{20}N_4O_6SCl_2)n$	Calcd	61.29	2.57	7.94	3.25
	(705.37)n	Found	59.30	3.00	7.84	
		Corrected	61.22	2.90	8.10	
IIIg	$(C_{42}H_{22}N_4O_8Cl_2)n$	Calcd	64.55	2.84	7.17	3.31
	(781.36)n	Found	62.41	3.20	7.33	
		Corrected	64.48	3.09	7.57	
IIIh	$(C_{42}H_{22}N_4O_8Cl_2)n$	Calcd	64.45	2.84	7.17	3.00
	(781.36)n	Found	62.61	3.27	7.42	
		Corrected	64.48	3.17	7.38	
IIIi	$(C_{51}H_{32}N_4O_8Cl_2)n$	Calcd	68.08	3.58	6.23	1.35
	(899.45)n	Found	67.16	3.89	5.97	
		Corrected	68.06	3.83	6.00	
IIIj	$(C_{51}H_{26}N_4O_8Cl_2F_6)n$	Calcd	60.79	2.60	5.56	1.28
	(1007.45)n	Found	60.01	2.99	5.25	
		Corrected	60.77	2.95	5.32	

a) For C and N : corrected value = found value × (100% + moisture intake%)
For H : corrected value = found value × (100% - moisture intake%)
b) Moisture intake(%) = $(W-W_0)/W_0 \times 100\%$
W = weight of polymer sample after standing at room temperature.
W_0 = weight of polymer sample after dried in vacuum at 100℃ for 10 hr.

Table 3. Solubility of Poly(amide-imide)s[a]

Polymer	DMAc	DMAc +5%LiCl	NMP	DMF	DMSO	m-cresol	pyridine	conc H_2SO_4
III-a,h	–	–	–	–	–	–	–	+
III-b,g	+	+	+	–	+	–	–	+
III-c,l	+	+	+	+	+	+	–	+
III-d	–	–	+	–	–	–	–	+
III-e,f,i	+	+	+	+	–	–	–	+
III-j,k	+	+	+	+	+	+	+	+
IV-a,d	–	–	–	–	–	–	–	+
IV-h~j	–	–	–	–	–	–	–	+
IV-b,c	–	+	–	–	–	–	–	+
IV-k,l	–	+	–	–	–	–	–	+

a) Solubility:(+) soluble at room temperature; (-) insoluble. DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethylsulfoxide.

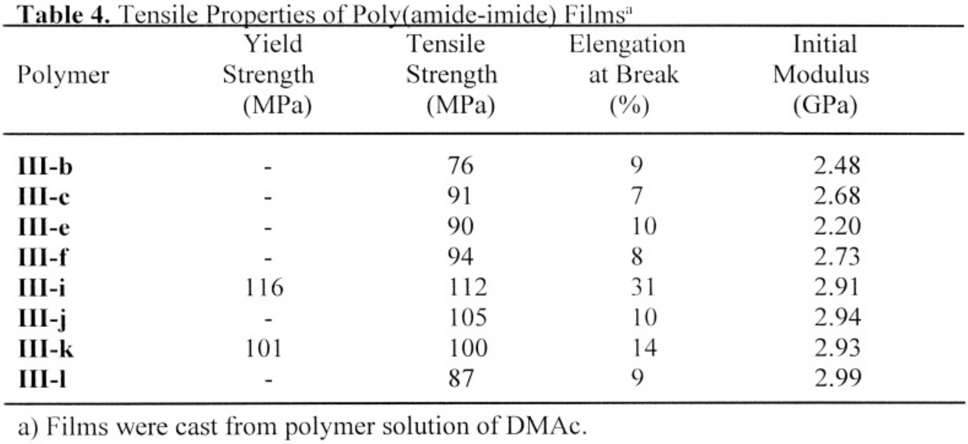


Table 4. Tensile Properties of Poly(amide-imide) Films[a]

Polymer	Yield Strength (MPa)	Tensile Strength (MPa)	Elengation at Break (%)	Initial Modulus (GPa)
III-b	-	76	9	2.48
III-c	-	91	7	2.68
III-e	-	90	10	2.20
III-f	-	94	8	2.73
III-i	116	112	31	2.91
III-j	-	105	10	2.94
III-k	101	100	14	2.93
III-l	-	87	9	2.99

a) Films were cast from polymer solution of DMAc.

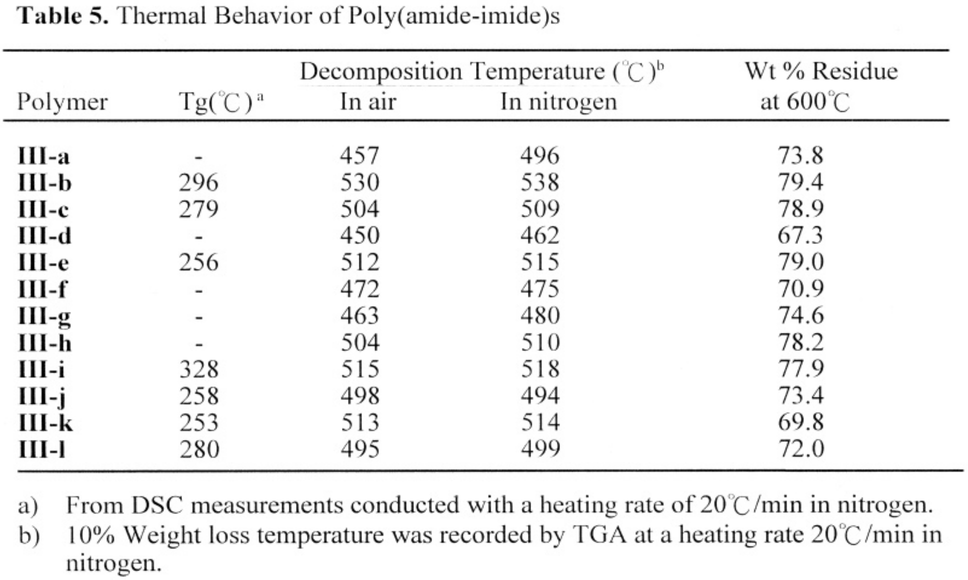


Table 5. Thermal Behavior of Poly(amide-imide)s

Polymer	Tg(℃)[a]	Decomposition Temperature (℃)[b] In air	Decomposition Temperature (℃)[b] In nitrogen	Wt % Residue at 600℃
III-a	-	457	496	73.8
III-b	296	530	538	79.4
III-c	279	504	509	78.9
III-d	-	450	462	67.3
III-e	256	512	515	79.0
III-f	-	472	475	70.9
III-g	-	463	480	74.6
III-h	-	504	510	78.2
III-i	328	515	518	77.9
III-j	258	498	494	73.4
III-k	253	513	514	69.8
III-l	280	495	499	72.0

a) From DSC measurements conducted with a heating rate of 20℃/min in nitrogen.
b) 10% Weight loss temperature was recorded by TGA at a heating rate 20℃/min in nitrogen.

Properties of Polymers

Table 3 shows the qualitative solubility of the PAIs in various solvents. Most polymers were soluble in aprotic polar solvents such as DMAc, NMP, DMF, and even in less polar solvents like m-cresol and pyridine; however, polymer **IIIa, IIId,** and **IIIh** with symmetrical p-phenylene and flexible ether linkage connecting para-aromatic ring structure, respectively, had somewhat limited solubility. This may be due to the semi-crystalline nature of these polymers, as evidenced by x-ray diffractograms discussed later. All the polymers are insoluble in common organic solvents such as chloroform, acetone, and benzene. The solubility behavior of the new poly(amide-imide)s derived from the diimide-diacid (**I**) with aromatic diamines were compared with those of the corresponding poly(amide-imide)s derived from diimide-diacid, 1,4-bis(trimellitimido)benzene, without methyl-substituent also summarized in Table 3. Thus, the solubility of poly(amide-imide)s was found to be greatly improved by the introduction of a bulky methyl-substituent into phenylene unit along polymer backbone.

The crystallinity of the prepared poly(amide-imide)s was measured by wide-angle X-ray diffraction studies. Figure.1 revealed that polymer **IIIa, IIId,** and **IIIh** had a fair degree of crystallinity, exhibiting crystalline peaks at around 15° and 25°, whereas all of the other polymers showed 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 decrease with increasing crystallinity. The semi-crystalline behavior of the above polymer was speculated that the introduction of rigid-rod p-phenylene (**IIa**) and flexible ether linkage connecting para-aromatic ring structure (**IId, IIh**).

Transparent, flexible, and yellowish films could be cast from the DMAc or NMP solutions of most PAIs and were subjected to tensile test. The tensile properties of some typical PAIs are summarized in Table 4. These films had tensile strength of 76-112 MPa, elongation to break of 7-31%, and initial modulus of 2.20-2.99 GPa. Some of polymers yielded during tensile testing and had fairly high elongation to break, indicative of high toughness.

The thermal stability of the poly(amide-imide)s was studied by thermogravimetric analysis (TGA). The temperatures of 10% weight loss in nitrogen and air atmosphere were determined from orginal thermograms and tabulated in Table 5. In general, all the polymers exhibited good thermal stability with no significant weight loss up to temperatures of approximately 400°C in nitrogen, and their 10% weight loss temperatures were recorded in the range of 460-540°C in nitrogen and 450-530°C in air, respectively. The amount of carbonized residue (char yield) of poly(amide-imide)s in nitrogen atmosphere was in the range of 67-79% weight at 600°C, showing high intrinsic fire-retardant characteristics.

Table 5 also summarizes the thermal transition data of the poly(amide-imide)s. Quenching from the elevated temperatures to room temperature in air yields more amorphous samples so that in most cases the glass transition temperatures (Tgs) could be easily measured in the second heating traces of DSC. The Tgs of the poly(amide-imide)s were in the range of 253-328°C. A broad melting (Tm) endotherm peak of polymer **IIIj** could be observed on its first DSC trace. Although the as-precipitated polymer melted, they failed to crystallize under the condition of the DSC measurement and exhibited clear Tgs in second heating runs. No cold crystallization was observed above Tg. Thus, it appears that the initial crystallinity results from the presence of solvent and the way the material was precipitated.

Conclusions

A series of new high molecular weight aromatic poly(amide-imide)s based on the diimide-diacid, 2,5-bis(trimellitimido)toluene, were successfully prepared by direct polycondensation with various aromatic diamines. Typical poly(amide-imide)s were noncrystalline. The introduction of bulky and symmetrical 2-methyl-p-phenylene unit into the polymer backbone lead to significantly improve solubility of the polymer in various organic solvents. Most of these polymers exhibited a desired combination of properties requiring for high performance materials that include good mechanical properties, high thermal stability, excellent solubility in organic solvents, and high Tgs.

Acknowledgment

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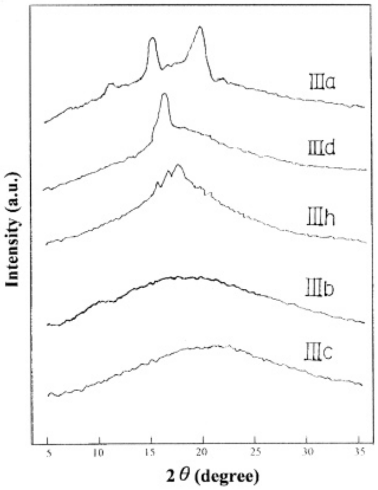

Figure. 1: Wide-angle X-ray diffrarogarms of some poly(amide-imide)s

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