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Organosoluble and light-colored fluorinated polyimides derived from 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic dianhydrides

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Abstract

A novel fluorinated bis(ether amine) monomer, 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was prepared through the nucleophilic aromatic substitution reaction of 2-chloro-5-nitrobenzotrifluoride and 2,3-dihydroxynaphthalene in the presence of potassium carbonate, followed by catalytic reduction with hydrazine and Pd/C. A series of new fluorine-containing polyimides having inherent viscosities of 0.54 to 1.10 dl/g were synthesized from the diamine with various commercially available aromatic dianhydrides using a standard two-stage process with thermal imidization of poly(amic acid) films. These polyimides were highly soluble in a variety of organic solvents, and most of them afforded transparent, light-colored, and tough films with good tensile strengths. These polyimides exhibited glass transition temperatures (T_gs) of 247–300 °C and showed no significant decomposition below 500 °C under either nitrogen or air atmosphere. Except for the polyimide derived from pyromellitic dianhydride, the polyimide films were almost colorless, with an ultraviolet–visible absorption cutoff wavelength below 400 nm and low b^* values (a yellowness index) of 10.7–41.9. These polyimides had dielectric constants of 3.09 to 3.65 (1 MHz) and moisture absorptions in the range of 0.2–0.3 wt%.
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1. Introduction

Aromatic polyimides are well known as high-performance polymeric materials for their excellent thermal stability, favorable dielectric properties and chemical resistance [1,2]. They are widely used as an interlayer dielectric in semiconductor devices or as substrates for flexible printed circuits. High optical transparency may expand the applications of polyimides; for example, to optoelectric materials such as flexible solar radiation protectors [3], orientation films in liquid crystal display devices [4], optical waveguides for communication interconnects [5], and optical half-waveplates for planar lightwave circuits [6]. However, most of the conventional aromatic polyimide films generally show considerable coloration from light yellow to dark brown due to chain–chain charge transfer and electronic polarization inter-

actions [7]; besides, they are difficult to process in their fully imidized form because of high softening temperatures and limited solubility in commercially available solvents. St Clair et al. [8,9] have shown that polymer backbone alternations that disrupt charge transfer complex formation generally lead to less color polyimide films. It has been demonstrated that polyimides containing hexafluoroisopropylidene (6F) group exhibit high transparency in the UV–Vis region [10]. In the past, a number of fluorine-containing dianhydrides and diamines have been introduced to prepare fluorinated polyimides with low moisture uptake, reflective index and dielectric constant without sacrificing other advantageous polymer properties [11–20]. The incorporation of fluorine-containing groups is also known to enhance the solubility and optical transparency of polyimides.

Recent studies demonstrated that polyimides derived from ether-bridged aromatic diamines with trifluoromethyl (CF$_3$) groups are soluble high temperature polymer materials with low moisture uptake, low dielectric constant, high optical transparency, and low birefringence [21–25].

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We have previously reported the synthesis of 2,3-bis(4-aminophenoxy)naphthalene (2,3-BAPON) and its derived polyimides [26]. However, unless flexible dianhydrides were incorporated, these polyimides showed a limited solubility. As part of our continuing efforts in developing tractable high-performance polymers containing naphthalene units, the present article describes the successful synthesis of a new CF₃-substituted bis(ether amine), 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, and its use for the preparation of soluble polyimides by the reaction of the diamine with dianhydrides. The polymers were subjected to solubility tests and thermal, optical, moisture absorption and dielectric property measurements and were compared to analogous counterparts prepared from a structurally similar bis(ether amine) without the CF₃ groups, 2,3-BAPON. The fluorinated polyimides were expected to exhibit enhanced solubility and optical transparency and decreased dielectric constants because of increased free volume caused by the CF₃ substituents [27].

2. Experimental

2.1. Reagents and solvents

2,3-Dihydroxynaphthalene (Janssen) and 2-chloro-5-nitrobenzotrifluoride (Lancaster) were used without previous purification. According to the synthetic procedure reported previously [26], 2,3-BAPONP (mp 176–177 °C) was prepared by the aromatic nucleophilic substitution reaction of 2,3-dihydroxynaphthalene with *p*-chloronitrobenzene in the presence of potassium carbonate and the subsequent Pd/C-catalyzed reduction using hydrazine as the reducing agent. Pyromellitic dianhydride (PMDA; **III$_a$**, from Lancaster), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; **III$_b$**, from Acros), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA; **III$_d$**, from New Japan Chemical Co.), 4,4′-oxydiphthalic dianhydride (ODPA; **III$_e$**, from Chriskev) were recrystallized from acetic anhydride before use. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA; **III$_c$**, from Chriskev) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA; **III$_f$**, from Chriskev) were purified by sublimation. *N,N*-Dimethylacetamide (DMAc; Fluka) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

2.2. Preparation of 2,3-bis(4-nitro-2-trifluoromethylphenoxy)naphthalene (I)

2,3-Dihydroxynaphthalene (15 g, 0.094 mol) and 2-chloro-5-nitrobenzotrifluoride (42.6 g, 0.189 mol) were dissolved in 90 ml of DMAc in a 300-ml flask. Potassium carbonate (21 g, 0.15 mol) was added to the solution, and the suspension solution was heated at 110 °C for 12 h. The solution was poured in 600 ml of methanol/water (volume ratio 1/1). The precipitated solid was collected, washed thoroughly with water, and dried. The crude product was recrystallized from DMF/methanol to give a off-white product (45 g, 89%), mp 173–174 °C by differential scanning calorimetry (DSC) at a scan rate of 10 °C/min. IR (KBr): 1529, 1348 (–NO₂ stretching), 1288, 1243, 1149, 1116 cm⁻¹ (C–F and C–O stretching). ¹H NMR (DMSO-d₆) δ : 8.42 (d, $J = 2.5$ Hz, 2H, H$_a$), 8.40 (dd, $J = 9.2$, 2.6 Hz, 2H, H$_b$), 8.14 (s, 2H, H$_d$), 8.04 (dd, $J = 6.2$, 3.2 Hz, 2H, H$_e$), 7.64 (dd, $J = 6.2$, 3.2 Hz, 2H, H$_f$), 7.27 (d, $J = 9.1$ Hz, 2H, H$_c$). ¹³C NMR (DMSO-d₆) δ : 159.45 (C⁴), 142.91 (C⁷), 141.93 (C¹), 131.79 (C²), 129.99 (C⁹), 127.66 (C¹⁰), 127.17 (C¹¹), 123.13 (C⁶), 121.95 (quartet, $^1J_{C-F} = 271$ Hz, C¹²), 121.04 (C⁸), 118.13 (quartet, $^2J_{C-F} = 33$ Hz, C⁵), 117.254 (C³). Anal. calcd for C₂₄H₁₂F₆N₂O₆ (538.36): C, 53.54%; H, 2.25%; N, 5.20%. Found: C, 53.59%; H, 2.51%; N, 5.26%.
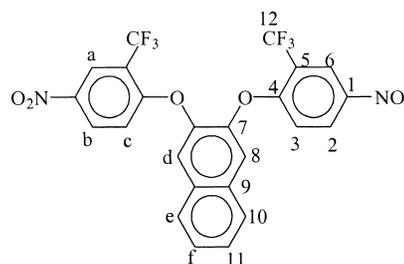
2.3. Preparation of 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (II)

A mixture of dinitro compound **I** (20 g, 0.037 mol), 10% Pd/C (0.2 g), hydrazine monohydrate (10 ml), and ethanol (120 ml) was heated at reflux temperature for 4 h. The resultant solution was filtered while hot to remove Pd/C, and the filtrate was then distilled to remove the solvent. The crude product was purified by recrystallization from ethanol/water to give off-white crystals (16 g, 90%), mp 175–176 °C according to DSC at 10 °C/min. IR (KBr): 3374, 3482 (–NH₂ stretching), 1278, 1226, 1157, 1103 cm⁻¹ (C–O and C–F stretching). ¹H NMR (DMSO-d₆) δ : 7.73 (dd, $J = 6.2$, 3.2 Hz, 2H, H$_e$), 7.34 (dd, $J = 6.2$, 3.2 Hz, 2H, H$_f$), 7.22 (s, 2H, H$_d$), 6.97 (d, $J = 2.5$ Hz, 2H, H$_a$), 6.93 (d, $J = 8.8$ Hz, 2H, H$_c$), 6.85 (dd, $J = 8.8$, 2.0 Hz, 2H, H$_b$). ¹³C NMR (DMSO-d₆) δ : 148.19 (C⁷), 145.64 (C⁴), 142.73 (C¹), 129.72 (C⁹), 126.65 (C¹⁰), 125.10 (C¹¹), 123.50 (quartet, $^1J_{C-F} = 271$ Hz, C¹²), 122.05 (C³), 120.89 (quartet, $^2J_{C-F} = 30$ Hz, C⁵), 118.62 (C²), 113.76 (C⁸), 110.93 (C⁶). Anal. calcd for C₂₄H₁₆F₆N₂O₂ (478.39): C, 60.26%; H, 3.37%; N, 5.86%. Found: C, 60.26%; H, 3.39%; N, 5.76%.
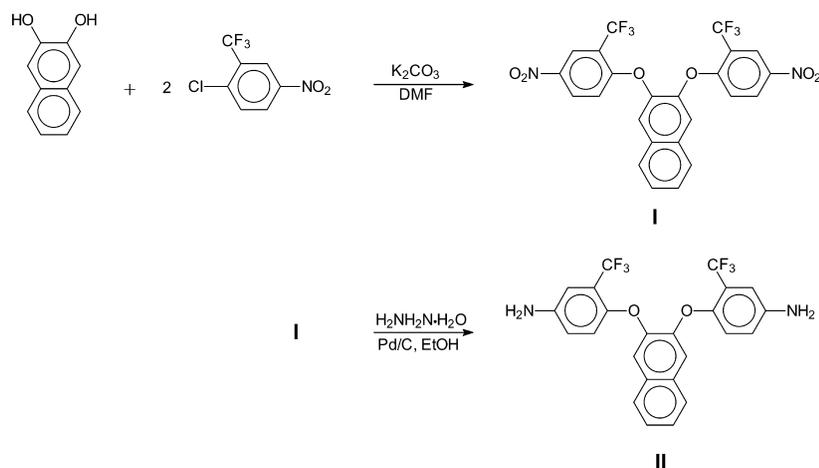
Scheme 1. Synthesis of diamine **II**.
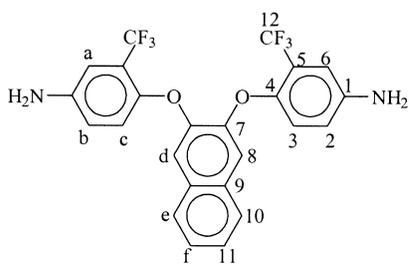
2.4. Polymer synthesis

The synthesis of polyimide V_a is used as an example to illustrate the general synthetic route used to prepare the polyimides. Diamine **II** (0.478 g, 1 mmol) was dissolved in 6.7 ml of dried DMAc in a 50-ml flask. After the diamine was dissolved completely, 0.218 g (1 mmol) PMDA (or III_a) was added to the solution in one portion. The mixture was stirred at room temperature for 12 h to form a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) (IV_a) was 0.96 dl/g, measured in DMAc at a concentration of 0.5 dl/g at 30 °C. The poly(amic acid) solution then was poured into a glass culture dish ($\phi = 9$ cm), which was placed in an 80 °C oven for 3 h for the slow release of the casting solvent. The semidried poly(amic acid) film was further dried and imidized by sequential heating at 120 °C for 10 min, 150 °C for 10 min, 180 °C for 10 min, 210 °C for 10 min, and 250 °C for 30 min. By being soaked in water, a flexible polyimide film of V_a was released from the glass surface. The inherent viscosity of V_a in DMAc at a 0.5 g/dl concentration at 30 °C was 0.87 dl/g. IR (film): 1778, 1720 (imide carbonyl asym. and sym. stretching), 1369 (C–N stretching), 1091, 722 cm^{-1} (imide ring deformation).

2.5. Characterization methods

Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were run in a Perkin–Elmer model 2400 C, H, N analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 500 MHz FT-NMR spectrometer. The inherent viscosities were determined at 0.5 g/dl concentration using a Cannon–Fenske viscometer at 30 °C. 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 (100 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a TA Instruments DSC 2010 in flowing nitrogen with heating rate of 15 °C/min. Glass transition temperatures (T_g) were read as the midpoint of the heat capacity jump and were taken from the second heating scan after quick cooling down from 400 °C. 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. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. The measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and 30–50 μm thick), and an average of at least three replicas was used. The color intensity of the polymers was evaluated by a Gretag-Macbeth Color-eye 3100 colorimeter (made in New Windor, NY, USA). Measurements were performed with films of 30–50 μm in thickness, using an observational angle of 10° and a CIE (Commission International de l'Eclairage)-D illuminant. A CIE LAB color difference equation was used. Ultraviolet–visible (UV–Vis) spectra of the polymer films were recorded on a Simadzu UV-1601 UV–Vis spectrophotometer. Dielectric property of the polymer films was measured by the parallel-plate capacitor method with an 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. The equilibrium moisture absorption was determined by weighing the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.
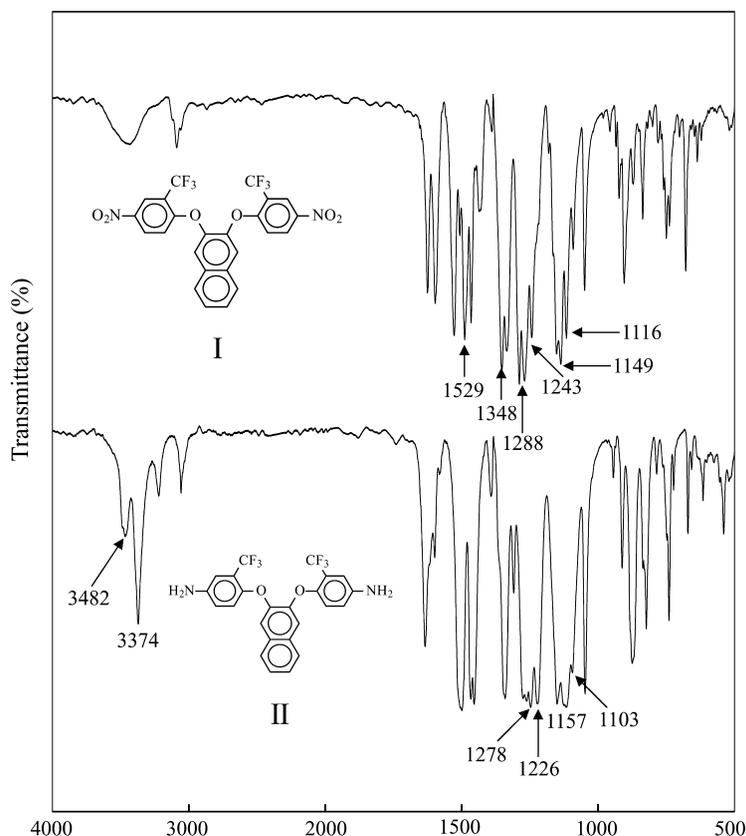
Fig. 1. FTIR spectra of dinitro compound **I** and diamine **II**.

3. Results and discussion

3.1. Monomer synthesis

The new CF_3-containing bis(ether amine) **II** was prepared in two steps according to a well-established procedure [28–31], as shown in Scheme 1. The first step involved a nucleophilic aromatic substitution reaction between 2-chloro-5-nitrobenzotrifluoride with 2,3-dihydroxynaphthalene in the presence of potassium carbonate. The diamine **II** was readily obtained in high yields by the Pd/C-catalyzed reduction of the intermediate dinitro compound **I** with hydrazine hydrate in refluxing ethanol. Characterization by IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis indicated high purity with the data consistent with the expected structure. The FTIR spectra of dinitro compound **I** and diamine **II** are illustrated in Fig. 1. The nitro group of compound **I** gave two characteristic bands at 1529 and 1348 cm^{-1} (NO$_2$ asym. and sym. stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical N–H stretching bands in the region of 3300–3500 cm^{-1}. Fig. 2 shows the ^{1}H and ^{13}C NMR spectra of diamine **II**. The ^{1}H NMR spectra confirm that the nitro groups were completely converted into the amino groups by the high field shift of the aromatic protons and by the signal at 5.44 ppm corresponding to the amino

protons. After reduction, most of the resonance signals of phenylene carbons shifted to a higher field due to the electron-donating nature of the amino group. The ^{13}C NMR spectra of **I** and **II** show two obvious quartets because of the heteronuclear ^{13}C–^{19}F coupling. The large quartets centered at about 121.95 ppm for **I** and 123.50 for **II** are peculiar to the CF$_3$ carbons. The one-bond C–F coupling constant in these cases is about 271 Hz. The CF$_3$-attached carbon C^5 also shows a clear quartet centered at about 118.13 ppm for **I** and at 120.89 ppm for **II** with a smaller coupling constant of about 30 Hz due to two-bond C–F coupling. All the spectroscopic data obtained were in good agreement with the proposed structures.

3.2. Polymer synthesis

All the fluorinated polyimides **V$_a$**–**V$_f$** were synthesized in two steps by the polymerization reactions of diamine **II** with six commercially available dianhydrides **III$_a$**–**III$_f$** to form poly(amic acid)s **IV$_a$**–**IV$_f$**, followed by thermal imidization (Scheme 2). The amino groups in diamine **II** were less basic than a normal aromatic diamine because of the inductive deactivation of the CF$_3$ group, a result confirmed by the slow polymerization rate inferred from the data in Fig. 3. As shown in Fig. 3, the reaction of BTDA with untrifluoromethylated 2,3-BAPON proceeded relatively fast and the inherent viscosity of the resulting
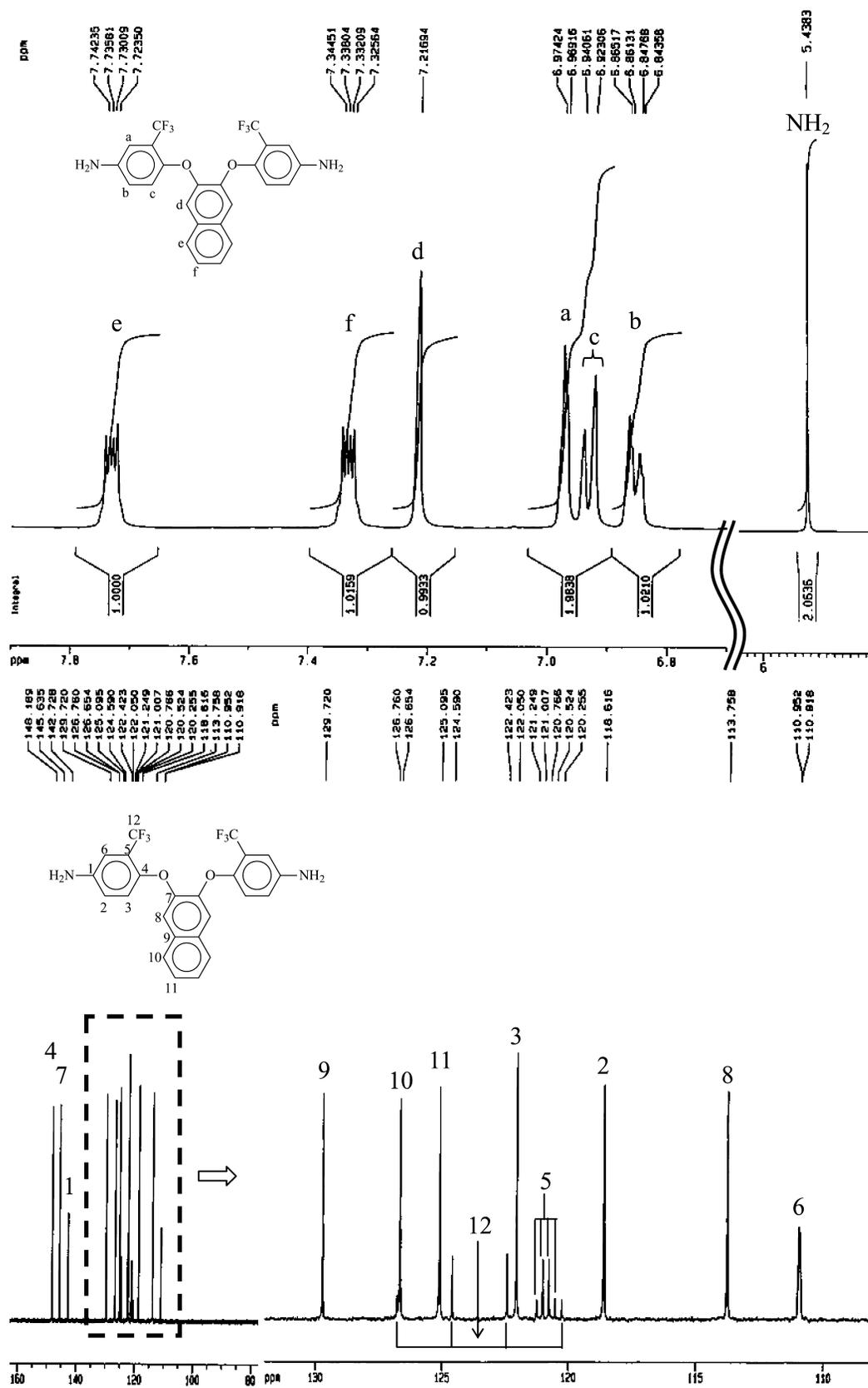
Fig. 2. ^{1}H and ^{13}C NMR spectra of diamine **II** in DMSO-d$_6$.

Scheme 2. Synthesis of polymides.
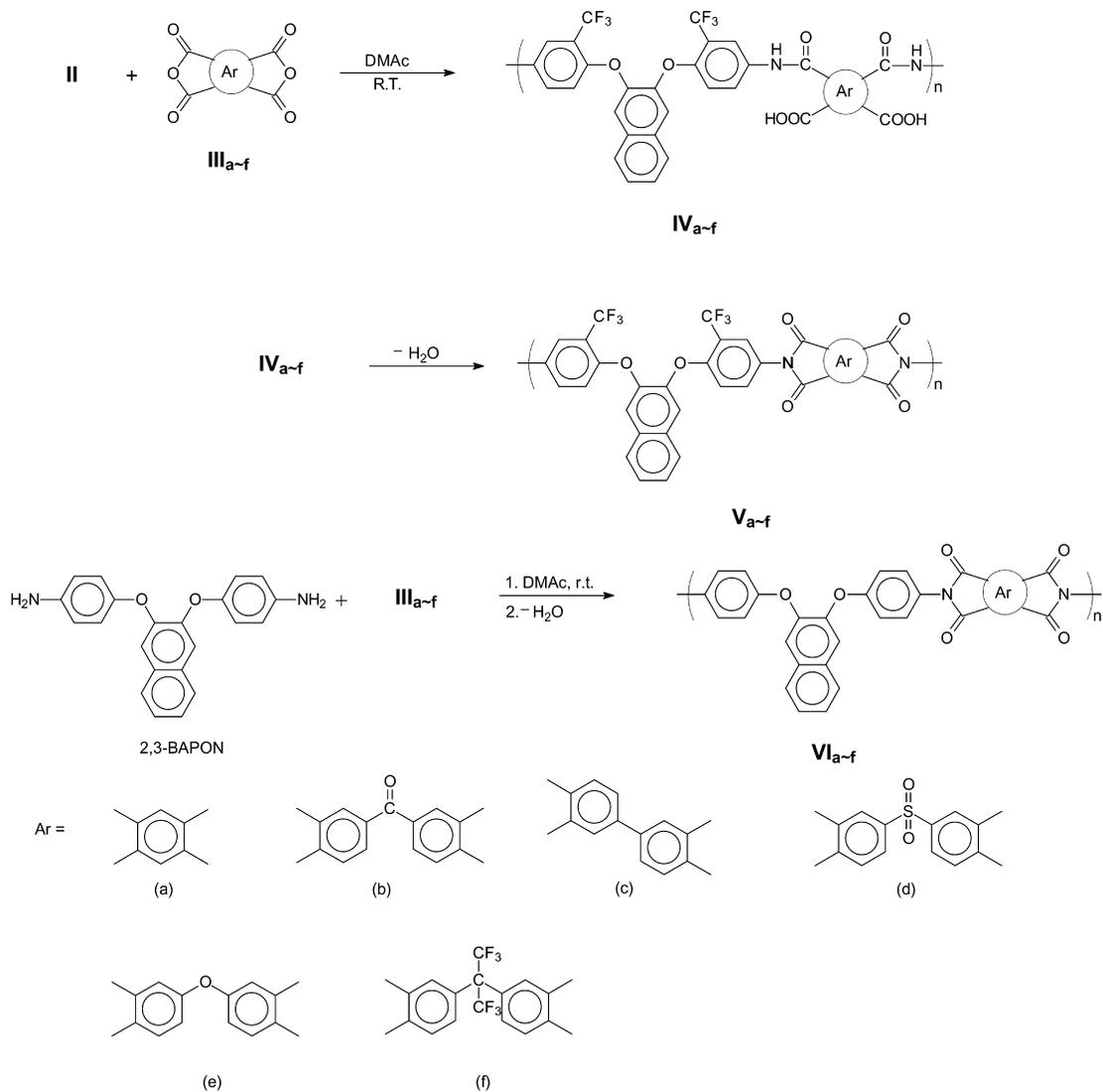
Table 1
Inherent viscosity of poly(amic acid)s and polyimides and elemental analysis of the fluorinated polyimides

Inherent viscosity of polymers				Elemental analysis (%) of polyimides				
Code	η_{inh}^{a} (dl/g)	Code	η_{inh}^{a} (dl/g)	Formula (formula weight)		C	H	N
IV$_a$	0.96	**V$_a$**	0.87	$(C_{34}H_{14}F_6N_2O_6)_n$	Calcd	61.81	2.14	4.24
				$(660.49)_n$	Found	60.14	2.09	4.18
IV$_b$	0.85	**V$_b$**	1.10	$(C_{40}H_{18}F_6N_2O_6)_n$	Calcd	65.21	2.46	3.80
				$(736.58)_n$	Found	64.77	2.40	3.85
IV$_c$	0.90	**V$_c$**	0.68	$(C_{41}H_{18}F_6N_2O_7)_n$	Calcd	64.39	2.37	3.67
				$(764.59)_n$	Found	63.58	2.39	3.84
IV$_d$	0.92	**V$_d$**	0.76	$(C_{40}H_{18}F_6N_2O_8S)_n$	Calcd	59.99	2.27	3.50
				$(800.64)_n$	Found	58.40	2.18	4.04
IV$_e$	0.73	**V$_e$**	0.54	$(C_{40}H_{18}F_6N_2O_7)_n$	Calcd	63.82	2.41	3.72
				$(752.58)_n$	Found	62.35	2.20	3.71
IV$_f$	0.82	**V$_f$**	0.54	$(C_{43}H_{18}F_{12}N_2O_6)_n$	Calcd	58.23	2.05	3.16
				$(886.61)_n$	Found	57.07	1.76	3.06

^{a} Measured at a polymer concentration of 0.5 g/dl in DMAc at 30 °C.
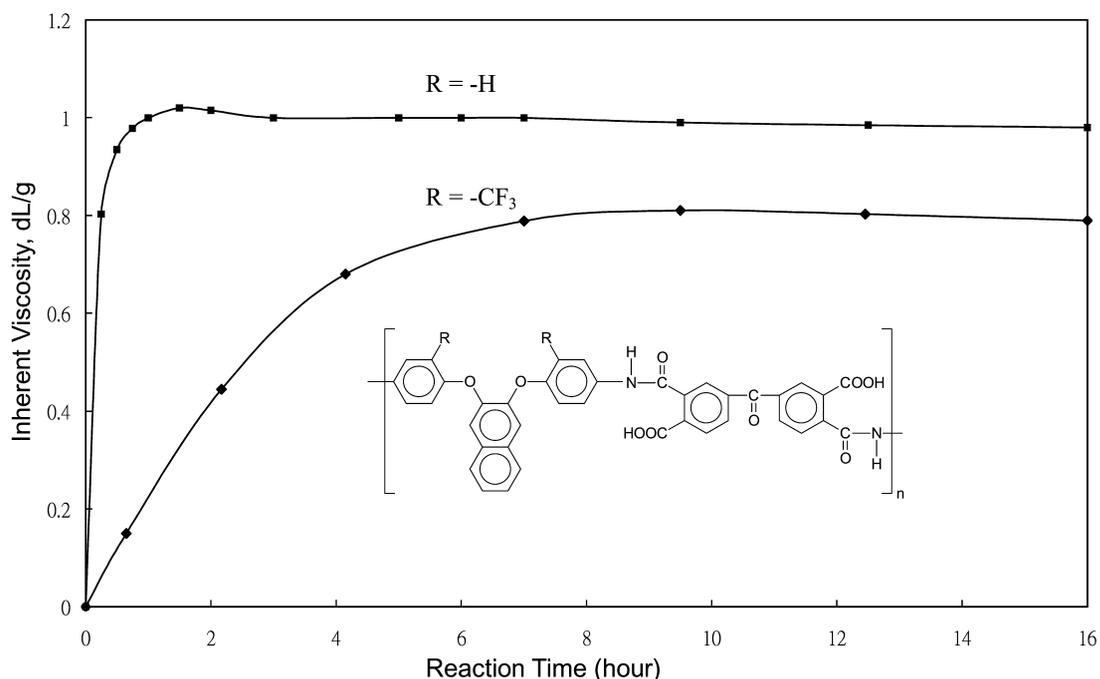
Fig. 3. Viscosity change of poly(amic acid)s prepared in DMAc at 10% solid content at room temperature.

poly(amic acid) increased rapidly within 30 min; the inherent viscosity reached about 1.0 dl/g after 1 h. In contrast, the reaction of BTDA with trifluoromethylated diamine **II** proceeded relatively slowly and the inherent viscosity reached only 0.8 dl/g after 7 h. However, such CF_3-substituted diamine was still sufficiently reactive to give high molecular weight poly(amic acid)s when they were allowed to polymerize for a sufficient length of time (ca. 12 h). Diamine **II** mostly likely retained its reactivity because the amino group is *meta* to the CF_3 group. As shown in Table 1, the inherent viscosities of the intermediate poly(amic acid)s were in the range of 0.73–0.96 dl/g.

The molecular weights of all the poly(amic acid)s are sufficiently high to permit the casting of flexible and tough poly(amic acid) films, which are subsequently converted into tough polyimide films by extended heating at elevated temperatures. These polyimides exhibited excellent solubility in polar solvents such as DMAc. Therefore, the characterization of solution viscosity was carried out without any difficulty, and the inherent viscosities of these polyimides were recorded in the range of 0.54–1.10 dl/g, as measured in DMAc. For the sake of comparison, a series of reference polyimides VI_a–VI_f were also synthesized from 2,3-BAPON and dianhydrides III_a–III_f. The inherent

Table 2
Solubility behavior of polyimides

Polymers	Solvents[a]										
	NMP	DMAc	DMF	DMSO	*m*-Cresol	Pyridine	Dioxane	THF	CH_2Cl_2	Acetone	H_2SO_4
V_a	++	++	++	++	++	++	++	++	++	++	++
V_b	++	++	++	++	+	+	+	++	+ −	+ −	++
V_c	++	++	++	++	++	+	+	+	++	+ −	++
V_d	++	++	++	++	++	++	++	++	++	++	++
V_e	++	++	++	++	++	++	++	++	++	++	++
V_f	++	++	++	++	++	++	++	++	++	++	++
VI_a	−	−	−	−	−	−	−	−	−	−	++
VI_b	+	+ −	+ −	−	+	−	−	−	−	−	++
VI_c	++	−	−	−	++	+ −	S	−	S	S	++
VI_d	++	++	+	−	++	−	S	−	S	S	++
VI_e	++	++	+	+	++	+ −	−	−	+ −	S	++
VI_f	++	++	++	++	++	++	++	++	++	++	++

[a] The qualitative solubility was tested with 10-mg samples in 1 ml of solvent. ++, soluble at room temperature; +, soluble on heating; + −, partial soluble on heating; S, swelling on heating; −, insoluble on heating. Solvents: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran.
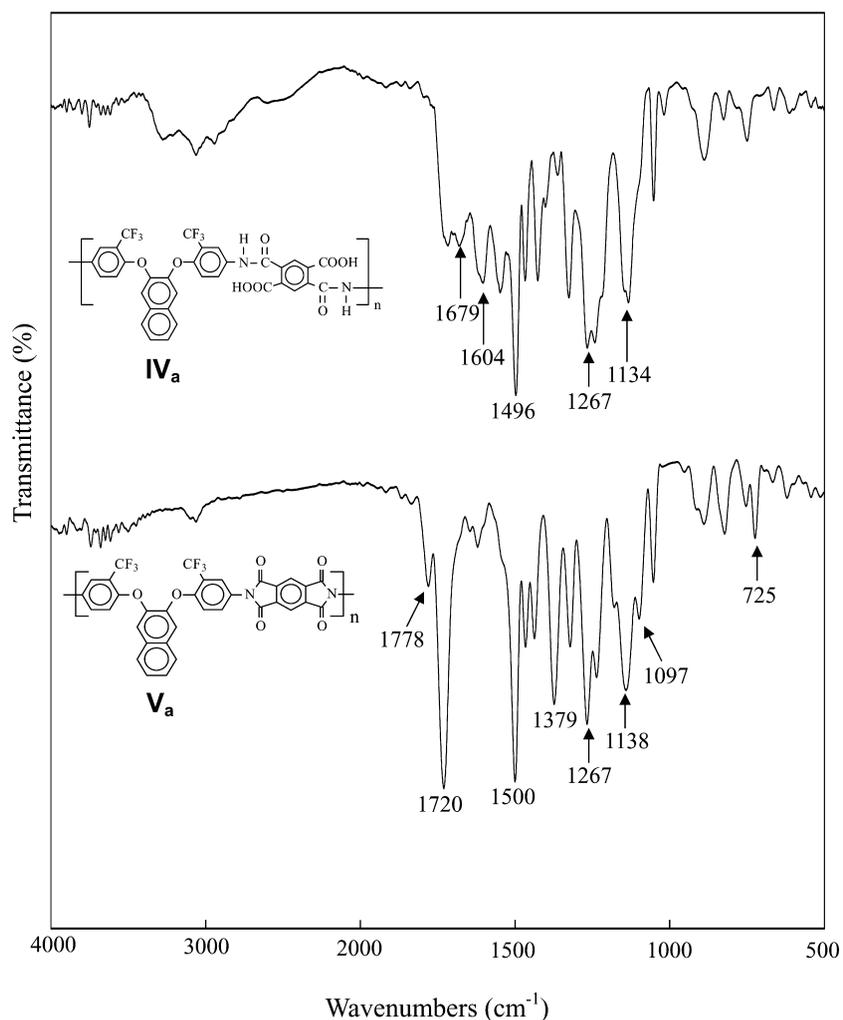
Fig. 4. FTIR spectra of poly(amic acid) IV_a and polyimide V_a.

viscosities of the precursor poly(amic acid)s of VI_a–VI_f were in the range of 1.02–1.85 dl/g, indicating high molecular weight polymer formation.

The formation of polyimides was confirmed by means of elemental analysis and IR and NMR spectroscopy. The results of elemental analyses of all the fluorinated polyimides are listed in Table 1. The elemental analysis values were in good agreement with the calculated values of the proposed structures. IR spectroscopy allows monitoring of the imide ring formation during thermal curing. A typical set of IR spectra for the thin films of poly(amic acid) IV_a and polyimide V_a is shown in Fig. 4. All the fluorinated polyimides exhibited characteristic imide group absorptions around 1780 and 1720 (typical of imide carbonyl asymmetrical and symmetrical stretching), 1380 (C–N stretching), and 1100 and 725 cm^{-1} (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. Fig. 5 shows a typical set of ^{1}H

and ^{13}C NMR spectra of polyimide V_a in DMSO-d$_6$, where all the peaks have been readily assigned to the hydrogen and carbon atoms of the repeating unit.

3.3. Solubility properties

The solubility properties of all polyimides are reported in Table 2. All the fluorinated polyimides V_a to V_f showed an excellent solubility in aprotic polar solvents such as NMP, DMAc, DMF, and DMSO and were also soluble in less polar solvents like *m*-cresol, pyridine, dioxane, and THF. Most of them were soluble even in dichloromethane and acetone. The excellent solubility associated with these polyimides might be due in part to the presence of the laterally attached 2,3-naphthalenediyl units and the bulky CF$_3$ substituents. On comparing the solubility behaviors with polyimides V_a–V_e, the analogous polyimides VI_a–VI_e revealed a relatively decreased solubility. The large differences in solubility between the V_a–V_e and VI_a–VI_e series could be attributable to the molecular asymmetry and the presence of bulky CF$_3$ groups in the former. Molecular
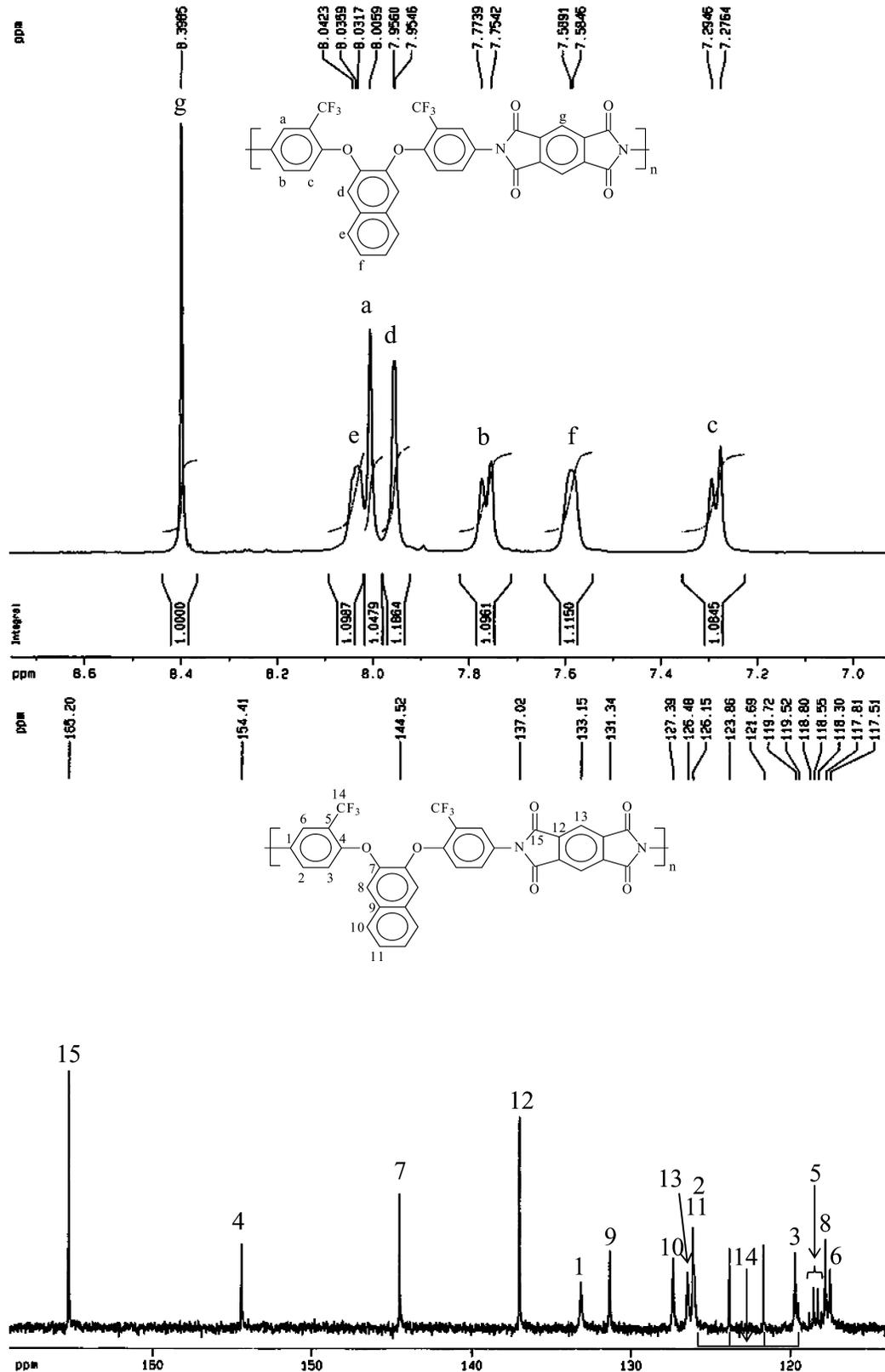
Fig. 5. ^{1}H and ^{13}C NMR-Spectra of polymide $\mathbf{V_a}$ in DMSO-d$_6$.

Table 3
Color coordinates and cutoff wavelength (λ_0) and transparency at 500 nm from UV–Vis spectra of polyimide films

Code	Film thickness (μm)	b^*	a^*	L^*	λ_0 (nm)	Transparency at 500 nm (%)
V_a	42	69.0	−13.9	97.1	412	79
V_b	31	41.9	−12.5	98.8	397	82
V_c	27	29.7	−8.6	98.6	394	86
V_d	32	37.8	−10.5	97.9	391	85
V_e	37	18.3	−7.1	99.4	370	87
V_f	38	10.7	−4.1	99.7	365	89
VI_a	27	84.3	−4.7	93.2	428	59
VI_b	31	88.2	−1.0	91.2	440	54
VI_c	43	54.7	−11.2	95.7	416	68
VI_d	63	67.3	−6.6	91.6	420	76
VI_e	45	33.5	−8.8	96.5	389	83
VI_f	49	30.0	−9.7	98.1	385	76
PMDA/ODA	41	83.9	5.1	88.1	444	60

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.

asymmetry and the CF_3 group inhibit close packing, thus reducing the chain–chain interactions to enhance solubility.

3.4. Color intensity and optical transparency

The color intensities of the polyimides were elucidated from the yellowness (b^*) or redness (a^*) indices observed by a colorimeter. For comparison, a standard polyimide from PMDA and 4,4′-oxydianiline (ODA) was also prepared and characterized by its color intensity. The color coordinates of these polyimides are given in Table 3. The results shown in Table 3 indicate that all the **V** series polyimides showed a lower b^* value in comparison with the **VI** series analogues without the CF_3 substituents. The 6FDA and ODPA produced nearly colorless polyimide films in contrast to other dianhydrides, and these can be explained from the decreased intermolecular interactions [31]. Thin films were also measured for optical transparency using UV–Vis spectroscopy. Fig. 6 shows the UV–Vis spectra of the polyimide films, and the cutoff wavelength (absorption

edge, λ_0) values and the percentage transmittance at 500 nm from these spectra are reported in Table 3. Except for V_a, the other **V** series polyimides had λ_0 shorter than 400 nm, and all the **V** series polyimides exhibited high optical transparency of 79–89%. Consistent with the results obtained from the colorimeter, all the **V** series polyimides containing pendant CF_3 group revealed shorter λ_0 and higher optical transparency than their respective CF_3-free analogous polyimides **VI**. The bulky and electron-withdrawing CF_3 group in the diamine moieties was presumably effective in decreasing charge-transfer complexes between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties).

3.5. Thermal and mechanical properties

DSC and TGA were used to evaluate the thermal properties of the polymers. The thermal behavior data of all the polyimides are summarized in Table 4. DSC
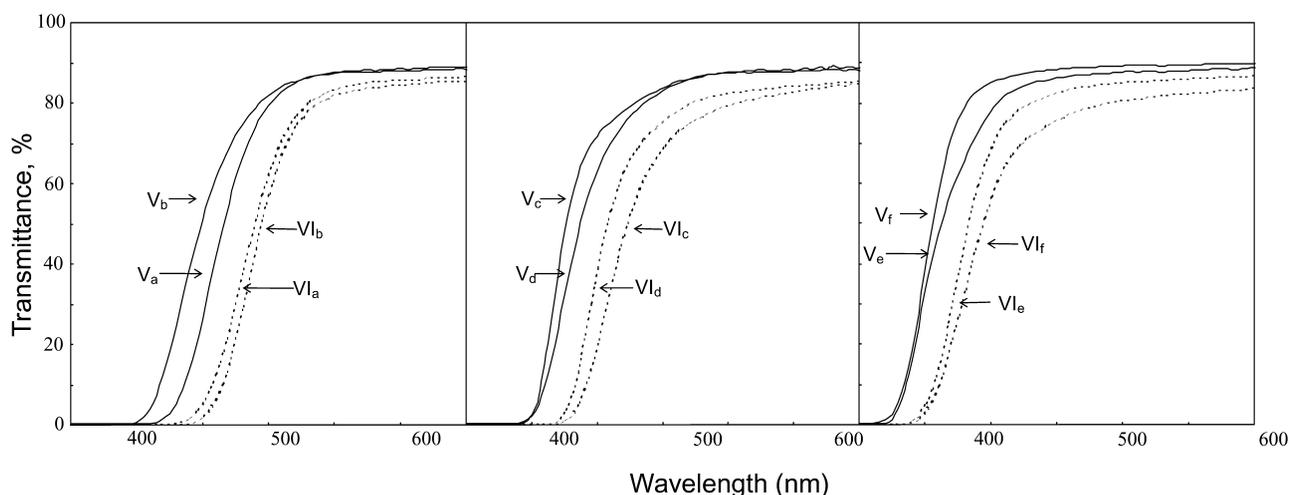

Fig. 6. UV–Vis spectra of polyimide films.

Table 4
Thermal and tensile properties of polyimides

Polymer	T_g^a (°C)	T_{10}^b (°C)		Char yield^c (%)	Tensile strength (MPa)	Elongation (%)	Modulus (GPa)
		In N$_2$	In air				
V_a	300	588	569	52	63	4	2.0
V_b	259	586	573	57	108	8	2.2
V_c	275	592	581	60	124	10	2.4
V_d	274	531	536	54	74	5	2.3
V_e	247	588	575	57	122	10	2.2
V_f	268	561	551	53	108	8	2.2
VI_a	315	570	570	57	89	8	2.0
VI_b	269	566	568	61	109	6	2.8
VI_c	267	578	582	65	109	8	2.5
VI_d	278	541	550	54	99	6	2.4
VI_e	241	571	573	55	122	9	2.3
VI_f	272	554	564	56	72	5	2.0

[a] Midpoint temperature of the baseline shift in the second DSC heating traces (rate = 15 °C/min) of the sample after quenching from 400 °C.
[b] Temperatures at which 10% weight loss were recorded by TG at a heating rate of 20 °C/min.
[c] Residual weight (%) when the sample were heated to 800 °C in nitrogen.

experiments were conducted at a heating rate of 15 °C/min in nitrogen. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so the glass transition temperatures (T_g) of all the polyimides could be easily read in the subsequent heating DSC traces. The T_g values of the fluorinated polyimides V_a–V_f were in the range of 247–300 °C. The decreasing order of T_g generally correlated with that of chain flexibility. As expected, the polyimide V_e obtained from ODPA showed the lowest T_g due to the presence of a flexible ether linkage between the phthalimide units, and the polyimide V_a derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit. The range of T_g values for the VI series polyimides was 241–315 °C. Slightly lower T_gs for the V series in comparison with the VI series might be a result of reduced chain–chain interactions and poor chain packing due to the bulky pendant CF$_3$ groups. The thermal stability

of the polyimides was evaluated by TGA. The temperatures for 10% weight loss (T_{10}) of the fluorinated polyimides (V_a–V_f) in nitrogen and air atmospheres stayed within 536–581 °C and within 531–588 °C, respectively. They left more than a 52% char yield at 800 °C in nitrogen. The TGA data indicated that these polyimides had fairly high thermal stability comparable with that of polyimides VI_a–VI_f derived from nonfluorinated 2,3-BAPON. As shown in Table 4, the polyimides had tensile strengths of 63–124 MPa, elongations to break of 5–10%, and initial moduli of 2.0–2.8 GPa, indicating that they could be cast into flexible and strong films.

3.6. Moisture absorption and dielectric properties

The moisture absorption and dielectric constants of all polyimides are presented in Table 5. In comparison,

Table 5
Moisture absorption and dielectric constants of the polyimides

Polymer	Film thickness (μm)	Moisture absorption (%)	Dielectric constants			
			1 kHz	10 kHz	1 MHz	40 MHz
V_a	30	0.22	3.61	3.59	3.53	3.57
V_b	30	0.30	3.24	3.21	3.15	3.07
V_c	32	0.25	3.23	3.24	3.19	3.21
V_d	40	0.30	3.77	3.76	3.65	3.64
V_e	45	0.25	3.61	3.62	3.56	3.74
V_f	48	0.21	3.16	3.14	3.09	3.05
VI_a	25	1.35	4.62	4.63	4.51	4.54
VI_b	45	1.29	4.25	4.29	4.21	4.28
VI_c	45	1.39	4.03	4.06	3.96	3.95
VI_d	55	1.39	4.51	4.54	4.45	4.50
VI_e	56	0.87	4.25	4.29	4.21	4.28
VI_f	42	0.73	3.86	3.91	3.83	3.85
PMDA/ODA	29	1.84	3.89	3.85	3.67	3.60

polyimides V_a–V_f exhibited lower moisture absorptions and dielectric constants than the corresponding VI_a–VI_f counterparts and PMDA/ODA polyimide film. The dielectric constant is minimized for polyimide V_f (6FDA + II) in which both the dianhydride and diamine portions of the polymer contain CF_3 groups. The decreased dielectric constants of the fluorinated polyimides could be attributed to the presence of bulky CF_3 groups, which result in a less efficient chain packing and an increase in the fractional free volume and hydrophobicity [27].

4. Conclusions

A new fluorinated bis(ether amine) monomer, 2,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (**II**), was prepared through the nucleophilic substitution reaction of 2,3-dihydroxynaphthalene and 2-chloro-5-nitrobenzotrifluoride, followed by hydrazine catalytic reduction of the dinitro intermediate. A series of organosoluble and light-colored fluorinated polyimides have been synthesized from **II** with various aromatic dianhydrides. These polyimides could be cast into flexible and strong films with excellent thermal stability, moderate to high T_gs (247–300 °C), and low dielectric constants. Thus, these polyimides exhibit a good combination of properties required for high-performance materials and demonstrate a promising potential for future applications.

Acknowledgements

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