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Synthesis and properties of soluble colorless poly(amide–imide)s based on *N,N′*-bis(3-carboxyphenyl)-4,4′-oxydiphthalimide and various aromatic diamines

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Abstract

The diimide–diacid monomer, *N,N′*-bis(3-carboxyphenyl)-4,4′-oxydiphthalimide (**I**), was prepared by azeotropic condensation of 4,4′-oxydiphthalic anhydride and *m*-aminobenzoic acid at a 1:2 molar ratio in polar solvent and toluene. A series of organosoluble and colorless poly(amide–imide)s with inherent viscosities ranging from 0.95 to 1.70 dl/g were synthesized from diimide–diacid **I** and various aromatic diamines by the direct polycondensation using triphenyl phosphite and pyridine as condensing agents. From UV–visible spectrum and resulting parameters of Macbeth Color-eye colorimeter, these polymers were much lighter in color than other analogous polymers. All the poly(amide–imide)s were readily soluble in a variety of organic solvents such as NMP, DMAc, DMF, and DMSO, and some even could be dissolved in less polar solvents such as *m*-cresol and pyridine. The cast films exhibited tensile strengths ranging from 82 to 106 MPa, elongations to break from 10 to 15%, and initial moduli from 1.9 to 2.3 GPa. Poly(amide–imide)s had glass transition temperatures of 221–276°C and 10% weight loss temperatures of 551–570°C in nitrogen and 548–578°C in air indicating excellent thermal stability.

Keywords: *N,N′*-Bis(3-carboxyphenyl)-4,4′-oxydiphthalimide; Colorless; Poly(amide–imide)s; Organosoluble

1. Introduction

Aromatic polyimides are well known as polymer materials of high performance for their excellent thermal stabilities and balanced mechanical and electric properties [1–7]. Polyimides are mainly used in the aerospace and electronics industries in the form of films and moldings. Optical transparency of polyimide films is of special importance in some applications such as flexible solar radiation protectors [8,9], orientation films in liquid crystal display devices [10,11], optical waveguides for communication interconnects [12], and optical half-waveplates for planar lightwave circuits [13]. However, the wholly aromatic polyimides strongly absorb in the visible region of their UV–visible spectra and are pale yellow or deep reddish yellow because of their highly conjugated aromatic structures and/or the intermolecular charge-transfer complex (CTC) formation [14].

In order to increase the optical application of polyimides, a number of very lightly colored to colorless, transparent polyimide films have been synthesized and characterized. Rogers first reported that optically transparent and colorless polyimides can be synthesized from a dianhydride and a diamine that have hexafluoroisopropyridene ($-C(CF_3)_2-$) groups [15]. Dinc-Hart et al. have shown the formation of CTC between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [14]. St. Clair et al. focused much attention on colorless polyimides from the viewpoint of the potential applications on space components such as multilayer insulation blankets, solar cells, and thermal control coating systems [16–18]. They demonstrated that polyimides containing the hexafluoroisopropylidene group and/or sulfone linkage exhibited high transparency in the visible region.

Many other examples have since been reported where dianhydrides with a biphenyl structure and fluorinated or aliphatic monomers were employed [19–24]. However, 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, one of them being poly(amide–imide), whose amide groups

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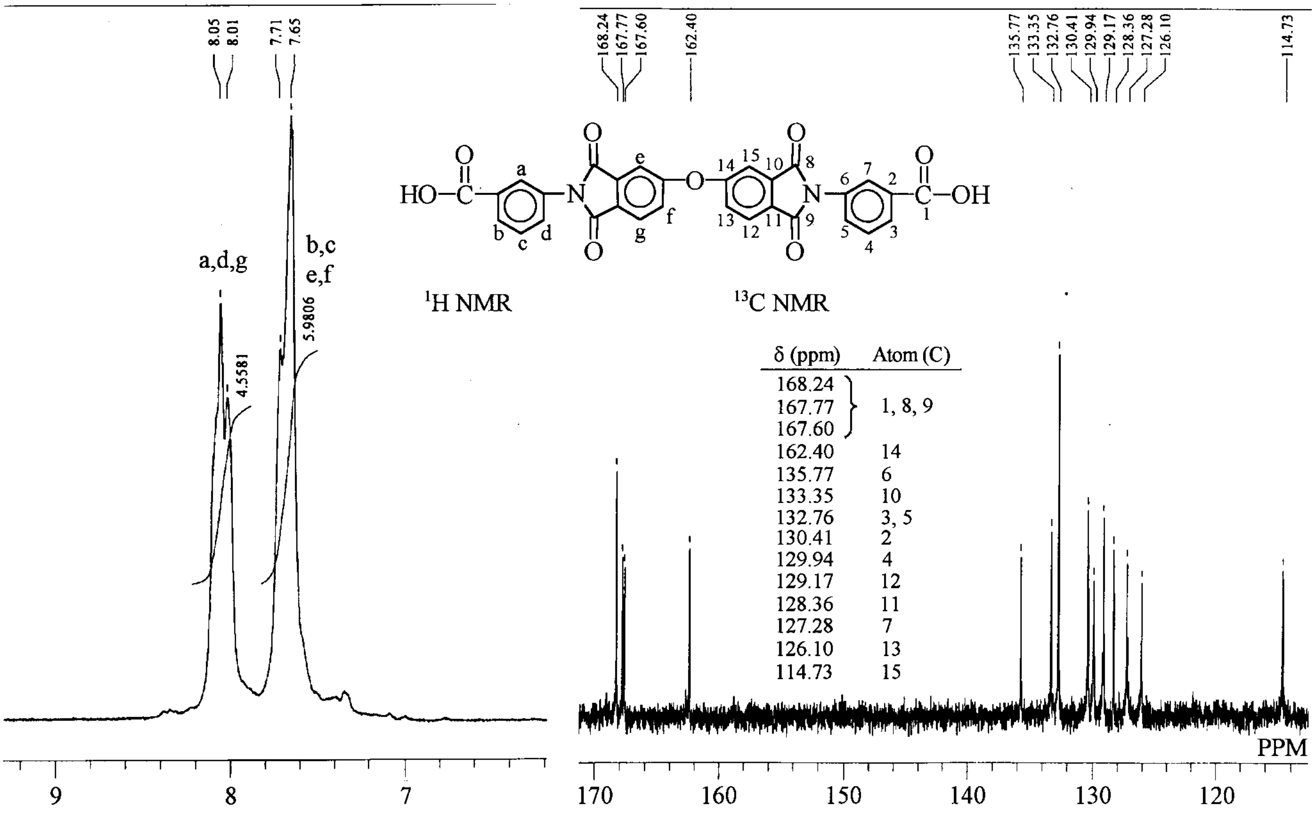


δ (ppm)	Atom (C)
168.24 167.77 167.60	1, 8, 9
162.40	14
135.77	6
133.35	10
132.76	3, 5
130.41	2
129.94	4
129.17	12
128.36	11
127.28	7
126.10	13
114.73	15

Fig. 1. NMR spectra of diimide–diacid **I**.

can improve solubilities [25,26]. Furthermore, poly(amide–imide)s were lighter in color than corresponding polyimides. In our previous report [27], *m*-phenylenediamine has been polycondensated with trimellitic anhydride and various diamines to synthesize poly(amide–imide)s, which were found to be of light color due to the *m*-phenylene group.

In this study, poly(amide–imide)s having light color and heat-resistant characters were synthesized. In general, the study of new polyimide or poly(amide–imide) syntheses using monomers with various structures has been carried out to improve the coloration of polymers. For example, dianhydrides with polyalicyclic structures are used [28] but heat resistance of polymers obtained is sacrificed. Although fluorinated monomers are effective in decreasing coloration [15], the monomers are too costly to be utilized. Therefore, commercially available and cheap monomers, 4,4′-oxydiphthalic anhydride and *m*-aminobenzoic acid, were used in this study to prepare an imide ring-performed dicarboxylic acid (**I**), which is then reacted with aromatic diamine to synthesize poly(amide–imide)s. Because this diacid monomer **I** had *m*-phenylene groups and flexible ether linkages, it was expected to decrease coloration and improve solubility of polymers. In addition, poly(amide–imide)s were prepared with low cost and could maintain good thermal stability. Some basic characterizations of the obtained polymers also are investigated in present article.

2. Experimental section

2.1. Materials

Aromatic diamines: *p*-Phenylenediamine (**II**$_a$; from Wako) and *m*-phenylenediamine (**II**$_b$; from TCI) were vacuum-distilled before use. All other diamines such as 4,4′-oxydianiline (**II**$_c$; from Wakayama), 4,4′-methylenedianiline (**II**$_d$; from TCI), 4,4′-thiodianiline (**II**$_e$; from TCI), and 4,4′-(1,4-phenylenedioxy)dianiline (**II**$_f$; from TCI) were used as received. The diamines 4,4′-(1,3-phenylenedioxy)dianiline (**II**$_g$), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**II**$_h$), 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (**II**$_i$), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**II**$_j$) were obtained from Chriskev Corp. and used without previous purification. *m*-Aminobenzoic acid (*m*-ABA; from TCI) and triphenyl phosphite (TPP; from TCI) were used as received. 4,4′-Oxydiphthalic anhydride (ODPA; from Chriskev) was recrystallized from acetic anhydride before use. Commercially available calcium chloride ($CaCl_2$) was dried under vacuum at 150°C for 6 h. *N*-methyl-2-pyrrolidone (NMP; from Fluka), *N*,*N*-dimethylacetamide (DMAc;

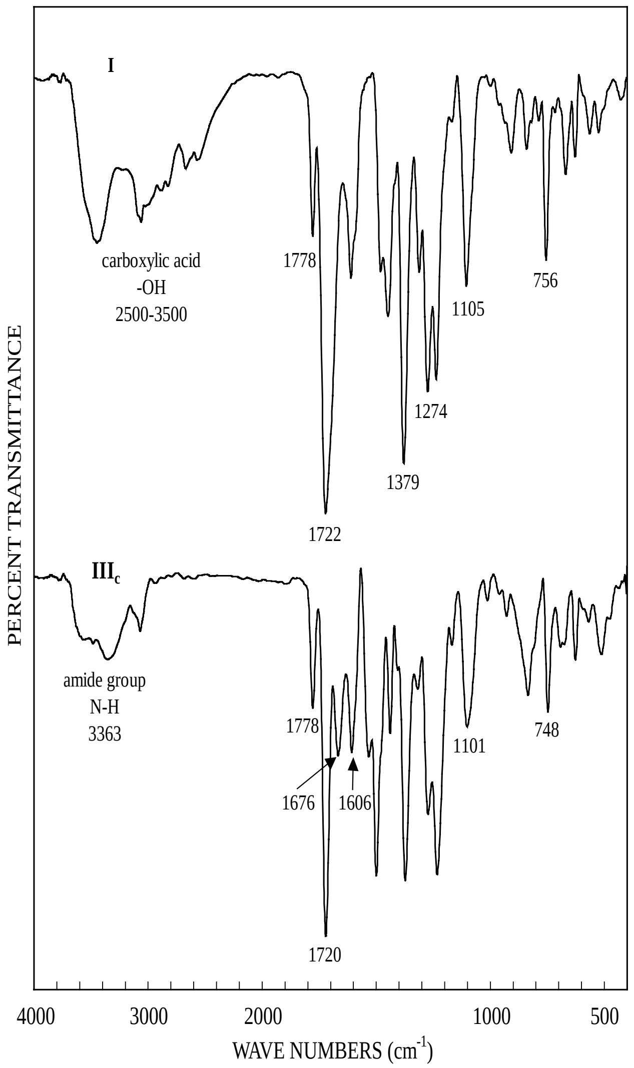


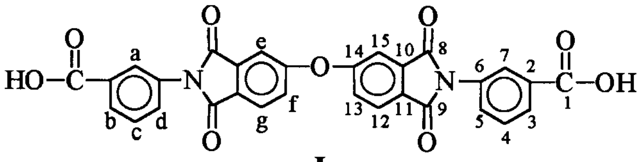
Fig. 2. IR spectra of diimide–diacid **I** and poly(amide–imide) **III$_c$**.

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 acid

m-ABA (8.22 g, 60 mmol) was dissolved in 45 ml of dried DMAc in a 150 ml flask. After *m*-ABA was dissolved completely, 9.30 g (30 mmol) ODPA was added to it in one portion. The mixture was stirred at room temperature for 1 h. Toluene (20 ml) was then added, and the mixture was heated at the reflux for about 3 h until about 1.08 ml of water was distilled off azeotropically in a Dean–Stark trap. Heating was continued to distill off the residual toluene. After cooling, methanol was added and the precipitated product was isolated by filtration, purified by recrystallization from DMF–methanol solution, and dried in vacuum, to give 15.86 g of diimide–diacid **I** (97% yield).

Diimide–diacid **I**: m.p. 381°C. IR (KBr): 2500–3500 (acid –OH), 1778 (imide, symmetric C=O stretching), 1722 (acid C=O stretching and asymmetric imide C=O stretching), 1274 (ether C–O–C), 1379, 1105, 756 cm^{-1} (imide, imide ring vibration, axial, transverse, and out of plane) (see Fig. 2). ^{1}H NMR (DMSO-d$_6$, δ, ppm): 8.05, 8.01 (3H, H$_a$ + H$_d$ + H$_g$), 7.71, 7.65 (4H, H$_b$ + H$_c$ + H$_e$ + H$_f$). ^{13}C NMR (DMSO-d$_6$, δ, ppm): 168.24, 167.77, 167.60 (C^1, C^8, C^9), 162.40 (C^{14}), 135.77 (C^6), 133.35 (C^{10}), 132.76 (C^3, C^5), 130.41 (C^2), 129.94 (C^4), 129.17 (C^{12}), 128.36 (C^{11}), 127.28 (C^7), 126.10 (C^{13}), 114.73 (C^{15}) (see Fig. 1).



I

Analysis (wt%): calculated for C$_{30}$H$_{16}$N$_2$O$_9$: C, 65.70; H, 2.95; N, 5.11; found: C, 65.09; H, 3.25; N, 5.20.

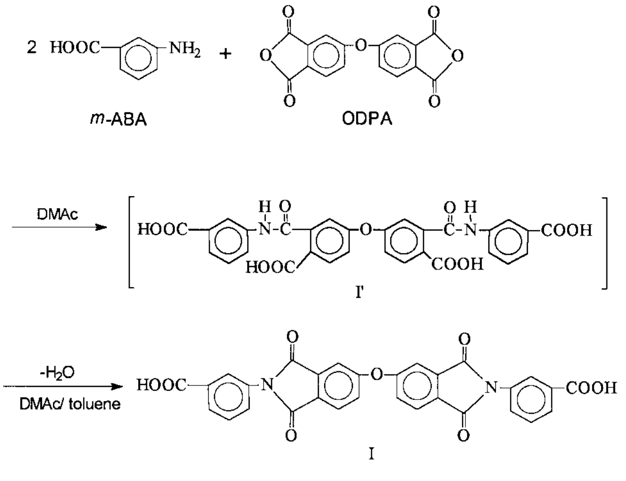
2.3. Synthesis of poly(amide–imide)s

Synthesis of poly(amide–imide) **III$_g$** is described as a typical procedure. A mixture of 0.822 g (1.5 mmol) of diimide–diacid **I**, 0.438 g (1.5 mmol) of 4,4′-(1,3-phenylenedioxy)dianiline (**II$_g$**), 0.38 g of CaCl$_2$, 1.4 ml of Py, 0.9 ml of TPP, and 5.0 ml of NMP was heated with stirring at 100°C for 3 h. The viscosity of reaction solutions increased after 1 h and an additional 6.0 ml of NMP was added to the reaction mixture. At the end of the reaction, the polymer solution was slowly 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 1.19 g (yield: 99%). The inherent viscosity of the polymer **III$_g$** was 1.70 dl/g at 30°C, measured at a concentration of 0.5 g/dl in DMAc.

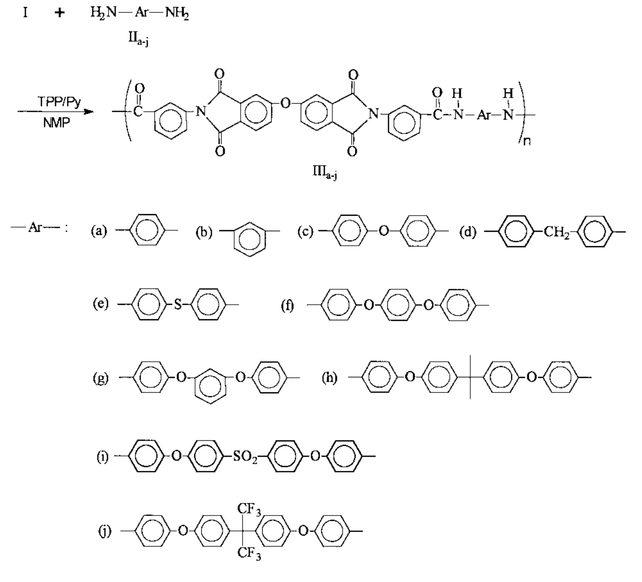
Other poly(amide–imide)s **III** were synthesized in a similar manner. A typical set of IR spectrum and the results of elemental analysis of polymers are shown in Fig. 2 and Table 2, respectively.

2.4. Measurements

Melting points were measured in capillaries on a Yamato mp apparatus (Model MP-21) without correction. Elemental analyses were run in a Perkin–Elmer Model 2400 C,H,N analyzer. IR spectra were recorded on a Horiba Fourier-Transform Infrared Spectrometer FTIR-720. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol EX-400 FT-NMR spectrometer. Inherent viscosities of all polymers were determined at 0.5 g/dl concentration using a Cannon–Fenske viscometer at 30°C. Solubilities were determined at 1% (w/w) concentration. Coloration of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films of about 0.06 mm in thickness, using an observational angle of 10°



Scheme 1.



Scheme 2.

and a CIE (Commission International de l'Eclairage)-D illuminant. A CIE LAB color difference equation was used. UV–visible spectra of the polymer films were recorded on a Shimadzu UV–visible recording spectrophotometer UV-1601 at room temperature in air. Differential scanning calorimeter (DSC) traces were measured on TA Instruments DSC 2010 at the rate of 15°C/min in flowing nitrogen (40 cm^3/min). Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (100 cm^3/min) at a heating rate of 20°C/min. An Instron Universal Tester Model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the sample. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.06 mm thick), and the average of at least five individual determinations was reported.

3. Results and discussion

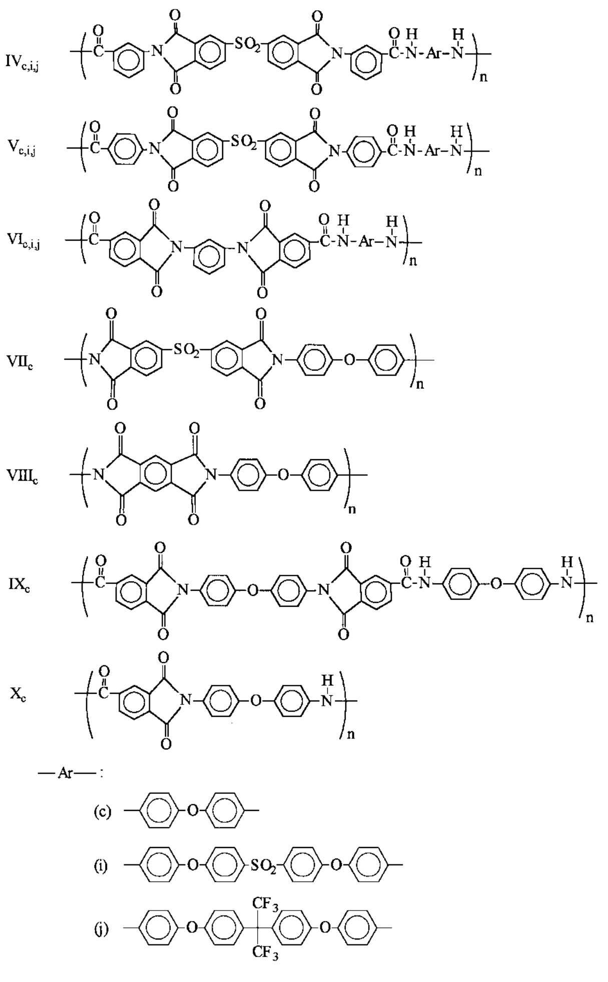
3.1. Synthesis

Poly(amide–imide)s **III$_a$–$_j$** were synthesized in two steps starting from *m*-ABA and ODPA to prepare a diimide–dicarboxylic acid **I**, which was then reacted with various aromatic diamines **II$_a$–$_j$** by direct polycondensation to prepare poly(amide–imide)s. *N,N′*-Bis(3-carboxyphenyl)-4,4′-oxydiphthalimide (**I**), the new polymer-forming diimide–diacid with preformed imide rings, was synthesized via the two-stage procedure that included the ring-opening addition of ODPA with two equivalents of *m*-ABA at room temperature in polar solvents (such as NMP or DMAc) to form the amide–amide intermediate, followed by thermal cyclodehydration to the diacid **I** at reflux temperature by toluene–water azeotropic distillation, as shown in Scheme 1. The crude **I** was purified by recrystallization from DMF. The structures of monomer **I** was confirmed by elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Fig. 1 shows the typical ^{1}H and ^{13}C NMR spectra of diacid **I**. The ^{1}H NMR spectrum of **I** was divided into two parts: one was the H_a, H_d, and H_g close to imide ring (*ortho*-oriented protons) at the downfield region, due to resonance; the other was the H_b, H_e, and H_f *ortho*-oriented to carboxylic acid or aromatic ether at the upfield region, due to the shielding effect. The ^{13}C NMR spectrum revealed fourteen peaks as a result of the overlap of C^3 and C^5 were in agreement with the predicted structure of **I**. The carbons C^1, C^8, and C^9 of carbonyl groups presented in the downfield at 167.60–168.24 ppm and the different shifts of C^8 and C^9 were caused by the asymmetric structure of *m*-phenylene. Due to the proximity with the aromatic ether, the C^{14} also appeared in the downfield.

Table 1
Synthesis of poly(amide–imide)s (polymerization was carried out with 1.5 mmol of each monomer, 0.9 ml of triphenyl phosphite and 1.4 ml of pyridine in NMP at 100°C for 3 h)

Polymer	Amount of reagents used			η_{inh} (dl/g)[a]
	NMP (ml)	Additional NMP (ml)	CaCl$_2$ (g)	
III$_a$	5.5	5	0.38	1.19
III$_b$	5.5	5	0.38	1.00
III$_c$	5.5	3	0.38	0.95
III$_d$	5.0	3	0.38	1.69
III$_e$	5.5	9	0.38	1.61
III$_f$	5.5	9	0.38	1.63
III$_g$	5.0	6	0.38	1.70
III$_h$	5.5	3	0.38	1.15
III$_i$	5.0	5	0.37	1.22
III$_j$	5.0	5	0.35	1.54

[a] Measured at 30°C on a concentration of 0.5g/dl in DMAc.



Scheme 3.

A series of poly(amide–imide)s was synthesized by a phosphorylation reaction using TPP as a promoter in NMP in the presence of pyridine and $CaCl_2$ (Scheme 2). The reaction condition and results of the polycondensation are summarized in Table 1. All polymerizations proceeded homogeneously throughout the reaction. The viscosity of 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 poly(amide–imide)s **III** had inherent viscosities of up to 1.70 dl/g. Except for **III$_c$**, all the polymers had inherent viscosities above 1.0 dl/g indicating high molecular weight. The formation of poly(amide–imide)s was confirmed by IR spectroscopy and elemental analysis. The typical IR spectrum of polymer **III$_c$** (Fig. 2) displayed characteristic absorption bands for the imide ring at 1778 and 1720 cm^{-1} because of the asymmetrical and symmetrical C=O stretching vibration and at 1101 and 748 cm^{-1} because of imide ring deformation. The absorptions of the amide groups appeared at 3363, 1676, and 1606 cm^{-1}. The results of elemental analysis of all the poly(amide–imide)s are listed in Table 2. In all cases, however, the carbon values were lower than the calculated values for the proposed structures. This possibly was caused by the hygroscopic nature of the amide groups of these polymers. The uptakes of water were in the range 1.66–4.60%; these were calculated from the weight change of the vacuum-dried polymer samples after they were exposed to air at room temperature for 8–10 h. When the found values were corrected by elimination of the amount of absorbed water, the correction values were in good agreement with the calculated ones.

3.2. Solubility

The solubility of poly(amide–imide)s **III$_a$–$_j$** was tested qualitatively in various solvents. The results are shown in Table 3. These polymers were soluble in aprotic polar solvents such as NMP, DMAc, DMF, and MDSO. In addition to highly polar solvents, they were also soluble or swelling in less polar solvents like *m*-cresol and pyridine. In THF and CH_2Cl_2, only **III$_j$** with fluorine atoms was soluble or swelling. Among these polymers, **III$_j$** showed the best solubility. This may be due to the existence of the bulky hexafluoropropane groups to prevent close chain-packing and allow solvent molecules to diffuse into the polymer chains. The high solubility of these poly(amide–imide)s was apparently due to the introduction of *m*-phenylene structures and flexible ether linkages, which resulted in increased free volume between the polymer chains and decreased intermolecular interactions. For comparing with analogous trimellitic anhydride–4,4′-oxydianiline (TMA–ODA) poly(amide–imide)s, **IX$_c$** and **X$_c$** were also prepared (Scheme 3). Although **IX$_c$** and **X$_c$** were soluble in aprotic polar solvents, they were insoluble in less polar solvents like *m*-cresol and pyridine. Therefore, polymers **III** had better solubility than typical poly(amide–imide)s obtained from TMA and ODA.

3.3. Coloration

The coloration of the polymers was elucidated from the yellowness or redness indices observed by a Macbeth Color-eye colorimeter and CIE LAB color system was applied. The color coordinates of poly(amide–imide)s **III** and corresponding polymers **IV**, **V**, and **VI** (Scheme 3) are given in Table 4. These parameters are generally used by the industry to describe the color, color intensity, and color difference. In Table 4, L^* is lightness; and the color is quantitatively described by parameter a^* and b^*. For instance, a red sample has a positive a^*, and a green sample reveals a negative a^*. Similarly, positive b^* means yellow color, while negative b^* implies blue color. The item ‘Paper’ referred 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. For colorless film, the values of a^* and b^* are 0 and the value of L^* is 100. In general, coloration of aromatic polymer is due to its conjugated aromatic structures and/or the intermolecular and intramolecular charge-transfer complex (CTC) formation. From

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

Polymer	Formula		Elemental analysis[a] (%)			Moisture uptake[b]
	M_w		C	H	N	
III$_a$	$(C_{36}H_{20}N_4O_7)_n$	Calcd	69.68	3.25	9.03	
	$(620.58)_n$	Found	66.54	3.71	8.45	4.34
		Corrected	69.43	3.55	8.82	
III$_b$	$(C_{36}H_{20}N_4O_7)_n$	Calcd	69.68	3.25	9.03	
	$(620.58)_n$	Found	66.74	3.42	8.70	4.22
		Corrected	69.56	3.28	9.07	
III$_c$	$(C_{42}H_{24}N_4O_8)_n$	Calcd	70.78	3.39	7.86	
	$(712.67)_n$	Found	68.54	3.76	7.54	3.16
		Corrected	70.71	3.64	7.78	
III$_d$	$(C_{43}H_{26}N_4O_7)_n$	Calcd	72.67	3.69	7.88	
	$(710.70)_n$	Found	70.35	4.06	7.56	3.19
		Corrected	72.59	3.93	7.80	
III$_e$	$(C_{42}H_{24}N_4O_7S)_n$	Calcd	69.22	3.32	7.69	
	$(728.74)_n$	Found	67.27	3.72	7.36	2.82
		Corrected	69.17	3.62	7.57	
III$_f$	$(C_{48}H_{28}N_4O_9)_n$	Calcd	71.64	3.51	6.96	
	$(804.77)_n$	Found	69.90	3.86	6.90	2.43
		Corrected	71.60	3.77	7.07	
III$_g$	$(C_{48}H_{28}N_{44}O_9)_n$	Calcd	72.64	3.51	6.96	
	$(804.77)_n$	Found	70.12	3.78	6.77	2.12
		Corrected	71.61	3.70	6.91	
III$_h$	$(C_{57}H_{38}N_4O_9)_n$	Calcd	74.18	4.15	6.07	
	$(922.95)_n$	Found	72.79	4.40	6.00	1.87
		Corrected	74.15	4.32	6.11	
III$_i$	$(C_{54}H_{32}N_4O_{11}S)_n$	Calcd	69.83	3.48	6.03	
	$(928.80)_n$	Found	66.62	3.71	5.72	4.60
		Corrected	69.68	3.54	5.98	
III$_j$	$(C_{57}H_{32}N_4O_9F_6)_n$	Calcd	66.41	3.13	5.43	
	$(1030.89)_n$	Found	65.31	3.31	5.64	1.66
		Corrected	66.39	3.26	5.73	

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

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

Table 3
Solubility of poly(amide–imide)s (solubility: +, soluble; ±, partially soluble; −, insoluble; S, swelling)

Polymer	Solvent[a]							
	NMP	DMAc	DMF	DMSO	*m*-Cresol	Py	THF	CH_2Cl_2
III$_a$	+	+	+	+	+	S	−	−
III$_b$	+	+	+	+	+	S	−	−
III$_c$	+	+	+	+	+	S	−	−
III$_d$	+	+	+	+	+	S	−	−
III$_e$	+	+	+	+	+	+	−	−
III$_f$	+	+	+	+	+	+	−	−
III$_g$	+	+	+	+	+	+	−	−
III$_h$	+	+	+	+	+	+	S	−
III$_i$	+	+	+	+	+	+	−	−
III$_j$	+	+	+	+	+	+	+	S
IX$_c$	+	+	+	±	−	−	−	−
X$_c$	+	+	+	+	−	−	−	−

[a] NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethylsulfoxide; Py, pyridine; THF, tetrahydrofuran.

Table 4
Color Coordinates of poly(amide–imide)s. (The color parameters were calculated according to a CIE LAB equation, using paper as a standard. L^* is lightness; 100 means white, while 0 implies black. A positive a^* means red color, while a negative a^* indicates green color. A positive b^* means yellow color, while a negative b^* implies blue color)

Code	b^*	a^*	L^*
Paper	−0.93	−0.56	90.88
$\mathbf{III}_{a}$	28.49	−1.12	76.93
$\mathbf{III}_{b}$	17.17	−4.06	87.01
$\mathbf{III}_{c}$	22.79	−3.52	83.36
$\mathbf{III}_{d}$	25.15	1.39	82.41
$\mathbf{III}_{e}$	32.53	−3.09	79.92
$\mathbf{III}_{f}$	22.34	−2.77	82.78
$\mathbf{III}_{g}$	18.54	−2.25	83.52
$\mathbf{III}_{h}$	22.39	0.59	78.35
$\mathbf{III}_{i}$	19.24	−0.94	81.74
$\mathbf{III}_{j}$	15.03	−2.97	87.03
$\mathbf{IV}_{c}$	33.04	−1.93	79.48
$\mathbf{IV}_{i}$	34.07	−4.69	82.02
$\mathbf{IV}_{j}$	31.25	2.55	73.97
$\mathbf{V}_{c}$	36.27	4.53	72.64
$\mathbf{V}_{i}$	35.53	−3.35	80.75
$\mathbf{V}_{j}$	33.25	2.55	73.97
$\mathbf{VI}_{c}$	73.59	−10.07	78.33
$\mathbf{VI}_{i}$	45.49	−12.87	88.54
$\mathbf{VI}_{j}$	56.09	−10.48	86.60

previous report [28,29], lighter color polymer films were gained when there are more *m*-phenylene groups in the polymer chain because *m*-phenylene can decrease the extent of conjugation. In this study, the differences of a^* (values are small) and L^* (affected by thickness and surface of film) values between these series were small, but the values of b^* (a yellowness index) were large. In series **III**, all the phenylene groups in diacid segments of poly(amide–imide)s **III** were *meta*-linked, so their b^* values were small ranging from 15.03 to 32.53. The smallest b^* value of $\mathbf{III}_{j}$ was due to the strong electron withdrawing groups $–C(CF_3)_2–$, which was effective in preventing the CTC formation. $\mathbf{III}_{b}$ also showed smaller b^* values than the other polymers **III** because of *m*-phenylene groups in diamine segments, which reduced the conjugation of polymer structures. $\mathbf{III}_{e}$ containing 4,4′-thiodianiline moieties had the largest b^* value in series **III**, indicating that 4,4′-thiodianiline moiety could increase the color intensity. This agreed with the previous reported result [28,29].

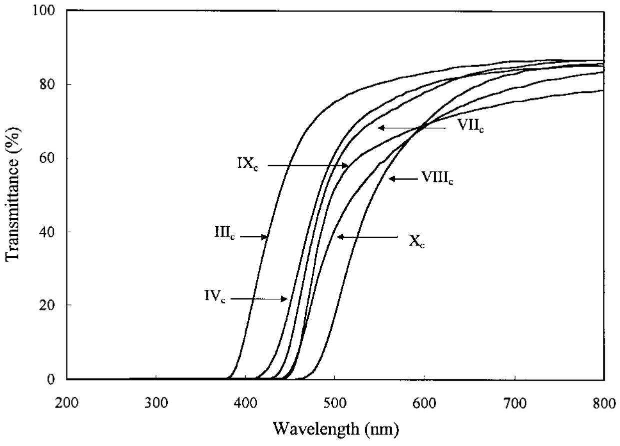


Fig. 3. Transmission UV–visible spectra of about 0.06 mm thick poly(amide–imide) and polyimide films.

The results shown in Table 4 indicate that the **III** series poly(amide–imide)s showed a smaller b^* value in contrast with the corresponding **IV**, **V**, and **VI** series polymers. Although the **VI** series poly(amide–imide)s had *m*-phenylene group between two imide rings in diacid segments, this structure was not effective in reducing color; so the **VI** series showed a larger b^* value than the other series, and $\mathbf{VI}_{c}$ had b^* value of up to 73.59. The a^* values of the **VI** series also were smaller than −10, indicating deeper color of the **VI** series. The **III** series showed a smaller b^* value than the **IV** and **V** series, and this may be due to the fact that ether groups are more effective than sulfone groups in reducing color. The transmission UV–visible spectra of 0.06-mm thick poly(amide–imide) and polyimide films are showed in Fig. 3. The $\mathbf{III}_{c}$ film exhibited a cutoff wavelength at around 375 nm and were highly transparent and colorless in the range from 400 to 800 nm. When dianhydride moieties in $\mathbf{III}_{c}$ were replaced by 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), the cutoff wavelength in the UV–visible spectrum shifted to 405 nm. This shift revealed that polymer based on ODPA had lighter color than that based on DSDA, so $\mathbf{III}_{c}$ showed higher transparency than $\mathbf{IV}_{c}$ in the visible region. Polyimide $\mathbf{VII}_{c}$ was prepared from DSDA and $\mathbf{II}_{c}$ (Scheme 3), and it colored deeper than poly(amide–imide) $\mathbf{IV}_{c}$. This is attributed to higher percentage of the imide group and absence of *m*-phenylene group in the polymer $\mathbf{VII}_{c}$. Polyimide $\mathbf{VIII}_{c}$ derived from pyromellitic dianhydride (PMDA) showed the deepest color than the other three polymers and the cutoff wavelength shifted to 460 nm, revealing the increase of CTC formation by PMDA. In general, TMA-based poly(amide–imide)s, such as synthesized from TMA and ODA, are deep yellow, so polymers **III** are superior to TMA–ODA polymers in optical transparency. For example, $\mathbf{III}_{c}$ were less colored than analogous TMA–ODA poly(amide–imide)s $\mathbf{IX}_{c}$ and $\mathbf{X}_{c}$, as shown in Fig. 3. On the whole, the **III** series poly(amide–imide)s contained *m*-phenylene groups and ether linkages in the polymer chain, so the extent of conjugation and CTC formation were much decreased; therefore, poly(amide–imide)s **III** showed lighter color than corresponding polymers.

3.4. Tensile properties

Transparent and tough films could be cast from the DMAc solutions of all the poly(amide–imide)s. The tensile properties are summarized in Table 5. Polymers $\mathbf{III}_{d,f,h,i}$ exhibited yield points on their stress–strain curves and

Table 5
Tensile properties of poly(amide–imide) films (films were cast from polymer solutions of DMAc)

Polymer	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
III$_a$	–	96	11	2.3
III$_b$	–	106	10	2.3
III$_c$	–	95	14	2.0
III$_d$	88	84	15	1.9
III$_e$	–	89	11	1.9
III$_f$	88	85	10	2.0
III$_g$	–	82	10	2.0
III$_h$	95	90	11	2.0
III$_i$	88	83	12	2.1
III$_j$	–	94	10	2.1

III$_{g,i}$ showed lower tensile strengths. This may be attributable to more phenyl-ether chains in the polymer chain. These films had tensile strengths of 82–106 MPa, elongations to break of 10–15%, and initial moduli of 1.9–2.3 GPa. From these results, this series of poly(amide–imide)s all possessed good tensile properties with strong and tough characters, suggesting that these poly(amide–imide)s can be applied as new materials for engineering plastics.

3.5. Thermal properties

The thermal properties of all the poly(amide–imide)s were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal behavior data of all polymers are listed in Table 6.

DSC measurements were conducted with a heating rate of 15°C/min in nitrogen. Quenching from the elevated temperatures (approximately 400°C) to room temperature in air gave predominantly amorphous samples so that the glass transition temperatures (T_g) of poly(amide–imide)s could be easily measured in the second heating traces of DSC. The T_g values of the poly(amide–imide)s **III**$_{a}$–$_{j}$ were in the range of 221–276°C, depending on the structure of diamine component. **III**$_a$ and **III**$_b$ containing the mono-phenylene group in diamine, which had higher rigidity, exhibited higher T_g values. **III**$_i$ having the polar sulfone groups in polymer backbones also showed high T_g value. **III**$_j$ based on **II**$_j$ with bulky hexafluoropropane group had increased steric hindrances, so their macromolecular chains rotated in higher temperature. **III**$_h$ had structures analogous to **III**$_j$, but substituent magnitude of $-CH_3$ was much smaller than $-CF_3$. Therefore, free volume between **III**$_h$ main chains may be increased without steric hindrance, leading to the lowest T_g value. In comparison with analogous poly-(amide–imide)s **III**$_c$ and **III**$_f$, **III**$_f$ exhibited lower T_g value than **III**$_c$. This may be due to **III**$_f$ had more ether linkages in the polymer chains.

Table 6
Thermal behavior data of poly(amide–imide)s

Polymer	DSC	TGA		
		Decomposition temperature[a] (°C)		Char yield[b] (%)
	T_g[c] (°C)	In air	In nitrogen	
III$_a$	276	564	576	54
III$_b$	265	561	556	62
III$_c$	250	570	578	66
III$_d$	253	570	571	64
III$_e$	251	561	561	65
III$_f$	233	551	567	63
III$_g$	254	563	562	63
III$_h$	221	553	548	62
III$_i$	258	561	556	58
III$_j$	255	553	567	61

[a] Temperature at which 10% weight loss was recorded by TG at heating rate of 20°C/min.

[b] Char yield in TGA at 800°C under nitrogen atmosphere.

[c] From the second heating traces of DSC measurements conducted with a heating rate of 15°C/min.

The thermal stability of the poly(amide–imide)s was characterized by TG analysis conducted at a heating rate of 20°C/min. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original thermograms and also tabulated in Table 6. The T_{10} values of these poly-(amide–imide)s remained in the range of 548–576°C in nitrogen and in the range of 551–570°C in air, respectively. They left more than 54% char yield at 800°C in nitrogen. The lowest thermal stability of **III**$_h$ was brought about by the easy degradation of the aliphatic isopropane group. However, the fluorine-containing poly(amide–imide) **III**$_j$ had a slightly better thermal stability than its nonfluoro analogous **III**$_h$ because the C–F bond of the CF_3 group is stronger than the C–H bond of the CH_3 group. A comparison of **III**$_{a,f}$ and **III**$_{b,g}$ revealed that *para*-oriented phenylene was more thermally stable than *meta*-oriented one. The T_{10} values of **III**$_h$ and **III**$_i$ in air were slightly higher than that in nitrogen, possibly because of the oxidative crosslinking of the isopropane group or the anti-oxidation of sulfone group when thermally degraded in air. Generally speaking, polymers exhibited good thermal stability with no significant weight loss up to approximately 500°C in both air and nitrogen atmospheres, and the anerobic char yield was in the range of 54–66 wt% showing a high intrinsic fire resistance.

4. Conclusions

Most conventional polymers of aromatic polyimide or poly(amide–imide) are colored (dark color). New poly(amide–imide)s containing *meta*-oriented phenylene rings and ether linkages in the polymer had light color, which became even more colorless if electron-withdrawing group is increased. All-*meta*-phenylene diimide–diacid **I** was successfully prepared from ODPA with *m*-ABA, and a total of 10 poly(amide–imide)s were synthesized from **I** with various diamines. These polymers showed excellent solubilities and could be made into transparent and tough films upon casting from DMAc solution. The tensile properties of the polymer films were flexible and tough, and all the polymers exhibited yield points. The glass transition temperatures were in the range of 221–276°C and the 10% weight loss temperatures were recorded higher than 550°C in nitrogen or in air indicating excellent thermal stability. Thus, this series of polymers demonstrates a good combination of physical properties and optical transparence and they are considered as new candidates for processable high-performance polymeric materials.

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