

New Poly(amide-imide) Syntheses XXII. Synthesis and Properties of Poly(amide-imide)s Based on 1,4-Bis(4-trimellitimidophenoxy)-2-*t*-butylbenzene and Aromatic Diamines

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ABSTRACT: A diimide dicarboxylic acid, 1,4-bis(4-trimellitimidophenoxy)-2-*t*-butylbenzene (**I**), was prepared by the condensation of 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene (BAP-*t*BB) and trimellitic anhydride (TMA) in 1:2 molar ratio. A series of novel poly(amide-imide)s (PAIs) **III**_{a-1} having inherent viscosities of 0.98—1.51 dL g⁻¹ were prepared by the triphenyl phosphite activated polycondensation from the diimide-diacid **I** with various aromatic diamines (**II**_{a-1}) in a medium consisting of *N*-methyl-2-pyrrolidone (NMP), pyridine, and calcium chloride. Most of polymers show excellent solubility in amide-type solvents such as NMP and *N,N*-dimethylacetamide (DMAc) and formed tough, transparent, and flexible films by casting from DMAc solution. These films had tensile strengths of 71—106 MPa, elongations at break of 5—45%, and initial moduli of 2.1—2.9 GPa. Most PAIs necked during the tensile testing. The glass transition temperatures of these polymers were in the range 228—286°C and the 10% weight loss temperatures were above 475°C in air or in nitrogen.

KEY WORDS 1,4-Bis(4-aminophenoxy)-2-*t*-butylbenzene / Trimellitic Anhydride / 1,4-Bis(4-trimellitimidophenoxy)-2-*t*-butylbenzene / Poly(amide-imide)s /

Aromatic polyimides have earned a reputation as high-performance materials based on their excellent thermal stability, chemical resistance, and outstanding mechanical properties.¹⁻⁴ However, poor handling and intractable characteristics have been major problems due to high melting point and insolubility. To extend the utility of such high performance materials, it has been a long-desired goal to synthesize soluble polymers without much sacrifice in their thermomechanical properties. It is well known that the synthesis of poly(amide-imide)s (PAIs) can offer a compromise between excellent thermal stability and processability.

In our previous studies,⁵⁻¹² we have successfully applied the phosphorylation polycondensation technique¹³⁻¹⁵ to prepare PAIs from imide-containing dicarboxylic acids and aromatic diamines. This route provides significant advantages in manufacturing operations compared with conventional methods. Thus, many new series of PAIs could be readily developed by this convenient technique in our laboratory. Polyamides on the basis of diamine 1,4-bis(4-aminophenoxy)-2-*t*-butylbenzene (BAP-*t*BB) have been claimed to possess the potential application as gas separation membranes.¹⁶ It has been reported that incorporating the residue of BAP-*t*BB into polyimide backbones led to decreased crystallinity and glass transition temperature.¹⁷ The present work was undertaken to synthesize and characterize a series of novel aromatic PAIs on the basis of the diimide-diacid derived from BAP-*t*BB and trimellitic anhydride. Thus, it is expected that the PAIs prepared from the diimide-diacid would give higher solubility compared to those of the corresponding PAIs without *t*-butyl substituent prepared from our previous study.⁷ These PAIs are also expected to be potential candidates for gas separation membranes because of the presence of pendent bulky *t*-butyl group.

EXPERIMENTAL

Materials

Trimellitic anhydride (TMA) (Wako) was used without previous purification. BAP-*t*BB (mp 129—130°C) was synthesized from *t*-butylhydroquinone and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction with a 10% Pd-C catalyst and hydrazine hydrate in our previous studies.⁸⁻¹² *p*-Phenylenediamine (**II**_a) (Wako) and *m*-phenylenediamine (**II**_b) (TCI) were vacuum-distilled, and benzidine (**II**_c) (TCI) was crystallized prior to use. Other diamines that included 4,4'-diaminobenzanilide (**II**_d), 4,4'-oxydianiline (**II**_e), 4,4'-diaminodiphenyl sulfide (**II**_f), 4,4'-diaminodiphenylmethane (**II**_g), 1,4-bis(4-aminophenoxy)benzene (**II**_h), 1,3-bis(4-aminophenoxy)benzene (**II**_i), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**II**_k), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**II**_l) were all from TCI and used without any further purification. Bis[4-(4-aminophenoxy)phenyl] ether (**II**_j) (mp 109—110°C) was prepared according to a reported method.¹⁸ *N,N*-Dimethylacetamide (DMAc; Fluka), *N,N*-dimethylformamide (DMF; Fluka), and pyridine (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 (CaCl₂; Wako) was dried under vacuum at 180°C for 10 h.

Synthesis of 1,4-Bis(4-trimellitimidophenoxy)-2-*t*-butylbenzene (**I**)

A mixture of 6.96 g (20 mmol) of diamine BAP-*t*BB and 7.69 g (40 mmol) of TMA were heated to dissolve in 50 mL of dry DMF. Stirring and heating at 40°C were continued for 1 h. Then, about 20 mL of toluene was added, and the mixture was heated with reflux for about 6 h until about 1.1 mL of water was distilled off azeo-

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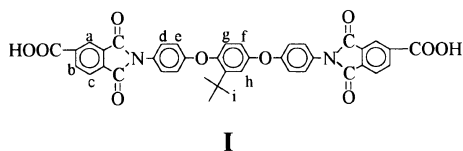
tropically under a Dean–Stark trap. After complete removal of water, the residual toluene was distilled off. After cooling, the precipitated yellowish solid was isolated by filtration, washed several times by hot water, and dried in vacuum to yield 13.6 g (98%) of pure diimide-diacid **I**; mp 338–339°C.

IR (KBr): 3500–2500 (carboxyl –OH), 1780 and 1726 (imide C=O), 1092 and 729 cm⁻¹ (imide ring C–N).

Anal. Calcd for C₄₀H₂₈O₁₀N₂ (696.67): C, 68.96%; H, 4.05%; N, 4.02%. Found: C, 68.54%; H, 4.3%; N, 3.67%.

¹H NMR (dimethyl sulfoxide (DMSO)-*d*₆): δ (ppm) = 8.38–8.42 (d, 2H, H_b), 8.28 (s, 2H, H_a), 8.04–8.07 (d, 2H, H_c), 7.45–7.49 (d, 4H, H_d), 7.15–7.11 (m, 5H, H_e + H_h), 6.98–6.99 (d, 2H, H_f + H_g), 1.38 (s, 9H, H_i).

¹³C NMR (DMSO-*d*₆): δ (ppm) = 166.52, 165.96, 157.47, 157.11, 151.845, 150.68, 143.12, 136.57, 135.57, 134.99, 132.12, 129.15, 126.58, 126.24, 123.85, 123.46, 122.64, 118.76, 118.21, 118.09, 117.80, 34.58, 29.83.



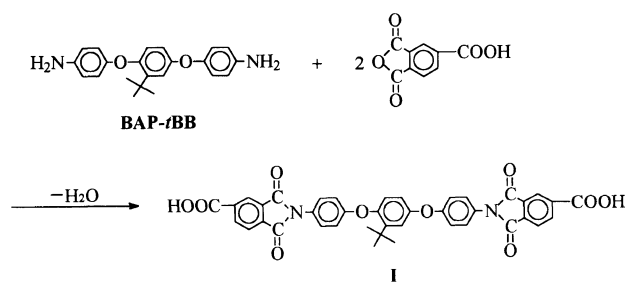
Polymerization

A typical example of polymerization is as follows. A mixture of 0.435 g (0.625 mmol) of diimide-diacid **I**, 0.126 g (0.625 mmol) of diamine **II_d**, 0.3 g of CaCl₂, 4 mL of NMP, 0.8 mL of pyridine and 0.4 mL of TPP was heated with stirring at 100°C for 3 h. The polymer solution was too viscous to stir after about 1 h and was diluted gradually with an additional 3 mL of *N*-methyl pyrrolidone (NMP) to maintain smooth stirring. The polymer solution obtained was trickled on 100 mL of stirring methanol giving rise to a stringy precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried under vacuum at 100°C. The yield was 0.55 g (98%). The inherent viscosity of the PAI **III_d** was 1.51 dL g⁻¹, as measured on 0.5 g dL⁻¹ in DMAc at 30°C.

Other PAIs were synthesized in an analogous procedure.

Measurements

Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N, analyzer. ¹H and ¹³C NMR spectra were determined on a JEOL EX-200 FT-NMR spectrometer. IR spectra were recorded on a JASCO FTIR-7000 Fourier-transform Infrared Spectrometer. The inherent viscosities were measured with a Cannon–Fenske viscometer at 30°C. DSC traces were measured on a Sinku Riko 7000 differential scanning calorimeter coupled to a basic component TA 7000 thermal analyzer at the rate of 10°C min⁻¹ in flowing nitrogen (30 cm³ min⁻¹). Thermogravimetry (TG) was conducted with TA Instruments TGA 2050. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. An Instron Universal Tester Model 1130 with a load cell of 5 kg was used to study the stress–strain behavior of the polymer films. A gauge of 2 cm and a strain rate of



Scheme 1. Preparation of diimide-diacid.

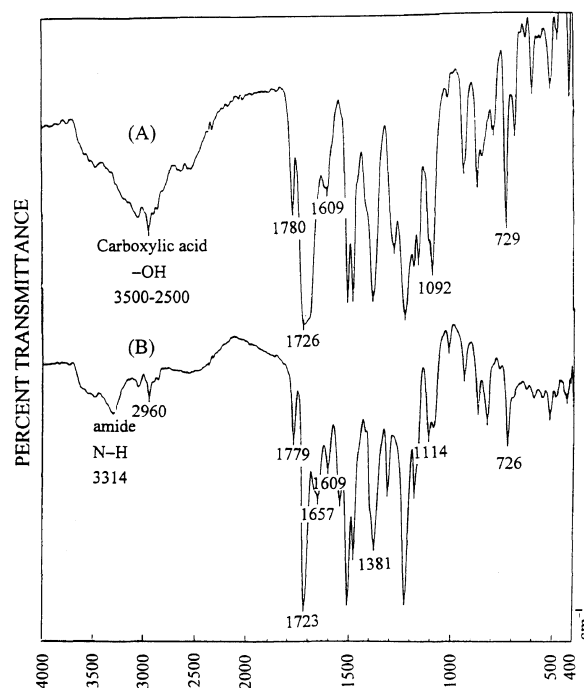


Figure 1. FT-IR spectra of (A) diimide-diacid **I** and (B) poly(amide-imide) **III_a**.

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 0.5 mm thick) and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Synthesis

1,4-Bis(4-trimellitimidophenoxy)-2-*t*-butylbenzene (**I**), the diimide-diacid monomer, was prepared *via* the two-stage procedure that included ring-opening addition of the diamine BAP-*t*BB with two equivalent amounts of trimellitic anhydride, followed by cyclodehydration to the diimide-diacid by means of toluene–water azeotropic distillation (Scheme 1). The structure of **I** was confirmed by elemental analysis and IR, ¹H, and ¹³C NMR spectroscopy. The FT-IR spectrum of diimide-diacid **I** is reproduced in Figure 1(A). The absorption bands appearing between 2500–3500 (carboxyl –OH), 1780 (imide, asymmetric C=O stretching), 1726 (carboxyl C=O and symmetric imide C=O stretching), 1092 and 729 cm⁻¹ (imide ring deformation) establish the presence of carboxyl group and imide rings in the structure of the monomer synthesized. The ¹³C NMR spectrum of

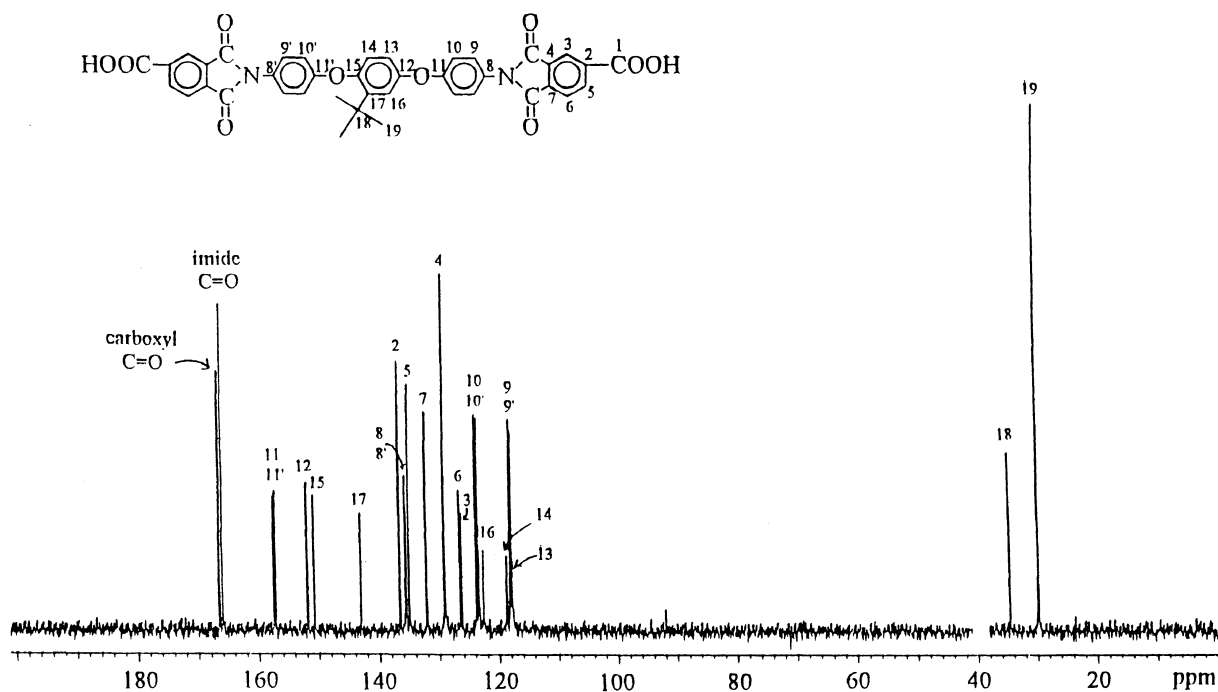
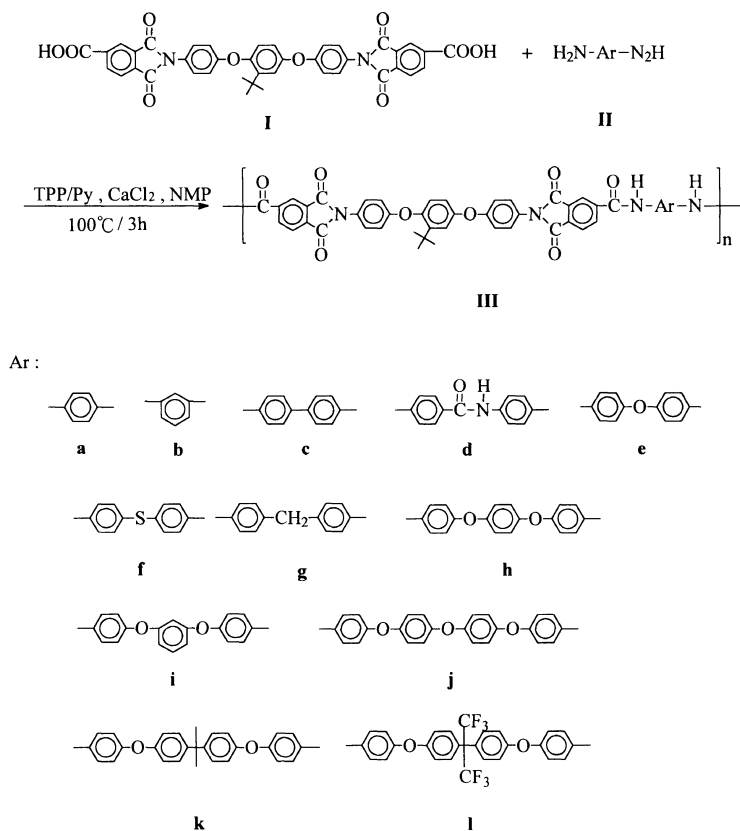


Figure 2. The 50 MHz ^{13}C NMR spectrum of diimide-diacid **I** in $\text{DMSO-}d_6$.



Scheme 2. Preparation of poly(amide-imide)s.

diimide-diacid **I** shown in Figure 2 was in good agreement with the proposed structure.

A series of novel PAIs **III**_{a-1} were prepared from diimide-diacid **I** and various aromatic diamines **II**_{a-1} by the direct condensation reaction using triphenyl phosphite and pyridine as condensing agent (Scheme 2). Synthesis conditions and inherent viscosities of the PAIs produced are shown in Table I. Under these conditions

the reaction solutions were homogeneously transparent throughout the reaction. The solubility of the polymer and the state of stirring affected the inherent viscosity of the resulting PAI significantly. In general, the molecular weight of the polymer obtained from the phosphorylation reaction is highly dependent on the reactant concentration. According to our earlier publications,⁵⁻¹⁰ it was repeatedly observed that the higher the concentration of

Table I. Synthesis of poly(amide-imide)s

Polymer code	Amount of each monomer mmol	Amounts of reagents used ^a					η_{inh}^b dL g ⁻¹
		NMP	Additional NMP	CaCl ₂	Py	TPP	
		mL	mL	g	mL	mL	
III_a	0.830	5.0		0.38	1.0	0.55	1.11
III_b	0.740	5.0		0.38	1.0	0.55	1.04
III_c	0.625	3.5	1.0	0.37	0.8	0.40	1.10 ^c
III_d	0.625	4.0	3.0	0.30	0.8	0.40	1.51
III_e	0.625	3.5	1.5	0.27	0.8	0.40	1.25
III_f	1.000	5.0		0.37	1.2	0.60	1.02
III_g	0.625	3.5		0.27	0.8	0.40	1.01
III_h	0.625	3.5	1.0	0.25	0.8	0.40	0.98
III_i	0.625	3.5		0.27	0.8	0.40	1.27
III_j	0.625	3.5	1.0	0.27	0.8	0.40	1.35
III_k	0.625	3.5	1.0	0.27	0.8	0.40	1.45
III_l	0.625	3.5		0.27	0.8	0.40	1.03

^a Polymerization was carried out at 100°C. ^b Measured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C. ^c Measured at a concentration of 0.5 g dL⁻¹ in H₂SO₄ at 30°C.

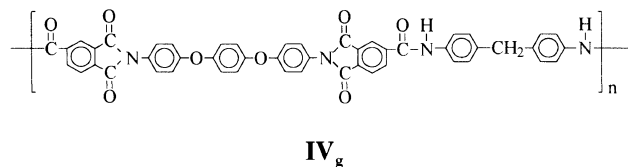
monomers, the higher the final inherent viscosity provided that no precipitation, or gelation, of the product from the reaction medium took place. It was anticipated that the bulky pendent *t*-butyl group-containing PAIs **III_{a-1}** would have increased solubility in organic solvents and a higher monomer concentration could be tolerated during the polymerization. In some cases, higher molecular weights 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. The series of PAIs **III_{a-1}** having inherent viscosities of 0.98–1.51 dL g⁻¹ were obtained in quantitative yield. Except for **III_c**, all the other PAIs could be solution cast into flexible and noncreasable films. These results indicated the formation of high molecular weights.

The structures of these polymers were confirmed by IR spectroscopy and elemental analysis. A typical IR spectrum for the representative PAI **III_a** is shown in Figure 1(B). The characteristic absorption bands for imide ring appear around 1780, 1726 cm⁻¹ (imide C=O), 1092 and 729 cm⁻¹ (imide ring deformation). Bands of amide groups appear at 3314 and 1657 cm⁻¹. The elemental analysis values of these PAIs are listed in Table II. 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 intake for these PAIs were in the range of 1.58–3.83%. The corrected values were in good agreement with the calculated ones after deducting the amount of moisture intake.

Properties of Polymers

The qualitative solubility of the PAIs is shown in Table III. Most PAIs were soluble in aprotic dipolar solvents such as NMP, DMAc, and DMF, and even in less polar solvents like *m*-cresol, pyridine, tetrahydrofuran (THF). The high solubility of these polymers may be due in part to the introduction of the pendent *t*-butyl group which hinders the close packing of polymer chains. However the PAIs **III_a**, **III_c**, and **III_d** derived from rigid diamines

such as *p*-phenylenediamine (**II_a**), benzidine (**II_c**), and 4,4'-diaminobenzanilide (**II_d**) revealed somewhat limited solubility. In general, the pendent group-containing PAIs **III** showed significantly higher solubility than their homologs based on hydroquinone-derived diimide-diacid.⁷ For example, polymer **IV_g** condensed from hydroquinone-based diimide-diacid and 4,4'-diaminodiphenylmethane (**II_g**) was insoluble in all the organic solvents tested and only soluble in concentrated sulfuric acid. This indicates that the incorporation of pendent *t*-butyl group led to a significant increase in solubility.



The thermal properties of all the PAIs were evaluated by TG and differential scanning calorimetry (DSC), and the results are summarized in Table IV. DSC measurements were conducted with a heating rate of 10°C min⁻¹ in nitrogen. Quenching from an elevated temperature (about 450°C) to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (*T_g*) of almost all the PAIs could be easily observed in the second heating traces of DSC. *T_g* values of these PAIs were recorded in the range 228–286°C. This order is correlative to the decreasing order of stiffness and polarity of the polymer backbones. For example, the *T_g* of the *p*-diphenoxybenzene residue-containing **II_h** is higher than that of its *m*-isomeric **III_i**, and the perfluoroisopropylidene-containing **III_l** reveals a higher *T_g* than its nonfluorinated counterpart **III_k**. In general, the *t*-butyl substituent-containing PAIs **III** showed lower *T_g*s in comparison with the corresponding PAIs without *t*-butyl substituent.⁷ Most of the unsubstituted PAIs did not show discernible *T_g*s before decomposition, probably due to high crystallinity as evidenced by X-ray diffraction patterns. The decrease in *T_g* owing to the introduction of the pendent group

Table II. Elemental analysis of poly(amide-imide)s

Polymer	Formula M_w	Elemental analysis ^a /%			Moisture intake ^b /%	
		C	H	N		
III _a	$(C_{46}H_{32}O_8N_4)_n$ (768.78) _n	Calcd	71.87	4.20	7.29	3.65
		Found	69.27	4.46	6.96	
		Corrected	71.89	4.30	7.22	
III _b	$(C_{46}H_{32}O_8N_4)_n$ (768.78) _n	Calcd	71.87	4.20	7.29	3.15
		Found	69.61	4.50	7.12	
		Corrected	71.87	4.36	7.35	
III _c	$(C_{52}H_{36}O_8N_4)_n$ (844) _n	Calcd	73.93	4.27	6.64	2.87
		Found	71.75	4.52	6.47	
		Corrected	73.87	4.39	6.67	
III _d	$(C_{53}H_{37}O_9N_5)_n$ (887.9) _n	Calcd	71.69	4.20	7.89	3.83
		Found	68.98	4.53	7.42	
		Corrected	71.73	4.36	7.72	
III _e	$(C_{52}H_{36}O_9N_4)_n$ (860.88) _n	Calcd	72.22	4.21	6.51	1.58
		Found	69.86	4.47	6.19	
		Corrected	70.98	4.40	6.29	
III _f	$(C_{52}H_{36}O_8N_4S_1)_n$ (876.94) _n	Calcd	71.22	4.14	6.39	2.79
		Found	69.20	4.32	6.19	
		Corrected	71.19	4.20	6.37	
III _g	$(C_{53}H_{38}O_8N_4)_n$ (858.91) _n	Calcd	74.12	4.46	6.52	2.86
		Found	72.00	4.66	6.33	
		Corrected	74.12	4.53	6.52	
III _h	$(C_{58}H_{40}O_{10}N_4)_n$ (952.98) _n	Calcd	73.10	4.23	5.88	2.46
		Found	71.25	4.50	5.70	
		Corrected	73.05	4.39	5.85	
III _i	$(C_{58}H_{40}O_{10}N_4)_n$ (952.98) _n	Calcd	73.10	4.23	5.88	3.21
		Found	70.75	4.40	5.57	
		Corrected	73.09	4.26	5.75	
III _j	$(C_{64}H_{44}O_{11}N_4)_n$ (1045.07) _n	Calcd	73.56	4.24	5.36	2.02
		Found	72.03	4.49	5.27	
		Corrected	73.51	4.40	5.38	
III _k	$(C_{67}H_{50}O_{10}N_4)_n$ (1071.15) _n	Calcd	75.13	4.70	5.23	2.10
		Found	73.44	4.84	5.10	
		Corrected	75.01	4.74	5.21	
III _l	$(C_{67}H_{44}O_{10}N_4F_6)_n$ (1179.10) _n	Calcd	68.25	3.76	4.75	1.61
		Found	67.10	4.00	4.76	
		Corrected	68.19	3.94	4.84	

^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 for 3 days, and W_0 = weight of polymer sample after dried in vacuum at 100°C for 10 h.

Table III. Solubility behavior of poly(amide-imide)s^a

Polymer	Solvent ^b							
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	THF	H ₂ SO ₄
III _a	+	+	-s	+	-	-	-	+
III _b	+	+	+	+	+	+	+	+
III _c	+ -	+ -	-	-	-	-	-	+
III _d	+	+	-	+	-	-	-	+
III _e	+	+	+	+	+	+	-	+
III _f	+	+	+	+	+	+	+ -	+
III _g	+	+	+	+	+	+	+	+
III _h	+	+	+	+	+	+	-	+
III _i	+	+	+	+	+	+	+	+
III _j	+	+	+	+	+	+	+	+
III _k	+	+	+	+	+	+	+	+
III _l	+	+	+	+	+	+	+	+
IV _g ^c	-	-	-	-	-	-	-	+

^a +, soluble; -, insoluble; -s, swelling; + -, partially soluble. ^b NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran. ^c Data from ref 7.

may be attributed to the effect of asymmetry, irregularity, and increased fractional free volume of the polymer chain.

The thermal stability of the PAIs was characterized

by TG analysis conducted at a heating rate of 20°C min⁻¹. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmosphere were determined from original thermograms and also tabulated in Table IV.

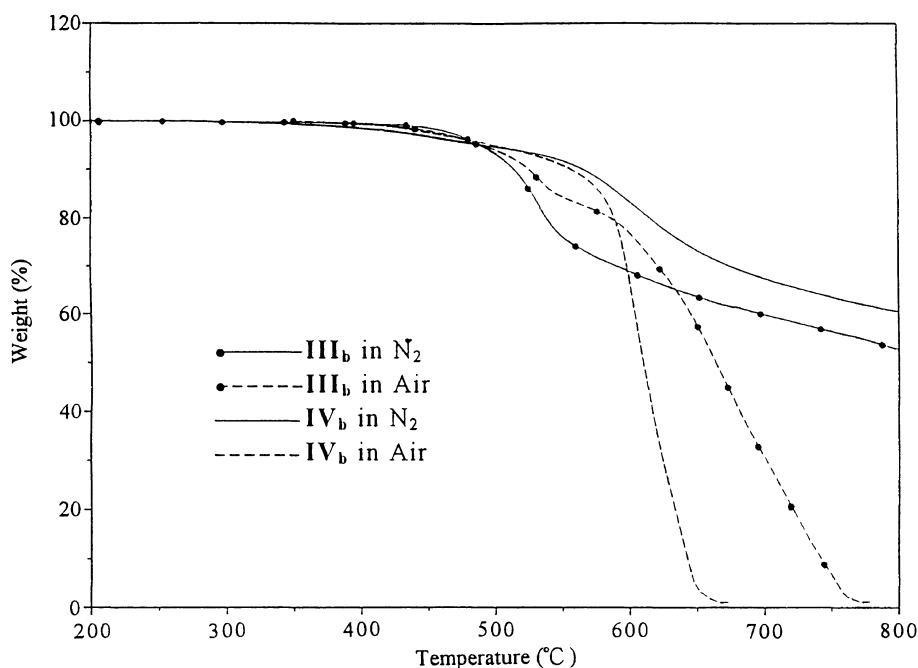


Figure 3. TG curves for PAIs **III_b** and **IV_b** with a heating rate of 20°C min⁻¹.

Table IV. Thermal properties of poly(amide-imide)s

Polymer	T_g^a	$T_{10}^b/^\circ\text{C}$		Char yield ^d
	$^\circ\text{C}$	In N_2	In air	
III_a	286	521	544	64
III_b	282	516	525	53
III_c	— ^c	512	475	49
III_d	270	512	510	58
III_e	262	525	530	65
III_f	272	490	496	60
III_g	256	511	521	68
III_h	266	517	522	59
III_i	228	520	522	62
III_j	244	516	514	55
III_k	252	510	518	55
III_l	260	521	521	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 TG at a heating rate 20°C min⁻¹. ^c Difficult to judge. ^d Residual weight (%) when heated to 800°C in nitrogen.

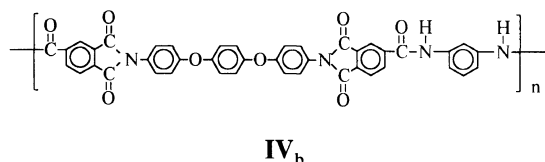
The T_{10} s of these PAIs stayed in the range of 490–521°C in nitrogen and 475–544°C in air, which is adequately high for an aliphatic group-containing aromatic polymer. In most cases, the T_{10} s of these PAIs in air were close to or even higher than those in nitrogen. Figure 3 shows the TG curves of PAI **III_b** and its corresponding PAI (**IV_b**) without the *t*-butyl group. As expected, polymer **III_b** started to lose weight at an earlier temperature than **IV_b** due to the presence of less stable aliphatic *t*-butyl group. PAI **III_b** did not show significant weight loss up to about 450°C in nitrogen and in air, whereas it decomposed rapidly above 500°C. In nitrogen, the rate of weight loss was slowed down above 550°C, and about 53% residual char left at 800°C. In air, the oxidative degradation continued above 600°C, and the polymer decomposed completely when heated to about 730°C. It also can be seen from the TG thermograms of PAI **III_b** that the decomposition rate in air is lower than in nitrogen in the temperature range 500–600°C. This

Table V. Tensile properties of poly(amide-imide)s films^a

Polymer	Strength at yield	Strength at break	Elongation to break	Initial modulus
	MPa	MPa	%	
III_a	—	71	16	2.1
III_b	—	83	17	2.3
III_c	—	—	—	—
III_d	—	85	5	2.7
III_e	—	106	13	2.9
III_f	—	93	13	2.3
III_g	100	101	44	2.7
III_h	93	95	45	2.7
III_i	99	89	11	2.6
III_j	101	103	31	2.7
III_k	95	96	25	2.7
III_l	—	91	6	2.5

^a Films were cast from polymer solutions of DMAc.

may be attributed to the effect of an earlier weight-gained oxidation and to some possible oxidative interchain crosslinking between aliphatic segments of the polymer chain when thermally degraded in air.



Transparent, flexible and tough films could be cast from the DMAc solutions of the obtained PAIs, except for **III_c** which had poor solubility. Table V summarizes the mechanical properties of the PAIs films. These films had tensile strengths of 71–106 MPa, elongations at break of 5–45%, and initial moduli of 2.1–2.9 GPa. Some PAIs such as **III_{g–k}** showed clear yield points on their stress-strain curves and had higher elongation-to-break, indicating high toughness. In comparison with

PAIs without the pendent group, PAIs **III** possessed excellent film-formability and superior mechanical properties due to the presence of *t*-butyl substituent.

CONCLUSIONS

The diimide-diacid 1,4-bis(4-trimellitimidophenoxy)-2-*t*-butylbenzene was used as a PAI building block. PAIs having moderate to high molecular weight were successfully prepared by direct polycondensation of the diimide-diacid with various aromatic diamines using triphenyl phosphite and pyridine. The PAIs generally showed good thermal stability and solubility, and their cast films exhibited excellent tensile properties. Thus, the present PAIs are considered as new candidates for processable high-performance polymeric materials. In comparison with the counterparts having no pendent group, this series of PAIs showed an enhanced solubility and film-formability, but slightly lower T_g s and initial decomposition temperatures due to the attachment of pendent *t*-butyl group.

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