

# Processable and Colorless Fluorinated Poly(ether imide)s Based on an Isopropylidene-containing Bis(ether anhydride) and Various Aromatic Bis(ether amine)s Bearing Trifluoromethyl Groups

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**ABSTRACT:** A series of novel organosoluble and light-colored fluorinated poly(ether imide)s (PEIs) (**IV**) having inherent viscosities of 0.43–0.59 dL/g were prepared from 4,4'-[1,4-phenylenebis(isopropylidene-1,4-phenyleneoxy)]diphthalic anhydride (**I**) and various trifluoromethyl-substituted aromatic bis(ether amine)s by a standard two-step process with thermal and chemical imidization of poly(amic acid) precursors. These PEIs showed excellent solubility in many organic solvents and could be solution-cast into transparent and tough films. These films were essentially colorless, with an UV–visible absorption edge of 361–375 nm and a very low  $b^*$  value (a yellowness index) of 15.3–17.0. They also showed good thermal stability with glass-transition temperature of 191–248°C, 10% weight loss

temperature in excess of 494°C, and char yields at 800°C in nitrogen more than 39%. The thermally cured PEI films showed good mechanical properties with tensile strengths of 83–96 MPa, elongations at break of 8–11%, and initial moduli of 1.7–2.0 GPa. They possessed lower dielectric constants of 3.25–3.72 (1 MHz). In comparison with the **V** series nonfluorinated PEIs, the **IV** series showed better solubility, lower color intensity, and lower dielectric constants. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 620–628, 2007

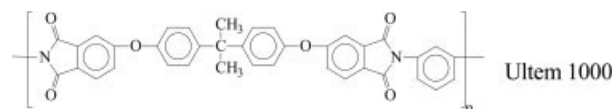
**Key words:** isopropylidene; bis(ether anhydride); bis(ether amine); fluorinated poly(ether imide)s; trifluoromethyl group; colorless polyimide; soluble polyimide

## INTRODUCTION

Aromatic polyimides are one of the most important classes of polymers used in the microelectronics and photoelectronics industries because they have excellent thermal, mechanical, and electrical properties as well as outstanding chemical resistance.<sup>1,2</sup> Despite the excellent combined properties, their widespread applications are often limited because of their poor solubility and high processing temperature, which are caused by the rigid polymer backbones and the strong inter-chain interactions. To overcome these limitations, many attempts have been made to improve the processability (melt processing properties and/or solubility in organic solvents) of polyimides while maintaining their excellent properties.<sup>3,4</sup> Another obstacle that may hinder extending the applications of aromatic polyimides in optoelectronic materials is the light or dark-yellow color of their films caused by the intramolecular and intermolecular charge transfer complex

(CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties.<sup>5</sup> By minimizing or eliminating CTC formation, low color or virtually colorless polyimide films with improved transparency can be obtained.<sup>6,7</sup> Colorless soluble polyimides can be obtained by using aliphatic dianhydride or diamine monomers<sup>8–11</sup>; however, the long term thermal stability is somewhat decreased because of the incorporation of less stable aliphatic segments.

Poly(ether imide)s (PEIs) have received great attention because they may provide good processability owing to the presence of flexible ether linkages. The development of nucleophilic displacement reactions, and nitrodisplacement reactions in particular, has led to the development of a large class of PEIs from bis(ether anhydride)s and various aromatic diamines.<sup>12–14</sup> An important example is Ultem 1000 resin developed and commercialized by General Electric Co.,<sup>15</sup> which exhibits reasonable thermal stability and good mechanical properties together with good moldability.



<sup>†</sup>The second author died on August 17, 2005, at the age of 75. This article is now dedicated to the memory of Professor Chin-Ping Yang, who cherished research and publications as his lifetime joys.

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found that the incorporation of bulky  $\text{CF}_3$  groups into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which attributed to low polarizability of the C—F bond and the increase in free volume. The fluorinated polyimides also provided other merits such as good thermal and thermo-oxidative stability and low moisture absorption.

As part of our continuing efforts to gain colorless and soluble polyimides with high thermal stability and low dielectric constant for advanced microelectronics and photoelectronics applications, a series of novel fluorinated PEIs were synthesized from 4,4'-[1,4-phenylenbis(isopropylidene-1,4-phenyleneoxy)]-diphthalic anhydride (**I**) with various  $\text{CF}_3$ -substituted aromatic bis(ether amine)s. These polymers were subjected to solubility, thermal and mechanical properties, color intensity, optical transparency, and dielectric constant. Since the designed PEIs are composed of less electron-accepting dianhydride and less electron-donating diamine moieties, they should exhibit light or no color and high transparency in the visible region, a property which should be helpful for optical applications. The PEIs would also be expected to possess an enhanced solubility and melt processability because of the incorporation of kinked isopropylidene groups and flexible ether links in the main chain. Moreover, the properties of the **IV** series PEIs are also compared with those of analogous nonfluorinated PEIs (**V** series) to investigate the effect of  $\text{CF}_3$  groups on coloration and solubility.

## EXPERIMENTAL

### Materials

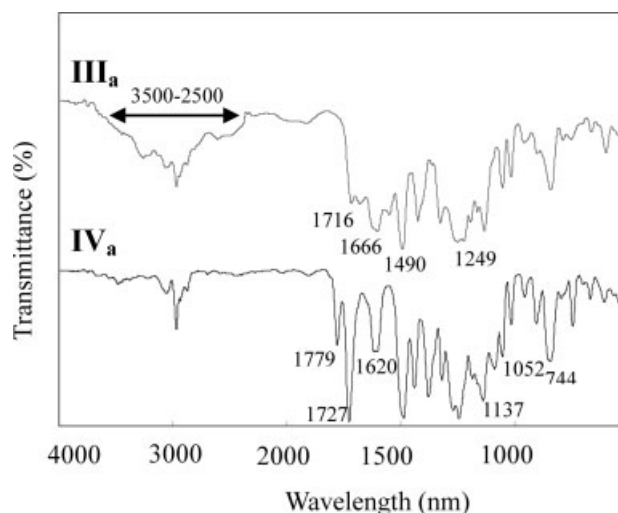
As reported previously,<sup>22</sup> the bis(ether anhydride) **I** (mp = 182–184°C) was synthesized starting from the nitro displacement of 4-nitrophthalonitrile with  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene in the presence of potassium carbonate in *N,N*-dimethylformamide (DMF), followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile), and the cyclodehydration of the resulting bis(ether diacid). The  $\text{CF}_3$ -substituted bis(ether amine)s **II<sub>a</sub>** to **II<sub>h</sub>** were prepared from the chloro-displacement reactions of 2-chloro-5-nitrobenzotrifluoride with the corresponding aromatic diols in the presence of potassium carbonate, followed by Pd/C-catalyzed hydrazine reduction; they included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (**II<sub>a</sub>**) (mp = 132–133°C),<sup>23</sup> 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2-*tert*-butylbenzene (**II<sub>b</sub>**) (mp = 164–165°C),<sup>24</sup> 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2,5-di-*tert*-butylbenzene (**II<sub>c</sub>**) (mp = 215–216°C),<sup>25</sup> 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**II<sub>d</sub>**) (mp = 155–156°C),<sup>26</sup> 4,4-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (**II<sub>e</sub>**) (mp = 256–257°C),<sup>27</sup>

4,4'-bis(4-amino-2-trifluoromethylphenoxy)benzophenone (**II<sub>f</sub>**) (mp = 152–153°C),<sup>28</sup> 2,2-Bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**II<sub>g</sub>**) (mp = 131–132°C),<sup>29</sup> 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (**II<sub>h</sub>**) (mp = 65–66°C).<sup>30</sup> *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

### Synthesis of PEIs

#### Thermal imidization

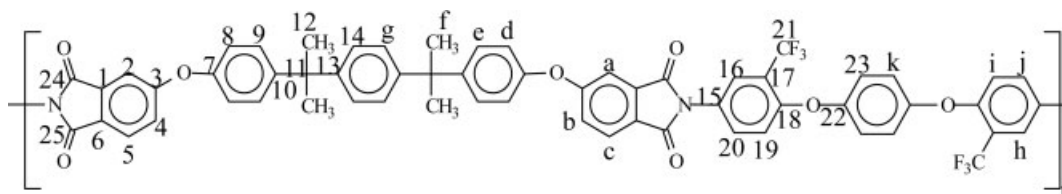
The synthesis of PEI **IV<sub>a</sub>(H)** is used as an example to illustrate the general synthetic route used to prepare the polyimides. To a solution of diamine **II<sub>a</sub>** (0.274 g, 1 mmol) in 7 mL of dried DMAc, an equimolar amount of bis(ether anhydride) **I** (0.6435 g, 1 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to form a viscous poly(amic acid) (PAA) solution. The PAA solution was then poured into a glass culture dish with a diameter of 10 cm, which was placed in an oven at 100°C for 2 h for the slow release of the casting solvent. The semidried PAA films were further dried and imidized by sequential heating from 130 to 250°C at a slow heating rate of 2°C/min and held at 250°C for 1 h. By being soaked in water, a flexible polymer film of PEI **IV<sub>a</sub>(H)** was released from the glass surface. The inherent viscosity of **IV<sub>a</sub>(H)** was 0.45 dL/g, as measured in DMAc on a 0.5 g/dL concentration at 30°C. IR (film) (see Fig. 1): 1779 (asymmetric C=O stretch), 1725 (symmetric imide C=O stretch), 1620–1490 (aromatic C=C stretch), 1379 (C—N stretch), 1242 (C—O stretch), 1052, 744  $\text{cm}^{-1}$  (imide ring deformation). <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.89 (d, *J* = 8.3 Hz, 2H,  $\text{H}_c$ ), 7.77 (d, *J* = 2.1 Hz, 2H,  $\text{H}_h$ ), 7.54 (dd, *J* = 8.9, 2.1 Hz, 2H,  $\text{H}_j$ ), 7.44 (d, *J* = 1.9 Hz,



**Figure 1** FTIR spectra of poly(ester imide) **IV<sub>a</sub>** and PAA **III<sub>a</sub>**.

2H, H<sub>a</sub>), 7.36 (dd,  $J = 8.3, 1.9$  Hz, 2H, H<sub>b</sub>), 7.32 (d,  $J = 8.6$  Hz, 4H, H<sub>c</sub>), 7.20 (s, 4H, H<sub>g</sub>), 7.15 (s, 4H, H<sub>k</sub>), 7.04 (d,  $J = 8.9$  Hz, 2H, H<sub>i</sub>), 7.01 (d,  $J = 8.6$  Hz, 4H, H<sub>d</sub>), 1.72 (s, 12H, H<sub>f</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 166.52 (C<sup>24</sup>), 166.43 (C<sup>25</sup>), 164.14 (C<sup>3</sup>), 155.03 (C<sup>18</sup>), 152.34 (C<sup>7,22</sup>), 148.20 (C<sup>13</sup>), 147.49 (C<sup>10</sup>), 133.99

(C<sup>15</sup>), 131.26 (C<sup>20</sup>), 128.80 (C<sup>9</sup>), 126.42 (C<sup>14</sup>), 126.27 (C<sup>1</sup>), 125.89 (C<sup>5</sup>), 125.65 (C<sup>16</sup>), 124.62 (C<sup>6</sup>), 123.13 (C<sup>4</sup>), 122.77 (C<sup>21</sup>, quartet,  $^1J_{C-F} = 273$  Hz), 121.54 (C<sup>23</sup>), 121.53 (C<sup>17</sup>, quartet,  $^2J_{C-F} = 31$  Hz), 119.80 (C<sup>8</sup>), 118.75 (C<sup>19</sup>), 111.95 (C<sup>2</sup>), 42.37 (C<sup>11</sup>), 30.88 (C<sup>12</sup>) ppm (see Fig. 2).



### Chemical imidization

The chemical imidization was carried out by adding a mixture of 2 mL of acetic anhydride and 1 mL of pyridine to a PAA solution prepared by a similar procedure mentioned earlier. The reaction mixture was heated at 80°C for 1 h to effect a complete imidization. Then, the obtained solution was poured into a glass culture dish, which was placed in a 100°C oven for 1 h to evaporate the solvent and form a thin solid film. The PEI film was then heated at 200°C for about 2 h to remove the residual solvent. By being soaked in water, a flexible and colorless PEI film of IV<sub>a</sub>(C) was released from the glass surface.

### Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a Heraeus VarioEL-III CHN analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30°C. Weight-average molecular weights ( $\overline{M}_w$ 's) and number-average molecular weights ( $\overline{M}_n$ 's) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and tetrahydrofuran (THF) as the eluent. Color intensity of the polymers was evaluated on a Nippon Denshoku Handy Colorimeter NR-3000. Measurements were performed for the films at an observational angle of 10° and with a Commission International de l'Eclairage (CIE)-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. Mechanical properties of the films were measured on an Instron model 4400R tensile tester with a 5 kg load cell at a crosshead speed of 5 mm/min on strips approximately 30–60  $\mu$ m thick and 0.5 cm wide with a 2 cm gauge length. An average of at least three replicates

was used. Glass-transition temperature ( $T_g$ ) of the polymer was measured on a TA Instruments DSC 2010 at a heating rate of 15°C/min under nitrogen. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Measurements were carried out on 9–11 mg film samples heated in flowing nitrogen or air (90 cm<sup>3</sup>/min) at a heating rate of 20°C/min. Dielectric property of the polymer films was tested by the parallel-plate capacitor method with a Hewlett-Packard 4284A Precision LCR meter. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25°C in a dry chamber.

## RESULTS AND DISCUSSION

### Polymer synthesis

The novel fluorinated PEIs IV<sub>a–h</sub> were synthesized from bis(ether anhydride) I and various CF<sub>3</sub>-containing bis(ether-amine)s II<sub>a–h</sub> via a conventional two-step procedure, as shown in Scheme 1. Both thermal and chemical imidization methods were employed to convert the PAA precursors to the PEIs, and the PEI samples are coded with IV(H) and IV(C), respectively. For comparison, a series of referenced PEIs (V<sub>a–h</sub>) were also prepared from bis(ether anhydride) I and CF<sub>3</sub>-free bis(ether amine)s II'<sub>a–h</sub> with the thermal imidization process. The formation of PEIs was confirmed by IR, NMR, and elemental analysis. The elemental analysis data of the thermally cured IV(H) series are listed in Table I, which are in good agreement with the calculated values for the proposed chemical structures. A typical FTIR spectrum for PEI IV<sub>a</sub> is shown in Figure 1. The PEI shows characteristic imide absorptions around 1779 and 1725 (asymmetrical and symmetrical carbonyl stretch), 1380 (C–N stretch), and 1052 and 744 cm<sup>-1</sup> (imide ring deformation), together with some strong absorption bands in the region of 1100–1300 cm<sup>-1</sup> due to the C–O and C–F stretching vibrations. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the PAA precursor into the polyimide. The <sup>1</sup>H NMR and

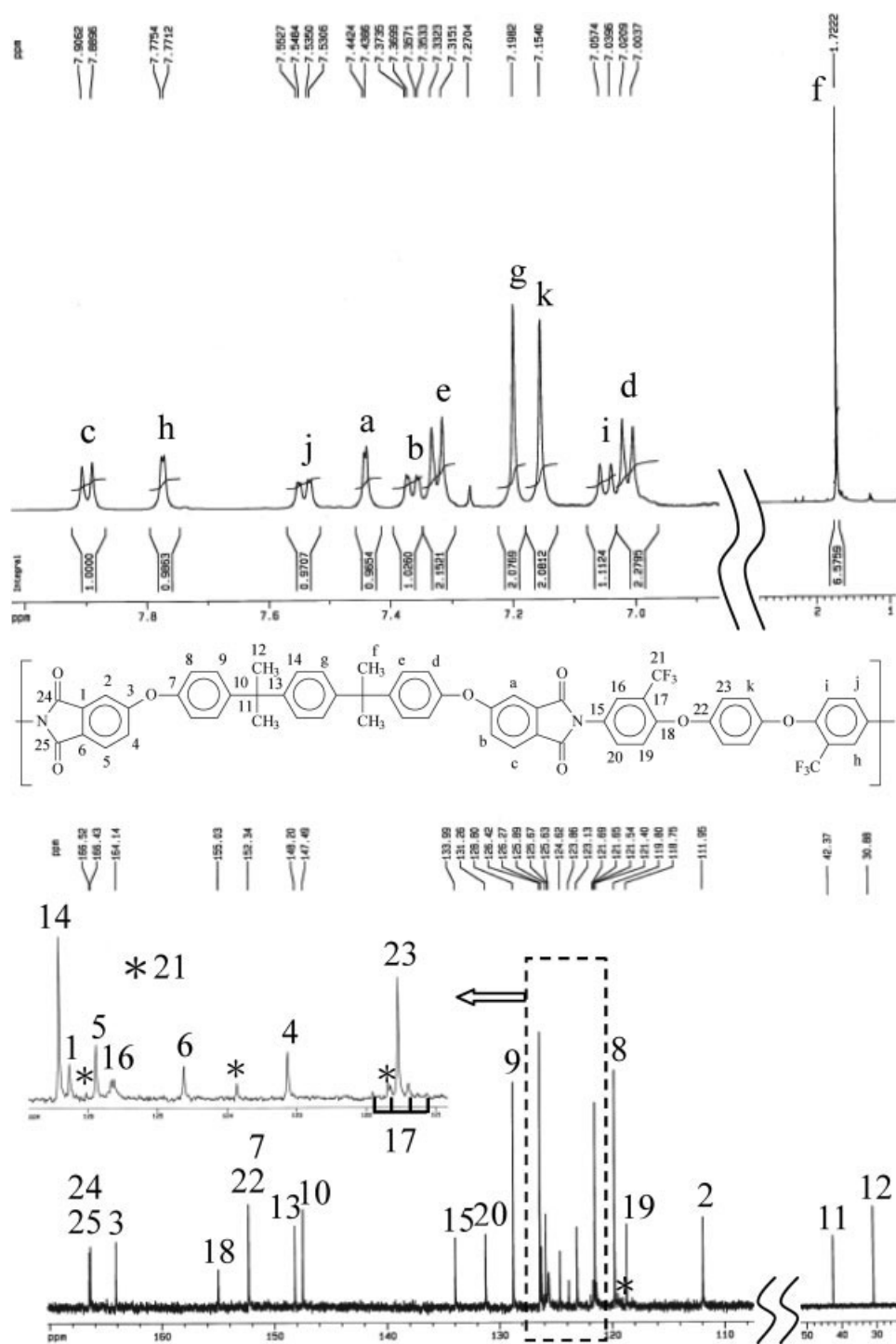


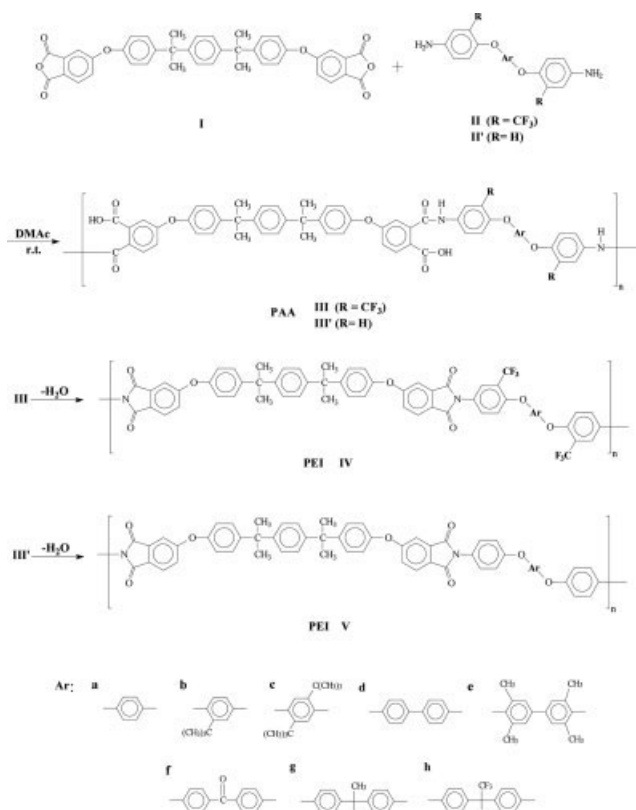
Figure 2  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PEI  $\text{IV}_a$  in  $\text{CDCl}_3$ .

$^{13}\text{C}$  NMR spectra of PEI  $\text{IV}_a$  are illustrated in Figure 2. Assignments of all carbon and proton resonance signals assisted by the 2D-NMR spectroscopy (Figs. 3 and 4) are also given in the figures, and these spectra are in complete agreement with the proposed polymer structure. As shown in Table II, the obtained PEIs exhibited inherent viscosities of 0.42–0.59 dL/g. The molecular weights of the fluorinated PEIs determined by GPC in THF using polystyrene as standard are in

the range of 12,000–22,000 for  $\overline{M}_n$  and 22,000–39,000 for  $\overline{M}_w$  with the  $\overline{M}_w/\overline{M}_n$  values of 1.80–1.94.

#### Polymer solubility and film property

The solubility of the polymers was tested in various solvents, and the results are listed in Table III. Except for  $\text{IV}_f(\text{H})$ , all the PEIs prepared by the chemical or thermal imidization method were readily soluble with



Scheme 1

a 10 wt % solid content in both strong dipolar solvents and common organic solvents such as NMP, DMAc, DMF, pyridine, dioxane,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and THF. The good solubility of these polymers in low boiling point solvents is a benefit to prepare the polymer films or coatings at low processing temperatures. The insolubility of thermal cured PEI  $\text{IV}_f(\text{H})$  might be attribut-

TABLE I  
Elemental Analysis of the Poly(ether imide)s

Polymer code	Formula of the repeating unit (formula weight)	Elemental analysis (%)			
		C	H	N	
$\text{IV}_a(\text{H})$	$(\text{C}_{62}\text{H}_{46}\text{F}_6\text{N}_2\text{O}_8)_n$ (1061.05) $_n$	Calcd	69.90	3.91	2.72
		Found	69.54	4.04	2.78
$\text{IV}_b(\text{H})$	$(\text{C}_{66}\text{H}_{54}\text{F}_6\text{N}_2\text{O}_8)_n$ (1117.15) $_n$	Calcd	70.71	4.45	2.58
		Found	70.66	4.30	2.56
$\text{IV}_c(\text{H})$	$(\text{C}_{70}\text{H}_{62}\text{F}_6\text{N}_2\text{O}_8)_n$ (1173.26) $_n$	Calcd	71.44	4.94	2.45
		Found	71.48	4.82	2.43
$\text{IV}_d(\text{H})$	$(\text{C}_{68}\text{H}_{50}\text{F}_6\text{N}_2\text{O}_8)_n$ (1137.14) $_n$	Calcd	71.61	4.01	2.53
		Found	71.55	3.69	2.58
$\text{IV}_e(\text{H})$	$(\text{C}_{72}\text{H}_{58}\text{F}_6\text{N}_2\text{O}_8)_n$ (1193.25) $_n$	Calcd	72.28	4.51	2.41
		Found	72.34	4.61	2.43
$\text{IV}_f(\text{H})$	$(\text{C}_{69}\text{H}_{50}\text{F}_6\text{N}_2\text{O}_9)_n$ (1165.15) $_n$	Calcd	70.90	3.91	2.47
		Found	70.63	3.87	2.56
$\text{IV}_g(\text{H})$	$(\text{C}_{71}\text{H}_{56}\text{F}_6\text{N}_2\text{O}_8)_n$ (1179.22) $_n$	Calcd	72.12	4.39	2.44
		Found	71.84	4.05	2.43
$\text{IV}_h(\text{H})$	$(\text{C}_{71}\text{H}_{50}\text{F}_{12}\text{N}_2\text{O}_8)_n$ (1287.17) $_n$	Calcd	65.93	3.53	2.23
		Found	65.93	3.14	2.25

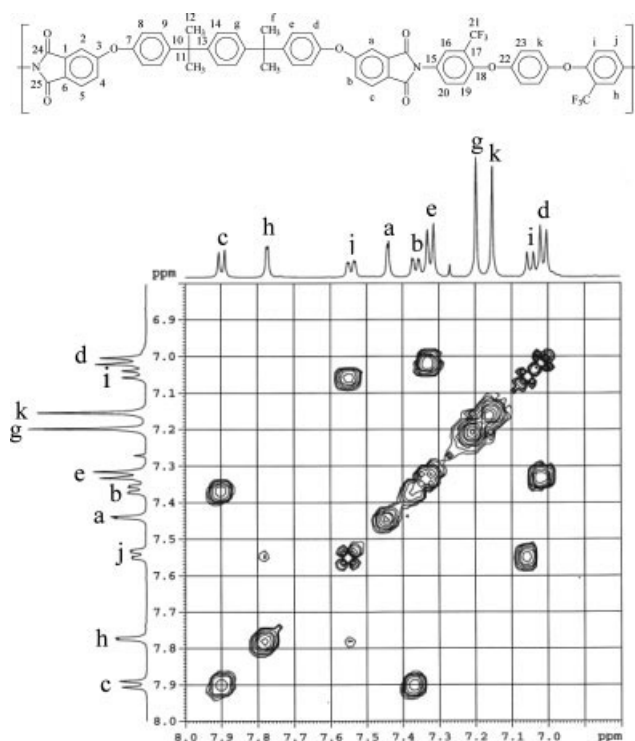


Figure 3 Aromatic region of H–H COSY NMR spectrum of PEI  $\text{IV}_a$  in  $\text{CDCl}_3$ .

able to the presence of benzophenone segment in the chain, which may lead to partial crosslinking within polymer chains during the imidization process at elevated temperatures.<sup>31</sup> The  $\text{IV}$  series PEIs generally showed better solubility when compared with the  $\text{V}$  series analogs. This result indicated that the incorporation of bulky  $-\text{CF}_3$  groups in the backbone increased

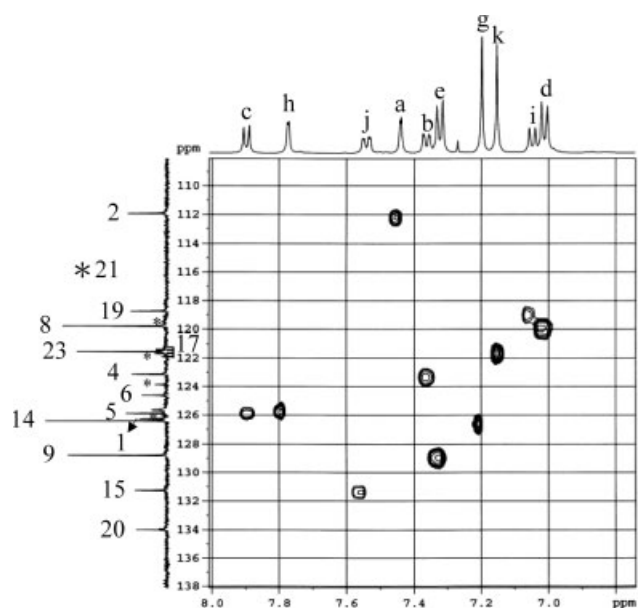


Figure 4 Aromatic region of H–C COSY NMR spectrum of PEI  $\text{IV}_a$  in  $\text{CDCl}_3$ .

**TABLE II**  
Inherent Viscosity and GPC Data of Poly(ether imide)s

Polymer code <sup>a</sup>	$\eta_{inh}^b$ (dL/g)	GPC data of PEIs <sup>c</sup>		
		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
IV <sub>a</sub> (H)	0.45	$1.26 \times 10^4$	$2.27 \times 10^4$	1.80
IV <sub>b</sub> (H)	0.45	$1.23 \times 10^4$	$2.23 \times 10^4$	1.82
IV <sub>c</sub> (H)	0.52	$2.10 \times 10^4$	$3.83 \times 10^4$	1.82
IV <sub>d</sub> (H)	0.59	$1.86 \times 10^4$	$3.62 \times 10^4$	1.94
IV <sub>e</sub> (H)	0.57	$2.21 \times 10^4$	$3.69 \times 10^4$	1.67
IV <sub>f</sub> (C)	0.42	$2.03 \times 10^4$	$3.57 \times 10^4$	1.76
IV <sub>g</sub> (H)	0.49	$1.57 \times 10^4$	$3.03 \times 10^4$	1.93
IV <sub>h</sub> (H)	0.51	$2.11 \times 10^4$	$3.89 \times 10^4$	1.84

<sup>a</sup> (H): thermal imidization; (C): chemical imidization.

<sup>b</sup> Measured at a polymer concentration of 0.5 g/dL in DMAc at 30°C.

<sup>c</sup> Relative to polystyrene standards, using THF as the eluent.

the disorder along the polymer chains, interfered with close chain packing, and diminished the chain-to-chain interactions.

All the PEIs could be processed into strong and tough films with low color. These films were subjected to tensile tests, and the tensile properties are

reported in Table IV. They exhibited good mechanical properties with tensile strengths of 83–96 MPa, elongations to break of 8–11%, and initial moduli of 1.7–2.0 GPa, comparable to those of the V series PEIs.

### Optical properties

The transmission UV–vis spectra were measured for tough and flexible films of all PEIs. All PEI films exhibited cut-off wavelengths (absorption edge,  $\lambda_0$ ) shorter than 380 nm (Table V) and were entirely transparent and colorless. For a comparative purpose, a standard polyimide film from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) and a referenced PEI film (with the same chemical structure of Ultem 1000) from bisphenol A bis(ether anhydride) and *m*-phenylenediamine were synthesized in this laboratory, and their optical properties are also included in Table V. Figure 5 depicts the UV–vis spectra of PEI IV<sub>a</sub>(C), IV<sub>a</sub>(H), V<sub>a</sub>(H), PMDA/ODA, and Ultem 1000. PEI IV<sub>a</sub> revealed a  $\lambda_0$  at 373 nm, similar to the Ultem 1000 film, slightly lower than V<sub>a</sub>, and much lower than the PMDA/ODA film (by 43 nm). The color coordinates  $L^*$

**TABLE III**  
Solubility Behavior of Poly(ether imide)s<sup>a</sup>

Polymer code	Solvent									
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
IV <sub>a</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>b</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>c</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>d</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>e</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>f</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>g</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>h</sub> (C)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>a</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>b</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>c</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>d</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>e</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>f</sub> (H)	–	–	–	–	–	–	–	–	–	–
IV <sub>g</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
IV <sub>h</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++
V <sub>a</sub> (H)	+	+	+	–	+	+++	–	+	+	+++
V <sub>b</sub> (H)	+++	+++	+	–	+	+++	+	+++	+	+++
V <sub>c</sub> (H)	–	–	–	–	+	+++	–	+++	+++	+++
V <sub>d</sub> (H)	+	+	–	–	+	+	–	+	+++	+++
V <sub>e</sub> (H)	+	–	–	–	+	+	–	++	+++	+++
V <sub>f</sub> (H)	–	–	–	–	–	–	–	–	–	–
V <sub>g</sub> (H)	+++	+++	++	–	+	+++	+++	+++	+++	+++
V <sub>h</sub> (H)	+++	+++	+++	–	+	+++	+++	+++	+++	+++

NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran; +++, soluble at 10 wt %; ++, soluble at 5 wt % solid; +, soluble at 1 wt % solid; –, insoluble.

<sup>a</sup> Determined at room temperature.

**TABLE IV**  
Tensile Properties of Poly(ether imide) Films

Polymer code <sup>a</sup>	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
IV <sub>a</sub> (H)	95	11	1.7
IV <sub>b</sub> (H)	85	8	2.0
IV <sub>c</sub> (H)	83	9	1.8
IV <sub>d</sub> (H)	89	8	1.8
IV <sub>e</sub> (H)	85	9	1.8
IV <sub>f</sub> (H)	92	10	1.7
IV <sub>g</sub> (H)	86	10	1.8
IV <sub>h</sub> (H)	96	11	1.9
V <sub>a</sub> (H)	94	11	1.8
V <sub>b</sub> (H)	91	10	1.4
V <sub>c</sub> (H)	84	9	1.6
V <sub>d</sub> (H)	88	20	1.7
V <sub>e</sub> (H)	85	12	1.4
V <sub>f</sub> (H)	86	10	1.5
V <sub>g</sub> (H)	84	13	1.6
V <sub>h</sub> (H)	90	9	1.8

$a^*$   $b^*$  values of all polymer films are listed in Table V. The slightly higher yellowness index ( $b^*$ ) of the thermally cured PEI films might be explained by thermal oxidation of chain-end amino groups. All the **IV** series fluorinated PEIs showed lower  $b^*$  values than their respective **V** series PEIs and the PMDA/ODA polyimide (Fig. 6). The low color intensity of the CF<sub>3</sub>-substituted PEIs could be attributable to the weakening CTC effect between the electro-donating components (dietheramine) and electro-accepting components (dietheranhydride) because of the existence of the —CF<sub>3</sub> groups, which were highly sterically hindered and electron-withdrawing substituents, capable of reducing the CTC formation. The use of bis(ether anhydride) **I** also contributed toward decreasing the overall electron affinity of the phthalimide units, and thus lowered the intra- and intermolecular CTC interactions.

### Thermal properties

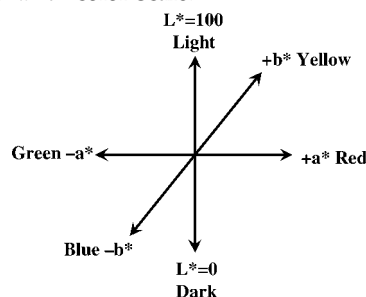
The thermal behavior data of the thermally imidized PEIs are presented in Table VI. The  $T_g$  values of the **IV(H)** series PEIs, determined by DSC, are in the range of 191–248°C. The decreasing order of  $T_g$  values generally correlated with the flexibility of the diamine moieties. PEI **IV<sub>g</sub>(H)** showed the lowest  $T_g$  values (191°C) because of the presence of flexible isopropylidene linkage, whereas PEI **IV<sub>e</sub>(H)** exhibited the highest  $T_g$  value of 248°C because of the presence of rigid tetramethylbiphenyl unit in the diamine moiety. As expected, the methyl- or *t*-butyl-substituted PEIs exhibited higher  $T_g$  values than the corresponding unsubstituted PEIs because of the hindrance effect of the chain rotation in the substituted polymers. In most cases, slightly decreased  $T_g$  values for the **IV** series when compared to the **V** series might be a result of reduced electronic interactions and less dense packing caused by the bulky pendent CF<sub>3</sub> groups.

The thermal stability of the thermally cured PEIs was evaluated by dynamic TGA 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 TGA thermograms. The  $T_{10}$  values of the **IV(H)** series were recorded in the range of 494–549°C in nitrogen and 494–547°C in air, comparable to or slightly higher than those of the **V** analogs. They left more than 39% char yield at 800°C in nitrogen. It is quite reasonable that the methyl- or *t*-butyl-substituted PEIs began to decompose at lower temperatures when compared with the unsubstituted ones. The TGA data indicate that these fluorinated PEIs had high thermal stability regardless of the introduction of CF<sub>3</sub> groups.

**TABLE V**  
Color Coordinates and the Cut-off Wavelengths ( $\lambda_0$ ) from the UV–visible Spectra of the Poly(ether imide) Films

Polymer code	Film thickness ( $\mu\text{m}$ )	Color coordinates <sup>a</sup>			$\lambda_0$ (nm)
		$b^*$	$a^*$	$L^*$	
Blank		7.5	−5.3	94.5	
IV <sub>a</sub> (C)	54	17.0	−4.8	84.8	375
IV <sub>b</sub> (C)	59	16.3	−5.0	85.2	374
IV <sub>c</sub> (C)	48	16.9	−5.3	84.6	363
IV <sub>d</sub> (C)	46	15.3	−4.9	85.7	361
IV <sub>e</sub> (C)	49	16.2	−5.3	85.9	364
IV <sub>f</sub> (C)	47	16.3	−5.5	85.5	374
IV <sub>g</sub> (C)	46	15.8	−5.4	85.7	365
IV <sub>h</sub> (C)	54	15.5	−4.8	85.5	365
IV <sub>a</sub> (H)	48	20.0	−5.8	85.1	373
IV <sub>b</sub> (H)	47	16.8	−5.8	86.7	367
IV <sub>c</sub> (H)	38	18.0	−6.7	86.1	368
IV <sub>d</sub> (H)	44	19.3	−6.0	84.7	370
IV <sub>e</sub> (H)	32	20.8	−7.6	83.2	362
IV <sub>f</sub> (H)	38	22.9	−7.1	84.7	376
IV <sub>g</sub> (H)	41	16.5	−5.9	86.1	368
IV <sub>h</sub> (H)	37	18.6	−6.7	85.8	367
V <sub>a</sub> (H)	56	23.0	−5.4	82.5	375
V <sub>b</sub> (H)	66	24.3	−5.5	82.1	374
V <sub>c</sub> (H)	51	19.6	−6.9	85.2	369
V <sub>d</sub> (H)	55	21.0	−5.2	85.4	366
V <sub>e</sub> (H)	38	22.0	−7.1	85.7	364
V <sub>f</sub> (H)	40	25.0	−1.5	77.4	374
V <sub>g</sub> (H)	40	18.0	−4.1	83.1	366
V <sub>h</sub> (H)	41	24.0	−5.4	85.9	365
Ultem 1000	50	18.1	−5.7	84.3	375
PMDA/ODA	32	49.3	−8.6	83.6	416

<sup>a</sup> The CIE  $L^*$   $a^*$   $b^*$  color scale:



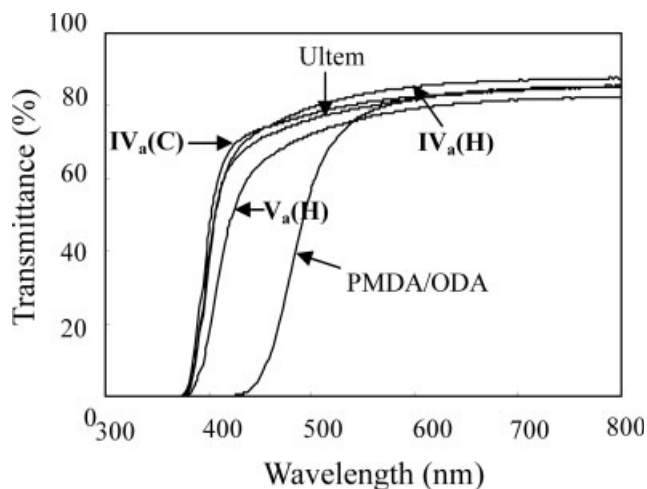


Figure 5 UV-vis spectra of PEIs films.

### Dielectric constants

The dielectric constants of the thermally imidized PEI films are listed in Table VII. The **IV(H)** series had lower dielectric constants (3.25–3.72 at 1 MHz) than the corresponding nonfluorinated homologues **V** series (3.70–4.19 at 1 MHz). The decreased dielectric constants could be attributable to the presence of bulky  $\text{CF}_3$  groups in the polymer chains. The strong electronegativity of the fluorine atom resulted in very low polarizability of the C–F bonds, combined with the high free volumes of the  $\text{CF}_3$  group, endowed the PEIs with lowered dielectric constants. Besides, **IV<sub>h</sub>** and **V<sub>h</sub>** exhibited the lowest dielectric constants in each series because of the additional bulky hexafluoroisopropylidene group in diamine moieties.

### CONCLUSIONS

A series of novel fluorine-containing PEIs (**IV** series) were synthesized from 4,4'-[1,4-phenylenbis(isopro-

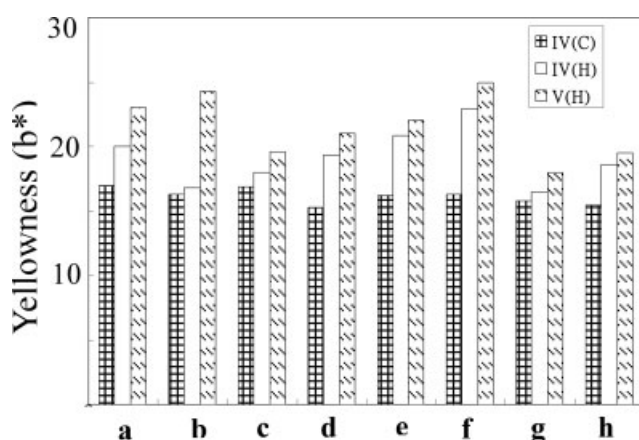


Figure 6 Comparison of the yellowness index ( $b^*$  value) between PEIs.

TABLE VI  
Thermal Behavior Data of Poly(ether imide)s

Polymer	$T_g$ ( $^{\circ}\text{C}$ ) <sup>a</sup>	$T_{10}$ ( $^{\circ}\text{C}$ ) <sup>b</sup>		Char yield (%) <sup>c</sup>
		In $\text{N}_2$	In air	
IV <sub>a</sub> (H)	193	546	543	50
IV <sub>b</sub> (H)	202	535	529	42
IV <sub>c</sub> (H)	215	523	514	39
IV <sub>d</sub> (H)	202	549	547	59
IV <sub>e</sub> (H)	243	494	494	53
IV <sub>f</sub> (H)	197	545	535	59
IV <sub>g</sub> (H)	191	543	537	55
IV <sub>h</sub> (H)	194	542	540	58
V <sub>a</sub> (H)	203	534	524	48
V <sub>b</sub> (H)	202	523	517	42
V <sub>c</sub> (H)	214	515	506	36
V <sub>d</sub> (H)	213	529	529	51
V <sub>e</sub> (H)	246	492	497	48
V <sub>f</sub> (H)	204	526	524	52
V <sub>g</sub> (H)	199	533	526	39
V <sub>h</sub> (H)	205	543	535	50

<sup>a</sup> Baseline shift in the second heating DSC traces, with a heating rate of  $15^{\circ}\text{C}/\text{min}$ .

<sup>b</sup> Temperatures at which 10% weight loss were recorded by TG at a heating rate of  $20^{\circ}\text{C}/\text{min}$ .

<sup>c</sup> Residual weight (%) when heated to  $800^{\circ}\text{C}$  in nitrogen.

pylidene-1,4-phenyleneoxy)]diphthalic anhydride (**I**) with various  $\text{CF}_3$ -substituted aromatic bis(ether amine)s by two-step thermal or chemical imidization method. These PEI films showed excellent solubility in various organic solvents, including low boiling point solvents, and could be cast into virtually colorless and strong films. They also exhibited moderately high  $T_g$ s and good thermal stability, together with low dielectric constants. Thus, this series of PEIs demonstrated a good combination of properties and may be of interest for optical and optoelectronic applications.

TABLE VII  
Dielectric Constants of Poly(ether imide) Films

Polymer	Film thickness ( $\mu\text{m}$ )	Dielectric constant (dry)		
		1 kHz	10 kHz	1 MHz
IV <sub>a</sub> (H)	45	3.91	3.83	3.65
IV <sub>b</sub> (H)	36	3.54	3.51	3.47
IV <sub>c</sub> (H)	44	3.47	3.45	3.31
IV <sub>d</sub> (H)	53	3.72	3.68	3.40
IV <sub>e</sub> (H)	36	3.78	3.74	3.66
IV <sub>f</sub> (H)	37	3.86	3.83	3.72
IV <sub>g</sub> (H)	38	3.71	3.67	3.57
IV <sub>h</sub> (H)	50	3.34	3.31	3.25
V <sub>a</sub> (H)	57	4.03	3.96	3.82
V <sub>b</sub> (H)	52	4.14	4.09	3.99
V <sub>c</sub> (H)	48	4.21	4.16	4.02
V <sub>d</sub> (H)	35	3.93	3.90	3.73
V <sub>e</sub> (H)	52	4.38	4.33	4.19
V <sub>f</sub> (H)	41	4.24	4.07	3.85
V <sub>g</sub> (H)	48	4.24	4.19	4.06
V <sub>h</sub> (H)	40	3.87	3.82	3.70



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