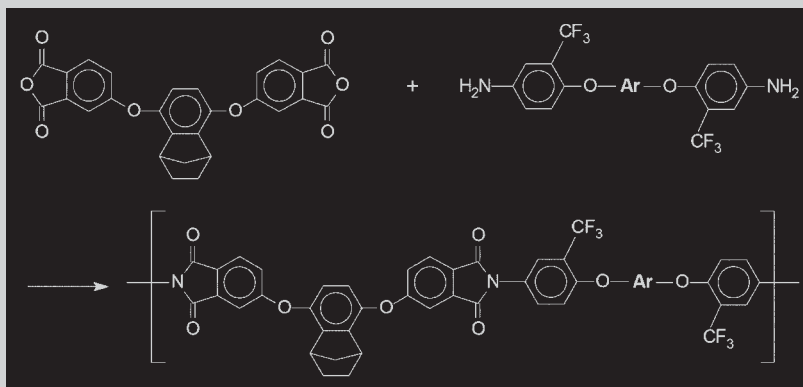


Summary: A series of organosoluble and colorless fluorinated poly(ether imide)s (**IV_{a-g}**) were prepared from 3,6-bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride (**I**) and various trifluoromethyl (CF₃)-substituted aromatic bis(ether amine)s **II_{a-g}** by a standard two-step process with thermal and chemical imidization of poly(amic acid) precursors. These poly(ether imide)s had inherent viscosities of 1.02–1.28 dL · g⁻¹ and showed excellent solubility in many organic solvents. They could be solution-cast into transparent, flexible, and tough films with good mechanical properties. These films were virtually colorless, with an ultraviolet-visible absorption edge of 372–381 nm and a very

low *b** value (a yellowness index) of 10.8 to 18.2. The glass-transition temperatures (*T_g*) and softening temperatures (*T_s*) were recorded between 216–292 °C and 209–285 °C, respectively. The decomposition temperature for 10% weight loss all occurred above 472 °C in nitrogen and 481 °C in air, and the char yields at 800 °C in nitrogen were more than 51%. They also showed low dielectric constants of 2.84–3.58 (1 MHz) and moisture absorptions in the range of 0.05–0.19%. In comparison with analogous **V** series poly(ether imide)s without the CF₃ substituents, the **IV** series ones showed better solubility, lower color intensity, and lower dielectric constants.



A novel series of fluorinated poly(ether imide)s.

Soluble and Colorless Poly(ether-imide)s Based on a Benzonorbornane Bis(ether anhydride) and Trifluoromethyl-Substituted Aromatic Bis(ether-amine)s

Dedicated to the memory of Prof. *Chin-Ping Yang*, who cherished research and publications as his lifetime joys

Ya-Yin Chen, *Chin-Ping Yang*^a, *Sheng-Huei Hsiao*^{*}

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan
Fax: +886 2 2586 1939; E-mail: shhsiao@ttu.edu.tw

Received: June 9, 2006; Revised: August 8, 2006; Accepted: August 15, 2006; DOI: 10.1002/macp.200600287

Keywords: benzonorbornane bis(ether anhydride); colorless polyimides; fluorinated poly(ether imide)s; low dielectric constants; soluble polyimides; trifluoromethyl-substituted bis(ether amine)s

^a Prof. Chin-Ping Yang passed away on Aug. 17, 2005, at the age of 75.

Introduction

Aromatic polyimides are widely used in the aerospace and microelectronics industries because of their unique combined physical and chemical properties.^[1–4] Regardless of the excellent combined properties, they are usually difficult to process in their imidized forms because of high softening temperature and limited solubility, which are caused by the rigid polymer backbones and the strong interchain interactions. To overcome these problems, many attempts have been made to improve the processability (melt processing properties and/or solubility in organic solvents) of

polyimides while maintaining their useful properties.^[5–7] Another obstacle that may hinder extending the applications of aromatic polyimides in optical and/or optoelectronic materials is the pale yellow to amber color of their films. The color in polyimide films may originate from chromophoric units or impurities within the starting material. However, studies have shown that charge-transfer complex (CTC) formation is the primary cause of color arising in polyimides.^[8–10] Bulky side groups and meta-substitution of the aromatic diamine moiety have been shown to reduce conjugation and electronic interactions between polyimide chains due to CTC formation.^[11–13] By

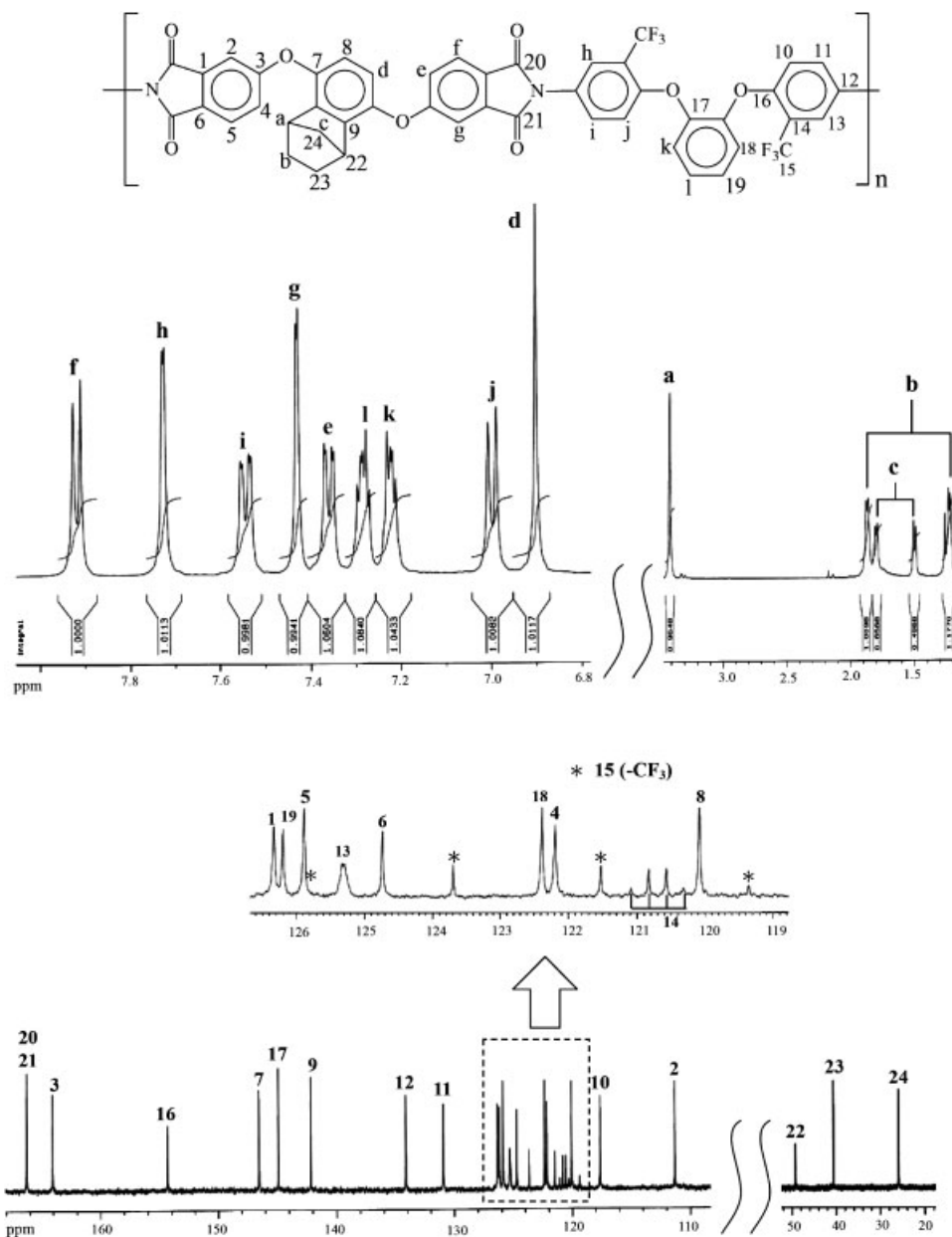
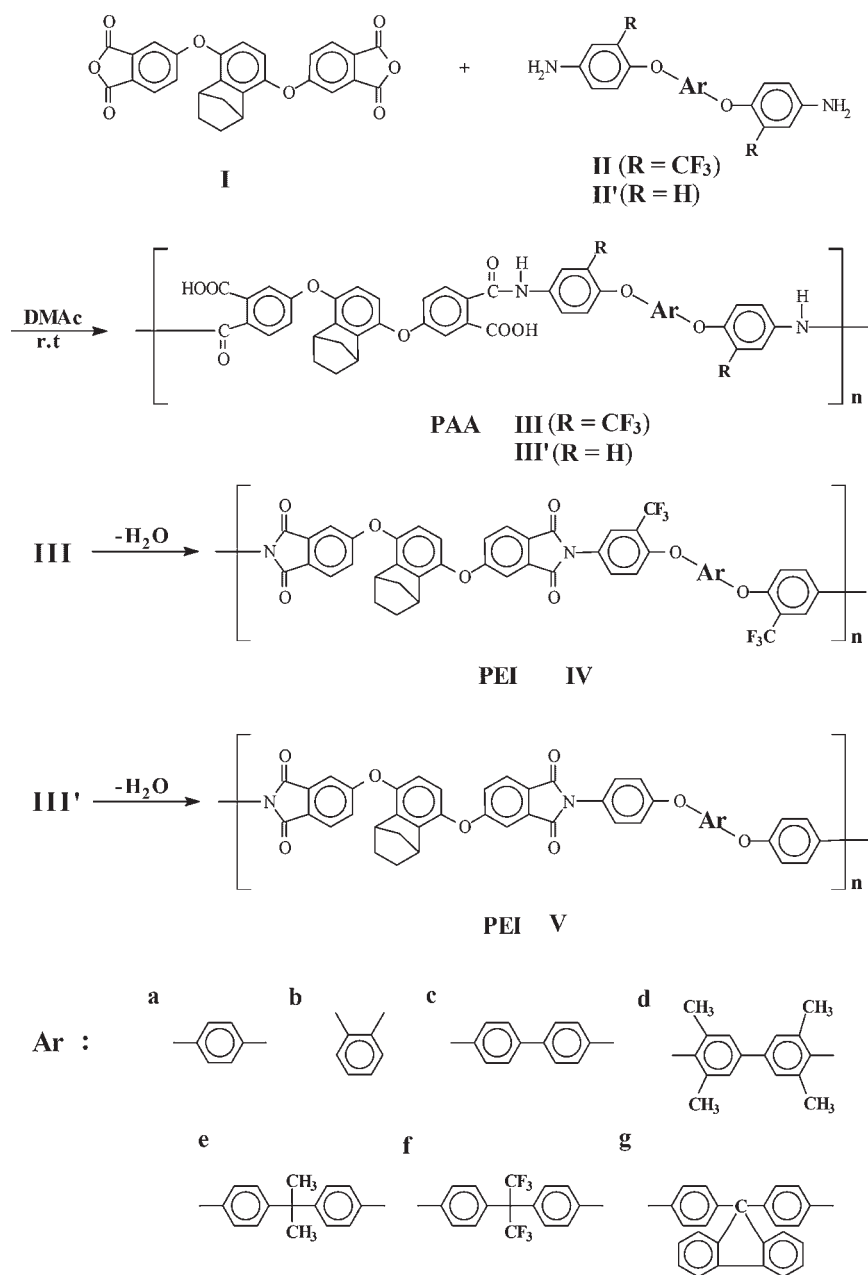


Figure 1. ¹H and ¹³C NMR spectra of PEI IV_b in CDCl₃.

minimizing or eliminating CTC formation, low color or colorless polyimides films with improved optical transparency can be obtained. Soluble and colorless polyimides were prepared by using aliphatic dianhydride or diamine monomers;^[14–17] however, the long term thermal stability was somewhat sacrificed due to the incorporation of less-stable aliphatic segments.

Recently, considerable attention has been paid to the fluorinated aromatic polyimides, especially trifluoromethyl (CF₃)-containing polyimides.^[18–28] It has been proved that the introduction of bulky CF₃ pendent groups into the

polyimide backbones resulted in great benefits for improving polymer solubility as well as optical transparency and dielectric performance, which attributed to the low polarizability of the C–F bond and the increase in free volume. Another effective approach to enhance solubility and/or melt processability of polyimides is to incorporate flexible linkages along the backbones, either in the diamine or the dianhydride component. The development of nucleophilic displacement reactions, and nitro displacement reactions in particular, has led to the development of a large class of poly(ether imide)s (PEIs) from bis(ether anhydride)s and



Scheme 1. Synthesis of poly(ether imide)s.

various diamines.^[29–34] The Ultem 1000 poly(ether imide) developed by General Electric Co. has achieved great commercial success, which exhibits reasonable thermal stability and good mechanical properties together with good moldability.^[35]

As part of our continuing efforts to develop colorless and soluble polyimides with high thermal stability and low dielectric constants, this work deals with the synthesis and characterization of a series of novel fluorinated PEIs from 3,6-bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride (**I**) and various CF₃-substituted aromatic bis(ether amine)s. In addition to the steric effect contributed to the bulky CF₃ groups and benzonorbornane segments, the prepared PEIs should exhibit reduced intra- and intermolecular CTC formation because of the decrease in both of the electron-donating ability of the diamine moiety (caused by the electron-withdrawing CF₃ pendants) and the electron-affinity of the dianhydride moiety (caused by the electron-donating ether group). Thus, the polymers would be expected to exhibit low color intensity, high optical transparency in the visible region, good solubility in organic solvents, and low dielectric constants.

Experimental Part

Materials

The bis(ether anhydride), 3,6-bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride (**I**) (mp = 215–216 °C), was prepared in three steps starting from the nitro displacement reaction of the dipotassium phenolate of 3,6-dihydroxybenzonorbornane with 4-nitrophthalonitrile, followed by alkaline

hydrolysis of the intermediate bis(ether dinitrile) and subsequent cyclodehydration of the resulting tetraacid. The synthetic details and characterization data have been reported previously.^[36] The CF₃-substituted bis(ether amine)s were prepared from the 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^[37] (**II_a**) (mp = 132–133 °C), 1,2-bis(4-amino-2-trifluoromethylphenoxy)benzene^[38] (**II_b**) (mp = 116–117 °C), 4,4'-bis(4-amino-2-trifluoromethylphenoxy)biphenyl^[39] (**II_c**) (mp = 155–156 °C), 4,4-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl^[40] (**II_d**) (mp = 256–257 °C), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane^[41] (**II_e**) (mp = 131–132 °C), 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]hexafluoropropane^[42] (**II_f**) (mp = 65–66 °C), 9,9-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]fluorene^[43] (**II_g**) (mp = 239–240 °C). *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride (CaH₂) and stored over 4 Å molecular sieves.

Synthesis of Poly(ether imide)s

The general polymerization procedure is illustrated by the following example. To a solution of bis(ether amine) **II_b** (0.214 g; 0.5 mmol) in CaH₂-dried DMAc (3.5 mL) in a 20 mL round-bottomed flask, bis(ether anhydride) **I** (0.234 g, 0.5 mmol) was added in one portion. The mixture was stirred at room temperature for 10 h to afford a highly 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

Table 1. Inherent viscosity, elemental analysis and GPC data of the PEIs.

Polymer code ^{a)}	η_{inh}^b dL · g ⁻¹	Formula (Formula weight)	Elemental analysis			GPC data ^{c)}			
			%			$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	PDI ^{d)}	
			C	H	N				
IV_a(H)	1.19	(C ₄₇ H ₂₆ N ₂ O ₈ F ₆) _n (860.72) _n	Calcd	65.59	3.04	3.25	2.61	5.03	1.92
			Found	65.64	3.10	2.29			
IV_b(H)	1.23	(C ₄₇ H ₂₆ N ₂ O ₈ F ₆) _n (860.72) _n	Calcd	65.59	3.04	3.25	2.95	5.46	1.85
			Found	65.02	3.03	3.60			
IV_c(C)	1.02	(C ₅₃ H ₃₀ N ₂ O ₈ F ₆) _n (936.82) _n	Calcd	67.95	3.23	2.99	1.53	2.96	1.94
			Found	68.00	3.21	3.05			
IV_d(H)	1.08	(C ₅₇ H ₃₈ N ₂ O ₈ F ₆) _n (992.93) _n	Calcd	68.95	3.86	2.82	1.63	3.82	2.34
			Found	68.54	3.86	3.06			
IV_e(H)	1.28	(C ₅₆ H ₃₄ N ₂ O ₈ F ₆) _n (978.90) _n	Calcd	68.71	3.71	2.86	3.89	6.07	1.56
			Found	67.99	3.59	2.92			
IV_f(H)	1.27	(C ₅₆ H ₃₀ N ₂ O ₈ F ₁₂) _n (1086.84) _n	Calcd	61.89	2.78	2.58	3.69	6.13	1.66
			Found	61.62	2.73	2.57			
IV_g(H)	1.16	(C ₆₆ H ₃₈ N ₂ O ₈ F ₁₂) _n (1101.03) _n	Calcd	72.00	3.48	2.54	2.19	4.49	2.04
			Found	71.38	3.47	2.79			

^{a)} (H): Samples prepared by the thermal imidization method; (C): by the chemical imidization method.

^{b)} Measured at a polymer concentration of 0.5 g · dL⁻¹ in DMAc at 30 °C.

^{c)} Relative to polystyrene standards, using THF as the eluent.

^{d)} Polydispersity index (PDI) = \bar{M}_w/\bar{M}_n .

PAA solution was poured into a glass culture dish of about 7 cm in diameter, which was placed in an 80 °C oven for 1 h to remove the solvent. The semidried PAA film was further dried and imidized by sequential heating from 120 °C to 250 °C at a heating rate of 3 °C · min⁻¹ and further heated at 250 °C for 1 h. The polyimide film was stripped from the glass substrate by immersion in water. Inherent viscosity (η_{inh}) in DMAc of PEI **IV_b** was 1.23 dL · g⁻¹, as measured at a concentration 0.5 g · dL⁻¹ at 30 °C. The 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 bring about a complete imidization and then poured into a glass culture dish, which was placed in an 80 °C oven for 1 h to evaporate the solvent and form a thin solid film. The polyimide film was then heated to 200 °C and held at that temperature for 2 h to remove the residual solvent.

Elemental analysis: (C₄₇H₂₆F₆N₂O₈)_n (860.72)_n Calcd. C 65.59, H 3.04, N 3.25; Found 65.02, H 3.03, N 3.60.

IR (film): 1779 (asymmetric C=O stretch), 1729 (symmetric C=O stretch), 1496–1617 (aromatic C=C stretch),

1379 (C–N stretch), 1083, 746 (imide ring deformation), 1100–1300 cm⁻¹ (C–O and C–F stretching).

¹H NMR (500 MHz, CDCl₃): δ = 7.92 (2H, H_f), 7.72 (2H, H_h), 7.54 (2H, H_i), 7.43 (2H, H_g), 7.36 (2H, H_e), 7.28 (2H, H_j), 7.22 (2H, H_k), 7.00 (2H, H_l), 6.90 (2H, H_d), 3.41 (2H, H_a), 1.87, 1.24 (2H, H_b), 1.80, 1.50 (2H, H_c).

¹³C NMR (125 MHz, CDCl₃): δ = 166.31 (C²¹), 166.28 (C²⁰), 164.07 (C³), 154.37 (C¹⁶), 146.52 (C⁷), 144.89 (C¹⁷), 142.16 (C⁹), 134.16 (C¹²), 130.97 (C¹¹), 126.34 (C¹), 126.21 (C¹⁹), 125.89 (C⁵), 125.33 (C¹³), 124.74 (C⁶), 122.61 (quartet, ¹J_{C-F} = 272 Hz, C¹⁵), 122.39 (C¹⁸), 122.20 (C⁴), 120.72 (quartet, ²J_{C-F} = 31 Hz, C¹⁴), 120.09 (C⁸), 117.64 (C¹⁰), 111.31 (C²), 49.25 (C²²), 40.66 (C²³), 25.95 (C²⁴) (Figure 1).

Measurements

Infrared spectra were recorded on a Perkin-Elmer Spectrum GX Fourier transform infrared (FT-IR) system. Elemental analyses were run on a Heraeus VarioEL-III CHN analyzer.

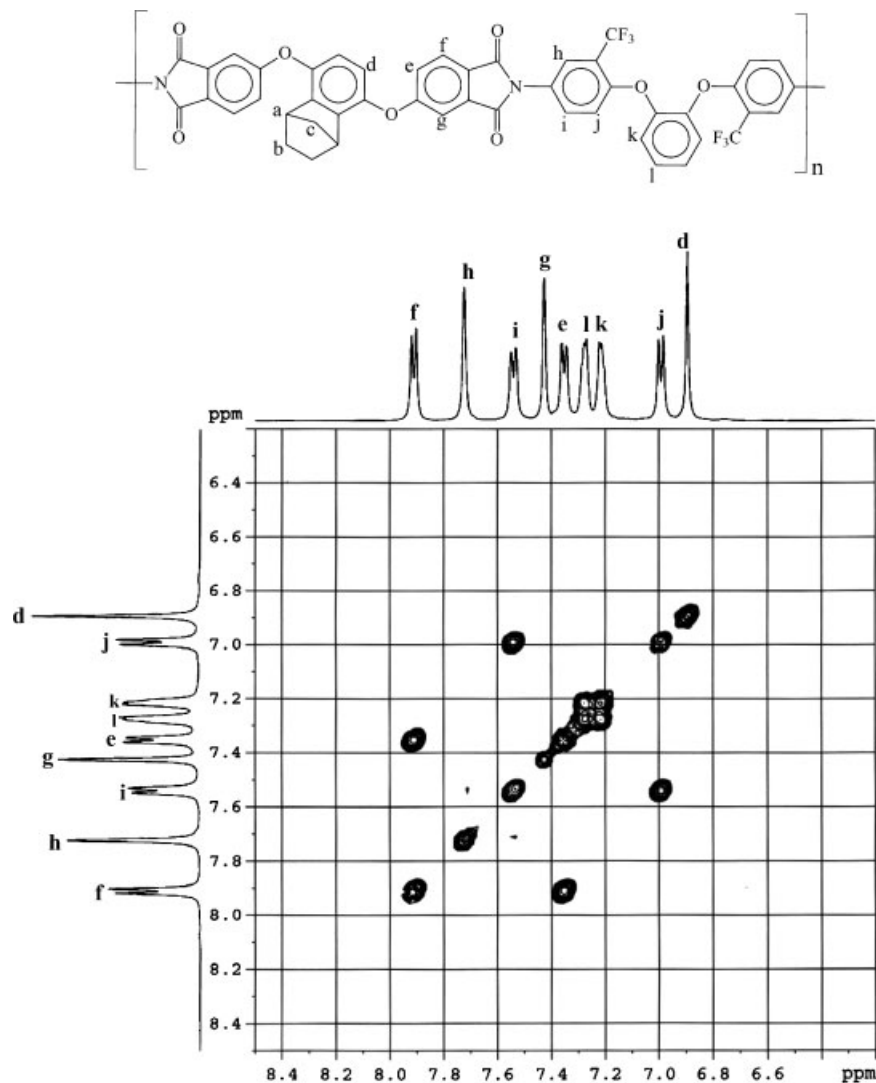


Figure 2. Aromatic region of H-H COSY NMR spectrum of PEI **IV_b** in CDCl₃.

^1H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at a $0.5 \text{ g} \cdot \text{dL}^{-1}$ 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 a Waters 2410 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 Jasco V-500 UV-Vis spectrophotometer. Tensile properties were determined from stress-strain curves obtained with a universal

testing machine (Instron, model 4400R) with a load cell of 5 kg. A gauge length of 2 cm and a strain rate of $5 \text{ mm} \cdot \text{min}^{-1}$ were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and $40\text{--}60 \mu\text{m}$ thick). An average of three to five replicates was used. Glass-transition temperatures (T_g) of the polymers were measured on a TA Instruments DSC 2010 at a heating rate of $15^\circ\text{C} \cdot \text{min}^{-1}$ 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 ($90 \text{ cm}^3 \cdot \text{min}^{-1}$) at a heating rate of $20^\circ\text{C} \cdot \text{min}^{-1}$. Thermomechanical analysis (TMA) was conducted with a Perkin-Elmer TMA 7 at a scan rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ with a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. Dielectric property of the polymer films was tested by the parallel-plate

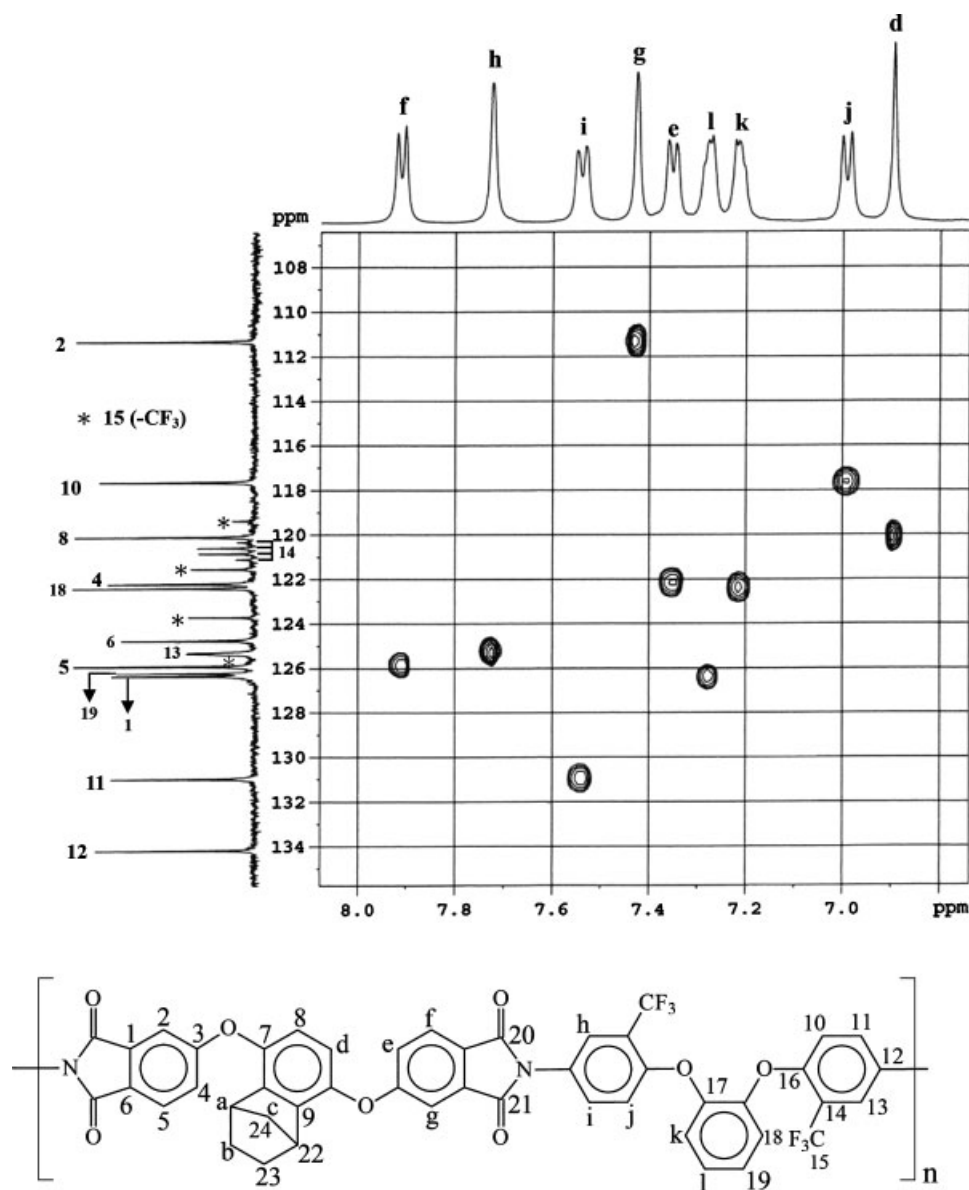


Figure 3. Aromatic region of H-C COSY NMR spectrum of PEI IV_b in CDCl₃.

capacitor method with a Hewlett Packard 4194A 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 moisture absorption was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 d.

Results and Discussion

Polymer Synthesis

The fluorinated PEIs **IV_{a-g}** were prepared from bis(ether anhydride) **I** and various CF₃-containing aromatic bis(ether-amine)s **II_{a-g}** in DMAc as shown in Scheme 1. Typically, the PAA was prepared by dissolving the diamine and then adding a molar equivalent of dianhydride as a solid. The solid content of the reaction solution was about 10 wt.-%. The reaction mixture was stirred at room temperature for 10 h followed by solution casting and thermal imidization/cyclo-dehydration at elevated temperatures or by chemical imidization using a mixture of acetic anhydride and pyridine. The resulting PEIs were isolated in almost quantitative yields. As shown in Table 1, the inherent viscosities of **IV_{a-g}** ranged from 1.02 to 1.28 dL · g⁻¹, indicating high molecular weight polymer formation. According to GPC analysis, their weight-

average molecular weights (\overline{M}_w) and number-average molecular weights (\overline{M}_n) were recorded in the ranges of 29 600–61 300 and 15 300–38 900, respectively, relative to polystyrene standards. The elemental analysis results of PEIs generally agreed with the calculated values for the proposed structures (Table 1). For a comparative study, a series of referenced PEIs (**V_{a-g}**) were also prepared from bis(ether anhydride) **I** and bis(ether amine)s **II'_{a-g}** without the CF₃ substituents via thermal imidization.

The complete imidization of polymers was confirmed with FT-IR and NMR spectra. The IR characteristic absorptions of the PAA appeared in the region of 3 700–2 700 cm⁻¹, and around 1 621 cm⁻¹ peculiar to amide and carboxyl groups. After dehydration, the above peak disappeared and showed the symmetrical and asymmetrical imide carbonyl peaks at 1 729 and 1 779 cm⁻¹ and imide-ring deformation absorptions at 1 083 and 746 cm⁻¹, together with some strong absorption bands in the region of 1 100–1 300 cm⁻¹ due to the C–O and C–F stretching. The disappearance of amide and carboxyl bands indicates a virtually complete conversion of PAA precursor into PEI. The ¹H NMR and ¹³C NMR spectra of a typical PEI **IV_b** are illustrated in Figure 1. The assignments of each carbon and proton were based on 2D-COSY experiments (Figure 2 and Figure 3), in good agreement with the proposed polymer structure.

Table 2. Solubility behavior of PEIs.

Polymer code	Solvent ^{a)}								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	CHCl ₃
IV_a(C)	◇	◇	◇	×	×	◇	◇	◇	◇
IV_b(C)	◇	◇	◇	◇	○	◇	◇	◇	◇
IV_c(C)	◇	○	○	×	×	◇	×	◇	◇
IV_d(C)	◇	◇	○	×	×	◇	×	◇	◇
IV_e(C)	◇	◇	◇	×	×	◇	◇	◇	◇
IV_f(C)	◇	◇	◇	×	×	◇	◇	◇	◇
IV_g(C)	◇	◇	◇	×	×	◇	◇	◇	◇
IV_a(H)	×	○	×	×	×	◇	×	+	◇
IV_b(H)	◇	◇	○	×	○	◇	×	○	◇
IV_c(H)	×	×	×	×	×	◇	×	×	×
IV_d(H)	×	○	○	×	×	◇	×	○	◇
IV_e(H)	×	○	+	×	×	◇	×	○	◇
IV_f(H)	◇	◇	○	×	×	◇	×	○	◇
IV_g(H)	×	○	+	×	×	◇	×	◇	◇
V_a(H)	×	×	×	×	×	×	×	×	×
V_b(H)	◇	◇	×	×	×	×	×	×	◇
V_c(H)	×	×	×	×	×	×	×	×	×
V_d(H)	×	×	×	×	×	×	×	×	◇
V_e(H)	×	×	×	×	×	×	×	×	×
V_f(H)	×	×	○	×	×	◇	×	○	◇
V_g(H)	×	×	×	×	×	×	×	×	◇

^{a)} Determined at room temperature. ◇, soluble at 10 wt.-%; ○, soluble at 5 wt.-% solid; +, soluble at 1 wt.-% solid; ×, insoluble. NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

Polymer Solubility and Film Property

The solubility of the polymers was tested in various solvents, and the results are summarized in Table 2. All the chemically imidized PEIs **IV_{a-g}(C)**, were readily soluble at a 5–10 wt.-% concentration both in strong dipolar solvents and in common organic solvents such as NMP, DMAc, DMF, pyridine, THF, and chloroform. The thermally imidized PEIs **IV_{a-g}(H)** revealed a slightly decreased solubility, possibly due to denser chain packaging and/or aggregation occurring during thermal treatment. From a comparison of the solubility for the **IV** series and the nonfluorinated **V** series analogs, the following order was found: **IV(C)** > **IV(H)** > **V(H)**. This can be attributed to the effect of the large volume of CF₃ groups, which disrupted regularity and dense chain packing leading to decreased interchain interactions. All of the **IV** series PEIs could afford good-quality and creasable films with almost no color. The thin film tensile properties of the thermally imidized PEIs are shown in Table 3. The films of PEIs **IV_{a-g}(H)** have tensile strengths of 104–130 MPa, elongations to break of 7–38%, and initial moduli of 1.9–2.5 GPa, comparable to those of the **V** series counterparts.

Color Intensities and Optical Transparency

The color intensities of the polymers were elucidated from the yellowness or redness indices observed by a colorimeter or from the cutoff wavelength observed in the UV-vis transmission spectra. Typical UV-vis transmission spectra of the films of PEIs **IV_r(C)**, **IV_r(H)** and **V_r(H)** and a standard PMDA/ODA polyimide are shown in Figure 4. All the **IV(C)** PEI films exhibited high optical transparency >80% at 500 nm. The color co-ordinates and cut-off wavelengths (absorption edge) of all the PEIs and

referenced Ultem 1000 and PMDA/ODA films are summarized in Table 4. All PEI films exhibited cut-off wavelengths shorter than 400 nm and were entirely transparent and colorless. The **IV(C)** PEIs shows a very low yellowness index (*b*^{*}) of 10.8–14.1. The slightly higher *b*^{*} of the thermally cured PEI films might be a result of denser chain packing/aggregates or thermal oxidation of chain-end amino groups. All the PEIs containing the CF₃ substituent revealed a slightly lower cut-off wavelength and *b*^{*} value than their respective CF₃-free analogs. The bulky and electron-withdrawing CF₃ group in the diamine moiety was presumably effective in disrupting the formation of charge transfer complexes between polymer chains through both the steric and inductive effects. The electron-donating ether groups in the dianhydride moiety also contribute to decreasing the electron-accepting property of the phthalimide units, and thus further lower the intermolecular electronic interactions. In a comparison, the prepared fluorinated PEI films showed a slightly lower *b*^{*} than Ultem 1000 and a much lower *b*^{*} and cut-off wavelength compared to standard PMDA/ODA polyimide.

Thermal Properties

The thermal behavior data of all PEIs are listed in Table 5. The *T_g* values of the **IV(H)** series PEIs obtained by DSC are in the range of 216–292 °C. PEIs **IV_b** showed relatively lower *T_g* values (216 °C), similar to that of Ultem PEI, because of the presence of kinked, flexible 1,2-phenyleneedioxy units. PEI **IV_d** possessed the highest *T_g* value of 292 °C due to the presence of rigid tetramethylbiphenyl segment in the diamine moiety. A 55 °C higher *T_g* of **IV_d** as compared to **IV_c** can be explained by the hindrance effect of the chain mobility caused by the methyl substitution. When comparing with the analogous **V** series PEIs, most of

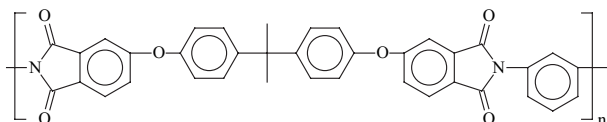
Table 3. Tensile properties of PEI films.

Polymer code	Strength at yield	Strength at break	Elongation to break	Initial modulus
	MPa	MPa	%	GPa
IV_a(H)	128	130	13	2.1
IV_b(H)	–	106	7	2.0
IV_c(H)	–	115	38	2.0
IV_d(H)	–	111	8	1.9
IV_e(H)	–	104	8	2.5
IV_r(H)	98	112	14	2.1
IV_g(H)	–	122	9	2.3
V_a(H)	–	125	7	3.1
V_b(H)	–	117	8	2.4
V_c(H)	124	131	21	2.6
V_d(H)	113	115	15	2.1
V_e(H)	–	109	11	2.0
V_r(H)	114	115	16	1.8
V_g(H)	–	117	12	2.4

Table 4. Color coordinates and cut-off wavelengths from UV-vis spectra of PEI films.

Polymer code	Film thickness μm	Color coordinates ^{c)}			Cut-off wavelength nm
		b^*	a^*	L^*	
Paper		1.9	-0.7	95.1	
IV _a (C)	53	13.9	-5.6	88.7	378
IV _b (C)	68	13.4	-6.3	87.8	378
IV _c (C)	55	11.3	-5.8	88.7	376
IV _d (C)	42	14.1	-5.4	89.1	379
IV _e (C)	65	11.1	-4.9	88.6	376
IV _f (C)	63	10.8	-4.6	87.1	372
IV _g (C)	45	11.9	-5.2	87.6	375
IV _a (H)	34	15.4	-6.5	87.7	379
IV _b (H)	44	17.0	-7.0	86.2	380
IV _c (H)	40	17.0	-7.2	85.8	381
IV _d (H)	39	18.2	-7.3	87.9	381
IV _e (H)	35	15.4	-6.6	86.6	379
IV _f (H)	55	14.6	-6.4	85.4	378
IV _g (H)	49	15.0	-7.1	87.6	380
V _a (H)	45	18.9	-7.3	84.8	384
V _b (H)	37	19.6	-7.1	85.8	384
V _c (H)	40	20.3	-8.3	84.8	386
V _d (H)	42	23.9	-8.6	83.3	386
V _e (H)	49	19.8	-5.6	81.0	384
V _f (H)	39	18.6	-6.0	83.9	382
V _g (H)	35	19.9	-5.1	83.7	384
Ultem 1000 ^{a)}	50	18.1	-5.7	84.3	398
PMDA/ODA ^{b)}	46	72.5	-9.2	82.5	443

a) Ultem 1000:



b) PMDA/ODA:

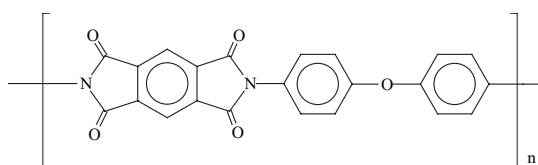
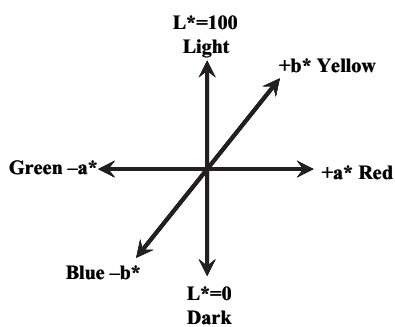
c) CIE L^* a^* b^* scale:

Table 5. Thermal properties of PEIs.

Polymer code	T_g $^{\circ}\text{C}^{\text{a)}$	T_s $^{\circ}\text{C}^{\text{b)}$	T_{10} $^{\circ}\text{C}^{\text{c)}$		Char yield % ^{d)}
			In N_2	In air	
IV _a (H)	224	209	503	498	53
IV _b (H)	216	209	494	498	54
IV _c (H)	237	224	504	513	58
IV _d (H)	292	285	472	481	60
IV _e (H)	233	228	499	519	52
IV _f (H)	218	210	495	510	51
IV _g (H)	250	250	507	527	61
V _a (H)	234	212	502	512	48
V _b (H)	218	201	496	508	53
V _c (H)	243	227	504	525	58
V _d (H)	284	274	505	510	56
V _e (H)	227	212	504	518	56
V _f (H)	219	217	504	505	58
V _g (H)	277	268	512	527	60

a) Midpoint temperature of the baseline shift on the second heating DSC traces, with a heating rate of $15^{\circ}\text{C}\cdot\text{min}^{-1}$.

b) Softening temperature taken as the onset temperature of the probe displacement on the TMA trace at a heating rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$. The film samples were heated at 300°C for 1 h prior to the TMA experiments.

c) Temperatures at which 10% weight loss were recorded by TGA at a heating rate of $20^{\circ}\text{C}\cdot\text{min}^{-1}$.

d) Residual weight (%) when heated to 800°C in nitrogen.

the IV series ones had a slightly lower T_g possibly attributable to reduced chain-to-chain charge transfer interactions and packing efficiency produced by the pendent CF_3 groups. The softening temperatures (T_s) of the PEI films were determined by the TMA method using a loaded penetration probe. They were taken as the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of PEI IV_g is

Table 6. Water absorption and dielectric constants of PEI films.

Polymer code	Film thickness μm	Water absorption %	Dielectric constant (dry)		
			1 kHz	10 kHz	1 MHz
IV _a (H)	41	0.11	3.67	3.64	3.58
IV _b (H)	50	0.17	3.16	3.14	3.01
IV _c (H)	43	0.15	3.08	3.05	2.99
IV _d (H)	33	0.09	2.97	2.95	2.90
IV _e (H)	48	0.11	3.59	3.58	3.52
IV _f (H)	51	0.05	2.90	2.89	2.84
IV _g (H)	46	0.19	3.20	3.19	3.17
V _a (H)	35	0.35	3.78	3.79	3.81
V _b (H)	55	0.39	3.54	3.53	3.49
V _c (H)	50	0.35	3.86	3.85	3.82
V _d (H)	40	0.36	3.44	3.41	3.31
V _e (H)	44	0.48	3.41	3.40	3.38
V _f (H)	37	0.22	3.36	3.35	3.21
V _g (H)	35	0.32	4.02	4.01	3.97

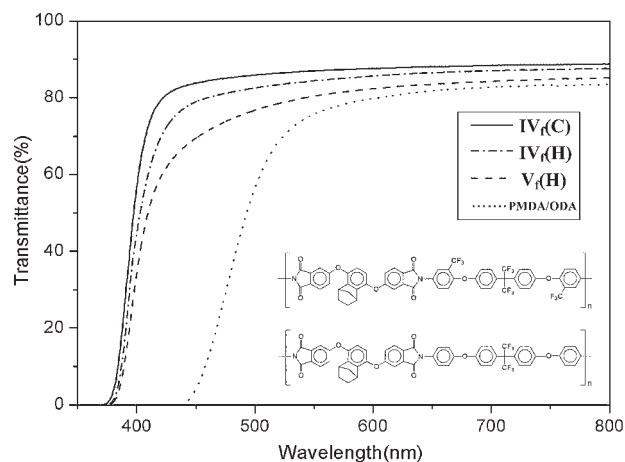


Figure 4. UV-visible transmission spectra of PEI **IV_f** and **V_f** and PMDA/ODA films.

illustrated in Figure 5. 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 DSC. The trend of T_s variation with the chain stiffness is similar to that of T_g observed in the DSC experiments.

The thermal stability of **IV_{a-g}** was evaluated by dynamic TGA conducted at a heating rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were determined from original TGA thermograms. The T_{10} values of CF_3 -substituted PEIs **IV_{a-g}** were recorded in the range of $472\text{--}507\text{ }^\circ\text{C}$ in nitrogen and $481\text{--}527\text{ }^\circ\text{C}$ in air. They left more than 51% char yield at $800\text{ }^\circ\text{C}$ in nitrogen. In all cases, the T_{10} values were higher in air than in nitrogen, possibly because of oxidative crosslinking or an early weight-gained oxidation of the aliphatic norbornane groups with thermal degradation in air. PEI **IV_g** showed the highest T_{10} and char yield because of a higher aromatic content. It is quite reasonable that the methyl-

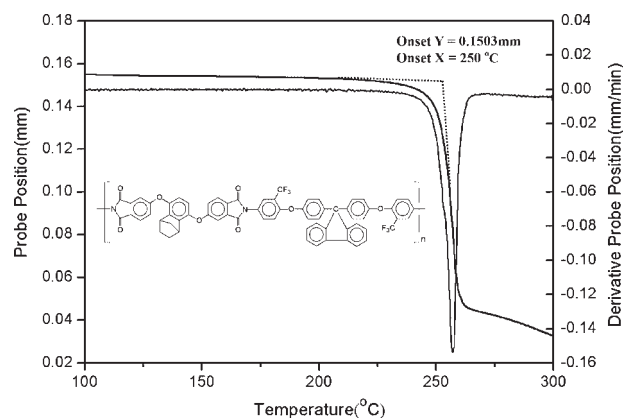


Figure 5. TMA curve of PEI **IV_g**.

substituted PEI **IV_d** began to decompose at lower temperatures compared to the corresponding methyl-free **IV_c** and the other PEIs. The TGA data indicated that these fluorinated PEIs still exhibited high thermal stability regardless of the introduction of CF_3 groups.

Dielectric Property and Water Absorption

The dielectric constants and water absorptions of the PEI films are reported in Table 6. The measurements of the dielectric constants were performed between gold layers. The polymer film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the film. This procedure excluded any contact problems. The **IV** series PEIs exhibited lower dielectric constants (2.84–3.58 at 1 MHz) than the **V** series analogs (3.21–3.97 at 1 MHz). The decreased dielectric constants might be attributed to the presence of bulky CF_3 group, which has low polarizability and increases the free volume of the polymer chain. PEI **IV_f** showed the lowest dielectric constant of 2.84 at 1 MHz, possibly due to further increased free volume caused by the hexafluoroisopropylidene linkage. As expected, the CF_3 -substituted **IV** PEIs exhibited lower water absorptions (0.05–0.19%) than the corresponding analogous **V** series (0.22–0.48%) due to the hydrophobic nature of the CF_3 group. In addition, PEIs **IV_f** and **V_f** exhibited the lowest water absorption in their own series because of the higher fluorine content in the repeat unit. The low water absorptions ensure that these fluorinated PEIs have stable dielectric performance.

Conclusion

A series of novel fluorinated PEIs **IV** were synthesized from 3,6-bis(3,4-dicarboxyphenoxy)benzonorbornane dianhydride (**I**) with various CF_3 -containing aromatic bis(ether amine)s by a two-step thermal or chemical imidization method. The combination of these dianhydride and diamine monomers was a successful process for reducing overall charge transfer complex formation due to either or both inter- and intramolecular electronic interactions. Thus, the prepared PEIs had high solubility and could be cast into colorless films compared to the bright yellow color of conventional/commercial aromatic polyimide films. This increased optical transparency in these aromatic PEIs has achieved at no sacrifice in thermal stability, flexibility, toughness, or mechanical properties. These PEIs also showed low dielectric constants and low water absorptions. Thus, they demonstrate a good combination of properties and should be useful for the applications where high optical transparency and thermal stability are needed requirements.

Acknowledgements: The authors are grateful to the National Science Council of Taiwan for the support of this work (Grant no. NSC 94-2216-E-036-014).

- [1] "Polyimides: Synthesis, Characterization, and Application, Vol. I and II", K. L. Mittal, Ed., Plenum, New York 1984.
- [2] "Polyimides", D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, Eds., Blackie, Glasgow 1990.
- [3] "Polyimides and Other High-Temperature Polymers", M. J. M. Adadie, B. Sillion, Eds., Elsevier, Amsterdam 1991.
- [4] "Polyimides: Fundamentals and Applications", M. K. Ghosh, K. L. Mittal, Eds., Marcel Dekker, New York 1996.
- [5] S. J. Huang, A. E. Hoyt, *Trends Polym. Sci.* **1995**, *3*, 262.
- [6] Y. Imai, *React. Funct. Polym.* **1996**, *30*, 3.
- [7] J. de Abajo, J. G. de la Campa, *Adv. Polym. Sci.* **1999**, *140*, 23.
- [8] R. A. Dine-Hart, W. W. Wright, *Makromol. Chem.* **1971**, *143*, 89.
- [9] S. Ando, T. Matsuura, S. Sasaki, *Polym. J.* **1997**, *29*, 69.
- [10] M. Hasegawa, K. Horie, *Prog. Polym. Sci.* **2001**, *26*, 259.
- [11] A. K. St Clair, T. L. St Clair, W. S. Slem, "Recent Advances in Polyimides Science and Technology", W. Weber, M. Gupta, Eds., Society of Plastics Engineers: Poughkeepsie, New York 1987, p. 16.
- [12] C. P. Yang, S. H. Hsiao, H. W. Yang, *Macromol. Chem. Phys.* **2000**, *201*, 409.
- [13] W. Huang, D. H. Yan, Q. H. Lu, P. Tao, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *40*, 229.
- [14] T. Matsumoto, T. Kurosaki, *Macromolecules* **1997**, *30*, 993.
- [15] T. Matsumoto, *Macromolecules* **1999**, *32*, 4933.
- [16] H. Seino, A. Mochizuki, M. Ueda, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3584.
- [17] J. Li, J. Kato, K. Kudo, S. Shiraishi, *Macromol. Chem. Phys.* **2000**, *201*, 2289.
- [18] K. Xie, J. G. Liu, H. W. Zhou, S. Y. Zhang, M. H. He, S. Y. Yang, *Polymer* **2001**, *42*, 7267.
- [19] S. Banerjee, M. K. Madhra, A. K. Salunke, G. Maier, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1016.
- [20] C. P. Yang, S. H. Hsiao, K. H. Chen, *Polymer* **2002**, *43*, 5095.
- [21] C. P. Yang, R. S. Chen, K. H. Chen, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 922.
- [22] C. P. Yang, S. H. Hsiao, K. L. Wu, *Polymer* **2003**, *44*, 7076.
- [23] S. H. Hsiao, C. P. Yang, C. L. Chung, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2001.
- [24] B. Y. Myung, J. S. Kim, J. J. Kim, T. H. Yoon, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3361.
- [25] B. J. Liu, W. Hu, T. Matsumoto, Z. H. Jiang, S. Ando, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3018.
- [26] H. S. Li, J. G. Lin, K. Wang, L. Fan, S. Y. Yang, *Polymer* **2006**, *47*, 1443.
- [27] H. S. Li, J. G. Lin, J. M. Rui, L. Fan, S. Y. Yang, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2665.
- [28] C. L. Chung, C. P. Yang, S. H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3092.
- [29] T. Takekoshi, J. E. Kochanowski, J. S. Manello, M. J. Webber, *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1759.
- [30] T. Takekoshi, J. E. Kochanowski, J. S. Manello, M. J. Webber, *J. Polym. Sci., Polym. Symp.* **1986**, *74*, 93.
- [31] T. Takekoshi, *Polym. J.* **1987**, *19*, 191.
- [32] G. C. Eastmond, J. Paprotny, *React. Funct. Polym.* **1996**, *30*, 27.
- [33] G. C. Eastmond, J. Paprotny, *J. Mater. Chem.* **1997**, *7*, 589.
- [34] G. C. Eastmond, M. Gibas, J. Paprotny, *Eur. Polym. J.* **1999**, *35*, 2097.
- [35] J. G. Wirth, "High Performance Polymers: Their Origin and Development", R. B. Seymour, G. S. Krishenbaum, Eds., Elsevier, Amsterdam 1986.
- [36] S. H. Hsiao, T. L. Huang, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1712.
- [37] K. Xie, S. Y. Zhang, J. G. Liu, M. H. He, S. Y. Yang, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2581.
- [38] C. P. Yang, R. S. Chen, H. C. Chiang, *Polym. J.* **2003**, *35*, 662.
- [39] C. P. Yang, S. H. Hsiao, M. F. Hsu, *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 524.
- [40] C. P. Yang, S. H. Hsiao, K. H. Chen, *Polymer* **2002**, *43*, 5095.
- [41] C. P. Yang, R. S. Chen, K. H. Chen, *J. Appl. Polym. Sci.* **2005**, *95*, 922.
- [42] C. P. Yang, R. S. Chen, K. H. Chen, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 922.
- [43] C. P. Yang, H. C. Chiang, *Colloid Polym. Sci.* **2004**, *282*, 1347.