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Novel organosoluble and colorless poly(ether imide)s based on 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]cyclohexane dianhydride and trifluoromethyl-substituted aromatic bis(ether amine)s

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Abstract

A series of novel fluorinated poly(ether imide)s (**IV**) having inherent viscosities of 0.70–1.08 dL/g were prepared from 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]cyclohexane dianhydride (**I**) and various trifluoromethyl (CF$_3$)-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 showed excellent solubility in many organic solvents and could be solution-cast into transparent, flexible, and tough films. These films were essentially colorless, with an ultraviolet-visible absorption edge of 375–380 nm and a very low b^* value (a yellowness index) of 5.5–7.3. They also showed good thermal stability with glass-transition temperatures of 207–269 °C, 10% weight loss temperatures in excess of 474 °C, and char yields at 800 °C in nitrogen more than 62%. In comparison with analogous **V** series poly(ether imide)s without the –CF$_3$ substituents, the **IV** series polymers showed better solubility, lower color intensity, and lower dielectric constants.
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1. 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 [1,2]. Despite the excellent combined properties, their widespread applications are often limited because of their poor solubility and high processing temperature, which are caused by the rigid polymer backbones and the strong 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

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maintaining their excellent properties [3,4]. 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 transfer charge (CT) interactions between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties [5–7]. 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 [7]. Soluble and colorless polyimides can be obtained by using alicyclic dianhydride or diamine monomers [8–11]; 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 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 poly(ether imide)s (PEIs) from bis(ether anhydride)s and various diamines [12–14]. An important example is Ultem 1000 resin developed and commercialized by General Electric Co. [15], which exhibits reasonable thermal stability and good mechanical properties together with good moldability. Recently, considerable attention has been devoted to the fluorinated aromatic polyimides, especially trifluoromethyl (CF$_3$)-containing polyimides [16–19]. It was found that the incorporation of bulky CF$_3$ into polyimide backbones resulted in an enhanced solubility and optical transparency together with a lowered dielectric constant, which attributed to low polarizability of the C–F bond and the increase in free volume. The fluorinated polyimides also provided other merits such as good thermal and thermo-oxidative stability and low moisture absorption.

As part of our continuing efforts to gain colorless and soluble polyimides with high thermal stability and low dielectric constant for advanced microelectronics and optoelectronics applications, this work deals with the synthesis and characterization of a series of fluorinated poly(ether imide)s from 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]cyclohexane dianhydride (**I**) and various CF$_3$-substituted aromatic bis(ether amine)s. The solubility, thermal

and mechanical properties, color intensity, and optical transparency of the resulting polymers were investigated. Since the designed poly(ether imide)s are composed of less electron-accepting dianhydride and less electron-donating diamine moieties, they should exhibit low or no color and high transparency in the visible region, a property which should be helpful for optical applications. The poly(ether imide)s would also be expected to possess an enhanced solubility and melt processability because of the incorporation of kinked cyclohexylidene cardo groups and flexible links in the main chain.

2. Experimental

2.1. Materials

The CF$_3$-substituted bis(ether amine)s were prepared from the chloro-displacement reaction of 2-chloro-5-nitrobenzotrifluoride with the corresponding aromatic diols in the presence of potassium carbonate, followed by Pd/C-catalyzed hydrazine reduction; they included 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (**II$_a$**) (mp = 132–133 °C) [20], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2-*tert*-butylbenzene (**II$_b$**) (mp = 164–165 °C) [21], 1,4-bis(4-amino-2-trifluoromethylphenoxy)-2,5-di-*tert*-butylbenzene (**II$_c$**) (mp = 215–216 °C) [22], 4,4′-bis(4-amino-2-trifluoromethylphenoxy)biphenyl (**II$_d$**) (mp = 155–156 °C) [23], 4,4-bis(4-amino-2-trifluoromethylphenoxy)-3,3′,5,5′-tetramethylbiphenyl (**II$_e$**) (mp = 256–257 °C) [24], 2,2-bis[4-(4-amino-2-trifluoromethylphenoxy)phenyl]propane (**II$_f$**) (mp = 131–132 °C) [25], 4,4′-bis(4-amino-2-trifluoromethylphenoxy)benzophenone (**II$_g$**) (mp = 152–153 °C) [26]. *N*,*N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular seives.

2.2. Synthesis of 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]cyclohexane dianhydride (*I*)

As shown in Scheme 1, bis(ether anhydride) **I** (mp = 200–201 °C) was prepared in three steps starting from the nitro displacement reaction of the dipotassium phenolate of 1,1-bis(4-hydroxyphenyl)cyclohexane with 4-nitrophthalonitrile, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) (**I′**) and subsequent dehydration of the resulting tetraacid (**I″**). The synthetic details and characterization data have been reported in a previous article [27].
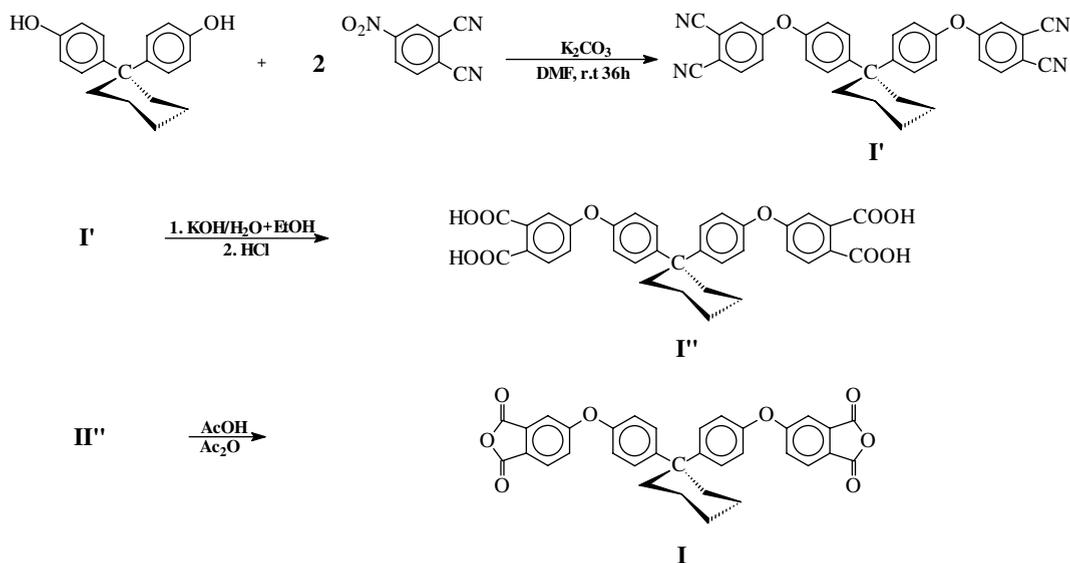
Scheme 1. Synthesis of 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]cyclohexane dianhydride (**I**).

The single crystals of bi(ether anhydride) **I** were grown during slow crystallization of its acetic anhydride solution. A crystal size of $0.25 \times 0.20 \times 0.15 \, mm^3$ was used for X-ray structure determination. Crystal data: triclinic $P2(1)/c$ with $a = 9.5575(3)$ Å, $b = 17.8246(4)$ Å, $c = 16.4628(4)$ Å; $\alpha = 90°$, $\beta = 102.1450(13)°$, $\gamma = 90°$, where $D_C = 1.358 \, Mg/m^3$ for $Z = 4$ and $V = 2741.81(13)$ Å^3. Least squares refinement based on 6252 independent reflections converged to final values of $R_1 = 0.0609$ and $wR_2 = 0.1383$. The refined crystal structure of **I** is shown in Fig. 1.

2.3. Synthesis of poly(ether imide)s

The general polymerization procedure is illustrated by the following example. To a solution of bis(ether amine) **II$_a$** (0.228 g, 0.5 mmol) in dried DMAc (3.2 mL) in a 20 mL round-bottomed flask, bis(ether anhydride) **I** (0.297 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 PAA solution was poured into a glass culture dish, 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 to 250 °C at a heating rate of 3 °C/min and then further heating at 250 °C for 30 min. The polyimide film was stripped from the glass substrate by immersion in water. Inherent viscosity (η_{inh}) in DMAc of
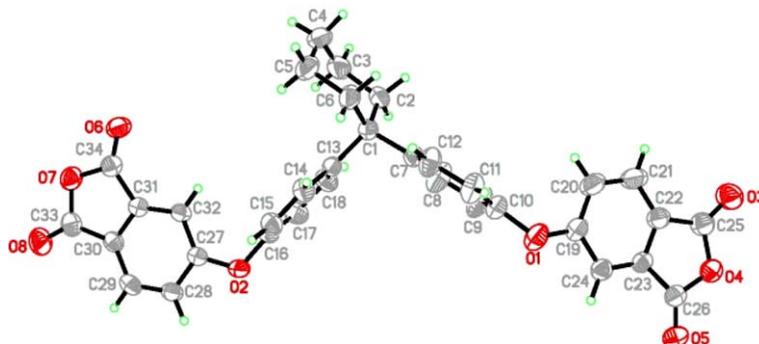
Fig. 1. Single crystal structure of bis(ether anhydride) **I** by X-ray diffraction analysis.

PEI IV_a was 0.98 dL/g, as measured at a concentration 0.5 g/dL 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 cause 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: Calcd. for $(C_{54}H_{35}F_6N_2O_8)_n$ $(953.87)_n$: C, 68.00%; H, 3.70%; N, 2.94%; Found: 67.90%; H, 3.75%; N, 2.87%.

IR (film): 1780 cm^{-1} (asymmetric C=O stretch), 1726 cm^{-1} (symmetric C=O stretch), 1478–1620 cm^{-1} (aromatic C=C stretch), 1378 cm^{-1} (C–N stretch), 1053, 745 cm^{-1} (imide ring deformation) 1100–1300 cm^{-1} (C–O and C–F stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.89 (2H, H$_b$),

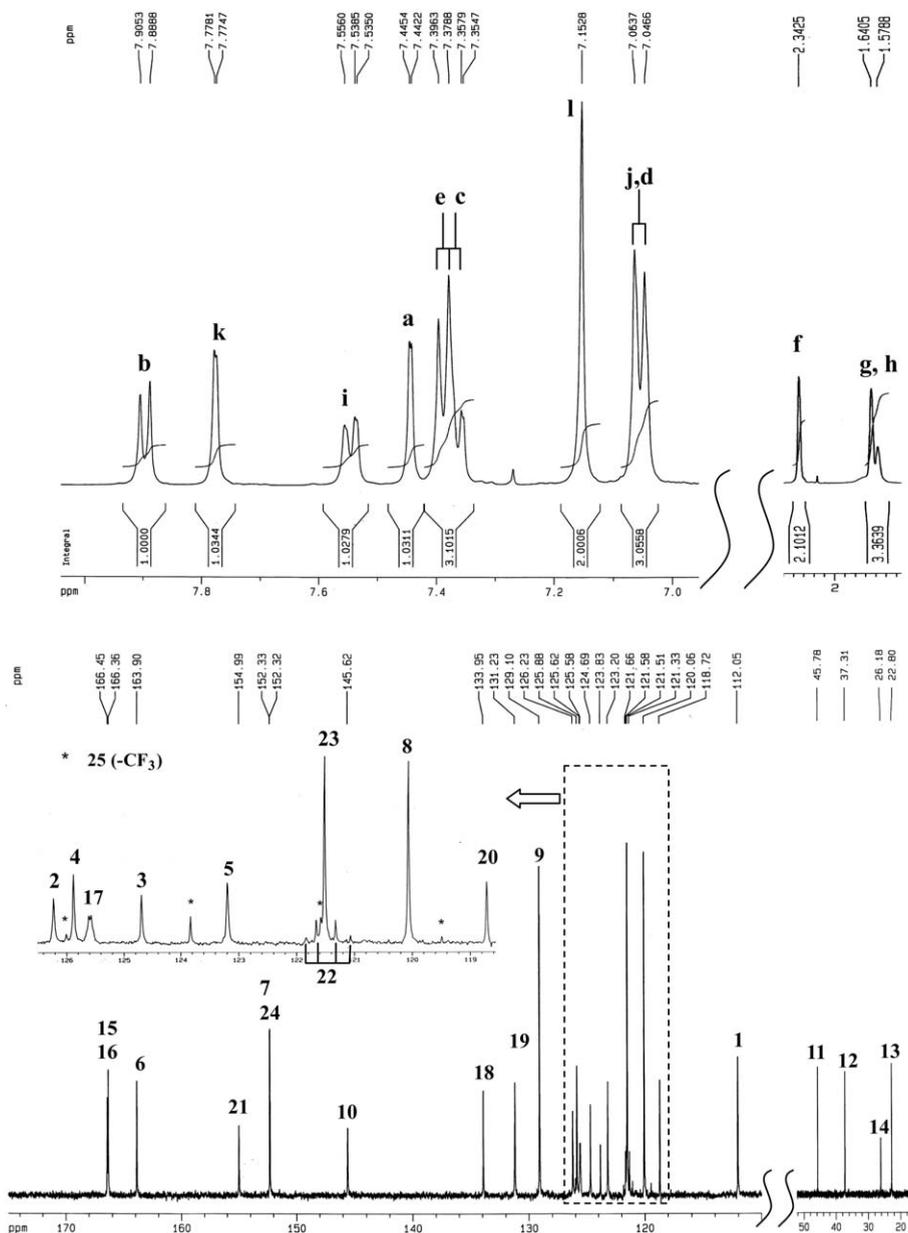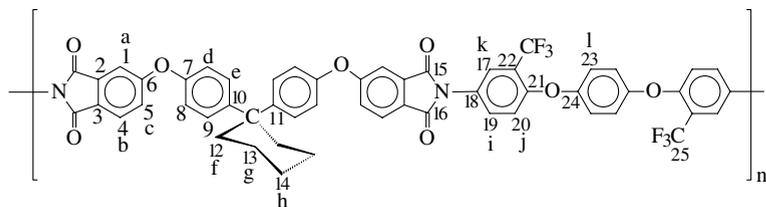Fig. 2. ^{1}H and ^{13}C NMR spectra of poly(ether imide) IV_a in CDCl$_3$.

7.77 (2H, H_k), 7.54 (2H, H_i), 7.44 (2H, H_a), 7.37 (4H, H_e), 7.36 (2H, H_c), 7.15 (4H, H_l), 7.05 (6H, $H_{d,j}$), 2.34 (4H, H_f), 1.64 (4H, H_g), 1.58 (2H, H_h). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm): 166.45 (C^{16}), 166.36 (C^{15}), 163.90 (C^6), 154.99 (C^{21}), 152.32, 152.33 (C^7, C^{24}), 145.62 (C^{10}), 133.95 (C^{18}), 131.23 (C^{19}), 129.10 (C^9), 126.23 (C^2), 125.88 (C^4), 125.62 (C^{17}), 124.69 (C^3), 123.20 (C^5), 122.74 (quartet, $^1J_{C-F} = 271$ Hz, C^{25}), 121.51 (C^{23}), 121.45 (quartet, $^2J_{C-F} = 31$ Hz, C^{22}), 120.06 (C^8), 118.72 (C^{20}), 112.05 (C^1), 45.78 (C^{11}), 37.31 (C^{12}), 26.18 (C^{14}), 22.80 (C^{13}) (Fig. 2).

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

2.4. Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run on a Heraeus VarioEL-III CHN analyzer. ^1H and ^{13}C NMR spectra were measured on a Bruker AV-500 FT-NMR spectrometer. Inherent viscosities were determined at a 0.5 g/dL concentration with an Ubbelohde viscometer at 30 °C. Weight-average molecular weights ($\overline{M}_w$'s) and number-average molecular weights ($\overline{M}_n$'s) were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using Waters 2410 as an apparatus and tetrahydrofuran (THF) as the eluent. Color intensity of the polymers was evaluated on a GretagMacbeth Color-Eye 3100 colorimeter. Measurements were performed for the films at an observational angle of 10° and with a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–Visible (UV–Vis) spectra of the polymer films were recorded on a Shimadzu UV-1601 UV–Vis spectrophotometer. Mechanical properties of the films were measured on an Instron model 1130 tensile tester with a 5 kg load cell at a crosshead speed of 5 mm/min on strips approximately 30–60 μm thick and 0.5 cm wide with a 2 cm gauge length. An average of at least five individual determinations was used. Glass-transition temperature (T_g) of the polymer was measured on a TA Instruments DSC 2010 at a heating rate of

3. Results and discussion

3.1. Polymer synthesis

A series of novel poly(ether imide)s IV_{a-g} were synthesized from bis(ether anhydride) I and various CF$_3$-containing bis(ether amine)s II_{a-g} via a conventional two-step procedure, as shown in Scheme 2. 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 –CF$_3$ 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 poly(amic acid) precursors to the PEIs, and the PEI samples are denoted as IV(H) and IV(C), respectively. As shown in Table 1, some of these PEIs exhibited inherent viscosities of 0.70–1.08 dL/g. 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 48,300–57,400 and 28,100–33,800, respectively. 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} via thermal imidization.

The complete imidization of polymers was confirmed with IR and NMR spectra. In the IR spectra, the fluorinated PEIs exhibited characteristic imide
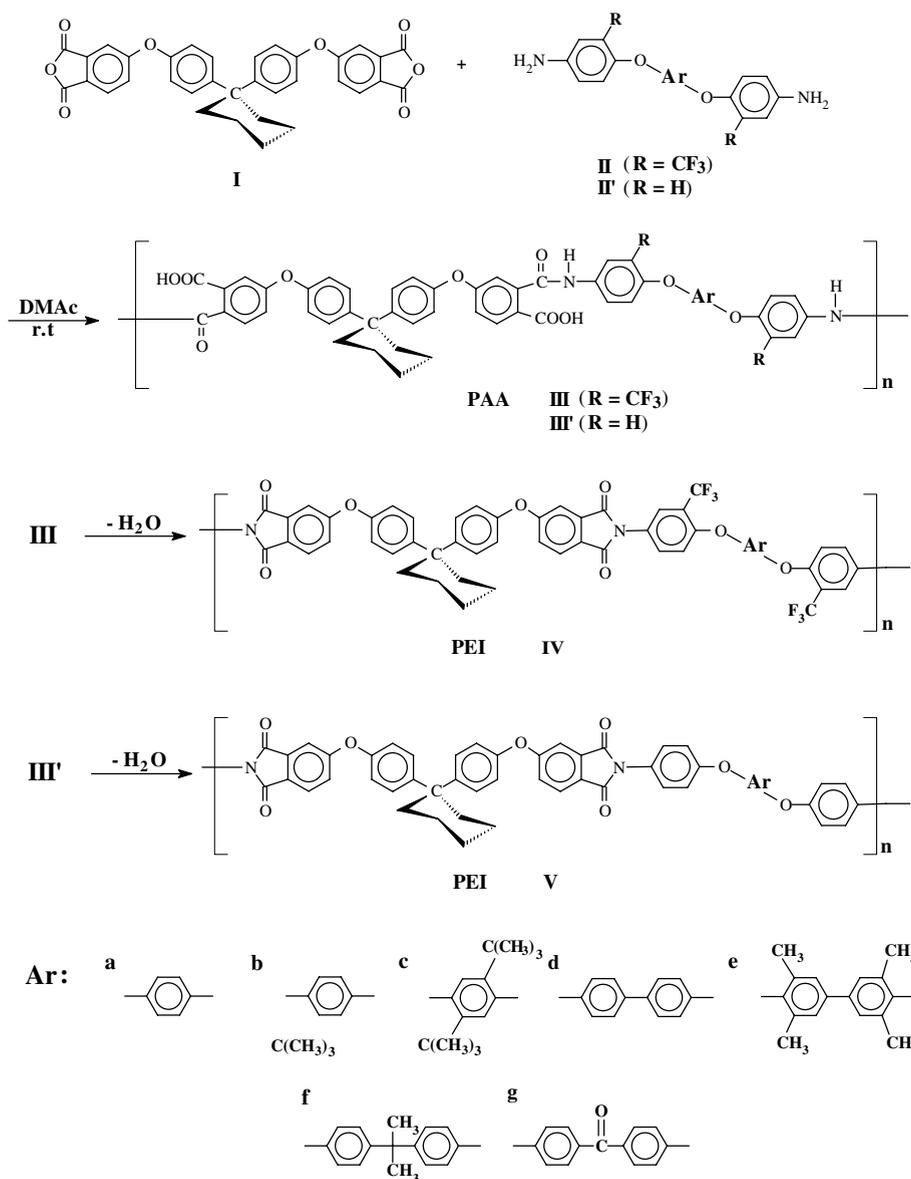
Scheme 2. Synthesis of poly(ether imide)s.

group absorptions around 1780 and 1725 cm^{-1} (typically 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 ^{1}H NMR and ^{13}C NMR spectra of a typical PEI IV_a are illustrated in Fig. 2. Assignments of each carbon and proton assisted by 2D-NMR spectra (Fig. 3)

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 also generally agreed with the calculated values for the proposed structures.

3.2. 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 PEIs prepared by the chemical

Table 1
Inherent viscosity and GPC data of poly(ether imide)s

Polymer code[a]	η_{inh}[b] (dL/g)	GPC data of poly(ether imide)s[c]		
		$\overline{M}_n \times 10^4$	$\overline{M}_w \times 10^4$	$\overline{M}_w/\overline{M}_n$
IV$_a$(H)	0.98	3.15	5.30	1.68
IV$_b$(H)	1.03	3.15	5.35	1.69
IV$_c$(H)	0.92	3.27	5.65	1.72
IV$_d$(H)	0.98	3.38	5.58	1.65
IV$_e$(H)	1.08	3.38	5.74	1.70
IV$_f$(H)	0.70	2.81	4.83	1.71
IV$_g$(C)	1.06	3.17	5.43	1.71

[a] (H): thermal imidization; (C): chemical imidization.
[b] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[c] Relative to polystyrene standards, using THF as the eluent.

imidization method, **IV$_{a-g}$(C)**, were readily soluble with a 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 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. The insolubility of thermally cured PEI **IV$_g$** might be attributable to the presence of benzophenone segment in the chain, which may lead to partial crosslinking within polymer chains during the imidization process at elevated temperatures [28]. The **IV** series PEIs generally showed better solubility, especially in strongly polar organic solvents such as NMP, DMAc, and DMF, as compared with the nonfluorinated **V** series analogs. This can be attributed to the effect of the large volume of CF$_3$ groups, which disrupted regularity and dense chain packing leading to
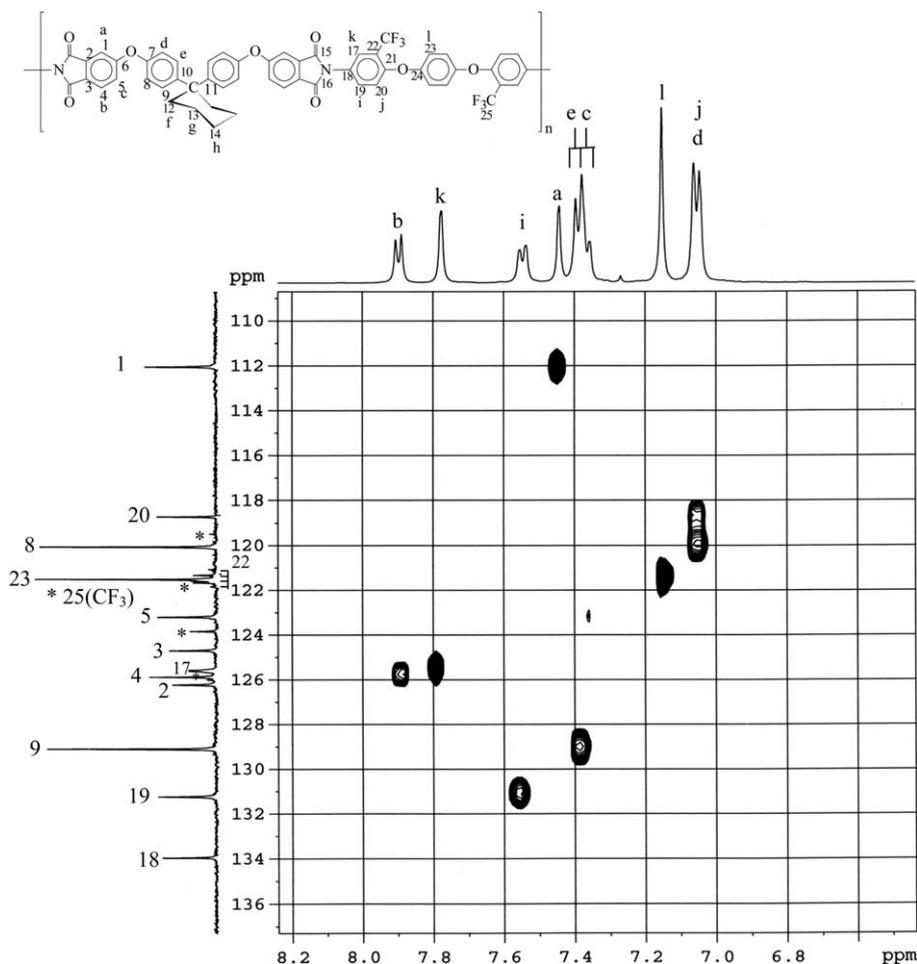

Fig. 3. Aromatic region of H–C COSY NMR spectrum of poly(ether imide) **IV$_a$** in CDCl$_3$.

Table 2
Solubility behavior of poly(ether imide)s[a]

Polymer code	Solvent[b]									
	NMP	DMAc	DMF	DMSO	m-Cresol	Py	Dioxane	THF	CHCl₃	Acetone
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.
[b] NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

decreased interchain interactions. The packing-disruptive cardo structure in the bis(ether anhydride) moiety also contributed to the enhancement in solubility. As shown in Fig. 1, the two inner aromatic rings of **I** are orthogonally arranged and are connected to the C-1 positions of cyclohexane. Thus, the resulting PEIs should have a periodically twisted polymer backbone, and this would lower the chain packing and increase the solubility.

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 80–113 MPa, elongations to break of 7–18%, and initial moduli of 1.5–1.9 GPa, comparable to those of the **V** series.

3.3. Optical properties

The transmission UV–Vis spectra were measured for tough and flexible films of all PEIs. All PEI films exhibited cut-off wavelengths shorter than 400 nm and were entirely transparent and colorless. As shown in Table 4, the **IV**(C) PEIs showed a very

Table 3
Tensile properties of poly(ether imide) films

Polymer code	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
IV$_a$(H)	113	17	1.9
IV$_b$(H)	98	15	1.9
IV$_c$(H)	100	18	1.5
IV$_d$(H)	86	7	1.7
IV$_e$(H)	80	9	1.5
IV$_f$(H)	81	12	1.8
IV$_g$(H)	105	10	1.9
V$_a$(H)	95	16	1.7
V$_b$(H)	73	7	1.6
V$_c$(H)	83	16	1.5
V$_d$(H)	87	11	1.7
V$_e$(H)	101	8	1.9
V$_f$(H)	87	9	1.9
V$_g$(H)	87	11	1.7

low yellowness index (b*) of 5.5–7.3. For comparison, the color coordinates and cut-off wavelength of a standard polyimide film from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) are also given in Table 4. The slightly higher

Table 4
Color coordinates and cut-off wavelengths from UV–Vis spectra of poly(ether imide)s

Polymers	Film thickness (μm)	Color coordinates[a]			Cut-off wavelength (nm)
		b^*	a^*	L^*	
Paper		1.1	−0.4	94.6	
IV$_a$(C)	68	6.2	−1.5	89.8	380
IV$_b$(C)	62	6.8	−1.9	91.0	376
IV$_c$(C)	57	6.3	−1.5	89.8	376
IV$_d$(C)	48	5.5	−1.5	89.9	376
IV$_e$(C)	44	5.7	−2.0	93.5	375
IV$_f$(C)	51	5.6	−1.5	90.9	375
IV$_g$(C)	55	7.3	−1.9	89.7	380
IV$_a$(H)	59	8.0	−1.9	89.5	378
IV$_b$(H)	51	11.1	−2.0	90.1	379
IV$_c$(H)	52	8.6	−2.1	91.2	382
IV$_d$(H)	45	12.1	−2.7	88.7	379
IV$_e$(H)	31	10.7	−2.7	90.5	379
IV$_f$(H)	32	9.5	−1.6	90.2	378
IV$_g$(H)	30	11.3	−2.5	89.3	382
V$_a$(H)	50	15.3	−3.4	88.1	381
V$_b$(H)	59	15.6	−3.2	90.2	380
V$_c$(H)	45	13.9	−2.8	89.8	384
V$_d$(H)	43	14.9	−2.6	88.3	382
V$_e$(H)	48	14.7	−2.4	83.6	383
V$_f$(H)	52	14.3	−1.8	88.5	380
V$_g$(H)	48	17.4	0.0	84.8	382
PMDA/ODA	38	85.1	0.3	90.1	443

[a] The CIE L^* a^* b^* color scale: **Green** - a*
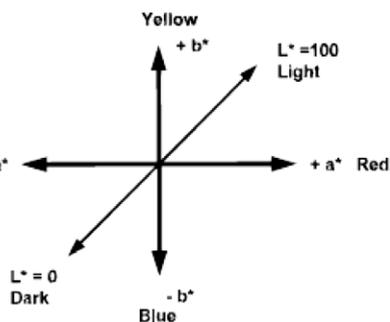
yellowness index of the thermally imidized PEI films might be a result of thermal oxidation of chain-end amino groups. All the **IV** series PEIs containing CF$_3$ group revealed slightly lower cut-off wavelengths and lower b^* values than their respective CF$_3$-free analogous PEIs **V** (Fig. 4). The bulky and electron-withdrawing 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 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 lower the intermolecular CT interaction. In addition, the aliphatic cardo

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

3.4. Thermal properties

The thermal behavior data of all PEIs are listed in Table 5. The T_g values of PEIs **IV$_{a-g}$** determined by DSC were in the range of 207–269 °C. The decreasing order of T_g generally correlated with that of the chain flexibility. PEI **IV$_f$** derived from bis(ether amine) **II$_f$** showed the lowest T_g value (207 °C) because of the presence of flexible
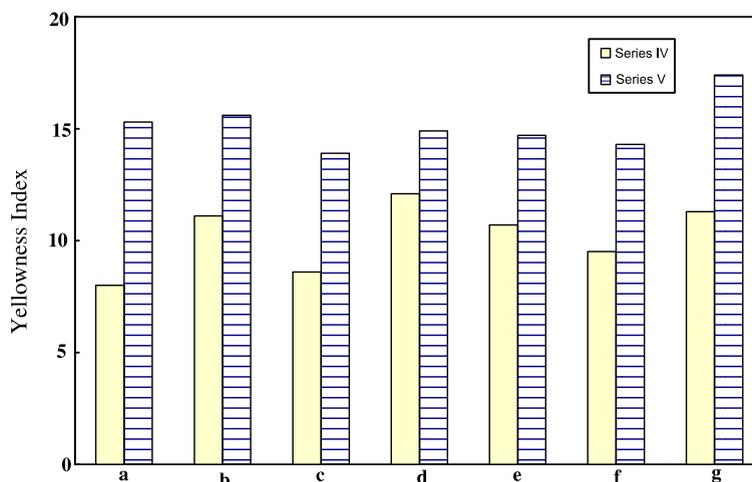
Fig. 4. Comparison of the yellowness index (b^* value) between the **IV**(H) and **V**(H) series poly(ether imide)s.

Table 5
Thermal properties of poly(ether imide)s

Polymers	T_g^a (°C)	T_{10}^b (°C)		Char yield^c (%)
		In N_2	In air	
IV$_a$(H)	212	513	518	60
IV$_b$(H)	224	502	488	54
IV$_c$(H)	237	490	483	53
IV$_d$(H)	223	517	529	60
IV$_e$(H)	269	474	475	59
IV$_f$(H)	207	515	518	53
IV$_g$(H)	213	516	502	62
V$_a$(H)	213	501	517	37
V$_b$(H)	224	510	514	37
V$_c$(H)	224	488	489	33
V$_d$(H)	226	498	500	47
V$_e$(H)	248	480	486	57
V$_f$(H)	210	513	522	42
V$_g$(H)	221	505	521	49

^{a} Baseline shift in the second heating DSC traces, with a heating rate of 15 °C/min.
^{b} Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min.
^{c} Residual weight (%) when heated to 800 °C in nitrogen.

isopropylidene linkage, whereas PEI **IV$_e$** exhibited the highest T_g value of 269 °C due to the presence of rigid tetramethylbiphenyl unit in the diamine moiety. As expected, the methyl- or t-butyl-substituted PEIs exhibited higher T_g value than the corresponding unsubstituted PEIs due to the hindrance effect of the chain rotation in the substituted polymers.

The thermal stability of **IV$_{a-g}$** was evaluated by dynamic TGA conducted at a heating rate of 20 °C/min. The temperatures of 10% weight loss (T_{10}) in nitrogen and air atmospheres were deter-

mined from original TGA thermograms. The T_{10} values of these **IV$_{a-g}$** were recorded in the range of 474–517 °C in nitrogen and 475–529 °C in air. They left more than 53% char yield at 800 °C in nitrogen. It is quite reasonable that the methyl- or t-butyl-substituted PEIs began to decompose at lower temperatures compared with the unsubstituted ones. The TGA data indicate that these fluorinated PEIs had fairly high thermal stability regardless of the introduction of CF_3 groups.

3.5. Dielectric property

The dielectric constants of all PEIs are reported in Table 6. The **IV** series PEIs exhibited the dielectric constants at 1 MHz in the range of 3.15–

Table 6
Dielectric constants of poly(ether imide) films

Polymer	Film thickness (μm)	Dielectric constant (dry)		
		1 kHz	10 kHz	1 MHz
IV$_a$	60	3.46	3.45	3.40
IV$_b$	52	3.51	3.47	3.41
IV$_c$	53	3.76	3.75	3.73
IV$_d$	50	3.21	3.19	3.15
IV$_e$	46	4.16	4.13	4.08
IV$_f$	51	3.79	3.75	3.69
IV$_g$	50	3.66	3.59	3.52
V$_a$	54	4.15	4.05	3.83
V$_b$	60	4.07	3.97	3.77
V$_c$	48	4.94	4.83	4.63
V$_d$	45	4.91	4.66	4.29
V$_e$	50	5.13	5.02	4.78
V$_f$	50	4.91	4.81	4.02
V$_g$	52	3.97	3.89	3.72

4.08. In comparison, the fluorinated PEIs IV_{a-g} showed a lower dielectric constant than the corresponding nonfluorinated V_{a-g}. 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. These results suggested that the CF_3 groups in the polymer chain play an important role in the dielectric property.

4. Conclusions

A series of novel fluorine-containing PEIs **IV** were synthesized from 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]cyclohexane dianhydride (**I**) with various fluorinated aromatic bis(ether amine)s by two-step thermal or chemical imidization method. The PEIs showed good solubility toward organic solvents and could be cast into colorless and strong films. They also exhibited moderately high T_gs and good thermal stability. Thus, this series of PEIs demonstrated a good combination of properties and may be of interest for microelectronics or optoelectronics applications.

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