

Organosoluble, low-dielectric-constant fluorinated polyimides based on 2,6-bis(4-amino-2-trifluoromethylphenoxy)naphthalene

Chin-Ping Yang, Sheng-Huei Hsiao* and Cheng-Lin Chung

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, Section 3, Taipei 104, Taiwan, China

Abstract: A novel fluorinated bis(ether amine) monomer, 2,6-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was prepared through the nucleophilic aromatic substitution reaction of 2-chloro-5-nitrobenzotrifluoride and 2,6-dihydroxynaphthalene in the presence of potassium carbonate, followed by catalytic reduction with hydrazine and Pd/C in ethanol. A series of novel trifluoromethylated polyimides were synthesized from the diamine with various commercially available aromatic tetracarboxylic dianhydrides using a two-stage process with thermal imidization of poly(amic acid) films. Most of the resulting polyimides were highly soluble in a variety of organic solvents and could afford transparent and tough films via solution casting. These polyimides exhibited moderately high glass transition temperatures (T_g s) of 249–311 °C, high thermal stability and good mechanical properties. Low moisture (0.19–0.85 %), low dielectric constants (2.49–3.59 at 10 kHz), and low color intensity were also observed. For a comparative study, a series of analogous polyimides based on 2,6-bis(4-aminophenoxy)naphthalene were also prepared and characterized.

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Keywords: fluorinated polyimides; solubility; optical transparency; low dielectric constants

INTRODUCTION

Aromatic polyimides are well known as high-performance polymeric materials for their excellent thermal, mechanical and electrical properties and they have been widely used in microelectronic and aerospace engineering.¹ Most of the conventional aromatic polyimide films generally show considerable coloration from light yellow to dark brown due to charge transfer between chains and electronic polarization interactions;² besides, they are difficult to process in their fully imidized form because of high softening temperatures and limited solubility in commercially available solvents, thus possibly narrowing down their applicability. To overcome these drawbacks, polymer structure modification is necessary. Much effort has been put into designing and synthesizing new dianhydrides^{3–11} and/or diamines,^{12–18} thus producing a great variety of soluble and processable polyimides for various purposes.

One of the most attractive properties of polyimide materials for microelectronic applications is their low dielectric constants. For a polymer structure with a low dielectric constant, recurring units with low polarity and low polarizability have to be used.¹⁹ For example,

the incorporation of the aliphatic adamantane or diamantane moiety is known to result in low dielectric constants because of high hydrophobicity, low polarity, and increased free volume.^{20–23} It is also well known that the incorporation of fluorinated substituents into polymers decreases the dielectric constant, due to the low electronic polarizability of the C–F bond, as well as the increase of fractional free volume which accompanies the replacement of methyl groups by trifluoromethyl (CF₃) groups. Thus, many fluorinated polyimides have been developed in order to reduce the dielectric constant.^{24–28} An additional positive effect of fluorinated substituents is to enhance the solubility and optical transparency of polyimides.

Recent studies demonstrated that polyimides derived from ether-bridged aromatic diamines with trifluoromethyl (CF₃) groups are soluble high-temperature polymeric materials with low moisture uptake, low dielectric constant, high optical transparency and low birefringence.^{29–43} As part of our recent efforts in developing new fluorinated polyimides containing naphthalene units,^{40–43} in the present study a new trifluoromethylated bis(ether amine), 2,6-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was synthesized and subsequently polycondensed with

* Correspondence to: Sheng-Huei Hsiao, Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, Section 3, Taipei 104, Taiwan, China

E-mail: shhsiao@ttu.edu.tw

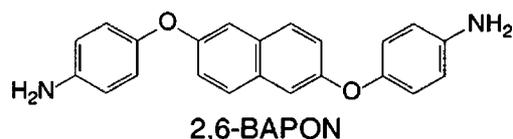
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various commercially available aromatic dianhydrides to produce a series of novel fluorinated polyimides. The polymers were subjected to solubility tests and thermal, optical, moisture-absorption and dielectric-property measurements, and were compared with analogous counterparts prepared from a structurally similar bis(ether amine) without the CF_3 groups, 2,6-bis(4-aminophenoxy)naphthalene (2,6-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 CF_3 substituents.



EXPERIMENTAL

General directions

2,6-Dihydroxynaphthalene (Tokyo Chemical Industry; TCI), potassium carbonate (K_2CO_3) (Fluka), 2-chloro-5-nitrobenzotrifluoride (Acros), *p*-chloronitrobenzene (Acros), 10 % palladium on charcoal (Pd/C) (Fluka), and hydrazine monohydrate (Acros) were used as received. As reported previously,⁴⁴ 2,6-BAPON (mp 202–203 °C) was prepared by the aromatic nucleophilic substitution reaction of 2,6-dihydroxynaphthalene with *p*-chloronitrobenzene in the presence of potassium carbonate, and subsequent reduction of the intermediate dinitro compound using hydrazine as the reducing agent and palladium as the catalyst. Pyromellitic dianhydride (PMDA) (**3a**) (Aldrich) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (**3c**) (Aldrich), were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) (**3b**) (Oxychem), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA) (**3d**) (New Japan Chemical Co), 4,4'-oxydiphthalic dianhydride (ODPA) (**3e**) (Oxychem) and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (**3f**) (Hoechst Celanese) were heated at 250 °C under vacuum for 3 h prior to use. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

Elemental analyses were run in a Perkin-Elmer model 2400 CHN analyzer. Infrared spectra were recorded on a Horiba FT-720 Fourier-transform infrared spectrometer.

¹H and ¹³C NMR spectra were measured on a Bruker Avance 500 MHz FT-NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane as the internal reference.

The inherent viscosities of the polymers were determined at 0.5 g dl⁻¹ concentration using an Ubbelohde viscometer at 30 °C.

Gel permeation chromatography (GPC) was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5- μm Styragel HR-2 and HR-4 columns (7.8 mm I.D. \times 300 mm) connected in series were used with tetrahydrofuran (THF) as eluent and were calibrated with narrow polystyrene standards.

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD 6000 X-ray diffractometer with a graphite monochromator, using nickel-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 20 mA).

An Instron universal tester model 4400R 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⁻¹ were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long and about 0.09 mm thick), and an average of at least five individual determinations was used.

The color intensity of the polymers was evaluated by a Gretag-Macbeth Color-eye 3100 colorimeter. Measurements were performed with films (28–42 μm thick) with an observational angle of 10° and a Commission International de l'Eclairage (CIE)-D illuminant. A CIE LAB color difference equation was used.

Ultraviolet-visible (UV-vis) spectra of the polymer films were recorded on a Shimadzu UV-visible spectrophotometer UV-1601.

Dielectric properties of the polymer films were tested by the parallel-plate capacitor method using a HP-4194A impedance/gain phase analyzer. Gold electrodes were vacuum deposited on both surfaces of dried films. Experiments were performed at 25 °C in a dry chamber.

Thermogravimetric analysis (TGA) was conducted with a Perkin-Elmer Pyris 1 TGA. Experiments were carried out on approximately 6–8-mg film samples heated in flowing nitrogen or air (flow rate 30 cm³ min⁻¹) at a heating rate of 20 °C min⁻¹.

Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer Pyris 1 DSC at a scan rate of 20 °C min⁻¹ in flowing nitrogen (20 cm³ min⁻¹). Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400 °C at a cooling rate of 200 °C min⁻¹. The equilibrium water uptake was determined by the weighing of the changes in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

Monomer synthesis

2,6-Bis(2-trifluoromethyl-4-nitrophenoxy)naphthalene (1)

2,6-Dihydroxynaphthalene (8.0 g, 0.05 mol) and 2-chloro-5-nitrobenzotrifluoride (23.0 g, 0.10 mol) were

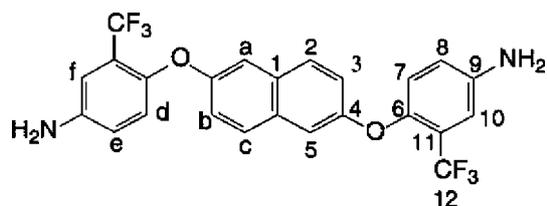
dissolved in 100 ml of *N,N*-dimethylformamide (DMF) in a 300-ml round-bottomed flask. Then, potassium carbonate (14.0 g, 0.10 mol) was added, and the suspension mixture was heated at 100 °C for 8 h. The mixture was allowed to cool and then poured into 600 ml of water to give a yellow solid, which was collected, washed repeatedly with water, and dried. The crude product was recrystallized from methanol/water to give pale-yellow crystals (22.0 g, 82 %); mp = 229–231 °C (onset to peak top temperature), by differential scanning calorimetry (DSC) at a scan rate of 2 °C min⁻¹; IR (KBr): 1529, 1340 (–NO₂), 1255 (C–O stretch), 1153 cm⁻¹ (C–F stretch); Anal Calcd for C₂₄H₁₂F₆N₂O₆ (538.36): C, 53.5; H, 2.24; N, 5.20 %; Found: C, 53.35; H, 2.10; N, 5.25 %.

2,6-Bis(4-amino-2-trifluoromethylphenoxy)naphthalene (2)

A mixture of the purified dinitro compound **1** (16.0 g, 0.03 mol), 10 % Pd/C (0.15 g), ethanol (100 ml), and hydrazine monohydrate (10 ml) was heated at reflux temperature for about 8 h. The resultant clear, darkened solution was filtered 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 pale-yellow (almost colorless) crystals (11.5 g, 82 %); mp = 188–189 °C by DSC (2 °C min⁻¹); IR (KBr): 3487, 3392 (N–H stretch), 1228 (C–O stretch), 1140 cm⁻¹ (C–F stretch); ¹H NMR (CDCl₃, δ, ppm): 7.78 (d, *J* = 9.7 Hz, 2H, H_c), 7.18 (d, *J* = 9.7 Hz, 2H, H_b), 7.19 (s, 2H, H_a), 6.96 (d, *J* = 2.6 Hz, 2H, H_f), 6.92 (d, *J* = 8.7 Hz, 2H, H_d), 6.84 (dd, *J* = 8.7, 2.4 Hz, 2H, H_e), 5.46 (s, 4H, –NH₂); ¹³C NMR (CDCl₃, δ, ppm): 155.4 (C⁴), 145.9 (C⁶), 142.4 (C⁹), 130.0 (C¹), 128.9 (C²), 123.5 (quartet, ¹*J*_{C–F} = 272 Hz, C¹²), 121.5 (quartet, ²*J*_{C–F} = 30 Hz, C¹¹), 123.2 (C⁵), 119.2 (C⁷), 118.7 (C⁸), 111.2 (C³), 110.8 (doublet, ³*J*_{C–F} = 5 Hz, C¹⁰); Anal Calcd for C₂₄H₁₆F₆N₂O₂ (478.39): C, 60.26; H, 3.37; N, 5.85 %; Found: C, 60.15; H, 2.78; N, 5.82 %.

Polymer synthesis

The polyimides were synthesized from various dianhydrides and the diamine **2** via a two-step method.

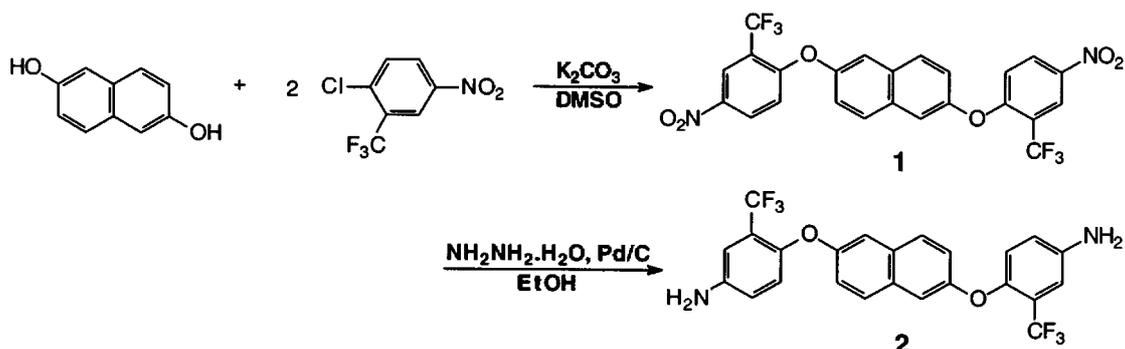


The synthesis of polyimide **6a** is used as an example to illustrate the general synthetic route used to prepare the polyimides. To a solution of 0.478 g (1 mmol) of diamine **2** in 6.7 ml of CaH₂-dried DMAc in a 50-ml flask, 0.218 g (1 mmol) of dianhydride PMDA (**3a**) was added in one portion. The mixture was stirred at room temperature overnight (for about 12 h) to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) **4a** was 2.16 dl g⁻¹, measured in DMAc at a concentration of 0.5 dl g⁻¹ at 30 °C. The poly(amic acid) solution was poured into a 9-cm glass culture dish, which was placed overnight in an 80 °C oven for 3 h for the slow release of the casting solvent. The semi-dried poly(amic acid) film was further dried and transformed into polyimide **6a** by sequential heating at 150 °C for 30 min, 200 °C for 30 min, and 250 °C for 1 h. The polyimide film was stripped from the glass substrate by soaking in water. For tensile test, dielectric and thermogravimetric analysis, the polyimide films were further heated at 300 °C for another 1 h.

RESULTS AND DISCUSSION

Monomer synthesis

The new CF₃-containing bis(ether amine) **2** was prepared according to a two-step procedure as shown in Scheme 1. The first step is an aromatic nucleophilic fluoro-displacement of 2-chloro-5-nitrobenzotrifluoride by the potassium salt of 2,6-dihydroxynaphthalene in DMSO. The diamine **2** was readily obtained in high yields by the catalytic reduction of intermediate dinitro compound **1** with hydrazine monohydrate and Pd/C catalyst in refluxing ethanol. The structures of the dinitro compound **1** and the diamine monomer **2** were confirmed by IR spectroscopy, ¹H and ¹³C NMR spectroscopy and elemental analysis. The nitro group of compound **1** gave two characteristic bands at 1529 and 1340 cm⁻¹ (NO₂



Scheme 1. Synthetic route used for the CF₃-substituted bis(ether amine) **2**.

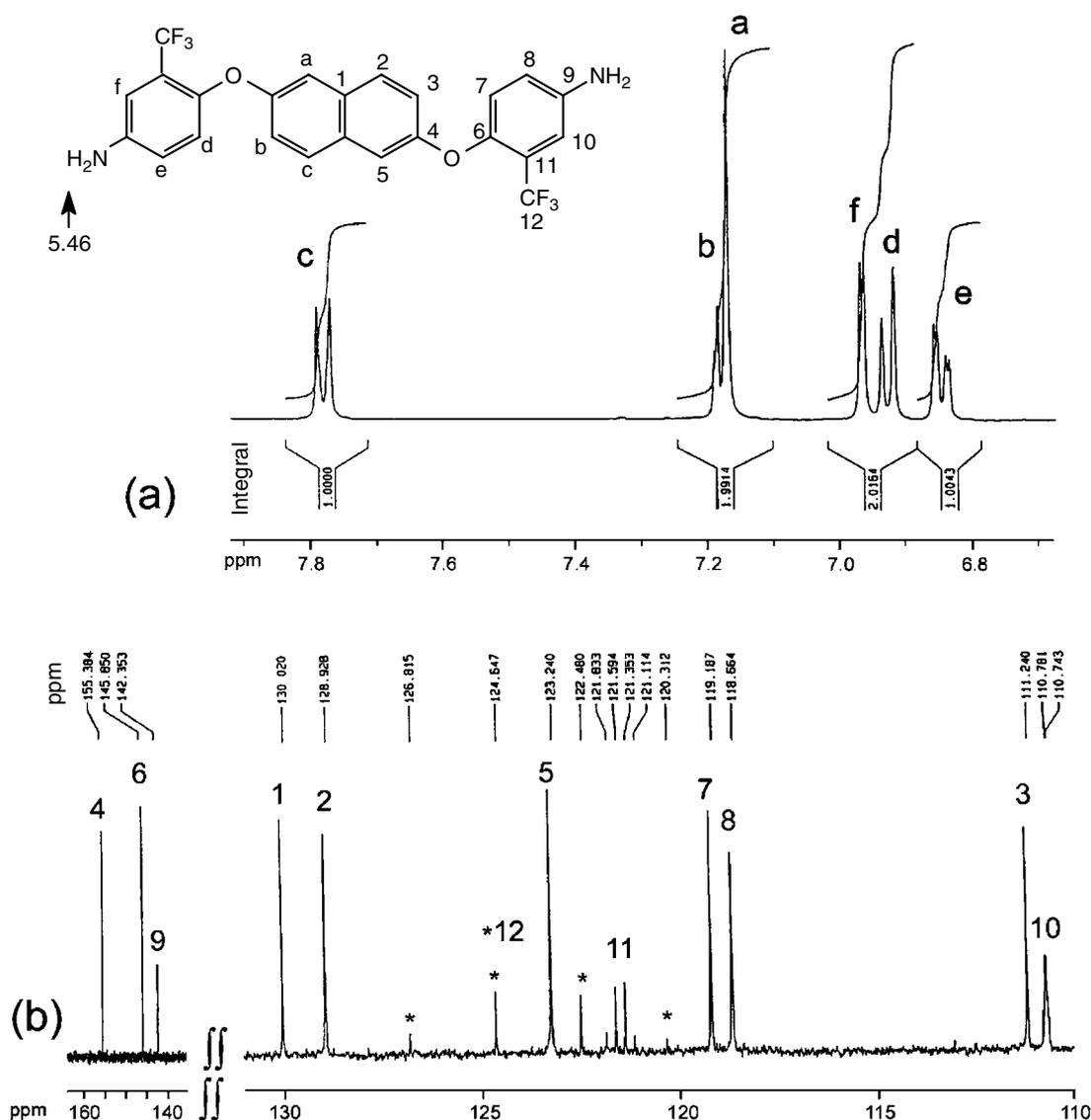


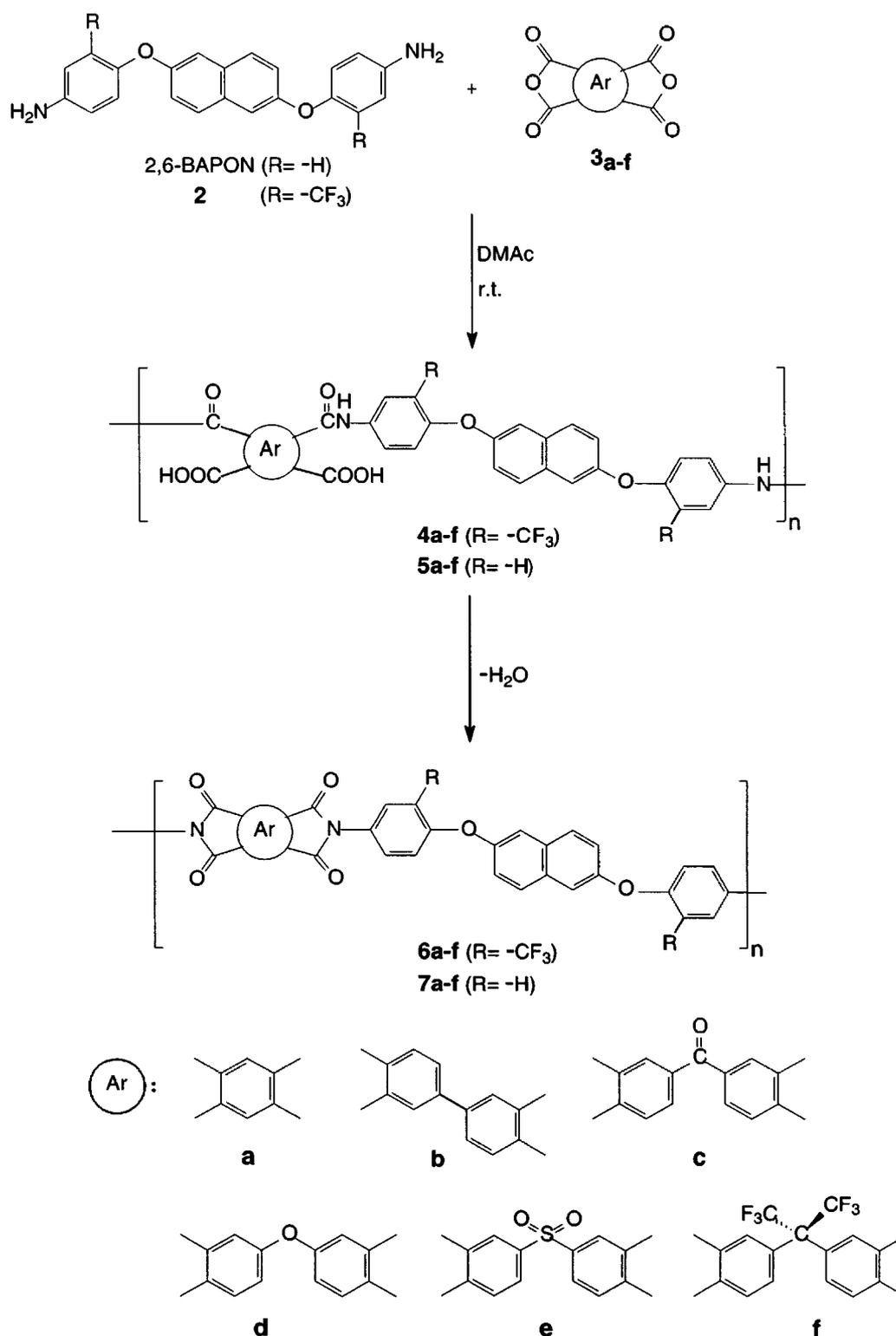
Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of diamine **2** in $\text{DMSO-}d_6$.

asymmetric and symmetric stretching) in its IR spectrum. After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical N–H stretching bands at 3392 and 3487 cm^{-1} . Figure 1 shows the ^1H NMR and ^{13}C NMR spectra of diamine **2**. The ^1H NMR spectra confirm that the nitro groups have been completely converted into amino groups by the high field shift of the aromatic protons and by the signal at 5.46 ppm corresponding to the primary aromatic amine 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 show two obvious quartets, because of the heteronuclear ^{13}C – ^{19}F coupling. The large quartets centered at about 123.5 ppm are due to the $-\text{CF}_3$ carbons. The one-bond C–F coupling constant in this case is about 272 Hz. The CF_3 -attached carbon C^{11} also shows a clear quartet centered at about 121.5 ppm with a smaller coupling constant of about 30 Hz from two-bond C–F coupling. Thus, all the

spectroscopic data obtained were in good agreement with the expected structures.

Polymer synthesis

The polyimides were prepared from diamine **2** and six commercially available dianhydrides **3a–f** by a conventional two-step synthetic method as shown in Scheme 2. Despite the presence of electron-withdrawing CF_3 substituents, the diamine **2** was still sufficiently reactive to give high molecular weight poly(amic acid)s when they were allowed to polymerize for a longer time (about 12 h). As shown in Table 1, the inherent viscosities of the intermediate poly(amic acid)s ranged from 1.10 to 2.16 dl g^{-1} . The molecular weights of all the poly(amic acid)s were sufficiently high to permit the casting of flexible and tough poly(amic acid) films, which were subsequently converted into tough polyimide films by extended heating at elevated temperatures. The diamine **2** is mostly likely retained its reactivity because the amino group is meta to the CF_3 group. For a comparative



Scheme 2. Synthesis of polyimides.

study, a series of referenced polyimides **7a–f** were also synthesized from 2,6-BAPON and dianhydrides **3a–f**. The inherent viscosities of precursor poly(amic acid)s of **5a–f** were in the range of 1.60–3.31 dl g⁻¹, indicating high molecular weight polymer formation. The very high inherent viscosities of some poly(amic acid)s derived from 2,6-BAPON ($\eta_{\text{inh}} > 3.0$ dl g⁻¹) may be attributable to the high reactivity of the diamine and the more symmetric or rigid polymer

backbones. In contrast, most of the poly(amic acid)s derived from CF₃-substituted diamine **2** showed relatively lower inherent viscosities because of the somewhat decreased basicity of the diamine caused by the electron-withdrawing CF₃ group. The weight-average molecular weights (M_w s) and number-average molecular weights (M_n s) of a THF-soluble polyimide **6f** were 54 000 and 33 000, respectively, as measured by GPC in THF relative to polystyrene standards.

Table 1. Inherent viscosity of poly(amic acid)s and elemental analysis of polyimides

Poly(amic acid)		Elemental analysis of polyimides (%)					
Code	η_{inh}^a (dl g ⁻¹)	Code	Formula (formula weight)		C	H	N
4a	2.16	6a	(C ₃₄ H ₁₄ F ₆ N ₂ O ₆) _n	Calcd	61.83	2.14	4.24
			(660.49) _n	Found	61.30	2.06	4.42
4b	1.20	6b	(C ₄₀ H ₁₈ F ₆ N ₂ O ₆) _n	Calcd	65.23	2.46	3.80
			(736.11) _n	Found	65.14	2.39	4.03
4c	1.41	6c	(C ₄₁ H ₁₈ F ₆ N ₂ O ₇) _n	Calcd	64.41	2.37	3.66
			(764.10) _n	Found	64.04	2.12	3.93
4d	1.89	6d	(C ₄₀ H ₁₈ F ₆ N ₂ O ₇) _n	Calcd	63.84	2.41	3.72
			(752.58) _n	Found	63.60	2.23	3.90
4e	1.10	6e	(C ₄₀ H ₁₈ F ₆ N ₂ O ₈ S) _n	Calcd	60.00	2.27	3.50
			(800.64) _n	Found	59.56	2.14	3.69
4f	1.69	6f	(C ₄₃ H ₁₈ F ₁₂ N ₂ O ₆) _n	Calcd	58.52	2.05	3.16
			(886.61) _n	Found	57.99	1.70	3.35
5a	3.31	7a	(C ₃₂ H ₁₆ N ₂ O ₆) _n	Calcd	73.28	3.07	5.34
			(524.49) _n	Found	72.41	3.00	5.44
5b	3.00	7b	(C ₃₈ H ₂₀ N ₂ O ₆) _n	Calcd	76.01	3.36	4.66
			(600.59) _n	Found	75.47	3.17	4.67
5c	1.67	7c	(C ₃₉ H ₂₀ N ₂ O ₇) _n	Calcd	74.52	3.21	4.46
			(628.60) _n	Found	73.82	3.09	4.60
5d	1.60	7d	(C ₃₈ H ₂₀ N ₂ O ₇) _n	Calcd	74.02	3.27	4.54
			(616.59) _n	Found	72.93	3.09	4.62
5e	3.20	7e	(C ₃₈ H ₂₀ N ₂ O ₈ S) _n	Calcd	68.67	3.03	4.21
			(664.65) _n	Found	67.59	2.87	4.32
5f	3.13	7f	(C ₄₁ H ₂₀ N ₂ O ₆ F ₆) _n	Calcd	65.61	2.69	3.73
			(750.61) _n	Found	64.58	2.51	3.89

^a Measured at a polymer concentration of 0.5 g dl⁻¹ in DMAc at 30 °C.

The formation of polyimides was confirmed with elemental analysis and IR spectroscopy. The results of the elemental analyses of all the polyimides are listed in Table 1. The values found were in good agreement with the calculated ones for the proposed structures. The IR spectra showed characteristic absorptions for the imide ring at around 1780 and 1720 cm⁻¹, indicative of the asymmetric and symmetric C=O stretching vibration, and at 1370, 1100 and 725 cm⁻¹ for imide-ring deformation, together with some strong absorption bands in the region of 1100–1300 cm⁻¹ for the C–O and C–F stretching vibration.

Polymer properties

Organo-solubility

The solubility of the polyimides **6a–f** was tested qualitatively in various organic solvents, and the results are summarized in Table 2. In addition, the solubility behavior for the analogous polyimides **7a–f** based on 2,6-BAPON is also listed for comparison. Because of the introduction of the bulky CF₃ group, all the **6** series polyimides, except for **6a**, were readily soluble in strong dipolar solvents, such as NMP, DMAc and DMSO at room temperature or upon heating. Some of the polyimides (**6d–f**) derived from less stiff dianhydride components were also soluble in less efficient *m*-cresol and pyridine upon heating. Polyimides **6a** and **6b** showed a relatively lower solubility than the other polymers of the same series; they were insoluble in DMF, *m*-cresol and some low-boiling solvents like THF and dichloromethane. The

Table 2. Solubility behavior of polyimides^a

Polymer Code	Solvents ^b							
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	THF	CH ₂ Cl ₂
6a	+	–	–	–	–	–	–	–
6b	++	+	–	+	–	–	–	–
6c	+	+–	+	+–	+–	–	+–	–
6d	++	+	+	+	+–	+–	–	+–
6e	++	+	+	+	+–	+	+–	–
6f	++	+	+	+	+	+	+	++
7a	–	–	–	–	–	–	–	–
7b	–	–	–	–	–	–	–	–
7c	–	–	–	–	–	–	–	–
7d	–	–	–	–	–	–	–	–
7e	–	–	–	–	–	–	–	–
7f	+	+	+	–	+	+	–	++

^a The solubility was determined with 10-mg sample in 1 ml of stirred solvent. (++) soluble at room temperature, (+) soluble on heating at 100 °C or the boiling temperature of the solution, (+–) partial soluble on heating, (–) insoluble even on heating.

^b NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

lower solubility associated with these two polymers could be ascribed to the more rigid nature of their backbones because of the rigid PMDA and BPDA moieties. For the **7** series, only the polyimide **7f** derived from 6FDA was soluble in the solvents tested. Poor solubility for the **7** series polyimides indicates either

strong intermolecular interactions or good packing ability. Therefore, the large differences in solubility between the **6** and **7** series are attributed to the bulky CF₃ groups, which increase the disorder in the chains and hinder dense chain-packing, thus, reducing the inter-chain interactions to enhance solubility.

Color intensity and optical transparency

The color intensities of the polyimides were elucidated from the yellowness (b^*) or redness (a^*) indices observed by a Macbeth color-eye colorimeter. For comparison, a standard polyimide from PMDA and 4,4'-oxydianiline (ODA) was also prepared and characterized by its color intensity. The results shown in Table 3 indicate that the **6** series fluorinated polyimides generally showed a lower b^* value than the **7** series analogues without the CF₃ substituents. Moreover, thin films were measured for optical transparency using UV-vis spectroscopy. The cutoff wavelengths (absorption edge; λ_0) from the UV-vis spectra are listed in Table 3. Consistent with the results obtained from colorimetry, all the fluorinated polyimides revealed a lower λ_0 than their respective non-fluorinated analogues. The 6FDA and ODPAs produced fairly transparent and almost colorless polyimide films in contrast to other dianhydrides. These results were attributed to the reduction of the intermolecular charge-transfer complex (CTC) between alternating electron-donor (diamine) and electron-acceptor (dianhydride) moieties. The light colors of the polyimides with the CF₃ groups in their diamine moieties can be explained from the decreased intermolecular interactions. The bulky and electron-withdrawing CF₃ group in diamine **2** was effective in decreasing CTC formation between polymer chains

Table 3. Color coordinates and cut-off wavelength (λ_0) from UV-vis spectra of polyimide films^a

Polymer code	Film thickness (μm)	L^*	a^*	b^*	λ_0 (nm)
6a	33	95	-10	76	430
6b	42	99	-10	29	410
6c	34	98	-15	53	418
6d	34	99	-6	17	383
6e	33	99	-12	37	405
6f	33	99	-5	14	380
7a	28	88	8	83	437
7b	37	91	-8	64	428
7c	38	88	6	83	443
7d	36	99	-9	23	383
7e	35	97	-15	67	416
7f	37	99	-11	28	387
Ref. ^b	38	90	0	85	443

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

^b A reference standard polyimide prepared from PMDA and 4,4'-oxydianiline (ODA).

through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). A secondary positive effect of the CF₃ groups on the film transparency is the weakened chain-to-chain cohesive force due to lower polarizability of the C-F bond. The decrease in intermolecular CTC formation is understandable also from the significant solubility of the polyimides prepared from CF₃-diamine **2**.

Crystallinity and tensile properties

The crystallinity of the polyimides was evaluated WAXD studies. As expected, all the **6** series polyimides failed to show any crystallinity apparently because the bulky CF₃ group interrupts the close chain-packing. In contrast to polyimides **6a** and **6c**, **7a** and **7c** displayed semi-crystalline WAXD patterns indicating a moderately ordered structure. All of the **6** series polyimides afforded good-quality and creasable films. These films were subjected to a tensile test, and their tensile properties are reported in Table 4. The films exhibited ultimate tensile strengths of 112–131 MPa, elongations to break of 10–18 %, and initial moduli of 2.1–2.3 GPa, indicating they are strong and tough material.

Thermal properties

DSC and TGA were used to evaluate the thermal properties of the polymers, and the thermal behavior data of all the polymers are summarized in Table 5. DSC experiments were conducted at a heating rate of 20 °C min⁻¹ in nitrogen. Rapid cooling from 400 °C to room temperature produced predominantly amorphous samples, so the T_g values of almost all the polyimides could be easily read in the subsequent heating DSC traces. The T_g values of the **6** series polyimides ranged from 249 to 311 °C. The decreasing order of T_g generally correlates with that of the chain flexibility. Thus, the polyimide **6d** obtained from ODPAs showed the lowest T_g (249 °C) owing to the presence of a flexible ether linkage between the phthalimide units, and the highest T_g of 311 °C was observed for polyimide **6a** derived from PMDA. No melting endothermic peak was observed from DSC curves before decomposition of polyimides **6a–f**. Thus, DSC measurements also revealed the amorphous nature of these fluorinated polyimides.

Table 4. Tensile properties of polyimide films

Polyimide code	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (GPa)
6a	112	13	2.2
6b	125	18	2.3
6c	131	13	2.3
6d	116	10	2.1
6e	122	11	2.3
6f	117	10	2.2

Table 5. Thermal behavior data of polyimides

Polymer	T_g^a (°C)	T_d^b (°C) in		Char yield ^c (%)
		Nitrogen	Air	
6a	311	612	591	57
6b	275	618	597	61
6c	256	616	590	60
6d	249	612	591	56
6e	275	548	561	55
6f	271	577	565	54
7a	—	610	601	63
7b	273	621	612	65
7c	269	600	605	62
7d	255	611	605	50
7e	295	560	575	50
7f	280	587	572	61

^a Midpoint temperature of the baseline shift on the heating DSC traces with a heating rate of 20 °C min⁻¹.

^b Decomposition temperature at which a 10 % weight loss were recorded by TGA at a heating rate of 20 °C min⁻¹.

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

DSC observed no T_g value for polyimide **7a**, possibly due to the rigid nature of backbone. The range of T_g values for other 7 series polyimides (**7b–f**) was 255–295 °C. Slightly lower T_g s for **6c–f** than for **7c–f** might be a result of decreased interactions and poor packing between polymer chains due to the bulky pendent CF₃ groups. The increased free volume caused by the CF₃ group also may affect the decrease of T_g values of these 6 series polyimides.

The thermal stability of the polyimides was evaluated by TGA measurements in both air and

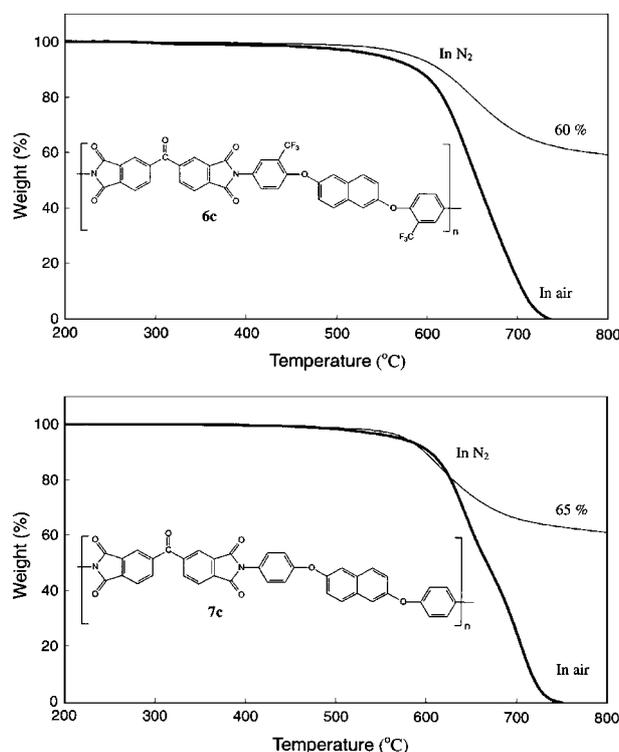


Figure 2. TGA thermograms of polyimides **6c** and **7c** at a heating rate of 20 °C/min in nitrogen and in air.

nitrogen atmospheres. Typical TGA curves for polyimides **6c** and **7c** are reproduced in Fig 2. The decomposition temperatures (T_d) at 10 % weight loss in nitrogen and in air atmospheres were determined from the original TGA thermograms and are given in Table 5. The T_d values at 10 % weight loss of the fluorinated polyimides (**6a–f**) in nitrogen and air stayed in the range of 548–618 °C and 561–597 °C, respectively. They left more than 54 % char yield at 800 °C in nitrogen. The TGA data indicate that these polyimides have fairly high thermal stability, comparable with that of polyimides **7a–f** derived from non-fluorinated 2,6-BAPON.

Dielectric constants and water uptake

The measurements of the dielectric constants were performed between gold layers: the polyimide film was dried carefully, and a thin gold layer was vacuum-deposited on both surfaces of the polymer film. This procedure excludes any contact problems. As shown in Table 6, polyimides **6a–f** revealed lower dielectric constants (2.49–3.59 at 10 kHz) compared to the corresponding analogous polyimides **7a–f** (3.09–3.91 at 10 kHz) and PMDA/ODA polyimide film (3.61 at 10 kHz). The decreased dielectric constants might be partly attributable to the bulky CF₃ groups, which resulted in less efficient chain packing and increased free volume. In addition, the strong electronegativity of fluorine results in permanent dipole moments of the CF₃ groups, thus decreasing the dielectric constant. Table 6 also presents the water uptake of the polyimides, which ranges from 0.19 to 0.85 %. In comparison, most of the polyimides **6a–f** exhibited lower water uptake than the corresponding polyimides **7a–f** and PMDA/ODA polyimide film. Polyimide **6f** exhibited the lowest water uptake due to the higher fluorine content in the repeat unit. Therefore, the 6FDA-derived polyimide **6f** exhibited the lowest dielectric constant of 2.49 at 10 kHz due to the higher free volume and hydrophobicity.

Table 6. Water uptake and dielectric constants of polyimides

Polymer code	Film Thickness (μm)	Water Uptake (wt%)	Dielectric constant (dry)	
			10 kHz	1 MHz
6a	29	0.25	3.07	3.06
6b	33	0.81	2.95	2.92
6c	31	0.81	3.20	3.18
6d	36	0.85	2.91	2.90
6e	31	0.74	3.59	3.56
6f	31	0.19	2.49	2.48
7a	26	0.73	3.65	3.63
7b	40	1.02	3.50	3.48
7c	36	1.10	3.67	3.60
7d	38	0.87	3.23	3.20
7e	35	1.20	3.91	3.82
7f	41	0.87	3.09	3.04
PMDA/ODA	29	1.20	3.61	3.59

CONCLUSIONS

A novel fluorinated bis(ether amine), 2,6-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was prepared through the nucleophilic substitution reaction of 2,6-dihydroxynaphthalene and 2-chloro-5-nitrobenzotrifluoride, followed by hydrazine catalytic reaction of the dinitro intermediate. A series of novel fluorinated polyimides have been obtained from the trifluoromethyl-substituted bis(ether amine) with various aromatic dianhydrides by two-step thermal imidization methods. These polyimides were characterized by high solubility, good film-forming ability, high optical transparency, excellent thermal stability and good mechanical properties together with low dielectric constants. It was concluded that this series of polyimides demonstrates a good combination of properties and processability.

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