

Organo-soluble and Lightly-colored Fluorinated Polyimides Based on 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride and Aromatic Bis(ether amine)s Bearing Pendent Trifluoromethyl Groups

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ABSTRACT: Two series of soluble and light-colored poly(ether imide)s (**III** and **IV**) were synthesized from 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (**I**) and various fluorinated and non-fluorinated aromatic diamines (**II_{a-g}** and **II'_{a-g}**) by a conventional two-step procedure that included a ring-opening polyaddition to give poly(amic acid)s, followed by chemical cyclodehydration to poly(ether imide)s. The **III** series were lighter-colored and higher optical transparency as compared with the non-fluorinated **IV** series. On comparing the **IV** series with the common lightly-colored aromatic polyimides (**V** series) based on 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), the **IV** series revealed less colored than the **V** series. This indicated that both the **III** and **IV** series were lightly-colored poly(ether imide)s. These polymer films showed the cutoff wavelength in the range of 364–371 nm. The **III** series showed good solubility in all testing solvents at a concentration of 5–10 wt/v % and most of **IV** series was soluble. These polymers exhibited glass-transition temperatures in the range of 194–264 °C, and the 10% weight-loss temperatures were higher than 492 °C under either nitrogen or air atmosphere. The **III** series also showed lower dielectric constants of 3.01–3.65 at 1 MHz and lower moisture absorption of 0.09–0.44 wt % than **IV** series.

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KEY WORDS 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride / Fluorinated Poly(ether imide) / Light Color Polyimide / Organo-soluble Polyimide / Bis(ether anhydride) /

Aromatic polyimides are widely used in the aerospace and electronic industries in the form of films and moldings because of high performance for their excellent thermal stabilities, chemical resistance, and electric properties.^{1,2} Optical transparency of polyimide films is of special importance in some application such as orientation films in liquid crystal display devices,³ and optical half-waveplates for planar light-wave circuits.⁴ However, most polyimides between UV and the visible area have strong absorption, rendering their color close to yellow or brown. In addition, they have poor processability in their imidized forms because of high softening temperatures and insolubility.

By introducing the ether chain^{5,6} or bulky group,^{7,8} the aromatic polyimide can raise the flexibility of polymer, reduce the melting point or T_g , and improve solubility. It was also proved that a lowering of the formation of the charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties provides polyimide with lighter color.^{9,10} Among the six kinds of commercially available aromatic dianhydrides including pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone-tetra-

carboxylic dianhydride (BTDA), 3,3',4,4'-biphenyl-tetracarboxylic dianhydride (BPDA), diphenylsulfone-3,3',4,4'-tetracarboxylic dianhydride (DSDA), 4,4'-oxydiphthalic dianhydride (ODPA) and 6FDA, the polyimides were deriving from ODPA or 6FDA with aromatic diamines showed lighter color than others. The reason was proposed that polyimides containing ether chains^{11–13} or hexafluoroisopropylidene group^{9,14} could reduce the CTC formation of polymer. Therefore, we synthesized the bis(ether anhydride) containing ether chains and hexafluoroisopropylidene group, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (**I**), and produced a series of lightly-colored poly(ether imide) films with various aromatic diamines. Though some poly(ether imide)s had been prepared from bis(ether anhydride) (**I**),^{15–17} their color and dielectric constants etc. were less discussed. Recently, it had also been proved that polyimide contained the trifluoromethyl or ether group can enhance the solubility and thermal stability, reduce dielectric constant and moisture absorption, and raise the optical transparency.^{18–22}

In this study, the bis(ether anhydride) **I** was prepared and a series of novel poly(ether imide)s (**III**)

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were prepared from **I** with CF₃-contained diamines **II_{a-g}**. These polymers were investigated in regard to their solubility, color, optical transparency, dielectric property, and moisture absorption, and they were compared to analogous non-fluorinated poly(ether imide)s **IV**. Moreover, these polymers were also compared with polyimide-6FDA in color.

EXPERIMENTAL

Materials

2,2-Bis(4-hydroxyphenyl)hexafluoropropane (6F-bisphenol-A; Acros), 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (mp 132–133 °C, **II_a**),²⁴ 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene (mp 116–117 °C, **II_b**),²⁵ 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (mp 155–156 °C, **II_c**),¹² 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (mp 256–257 °C, **II_d**),²⁶ 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (mp 131–132 °C, **II_e**),²⁷ 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (mp 65–66 °C, **II_f**),²⁸ 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene (mp 239–240 °C, **II_g**),²⁹ 4,4'-bis(4-aminophenoxy)biphenyl (mp 137–138 °C, **II'_c**),³⁰ 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl (mp 227–228 °C, **II'_d**)³¹ and 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene (mp 239–240 °C, **II'_g**)³² were prepared according to the literature procedures. Other aromatic diamines 1,4-bis(4-aminophenoxy)benzene (**II'_a**, TCI), 1,2'-bis(4-aminophenoxy)benzene (**II'_b**, Chriskev), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**II'_e**, Chriskev) and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**II'_f**, Chriskev) were used as received. Commercially available aromatic dianhydrides including PMDA (Lancaster), BTDA (Acros), and ODPA (Chriskev) were recrystallized from acetic anhydride before use. BPDA (Chriskev), DSDA (New Japan Chemical Co.), and 6FDA (Chriskev) were used as received. Others including 2-chloro-5-nitrobenzotrifluoride (Acros), *p*-chloronitrobenzene (TCI), 4-nitrophthalodinitrile (Acros), acetic anhydride (Ac₂O, Fluka), *N,N*-dimethylacetamide (DMAc, Fluka) and *N,N*-dimethyl formamide (DMF, Fluka) were used as received.

Synthesis of Monomers

2,2-Bis[4-(3,4-dicyanophenoxy)phenyl]hexafluoropropane (**I'**). 6F-bisphenol-A (8.40 g, 25 mmol), 4-nitrophthalonitrile (8.65 g, 50 mmol) and K₂CO₃ (6.90 g, 50 mmol) were suspended in 50 mL of DMF in a 250-mL flask. The suspension solution was stirred at room temperature for 24 h. Then, the reaction mixture was poured into 600 mL of water, and the precipitated white solid was collected and washed thoroughly with

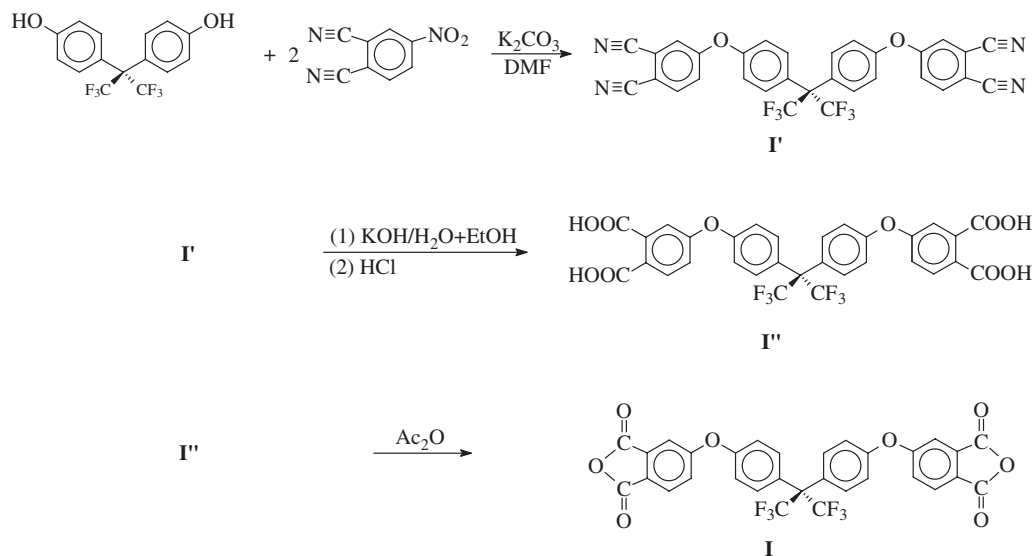
water, methanol and acetonitrile. The yield of the product was 14.26 g (97% yield). The crude product was purified by recrystallization from acetonitrile. The yield of the purified product was 9.64 g (74% yield) (mp 235 °C [Lit.¹⁵ 230 °C]). IR (KBr): 2235 (CN) and 1243 cm⁻¹ (C–O). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 8.15 (d, *J* = 8.7 Hz, 2H, H_b), 7.94 (d, *J* = 2.3 Hz, 2H, H_a), 7.54 (dd, *J* = 8.7, 2.3 Hz, 2H, H_c), 7.50 (d, *J* = 8.6 Hz, 4H, H_e), 7.30 (d, *J* = 8.6 Hz, 4H, H_d). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 159.9 (C³), 154.9 (C⁷), 136.4 (C⁹), 132.0 (C¹⁰), 128.8 (C⁵), 124.0 (C¹², quartet, ¹*J*_{C–F} = 285 Hz), 123.6 (C⁴), 123.1 (C²), 119.9 (C⁸), 116.7 (C¹), 115.7, 115.3 (C^{13,13'}), 109.2 (C⁶), 63.4 (C¹¹, septet, ²*J*_{C–F} = 25 Hz).

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane (**I''**). A suspension of bis(ether dinitrile) **I'** (9.40 g, 16 mmol) in an ethanol/water mixture (110 mL/110 mL) containing KOH (27 g, 0.48 mol) in a 500-mL flask was boiled under reflux at 80–100 °C. The mixture was refluxed for about 24 h until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any possible insoluble impurities. After cooling, the filtrate was acidified by addition of concentrated HCl to pH = 1–2. The resulting precipitate was filtered, washed with boiling water and dried under vacuum (100 °C) (10.10 g, 96% two endothermic peaks 110–170 °C and 233 °C, and one exothermic peak 184 °C. IR (KBr): 2500–3600 (O–H), 1714 (C=O) and 1288 cm⁻¹ (C–O–C). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.86 (d, *J* = 8.5 Hz, 2H, H_b), 7.42 (d, *J* = 8.4 Hz, 4H, H_c), 7.35 (d, *J* = 2.3 Hz, 2H, H_a), 7.23 (dd, *J* = 8.5, 2.3 Hz, 2H, H_c), 7.18 (d, *J* = 8.4 Hz, 4H, H_d). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 168.4, 167.8 (C^{13,13'}), 157.9 (C³), 156.7 (C⁷), 136.8 (C¹⁰), 132.2 (C¹), 131.9 (C⁹), 127.9 (C⁵), 127.8 (C⁶), 124.2 (C¹², quartet, ¹*J*_{C–F} = 285 Hz), 120.4 (C⁴), 119.1 (C⁸), 118.8 (C²), 63.5 (C¹¹, septet, ²*J*_{C–F} = 25 Hz).

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride (**I**). Bis(ether diacid) **I''** (9.96 g, 15 mmol) was suspended in 30 mL of acetic anhydride and 30 mL of glacial acetic acid in a 200-mL flask. The suspension was boiled under reflux until turning into a clear solution. During cooling, the crystallized white crystals were collected, washed with dry toluene, and dried in vacuum to give **I** (8.70 g, 92%; mp 233 °C [Lit.¹⁵ 228 °C]). IR (KBr): 1849 (asym. C=O str.), 1781 (sym. C=O str.) and 1288 cm⁻¹ (C–O–C). ¹H NMR and ¹³C NMR of **I** were shown in Figure 2.

Synthesis of Poly(ether imide)s

Diamine **II_a** (0.213 g, 0.5 mmol) was dissolved in 4.1 mL dried DMAc in a 25-mL flask. After the diamine had completely dissolved, bis(ether anhydride) **I** (0.308 g, 0.5 mmol) was added in one portion. The



Scheme 1.

mixture was stirred at room temperature for 12 h to form a viscous poly(amic acid) (PAA) solution. Then a 0.5-mL mixture of $\text{Ac}_2\text{O}/\text{Py}$ (volume ratio 2/1) was added to PAA solution. The mixture was stirred at 80°C for 1 h, and resulting solution then was poured into a glass culture dish, which was placed in an 110°C oven for 1 h to remove solvent. The semidried polyimide film was further dried to 200°C gradually, and heated at 200°C for 1 h to remove residual solvent. Then, the polymer film was stripped from the glass substrate by soaked in water. Inherent viscosity of **III_a** was 0.83 dL/g in DMAc at a 0.5 g/dL concentration at 30°C .

IR (film): 1780, 1728, 1489, 1379, 1234, 1054, 744 cm^{-1} . $^1\text{H NMR}$ (500 MHz, CDCl_3 , δ , ppm): 8.01 (d, $J = 7.9\text{ Hz}$, 2H, H_b), 7.93 (s, 2H, H_f), 7.72 (d, $J = 8.1\text{ Hz}$, 2H, H_g), 7.56 (s, 2H, H_a), 7.53 (d, $J = 8.5\text{ Hz}$, 4H, H_c), 7.52 (d, $J = 7.9\text{ Hz}$, 2H, H_e), 7.29 (d, $J = 8.5\text{ Hz}$, 4H, H_d), 7.27 (s, 4H, H_i), 7.23 (d, $J = 8.1\text{ Hz}$, 2H, H_h). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$, δ , ppm): 166.1, 166.0 ($\text{C}^{22,23}$), 161.4 (C^3), 156.0 (C^7), 154.5 (C^{20}), 152.0 (C^{16}), 134.3 (C^{10}), 133.2 (C^1), 132.0 (C^9), 128.3 (C^{13}), 126.7 (C^5), 126.3 (C^6), 126.0 (C^{18}), 124.0 (C^4), 123.9 (C^{12} , quartet, $^1J_{\text{C-F}} = 284\text{ Hz}$), 123.0 (C^{19} , quartet, $^1J_{\text{C-F}} = 273\text{ Hz}$), 121.9 (C^{14}), 121.6 ($\text{C}^{8,17}$), 119.7 (C^{21}), 119.6 (C^{15} , quartet, $^2J_{\text{C-F}} = 31\text{ Hz}$), 113.1 (C^2), 63.5 (C^{11} , septet, $^2J_{\text{C-F}} = 25\text{ Hz}$).

Measurements

IR spectra were recorded on a Horiba Fourier-Transform Infrared Spectrometer FT-IR-720. Elemental analyses were run in a Perkin-Elmer Model 2400 CHN analyzer. ^1H and ^{13}C spectra were recorded on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at a 0.5 g/dL concentration using a Cannon-Fenske viscometer at 30°C . Gel

permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters $5\text{ }\mu\text{m}$ styragel HR-2 and HR-4 columns ($7.8\text{ mm I.D.} \times 300\text{ mm}$) connected in series were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow polystyrene standard. Thermogravimetry analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on 9–11-mg film samples heated in flowing nitrogen or air ($90\text{ cm}^3/\text{min}$) at a heating rate of $20^\circ\text{C}/\text{min}$. Glass transition temperature (T_g) were read as the midpoint of the heat capacity jump and were measured on a TA Instruments DSC 2010 at the rate of $15^\circ\text{C}/\text{min}$ in flowing nitrogen ($40\text{ cm}^3/\text{min}$). Mechanical properties of the films were measured with an Instron model 1130 tensile tester with a 5-kg load cell at a crosshead speed of $5\text{ cm}/\text{min}$ on strips approximately $40\text{--}50\text{ }\mu\text{m}$ thick and 0.5 cm wide with a 2-cm gauge length. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films, using an observational angle of 10° and a CIE (Commission International de l'Eclairage)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–vis spectrophotometer. The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a Hewlett Packard 4194A dielectric analyzer. Experiments were performed at 25°C in a dry chamber. The equilibrium moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25°C for 3 d.

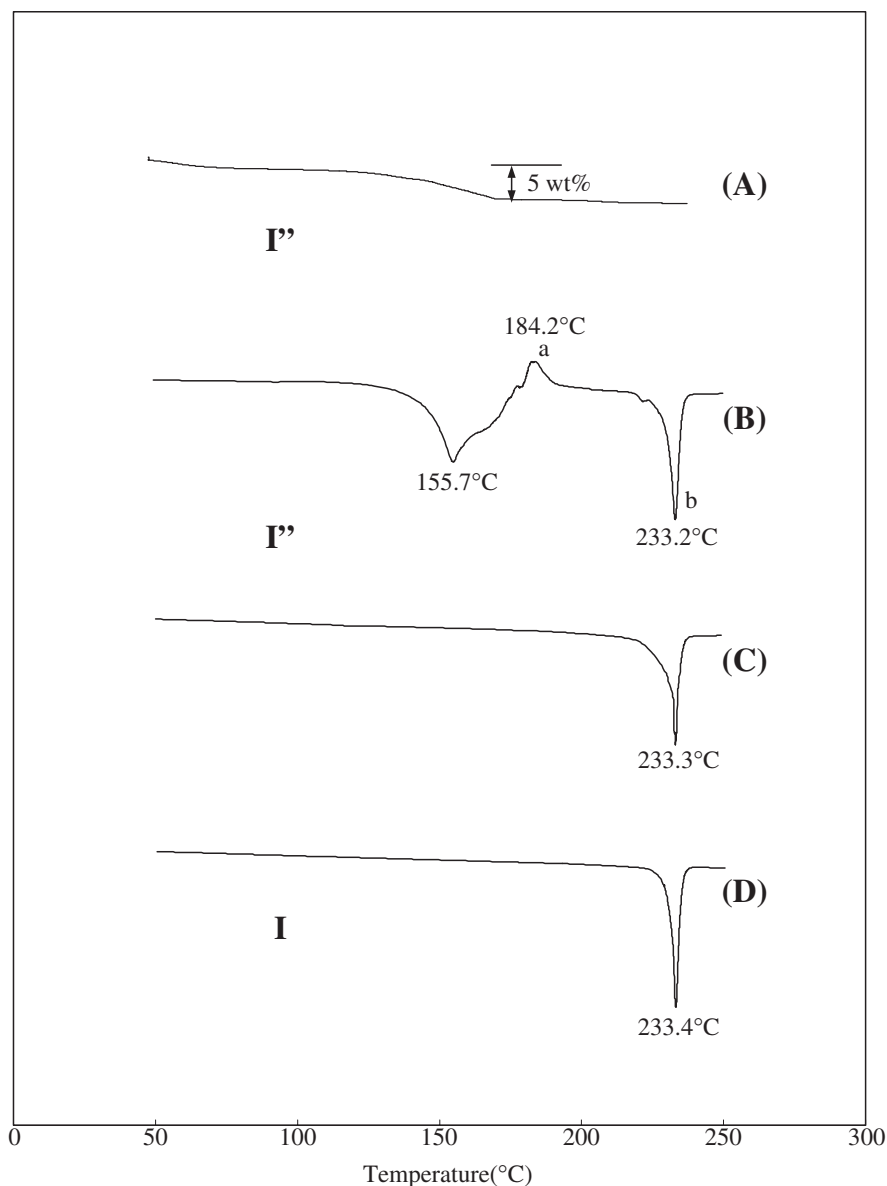


Figure 1. The melt temperature of bis(ether diacid) monomer **I''** and dianhydride **I**. The curve (A) was measured by TGA. The curves (B) and (D) were the first DSC scanning curve. The curve (C) was the second DSC scanning curve of **I''**.

RESULTS AND DISCUSSION

Monomer Synthesis

Bis(ether anhydride) **I** containing was prepared by a three-step reaction sequence as shown in Scheme 1 starting from the nitro displacement of 4-nitrophthalonitrile with 6F-bisphenol-A to form bis(ether dinitrile) **I'**. Then, the purified compound of **I'** was hydrolyzed with KOH solution of ethanol/water to form the bis(ether diacid) **I''**.

The thermal behavior of **I''** was investigated with DSC measurement and the result is shown in Figure 1. There are three peaks including of two endothermic peaks and one exothermic peak. The first endothermic peak showed in the range of 110–170 °C [Figure 1,

curve (B)], and its weight loss was about 5% from the TGA curve [Figure 1(A)]. Therefore, we could presume this temperature range might be the dehydration process of **I''** by the thermal cyclodehydration to **I**. On curve (B), the point was exothermic one, indicating the solidification of the dianhydride; the point b was a melting point of the dianhydride **I**. The curve (C) was the second DSC scanning curve of **I''**. There is only one endothermic been found and exhibited the melting point of the dianhydride **I**. It expressed the dianhydride **I** could be prepared by thermal method. Besides, **I''** also could be cyclodehydrated by acetic anhydride to obtain the high purity and quantity **I**, and the melt point of **I** was the same with **I** which formed by thermal one.

Above-mentioned, the higher purity of the bis(ether

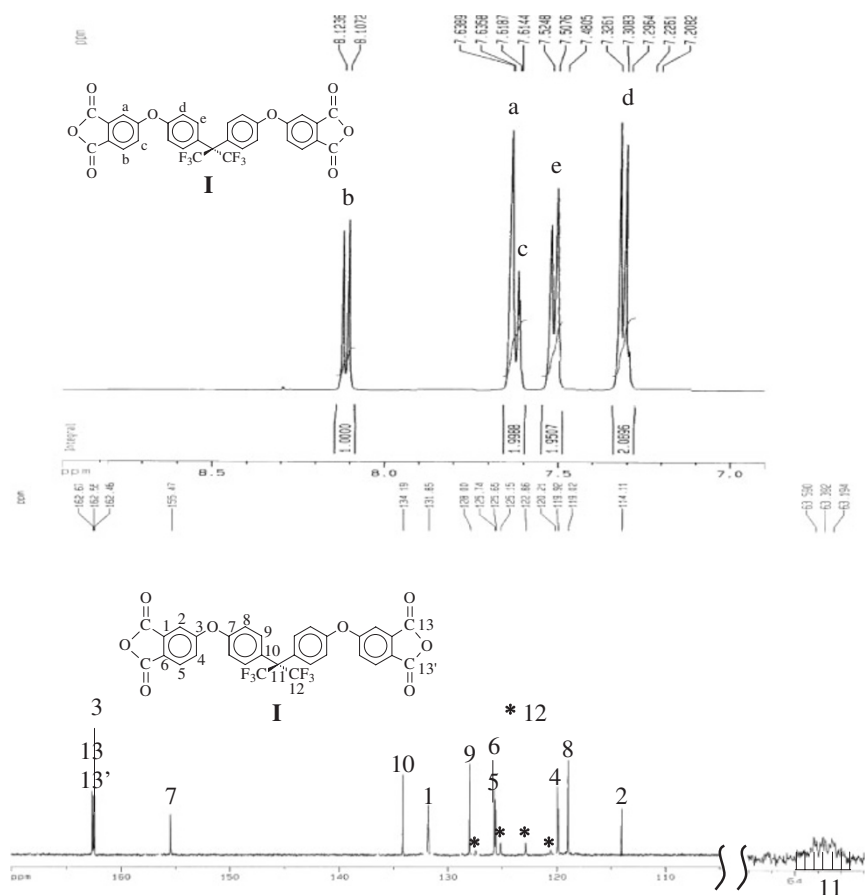


Figure 2. The ¹H NMR and ¹³C spectra of **I** in DMSO-*d*₆.

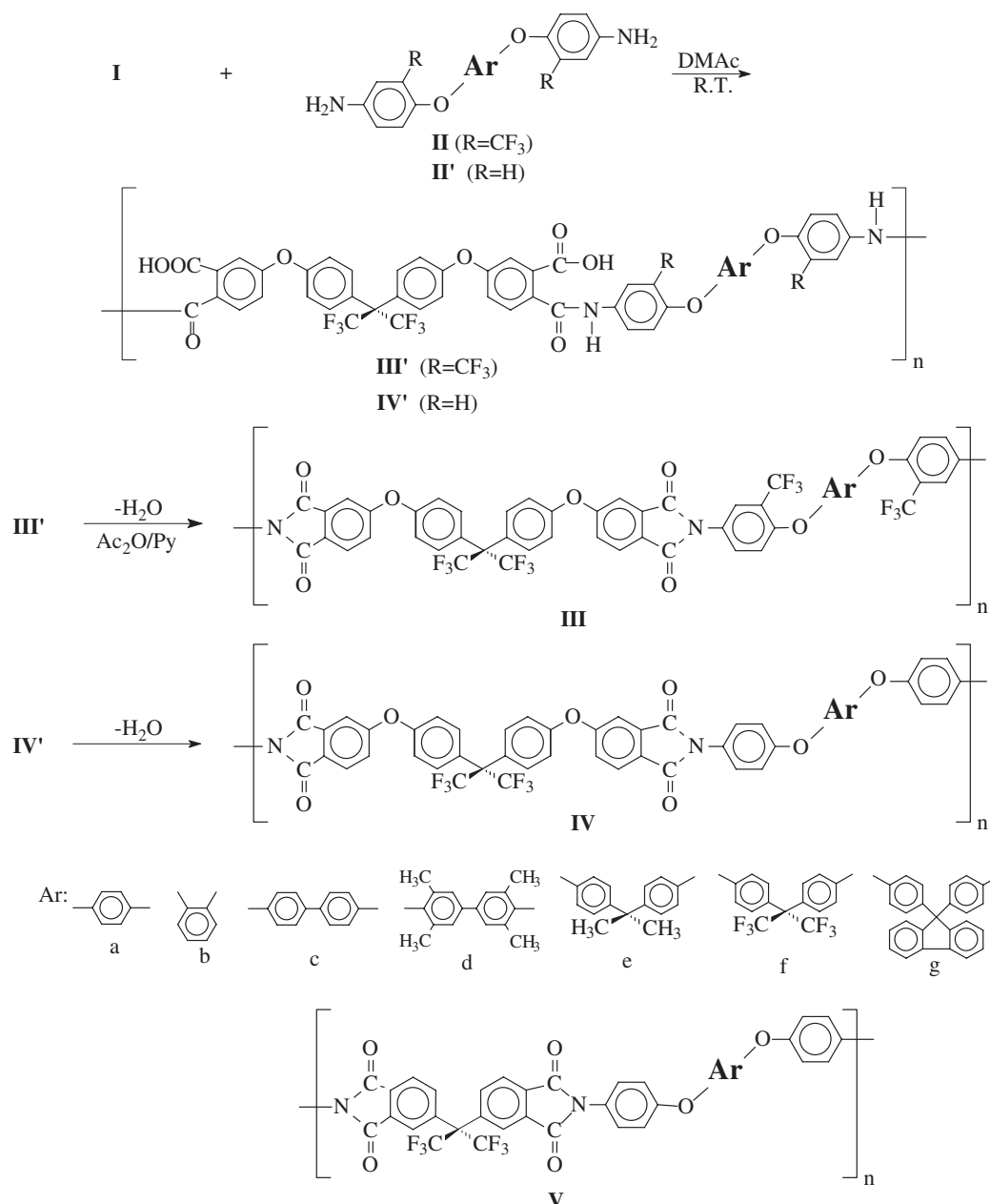
anhydride) **I** could be obtained by thermal or chemical cyclodehydration. However, a polyimide deriving from **I** which formed by the former method possessed a lower inherent viscosities of 0.51 dL/g than polyimide derived from **I** which formed by the latter method (0.79 dL/g). This indicated that the reactivity and the degree of polymerization of **I** from chemical method with aromatic diamine were better than thermal one. Therefore, these poly(ether imide)s were prepared from the bis(ether anhydride) **I** which was synthesized by chemical treatment.

In the IR spectrum during the formation of the monomer **I**, the characteristic peak of cyanide group (2235 cm⁻¹) of **I'** would be transformed into carbonyl group (3600–2500 cm⁻¹) of **I''**, then changed into anhydride group (1851, 1770 cm⁻¹). In ¹H NMR spectra of **I'**, **I''** and **I**, the aromatic protons of **I'** resonated in the region of 7.28–8.16 ppm. H_b closed cyanide group appeared at the farthest downfield, owing to the electron-withdrawing effect of cyanide group. H_{a,c,d} shifted to higher field due to the electron-donating property of aromatic ether. After **I'** was hydrolyzed into **I''**, all the aromatic protons of **I''** shifted to upfield (7.17–7.88 ppm). The last step, **I''** was cyclodehydrated to form **I**, all the protons of **I** shifted downfield (7.29–8.13 ppm). Compared with the chemical shift of three

compounds, **I'** had the largest chemical shifts and **I''** had the smallest one. The reason was probably that the electron-withdrawing effect of cyanide group was larger than others. In ¹³C NMR spectra, **I'**, **I''** and **I** all showed 14 main peaks, and the number of carbons was consistent with structures. By comparing the chemical shift of three compounds, it was found that the differences in C¹³ and C^{13'} were much. C^{13,13'} of cyano group in **I'** were evidenced in the upfield and C^{13,13'} of carbonyl group in **I''** and **I** were evidenced in the downfield. ¹³C NMR spectra of these three monomers showed the quartet and septet because of the heteronuclear ¹³C–¹⁹F coupling. The quartet occurred in 123 ppm due to the CF₃ carbons (C¹²). The one-bond C–F coupling constant in this case was about 285 Hz. The CF₃-attached carbons (C¹¹) showed a septet in about 63 ppm with a smaller coupling constant of about 25 Hz due to two-bond C–F coupling. All the spectroscopic data obtained were in good agreement with the expected structures.

Polymer Synthesis

Poly(ether imide)s **III**_{a-g} and **IV**_{a-g} containing the hexafluoropropane group were synthesized from the bis(ether anhydride) **I** and various fluorinated or non-fluorinated bis(ether amine)s (**II**_{a-h} or **II'**_{a-g}) *via* a con-



Scheme 2.

ventional two-step procedure of ring-opening polyaddition at room temperature to form PAAs, followed by thermal or chemical imidization (Scheme 2).

These polymers had inherent viscosity in the range of 0.37–0.85 dL/g. The elemental analyses of **III_{a-g}** are listed in Table I, showing that the measured values are close to the calculated ones. The GPC curves of the **III** series indicated that M_w and M_n values were in the range of $2.85\text{--}6.29 \times 10^4$ (g/mol) and $1.64\text{--}4.02 \times 10^4$ (g/mol), respectively, relative to the polystyrene standards, and their polydispersity index (M_w/M_n) values were 1.57–1.83 (Table II).

A typical IR spectrum of PAA **III_{a'}** and poly(ether imide) **III_a** is shown in Figure 3. As the PAA was converted into poly(ether imide), the characteristic

absorption bands of the imide ring were observed near 1780, 1728 cm⁻¹ (asym. and sym. C=O str.), and those of amide and carboxyl group in the regions of 2500–3500 cm⁻¹ (O–H and N–H str.) and 1716, 1668 cm⁻¹ (C=O str.) disappeared (Figure 3). Because the chemical imidization method can prevent oxidation during heating process, and obtain polyimide films with lighter color. Thus, these polymers were prepared by chemical imidization and cast into film directly. ¹H NMR and ¹³C NMR spectra of soluble **III_a** are shown in Figure 4. In ¹H NMR spectrum, all the protons of aromatic ring resonated in the region of 7.00–7.95 ppm. H_b and H_f closed to the imide ring appeared at the farthest downfield, owing to the inductive effect of electron-withdrawing imide group. Then

Table I. Inherent viscosity and elemental analysis of the poly(ether imide)s

Poly(ether imide) ^a				Formula	Elemental analysis (%)			
Code	η_{inh} (dL/g) ^b	Code	η_{inh} (dL/g) ^b	M_w		C	H	N
IV_a	0.62	III_a	0.72	(C ₅₁ H ₂₄ O ₈ N ₂ F ₁₂) _n	Calcd	60.01	2.37	2.74
				(1020.74) _n	Found	59.64	2.43	3.04
IV_b	0.55	III_b	0.37	(C ₅₁ H ₂₄ O ₈ N ₂ F ₁₂) _n	Calcd	60.01	2.37	2.74
				(1020.74) _n	Found	60.05	2.92	3.07
IV_c	0.85	III_c	0.62	(C ₅₇ H ₂₈ O ₈ N ₂ F ₁₂) _n	Calcd	62.42	2.57	2.55
				(1096.84) _n	Found	62.42	2.99	2.83
IV_d	0.76	III_d	0.75	(C ₆₁ H ₃₆ O ₈ N ₂ F ₁₂) _n	Calcd	63.55	3.15	2.43
				(1152.95) _n	Found	63.22	3.40	2.34
IV_e	0.55	III_e	0.43	(C ₆₀ H ₃₄ O ₈ N ₂ F ₁₂) _n	Calcd	63.28	3.01	2.46
				(1138.92) _n	Found	62.83	3.15	2.72
IV_f	0.57	III_f	0.43	(C ₆₀ H ₂₈ O ₈ N ₂ F ₁₈) _n	Calcd	57.80	2.26	2.25
				(1246.86) _n	Found	57.79	2.67	2.34
IV_g	0.49	III_g	0.51	(C ₆₉ H ₃₆ O ₈ N ₂ F ₁₂) _n	Calcd	66.35	2.91	2.24
				(1249.03) _n	Found	66.04	2.94	2.59

^aPoly(ether imide)s were obtained by chemical imidization method with DMAc as solvent. ^bMeasured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

Table II. GPC data of poly(ether imide)s **III**

Polymer ^b	M_n ($\times 10^4$) (g/mol)	M_w ($\times 10^4$) (g/mol)	M_w/M_n
III_a	3.45	5.74	1.59
III_b	2.35	4.31	1.83
III_c	2.95	4.87	1.65
III_d	4.02	6.29	1.57
III_e	1.64	2.85	1.74
III_f	1.95	3.12	1.60
III_g	2.60	4.67	1.64

^aRelative to polystyrene standard, using THF as the eluent.

^bPoly(ether imide)s were obtained by chemical imidization method with DMAc as solvent.

H_{c,d,i} and H_h shifted to the higher field due to the electron-donating property of aromatic ether. In ¹³C NMR spectra, because C²² and C⁸ overlaps of C²³ and C¹⁷, respectively, it showed 21 signals and the peaks of the spectra were less than calculation. Carbons C²² and C²³ of the carbonyl group were evidenced in the downfield. Moreover, there were three quartets and one septet because of the heteronuclear ¹³C–¹⁹F coupling. The large quartet centered at about 123 and 124 ppm was due to the CF₃ carbon (C¹², C¹⁹). The one-bond C–F coupling constant in this case was about 285 and 271 Hz. Another quartet centered at about 119 ppm was the CF₃-attached carbon (C¹⁵) with a smaller coupling constant of about 31 Hz due to two-bond C–F coupling. The CF₃-attached carbons (C¹¹) showed a septet centered at about 63.5 ppm had a coupling constant (*ca.* 25 Hz) because two-bond C–F coupling. Above-cited results evidence that the **III** series been synthesized successfully.

Properties of Polymers

Solubility of the poly(ether imide)s **III** and **IV** series was studied quantitatively, and the results are listed in Table III. Because of the monomers dianhydride and diamine both contained CF₃ group and ether chains, all **III** series exhibited excellent solubility above 10 wt/v % concentration in the amide-type solvents including NMP, DMAc and DMF, and in dichloromethane, chloroform, THF, pyridine, and *m*-cresol. Most of the **III** series also showed good solubility in DMSO at a concentration of 10 wt/v % except for **III_d** with 3,3',5,5'-tetramethylbiphenyl group being insoluble. The **IV** series could be dissolved in THF and chloroform at 10 wt/v % concentration, but the solubility of the **IV** series in other solvents was lower in comparison with the **III** series. For example, most of the **III** series were soluble in the amide-type solvents above 10 wt/v %, but the **IV** series only could dissolve above 5 wt/v %. The solubility of the **III** and **IV** series was much different in DMSO and acetone. Most of the **III** series could be dissolved in DMSO and acetone except **III_d**, but most of the **IV** series could not. **IV_b** showed better solubility in DMSO, *m*-cresol and CH₂Cl₂ because the Ar was ortho substitute as compared with **IV_a**.

The color intensities of the polymer films were elucidated from the yellowness (b*), redness (a*) or lightness (L*) indices observed by a colorimeter. In this case, we based our judgment of the degree of yellowness on the b* value. The color coordinates of the **III** and **IV** series are given in Table IV.

The b* value of the **III(C)** series prepared *via* chemical imidization was in the range of 6.2–7.0 and the lightness (L*) value was above 98.5%, and

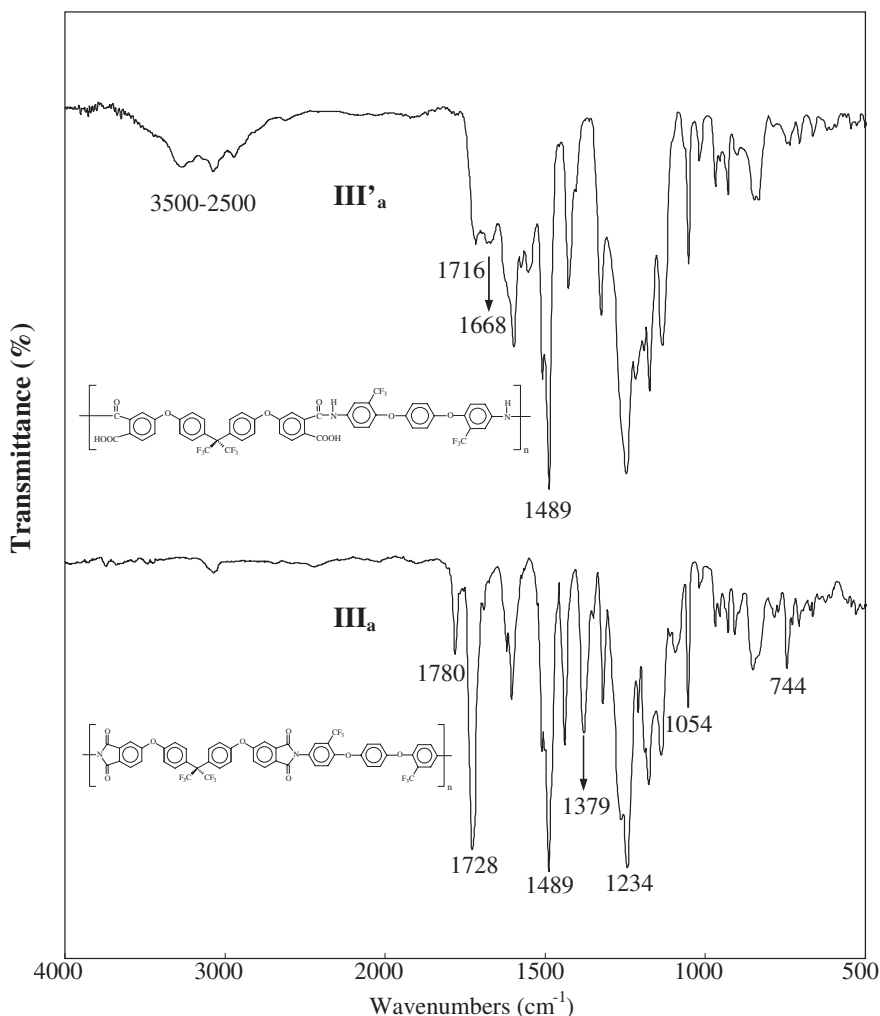


Figure 3. FT-IR spectra of representative poly(amic acid) **III'**_a and poly(ether imide) **III**_a.

showed high lightness. The difference in b^* value between the **III** series was unobvious, indicated that the influence on color by the structure of diamines was slight. On comparing with the **III(H)** series prepared by thermal imidization, the **III(C)** series showed lighter color (Δb^* is in the range of 3.2–5.1). Compared **III(C)** series with **IV(C)** series, the nonfluorinated **IV(C)** series had the b^* value of 12.0–13.1 except **IV_f**, and were higher than **III(C)** about 5–6. The b^* value of **IV_f(C)** was close to the **III(C)**. It was attributed to the Ar structure with hexafluoroisopropylidene group. The b^* value of the **IV(H)** showed higher than **IV(C)** about 3.0. Though the increasing of the Δb^* value in the **IV** series was smaller than it in the **III** series, the b^* value of the **IV(H)** series was higher than **III(H)** series about 5.0. The polyimide **V(C)** series, based on 6FDA, is general considered as the most transparent and color-lighted polyimide. Compare the color of the **IV(C)** series with the **V(C)** series, the b^* values of the **V** series ranging 21.4–28.7 except **V_f** and were higher than **IV(C)** series ($\Delta b^* = 8.9$ –14.8). Therefore, the polyimides de-

rived from bis(ether anhydride) containing hexafluoroisopropylidene group were lighter than polyimide based on 6FDA (**V** series). The color of polyimide is also related to the structure of dianhydride components. For example, **IV_a** derived from **II'**_a showed lower b^* value than six corresponding polyimides as shown in Table IV. The polyimide films of PMDA/**II'**_a and BTDA/**II'**_a appeared a deeper yellow and showed relatively high b^* values above 80. BPDA/**II'**_a and DSDA/**II'**_a revealed a slightly reduced b^* values of 65.9 and 60.1, respectively. 6FDA/**II'**_a (the **V_a(H)**) and ODPDA/**II'**_a were pale yellow in color and showed the b^* values of 34.7 and 30.4, respectively. In contrast with the b^* value of common polyimides, the **IV_a** had a low value (16.1). Moreover, **III_a(H)** derived from **I** with **II_a** had the lower b^* value of 11.5. If **III_a** was prepared *via* chemical imidization, **III_a(C)** could obtain the lowest b^* value and was close to colorless.

Moreover, the color intensity of the **III** series could also be elucidated from the cutoff (λ_0) observed in UV–vis absorption spectra. The λ_0 values of the **III**

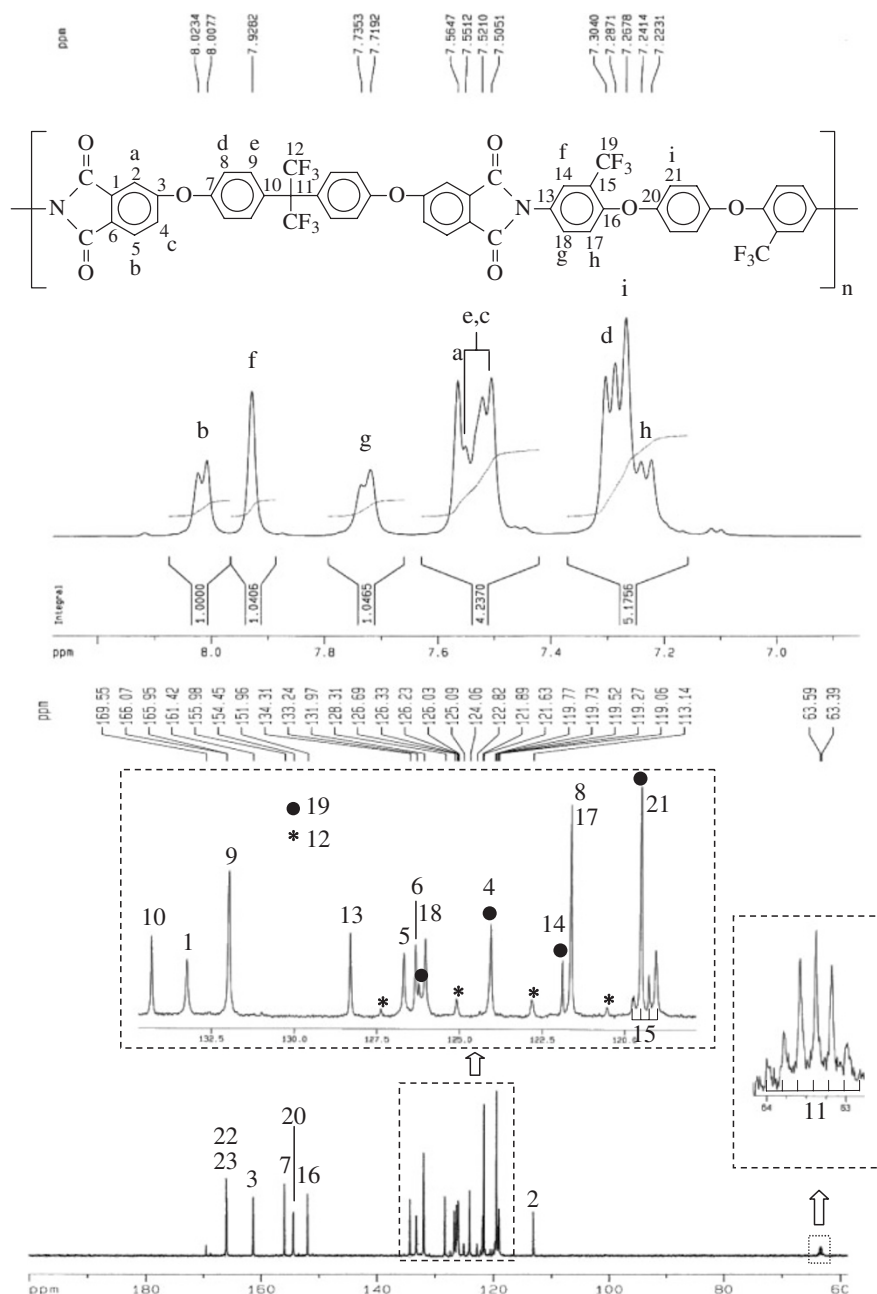


Figure 4. The ¹H and ¹³C NMR spectra of poly(ether imide) **III_a** in DMSO-*d*₆.

and **IV** series were recorded in the range of 364–367 and 368–371 nm, respectively, and they exhibited high transparency and colorless in visible region (Table IV). The λ_0 values of the **III** series were shorter than the **IV** series and the difference in λ_0 value between these two series is 2–4 nm. Compared the **IV** with **V** series and common polyimides, the **IV** series showed the lower λ_0 value. Consistent with the results obtained from the colorimeter. To summarize, both the **III** and **IV** series were lightly-colored, the **III** series especially. The results of colorless polyimide films (the **III** and **IV** series) were attributed to the structures of bis(ether anhydride). The high purity and colorless bis(ether anhydride) containing hexafluoroisopropyl-

dene and ether chains can be prepared and is effective in preventing the CTC formation. Then, the **III** series is lighter-colored than the **IV** series because of the bis(ether amine) with the pendent CF₃ group also can reduces CTC formation to form colorless polyimide films.

The results of tensile test are summarized in Table V. The films **III** and **IV** series had tensile strength of 77–102 MPa, initial modulus of 1.5–2.1 GPa, and elongation at break above 8% except **III_b**. **IV_e** and **IV_f** showed distinct yield point on stress-strain curves (the yield strength of 96 and 100 MPa) and moderate elongation at break. The incorporation of the CF₃ group into the structure of poly(ether

Table III. Solubility^a of poly(ether imide)s

Polymer ^c	Solvents ^b							
	NMP DMAc DMF	DMSO	<i>m</i> -Cresol	Py	THF	CH ₂ Cl ₂	CHCl ₃	Acetone
III_a	+++	+++	++	+++	+++	+++	+++	S
III_b	+++	+++	+++	+++	+++	+++	+++	+++
III_c	+++	++	++	+++	+++	+++	+++	S
III_d	+++	–	++	+++	+++	+++	+++	S
III_e	+++	+++	+++	+++	+++	+++	+++	+++
III_f	+++	+++	+++	+++	+++	+++	+++	+++
III_g	+++	+++	+++	+++	+++	+++	+++	+++
IV_a	++	–	–	++	+++	S	+++	–
IV_b	+++	+	+	+++	+++	+++	+++	–
IV_c	++	–	–	+	+++	S	+++	–
IV_d	++	–	–	++	+++	+++	+++	–
IV_e	++	–	–	++	+++	+++	+++	–
IV_f	++	–	+	+++	+++	+++	+++	–
IV_g	++	–	–	+++	+++	+++	+++	–

^aQuantitative solubility: (+++) 100 mg dissolved in 1 mL (10%), (++) 5%, (+) 1%, (S) swelling, (–) insoluble. ^bNMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethylsulfoxide; Py: pyridine; THF: tetrahydrofuran. ^cPoly(ether imide)s were obtained by chemical imidization method with DMAc as solvent.

imide)s would not reduce mechanical properties obviously. These results indicate that all these polymer films possess good tensile properties with strong and tough character.

The thermal behavior data of all the poly(ether imide)s are summarized in Table VI. DSC experiment were rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so the T_g of all the polymers could be easily read in the second heating DSC traces. The T_g values of the **III** and **IV** series were in the range of 196–265 °C, correlating with that of chain flexibility and depending on the structure of the diamine moieties. When the Ar of the phenylene structures of **III_a**(**IV_a**) and **III_b**(**IV_b**) were compared, the **III_b**(**IV_b**) showed lower T_g value, owing to the asymmetrical *o*-phenylene unit of polymer chain and made rotation difficulty. Those derived from biphenyl in diamine moieties such as **III_{c,d}**, **IV_{c,d}**, the **III_d** and **IV_d** showed the highest T_g value due to the structure of 3,3',5,5'-tetramethylbiphenyl group which hinder the segmental mobility and hence leads to a high T_g value. As the “Ar” containing tetraphenylene-diether of **III_e**(**IV_e**), **III_f**(**IV_f**) and **III_g**(**IV_g**), **III_g**(**IV_g**), they uneasily rotate by the asymmetrical bulky group, so the T_g of **III_g**(**IV_g**) are higher than **III_e**(**IV_e**) and **III_f**(**IV_f**). The T_g values of **III_f** and **IV_f** were higher than **III_e** and **IV_e** respectively, due to the of C–F bond of CF₃ group is stronger than C–H bond of CH₃ group. Comparison the T_g values between the **III** and **IV** series, all **III_{a–g}** bearing pendent

CF₃ group so that the packing density of polymer was decreased and free volume between polymers was increased, which generally resulted in reduced T_g .

The decomposition temperatures of all poly(ether imide)s at 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA curves. The T_{10} values of **III_{a–g}** in nitrogen and air stayed within 495–567 °C and within 492–558 °C, respectively. All T_{10} values of **IV_{a–g}** were above 500 °C in nitrogen and air. **III_g** and **IV_g** showed the highest T_{10} value in nitrogen or in air due to the Ar containing more aromatic rings. **III_d** and **IV_d** showed the lowest T_{10} value in nitrogen or in air, because the methyl group linkages to the side chain of phenyl is decomposed easily in the heating process. The T_{10} values of all polymers in nitrogen were higher than in air except **III_b**, **IV_d** and **IV_e**. The phenomenon of **IV_d** was especially obvious, and its TGA curves were shown in Figure 5. **IV_d** showed higher char yield in air than in N₂ within 490–570 °C, possibly due to the methyl groups were easily oxidized to form a free radical, causing cross-linking between intermolecular and delaying the decomposition rate of the polymer. The **III** and **IV** series had the char yield in the range of 49–57 and 53–62 wt % at 800 °C in nitrogen, respectively. Both **III_g** and **IV_g** containing fluorene group exhibited better thermal stability than others’.

The results of dielectric properties and moisture absorptions of the **III** and **IV** series are shown in Table VII. The dielectric constants of the **III** series

Table IV. Color coordinates and cut-off wavelength (λ_0) from UV-vis spectra for **III** and **IV** series poly(ether imide) films

Polymer ^{b,c}	Color Coordinates ^a			Δb^*	λ_0 (nm)	Film thickness (μm)
	b^*	a^*	L^*			
Ref. Std	0.09	-0.02	100.0			
III_a(C)	7.0	-1.0	98.5		367	53
III_b(C)	6.7	-1.4	98.9		367	59
III_c(C)	6.6	-1.1	98.9		366	48
III_d(C)	6.9	-1.8	99.3		366	46
III_e(C)	6.7	-1.4	99.6		367	41
III_f(C)	6.2	-1.1	98.7		362	65
III_g(C)	6.4	-1.4	98.9		365	62
III_a(H)	11.5	-1.6	97.0	4.5	371	62
III_c(H)	9.8	-1.9	98.3	3.2	368	69
III_d(H)	12.0	-2.8	98.3	5.1	369	60
IV_a(C)	13.1	-3.3	97.7	6.1	371	55
IV_b(C)	12.1	-3.4	98.4	5.4	369	46
IV_c(C)	12.0	-3.3	97.9	5.4	369	54
IV_d(C)	12.8	-4.3	97.8	5.9	370	52
IV_e(C)	12.7	-3.1	98.0	6.0	370	43
IV_f(C)	8.3	-1.8	98.3	2.1	368	43
IV_g(C)	12.3	-3.3	97.8	5.9	370	58
IV_a(H)	16.1	-3.3	97.0	2.2	374	30
VI_c(H)	15.0	-3.4	97.6	3.0	373	32
V_a(C)	28.7	-10.2	98.3	14.8	393	76
V_b(C)	22.9	-8.8	99.1	10.8	383	47
V_c(C)	25.4	-9.5	98.6	13.4	389	52
V_d(C)	27.9	-10.6	99.2	11.1	388	42
V_e(C)	22.1	-8.4	99.0	9.4	382	53
V_f(C)	12.6	-5.0	99.3	4.3	370	48
V_g(C)	21.4	-7.7	98.6	4.8	379	54
V_a(H)	34.7	-5.2	92.2	11.6	388	47
PMDA-II'_a(H)	80.5	3.7	88.1		440	39
BTDA-II'_a(H)	87.8	2.3	90.0		446	37
BPDA-II'_a(H)	65.9	-11.7	94.2		424	38
DSDA-II'_a(H)	60.1	-11.8	94.8		417	54
ODPA-II'_a(H)	30.4	-7.6	85.0		387	50

^a L^* is lightness. A positive a^* means red color, while a negative a^* indicated green color. A positive b^* means yellow color, while a negative b^* implies blue color. ^b(H): Poly(ether imide)s were obtained by thermal imidization method. (C): Poly(ether imide)s were obtained by chemical imidization with DMAc as solvent.

(3.01–3.65 at 1 MHz) were lower than the analogous nonfluorinated **IV** series (3.40–3.73 at 1 MHz). Both two series showed lower dielectric constants than the common polyimide, Kapton[®], because the dianhydride moieties contained the hexafluoropropane and ether group. The **III** series showed lower dielectric constants might be attributable to the presence of bulky CF_3 group, which resulted in less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine resulted in very low polarizability of the C–F bonds, thereby decreasing the dielectric constant. **III_{a-g}** also exhibited lower moisture absorptions (0.09–0.44%) as a result of the

hydrophobicity of the CF_3 group than **IV_{a-g}**. Moreover, **III_f** and **IV_f** exhibited the lowest moisture in the two series because of contained the higher CF_3 group in the repeat unit.

CONCLUSIONS

Two series of poly(ether imide)s **III** and **IV** are synthesized from the bis(ether anhydride) (**I**) with various aromatic diamines (**II_{a-g}**) bearing the pendent trifluoromethyl group or non-fluorinated diamines (**II'_{a-g}**) via chemical or thermal imidization. The **III** series is a kind of colorless polymer films and shows lighter col-

Table V. Tensile properties of poly(ether imide) films

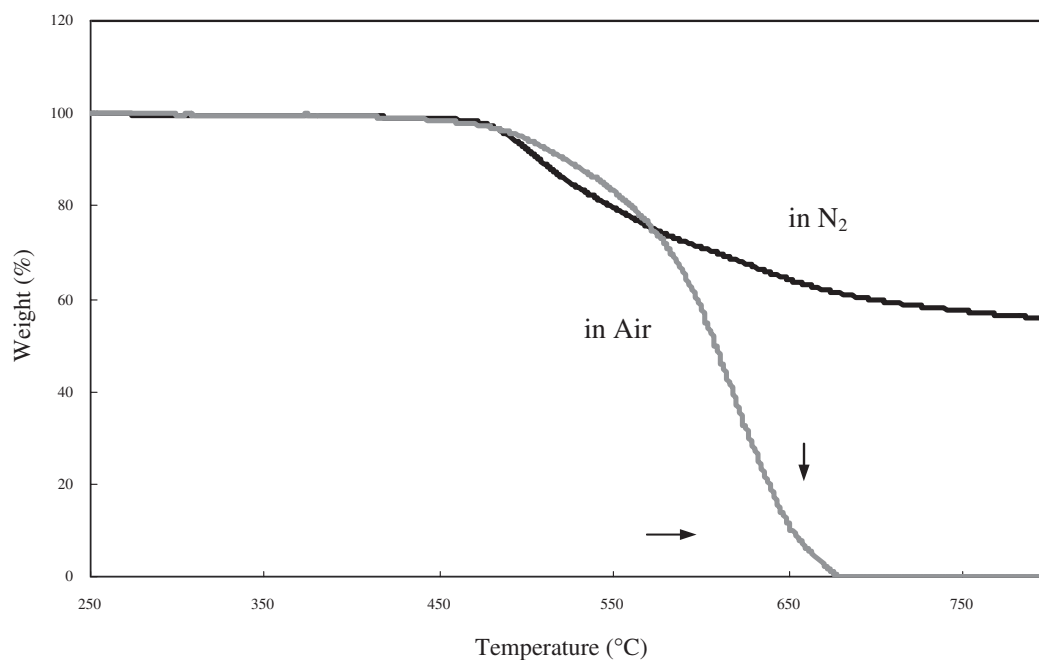
Polymer ^a	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
III _a	—	102	11	1.7
III _b	—	82	5	2.1
III _c	—	83	10	1.7
III _d	—	78	8	1.6
III _e	—	93	12	1.6
III _f	—	98	15	1.5
III _g	—	91	12	1.6
IV _a	—	84	9	1.8
IV _b	—	88	8	1.8
IV _c	—	101	11	1.9
IV _d	—	77	9	1.6
IV _e	96	81	10	2.0
IV _f	100	86	12	1.9
IV _g	—	87	8	1.8

^aPoly(ether imide)s were obtained by chemical imidization method with DMAc as solvent.

Table VI. Thermal behavior data of poly(ether imide)s

Polymer ^a	DSC T_g^b (°C)	TGA		Char Yield ^d (wt %)
		Decomposition Temp ^c (°C)		
		In Air	In Nitrogen	
III _a	199	553	556	49
III _b	201	550	549	50
III _c	205	554	559	55
III _d	263	492	495	53
III _e	199	537	539	56
III _f	196	538	541	51
III _g	239	558	567	57
IV _a	216	555	557	56
IV _b	201	550	551	53
IV _c	228	556	562	60
IV _d	265	522	507	56
IV _e	209	546	545	56
IV _f	215	547	548	54
IV _g	258	558	564	62

^aPoly(ether imide)s were obtained by chemical imidization method with DMAc as solvent. ^bBaseline shift in the second heating DSC traces, with a heating rate of 15 °C/min. ^cTemperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min. ^dResidual weight (%) when heated to 800 °C in nitrogen.


Figure 5. Typical TGA curves of poly(ether imide) IV_a with a heating rate of 20 °C/min.

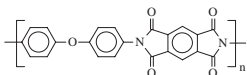
or and greater transparency than the analogous non-fluorinated IV series. Moreover, the IV series shows lighter color than the common polyimide V series. In addition, the III series shows excellent solubility in the organic solvents at a concentration of 5–10%. The solubility of IV series was lower than the III ser-

ies but IV series could be dissolved in the most of testing solvents. This exhibits that these two series possess good solubility. The III series are also characteristics of good mechanical properties and thermal properties together with lower dielectric constants and moisture absorptions.

Table VII. Moisture absorption and dielectric constants of poly(ether imide)s

Polymer ^a	Film thickness (μm)	Moisture Absorption (%)	Dielectric Constant ^b			
			1 KHz	10 KHz	1 MHz	40 MHz
III_a	61	0.15	3.27	3.25	3.20	3.23
III_b	107	0.20	3.74	3.70	3.65	3.67
III_c	65	0.21	3.33	3.29	3.24	3.26
III_d	50	0.18	3.12	3.04	3.01	3.05
III_e	105	0.12	3.56	3.51	3.45	3.47
III_f	71	0.09	3.14	3.08	3.04	3.07
III_g	76	0.44	3.45	3.35	3.30	3.33
IV_a	39	0.30	3.68	3.66	3.63	3.65
IV_b	62	0.34	3.73	3.71	3.64	3.71
IV_c	50	0.43	3.78	3.75	3.70	3.72
IV_d	46	0.47	3.74	3.67	3.63	3.65
IV_e	45	0.86	3.48	3.45	3.40	3.43
IV_f	58	0.26	3.69	3.64	3.59	3.62
IV_g	58	1.37	3.83	3.78	3.73	3.75
Kapton^b	40	0.42	3.89	3.85	3.80	3.75

^aPoly(ether imide)s were obtained by the chemical imidization with DMAc as solvent. ^bA reference polyimide (Kapton) prepared from PMDA and 4,4'-oxydianiline (η_{inh} of the poly(amic acid) precursor 1.90 dL/g).



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