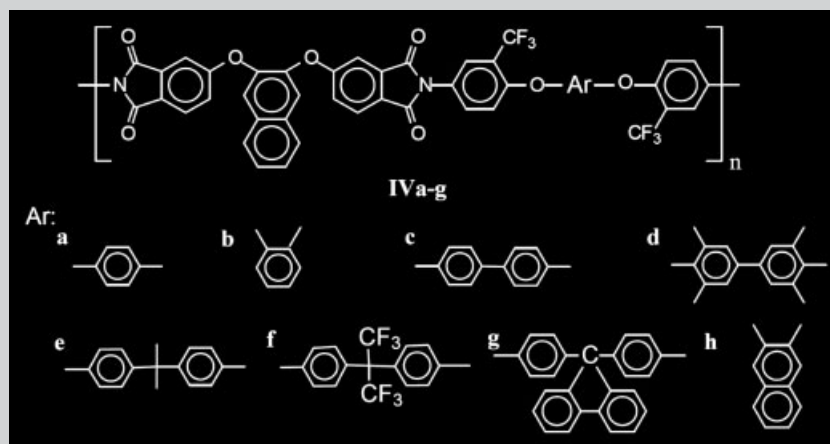


**Summary:** A novel series of aromatic poly(ether imide)s (PEIs) **IVa–h** containing *ortho*-linked aromatic units and pendent trifluoromethyl ( $\text{CF}_3$ ) groups were prepared from 2,3-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride (**I**) with various  $\text{CF}_3$ -substituted aromatic bis(ether amine)s **IIa–h** via a conventional two-stage process including ring-opening polyaddition to form the poly(amic acid)s followed by either chemical or thermal imidization to the PEIs. The inherent viscosities of PEIs **IVa–h** were in the range of  $0.43\text{--}0.86\text{ dL}\cdot\text{g}^{-1}$  that corresponded to weight-average and number-average molecular weights (by gel permeation chromatography) of  $36\,000\text{--}73\,000$  and  $23\,000\text{--}51\,000$ , respectively. All the **IV** series were highly soluble in several

organic solvents and could be solution-cast into transparent, flexible, and strong films. These films were essentially colorless; their cut-off wavelengths were between 368 and 377 nm and a very low  $b^*$  value (a yellowness index) ranging from 4.1 to 5.5. They had useful levels of thermal stability associated with moderately high-glass transition temperatures (208–281 °C), 10% weight-loss temperatures in excess of 492 °C, and char yields at 800 °C in nitrogen higher than 51%. They also showed low water uptakes of 0.25–0.48% and low dielectric constants of 3.06–3.67 at 10 kHz. For a comparative study, a series of structurally similar, non-fluorinated PEIs **Va–h** from dianhydride **I** and bis(ether amine)s **II'a–h** were also prepared and characterized.



A novel series of aromatic poly(ether imide)s (PEIs) **IVa–h**.

# Thermally Stable, Organosoluble, and Colorless Poly(ether imide)s Having *Ortho*-Linked Aromatic Units in the Main Chain and Trifluoromethyl Pendent Groups

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**Keywords:** films; fluorinated bis(ether-amine)s; low color; *ortho*-linked aromatic units; poly(ether imide)s; polyimides; solubility

## Introduction

Aromatic polyimides are one of the most important classes of high-performance polymers used in the microelectronics and optoelectronics 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 temperatures which are caused by the rigid polymer backbones and the strong interchain 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 pale yellow to deep brown color of their films caused by the intramolecular and intermolecular charge transfer (CT) interactions between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties.<sup>[5–7]</sup> A strategy for obtaining less colored or colorless polyimides is to use dianhydrides of lower electron-acceptability and diamines of lower electron-donatability as monomers for weakening both intra- and intermolecular CT interactions.<sup>[7]</sup> Soluble and colorless polyimides can be obtained by using alicyclic dianhydride or diamine monomers;<sup>[8–12]</sup> however, the high-temperature stability is somewhat sacrificed due to the incorporation of less-stable aliphatic segments. Thus, polyimides derived from aliphatic monomers are mostly used for applications that have less-stringent thermal requirements.

Poly(ether imide)s (PEIs) have attracted great attention as they may provide good processability owing to the presence of flexible ether links. The development of nucleophilic-displacement reactions, and nitro-displacement reactions in particular, has led to the development of a large class of PEIs from bis(ether anhydride)s and various diamines.<sup>[13–15]</sup> An important example is Ultem 1000 resin developed and commercialized by General Electric Co.,<sup>[16]</sup> which exhibits reasonable thermal stability and good mechanical properties together with good moldability. Recently, considerable attention has been paid to the fluorinated aromatic polyimides, especially trifluoromethyl (CF<sub>3</sub>)-containing polyimides.<sup>[17–22]</sup> It was found that the incorporation of bulky CF<sub>3</sub> into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which was attributed to low polarizability of the C–F bond and the increase in free volume. The fluorinated polyimides also had other merits, such as good thermal and thermooxidative stability and low moisture absorption.

As part of our recent efforts to develop soluble and colorless polyimides with high thermal stability and low dielectric constant for advanced microelectronics and optoelectronics applications, the current work reports the synthesis and characterization of a series of fluorinated PEIs

from 2,3-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride with various structurally different CF<sub>3</sub>-substituted aromatic bis(ether amine)s. The obtained PEIs should have diminished intra- and intermolecular CT interactions not only because of the decrease in electron-accepting property of the dianhydride moieties caused by the electron-donating ether groups, but also due to the decrease in electron-donating property of diamine moieties caused by the electron-withdrawing –CF<sub>3</sub> groups. In addition to the bulky, packing-disruptive –CF<sub>3</sub> groups, the formation of bent structures due to the presence of *ortho*-links will help to prevent the extended close chain packing, and consequently, the CT interactions. Thus, the polymers would be expected to exhibit low coloration, high optical transparency in the visible region, good solubility in organic solvents, and low dielectric constants.

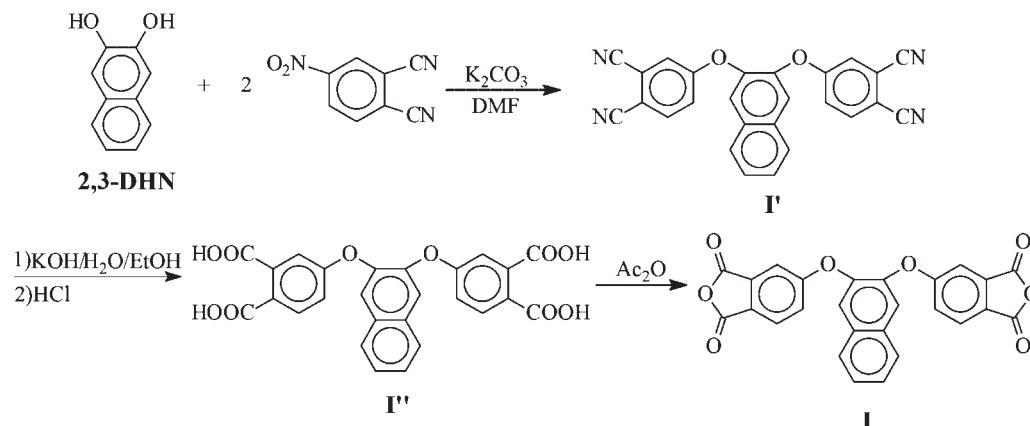
## Experimental Part

### Materials

According to well-established procedures,<sup>[23–34]</sup> all the CF<sub>3</sub>-substituted bis(ether amine)s and some of the CF<sub>3</sub>-free bis(ether amine)s were prepared from the chloro-displacement reactions of 2-chloro-5-nitrobenzotrifluoride and 4-chloronitrobenzene, respectively, with the corresponding aromatic diols in the presence of potassium carbonate, followed by Pd/C-catalyzed hydrazine reduction of the dinitro intermediates; they included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene<sup>[23]</sup> (**IIa**) (m.p.: 133–134 °C), 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene<sup>[24]</sup> (**IIb**) (m.p.: 116–117 °C), 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl<sup>[25]</sup> (**IIc**) (m.p.: 155–156 °C), 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl<sup>[26]</sup> (**IId**) (m.p.: 256–257 °C), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane<sup>[27]</sup> (**IIe**) (m.p.: 131–132 °C), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane<sup>[28]</sup> (**IIIf**) (m.p.: 65–66 °C), 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene<sup>[29]</sup> (**IIg**) (m.p.: 239–240 °C), 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene<sup>[30]</sup> (**IIh**) (m.p.: 175–176 °C), 1,2-bis(4-aminophenoxy)benzene<sup>[31]</sup> (**II' b**) (m.p.: 137–138 °C), 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl<sup>[32]</sup> (**II' d**) (m.p.: 225–226 °C), 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene<sup>[33]</sup> (**II' g**) (m.p.: 177–178 °C), and 2,3-bis(4-aminophenoxy)naphthalene<sup>[34]</sup> (**II' h**) (m.p.: 176–177 °C). 1,4-Bis(4-aminophenoxy)benzene (**II' a**; TCI), 4,4'-bis(4-aminophenoxy)biphenyl (**II' c**; 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. *N,N*-Dimethylacetamide (DMAc) (Fluka) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. All other reagents and solvents were used as received from commercial sources.

### Synthesis of 2,3-Bis(3,4-dicarboxyphenoxy)naphthalene Dianhydride (**I**)

According to a previously reported procedure,<sup>[35,36]</sup> the bis(ether anhydride) monomer **I** (m.p.: 266–267 °C) was

Scheme 1. Synthetic route to bis(ether anhydride) **I**.

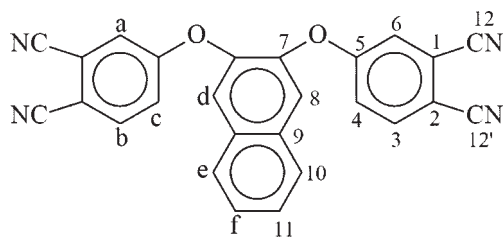
synthesized starting from the nitro-displacement reaction of 4-nitrophenalodinitrile with 2,3-dihydroxynaphthalene (2,3-DHN) in *N,N*-dimethylformamide (DMF) in the presence of potassium carbonate as the base, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) (**I'**) and the cyclodehydration of the resulting bis(ether diacid) (**I''**). The synthetic route is outlined in Scheme 1.

IR of **I'** (KBr): 2235 (C≡N), 1591, 1489 (arom. C–C), 1243  $\text{cm}^{-1}$  (C–O).

Anal. Calcd. for  $\text{C}_{26}\text{H}_{12}\text{N}_4\text{O}_2$  (412.41): C 75.72, H 2.93, N 13.58; Found C 75.68, H 2.90, N 13.49.

$^1\text{H}$  NMR of **I'** (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 8.02 (d, 2H,  $\text{H}_b$ ,  $J = 8.65$  Hz), 8.01–7.99 (2H,  $\text{H}_c$ ), 7.99 (s, 2H,  $\text{H}_d$ ), 7.78 (d, 2H,  $\text{H}_a$ ,  $J = 1.80$  Hz), 7.62 (dd, 2H,  $\text{H}_f$ ,  $J = 6.20, 6.20$  Hz), 7.43 (dd, 2H,  $\text{H}_e$ ,  $J = 8.75, 2.55$  Hz).

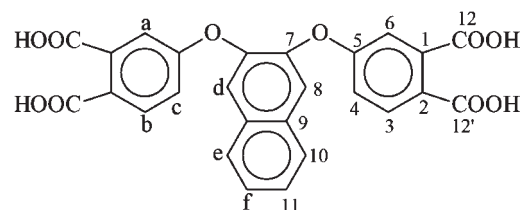
$^{13}\text{C}$  NMR of **I'** (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 160.7 ( $\text{C}^5$ ), 143.8 ( $\text{C}^7$ ), 136.5 ( $\text{C}^3$ ), 131.9 ( $\text{C}^9$ ), 127.9 ( $\text{C}^{10}$ ), 127.2 ( $\text{C}^{11}$ ), 122.2 ( $\text{C}^{12}, 12'$ ), 121.1 ( $\text{C}^4$ ), 116.9 ( $\text{C}^6$ ), 116.2 ( $\text{C}^1$ ), 115.5 ( $\text{C}^8$ ), 109.1 ( $\text{C}^2$ ).



IR of **I''** (KBr): 3600–2500 (O–H), 1701 (C=O), 1603, 1468 (arom. C=C), 1211  $\text{cm}^{-1}$  (C–O).

$^1\text{H}$  NMR of **I''** (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 7.90 (dd, 2H,  $\text{H}_e$ ,  $J = 6.15, 5.90$  Hz), 7.79 (s, 2H,  $\text{H}_d$ ), 7.73 (d, 2H,  $\text{H}_b$ ,  $J = 8.20$  Hz), 7.49 (dd, 2H,  $\text{H}_f$ ,  $J = 6.20, 5.98$  Hz), 7.08–7.06 (4H,  $\text{H}_c, a$ ).

$^{13}\text{C}$  NMR of **I''** (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 168.9, 168.0 ( $\text{C}^{12}, 12'$ ), 159.4 ( $\text{C}^5$ ), 145.5 ( $\text{C}^7$ ), 136.7 ( $\text{C}^1$ ), 131.8 ( $\text{C}^9$ ), 131.6 ( $\text{C}^3$ ), 127.7 ( $\text{C}^{10}$ ), 126.9 ( $\text{C}^2$ ), 126.6 ( $\text{C}^{11}$ ), 119.9 ( $\text{C}^4$ ), 118.7 ( $\text{C}^6$ ), 116.3 ( $\text{C}^8$ ).

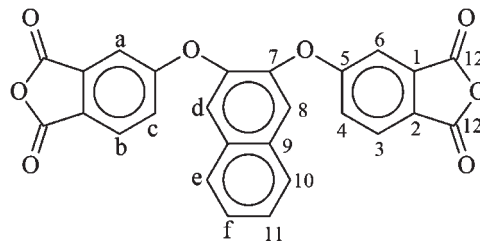


IR of **I** (KBr): 1855 (asym. C=O str.), 1780 (sym. C=O str.), 1616, 1487 (arom. C=C), 1288  $\text{cm}^{-1}$  (C–O).

Anal. Calcd. for  $\text{C}_{26}\text{H}_{12}\text{O}_8$  (452.37): C 69.09, H 2.67; Found C 68.65, H 2.64.

$^1\text{H}$  NMR of **I** (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 7.94 (dd, 2H,  $\text{H}_e$ ,  $J = 6.15, 6.15$  Hz), 7.84 (s, 2H,  $\text{H}_d$ ), 7.74 (d, 2H,  $\text{H}_b$ ,  $J = 8.25$  Hz), 7.53 (dd, 2H,  $\text{H}_f$ ,  $J = 6.25, 6.25$  Hz), 7.12–7.10 (2H,  $\text{H}_c$ ), 7.10 (s, 2H,  $\text{H}_a$ ).

$^{13}\text{C}$  NMR of **I** (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 168.5, 167.6 ( $\text{C}^{12}, 12'$ ), 159.0 ( $\text{C}^5$ ), 145.3 ( $\text{C}^7$ ), 136.5 ( $\text{C}^1$ ), 131.4 ( $\text{C}^9$ ), 131.2 ( $\text{C}^3$ ), 127.4 ( $\text{C}^{10}$ ), 126.5 ( $\text{C}^2$ ), 126.2 ( $\text{C}^{11}$ ), 119.5 ( $\text{C}^4$ ), 118.3 ( $\text{C}^6$ ), 116.1 ( $\text{C}^8$ ).



#### Synthesis of Poly(ether imide)s

The preparation of PEI **IVa** is used as an example to illustrate the general synthetic route. Diamine **IIa** (0.1966 g, 0.7 mmol) was dissolved in 3.9 mL of dried DMAc in a 25-mL flask at room temperature. After **IIa** was completely dissolved, an equimolar amount of bis(ether anhydride) **I** (0.3030 g, 0.7 mmol) was added in one portion. The mixture was stirred

at room temperature for 10 h to obtain a viscous poly(amic acid) (PAA) solution. The PAA was converted into polyimide either by the thermal imidization or chemical imidization method. For the thermal imidization method, the PAA solution was poured into a glass culture dish, which was placed in an oven and heated at 80 °C for 1 h to remove the solvent. The semi-dried PAA film was further dried and imidized by sequential heating from 120 to 250 °C at a heating rate of 3 °C · min<sup>-1</sup> and then further heated at 250 °C for 1 h. The polyimide film was stripped from the glass substrate by immersion in water. Inherent viscosity ( $\eta_{inh}$ ) in DMAc of PEI **IVa** was 0.83 dL · g<sup>-1</sup>, as measured at a concentration of 0.5 g · dL<sup>-1</sup> at 30 °C. Chemical imidization was carried out by adding a mixture of 1 mL of acetic anhydride and 0.5 mL of pyridine to the PAA solution. The mixture was heated at 80 °C for 1 h to cause a complete imidization and then poured into a glass culture dish, which was placed in an oven and heated at 80 °C for 1 h so that the solvent evaporates and a thin solid film is formed. The polyimide film was then heated to 200 °C and held at that temperature for 2 h to remove the residual solvent. By soaking in water, a flexible polymer film **IVa(C)** was stripped from the glass surface. Inherent viscosity ( $\eta_{inh}$ ) of **IVa(C)** in DMAc at a 0.5 g · dL<sup>-1</sup> concentration at 30 °C was 0.86 dL · g<sup>-1</sup>.

IR (film): 1779 (asymmetric C=O stretch), 1727 (symmetric imide C=O stretch), 1488 (aromatic C=C stretch), 1378 (C–N stretch), 1244 (C–O), 744 and 1052 cm<sup>-1</sup> (imide ring deformation).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 7.88–7.86 (4H, H<sub>b</sub> + H<sub>e</sub>), 7.76 (s, 4H, H<sub>d</sub> + H<sub>g</sub>), 7.59 (dd, 2H, H<sub>f</sub>,  $J$  = 5.70, 2.75 Hz), 7.52 (d, 2H, H<sub>h</sub>,  $J$  = 9.65 Hz), 7.32 (s, 2H, H<sub>a</sub>), 7.23 (d, 2H, H<sub>c</sub>,  $J$  = 9.15 Hz), 7.14 (s, 4H, H<sub>j</sub>), 7.03 (d, 2H, H<sub>i</sub>,  $J$  = 8.90 Hz).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 166.1 (C<sup>21</sup>, 21'), 163.1 (C<sup>5</sup>), 155.1 (C<sup>15</sup>), 152.3 (C<sup>19</sup>), 144.5 (C<sup>7</sup>), 134.0 (C<sup>12</sup>), 131.8 (C<sup>9</sup>), 131.3 (C<sup>13</sup>), 127.4 (C<sup>3</sup>), 127.1 (C<sup>11</sup>), 126.1 (C<sup>1</sup>), 125.9 (C<sup>10</sup>), 125.6 (C<sup>17</sup>), 125.3 (C<sup>2</sup>), 122.8 (C<sup>18</sup>, quartet, <sup>1</sup>J<sub>C–F</sub> = 272 Hz), 122.2 (C<sup>4</sup>), 121.5 (C<sup>20</sup>), 121.4 (C<sup>16</sup>, quartet, <sup>2</sup>J<sub>C–F</sub> = 32 Hz), 120.9 (C<sup>8</sup>), 118.7 (C<sup>14</sup>), 111.4 (C<sup>6</sup>).

### Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FT-IR) spectrometer. Elemental analyses were run in 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 0.5 g · dL<sup>-1</sup> concentration with an Ubbelohde viscometer at 30 °C. Weight-average molecular weights ( $\bar{M}_w$ ) and number-average molecular weights ( $\bar{M}_n$ ) 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. 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<sup>-1</sup>) at a heating rate of 20 °C · min<sup>-1</sup>. DSC analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen at a heating rate of 15 °C · min<sup>-1</sup>. 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 mm · min<sup>-1</sup> on approximately

40–70 μm thick, 0.5 cm wide, and 6 cm long strips. An average of at least five individual determinations was used. The color intensity of the polymers was evaluated by a GretagMacbeth COLOR-EYE 3100 colorimeter. Measurements were performed with an observational angle of 10° and 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. The dielectric property of the polymer films was tested by the parallel-plate capacitor method with a TA Instruments DEA 2970 dielectric analyzer. Gold electrodes were vacuum-deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. The equilibrium water uptake was determined by weighing of changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 d.

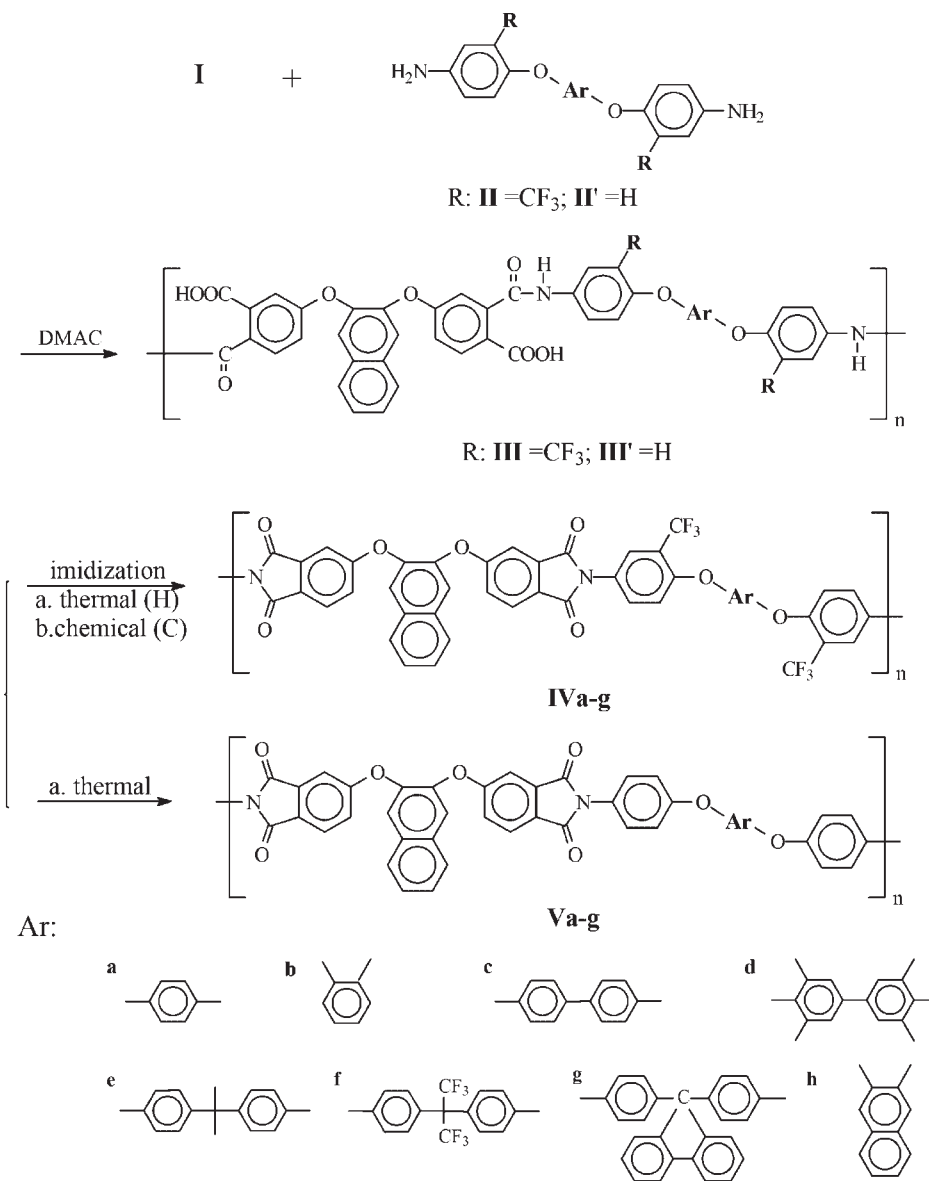
## Results and Discussion

### Polymer Synthesis

All the PEIs **IVa–h** were synthesized from bis(ether anhydride) (**I**) and various fluorinated diamines (**IIa–h**) via a conventional two-stage procedure of ring-opening polyaddition at room temperature to obtain PAAs, followed by sequential heating to 250 °C or treatment with a mixture of Ac<sub>2</sub>O/pyridine to obtain the corresponding polymers as shown in Scheme 2. In the first stage, the viscosities of the reaction mixtures became high as PAAs were formed, indicating the formation of a high-molecular-weight polymer. In spite of the presence of electron-withdrawing –CF<sub>3</sub> substituents, the maintained reactivity of these bis(ether amine)s is most likely based on the *meta*-substitution to the amino group. Both thermal and chemical imidization methods were employed to convert the PAA precursors to the PEIs, and the PEI samples are denoted as **IV(H)** and **IV(C)**, respectively. Almost all polymers remained in solution when imidized by acetic anhydride and pyridine. These PEIs exhibited excellent solubility in polar solvents such as NMP and DMAc. Therefore, the characterization of solution viscosity was carried out without any difficulty, and their inherent viscosities were recorded in the range of 0.43–0.86 dL · g<sup>-1</sup>, as measured in DMAc at 30 °C (Table 1). The weight-average molecular weights ( $\bar{M}_{ws}$ ) and number-average molecular weights ( $\bar{M}_n$ ) of these polymers were recorded in the range of 36 000–74 000 and 23 000–51 000, respectively, relative to polystyrene standards. For a comparative study, a series of referenced PEIs (**Va–h**) were also prepared from bis(ether anhydride) **I** and non-trifluoromethylated bis(ether amine)s **II'a–h** via thermal imidization.

The complete imidization of polymers was confirmed by IR and NMR spectra. Typical FT-IR spectra of PAA **IIIa** and PEI **IVa** are shown in Figure 1. In the IR spectra, the fluorinated PEIs exhibited characteristic imide group absorptions around 1780 and 1725 cm<sup>-1</sup> (typical of imide





Scheme 2. Synthesis of PEIs.

carbonyl asymmetrical and symmetrical stretch), 1 380 (C–N stretch), and 1 100 and 750 (imide ring deformation), together with some strong absorption bands in the region of 1 100–1 300  $\text{cm}^{-1}$  due to the C–O and C–F stretching. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of the PAA precursor into polyimide. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of a typical PEI **IVa** are shown in Figure 2. Assignments of each carbon and proton assisted by 2D-NMR spectra (Figure 3 and 4) are also given in the figures, and these spectra are in complete agreement with the proposed polymer structure. In addition to IR and NMR spectra, the elemental analysis results of PEIs were also generally in agreement with the calculated values for the proposed structures (Table 1).

### Polymer Solubility

The qualitative solubility of the PEIs was determined for the film samples in various organic solvents, and the results are listed in Table 2. Most of the PEIs prepared either by the thermal imidization method or the chemical imidization method were readily soluble with a 5 or 10 wt.-% solid content both in strong dipolar solvents and in common organic solvents such as NMP, DMAc, DMF, pyridine, dioxane, THF, and chloroform. 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 **IV** series PEIs generally showed better solubility, especially in DMF and DMSO, as compared with

Table 1. Elemental analysis, inherent viscosity, and GPC data of the PEIs.

Polymer code <sup>a)</sup>	Formula (weight)	Elemental analysis			$\eta_{inh}^{b)}$ dL · g <sup>-1</sup>	GPC data <sup>c)</sup>			
		%				$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$ (PDI)	
		C	H	N					
<b>IVa</b>	C <sub>46</sub> H <sub>22</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (844.68) <sub>n</sub>	Calcd	65.41	2.63	3.32	0.83	5.0	7.3	1.46
		Found	65.12	2.26	3.35	–	–	–	–
<b>IVb</b>	C <sub>46</sub> H <sub>22</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (844.68) <sub>n</sub>	Calcd	65.41	2.63	3.32	0.67	3.0	4.6	1.53
		Found	65.12	2.13	3.45	–	–	–	–
<b>IVc</b>	C <sub>52</sub> H <sub>26</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (920.78) <sub>n</sub>	Calcd	67.83	2.85	3.04	0.62	4.0	5.9	1.47
		Found	67.58	2.30	3.17	–	–	–	–
<b>IVd</b>	C <sub>56</sub> H <sub>34</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (976.88) <sub>n</sub>	Calcd	68.85	3.51	2.87	0.86	5.1	7.4	1.45
		Found	68.62	2.79	2.94	–	–	–	–
<b>IVe</b>	C <sub>55</sub> H <sub>32</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (962.86) <sub>n</sub>	Calcd	68.61	3.35	2.91	0.62	4.0	6.2	1.55
		Found	68.18	2.72	2.91	–	–	–	–
<b>IVf</b>	C <sub>55</sub> H <sub>26</sub> O <sub>8</sub> N <sub>2</sub> F <sub>12</sub> (1070.80) <sub>n</sub>	Calcd	61.69	2.45	2.62	0.46	2.3	3.6	1.56
		Found	61.43	2.61	2.67	–	–	–	–
<b>IVg</b>	C <sub>65</sub> H <sub>34</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (1084.98) <sub>n</sub>	Calcd	71.96	3.16	2.58	0.52	2.6	4.1	1.57
		Found	71.85	2.82	2.65	–	–	–	–
<b>IVh</b>	C <sub>50</sub> H <sub>24</sub> O <sub>8</sub> N <sub>2</sub> F <sub>6</sub> (894.74) <sub>n</sub>	Calcd	67.12	2.70	3.13	0.43	3.4	5.1	1.50
		Found	66.67	2.07	3.30	–	–	–	–

<sup>a)</sup> PEIs **IVa** was obtained by the thermal imidization method, and **IVb–h** were obtained by the chemical imidization method.

<sup>b)</sup> Measured at a polymer concentration of 0.5 g · dL<sup>-1</sup> in DMAc at 30 °C.

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

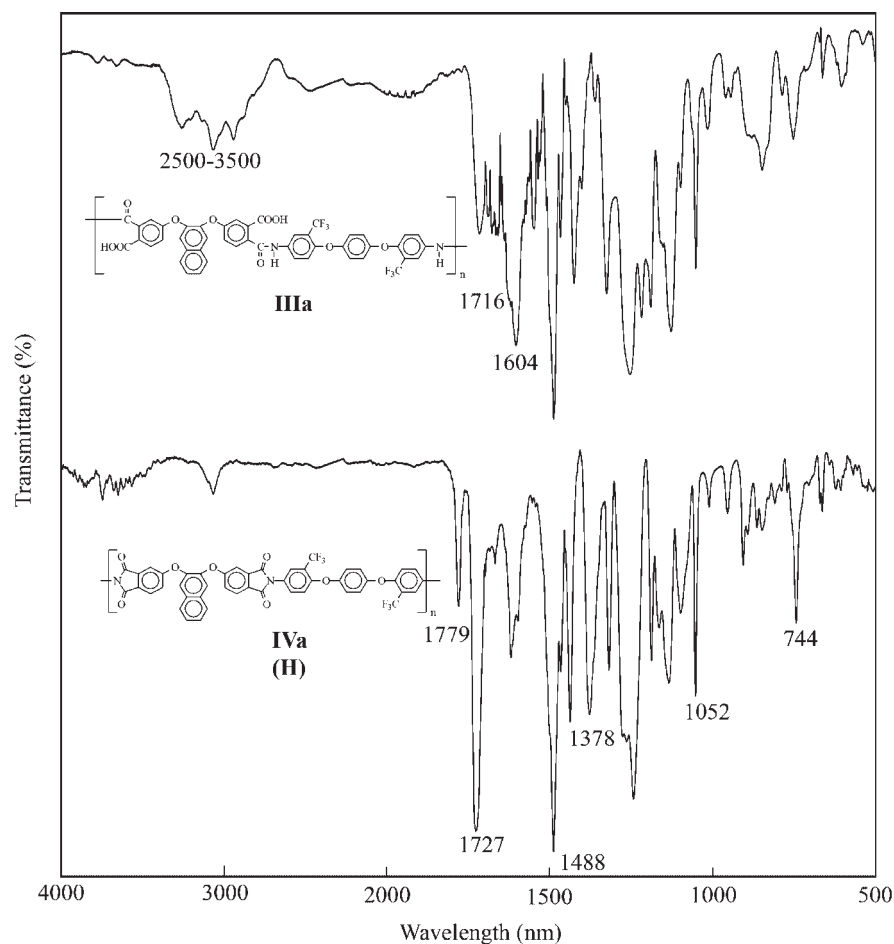


Figure 1. FT-IR spectra of PAA **IIIa** and its thermally imidized PEI **IVa**.

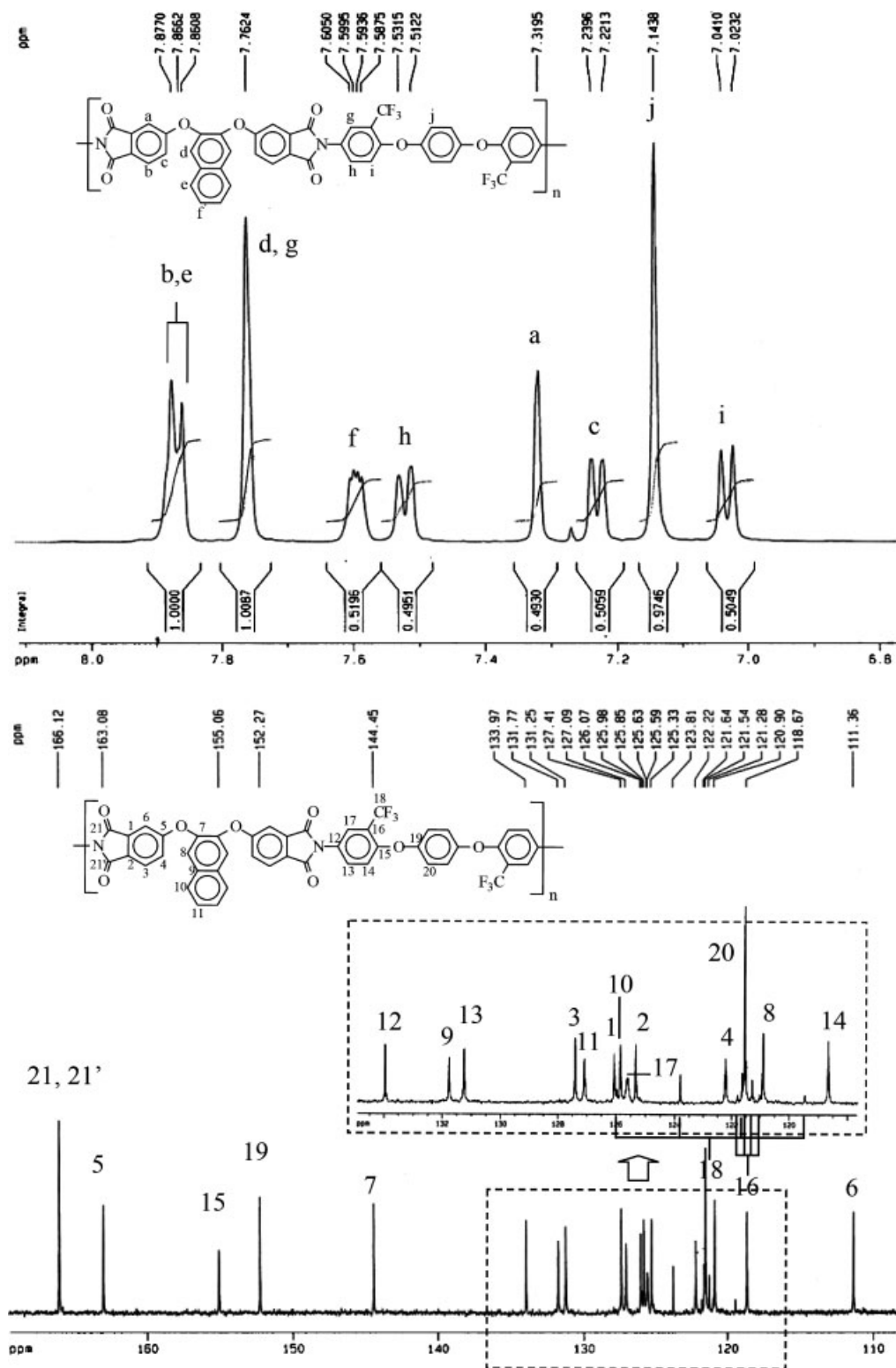


Figure 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PEI **IVa** in  $\text{CDCl}_3$ .

the non-fluorinated **V** series analogs. The difference between the **IV** and **V** series PEIs can be attributed to the effect of the large volume of  $\text{CF}_3$  groups, which disrupted the regularity and dense chain packing leading to decreased

interchain interactions. The packing-disruptive *ortho*-linked 2,3-naphthalenedioxy structure in the bis(ether anhydride) moiety also contributed to the enhancement in solubility.

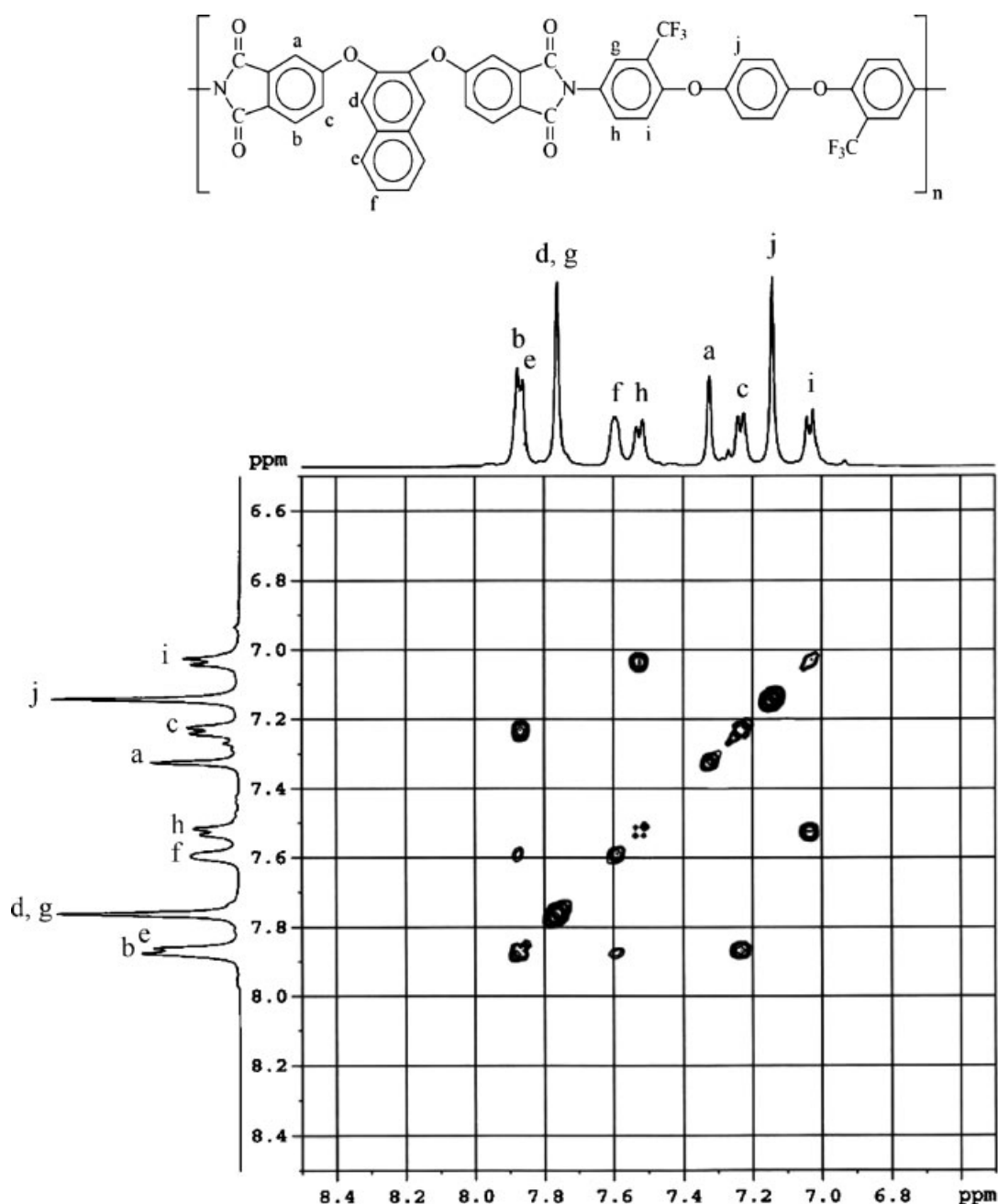


Figure 3. COSY spectrum of PEI **IVa** in  $\text{CDCl}_3$ .

### Optical Properties

The transmission UV-Vis spectra were measured for tough and flexible films of all PEIs. Typical UV-Vis spectra of the **IV(H)**, **IV(C)**, and **V(H)** films are shown in Figure 5. All fluorinated PEI films exhibited cut-off wavelengths shorter than 400 nm and were entirely transparent and colorless. As shown in Table 3, the **IV(C)** PEIs showed a very low yellowness index ( $b^*$ ) of 4.1–5.5. For comparison, the color co-ordinates and cut-off wavelength of a polyarylate and some common polyimides synthesized from commercially

available aromatic dianhydrides with non-fluorinated bis(ether amine) **II'a** are also given in Table 3. The slightly higher yellowness index of the thermally imidized PEI films might be a result of thermal oxidation of chain-end amino groups. All the **IV** series PEIs, containing a  $\text{CF}_3$  group, revealed slightly lower cut-off wavelengths and lower  $b^*$  values than their respective  $\text{CF}_3$ -free analogous PEIs **V**. The bulky and electron-withdrawing  $\text{CF}_3$  group in the diamine moieties was presumably effective in decreasing CT complexes between polymer chains through steric hindrance and the inductive effect (by decreasing



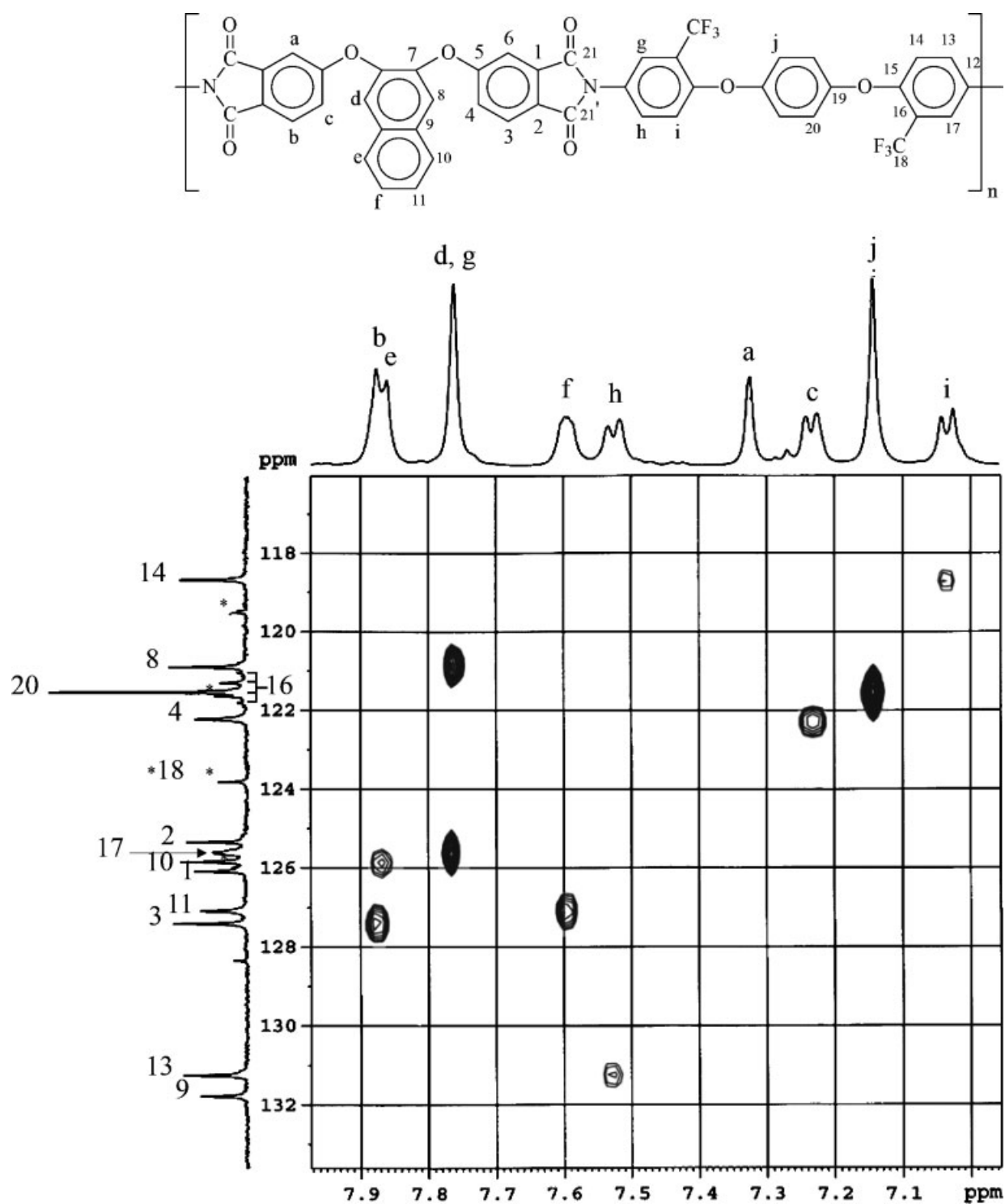


Figure 4. HETCOR spectrum of PEI IVa in  $\text{CDCl}_3$ .

the electron-donating property of diamine moieties). The electron-donating ether groups in the dianhydride moiety also contribute somewhat toward decreasing the overall electron affinity of the phthalimide units, and subsequently decrease the intermolecular CT interaction. In addition, the *ortho*-catenated aromatic structure in the

dianhydride moiety is not sterically favorable for the electronic interaction. Indeed, the prepared PEI films were found to be as colorless as the common polyarylate and 6FDA polyimide films also prepared in our laboratory [6FDA = hexafluoroisopropylidene 2,2-bis(phthalic anhydride)].

Table 2. Solubility of PEIs. Qualitative solubility. +++: 100 mg dissolved completely in 1 mL of the solvent (10%); ++: 5%; +: 1%; -: insoluble; S: swelling. (H): PEI samples prepared by the thermal imidization method. (C): PEI samples prepared by the chemical imidization method. Py: pyridine.

Polymer code	Solvents									
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
IVa(C)	++	+	-	-(S)	-	-	-	-	-	-
IVb(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
IVc(C)	+++	+++	+	-	-	+	-	+	-	-
IVd(C)	+++	+++	+++	++	+++	+++	+++	+++	+++	+++
IVe(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
IVf(C)	+++	+++	+++	+++	+++	+++	+++	+++	+++	+++
IVg(C)	+++	+++	+++	+++	++	+++	+++	+++	+++	+++
IVh(C)	+++	+++	+++	+++	++	+++	+++	+++	+++	+++
IVa(H)	+++	+++	+++	-(S)	++	++	+++	+++	-	++
IVb(H)	+++	+++	+++	+	+++	+++	+++	+++	+++	+++
IVc(H)	+++	+++	+++	-(S)	+	+++	+++	+++	+	++
IVd(H)	+++	+++	+++	-	+	+++	+++	+++	++	+++
IVe(H)	+++	+++	+++	+	+++	+++	+++	+++	+++	+++
IVf(H)	+++	+++	+++	++	+++	+++	+++	+++	+++	+++
IVg(H)	+++	+++	+++	++	++	+++	+++	+++	++	+++
IVh(H)	+++	+++	+++	+	+	+++	+++	+++	++	++
Va(H)	+++	+++	++	-	++	-(S)	-(S)	-	-	-
Vb(H)	+++	+++	+++	+	-(S)	-(S)	-	-	-	-
Vc(H)	+++	+++	++	-	++	-(S)	+	-(S)	-(S)	-
Vd(H)	+++	+++	+	-	-	++	+	+++	+++	+++
Ve(H)	+++	+++	+	-	++	+++	+++	+++	+++	+++
Vf(H)	+++	+++	+++	-	++	+++	+++	+++	+++	+++
Vg(H)	+++	++	+	-	-	+++	+	++	+++	+++
Vh(H)	+++	+++	++	-(S)	-	-(S)	-	-	-	-

### Mechanical and Thermal Properties

The mechanical properties and the thermal behavior data of the **IV** series are summarized in Table 4. These films had tensile strength of 75–104 MPa, 5–9% elongations to break, and initial moduli of 1.7–2.2 GPa. The fluorinated **IV** series PEIs not only had good solubility and low color

but also retained the good tensile properties comparable to those of the non-fluorinated **V** series.

DSC experiments revealed that rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so that  $T_g$  of all the polymers could be easily read in the subsequent heating traces. The  $T_g$  values of the **IV** series were in the range of 208–281 °C. The

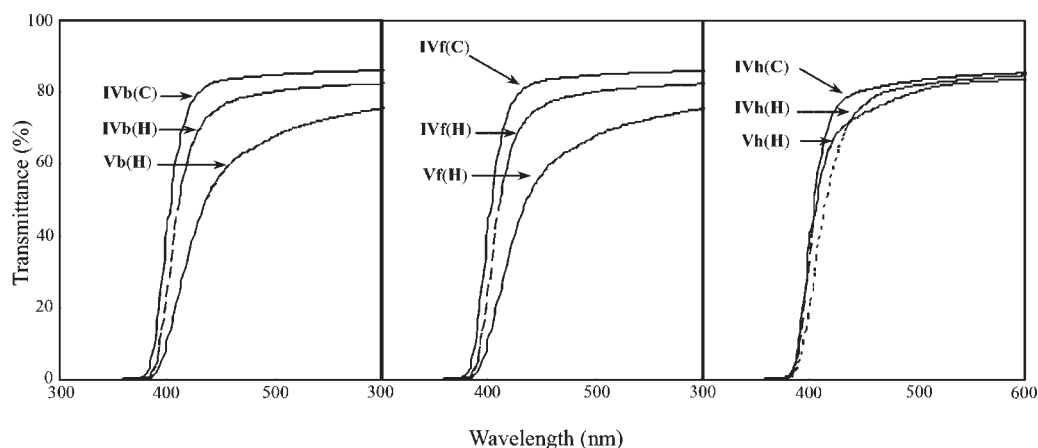


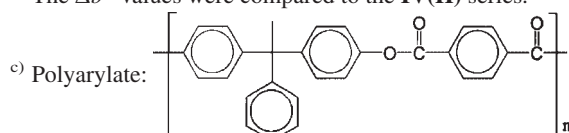
Figure 5. UV-Vis spectra of PEI films of **IV(C)**, **IV(H)**, and **V(H)**.

Table 3. Color co-ordinates and cut-off wavelengths ( $\lambda_0$ ) from UV-Vis spectra for the PEI films.

Polymer code	Film thickness $\mu\text{m}$	Color co-ordinates <sup>a)</sup>				$\lambda_0$ nm
		$b^*$	$\Delta b^{*b)}$	$a^*$	$L^*$	
Blank	–	1.0	–	–0.4	96.2	
Polyarylate <sup>c)</sup>	51	3.3	–	–0.8	98.9	
IVa(H)	43	8.2	–	–2.2	94.8	378
IVb(H)	65	7.9	–	–2.9	95.1	378
IVc(H)	44	8.2	–	–3.0	95.8	377
IVd(H)	55	7.3	–	–2.8	93.5	376
IVe(H)	47	7.4	–	–2.7	95.4	376
IVf(H)	62	6.9	–	–2.3	95.0	368
IVg(H)	55	8.1	–	–2.8	94.9	377
IVh(H)	70	8.0	–	–2.9	94.0	378
IVb(C)	70	5.1	–2.8	–2.0	96.1	376
IVc(C)	63	5.5	–2.7	–2.0	95.9	376
IVd(C)	54	4.3	–3.0	–1.8	94.8	374
IVe(C)	67	4.8	–2.6	–1.8	96.1	374
IVf(C)	79	4.1	–2.8	–1.4	96.1	367
IVg(C)	45	4.8	–3.3	–1.8	96.0	375
IVh(C)	68	5.5	–2.5	–1.9	95.0	377
Va(H)	44	17.8	9.6	–3.6	93.0	382
Vb(H)	45	17.6	9.7	–3.2	92.5	380
Vc(H)	44	17.3	9.1	–2.9	92.3	379
Vd(H)	57	19.2	11.9	–5.6	93.1	380
Ve(H)	45	14.0	6.6	–3.5	94.0	379
Vf(H)	46	10.2	3.3	–2.6	94.6	370
Vg(H)	45	15.1	7.0	–4.0	94.1	381
Vh(H)	47	14.4	6.4	–3.7	93.6	381
PMDA-II'a(H) <sup>d)</sup>	49	80.5	–	3.7	84.8	440
BTDA-II'a(H) <sup>d)</sup>	47	87.8	–	2.3	86.5	446
BPDA-II'a(H) <sup>d)</sup>	48	65.9	–	–11.7	90.6	424
DSDA-II'a(H) <sup>d)</sup>	54	60.1	–	–11.8	91.2	417
ODPA-II'a(H) <sup>d)</sup>	50	30.4	–	–7.4	81.8	387

<sup>a)</sup> The color parameters were calculated according to a CIE LAB equation.  $L^*$  is lightness; 100 means white, while 0 implies black. 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.

<sup>b)</sup> The  $\Delta b^*$  values were compared to the **IV(H)** series.



<sup>d)</sup> PMDA: pyromellitic dianhydride; BTDA: 3,3',4,4'-benzophenonetetracarboxylic dianhydride; BPDA: 3,3',4,4'-biphenyltetracarboxylic dianhydride; DSDA: 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride; ODPA: 4,4'-oxydiphthalic dianhydride.

decreasing order of  $T_g$  generally correlated with that of the chain flexibility. PEIs **IVb**, **IVe**, and **IVf** showed relatively lower  $T_g$  values (208–215 °C), similar to that of Ultem PEI, because of the presence of additional flexible 1,2-phenylene, isopropylidene, or hexafluoroisopropylidene groups. PEI **IVd** exhibited the highest  $T_g$  value of 281 °C due to the presence of rigid tetramethylbiphenyl unit in the diamine moiety. As expected, the methyl-substituted PEI **IVd** exhibited a higher  $T_g$  value than the corresponding unsubstituted PEI **IVc** due to the hindrance effect of the chain rotation in the substituted polymers. The range of  $T_g$  values for the referenced **V** series PEIs was 219–274 °C. In most of the cases, slightly lower  $T_g$

values for the **IV** series in comparison with the **V** series might be a result of reduced electronic interactions and poor packing due to the bulky pendant  $\text{CF}_3$  groups.

The thermal stability of PEIs was evaluated by dynamic TGA conducted at a heating rate of 20 °C · min<sup>–1</sup>. The temperatures of 10% weight loss ( $T_{10}$ ) in nitrogen and air atmospheres were determined from original TGA thermograms. The  $T_{10}$  values of these **IVa–h** were recorded in the range of 492–595 °C in nitrogen and 506–580 °C in air. They left more than 50% char yield at 800 °C in nitrogen. It is quite reasonable that the methyl-substituted PEI **IVd** began to decompose at lower temperatures compared with

Table 4. Tensile properties and thermal properties data of PEI films.

Polymer code <sup>a)</sup>	Strength at yield	Strength at break	Elongation to break	Initial modulus	$T_g$ <sup>b)</sup>	$T_{10}$ <sup>c)</sup>		Char yield <sup>d)</sup>
						In N <sub>2</sub>	In air	
						°C	°C	
MPa	MPa	%	GPa	°C	°C	°C	%	
<b>IVa</b>		83	5	2.0	224	584	565	54
<b>IVb</b>	81	80	6	1.9	215	582	576	51
<b>IVc</b>		93	9	1.8	229	590	580	58
<b>IVd</b>	107	104	9	2.2	281	492	506	57
<b>IVe</b>		103	9	1.7	213	549	548	60
<b>IVf</b>		95	8	1.9	208	560	548	55
<b>IVg</b>		82	6	2.0	254	587	580	64
<b>IVh</b>		75	5	2.1	237	582	576	60
<b>Va</b>		101	9	1.9	230	562	571	54
<b>Vb</b>		83	6	1.8	219	561	566	54
<b>Vc</b>		102	8	1.8	236	574	578	61
<b>Vd</b>		114	12	1.9	274	504	511	56
<b>Ve</b>		98	8	2.1	224	535	544	54
<b>Vf</b>		91	7	1.9	228	565	561	60
<b>Vg</b>		85	5	2.8	270	573	574	63
<b>Vh</b>		63	5	2.5	236	544	553	56

<sup>a)</sup> All the PEI samples were obtained by the thermal imidization method.

<sup>b)</sup> Baseline shift in the second heating DSC traces, with a heating rate of 15 °C · min<sup>-1</sup>.

<sup>c)</sup> Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C · min<sup>-1</sup>.

<sup>d)</sup> Residual weight (%) when heated to 800 °C in nitrogen.

the unsubstituted **IVc**. The TGA data indicate that these fluorinated PEIs had fairly high thermal stability regardless of the introduction of CF<sub>3</sub> groups.

Table 5. Water uptake and dielectric constants of PEIs.

Polymer <sup>a)</sup>	Film		Dielectric constant (dry) <sup>b)</sup>			
	thickness	uptake				
	μm	%	1 kHz	10 kHz	1 MHz	40 MHz
<b>IVa</b>	45	0.48	3.40	3.36	3.25	3.29
<b>IVb</b>	65	0.31	3.29	3.18	3.14	3.17
<b>IVc</b>	47	0.42	3.23	3.21	3.58	3.10
<b>IVd</b>	55	0.50	3.31	3.24	3.20	3.00
<b>IVe</b>	48	0.25	3.42	3.41	3.34	3.40
<b>IVf</b>	60	0.24	3.11	3.06	3.02	3.09
<b>IVg</b>	55	0.36	3.77	3.67	3.58	3.57
<b>IVh</b>	68	0.30	3.54	3.48	3.44	3.48
<b>Va</b>	46	0.51	3.52	3.50	3.44	3.49
<b>Vb</b>	48	0.40	3.67	3.64	3.58	3.65
<b>Vc</b>	48	0.46	3.95	3.92	3.87	3.93
<b>Vd</b>	53	0.56	3.46	3.43	3.38	3.43
<b>Ve</b>	48	0.29	3.46	3.44	3.38	3.43
<b>Vf</b>	56	0.27	3.33	3.29	3.25	3.31
<b>Vg</b>	50	0.41	3.98	3.97	3.91	3.97
<b>Vh</b>	51	0.38	3.70	3.68	3.63	3.70
<b>PMDA-ODA</b>	48	0.52	3.89	3.85	3.67	3.69

<sup>a)</sup> PEI samples obtained by the thermal imidization method.

<sup>b)</sup> Measured by DEA at room temperature (dry dielectric constant).

### Dielectric Constants and Water Uptakes

The dielectric constants and water uptakes of all PEIs are reported in Table 5. For comparison, the data of a standard polyimide film from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) are also given in Table 5. The **IV** series PEIs exhibited the dielectric constants at 10 kHz in the range of 3.06–3.67. In comparison, the fluorinated PEIs **IVa–h** showed a lower dielectric constant than the corresponding non-fluorinated **Va–h** and the standard PMDA-ODA polyimide. The decreased dielectric constants of the fluorinated PEIs could be attributed to the low polarizability of the C–F bond and the increase in free volume. PEIs **IVa–h** exhibited lower water uptakes (0.24–0.50%) than the corresponding non-fluorinated **V** series (0.27–0.56%) due to the hydrophobicity of the CF<sub>3</sub> group. Moreover, **IVf** and **Vf** exhibited the lowest water uptake and dielectric constant in each polymer series because of the higher fluorine content in the repeat unit. The low-water uptake values ensure that the polymers have stable dielectric performance.

### Conclusion

A series of novel fluorinated PEIs have been synthesized from 2,3-bis(3,4-dicarboxyphenoxy)naphthalene dianhydride and various structurally different CF<sub>3</sub>-containing aromatic bis(ether amine)s. These PEIs were characterized

by high solubility, good film-forming ability, low color, high optical transparency, excellent thermal stability, and good mechanical properties together with low dielectric constants. Therefore, this series of PEIs demonstrated a good combination of properties and may be of interest for optoelectronics applications.

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