

Preparation and characterization of colourless alternate poly(amide-imide)s based on trimellitic anhydride and *m*-phenylenediamine

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Abstract

Alternate copoly(amide-imide) was synthesized from two aromatic diamines and trimellitic anhydride (TMA). When the diamine was *m*-phenylenediamine (*m*-PDA), the resulted poly(amide-imide) [P(A-alt-I)] was found to be of light colour. Specifically, when *m*-PDA was located between two amide groups in the P(A-alt-I) chain, the P(A-alt-I) was colourless. Using triphenyl phosphite (TPP) and pyridine as condensing agents, a series of P(A-alt-I)s (series **III**) containing *m*-PDA was synthesized through direct polycondensation of an aromatic dicarboxylic acid (**II_b**) prepared from *m*-PDA and TMA, as well as various aromatic diamines. The isomeric series of P(A-alt-I)s (series **IV**) was synthesized from diacid monomers that had been prepared from various diamines and TMA, as well as *m*-PDA. The colour (yellow) of P(A-alt-I)s **IV** was lighter than that of the isomeric series of P(A-alt-I)s **III**. The 24 P(A-alt-I)s (series **III** and series **IV**) had inherent viscosities ranging 1.01–1.88 dl g⁻¹. The tensile strengths, elongations to break and initial moduli of the films were 86–112 MPa, 6%–42% and 1.74–2.81 GPa, respectively, and most of the films had yielding. Polymers of Series **IV** had glass transition temperatures 228°C–293°C, which were higher than those of Series **III** ranging 223°C–278°C. The 10% weight loss temperatures in nitrogen of these two series were similar in the range 472°C–561°C. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Alternate copoly(amide-imide); Colourless

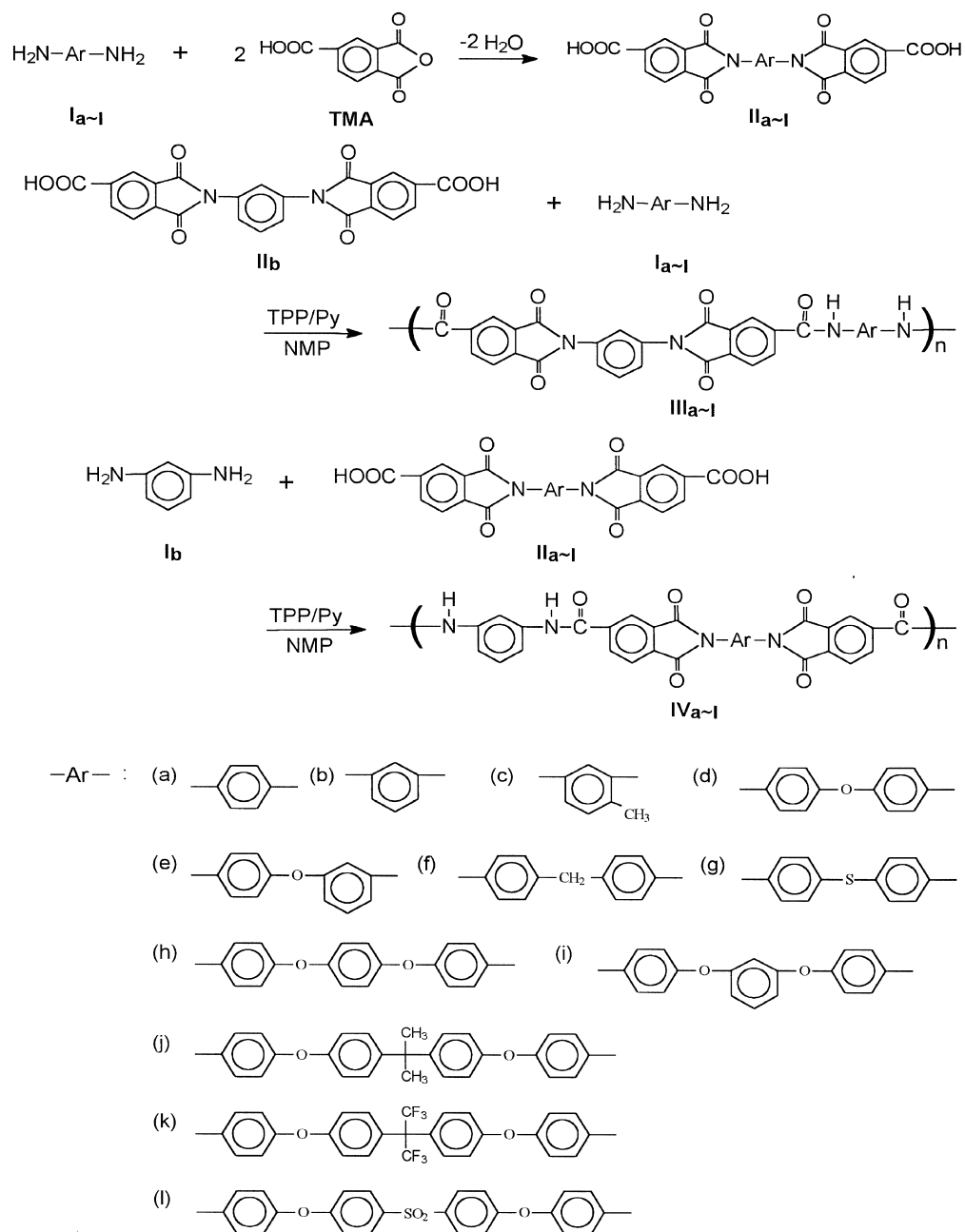
1. Introduction

Aromatic polyimides are polymers resistant to high temperature and noted for their mechanical strength and excellent electrical insulating properties [1,2]. Polyimides are difficult to process due to their high softening or melting temperatures and their insoluble nature in most organic solvents. To overcome this drawback, various copolymers have been developed and reported, among them being poly(amide-imide) [P(A-alt-I)] [3,4], whose amide groups can improve the solubilities. P(A-alt-I)s can be synthesized from various monomers containing anhydride, carboxylic acid or aromatic amino groups by polycondensation [5,6]. To synthesize P(A-alt-I)s, one can usually use dicarboxylic acid, dianhydride, diamine, aminoacid or anhydride-acid, among which trimellitic anhydride (TMA) is an aromatic anhydride commercially available. TMA and diisocyanate

or diamine can produce P(A-alt-I) [7–9]. However, resulting polymers have low inherent viscosities due to the above-described monomers' moisture uptake.

Our laboratory has developed a convenient method for P(A-alt-I)s' synthesis, and many kinds of alternate PAIs can be synthesized. The method involves using 2 mol TMA and 1 mol diamine to prepare an imide ring-preformed dicarboxylic acid, which is then reacted with another aromatic diamine to prepare P(A-alt-I)s. The direct polycondensation utilizes triphenyl phosphite and pyridine as condensing agents in the presence of CaCl₂ or LiCl in *N*-methyl-2-pyrrolidone [10–12]. In general, the study [3–9] of new polyimides or P(A-alt-I) syntheses using various diamines has been carried out to improve polymers' processability, mechanical strength, crystallinity and high temperature resistance, but the colouration of polymers has been investigated less often [13]. Among the conventional diamines, such as *p*-phenylenediamine, *m*-phenylenediamine (*m*-PDA), 4,4'-oxydianiline, 4,4'-methylenedianiline, 4,4'-thiodianiline, etc. *m*-PDA can give colourless polymers. Because of

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Scheme 1. Procedure of alternate poly(amide-imide) synthesis.

m-PDAs larger amino group ^{15}N NMR chemical shifts (δ_{N}) [13], its polymers have a lighter colour. Being commercially available and cheap, *m*-PDA was chosen to investigate P(A-alt-I)'s colouration in this study. When *m*-PDA and TMA are used as main ingredients, alternate PAI can be synthesized with another diamine by the method described earlier. The resultant polymers have some characteristics: colourless [aromatic P(A-alt-I)s or polyimides are yellow], good solubility, mechanical properties, and thermal behaviour. In this study, two series of P(A-alt-I)s containing *m*-phenylene groups were synthesized and their properties of polymers characterized.

2. Experimental

2.1. Materials

Aromatic diamines: *p*-Phenylenediamine (I_a; from Wako) and *m*-phenylenediamine (I_b; from TCI) were vacuum-distilled before use. All other diamines such as 2,4-tolylenediamine (I_c; from TCI), 4,4'-oxydianiline (I_d; from TCI), 3,4'-oxydianiline (I_e; from Teijin Ltd, Tokyo), 4,4'-methylenediamine (I_f; from TCI), 4,4'-thiodianiline (I_g; from TCI), 4,4'-(1,4-phenylenedioxy) dianiline (I_h; from TCI) were used as received. The diamines 4,4'-(1,3-phenylenedioxy) dianiline

Table 1
Synthesis of poly(amide-imide)s

Polymer ^a	Amount of each monome (mmol)	Amount of reagents used ^c					η_{inh}^d (dl g ⁻¹)
		NMP (ml)	Additional NMP (ml)	CaCl ₂ (g)	Py (ml)	TPP (ml)	
III_a	1.25	9.0	3.0	0.70	2.0	0.8	0.57
III_b	1.5	7.0	0	0.45	1.5	0.9	1.09
III_c	1.5	7.0	0	0.46	1.5	1.0	1.19
III_d	1.5	7.5	0	0.45	1.5	0.9	1.36
III_e	1.0	4.5	0	0.30	1.0	0.6	1.35
III_f	1.5	7.0	0	0.45	1.5	0.9	1.02
III_g	1.5	5.0	0	0.30	1.0	0.6	1.07
III_h	1.5	7.5	2.0	0.46	1.5	0.9	1.39
III_i	1.5	7.5	0	0.45	1.5	0.9	1.71
III_j	1.0	5.0	1.5	0.30	1.0	0.6	1.64
III_k	1.0	5.0	1.0	0.30	1.0	0.6	1.14
III_l	1.0	4.5	1.5	0.30	1.0	0.6	1.42
IV_a	1.07	6.0	0	0.50	1.2	0.6	0.37 ^e
IV_b	1.50	7.0	0	0.45	1.5	0.9	1.09
IV_c	1.29	6.0	0	0.30	1.5	0.9	1.44
IV_d	1.33	6.0	0	0.45	1.2	0.9	1.54
IV_e	1.14	5.0	2.5	0.30	1.2	0.7	1.88
IV_f	1.14	5.0	1.5	0.38	1.2	0.7	1.72
IV_g	1.06	4.5	0	0.30	1.0	0.6	1.25
IV_h	1.05	5.0	1.5	0.40	1.0	0.6	1.69
IV_i	1.54	7.5	1.5	0.45	1.5	1.0	1.01
IV_j	1.18	5.0	1.5	0.32	1.2	0.7	1.39
IV_k	1.00	5.0	0	0.30	1.0	0.6	1.37
IV_l	1.25	6.0	1.5	0.38	1.2	0.8	1.27

^a All polymers were soluble throughout the reaction, besides **II_a**.

^b **III_b** and **IV_b** are the same.

^c Polymerization was carried out at 100°C for 3 h.

^d Measured at 30°C on a concentration of 0.5 g dl⁻¹ in DMAc + 5% LiCl.

^e Measured at 30°C in conc. H₂SO₄.

(**I_i**), 4,4'-[isopropylidenebis(1,4-phenyleneoxy)]dianiline (**I_j**) and 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (**I_k**) were obtained from Chriskev Corp. and used without further purification. According to a reported method [14], 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (**I_k**) were prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursors and *p*-chloronitrobenzene in the presence of potassium carbonate, and subsequent reduction of the dinitro compound. Trimellitic anhydride (from Wako) and triphenyl phosphite (from TCI) were used without further purification. Commercially available calcium chloride (CaCl₂) was dried under vacuum at 150°C for 6 h. *N*-methyl-2-pyrrolidone (NMP, from Fluka), *N,N*-dimethylformamide (DMF, from Fluka), and pyridine (Py, from Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å; molecular sieves.

2.2. Synthesis of diimide-dicarboxylic acids

In our laboratorys previous reports [15–19], diimide-dicarboxylic acids were synthesized from TMA with various aromatic diamines as follows: a mixture of TMA

(120 mmol, 23.04 g) and *m*-phenylenediamine (**I_b**) (60 mmol, 6.48 g) was dissolved in 120 ml of dry DMAc and stirred till the solution was clear. Toluene (20 ml) was then added, and the mixture was heated to 140°C until water (about 2.1 ml) was distilled off. Heating was continued to distill off the residual toluene. After cooling, the precipitate of **II_b** was isolated by filtration and recrystallization from *N,N*-dimethylformamide (DMF), and was dried to give 29.3 g of **II_b** (yield: 99%). Other diimide-dicarboxylic acids were synthesized similarly.

2.3. Synthesis of poly(amide-imide)s

As an example of polymer **III_c**, a mixture of 0.183 g (1.5 mmol) of 2,4-tolylenediamine (**I_c**), 0.684 g (1.5 mmol) of diimide-diacid **II_b**, 0.46 g of calcium chloride, 1.5 ml of pyridine, 1.0 ml of triphenyl phosphite and 7.0 ml of NMP was heated while being stirred at 100°C for 3 h. At the end of the reaction, the polymer solution was trickled into stirred methanol, giving rise to a stringy precipitate, which was washed thoroughly with hot water and methanol, collected by filtration and dried. The product obtained was 0.86 g (yield: 99%). The inherent

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

Polymer	Formula (mol. weight)		Elemental analysis ^a (%)			Moisture uptake ^b (%)
			C	H	N	
III _a	(C ₃₀ H ₁₆ N ₄ O ₆) _n (528.48) _n	Calcd	68.18	3.05	10.60	5.46
		Found	64.46	3.68	9.27	
		Corrected	67.98	3.48	9.78	
III _b	(C ₃₀ H ₁₆ N ₄ O ₆) _n (528.48) _n	Calcd	68.18	3.05	10.60	5.94
		Found	64.13	3.65	9.11	
		Corrected	67.94	3.43	9.65	
III _c	(C ₃₁ H ₁₈ N ₄ O ₆) _n (542.51) _n	Calcd	68.63	3.34	10.33	4.87
		Found	65.29	3.81	9.15	
		Corrected	68.47	3.62	9.60	
III _d	(C ₃₆ H ₂₀ N ₄ O ₇) _n (620.58) _n	Calcd	69.68	3.25	9.03	3.83
		Found	67.01	3.62	8.20	
		Corrected	69.58	3.48	8.51	
III _e	(C ₃₆ H ₂₀ N ₄ O ₇) _n (620.58) _n	Calcd	69.68	3.25	9.03	3.49
		Found	67.25	3.58	8.32	
		Corrected	69.60	3.46	8.61	
III _f	(C ₃₇ H ₂₂ N ₄ O ₆) _n (618.60) _n	Calcd	71.84	3.58	9.06	4.16
		Found	68.85	3.88	8.15	
		Corrected	71.71	3.72	8.49	
III _g	(C ₃₆ H ₂₀ N ₄ O ₆ S) _n (636.64) _n	Calcd	67.92	3.17	8.80	3.67
		Found	65.43	3.55	7.93	
		Corrected	67.83	3.42	8.22	
III _h	(C ₄₂ H ₂₄ N ₄ O ₈) _n (712.67) _n	Calcd	70.78	3.39	7.86	3.33
		Found	68.42	3.72	7.32	
		Corrected	70.70	3.60	7.56	
III _i	(C ₄₂ H ₂₄ N ₄ O ₈) _n (712.67) _n	Calcd	70.78	3.39	7.86	3.36
		Found	68.40	3.68	7.22	
		Corrected	70.70	3.56	7.46	
III _j	(C ₅₁ H ₃₄ N ₄ O ₈) _n (830.85) _n	Calcd	73.73	4.12	6.74	2.69
		Found	71.75	4.31	6.32	
		Corrected	73.68	4.19	6.49	
III _k	(C ₅₁ H ₂₈ N ₄ O ₈ F ₆) _n (938.80) _n	Calcd	65.25	3.01	5.97	2.67
		Found	63.51	3.31	5.53	
		Corrected	65.21	3.22	5.68	
III _l	(C ₄₈ H ₂₈ N ₄ O ₁₀ S) _n (852.83) _n	Calcd	67.60	3.31	6.57	2.78
		Found	65.72	3.59	6.13	
		Corrected	67.55	3.49	6.30	
IV _a	(C ₃₀ H ₁₆ N ₄ O ₆) _n (528.48) _n	Calcd	68.18	3.05	10.60	4.69
		Found	64.98	3.52	9.71	
		Corrected	68.03	3.35	10.17	
IV _b	(C ₃₀ H ₁₆ N ₄ O ₆) _n (528.48) _n	Calcd	68.18	3.05	10.60	5.94
		Found	64.13	3.65	9.11	
		Corrected	67.94	3.43	9.65	
IV _c	(C ₃₁ H ₁₈ N ₄ O ₆) _n (542.51) _n	Calcd	68.63	3.34	10.33	4.60
		Found	65.47	3.78	9.60	
		Corrected	68.48	3.61	10.04	
IV _d	(C ₃₆ H ₂₀ N ₄ O ₇) _n (620.58) _n	Calcd	69.68	3.25	9.03	3.95
		Found	66.93	3.68	8.56	
		Corrected	69.57	3.53	8.90	
IV _e	(C ₃₆ H ₂₀ N ₄ O ₇) _n (620.58) _n	Calcd	69.68	3.25	9.03	3.67
		Found	67.12	3.61	8.41	
		Corrected	69.58	3.48	8.72	
IV _f	(C ₃₇ H ₂₂ N ₄ O ₆) _n (618.60) _n	Calcd	71.84	3.58	9.06	3.95
		Found	69.00	3.91	8.45	
		Corrected	71.73	3.76	8.78	
IV _g	(C ₃₆ H ₂₀ N ₄ O ₆ S) _n (636.64) _n	Calcd	67.92	3.17	8.80	3.92
		Found	65.26	3.60	8.08	
		Corrected	67.82	3.46	8.40	
IV _h	(C ₄₂ H ₂₄ N ₄ O ₈) _n (712.67) _n	Calcd	70.78	3.39	7.86	3.67
		Found	68.18	3.68	7.53	
		Corrected	70.68	3.54	7.81	

Table 2 (continued)

Polymer	Formula (mol. weight)		Elemental analysis ^a (%)			Moisture uptake ^b (%)
			C	H	N	
IV _i	(C ₄₂ H ₂₄ N ₄ O ₈) _n (712.67) _n	Calcd	70.78	3.39	7.86	2.64
		Found	68.91	3.62	7.56	
		Corrected	70.73	3.52	7.76	
IV _j	(C ₅₁ H ₃₄ N ₄ O ₈) _n (830.85) _n	Calcd	73.73	4.12	6.74	3.49
		Found	71.16	4.37	6.45	
		Corrected	73.64	4.22	6.68	
IV _k	(C ₅₁ H ₂₈ N ₄ O ₈ F ₆) _n (938.80) _n	Calcd	65.25	3.01	5.97	3.60
		Found	62.90	4.12	5.57	
		Corrected	65.16	3.97	5.77	
IV _l	(C ₄₈ H ₂₈ N ₄ O ₁₀ S) _n (852.83) _n	Calcd	67.60	3.31	6.57	3.05
		Found	65.54	3.59	6.35	
		Corrected	67.54	3.48	6.54	

^a For C and N: corrected value = found value × (100% + moisture uptake %). For H: corrected value = found value × (100% – moisture uptake %).

^b Moisture uptake (%) = [(W – W₀)/W₀] × 100%; W = weight of polymer sample after standing at room temperature, and W₀ = weight of polymer sample after dried in vacuum at 120°C for 10 h.

viscosity of the polymer solution was 1.19 dl g⁻¹ at 30°C, measured at a concentration of 0.5 g dl⁻¹ in *N,N*-dimethylacetamide (DMAc) containing 5 %wt LiCl. Other poly-(amide-imide)s **III**_{a-1} and **IV**_{a-1} were synthesized in a similar manner.

3. Measurements

Elemental analyses were carried out a perkin-elmer model 2400 C,H,N analyser. Inherent viscosities of all polymers were determined at 0.5 g dl⁻¹ concentration using a

Table 3
Solubility of poly(amide-imide)s^a

Polymer ^c	Solvent ^b								
	DMAc	DMAc +5% LiCl	NMP	DMF	DMSO	<i>m</i> -Cresol	Py	THF	Conc. H ₂ SO ₄
III _a	–	+	±	–	–	–	–	–	+
III _b	+	+	+	–	+	+	+ h	–	+
III _c	+	+	+	+	+ h	+ h	+	–	+
III _d	+	+	+	+	+	+	+	–	+
III _e	+	+	+	+	+	+	+	–	+
III _f	+	+	+	+	–	+	+	–	+
III _g	+	+	+	–	+	+	+	–	+
III _h	+	+	+	+	+ h	+	+	–	+
III _i	+	+	+	±	+	+	+	–	+
III _j	+	+	+	±	+	+	+	–	+
III _k	+	+	+	+	+	+	+	+	+
III _l	+	+	+	+	+	+	+	–	+
IV _a	–	–	–	–	–	–	–	–	+
IV _b	+	+	+	–	+	+	+ h	–	+
IV _c	+	+	+	+	+	+	+	–	+
IV _d	+	+	+	–	–	+	+	–	+
IV _e	+	+	+	+	+	+	+	–	+
IV _f	+	+	+	+	+	+	+	–	+
IV _g	+	+	+	–	+	+	+	–	+
IV _h	+	+	+	±	+ h	+	–	–	+
IV _i	+	+	+	–	+ h	–	–	–	+
IV _j	+	+	+	+	+ h	+	+	–	+
IV _k	+	+	+	+	+	+	+	+	+
IV _l	+	+	+	+	+ h	+	+	–	+

^a Solubility: +, soluble; + h, soluble on heating; ±, partially or swelling; –, insoluble at room temperature.

^b DMAc, *N,N'*-dimethylacetamide; DMF, *N,N*-dimethylformamide; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethylsulfoxide; Py, pyridine; THF, tetrahydrofuran.

^c All of polymers are insoluble in dioxane, CHCl₃, xylene, acetone and MeOH.

Cannon–Fenske viscometer. Solubilities were determined at 1% (w/w) concentration. Colouration of all polymers was determined by Macbeth Colour-eye. Measurements were performed with films about 0.05 mm thick, observational angle was 10°, illuminant was CIE-D, and colour difference equation used was CIE LAB. 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 cm³ min⁻¹) at a heating rate of 20°C min⁻¹. The samples were heated to 400°C, then quenched from the elevated temperature to room temperature in air to yield more amorphous samples so that T_g of polymers could be easily detected in the second heating. Thermogravimetry (TG) was done on a rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100. Measurements were performed with 10 ± 2 mg samples 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 5 kg was used to study the stress–strain behaviour of the sample. A gauge 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 the average of at least five individual determinations was reported.

4. Results and discussion

4.1. Polymer synthesis

A diimide-diacid was prepared from *m*-phenylenediamine (*m*-PDA) and trimellitic anhydride (TMA), and then was directly polycondensated with various aromatic diamines to synthesize alternate poly(amide-imide)s [P(A-alt-I)s] **III**. Another series of isomeric P(A-alt-I)s **IV** was synthesized from *m*-PDA with various diimide-diacids, which were prepared from TMA with various aromatic diamines, as shown in Scheme 1. Direct polycondensation was performed using triphenyl phosphite and pyridine as condensing agents. The reaction conditions were shown in Table 1. In high monomers concentration, the reaction solutions were homogeneously transparent in the presence of CaCl₂ in NMP. The viscosity of some reaction solutions increased after about 1 h, and an additional volume of NMP was added to the reaction mixture to reduce the viscosity of polymer solution for smooth stirring. The series of P(A-alt-I)s **III** had inherent viscosities of up to 1.71 dl g⁻¹ and 1.88 dl g⁻¹ for series of P(A-alt-I)s **IV**. Due to the rigid structure of *p*-phenylene unit, **III_a** and **IV_a** were insoluble in the solvent and had low inherent viscosities. Except for **III_a** and **IV_a**, all of the polymers had inherent viscosities above 1.0 dl g⁻¹. The results of elemental analyses of the two series polymers were listed in Table 2. In all cases, the observed values of carbon and nitrogen were lower than the calculated ones for the

Table 4
Colour data of poly(amide-imide) films

Code	Calculated data ^a		
	DB	DA	DL
Paper	-9.77	0.92	92.67
Kapton	62.88	10.98	76.23
III_a	—	—	—
III_b	39.83	-8.16	86.97
III_c	49.76	-9.99	86.53
III_d	73.59	-10.07	78.33
III_e	71.98	-4.10	83.64
III_f	61.75	-6.33	83.43
III_g	56.92	-5.70	83.78
III_h	68.43	-8.96	85.87
III_i	63.72	-5.52	82.11
III_j	54.98	-12.94	88.94
III_k	56.09	-10.48	86.60
III_l	45.49	-12.87	88.54
IV_a	—	—	—
IV_b	39.83	-8.16	86.97
IV_c	40.61	-8.02	86.66
IV_d	44.51	-6.86	82.23
IV_e	40.74	-9.45	86.02
IV_f	57.90	-7.53	84.29
IV_g	36.16	-8.38	87.42
IV_h	47.69	-6.71	84.04
IV_i	36.87	-0.14	73.98
IV_j	28.94	-7.86	86.91
IV_k	36.20	-8.74	86.73
IV_l	38.90	-7.17	85.32

^a Standard, Paper; Calculation Eq., CIE LAB. DB values '+' tend to yellow, '-' tend to blue; DA values '+' tend to red, '-' tend to green; DL values from 100 to 0 mean white to black.

proposed structures, but the hydrogen values were higher. This could result from the hygroscopic nature of the samples, something attributed to the amide groups of polymers. The amounts of absorbed water for the two series polymers were in the range of 2.64%–5.94%. The moisture uptake was calculated from the weight loss of the polymer samples at 120°C under vacuum after they were exposed to the air at room temperature for 5 min. The corrected values were in agreement with the calculated ones after deducting the amount of moisture uptake.

4.2. Solubility

The solubility of these two series polymers (**III** and **IV**) was tested qualitatively in various solvents. The results were shown in Table 3. The polymers of the two series containing *m*-phenylene structure exhibited excellent solubility in polar amide solvents and *m*-cresol. Due to the rigid structure of *p*-phenylene moiety, the solubility of **III_a** and **IV_a** was limited. The solubility in amide solvents was in the order of NMP > DMAc > DMF. DMSO was similar to DMF. Polymers **III_{a-1}** and isomeric **IV_{a-1}** had similar solubility in the amide solvents, but were insoluble in general organic solvents such as xylene, dioxane, CHCl₃, and

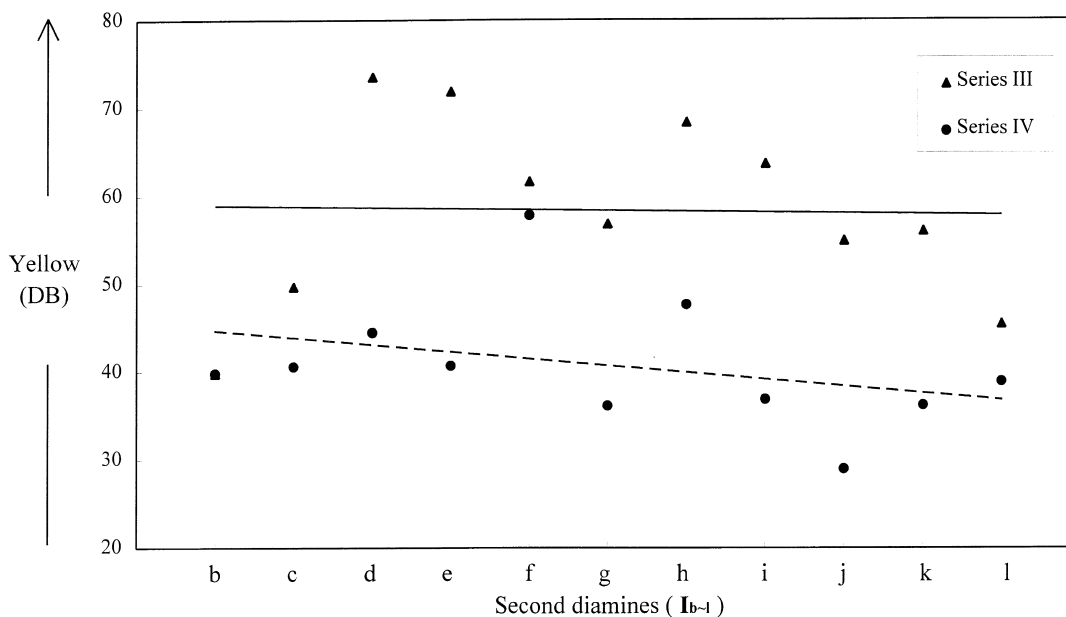


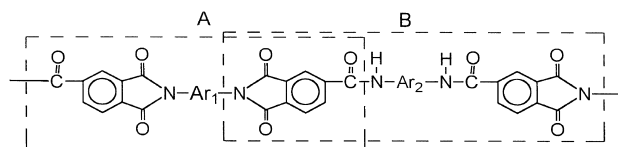
Fig. 1. Colour data of DB values for series **III** and **IV**.

acetone. In THF, only **III_k** and **IV_k** with fluorine atoms were soluble.

4.3. Colouration

Colouration of all polymers was determined by Macbeth Colour-eye, and CIE LAB colour system was applied. The results were shown in Table 4. These parameters are generally used by the industry to describe the colour, colour intensity, and colour difference. In Table 4, DL is lightness. The colour is quantitatively described by parameters DA and DB. For instances, a red sample has a positive DA, and a green sample possesses a negative DA value. Similarly, positive DB means yellow colour, while negative DB implies blue colour. For colourless film, the values of DA and DB are 0 and the value of DL is 100. The item Paper refereed to in Table 4 was the result of white paper that was used as a standard. When polymer films were tested, a white paper was placed behind the films as a ground. The popular polymer, Kapton, was also tested and it had a little red and much yellow. The differences of DA (values are small) and DL (affected with thickness and surface of film) between the two series polymers were small, but the values of DB (colouration of yellow) were large. The DB changed according to the type of polymer as follows, **III_d** > **III_e**, **III_h** > **III_i**, **IV_d** > **IV_e**, and **IV_h** > **IV_i**. With increasing percentage of the *m*-phenylene group in the polymer, the colour of films became light. It was clearer in series **III**, where high percentage polymers **III_{b,c}** were lighter coloured than others. From DB of the two series, polymers of series **III** were larger than those of the isomeric **IV** series, as shown in Fig. 1. The differences were in the range of 20–30 DB, but were reduced when the second diamines were **I_{c,f,l}**. From the above results, we found that

the colouration of polymers was caused by A and B segments:



The Ar_2 in the B segment affected the colouration more strongly than Ar_1 in the A segment. The weaker the electron-donating nature of a diamine in the B segment is, the lighter coloured the polymer is. From the data, the polymers of series **IV** containing *m*-phenylene moiety between two amide groups have lighter colour than the isomeric **III** series containing *m*-phenylene between two imide groups, and it corresponds with the above result. To reduce colour, not only do the polymers need a high percentage of the *m*-phenylene group but the *m*-phenylene group has to be located between two amide groups in P(A-alt-I).

4.4. Mechanical properties

Except for **III_a**, **IV_a** and **IV_i**, transparent and tough films could be cast from the DMAc solutions of all the poly-(amide-imide)s. The tensile properties were summarized in Table 5. Some polymers of the **III** series, in which the linkages (-Ar-) of second diamines had more phenyl-ether chains, such as **III_{h-1}**, exhibited yield points and had strengths of 90–117 MPa. The films of series **III** had tensile strengths of 87–112 MPa, elongations to break of 6%–39%, and initial moduli of 1.74–2.81 GPa. The films of series **IV** had yield strengths of 92–103 MPa, tensile strengths of 86–105 MPa, elongations to break of 7%–42%, and initial moduli of 2.31–2.60 GPa. Most of the **III** series films had

Table 5
Tensile properties of poly(amide-imide) films^a

Code ^b	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
III _a	—	—	—	—
III _b	—	110	8	1.74
III _c	—	112	9	2.81
III _d	—	87	6	1.77
III _e	—	99	13	1.77
III _f	—	103	7	2.16
III _g	—	110	7	2.43
III _h	106	103	12	2.71
III _i	117	109	14	2.58
III _j	97	96	39	1.98
III _k	90	88	11	1.91
III _l	96	89	15	2.34
IV _a	—	—	—	—
IV _b ^c	—	110	8	1.74
IV _c	98	91	9	2.48
IV _d	100	95	42	2.48
IV _e	97	86	37	2.31
IV _f	96	93	20	2.60
IV _g	—	105	7	2.54
IV _h	92	91	12	2.39
IV _i ^d	—	—	—	—
IV _j	103	101	35	2.36
IV _k	—	97	7	2.60
IV _l	96	90	29	2.60

^a Films were cast from polymer solutions of DMAC.

^b Films of polymers III_a and IV_a could not be obtained.

^c III_b and IV_b are the same.

^d Film was brittle.

higher tensile strengths, and most of the IV series films exhibited yielding. Elongations to break and initial moduli of the IV series films were also higher than those of the III series films, and the IV series films were stronger and tougher than the III series films. Except for III_a and IV_a, Series III and IV polymers had good mechanical properties. Especially, III_j and IV_{d,e,j} had yield points, high tensile strengths, long elongations to break and high initial moduli.

4.5. Thermal properties

The thermal behaviour data of all polymers were listed in Table 6. Due to the symmetry and stiffness of *p*-phenylene moiety, transitions were not observed for polymers III_a and IV_a. III_{a-g} and IV_{a-g}, which had shorter linkages (-Ar-) of second diamines than those of III_{h-k} and IV_{h-k} containing more phenyl-ether chains, showed higher T_g values. III_l and IV_l containing the -SO₂- group, which had higher polarity and increased the intermolecular forces, exhibited higher T_g values. Except for IV_e, series of polymers IV exhibited the same or higher T_g than did the isomeric III series. The T_g s of series III were in the range of 223–278°C, and series IV were higher T_g s of 228°C–293°C. This may be due to the effect of the chain rotation of polymers.

The 10% decomposition temperatures ($T_{d,10\%}$) of two

series polymers were recorded in the range of 472°C–561°C in nitrogen. The TGA curves for two series polymers indicated that all of the polymers did not significantly lose weight below 450°C in nitrogen and the air atmosphere. Most of the polymers decomposed faster in the air, so $T_{d,10\%}$ s were lower in the 472°C–574°C range. III_a and IV_a containing the *p*-phenylene structure had higher $T_{d,10\%}$ s than other polymers, and polymers containing I_{h,k,l} as second diamines also had higher $T_{d,10\%}$ s. This may be due to the fact that the long chain will bring polymers closer. In addition, the polymers with fluorine atoms were heat-resistant. The char yields of polymers at 800°C in nitrogen were as high as 58%, indicating good thermal stability. Because the degree of polymerization of IV_a was low, its char yield and $T_{d,10\%}$ in the air were affected. From the data, the polymers with more phenyl-ether chains had no effect on the resistance of heating, but the polymers with short linkages (-Ar-) (III_{b,c} and IV_{b,c}) had worse thermal stability than others.

5. Conclusion

Most polymers of aromatic polyimide or polyamide-imide [P(A-alt-I)] are coloured (dark colour). When alternate

Table 6
Thermal behaviour data of poly(amide-imide)s

Code	DSC T_g^a (°C)	TG		Char Yield ^c (%)
		Decomposition temperature ^b (°C)		
		In air	In nitrogen	
III _a	—	574	560	64
III _b	278	472	472	62
III _c	277	477	480	63
III _d	254	488	495	66
III _e	270	511	550	66
III _f	251	507	506	67
III _g	242	496	505	63
III _h	244	537	535	64
III _i	223	516	509	63
III _j	225	522	525	66
III _k	229	537	545	60
III _l	256	524	536	60
IV _a	—	527	553	51
IV _b ^d	278	472	472	62
IV _c	293	490	480	60
IV _d	277	500	504	64
IV _e	258	492	492	63
IV _f	262	513	508	67
IV _g	253	484	498	67
IV _h	247	536	550	63
IV _i	254	522	561	60
IV _j	245	516	515	67
IV _k	228	506	540	58
IV _l	261	513	528	61

^a From the second heating traces of DSC measurements conducted with a heating rate of 20°C min⁻¹ in nitrogen.

^b Temperatures at which 10% weight loss was recorded by TG at heating rate of 20°C min⁻¹.

^c Char yield in TGA at 800°C under nitrogen atmosphere.

^d III_b and IV_b are the same.

P(A-alt-I) was synthesized of trimellitic anhydride and two aromatic diamines, the P(A-alt-I) synthesized had light colour was even colourless if one of the diamines was *m*-phenylenediamine (*m*-PDA). For polymers' structure, *m*-PDA between two amide groups (the IV series) had less colouration than *m*-PDA between two imide groups (the III series). In this research, 12 aromatic diamines are used by direct polycondensation to synthesize 24 P(A-alt-I)s. Most polymers are soluble in polar solvent, such as DMAc, DMSO, NMP, etc., and can be made into transparent, flexible, and tough films upon casting from DMAc solution. Either the degree of polymerization or structure of second diamine affects mechanical properties of films. Most of them exhibit yielding, and they have tensile strengths of 86–112 MPa, elongations to break of 6%–42%, and initial moduli of 1.74–2.81 GPa. The glass transition temperatures of Series IV are in the range of 228°C–293°C, which are higher than Series III in the range of 223°C–278°C. The 10% weight loss temperatures for these two series are close and in the range of 472–561°C

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