Synthesis and characterization of new aromatic poly(amide–imide)s derived from 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene and various bis(trimellitimide)s ☆

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Abstract

A series of novel *t*-butyl group-containing poly(amide–imide)s **III$_{a-m}$** were synthesized by the direct polycondensations of 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene (BAP-*t*BB) with various aromatic bis(trimellitimide)s **II$_{a-m}$** in *N*-methyl-2-pyrrolidone (NMP) using triphenyl phosphite and pyridine as condensing agents. Poly(amide–imide)s **III** having inherent viscosities between 0.67 and 1.77 dl g^{-1} were obtained in quantitative yields. Most of the resulting polymers were readily soluble in polar solvents such as NMP and *N*,*N*-dimethylacetamide. All of the soluble poly(amide–imide)s afforded transparent, flexible, and tough films. The glass transition temperatures of these polymers were in the range of 243–300°C, and the 10% weight loss temperatures were above 490°C in nitrogen. The properties of poly(amide–imide)s **III** were compared with those of the corresponding poly(amide–imide)s **III′** prepared from the bis(trimellitimide) of BAP-*t*BB and various aromatic diamines. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene; Bis(trimellitimide); Poly(amide–imide)s

1. Introduction

Aromatic polyimides are an important class of high-performance materials due to their excellent thermo-oxidative stability, mechanical strength, electrical properties, and high radiation and solvent resistance [1–3]. However, poor handling and intractable characteristics have been major problems due to high melting point and insolubility. To overcome this drawback, various copolyimides have been developed. For example, a poly(amide–imide) (PAI) was developed as one of alternative materials offering a compromise between excellent thermal stability and processability.

A number of PAIs have been synthesized through two main routes: via amide–imide-forming reaction from trimellitic anhydride, and through amide-forming reaction from imide-containing monomers such as imide-preformed dicarboxylic acid or their acid chlorides [4]. One of the more facile approaches to prepare PAIs with high molecular weights is the direct polycondensation between imide-bearing dicarboxylic acids with aromatic diamines following the Yamazaki–Higashi phosphorylation technique [5–7]. The direct polycondensation route avoids using moisture-sensitive acid chlorides or isocyanates and provides significant advantages in laboratory preparation of

PAIs as well as aromatic polyamides. Thus, several series of novel PAIs have been easily synthesized by this convenient technique in our laboratory [8–14]. Furthermore, this synthetic approach to PAIs can offer us the option of introduction of specific diamine residues between amide or imide groups into the polymer backbone. The incorporation of such diamine residues may provide an easy method of controlling the physical properties of PAIs.

Polyamides were reported from the *t*-butylhydroquinone-based diamine, 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene (BAP-*t*BB), that have been claimed to possess the potential application as gas separation membranes [15]. Recently, it has been reported that incorporating the diamine residue of BAP-*t*BB into polyimide backbones led to a relative decrease in T_g and crystallinity; however, the polyimides obtained from BAP-*t*BB only showed limited enhancement in solubility with less rigid dianhydrides [16]. Very recently, we have demonstrated that the poly(amide–imide)s (**III′**) prepared from the bis(trimellitimide) of BAP-*t*BB with aromatic diamines showed a significant solubility with retention of high thermal stability [14]. As a continuation of our efforts on screening new, easily tractable poly(amide–imide)s, the present article describes the synthesis of a series of novel poly(amide–imide)s obtained from BAP-*t*BB and the bis(trimellitimide)s of various aromatic diamines. A comparative study on the properties of the two analogous series of poly(amide–imide)s, **III** and **III′**, is also presented.

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2. Experimental

2.1. Materials

Trimellitic anhydride (TMA, Wako) was used without previous purification. According to a well-developed procedure [17], 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene (BAP-*t*BB) (mp 129–130°C) was synthesized from the chloro-displacement reaction of *t*-butylhydroquinone and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction with a 10% Pd–C catalyst and hydrazine hydrate. *p*-Phenylenediamine (**I$_a$**, Wako), *m*-phenylenediamine (**I$_b$**, TCI) were vacuum-distilled and benzidine (**I$_d$**, TCI) was recrystallized prior to use. The other diamines: 2,4-diaminotoluene (**I$_c$**, TCI), 3,3′-dimethyl-4,4′-diamonobiphenyl (**I$_e$**, TCI), 4,4′-oxydianiline (**I$_f$**, TCI), 3,4′-oxydianiline (**I$_g$**, Teijin, Tokyo) 4,4′-thiodianiline (**I$_h$**, TCI), 4,4′-methylenedianiline (**I$_i$**, TCI), 1,4-bis(4-aminophenoxy)benzene (**I$_j$**, TCI), 1,3-bis(4-aminophenoxy)benzene (**I$_k$**, Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**I$_l$**, TCI), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**I$_m$**, TCI) were used without any further purification. Diimide-dicarboxylic acids **II$_{a-m}$** were obtained by a procedure described previously [18] from TMA and the corresponding diamines. *N*-methyl-2-pyrrolidone (NMP, Fluka), *N,N*-dimethylacetamide (DMAc, Fluka), *N,N*-dimethylformamide (DMF, Fluka), and pyridine (Py, Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP, TCI) was purified by vacuum-distillation. Commercially-obtained calcium chloride (CaCl$_2$, Wako) was dried under vacuum at 180°C for 10 h.

2.2. Polymerization

Synthesis of PAI **III$_f$** is described as a typical procedure. A mixture of 0.217 g (0.625 mmol) of diamine BAP-*t*BB, 0.125 g (0.625 mmol) of diimide–diacid **II$_f$**, 0.36 g of calcium chloride, 4 ml of NMP, 1.0 ml of pyridine and 0.4 ml of TPP were heated with stirring at 100°C. An additional 1.5 ml of NMP was added as the solution became too viscous such that the magnetic stirrer could no longer work. After 4 h of stirring at 100°C, the resulting polymer solution was poured slowly into 100 ml of stirring methanol giving rise to a stringy, fiber-like precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried under vacuum at 100°C. The yield was 0.34 g (99%). Inherent viscosity of the polymer **III$_f$** was 1.49 dl g^{-1}, as measured in DMAc at 30°C on 0.5 g dl^{-1}.

All other PAIs were synthesized in an analogous procedure.

2.3. Measurements

Elemental analyses were run in a Perkin–Elmer Model 2400 C, H, N, analyzer. Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier-transform Infrared Spectrometer. The inherent viscosities were measured using a Cannon-Fenske viscosimeter at 30°C. DSC traces were obtained with a TA Instrument DSC 2010 at the rate of 20°C min^{-1} in flow nitrogen (40 cm^3 min^{-1}). Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 10±2 mg samples heated in flowing nitrogen 50 cm^3 min^{-1} at a heating rate of 20°C min^{-1}. A LLOYD instrument with a load cell of 500 N was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a strain rate of 5 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.05 mm thick), and an average of at least five individual determinations was used.

3. Results and discussion

3.1. Polymer synthesis

Poly(amide–imide)s with perfectly alternating (amide–amide)-(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 [14], the diamine BAP-*t*BB served as a specific diamine and was first condensed with TMA to give a bis(trimellitimide) **II′** (Scheme 1), which was directly polycondensated with various aromatic diamines to prepare PAIs **III′$_{a-m}$** having BAP-*t*BB residues in the imide segments. In the present study, another series of analogous PAIs **III$_{a-m}$** bearing BAP-*t*BB residues in the amide segments were synthesized from diamine BAP-*t*BB with various aromatic diamines-derived bis(trimellitimide)s **II$_{a-m}$**. These polymers were synthesized by the triphenyl phosphite-activated method, the same as that used in the synthesis of PAIs **III′$_{a-m}$**.

Synthesis conditions and inherent viscosities of the produced polymers are shown in Table 1. With the exception of **III$_a$** and **III$_d$**, all polymerizations proceeded in homogeneous, transparent, and viscous solutions throughout the reaction, and the PAIs were isolated as fibers or powders in quantitative yields. Inherent viscosities for **III$_a$** and **III$_d$** were 0.75 and 0.67 dl g^{-1} in concentrated sulfuric acid, and for the other PAIs it ranged from 0.94 to 1.77 dl g^{-1} in DMAc, indicating high molecular weight polymers. In general, the molecular weight of the polymer obtained from the phosphorylation reaction is highly dependent on the reactant concentration. According to our earlier papers [8–14], it was repeatedly observed that the higher the concentration of monomers, the higher was the final inherent viscosity if no precipitation or gelation of the product from the reaction medium took place. It was anticipated that the bulky pendant *t*-butyl group and flexible ether group-containing PAIs **III** would have increased solubility in the reaction media and a higher reactant concentration could be tolerated dur-
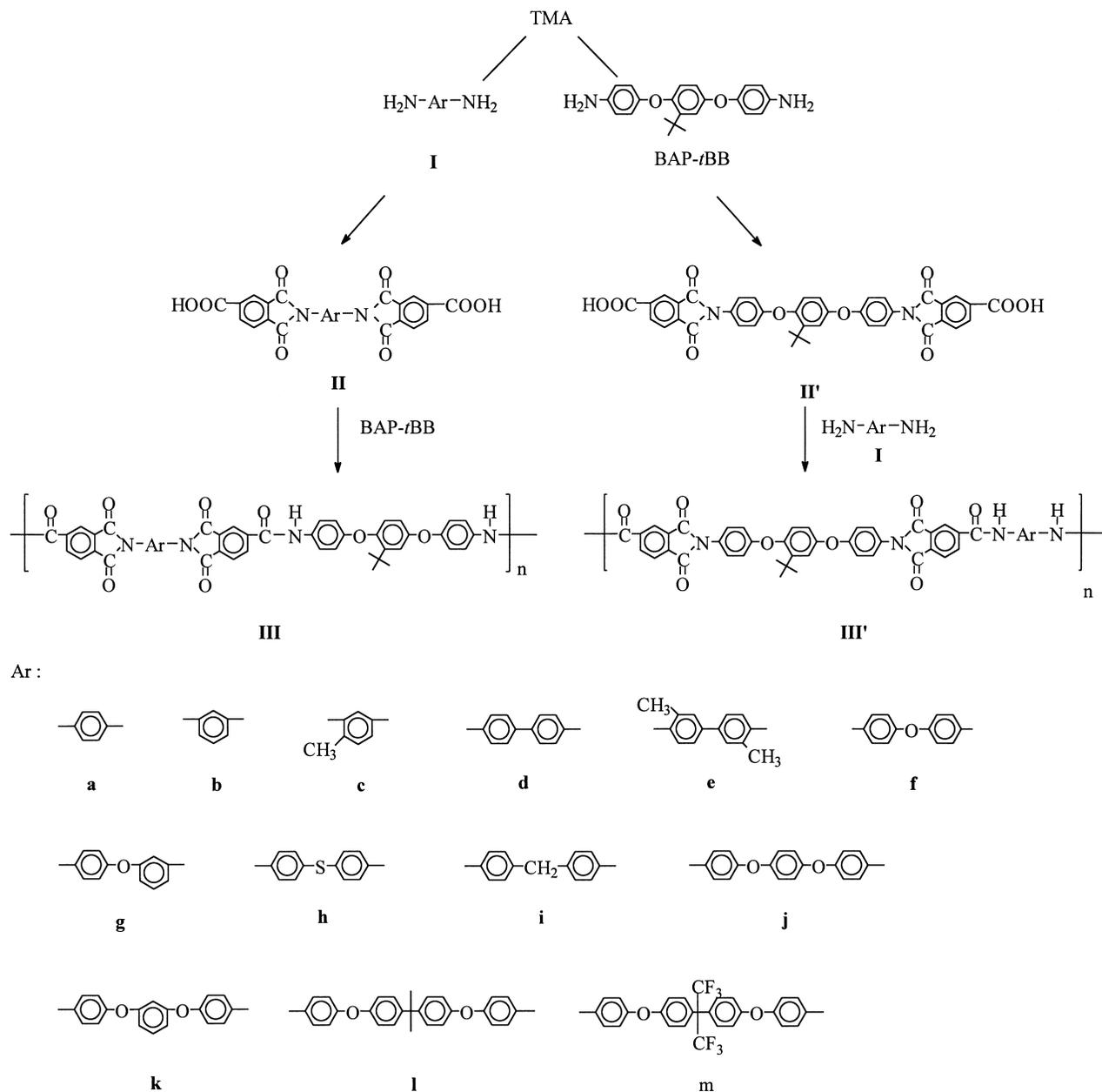
Scheme 1. Polycondensation of poly(amide–imide)s.

ing the polymerization. In some cases such as **III_f**, **III_i**, and **III_l**, higher inherent viscosities of the polymers could be obtained by using a higher initial reaction concentration and adding an additional amount of NMP to the highly viscous reaction medium before the formation of swollen gel. However, in the cases of **III_a** and **III_d**, an early precipitation occurred during polymerization, and increasing the amount of CaCl$_2$ 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, and the polymers showed a lower inherent viscosity. The unsatisfactory results may be attributed to their

poor solubility, due to the presence of rigid planar imide segments in their polymer backbone, leading to better packing of polymer chains. For comparison, the inherent viscosities of the corresponding **III′** are also listed in Table 1.

PAI structures were verified by IR spectroscopy and elemental analysis. Representative FTIR spectra of isomeric PAIs **III_b** and **III′_b** are shown in Fig. 1. The IR spectrum shows characteristic absorptions for the imide ring at 1779 and 1724 cm^{-1}, due to the asymmetrical and symmetrical carbonyl stretching vibration, and at 1110 and 726 cm^{-1}, due to ring deformation. As can be seen from Fig. 1, even though the spectra of these two isomeric PAIs look very similar, the relative strengths and positions of some absorp-

Table 1
Synthesis of poly(amide–imide)s

Polymer	Amount of each monomer (mmol)	Amounts of reagents used[a]					η_{inh}[b] (dl g^{-1})	Remarks[c]
		NMP (ml)	Additional NMP (ml)	Py (ml)	TPP (ml)	CaCl$_2$ (g)		
III$_a$	1.250	6.0	–	1.8	0.80	0.50	0.75[d] (1.11)	Powder
III$_b$	1.000	6.0	–	1.2	0.60	0.43	1.01 (1.04)	String
III$_c$	1.000	4.5	–	1.0	0.60	0.38	1.05	String
III$_d$	1.250	6.0	–	1.8	0.80	0.52	0.67[d] (1.10[d])	Powder
III$_e$	1.000	5.5	–	1.2	0.60	0.37	1.34	String
III$_f$	0.625	4.0	1.5	1.0	0.40	0.36	1.49 (1.25)	String
III$_g$	1.000	5.0	–	1.2	0.60	0.39	1.42	String
III$_h$	1.000	5.0	–	1.2	0.60	0.35	1.21 (1.02)	String
III$_i$	0.625	4.0	1.0	0.8	0.40	0.37	1.10 (1.01)	String
III$_j$	0.625	4.0	–	1.0	0.40	0.35	1.26 (0.98)	String
III$_k$	0.625	4.0	–	0.8	0.40	0.35	1.38 (1.27)	String
III$_l$	0.625	4.0	3.0	0.8	0.40	0.28	1.77 (1.45)	String
III$_m$	0.625	4.0	–	0.8	0.40	0.23	0.94 (1.03)	String

[a] Polymerization was carried out at 100°C for 3 h.

[b] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C, unless otherwise indicated. Data in parentheses are the values of the corresponding isomeric III′ polymers reported in [14].

[c] Appearance of the polymer product when precipitated in stirred methanol.

[d] Measured at a concentration of 0.5 g dl^{-1} in concentrated H$_2$SO$_4$ at 30°C.

tions also can be distinguished in the spectra. The elemental analysis values of PAIs **III** are listed in Table 2. In most cases, the found values of carbon and nitrogen were lower than the calculated ones for the proposed structures, but the hydrogen values were found to be higher. This may be due to the hygroscopic nature of the amide group. The moisture intakes for these PAIs were in the range of 2.17–3.64% 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.
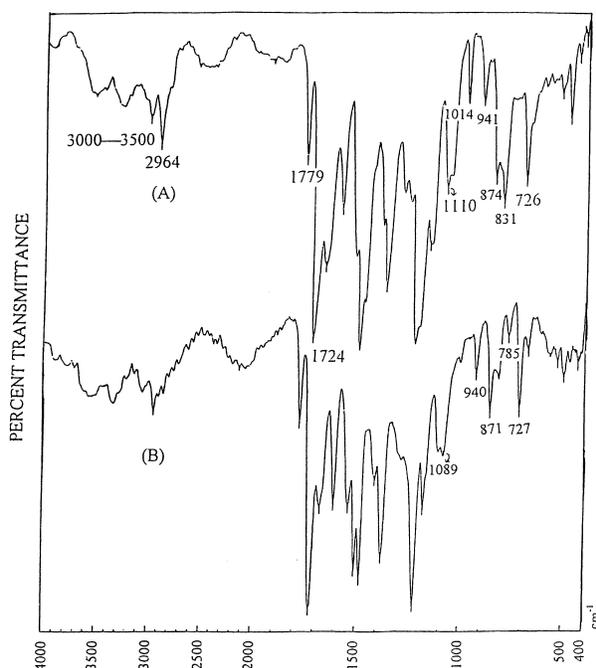

Fig. 1. FTIR spectra of PAIs: (A) **III$_b$** and (B) **III$_b$′**.

3.2. Polymer properties

The qualitative solubility of the PAIs **III** in various solvents was shown in Table 3. Most polymers were soluble in aprotic dipolar solvents such as NMP, DMAc, DMF and DMSO, and even in less polar *m*-cresol and pyridine. PAIs **III$_l$** and **III$_m$** were also soluble in THF, probably due to their non-planar structures and low cohesive energies caused by the –CH$_3$ and –CF$_3$ groups. The improved solubility of these polymers as compared to that of related PAIs [12] can be explained by the presence of the pendant *t*-butyl groups. Due to these groups, the packing of polymer chains in tight structures through hydrogen bonding between amide groups is probably disturbed and, consequently, the solvent molecules can penetrate easily to solubilize the chains. PAIs **III$_a$** and **III$_d$** were insoluble in all the tested solvents, probably due to the presence of rigid planar 1,4-bis(phthalimido)phenylene or 4,4′-bis(phthalimido)biphenylene units in the polymer main chain. Although the aromatic rings of diamine BAP-*t*BB cannot be co-planar, poor solubility of PAIs **III$_a$** and **III$_d$** indicates either strong intermolecular interactions or good packing ability. A comparison of the solubilities of the polymers **III** with the corresponding polymers **III′** shows that differ only by incorporation of the BAP-*t*BB moiety in the amide or imide segment, their solubilities are virtually identical in most cases. The slight solubility differences between **III$_a$** and **III$_a$′** and **III$_d$** and **III$_d$′** are believed to be related to the molecular rigidity in **III$_a$** and **III$_d$** due to the reason cited above.

The thermal properties of the polymers were evaluated using TGA and DSC. The results are summarized in Table 4. DSC measurements were conducted with a heating rate of 20°C min^{-1} in nitrogen. Quenching from an elevated tem-

Table 2
Elemental analysis of poly(amide–imide)s

Polymer	Formula (Molecular weight)		Elemental analysis[a] (%)			Moisture intake[b] (%)
			C	H	N	
$\mathbf{III_a}$	$(C_{46}H_{32}N_4O_8)_n$	Calculated	71.87	4.20	7.29	
	$(768.78)_n$	Found	72.72	4.39	6.87	3.55
		Corrected	71.12	4.32	7.11	
$\mathbf{III_b}$	$(C_{46}H_{32}N_4O_8)_n$	Calculated	71.87	4.20	7.29	
	$(768.78)_n$	Found	69.43	4.36	6.98	3.51
		Corrected	71.87	4.05	7.22	
$\mathbf{III_c}$	$(C_{47}H_{34}N_4O_8)_n$	Calculated	72.11	4.38	7.16	
	$(782.81)_n$	Found	69.51	4.47	6.90	3.64
		Corrected	72.04	4.31	7.15	
$\mathbf{III_d}$	$(C_{52}H_{36}N_4O_8)_n$	Calculated	73.92	4.29	6.63	
	$(844.88)_n$	Found	71.71	4.46	6.33	2.98
		Corrected	73.84	4.33	6.52	
$\mathbf{III_e}$	$(C_{54}H_{40}N_4O_8)_n$	Calculated	74.29	7.62	6.42	
	$(872.93)_n$	Found	74.74	4.59	6.23	3.45
		Corrected	74.22	4.43	6.44	
$\mathbf{III_f}$	$(C_{52}H_{36}N_4O_9)_n$	Calculated	72.55	4.21	6.51	
	$(860.88)_n$	Found	70.07	4.21	6.31	3.44
		Corrected	72.49	4.06	6.52	
$\mathbf{III_g}$	$(C_{52}H_{36}N_4O_9)_n$	Calculated	72.55	4.21	6.51	
	$(860.88)_n$	Found	69.94	4.24	6.27	3.53
		Corrected	72.41	4.09	6.49	
$\mathbf{III_h}$	$(C_{52}H_{36}N_4O_8S_1)_n$	Calculated	71.22	4.14	6.39	
	$(876.94)_n$	Found	69.29	4.12	6.20	2.59
		Corrected	71.08	4.01	6.36	
$\mathbf{III_i}$	$(C_{53}H_{38}N_4O_8)_n$	Calculated	74.12	4.46	6.52	
	$(858.91)_n$	Found	71.37	4.45	6.21	3.55
		Corrected	73.90	4.29	6.43	
$\mathbf{III_j}$	$(C_{58}H_{40}N_4O_{10})_n$	Calculated	73.10	4.23	5.88	
	$(952.98)_n$	Found	70.91	4.21	5.78	2.89
		Corrected	72.96	4.88	5.95	
$\mathbf{III_k}$	$(C_{58}H_{40}N_4O_{10})_n$	Calculated	73.10	4.23	5.88	
	$(952.98)_n$	Found	71.00	4.30	5.67	2.85
		Corrected	73.02	4.18	5.83	
$\mathbf{III_l}$	$(C_{67}H_{50}O_{10}N_4)_n$	Calculated	75.13	4.70	5.23	
	$(1071.15)_n$	Found	73.12	4.68	5.15	2.55
		Corrected	74.98	4.56	5.28	
$\mathbf{III_m}$	$(C_{67}H_{44}N_4O_{10}F_6)_n$	Calculated	68.25	3.76	4.75	
	$(1179.10)_n$	Found	66.73	3.83	4.67	2.17
		Corrected	68.18	3.75	4.77	

[a] For C and N: Corrected value=found value×(100%+moisture intake %). For H: Corrected value=found value×(100%−moisture intake %).

[b] Moisture intake (%)=$[(W-W_0)/W_0]\times100\%$; W=weight of polymer sample after standing at room temperature for 3 days, and W_0=weight of polymer sample after having dried in vacuum at 100°C for 10 h.

perature of about 450°C to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (T_g) of almost all PAIs could be easily measured in the second DSC heating traces. No discernible T_g was observed for PAI $\mathbf{III_e}$ by DSC. The other PAIs of the $\mathbf{III}$ series showed clear glass transitions between 243 and 300°C, following the decreasing order of chain flexibility and steric hindrance of the polymer backbones. In general, incorporation of less symmetric *m*-phenylene unit or flexible ether linkage leads to a decrease in T_g. For example, polymers $\mathbf{III_a}$, $\mathbf{III_f}$ and $\mathbf{III_j}$ which contain all *para*-substituted phenylene rings, have higher T_g, 282, 276, and 264°C, respectively, than do the analogous polymers $\mathbf{III_b}$, $\mathbf{III_g}$ and $\mathbf{III_k}$, which contain some *meta*-substituted phenylene units

and whose T_g are 276, 263, and 243°C, respectively. When comparing the T_g values of PAIs $\mathbf{III}$ with their analogous $\mathbf{III'}$, their T_g do not show any clear dependence on the site of the BAP-*t*BB moiety. Polymers $\mathbf{III_f}$, $\mathbf{III_i}$ and $\mathbf{III_j}$, which contain all *para*-substituted phenylene rings, showed higher T_g than their corresponding $\mathbf{III'}$ counterparts. However, polymers $\mathbf{III_b}$ and $\mathbf{III_k}$, which contain *m*-phenylene units, exhibited lower T_g compared to their $\mathbf{III'}$ analogs. The difference in T_g between these two series of analogous PAIs may be a reflection of the deviation of interchain hydrogen bonding caused by the different lengths and structures of the amide segment.

The thermal stability of the PAIs was characterized by TGA conducted at a heating rate of 20°C min^{-1}. The tem-

Table 3
Solubility behavior of poly(amide imide)s[a]

Polymer	Solvent[b]							
	NMP	DMAc	DMF	DMSO	m-Cresol	Py	THF	H$_2$SO$_4$
III$_a$	−	−	−	−	−	−	−	+
(**III$'_a$**)	(+)	(+)	(−s)	(+)	(−)	(−)	(−)	(+)
III$_b$	+	+	+	+	+	+	−	+
(**III$'_b$**)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)
III$_c$	+	+	+	+	+	+	−	+
III$_d$	−	−	−	−	−	−	−	+
(**III$'_d$**)	(±)	(±)	(−)	(−)	(−)	(−)	(−)	(+)
III$_e$	+	+	+	+	+	+	−	+
III$_f$	+	+	+	+	+	+	−	+
(**III$'_f$**)	(+)	(+)	(+)	(+)	(+)	(+)	(−)	(+)
III$_g$	+	+	+	+	+	+	−	+
III$_h$	+	+	+	±	+	+	−	+
(**III$'_h$**)	(+)	(+)	(+)	(+)	(+)	(+)	(±)	(+)
III$_i$	+	+	+	+	+	+	−	+
(**III$'_i$**)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)
III$_j$	+	+	+	+	+	+	−	+
(**III$'_j$**)	(+)	(+)	(+)	(+)	(+)	(+)	(−)	(+)
III$_k$	+	+	+	+	+	−s	−	+
(**III$'_k$**)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)
III$_l$	+	+	+	−s	+	+	+	+
(**III$'_l$**)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)
III$_m$	+	+	+	+	+	+	+	+
(**III$'_m$**)	(+)	(+)	(+)	(+)	(+)	(+)	(+)	(+)

[a] '+': soluble; '−': insoluble; '−s': swelling; '±': partially soluble. Solubility behavior indicated in parentheses is that of polymers **III'** reported in [14].

[b] NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide, DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide; Py: pyridine; THF: tetrahydrofuran.

Table 4
Thermal properties of poly(amide–imide)s

Polymer	$T_g{}^a$ (°C)	$T_{10}{}^b$ (°C)		Residual wt.% at 800°C in N$_2$
		In N$_2$	In air	
III$_a$	282 (286)[c]	528 (521)	511 (544)	64 (64)
III$_b$	276 (282)	512 (516)	525 (525)	60 (53)
III$_c$	300	506	506	55
III$_d$	280 (–)	510 (512)	504 (475)	60 (49)
III$_e$	–[d]	499	499	65
III$_f$	276 (262)	508 (525)	531 (530)	58 (65)
III$_g$	263	507	508	65
III$_h$	277 (272)	494 (490)	492 (496)	64 (60)
III$_i$	280 (256)	512 (511)	506 (521)	66 (68)
III$_j$	264 (228)	516 (517)	516 (522)	56 (59)
III$_k$	243 (266)	511 (520)	516 (522)	58 (62)
III$_l$	252 (252)	515 (510)	513 (518)	58 (55)
III$_m$	251 (260)	527 (521)	527 (521)	59 (58)

[a] Baseline shift in the second heating DSC traces, with a heating rate of 20°C min^{-1}.

[b] Decomposition temperatures at which 10% weight loss were recorded by TGA at a heating rate 20°C min^{-1}.

[c] Data in the parentheses are those of the corresponding isomeric poly(amide–imide)s of the **III'** series.
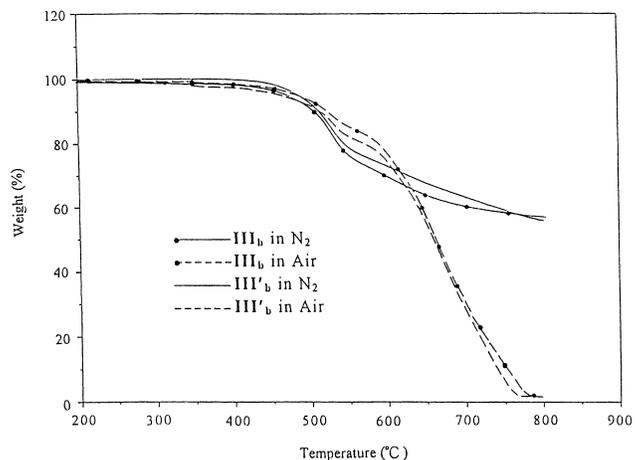
[d] Difficult to judge.

Fig. 2. TGA curves for PAIs **III$_b$** and **III$'_b$** at a heating rate of 20°C min^{-1}.

peratures at 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from the original thermograms and also tabulated in Table 4. The T_{10} of these PAIs stayed in the range of 494–528°C in nitrogen and 492–531°C in air, which are reasonable values considering the aliphatic content of these polymers. It is interesting to note that in some cases the temperature at which 10% weight loss occurred in air was higher than that in nitrogen. This may be attributable to an early weight-gained oxidation and possible oxidative interchain cross-linking of the aliphatic segments in the polymer chain when thermally degraded in air. There is no significant difference in thermal stability between polymers **III** and **III'**. Fig. 2 shows typical TGA curves of PAI **III$_b$** and its isomeric **III$'_b$**.

With the exception of organic-insoluble **III$_a$** and **III$_d$**, all the other PAIs possess outstanding film-forming properties. Transparent, flexible, and tough films could be obtained by casting polymer solutions from DMAc. Table 5 summarizes the tensile properties of the films of PAIs **III$_{a-m}$**. These films had tensile strengths of 55–107 MPa, elongations to break of 7–65%, and initial moduli of 1.8–2.9 GPa. Some PAIs such as **III$_{f-m}$**, which contain more flexible links in the polymer chain, showed clear yield points on their stress–strain curves and moderate elongations to break, indicative of high toughness.

4. Conclusion

Poly(amide–imide)s having moderate to high inherent viscosities were successfully prepared by the direct polycondensation of 1,4-bis(4-aminophenoxy)-2-t-butylbenzene (BAP-tBB) with various aromatic bis(trimellitimide)s by means of triphenyl phosphite and pyridine. These polymers generally showed good thermal stability and excellent solubility, and the cast films exhibited excellent tensile properties. Thus, the present poly(amide–imide)s are con-

Table 5
Tensile properties of poly(amide–imide) films[a]

Polymer	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
III$_b$	–	103	8	2.9
III$_c$	–	107	8	2.9
III$_e$	–	96	7	2.7
III$_f$	85	84	22	2.3
III$_g$	93	87	65	2.4
III$_h$	79	70	32	1.8
III$_i$	99	83	29	2.6
III$_j$	86	81	21	2.5
III$_k$	79	55	18	2.1
III$_l$	88	78	12	2.5
III$_m$	85	80	28	2.5

[a] Films were cast from slow evaporation of the polymer solutions in DMAc.

sidered as new candidates for processable high-performance polymeric materials.

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