

Organosoluble and Colorless Fluorinated Poly(ether imide)s from 1,2-Bis(3,4-dicarboxyphenoxy)benzene Dianhydride and Trifluoromethyl-Substituted Aromatic Bis(ether amine)s

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ABSTRACT: A series of novel aromatic poly(ether imide)s (PEI) containing ortho-catenated phenylene rings and pendant trifluoromethyl group have been prepared from 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride (1) with seven trifluoromethyl-substituted aromatic bis(ether amine)s (**2a-g**) via a conventional two-stage process that included ring-opening polyaddition to form the poly(amic acid)s followed by chemical imidization to the polyimides. These PEIs had inherent viscosities in the range of 0.45–1.17 dL/g that corresponded to weight-average and number-average molecular weights (by gel-permeation chromatography) of 42,000–102,000 and 28,500–67,500, respectively. All the PEIs were readily soluble in many organic solvents and could be solution-cast into transparent, flexible, and strong films. These films were essentially colorless; they had a very low yellowness index of 4.34–6.55 and an UV-vis absorption cut-off wavelength at 361–370 nm. The PEIs exhibited moderate-to-high glass-transition temperatures (T_g) in the range of 185–270 °C, softening temperatures (T_s) in the range of 184–275 °C, and 10% weight loss temperatures higher than 466 °C in nitrogen or in air. They also showed low moisture absorptions of 0.49–0.70% and low dielectric constants of 2.78–3.26 (measured at 10 kHz). © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 3092–3102, 2006

Keywords: catechol; bis(ether anhydride); fluorinated bis(ether amine); poly(ether imide); solubility; colorless polyimide

INTRODUCTION

Aromatic polyimides are one of the most important high-performance polymers that have many desirable properties, such as high thermal and thermooxidative stability, excellent dimensional stability, low dielectric constants, and outstanding chemical resistance. They have found diverse applications in the electronics industry as flexible circuitry sub-

strates, stress buffers, interlayer dielectrics, and passivation layers.^{1,2} However, the widespread applications of polyimides are often limited by processing difficulties because of their poor solubility and high processing temperature, which are caused by rigid polymer backbones and the strong inter-chain interaction. 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.^{3–18} Another obstacle that may hinder extending the applications of aromatic polyimides in optoelectronic materials is the pale yellow to amber color of their films caused

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by the intramolecular and intermolecular charge transfer complex (CTC) formation between electron-donor (diamine) and electron-acceptor (dianhydride) fragments of the polymer.^{19–21} By minimizing or eliminating CTC formation, low color or virtually colorless polyimide films with improved transparency can be obtained.^{22,23} Soluble and colorless polyimides can be obtained by using aliphatic dianhydride or diamine monomers^{24–27}; however, the high-temperature stability is somewhat sacrificed due to the incorporation of less stable aliphatic segments. Thus, polyimides derived from aliphatic monomers are most used for applications that have less-stringent thermal requirements.

Poly(ether-imide)s (PEIs) have received great attention as they may provide good processability owing to the presence of flexible ether links. 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 diamines.^{28–30} An important example is Ultem 1000 resin developed and commercialized by General Electric Co.,³¹ which exhibits reasonable thermal stability and good mechanical properties together with good moldability. Eastmond and coworkers^{32–34} have demonstrated that PEIs based on catechol bis(ether anhydride) exhibited a good combination of properties and processability, either by solution or melt processing. Recently, considerable attention has been devoted to the fluorinated aromatic polyimides, especially trifluoromethyl (CF₃)-containing polyimides.^{35–49} It was found that the incorporation of bulky CF₃ 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 thermooxidative stability and low moisture absorption.

As part of our continuing 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 catechol-derived bis(ether anhydride), 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride, with various structurally different CF₃-substituted aromatic bis(ether amine)s. The obtained PEIs should have diminished intra- and intermolecular CTC formation not only because of the decrease in electron-accepting property of the dianhydride moieties

caused by the electron-donating ether groups but also the decrease in electron-donating property of diamine moieties caused by the electron-withdrawing –CF₃ groups. In addition to the bulky, packing-disruptive –CF₃ groups, the formation of bent structures due to the presence of ortho links will help prevent the extended close chain packing, and consequently, the charge transfer 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

Materials

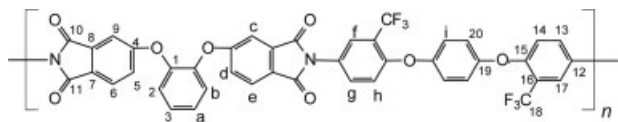
According to a reported procedure,³² 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride (m.p. = 187–188 °C) was synthesized starting from the nitro displacement of 4-nitrophthalonitrile with catechol in the presence of potassium carbonate, followed by the alkaline hydrolysis of the intermediate bis(ether dinitrile) and the cyclodehydration of the resulting bis(ether diacid). As reported previously, the trifluoromethyl-substituted bis(ether-amine)s that included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (**2a**) (m.p. = 132–133 °C),³⁶ 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene (**2b**) (m.p. = 116–117 °C),⁵⁰ 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**2c**) (m.p. = 155–156 °C),³⁷ 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (**2d**) (m.p. = 256–257 °C),⁵¹ 2,2-[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**2e**) (m.p. = 131–132 °C),⁵² 2,2-[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane (**2f**) (m.p. = 65–66 °C),⁵³ and 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene (**2g**) (m.p. = 239–240 °C)⁵⁴ were prepared by the chloro displacement of 2-chloro-5-nitrobenzotrifluoride with the potassium salts of corresponding aromatic diols and subsequent reduction of the intermediate dinitro compounds, using hydrazine as the reducing agent and palladium as the catalyst. *N,N*-Dimethylacetamide (DMAc) (Fluka) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Synthesis of PEIs

Polyimides syntheses are exemplified by the specific synthesis of **3a** from **1** and **2a**; other poly-

imides were prepared similarly. To a solution of 0.428 g (1 mmol) of the CF₃-substituted bis(ether amine) **2a** in 7.8 mL of CaH₂-dried DMAc in a 50-mL flask, 0.402 g (1 mmol) of the catechol-derived dianhydride **1** was added in one portion. Thus, the solid content of the solution is approximately 10 wt %. The mixture was stirred at room temperature overnight (for about 12 h) to afford a highly viscous poly(amic acid) solution. Then, 2 mL of acetic anhydride and 1 mL of pyridine were added to the poly(amic acid) solution. The mixture was heated at 80 °C for 1 h to ensure a complete imidization and then poured into a glass culture dish, which was placed in a 100 °C oven for 1 h to evaporate the solvent and to form a thin solid film. The polyimide film was sequentially heated to 200 °C and held at that temperature for 2 h to remove the residual solvent. The resulting polyimide film was flexible and creasable with an inherent viscosity of 1.17 dL/g in DMAc. ELEM. ANAL. Calcd. for (C₄₂H₂₀F₆N₂O₈)_n: C, 63.47%; H, 2.54%; N, 3.53%; Found: 63.01%; H, 2.32%; N, 3.57%.

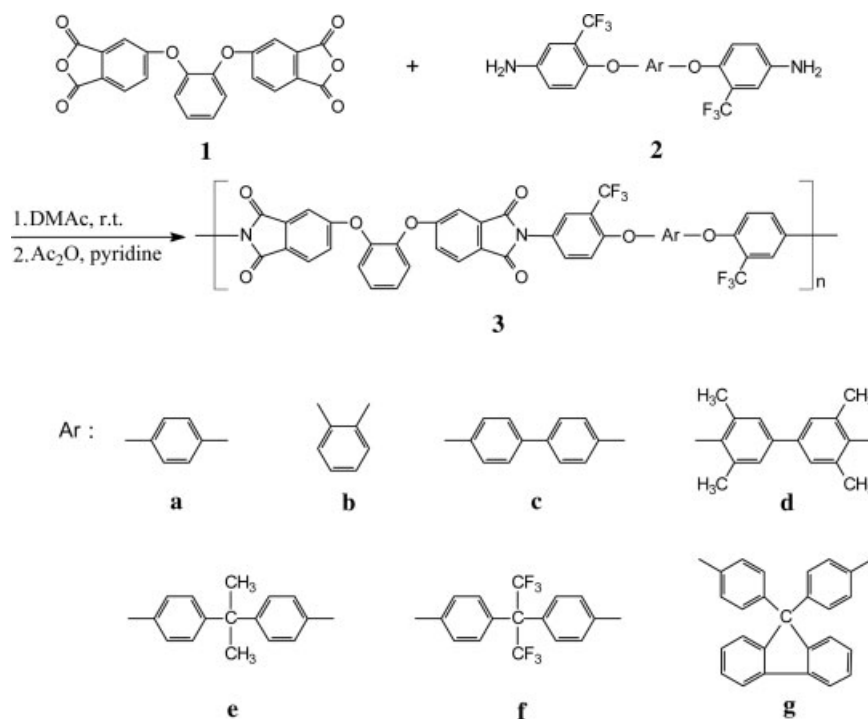
IR (film): 1778 cm⁻¹ (imide C=O asymmetric stretching), 1724 cm⁻¹ (imide C=O symmetric stretching), 1594–1486 cm⁻¹ (aromatic skeletal vibration), 1379 cm⁻¹ (C–N stretching), 1242 cm⁻¹ (C–O stretching). ¹H NMR (CDCl₃, δ, ppm): 7.84 (d, *J* = 8.3 Hz, 2H, H_e), 7.75 (d, *J* = 2.1 Hz, 2H, H_f), 7.52 (dd, *J* = 8.2, 2.1 Hz, 2H, H_g), 7.42 (dd, *J* = 6.0, 3.6 Hz, 2H, H_a), 7.33 (dd, *J* = 6.0, 3.6 Hz, 2H, H_b), 7.27 (d, *J* = 2.2 Hz, 2H, H_c), 7.18 (dd, *J* = 8.2, 2.1 Hz, 2H, H_d), 7.15 (s, 4H, H_i), 7.03 (d, *J* = 8.9 Hz, 2H, H_h). ¹³C NMR (CDCl₃, δ, ppm): 166.2 (C¹⁰), 166.1 (C¹¹), 162.9 (C⁴), 155.1 (C¹⁵), 152.3 (C¹⁹), 145.7 (C¹), 133.9 (C¹²), 131.2 (C¹³), 127.6 (C³), 126.1 (C⁸), 125.8 (C⁶), 125.6 (C¹⁷), 125.1 (C⁷), 123.6 (C²), 122.7 (quartet, ¹*J*_{C–F} = 272 Hz, C¹⁸), 122.1 (C⁵), 121.6 (C²⁰), 121.4 (quartet, ²*J*_{C–F} = 31 Hz, C¹⁶), 118.6 (C¹⁴), 111.1 (C⁹).



Measurements

Elemental analyses were run in a PerkinElmer model 2400 C, H, N analyzer. Infrared spectra were recorded on a PerkinElmer spectrum GX FTIR system. ¹H and ¹³C NMR spectra were measured on a JEOL EX 400 spectrometer with CDCl₃ as the solvent and tetramethylsilane as

the internal reference. The inherent viscosities of the polymers were measured with an Ubbelohde viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD 6000 X-ray diffractometer (40 kV, 20 mA), using graphite-monochromatized Cu-K_α radiation. Gel-permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μm Styragel HR-2 and HR-4 columns (7.8 mm I.D. × 300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent. The data were calibrated with narrow polystyrene standards. An Instron universal tester model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the polyimide film samples. The test specimens gauge length was 2 cm, and the crosshead speed for film testing was 5 mm/min. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.05 mm thick), and an average of three to five replicas was used. The color intensity of the polymers was evaluated by a Gretag-Macbeth COLOR-EYE 3100 colorimeter. Measurements were performed with films (50 ± 5 μm thick) with an observational angle 10° and a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. UV-vis spectra of the polymer films were recorded on a Shimadzu UV-visible spectrophotometer UV-1601. Dielectric property of the polymer films was tested by the parallel-plate capacitor method using a HP-4194A Impedance/Gain Phase Analyzer. Gold electrodes were vacuum deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate 30 cm³/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen (20 cm³/min). Glass transition temperatures (*T*_g) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400 °C at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was performed on a PerkinElmer TMA 7 instrument with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. The TMA experiments were conducted from 50 to 300 °C at a scan rate of



Scheme 1. Synthesis of the PEIs.

10 °C/min, and softening temperatures (T_g) of the polymer films were taken as the onset temperature of probe displacement on the TMA traces. The equilibrium water 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 days.

RESULTS AND DISCUSSION

Polymer Synthesis

The PEIs **3a–g** were prepared from the catechol-derived bis(ether anhydride) **1** with various CF_3 -containing bis(ether amine)s **2a–g** by a conventional two-step synthetic method as shown in Scheme 1. In the first stage, the viscosities of the reaction mixtures became high as poly(amic acid)s were formed, indicating the formation of high-molecular-weight polymer. In spite of the presence of electron-withdrawing $-\text{CF}_3$ substituents, the maintained reactivity of these bis(ether amine)s is most likely based on the meta-substitution to the amino group. 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 0.45–1.17 dL/g, as measured in DMAc at 30 °C (Table 1). The weight-average molecular weights (M_w 's) and number-average molecular weights (M_n 's) of these polymers were recorded in the range of 42,000–102,000 and 27,500–67,500, respectively, relative to polystyrene standards.

Table 1. Inherent Viscosity and Average Molecular Weights of PEIs

Polymer Code	$\eta_{\text{inh}}^{\text{a}}$ (dL/g)	M_w^{b}	M_n^{b}	M_w/M_n
3a	1.17	102,000	67,500	1.51
3b	0.47	42,000	27,500	1.53
3c	0.93	70,500	47,000	1.50
3d	0.45	47,500	28,500	1.67
3e	0.71	65,000	43,500	1.49
3f	0.70	60,500	38,500	1.57
3g	1.01	81,000	55,000	1.47

^a Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

^b Measured by GPC in THF, relative to polystyrene standards.

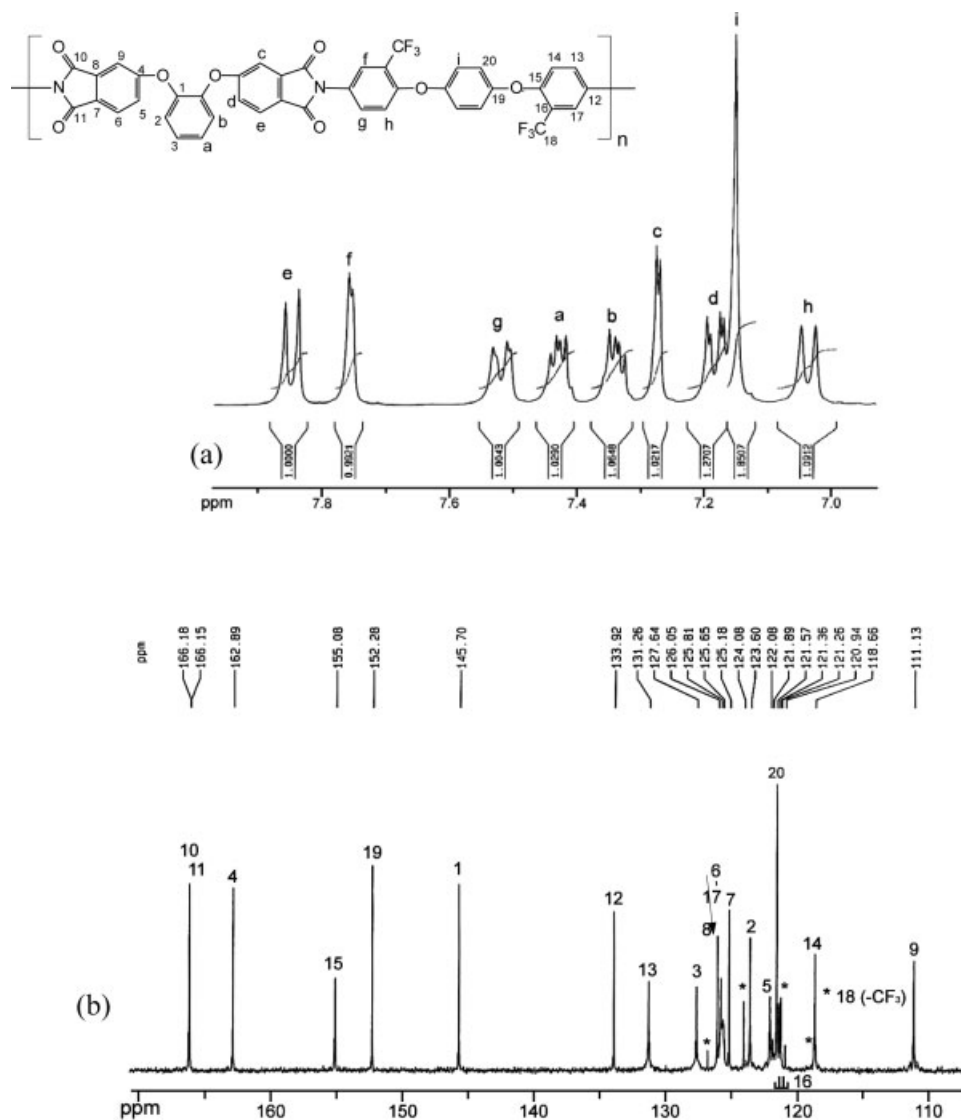


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of PEI 3a in CDCl_3 .

The complete imidization of polymers was confirmed with IR and NMR spectra. The PEIs exhibited characteristic imide group absorptions around 1780 and 1725 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretch), 1380 (C—N stretch), and 1100 and 750 (imide ring deformation), together with some strong absorption bands in the region of 1100 – 1300 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 poly(amic acid) precursor into polyimide. The typical ^1H NMR and ^{13}C NMR spectra of a representative PEI 3a are illustrated in Figure 1. Assignments of each carbon and proton assisted by 2D-

NMR spectra are also given in the figures, and these spectra are in good agreement with the proposed polymer structure. In addition to IR and NMR spectra, the elemental analysis results of PEIs also generally agreed with the calculated values for the proposed structures.

Polymer Solubility and Film Property

The solubility of these fluorinated PEIs was tested qualitatively in various organic solvents, and the results are reported in Table 2. All the PEIs exhibited excellent solubility; they were easily dissolved in strong dipolar solvents, such as NMP, DMAc, DMF, and DMSO, phenol sol-

Table 2. Solubility Behavior of PEIs^a

Solvent	PEI						
	3a	3b	3c	3d	3e	3f	3g
NMP	+	+	+	+	+	+	+
DMAc	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+
DMSO	+	+	+	+h	+	+	+
<i>m</i> -Cresol	+	+	+	+	+	+	+
2-Chlorophenol	+	+	+	+	+	+	+
THF	+	+	+	+	+	+	+
1,4-Dioxane	+	+	+	+	+	+	+
Dichloromethane	+	+	+	+	+	+	+
Acetone	-	+	-	-	-	+	-

NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfide; THF, tetrahydrofuran. +, soluble at room temperature; +h, soluble on heating at 100 °C or boiling temperature; -, insoluble even on heating.

^a The solubility was determined by using 10 mg sample in 1 mL of stirred solvent.

vents like *m*-cresol and 2-chlorophenol, and common organic solvents, such as THF, 1,4-dioxane, and dichloromethane. Thus, all these PEIs can be readily processed from solution.

All the PEI films prepared were tough and creasable and exhibited low color. Thin film tensile properties are presented in Table 3. The films exhibited ultimate tensile strengths of 72–108 MPa, elongations to break of 7–121%, and initial moduli of 1.69–2.04 GPa. It is interesting to note that PEI **3c** exhibited 121% elongation to break, indicative of a highly tough material. The superior extensibility of **3c** corresponds to that reported for a structurally similar PEI prepared from dianhydride **1** and 4,4'-bis(4-amino-

Table 3. Thin Film Tensile Properties of the PEI Films

Polyimide Code	Tensile Strength (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
3a	89	26	1.96
3b	80	7	1.88
3c	99	121	1.87
3d	72	7	1.69
3e	83	9	1.80
3f	98	10	2.04
3g	108	11	1.91

phenoxy)biphenyl (BAPB) reported previously by us⁵⁵ and Eastmond's group.³⁴ It has been explained by that the BAPB unit adopts a conformation that causes the polymer chain to coil strongly, though the disposition of the aromatic rings adjacent to the ether linkages, but that under stress these conformations are modified to give a more linear in-chain structure; the effective uncoiling of the long BAPB unit about its ether linkages could provide a mechanism for considerable chain extension.³⁴ The morphology of these PEI films was characterized by WAXD studies, and all the PEIs revealed amorphous patterns. We can interpret the result by the presence of ortho-linked phenylenedioxy units and the bulky pendent CF₃ groups, which resulted in poor chain packing and decreased interchain interactions. The high solubility of these PEIs is also affected by the amorphous structure.

Color Intensity and Optical Transparency

The coloration of the polyimide films were elucidated from the yellowness or redness indices observed by a GretagMacbeth color-eye colorimeter. The results shown in Table 4 indicate that these fluorinated PEIs **3a–g** showed a very low *b** value (a yellowness index) of 4.34–6.55. Moreover, thin films were measured for optical transparency using UV–vis spectroscopy. Figure 2 depicts the UV–vis spectra of the polyimide films,

Table 4. Color Coordinates and Cut-off Wavelength (λ_0) from UV–Vis Spectra for the PEI Films^a

Polymer	Film Thickness (μm)	<i>a</i> *	<i>b</i> *	<i>L</i> *	λ_0 (nm)
Paper		-0.39	0.99	96.21	
3a	48	-1.84	5.59	95.62	366
3b	51	-1.75	6.03	95.30	370
3c	54	-1.66	4.68	96.02	367
3d	48	-2.20	6.53	95.86	365
3e	55	-1.46	4.38	95.92	366
3f	47	-1.46	6.55	96.21	364
3g	51	-1.62	4.34	96.20	361

^a The color parameters were calculated according to a CIE LAB equation, using paper as a standard. *L** is lightness; 100 means white, while 0 implies black. A positive *a** means red color, while a negative *a** indicated green color. A positive *b** means yellow color, while a negative *b** implies blue color.

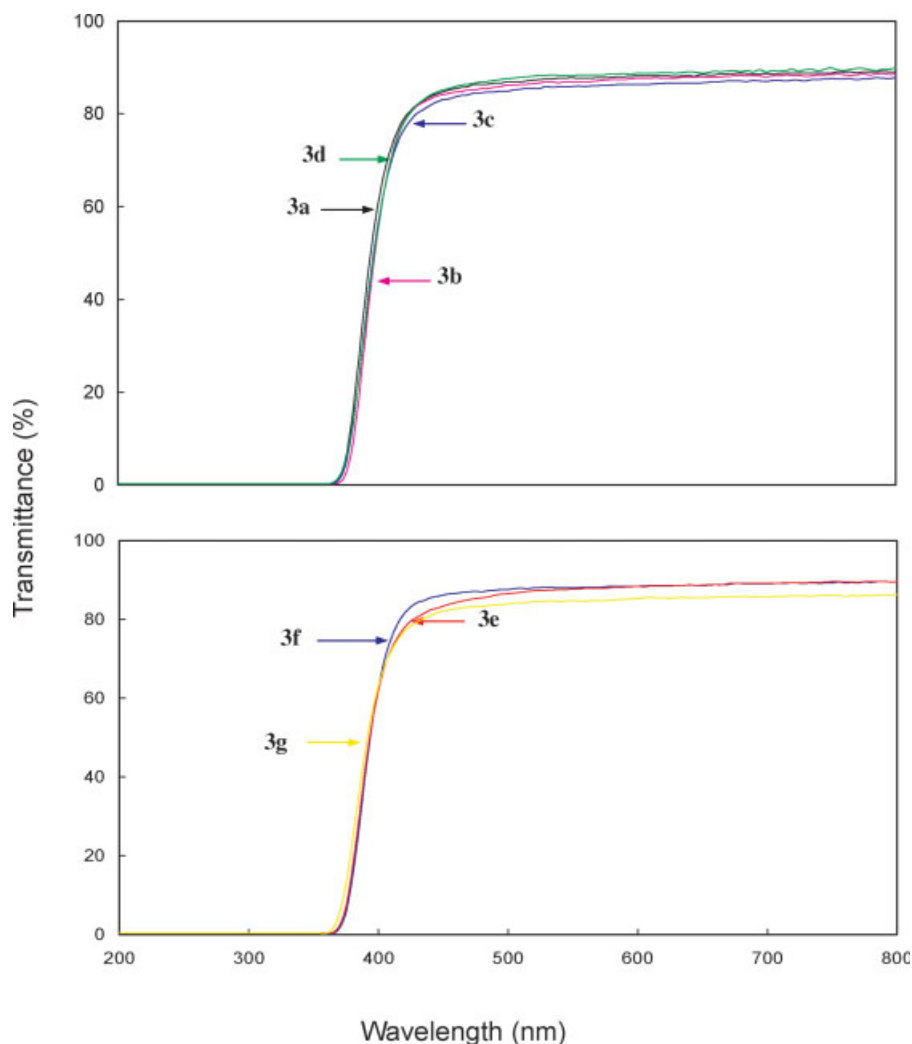


Figure 2. Transmission UV-vis absorption spectra of the PEI films (47–55 μm thick).

and the cutoff wavelengths (absorption edge, λ_0) from the UV-vis spectra are listed in Table 4. In accordance with the results obtained from colorimeter, all the fluorinated PEIs revealed a low λ_0 from 361 to 370 nm. The polymer films were colorless and transparent in the visible region, and the light transmittance was over 80–85%. The low color of these PEIs can be explained from the decreased intra- and intermolecular electronic interactions. The bulky and electron-withdrawing CF_3 group in diamines **2a–g** was effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating character of diamine moieties). The decrease in intermolecular CTC formation is understandable also from the signifi-

cant solubility of the PEIs prepared from the CF_3 -substituted bis(ether amine)s **2a–g**.

Thermal Properties

DSC, TMA, and TGA were used to evaluate the thermal properties of the PEIs. The results are reported in Table 5. DSC experiments were conducted at a heating rate of 20 $^\circ\text{C}/\text{min}$ in nitrogen. Rapid cooling from 400 $^\circ\text{C}$ to room temperature produced predominantly amorphous samples, so the T_g s of all the polymers could be easily read in the subsequent heating traces. These PEIs exhibited T_g values ranging from 191 to 270 $^\circ\text{C}$. In general, the T_g s are considered to be affected by both molecular packing and chain rigidity. Compared to conventional aro-

Table 5. Thermal Behavior Data of the PEIs

Polymer	T_g^a (°C)	T_s^b (°C)	T_d^c at 5 wt% Loss (°C)		T_d at 10 Wt % Loss (°C)		Char Yield ^d (%)
			In Air	In N ₂	In Air	In N ₂	
3a	197	196	500	538	526	559	56
3b	185	186	531	566	538	572	55
3c	208	211	536	572	580	610	61
3d	270	270	463	500	466	494	58
3e	192	184	513	548	526	546	58
3f	191	190	533	557	550	570	51
3g	241	245	545	578	559	589	61

^a Midpoint temperature of baseline shift on the second DSC heating trace (rate 20 °C/min) of the sample after quenching from 400 °C.

^b Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min. The film samples were heated at 300 °C for 30 min prior to the TMA experiments.

^c Decomposition temperatures recorded by TGA at a heating rate of 20 °C/min.

^d Residual weight percentage at 800 °C in nitrogen.

matic polyimides, most of the PEIs **3a–g** revealed a relatively low T_g value due to the flexible ether linkages and the less linear ortho-linked phenylene units. In comparison, the PEIs **3b**, **3e**, and **3f** showed lower T_g values than the other PEIs due to their less rigid backbones. PEI **3g** possessed a high T_g value of 241 °C because of the effect of rigid fluorene segment. PEI **3d** exhibited the highest T_g value (270 °C), which can be attributable to the increase of chain stiffness caused by the tetramethyl substi-

tution in the diamine moiety. The softening temperatures (T_s) (may be referred as apparent T_g) of the PEI films were determined by the TMA method using a loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of PEI **3d** is illustrated in Figure 3. As can be seen from Table 5, in most cases the T_s values obtained by TMA are comparable to the T_g values measured by the DSC experiments. The trend of T_s varia-

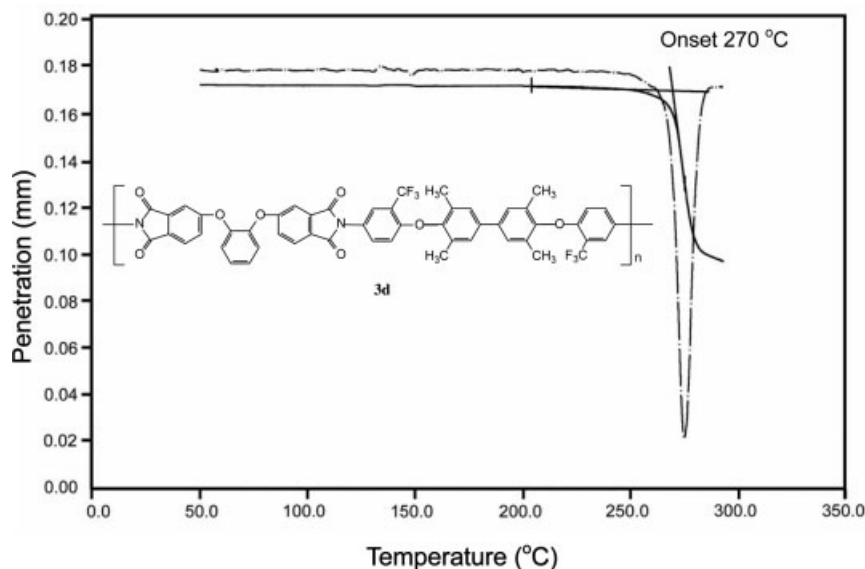


Figure 3. Typical TMA thermogram for PEI **3d** (heating rate = 10 °C/min; applied force = 10 mN)

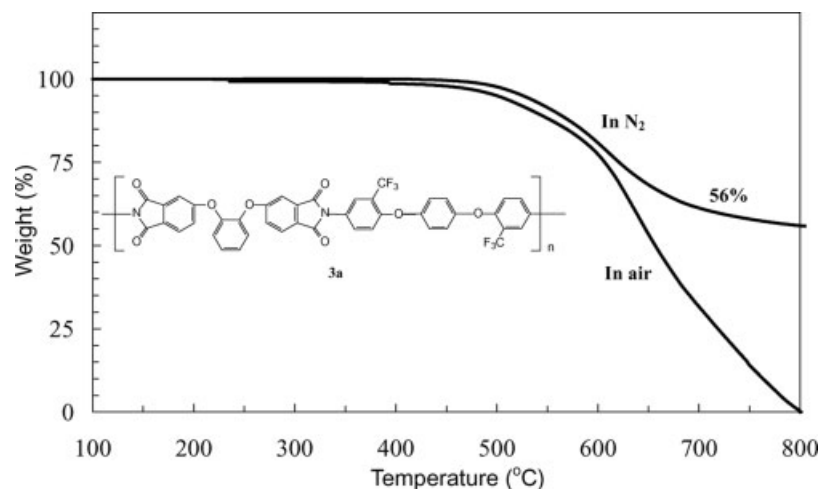


Figure 4. TGA thermograms of PEI **3a** at a heating rate of 20 °C/min.

tion with the chain stiffness is similar to that of T_g observed in the DSC measurements.

The thermal stability of the PEIs was evaluated by TGA measurements in both air and nitrogen atmospheres. Typical TGA curves of PEI **3a** are reproduced in Figure 4. The decomposition temperatures (T_d) at 5 and 10 wt % loss in nitrogen and in air atmospheres were determined from the original TGA thermograms and are given in Table 5. The T_d s at 10 wt % loss of these PEIs in nitrogen and air stayed in the range of 494–610 and 466–580 °C, respectively. They left more than 55% char yield at 800 °C in nitrogen. It is quite reasonable that the methyl-containing PEI **3d** began to decompose at lower temperatures compared to the corresponding methyl-free **3c** and the other PEIs. In comparison with the semiaromatic or nonaromatic polyimides reported in literatures,^{24,25} the prepared PEIs in this work revealed a higher decomposition temperature due to the absence of aliphatic

segments, but a lower T_g value because of the incorporation of flexible ether links in the polymer chain.

Dielectric Constants and Water Absorption

The measurements of the dielectric constants were performed between gold layers: the PEI film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the polymer film. This procedure excludes any contact problems. As shown in Table 6, PEIs **3a–g** revealed low dielectric constants (2.78–3.32 at 10 kHz). The results suggested that the CF_3 groups could improve the dielectric performance because of less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine results in very low polarizability of the C–F bonds, thus decreasing the dielectric constant. PEI **3f** exhibited the lowest dielectric constant of 2.78 at 10 kHz, possibly due to the

Table 6. Water Absorption and Dielectric Constants of PEIs

Polymer Code	Film Thickness (μm)	Fluorine Content (%)	Water Absorption (%)	Dielectric Constant (Dry)	
				10 kHz	40 MHz
3a	48	14.4	0.66	3.23	3.29
3b	51	14.4	0.57	3.32	3.37
3c	54	13.1	0.52	3.04	3.08
3d	48	12.3	0.49	3.31	3.40
3e	55	12.5	0.63	3.26	3.34
3f	47	22.3	0.50	2.78	2.82
3g	51	11.0	0.70	2.95	3.07

further increased free volume caused by the higher free volume and hydrophobicity. The reason also could be that the hexafluoroisopropylidene moiety in polymer **3f** can separate the chromophoric groups and reduce electronic interaction. Table 6 also presents the water absorption of the PEIs, which ranges from 0.49 to 0.70%. The low water uptake values ensure that the polymers have stable dielectric performance.

CONCLUSIONS

A series of novel fluorinated PEIs have been synthesized from 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride and various structurally different CF₃-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 interest for optoelectronics applications.

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