

Polyimides from 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic tetracarboxylic dianhydrides

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Abstract

A new trifluoromethylated bis(ether amine), 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was synthesized in two steps starting from 1,5-dihydroxynaphthalene and 2-chloro-5-nitrobenzotrifluoride via nucleophilic aromatic substitution and catalytic reduction. A series of novel fluorinated polyimides with moderate to high molecular weights were synthesized from the diamine with various aromatic tetracarboxylic dianhydrides using a conventional two-stage process. All polyimides could afford flexible and tough films and most of them were soluble in strong polar solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc). The polyimides showed glass-transition temperatures (T_g) in the range of 253–315 °C (by DSC) and softening temperatures (T_s) in the range of 250–300 °C (by TMA). Decomposition temperatures for 5% weight loss all occurred above 500 °C in both air and nitrogen atmospheres. The dielectric constants of these polymers ranged from 3.17 to 3.64 at 1 MHz. The properties of these fluorinated polyimides were also compared with those of polyimides prepared from 1,5-bis(4-aminophenoxy)naphthalene with the same dianhydrides.

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1. Introduction

High-performance polymeric materials are currently receiving considerable attention for their potential applications in advanced technologies demands. Aromatic polyimides are well known high-performance polymers that have excellent thermal, mechanical and electrical properties [1,2]. However, one of the problems with most aromatic polyimides is their poor processability caused by limited solubility in organic solvents and high melting and softening temperatures. Therefore, much effort has been spent on preparing tractable aromatic polyimides by changing the chemical nature of the

macrochain to some degree while maintaining their desired properties [3–14]. One of the strategies to increasing solubility and lowering melting and softening temperature is introduction of flexible bonds in the polymer backbone [13,14]. Ether linkages are the most popularly flexible linkages introduced into the polymer backbone. It has been generally recognized that aryl-ether linkage imparts properties such as better solubility and melt-processing characteristics. On the other hand, the attachment of bulky lateral groups can increase the solubility due to decreasing packing and crystallinity [15–18].

In our previous publications [19,20], we have demonstrated that 1,5-bis(4-aminophenoxy)naphthalene could be successfully synthesized starting from the aromatic substitution reaction of 1,5-dihydroxynaphthalene with *p*-fluoronitrobenzene and used to

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prepare aromatic polyamides and polyimides containing 1,5-bis(phenoxy)naphthalene in the backbones. However, all the obtained polyimides and the polyamides derived from rigid diacids showed a limited solubility, possibly due to the rigid nature of polymer backbones. Recent studies demonstrated that polyimides derived from ether-bridged diamines with trifluoromethyl (CF₃) groups are soluble high temperature polymeric materials with low moisture uptake, low dielectric constant, and high optical transparency [21–25]. As part of our continuing efforts in developing tractable high-performance polymers containing naphthalene units, we decided to incorporate CF₃ groups along the backbones of polyimides by using a new CF₃-substituted bis(ether amine), 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, aiming to enhance their solubility while maintaining their positive properties.

2. Experimental

2.1. Reagents and solvents

1,5-Dihydroxynaphthalene (TCI), potassium carbonate (K₂CO₃) (Fluka), 2-chloro-5-nitrobenzotrifluoride (Acros), 10% palladium on charcoal (Pd/C) (Fluka), and hydrazine monohydrate (Acros) were used as received. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Commercially available aromatic tetracarboxylic dianhydrides such as pyromellitic dianhydride (**3a**; PMDA) (Aldrich) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**3c**; BTDA) (Aldrich) were purified by recrystallization from acetic anhydride. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (**3b**; BPDA) (Oxychem), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (**3e**; DSDA) (New Japan Chemical Co.), 4,4'-oxydiphthalic dianhydride (**3d**; ODPDA) (Oxychem), and 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**3f**; 6FDA) (Hoechst Celanese) were heated at 250 °C under vacuum for 3 h prior to use. As reported previously [26], 4,4'-(1,5-naphthalenedioxy)diphthalic anhydride (**3g**) (mp 252–253 °C) was prepared in three main steps starting from the nucleophilic nitro-displacement reaction of 4-nitrophthalonitrile with 1,5-dihydroxynaphthalene.

2.2. Characterization methods

Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental analysis was made on a PerkinElmer 2400 CHN analyzer. ¹H and ¹³C NMR spectra were measured on a JEOL EX 400 spectrometer at 399.65 and 99.00 MHz frequencies, respectively. The inherent viscosities of the polymers were determined with an Ubbelohde viscom-

eter 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 inside diameter × 300 mm) connected in series were used with tetrahydrofuran (THF) as the eluent and were calibrated with narrow polystyrene standards. The measurements were done at 35 °C with a flow rate of 1.0 ml/min. An Instron universal tester machine model 4400R with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 0.08 mm thick), and an average of at least three replicas was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (≈25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite-monochromatized Cu Kα radiation (λ = 1.5418 Å). The scanning rate was 3°/min over a range of 2θ = 10–40°. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 4–6 mg of samples in flowing nitrogen (flow rate 20 cm³/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a Perkin Elmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. Glass-transition temperatures (*T*_g) were read at the middle of the transition in the heat capacity from the second heating scan after quick cooling from 400 °C at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 40 to 300 °C at a scanning rate of 10 °C/min using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (*T*_s) were taken as the onset temperature of probe displacement on the TMA traces. The dielectric property of the polyimide films was tested by the parallel-plate capacitor method with a HP-4194 Impedance/Gain Phase analyzer. The moisture absorption was determined by the change of the weight in vacuum-dried film specimens before and after immersion in deionized water at 25 °C for 3 days.

2.3. Synthesis of diamine monomer

1,5-Bis(4-nitro-2-trifluoromethylphenoxy)naphthalene (**1**). In a 250-ml flask, 1,5-dihydroxynaphthalene (8 g, 0.05 mol) and potassium carbonate were dissolved in 80 ml of dimethylsulfoxide (DMSO) with stirring. Then, 2-chloro-5-nitrobenzotrifluoride (22.5 g, 0.1 mol) was added, and the reaction solution was stirred at room temperature for 24 h. Then, the reaction mixture was poured into 700 ml of methanol/water (6:1 by volume), and the precipitated brown solid was collected by fil-

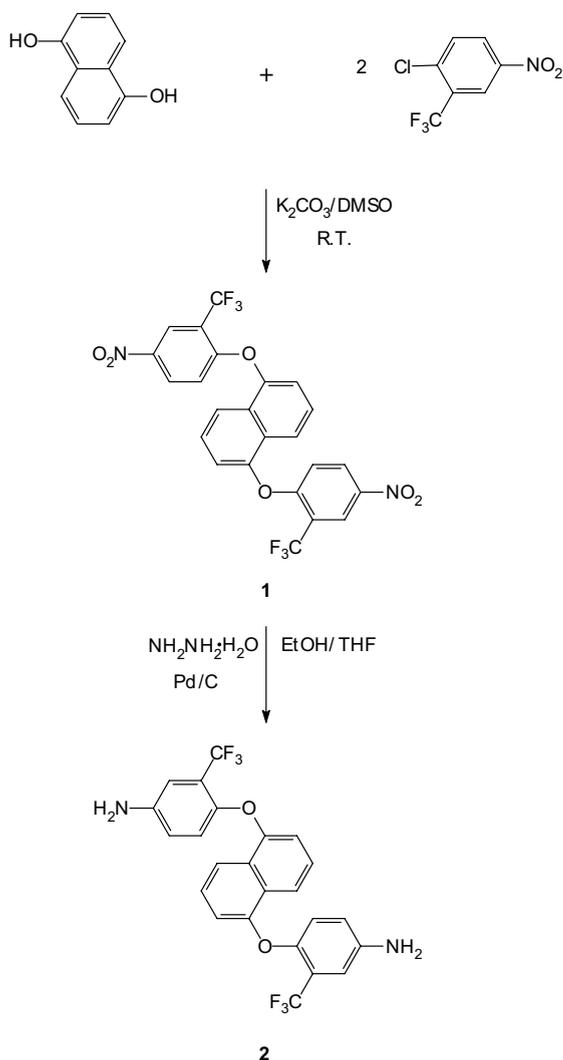
tration. The yield of the product was 24.5 (91%). The crude product was recrystallized from *N,N*-dimethylformamide (DMF)/water to afford 22.9 g of pale-brown crystals; mp = 216–218 °C.

ANAL. Calcd for $C_{24}H_{12}N_2O_6F_6$ (538.36): C, 53.54%; H, 2.24%; N, 5.20%. Found: C, 53.60%; H, 2.33%; N, 5.19%. IR (KBr): 1533, 1351 ($-\text{NO}_2$), 1255 (C—O), 1133 cm^{-1} (C—F). $^1\text{H NMR}$ (DMSO- d_6 , δ ppm) (for the assignment of peaks, see Fig. 2a): 8.61 (d, $J = 2.5$ Hz, 2H, H_f), 8.42 (dd, $J = 8.4, 2.5$ Hz, 2H, H_e), 7.87 (d, $J = 8.4$ Hz, 2H, H_c), 7.71 (dd, $J = 8.4, 7.6$ Hz, 2H, H_b), 7.53 (d, $J = 7.6$ Hz, 2H, H_a), 7.10 (d, $J = 8.4$ Hz, 2H, H_d). $^{13}\text{C NMR}$ (DMSO- d_6 , δ ppm) (for the assignment of peaks, see Fig. 3a): 160.0 (C^6), 149.4 (C^1), 142.0 (C^9), 130.2 (C^5), 127.8 (C^3), 127.6 (C^9), 123.5 (C^{10}),

122.4 (q, $^1J_{\text{C-F}} = 272$ Hz, C^{12}), 118.9 (C^7), 118.0 (C^4), 118.7 (q, $^2J_{\text{C-F}} = 33$ Hz, C^{11}), 117.6 (C^2).

1,5-Bis(4-amino-2-trifluoromethylphenoxy)naphthalene (2). A mixture of the obtained dinitro compound **1** (20 g, 0.037 mol), 10% Pd/C (0.2 g), ethanol (150 ml), THF (50 ml), and hydrazine monohydrate (20 ml) was heated at reflux temperature for about 4 h. The reaction solution was filtered when hot to remove Pd/C, and the filtrate was dried by rotary evaporation. The crude product was recrystallized from ethanol/THF to afford 15 g (84%) of pale-yellow crystals; mp = 213–214 °C.

ANAL. Calcd for $C_{24}H_{16}N_2O_2F_6$ (478.39): C, 60.26%; H, 3.37%; N, 5.85%. Found: C, 60.28%; H, 3.65%; N, 5.93%. IR (KBr): 3446, 3313, 3212 ($-\text{NH}_2$), 1259 (C—O), 1153 cm^{-1} (C—F). $^1\text{H NMR}$ (DMSO- d_6 , δ ppm) (for the assignment of peaks, see Fig. 2b): 7.94 (d, $J = 8.4$ Hz, 2H, H_c), 7.46 (dd, $J = 8.4, 7.7$ Hz, 2H, H_b), 7.06 (d, $J = 2.6$ Hz, 2H, H_f), 7.00 (d, $J = 8.8$ Hz, 2H, H_d), 6.91 (dd, $J = 8.8, 2.6$ Hz, 2H, H_e), 6.79 (d, $J = 7.7$ Hz, 2H, H_a), 5.54 ($-\text{NH}_2$, 4H). $^{13}\text{C NMR}$ (DMSO- d_6 , δ ppm) (for the assignment of peaks, see Fig. 3b): 154.7 (C^1), 144.7 ($C^6 + C^9$), 127.3 (C^5), 125.6 (C^3), 123.5 (q, $^1J_{\text{C-F}} = 271$ Hz, C^{12}), 122.3 (C^9), 122.2 (q, $^2J_{\text{C-F}} = 31$ Hz, C^{11}), 119.0 (C^7), 116.2 (C^4), 112.3 (C^{10}), 111.0 (C^2).



Scheme 1. Synthesis of diamine **2**.

2.4. General polyimide synthesis

The typical example of polymerization is as follows. Into a solution of 0.6868 g (1.44 mmol) of fluorinated

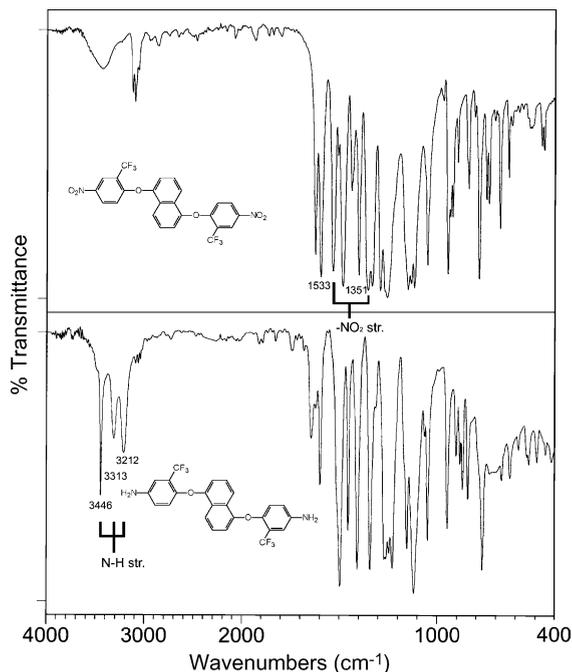


Fig. 1. FTIR spectra of dinitro compound **1** and diamine **2**.

diamine **2** in 9.5 ml of CaH₂-dried DMAc, 0.3132 g (1.44 mmol) of PMDA was added in one portion. The mixture was stirred at ambient temperature for about 24 h to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) **4a** was 1.31 dl/g, measured in DMAc at a concentration of 0.5 g/dl. The poly(amic acid) was converted into polyimide by either thermal or chemical imidization method.

For the thermal imidization method, the poly(amic acid) solution was spread on a glass plate and baked at 90 °C for the removal of the casting solvent. The semi-dried poly(amic acid) film was further dried and converted to the polyimide by sequential heating at 150 °C for 30 min, 200 °C for 30 min, and 250 °C for 1 h. The inherent viscosity of the resulting polyimide (**5a**) was 1.06 dl/g, measured in concentrated H₂SO₄ at a concentration of 0.5 g/dl.

For chemical imidization, 5 ml of acetic anhydride and 2 ml of pyridine were added to the poly(amic acid) solution and the mixture was reacted at 100 °C for 1 h to effect a complete imidization. The resultant solution of the polymer was poured slowly into 250 ml methanol giving rise to a fibrous precipitate, which was washed thoroughly with methanol, collected by filtration, and dried.

3. Results and discussion

3.1. Monomer synthesis

The new CF₃-containing diamine 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene (**2**) was prepared from 1,5-dihydroxynaphthalene and 2-chloro-5-nitro-

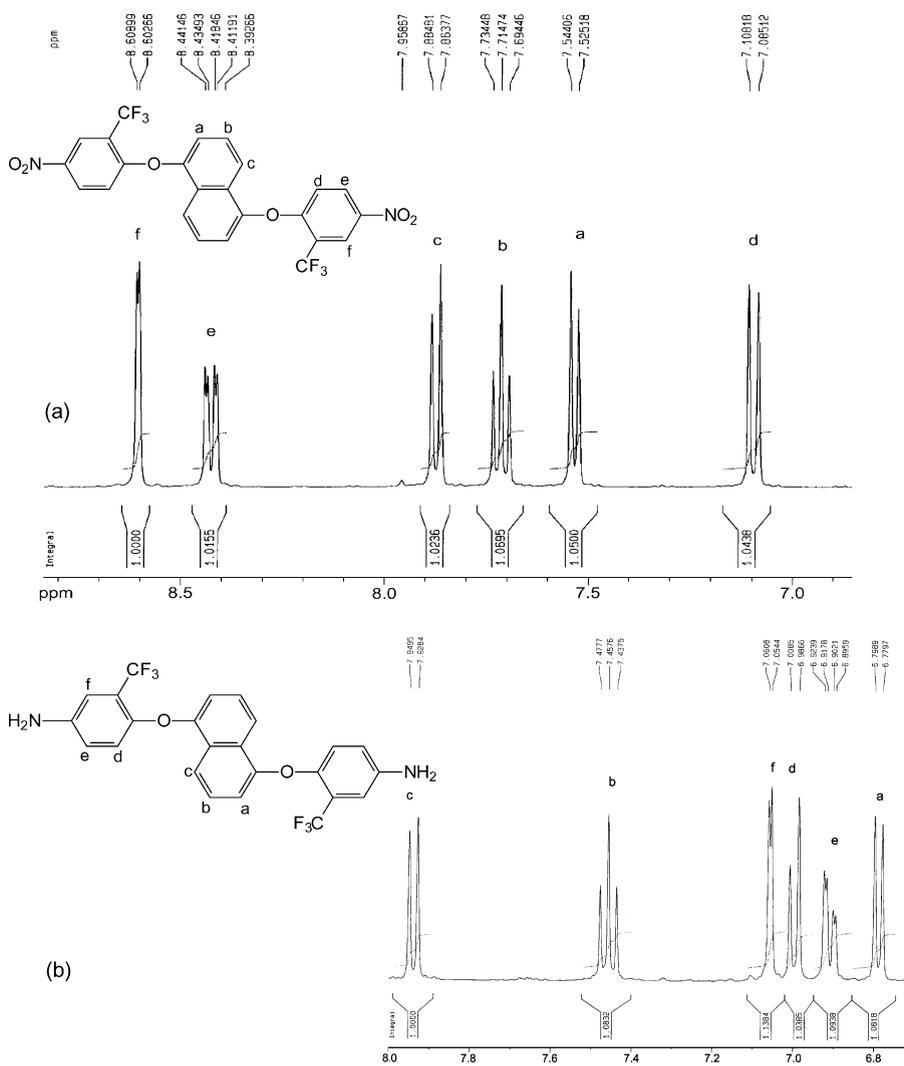
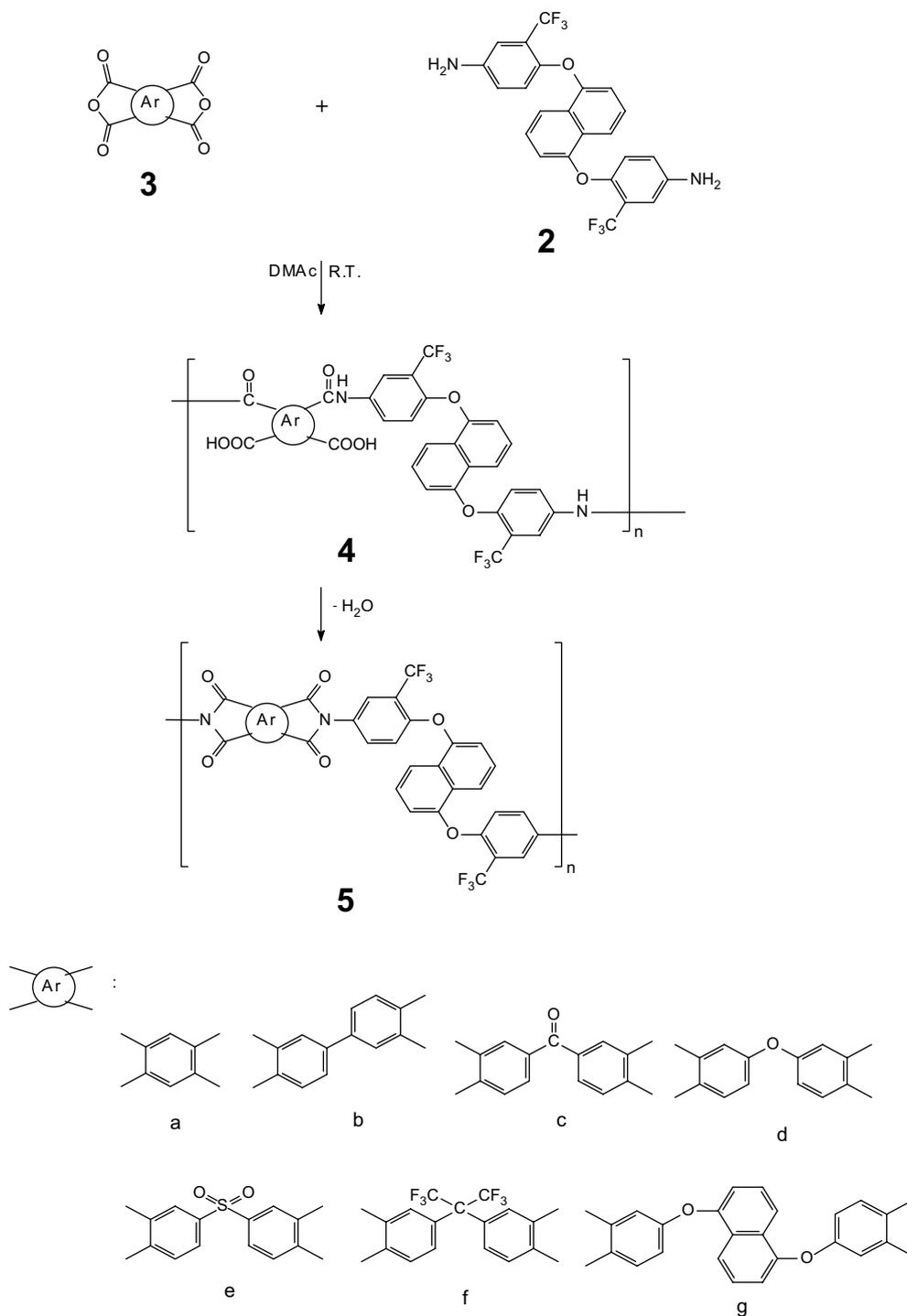


Fig. 2. ¹H NMR spectra of (a) dinitro compound **1** and (b) diamine **2** in DMSO-*d*₆.

molecular structures. The ^1H NMR spectra confirm that the nitro groups have been converted into amino groups by the high field shift of the aromatic protons and by the

signal at 5.54 ppm corresponding to the amino protons. The ^{13}C NMR spectra of **1** and **2** show two clear quartets because of the heteronuclear ^{13}C – ^{19}F coupling.



Scheme 2. Synthesis of polyimides.

In the ^{13}C NMR spectrum of diamine **2**, upfield shifts of the aromatic carbons, especially for those *para* (C^6) and *ortho* (C^9 , C^{10}) to the amino group, were also observed because of the resonance effect caused by the electron-donating amino group.

3.2. Polymer synthesis

The fluorinated diamine **2** was reacted with different dianhydrides **3a–3g** via a conventional two-step procedure to give the polyimides **5a–5g** displayed in Scheme 2. The imidization of the poly(amic acid) precursors was performed by thermal cyclization in solid film or by chemical cyclodehydration in solution. As shown in Table 1, inherent viscosities of the poly(amic acid)s were in the range of 0.76–1.31 dl/g, and those of the thermally cured polyimides stayed in the range of 0.42–1.06 dl/g. The weight average molecular weights of four THF-soluble polyimides (**5c–5f**) were recorded in the range of 57,000–69,000 g/mol based on polystyrene standards. The results of the elemental analyses of all the polyimides are also listed in Table 1. The values found were in good agreement with the calculated ones of the proposed structures. Complete imidization was confirmed with the aid of IR spectra of the resulting fluorinated polyimides. A typical set of IR spectra of poly(amic acid) **4a** and polyimide **5a** is given in Fig. 4. The IR spectra of the polyimides showed clearly the characteristic imide absorption bands around 1780 and 1720 cm^{-1} attributed respectively to the asymmetric stretching and

symmetric stretching of the carbonyl groups of the imide rings, the absorption band near 1380 cm^{-1} due to the C–N stretching and the absorption around 720 cm^{-1} for the C=O bending. The lack of absorptions in the region from 2500 to 3500 cm^{-1} (O–H and N–H stretch) and around 1680 cm^{-1} (amide C=O stretch) indicated that the polymers were fully imidized. All the polyimides also exhibited some strong absorption bands in the region of 1100–1300 cm^{-1} attributed to the C–O and C–F stretching.

3.3. Properties of polyimides

The solubility of the polyimides was determined qualitatively in various organic solvents, and the results are listed in Table 2. The CF_3 side groups seem to decrease the interactions between polymer chains and lead to an enhanced solubility. The solubility of the polyimides synthesized from PMDA and BPDA is lower than the solubility of polyimides prepared from the other dianhydrides. In addition, the polyimides prepared by chemical imidization method using acetic anhydride and pyridine exhibited better solubility than the thermally cured ones. The lower solubility of thermally cured polyimides might be attributed to partial cross-linking within polymer chains or denser packing of polymer chains during the thermal imidization. For comparison, the solubility behavior of the corresponding non-fluorinated **5'** series polyimides reported previously [19] was also presented in Table 2. All these

Table 1
Inherent viscosity of poly(amic acid)s and polyimides and elemental analyses of the polyimides

Poly(amic acid)		Polyimide		GPC data of polyimides ^a			Elemental analysis (%) of polyimides				
Code	$\eta_{\text{inh}}^{\text{b}}$ (dl/g)	Code	$\eta_{\text{inh}}^{\text{b}}$ (dl/g)	Mn	Mw	Mw/Mn	Formula (Formula weight)	C	H	N	
4a	1.31	5a	1.06 ^c	– ^d			($\text{C}_{34}\text{H}_{14}\text{N}_2\text{O}_6\text{F}_6$) _n (660.48) _n	Calcd Found	61.83 61.01	2.14 2.04	4.24 4.48
4b	0.76	5b	0.68				($\text{C}_{40}\text{H}_{18}\text{N}_2\text{O}_6\text{F}_6$) _n (736.58) _n	Calcd Found	65.23 64.70	2.46 2.71	3.80 3.90
4c	0.81	5c	0.60	35,000	57,000	1.63	($\text{C}_{41}\text{H}_{18}\text{N}_2\text{O}_7\text{F}_6$) _n (764.59) _n	Calcd Found	64.41 63.81	2.37 2.57	3.66 3.69
4d	1.21	5d	0.74	48,000	69,000	1.44	($\text{C}_{40}\text{H}_{18}\text{N}_2\text{O}_7\text{F}_6$) _n (752.58) _n	Calcd Found	63.84 63.36	2.41 2.43	3.72 3.75
4e	0.87	5e	0.53	43,000	63,500	1.48	($\text{C}_{40}\text{H}_{18}\text{N}_2\text{O}_8\text{S}_1\text{F}_6$) _n (800.64) _n	Calcd Found	60.01 59.38	2.27 2.35	3.50 3.66
4f	0.99	5f	0.42	41,000	59,500	1.47	($\text{C}_{43}\text{H}_{18}\text{N}_2\text{O}_6\text{F}_{12}$) _n (886.60) _n	Calcd Found	58.25 57.87	2.05 2.00	3.16 3.24
4g	0.92	5g	0.85				($\text{C}_{50}\text{H}_{24}\text{N}_2\text{O}_8\text{F}_6$) _n (894.73) _n	Calcd Found	67.12 66.76	2.70 2.62	3.13 3.29

^a Relative to polystyrene standards, using THF as the eluent.

^b Measured in DMAc at a concentration of 0.5 g/dl at 30 °C unless otherwise indicated.

^c Measured in concentrated sulfuric acid.

^d Insoluble in THF.

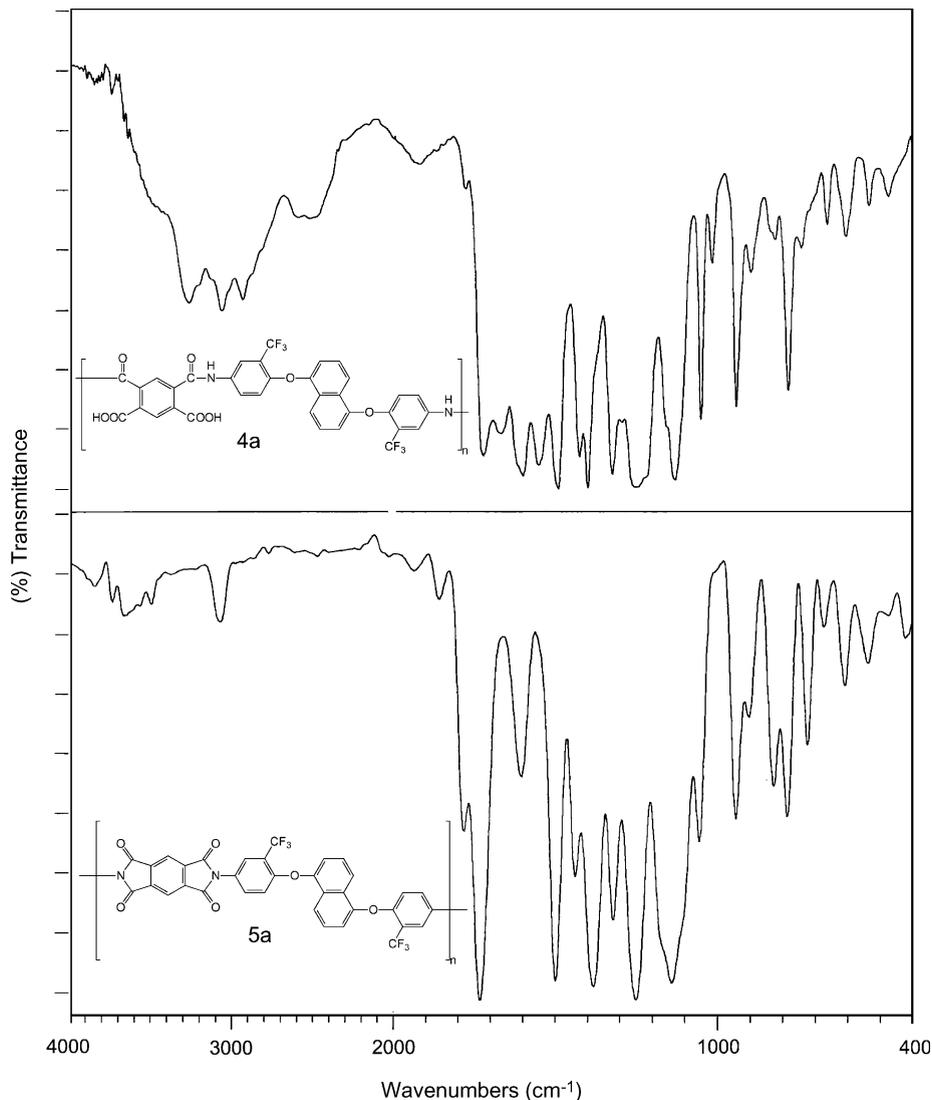


Fig. 4. IR spectra of poly(amic acid) **4a** and polyimide **5a**.

referenced polyimides were insoluble in NMP, DMAc, DMF, DMSO, *m*-cresol, and THF. The large differences in solubility between **5** and **5'** series could be apparently attributable to the bulky CF₃ substituents, which increased the disorder in the chains and hindered dense packing, thereby decreasing the intermolecular interactions to enhance solubility. All the polyimides were characterized by WAXD studies. As expected, these polyimides showed completely amorphous diffraction patterns. The tough and flexible films of polyimides **5a–5g** prepared by thermal imidization had tensile strengths of 118–135 MPa, elongations at break of 9–21%, and initial moduli of 2.04–2.53 GPa (Table 3), indicating that they could be cast into transparent, flexible and tough films.

DSC, TMA and TGA analyses were used to evaluate the thermal properties of the polymers. The results are collected in Table 4. Polyimides **5a–5g** showed T_g values in the range of 253–315 °C, following the decreasing order of chain flexibility and steric hindrance of the dianhydrides. For example, polyimide **5a**, obtained from PMDA, showed the highest T_g (315 °C) because of the presence of rigid pyromellitimide units, and polyimides **5d** and **5g** revealed lower T_g values due to the higher flexibility in their dianhydride moieties. The softening temperatures (T_s s) of all the polyimide films were also measured by the TMA method using a loaded penetration probe. A typical TMA thermogram for polyimide **5a** is reproduced in Fig. 5. The T_s values of these polymers were observed from 250 to 300 °C. In most cases,

Table 2
Solubility behavior of the polyimides prepared by thermal/or chemical imidization^a

Polyimide	Solvent							
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	2-Chlorophenol	THF	1,4-Dioxane
5a	±/± (-) ^b	±/± (-)	±/± (-)	-/- (-)	-/- (-)	-/- (-)	-/- (-)	-/-
5b	+h/+ (-)	+h/+h (-)	-/- (-)	-/- (-)	-/+h (-)	+h/+ (-)	-/- (-)	-/-
5c	+h/+ (-)	+/+ (-)	+/+ (-)	+h/+h (-)	+h/+h (-)	+h/+ (-)	+/+ (-)	+h/+h
5d	+h/+ (-)	+h/+ (-)	+/+ (-)	+/+h (-)	-/+h (-)	+h/+ (-)	+h/+ (-)	+h/+h
5e	+/+ (-)	+/+ (-)	+/+ (-)	+h/+ (-)	+h/+h (-)	+h/+ (-)	+/+ (-)	+h/+h
5f	+/+	+/+	+/+	+h/+	-/-	+/+	+/+	+/+
5g	+h/+h	+h/+h	+h/+	-/+h	-/+h (-)	+h/+h	-/+h	-/+h

^a Qualitative solubility was tested with 10 mg sample in 1 ml of solvent with stirring. + = soluble at room temperature; +h = soluble on heating at 100 °C (for THF, at boiling temperature); ± = partially soluble; - = insoluble even on heating.

^b Data in parentheses are those for analogous thermally cured polyimides (**5'**) having the corresponding Ar unit in the **5** series (see Ref. [19]).

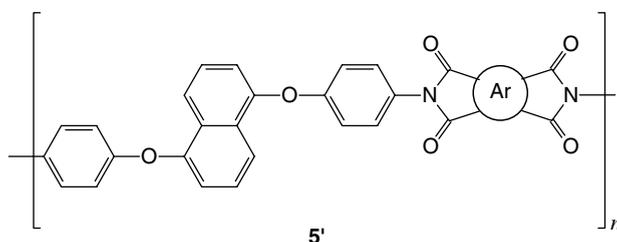


Table 3
Tensile properties of the polyimide films

Polyimide	Tensile strength (MPa)	Elongation to break (%)	Initial modulus (GPa)
5a	125	21	2.27
5b	135	25	2.29
5c	127	13	2.21
5d	139	15	2.19
5e	118	11	2.04
5f	129	9	2.53
5g	130	10	2.06

Table 4
Thermal properties of the polyimides

Polyimide	T_g^a (°C)	T_s^b (°C)	T_d at 5% weight loss (°C) ^c		T_d at 10% weight loss (°C) ^c		Char yield ^d (%)
			In N ₂	In air	In N ₂	In air	
5a	315 (-) ^e	300	601	535	630 (574)	576 (561)	59 (62)
5b	276 (-)	274	599	559	633 (571)	600 (566)	63 (65)
5c	266 (275)	256	593	541	624 (555)	585 (540)	61 (63)
5d	254 (260)	250	594	548	622 (560)	585 (551)	61 (62)
5e	275 (295)	275	559	521	592 (543)	561 (540)	58 (60)
5f	271 (285)	270	568	545	594	574	55
5g	253	250	624	574	648	602	67

^a The samples were heated from 40 to 400 °C at a scan rate of 20 °C/min; this was followed by rapid cooling to 40 °C at -200 °C/min in N₂. The midpoint temperature of heat capacity jump on the subsequent DSC trace (from 40 to 400 °C at 20 °C/min) was defined as T_g .

^b Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace. The film samples were heated at 300 °C for 30 min prior to the TMA experiment.

^c Decomposition temperatures, recorded via TGA at a heating rate of 20 °C/min and a gas flow rate of 40 cm³/min.

^d Residual weight percentage at 800 °C under nitrogen flow.

^e Values in parentheses are T_g s of analogous polyimides (**5'**) without the CF₃ groups. Polyimides **5a'** and **5b'** did not show discernible transition on the DSC curves.

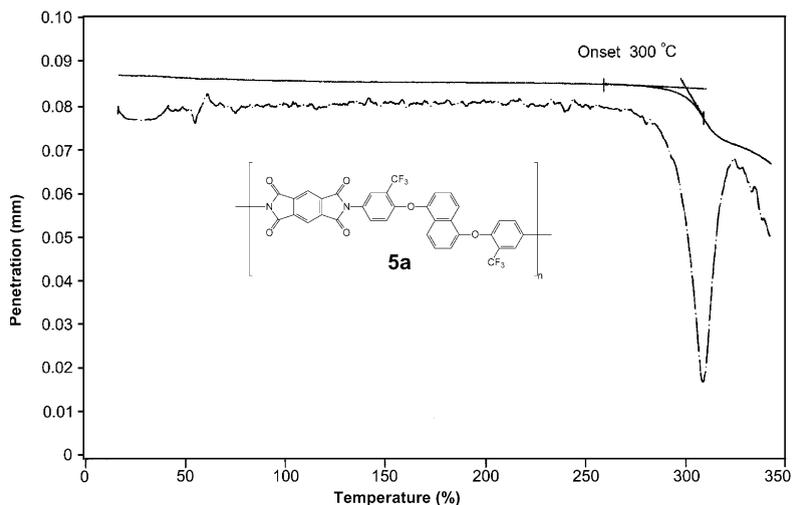
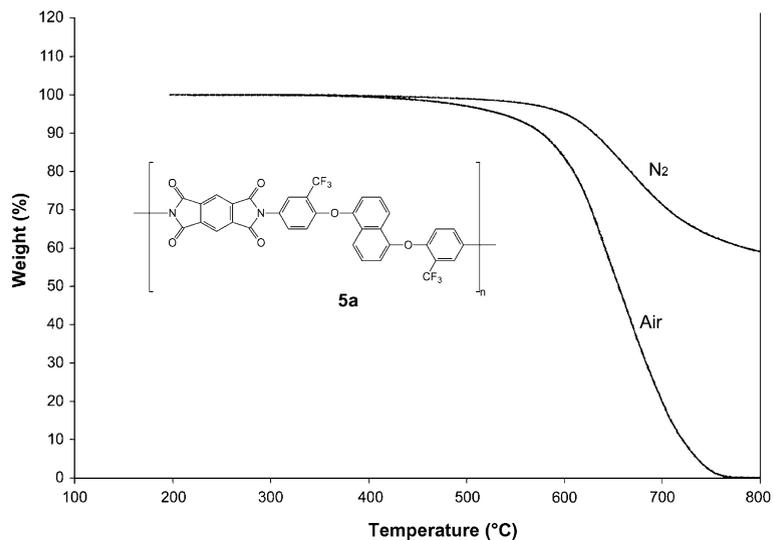
Fig. 5. The TMA curve of polyimide **5a** at a heating rate of 10 °C/min.Fig. 6. TGA curves of polyimide **5a** at a heating rate of 20 °C/min.

Table 5
Moisture absorption and dielectric constants of the polyimides

Polyimide	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (Dry)		
			1 kHz	10 kHz	1 MHz
5a	69	2.0	3.62	3.62	3.55
5b	110	1.6	3.59	3.57	3.52
5c	82	1.9	3.61	3.61	3.54
5d	79	1.5	3.39	3.39	3.34
5e	82	2.2	3.70	3.71	3.64
5f	103	0.5	3.13	3.21	3.17
5g	90	0.7	3.31	3.35	3.32
Ref ^a	80	2.1	3.89	3.85	3.67

^a A reference polyimide prepared from PMDA and 4,4'-oxydianiline (η_{inh} of the poly(amic acid) precursor = 2.90 dl/g).

the T_g values obtained by the TMA method are comparable to the T_g values measured by the DSC experiments. For comparison, the T_g values of the structurally similar polyimides **5'** are also listed in Table 4. Because T_g of a polymer might vary with the different instrument sensitivity and heating story, the T_g values of the **5'** series polyimides reported here were obtained by the same DSC instrument and heating story as those used for the **5** series. The T_g values of polymers **5c–5f** are lower than those of **5c'–5f'**, probably can be explained by the fact that the bulky CF_3 side groups decreased intermolecular interactions, thus leading to a decreased T_g . Thermal and thermo-oxidative stability of the polyimides was evaluated by TGA under both nitrogen and air atmospheres using 5 and 10 wt% loss values for comparison. Typical TGA curves in nitrogen and air of the representative polyimide **5a** are illustrated in Fig. 6. All polyimides exhibited good thermal stability with the decomposition temperature (T_d) at 5% weight loss above 500 °C in both air and nitrogen atmospheres and with more than 50 wt% residue remaining when heated to 800 °C in nitrogen. Slightly higher T_d 's at 10% weight loss for the **5** series polyimides in comparison to the **5'** series might be a result of strong C–F bonding.

The moisture absorption and dielectric constants of the fluorinated polyimides are reported in Table 5. Polyimides **5a–5g** had slightly lower dielectric constants (3.21–3.71 at 10 kHz) compared with standard polyimides such as PMDA/ODA (3.85). The decreased dielectric constants could be attributed to the presence of the bulky CF_3 groups, which resulted in less efficient chain packing and increased free volume [27,28]. In addition, the strong electronegativity of fluorine atom resulted in very low polarizability of C–F bonds, thereby decreasing the dielectric constant. These fluorine-containing polyimides showed low moisture absorption values of 0.5–2.2 wt%. The polyimide **5f** exhibited the lowest moisture absorption due to the highest fluorine content in the repeat unit; therefore, it showed the lowest dielectric constant among this series polyimides.

4. Conclusions

A novel fluorine-containing diamine, 1,5-bis(4-amino-2-trifluoromethylphenoxy)naphthalene, was successfully synthesized from available reagents in high purity and high yield. A series of novel fluorinated aromatic polyimides with moderate to high molecular weights were prepared from the diamine with aromatic tetracarboxylic dianhydrides. Because of the presence of CF_3 and aryl ether groups along the polymer main chain, most of the polyimides had good solubility and could be processed into transparent, flexible, and tough films. The data of TGA, DSC, and TMA analyses indicated that these polyimides have excellent thermal

stability. Thus, these polyimides exhibit a good combination of properties required for high-performance materials and demonstrate a promising potential for future applications.

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