

# Organosoluble and optically transparent fluorine-containing polyimides based on 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl

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## Abstract

A novel fluorinated diamine monomer, 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl, was prepared by a nucleophilic chloro-displacement reaction of 3,3',5,5'-tetramethyl-4,4'-biphenol with 2-chloro-5-nitrobenzotrifluoride and subsequent reduction of the intermediate dinitro compound. The diamine was reacted with aromatic dianhydrides to form polyimides via a two-step polycondensation method; formation of poly(amic acid)s, followed by thermal imidization. All the resulting polyimides were readily soluble in many organic solvents and exhibited excellent film forming ability. The polyimides exhibited high  $T_g$  (312–351 °C), good thermal stability, and good mechanical properties. Low moisture absorptions (0.2–1.1 wt%), low dielectric constants (2.54–3.64 at 10 kHz), and low color intensity were also observed. © 2002 Elsevier Science Ltd All rights reserved.

**Keywords:** Fluorine-containing polyimides; Solubility; Color intensity

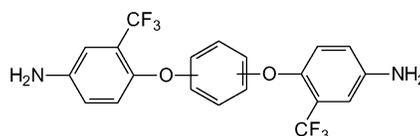
## 1. Introduction

Aromatic polyimides exhibit excellent thermal, mechanical and electrical properties and have been widely used in microelectronic and aerospace engineering [1]. However, one of the problems with most polyimides is their poor processability caused by limited solubility in organic solvents and high melting and softening temperatures, thus narrowing down their applicability. To overcome such a difficulty, polymer structure modification becomes necessary. Much effort has been achieved in designing and synthesizing new dianhydrides [2–9] and/or diamines [10–13], thus, producing a great variety of soluble and processable polyimides for various purposes.

On the other hand, a low dielectric constant is one of the most attractive properties of polyimide materials for microelectronics applications. In order to achieve a polymer structure with a low dielectric constant, repeating units with low polarity and low polarizability have to be used [14]. This also decreases water uptake. The incorporation of aliphatic adamantane or diamantane moiety is known to

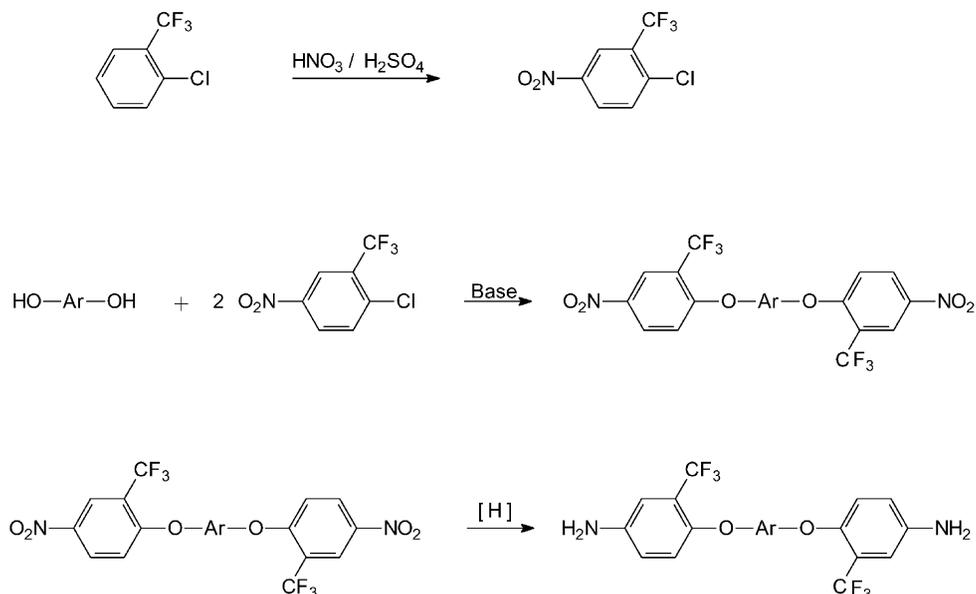
result in low dielectric constants because of high hydrophobicity, low polarity and increased free volume [15–18]. Another effective approach to decrease the dielectric constant is to introduce fluorine substituents or perfluoroalkyl side groups into polyimide materials. As is well known, the strong electronegativity of fluorine results in very low polarizability of the C–F bonds. In the past two to three decades, a number of fluorine-containing dianhydrides and diamines have been introduced to prepare fluorinated polyimides with low water uptake, low refractive index and low dielectric constant while maintaining many of the advantages of polyimides [19–23]. The incorporation of fluorine-containing substituents 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 (3F) groups, such as 1,3- or 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene with the following formula, are soluble high temperature polymer materials with low moisture uptake, low



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Scheme 1. General synthesis strategy for the 3F-substituted bis(ether amine)s.

dielectric constant, high optical transparency, and low birefringence [24–26]. These 3F-bis(ether amine)s can be synthesized easily by halo displacement from halonitrobenzotrifluorides such as 2-chloro-5-nitrobenzotrifluoride with resorcinol or hydroquinone followed by reduction of the resulting dinitro compounds (Scheme 1). This strategy allows the use of any sufficiently nucleophilic bisphenol for the synthesis and thus opens up the path to a large number of 3F-bis(ether amine)s. In the present study, a new 3F-bis(ether amine), 4,4'-bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl, was synthesized and was subsequently reacted with dianhydrides to prepare polyimides. The polymers were subjected to the solubility test and thermal, optical and dielectric property measurements, and compared to analogous counterparts prepared from a structurally similar bis(ether amine), 4,4'-bis(4-aminophenoxy)-3,3',5,5'-tetramethylbiphenyl (TMBAPB). The presence of methyl substituents on a ring unit at *ortho* positions to the ether linkage was expected to increase  $T_g$  of the polymers, due to the hindrance effect of the chain rotation. In addition, these 3F and methyl-substituted polyimides may exhibit enhanced solubility and diminished dielectric constants because of increased free volume caused by the 3F and methyl substituents.

## 2. Experimental

### 2.1. Materials

3,3',5,5'-Tetramethyl-4,4'-biphenol (Mitsubishi Petrochemical Co., Japan) and 2-chloro-5-nitrobenzotrifluoride (Acros) were used as received. As described in a previous article [27], TMBAPB (mp = 227–228 °C) was prepared by the aromatic nucleophilic substitution reaction of 4-

chloronitrobenzene with 3,3',5,5'-tetramethyl-4,4'-biphenol 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) (**3b**) (Aldrich) were recrystallized from acetic anhydride before use. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) (**3c**) (Oxychem) were purified by sublimation. 3,3',4,4'-Diphenylsulfonetetracarboxylic dianhydride (DSDA) (**3d**) (New Japan Chemical Co.) and 4,4'-oxydiphthalic anhydride (OPDA) (**3e**) (Oxychem) were purified by recrystallization from acetic anhydride prior to use. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (**3f**) (Hoechst) was purified by sublimation. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

### 2.2. Monomer synthesis

#### 2.2.1. 4,4'-Bis(4-nitro-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (**1**)

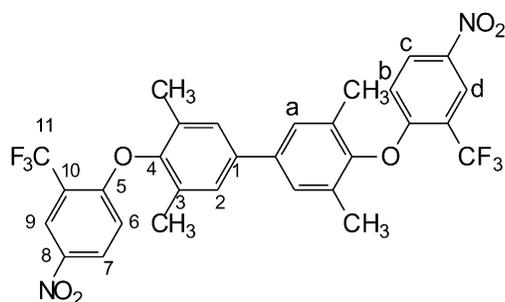
3,3',5,5'-Tetramethyl-4,4'-biphenol (12.1 g, 0.05 mol) and 2-chloro-5-nitrobenzotrifluoride (23 g, 0.1 mol + 0.4 g) were dissolved in 100 ml of *N,N*-dimethylformamide (DMF) in a 300 ml flask with stirring. Then, potassium carbonate (13.8 g, 0.1 mol) was added, and the suspension mixture was heated at 120 °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 with water, and dried (30.3 g, 97%). The crude product was recrystallized from DMF/methanol to give pale-yellow fine needles (24.1 g, 78%); mp = 266–267 °C (onset to peak top

temperature), by differential scanning calorimetry (DSC) at a scan rate of 2 °C/min.

IR (KBr): 1523, 1357 (–NO<sub>2</sub> stretch), 1270 (C–O stretch), 1139 cm<sup>-1</sup> (C–F stretch).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ, ppm): 8.55 (d, *J* = 2.4 Hz, 2H, Hd), 8.47 (dd, *J* = 8.0, 2.4 Hz, 2H, Hc), 7.64 (s, 4H, Ha), 6.80 (d, *J* = 8.0 Hz, 4H, Hb), 2.15 (s, 12H, –CH<sub>3</sub>).

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ, ppm): 161.17 (C<sup>5</sup>), 150.39 (C<sup>4</sup>), 142.99 (C<sup>8</sup>), 139.19 (C<sup>1</sup>), 132.20 (C<sup>2</sup>), 131.50 (C<sup>3</sup>), 129.46 (C<sup>7</sup>), 125.26 (C<sup>9</sup>), 118.33 (C<sup>6</sup>), 15.69 (methyl carbons). The quartet signals of C<sup>10</sup> and C<sup>11</sup> carbons are too weak to be assigned because of low solubility of dinitro compound **1** in DMSO-d<sub>6</sub>.



Anal. calcd for C<sub>30</sub>H<sub>22</sub>F<sub>6</sub>N<sub>2</sub>O<sub>6</sub> (620.50): C, 58.07; H, 3.57; N, 4.51. Found: C, 58.16; H, 3.47; N, 4.74.

#### 2.2.2. 4,4'-Bis(4-amino-2-trifluoromethylphenoxy)-3,3',5,5'-tetramethylbiphenyl (**2**)

A mixture of the purified dinitro compound **1** (21 g, 0.03 mol), 10% Pd/C (0.2 g), ethanol (200 ml), tetrahydrofuran (THF) (50 ml), and hydrazine monohydrate (10 ml) was heated at reflux temperature for about 6 h. The reaction 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 to give off-white crystals (13.8 g, 82%); mp = 256–257 °C by DSC (2 °C/min).

IR (KBr): 3477, 3384 (N–H stretch), 1255 (C–O stretch), 1137 cm<sup>-1</sup> (C–F stretch).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, δ, ppm): 7.49 (s, 4H), 6.99 (d, *J* = 2.4 Hz, 2H), 6.70 (dd, *J* = 8.0, 2.4 Hz, 2H), 6.23 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 4H, –NH<sub>2</sub>), 2.13 (s, 12H, –CH<sub>3</sub>).

<sup>13</sup>C NMR (DMSO-d<sub>6</sub>, δ, ppm): 151.10, 146.70, 144.45, 137.84, 132.33, 128.50, 125.13 (quartet, <sup>1</sup>*J*<sub>C–F</sub> = 271 Hz), 119.63, 117.52 (quartet, <sup>2</sup>*J*<sub>C–F</sub> = 30 Hz), 114.95, 112.81 (quartet, <sup>3</sup>*J*<sub>C–F</sub> = 5 Hz).

Anal. calcd for C<sub>30</sub>H<sub>26</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub> (560.54): C, 64.28; H, 4.67; N, 4.99. Found: C, 64.44; H, 4.58; N, 5.00.

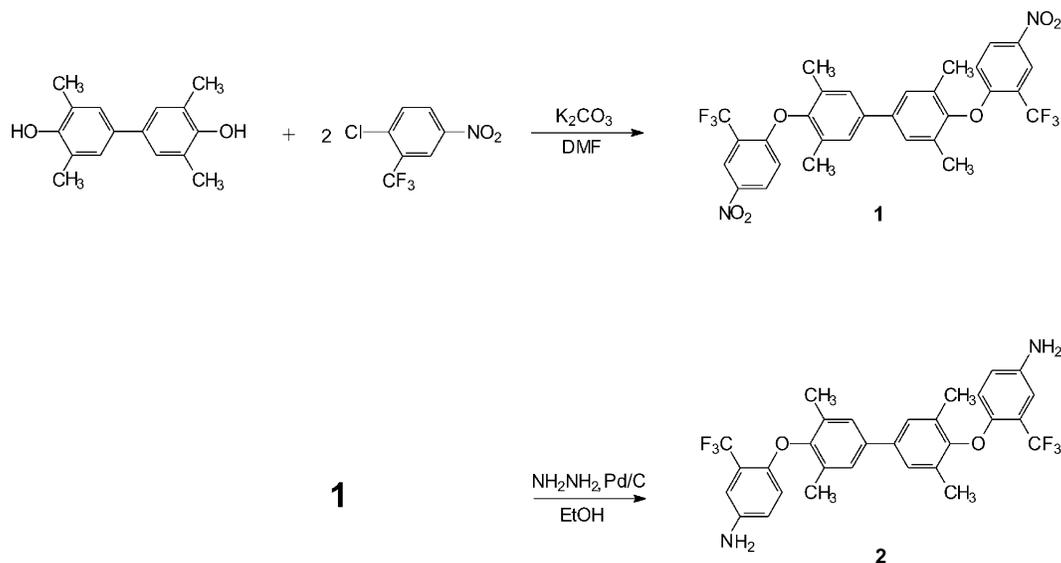
#### 2.3. Polymer synthesis

The general polymerization procedure is illustrated by the following example. To a solution of 0.7199 g (1.28 mmol) of 3F-diamine **2** in 9.5 ml of dried DMAc in

a 50 ml flask, 0.2801 g (1.28 mmol) of PMDA 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 1.61 dl/g, as measured in DMAc at a concentration of 0.5 g/dl at 30 °C. The poly(amic acid) was subsequently converted to polyimide either by thermal or chemical imidization process. For the thermal imidization process, about 7 g of the obtained poly(amic acid) solution was poured into a 9 cm glass culture dish which was placed overnight in a 90 °C oven for removal of the solvent. The semi-dried poly(amic acid) film was further dried and transformed into polyimide **5a** by 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 being soaked in water. The inherent viscosity of the thermally cured polyimide **5a** was 0.84 dl/g in DMAc at a concentration of 0.5 g/dl at 30 °C. For tensile test, the polyimide films were further heated at 300 °C for another 1 h. Chemical imidization was carried out via the addition of 2 ml of pyridine and 5 ml of acetic anhydride into the remaining poly(amic acid) solution (about 3 g) at room temperature overnight. The resulting homogeneous polyimide solution was poured into methanol to give a pale-yellow fibrous precipitate, which was collected by filtration, washed thoroughly with methanol, and dried. The inherent viscosity of the chemically imidized polyimide **5a** was 1.22 dl/g in DMAc at a concentration of 0.5 g/dl at 30 °C.

#### 2.4. Measurements

Infrared spectra were recorded on a Horiba Fourier transform infrared spectrometer FT-720. Elemental analyses were run in a Perkin–Elmer model 2400 C, H, N analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Jeol EX-400 spectrometer. The inherent viscosities were determined at 0.5 g/dl concentration using an Ubbelohde 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 (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. DSC analyses were performed on a Perkin–Elmer Pyris 1 DSC in flowing nitrogen with heating rate of 20 °C/min. Glass transition temperatures (*T*<sub>g</sub>) 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. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu K<sub>α</sub> radiation (40 kV, 15 mA) with a scanning rate of 2°/min. Measurements were performed with film specimens of 30–50 μm in thickness. Mechanical properties of the films were measured with an Instron tensile tester model 1130 with a 5 kg load cell at a crosshead speed of 5 cm/min on strips approximately 80–100 μm and 0.5 cm wide, with a 2 cm gauge length. An average of at least five individual determinations was used.



Scheme 2. Synthesis of 3F-diamine 2.

Colorimetry of the polymers was evaluated by a Macbeth Color-eye colorimeter. Measurements were performed with films of 30–50  $\mu\text{m}$  in thickness, using an observational angle of  $10^\circ$  and a CIE (Commission International de l'Eclairage)-D illuminant. A CIE LAB color difference equation was used. UV–visible spectra of the polymer films were recorded on a Simadzu UV–visible spectrophotometer UV-1601. Dielectric property of the polymer films was 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  $25^\circ\text{C}$  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  $25^\circ\text{C}$  for 3 days.

### 3. Results and discussion

#### 3.1. Monomer synthesis

The 3F-containing bis(ether amine) 2 was prepared in two steps according to a well-developed method (Scheme 2) [10,11]. The first step is a Williamson etherification reaction of 3,3',5,5'-tetramethyl-4,4'-biphenol and 2-chloro-5-nitrobenzotrifluoride in the presence of potassium carbonate in DMF. The diamine 2 was readily obtained in a good yield by the catalytic reduction of the intermediate dinitro compound 1 with hydrazine hydrate and Pd/C catalyst in refluxing ethanol.

FTIR, NMR, and elemental analysis were used to confirm the structures of the intermediate 1 and the diamine monomer 2. Fig. 1 shows the FTIR spectra of dinitro compound 1 and diamine 2. The nitro group of compound 1 gave two typical absorption bands at  $1531$  and  $1330\text{ cm}^{-1}$  ( $\text{NO}_2$  asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed the typical pair of N–H stretching bands in the region of  $3300$ – $3500\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectrum (Fig. 2) confirms 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  $5.16\text{ ppm}$  corresponding to the primary aromatic amine protons. Fig. 3 presents the  $^{13}\text{C}$  NMR spectrum of diamine 2 in  $\text{DMSO-d}_6$ . Most of the carbon-13 atoms in 3F-diamine 2 resonated in the region of  $112.8$ – $151.1\text{ ppm}$ . The methyl carbon resonated at  $15.4\text{ ppm}$ , and the carbons  $\text{C}^{10}$  and  $\text{C}^{11}$  of 2 showed clear quartets because of the heteronuclear  $^{13}\text{C}$ – $^{19}\text{F}$  coupling. Thus, all the spectroscopic data obtained were in good agreement with the expected structures.

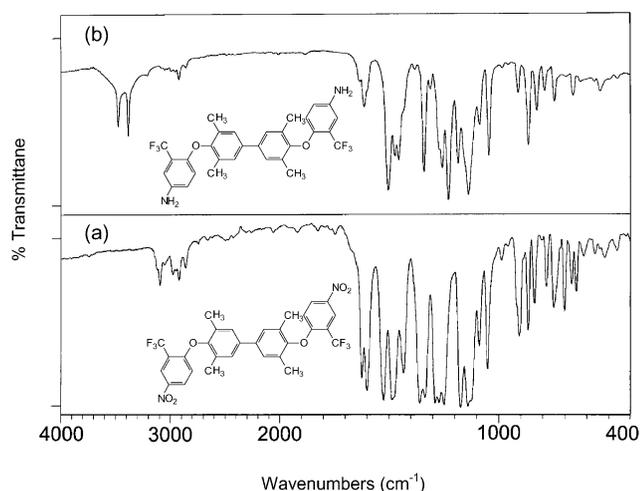


Fig. 1. IR spectra of (a) 3F-dinitro compound 1 and (b) 3F-diamine 2.

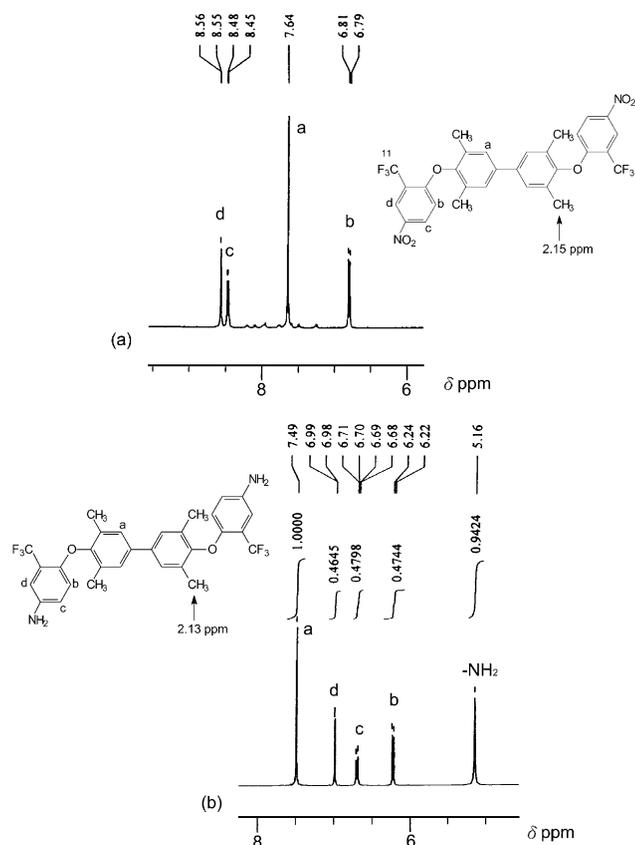


Fig. 2.  $^1\text{H}$  NMR spectra of (a) 3F-dinitro compound **1** and (b) 3F-diamine **2** in  $\text{DMSO-d}_6$ .

### 3.2. Polymer synthesis

The 3F-diamine **2** is polycondensed with various dianhydrides to give the fluorinated polyimides **5a–f** displayed in Scheme 3. No difficulty was encountered in obtaining high molecular weight poly(amic acid)s from the reactions of 3F-diamine **2** with aromatic dianhydrides **3a–f**. Although the amino groups in diamine **2** is less basic than a normal aromatic amine due to the inductive deactivation of the 3F group, such 3F-diamine was still sufficiently reactive to give high molecular weight poly(amic acid)s when they were allowed to polymerize for sufficient of time. As shown in Table 1, the inherent viscosities of the intermediate poly(amic acid)s were in the range of 1.49–2.24 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 the polyimides were recorded in the range of 0.65–1.19 dl/g for those obtained by thermal imidization and of 0.74–1.31 dl/g for those obtained by chemical imidization. The inherent viscosity of the thermally imidized polyimide was generally

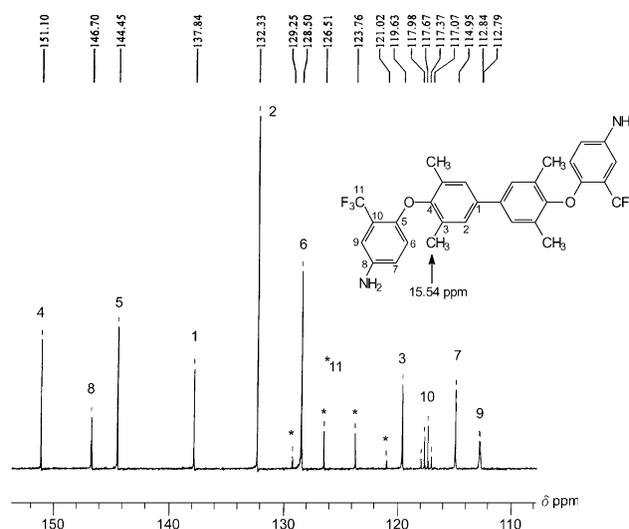


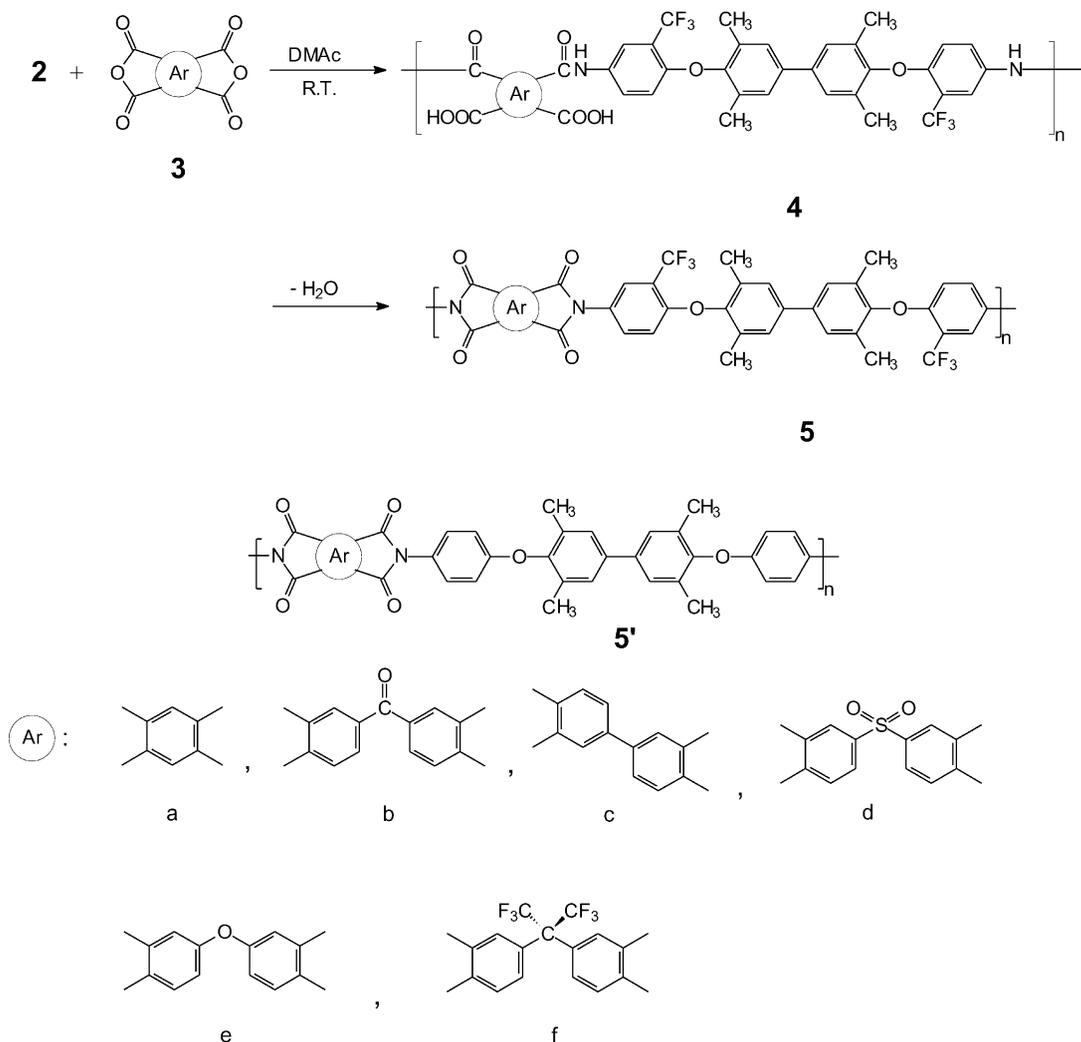
Fig. 3. The  $^{13}\text{C}$  NMR spectrum of 3F-diamine **2** in  $\text{DMSO-d}_6$ .

lower than that of the chemically imidized one, possibly due to the fact that the molecular weight of the poly(amic acid) drops during thermal cure of polyimide.

The formation of polyimides was confirmed by means of elemental analysis and IR and NMR spectroscopy. Fig. 4 shows a typical set of IR and  $^1\text{H}$  NMR spectra for polyimide **5a**. All polyimides exhibited characteristic imide group absorptions around 1780 and 1730 (typical of imide carbonyl asymmetrical and symmetrical stretch), 1380 (C–N stretch), and 1100 and 725  $\text{cm}^{-1}$  (imide ring deformation), together with some strong absorption bands in the region of 1100–1300  $\text{cm}^{-1}$  due to the C–O and C–F stretching. The lack of amide and carboxyl bands indicated that the polymers were fully imidized, as also confirmed by the fact that the  $^1\text{H}$  NMR spectrum showed no residual resonance in the region of 10–11 ppm, indicating the absence of amide NH protons. The results of elemental analyses of all polyimides are also listed in Table 1. The values found were in good agreement with the calculated ones of the proposed structures.

### 3.3. Properties of the polyimides

All the fluorinated polyimides **5a–f** revealed an amorphous nature, as evidenced by the X-ray diffraction patterns. The solubility of the thermally cured polyimides was tested qualitatively in various organic solvents, and the results are summarized in Table 2. In addition, the solubility behaviors for the analogous nonfluorinated polyimides **5a–f'** reported previously [23] have been listed for comparative purposes. Because of the introduction of the bulky 3F group, most polyimides were readily soluble in polar solvents such as NMP and DMAc at room temperature or upon heating. Conversely, for the **5a–f'** series, only the polyimide (**5f'**) derived from 6FDA was soluble in most of the solvents upon heating. Poor solubility for the **5'** polyimides indicates either strong intermolecular interactions or good packing



Scheme 3. Synthesis of polyimides.

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

Poly(amic acid)		Polyimide		Elemental analysis (%) of polyimides <sup>a</sup>				
Code	$\eta_{inh}^b$ (dl/g)	Code	$\eta_{inh}^b$ (dl/g)	Formula (formula weight)	C	H	N	
<b>4a</b>	1.61	<b>5a</b>	0.84 <sup>a</sup> (1.22) <sup>c</sup>	(C <sub>40</sub> H <sub>24</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	64.69	3.26	3.77
				(742.63) <sub>n</sub>	Found	63.63	3.02	3.96
<b>4b</b>	1.58	<b>5b</b>	1.19 (1.31)	(C <sub>47</sub> H <sub>28</sub> N <sub>2</sub> O <sub>7</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.67	3.33	3.31
				(846.74) <sub>n</sub>	Found	66.06	3.23	3.39
<b>4c</b>	2.24	<b>5c</b>	1.04 (1.25)	(C <sub>46</sub> H <sub>28</sub> N <sub>2</sub> O <sub>6</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	67.48	3.45	3.42
				(818.73) <sub>n</sub>	Found	66.72	3.34	3.45
<b>4d</b>	1.72	<b>5d</b>	0.83 (1.23)	(C <sub>42</sub> H <sub>28</sub> N <sub>2</sub> O <sub>8</sub> SF <sub>6</sub> ) <sub>n</sub>	Calcd	62.59	3.20	3.17
				(882.79) <sub>n</sub>	Found	62.08	3.07	3.29
<b>4e</b>	1.70	<b>5e</b>	0.84 (1.31)	(C <sub>46</sub> H <sub>28</sub> N <sub>2</sub> O <sub>7</sub> F <sub>6</sub> ) <sub>n</sub>	Calcd	66.19	3.38	3.36
				(834.73) <sub>n</sub>	Found	66.08	3.09	3.45
<b>4f</b>	1.49	<b>5f</b>	0.65 (0.74)	(C <sub>49</sub> H <sub>28</sub> N <sub>2</sub> O <sub>6</sub> F <sub>12</sub> ) <sub>n</sub>	Calcd	60.75	2.91	2.89
				(968.75) <sub>n</sub>	Found	60.16	2.78	2.97

<sup>a</sup> Prepared by thermal imidization.

<sup>b</sup> Measured at a polymer concentration of 0.5 g/dl in DMAc at 30 °C.

<sup>c</sup> Prepared by chemical imidization.

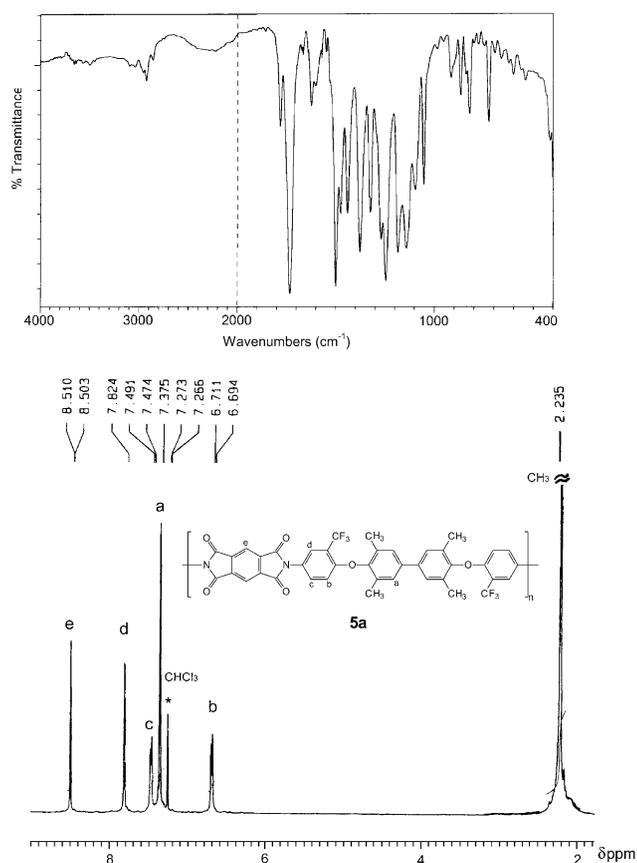


Fig. 4. IR (film) and  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) spectra of polyimide **5a**.

ability. Obviously, the large differences in solubility between the **5** and **5'** series are attributed to the bulky 3F groups, which increased the disorder in the chains and hindered dense chain stacking, thus reducing the interchain

interactions to enhance solubility. All the fluorinated polyimides afforded good-quality and creasable films. The tensile properties of flexible films are summarized in Table 3. They showed an ultimate tensile strength of 80–102 MPa, an elongation to break of 8–16%, and an initial modulus of 1.6–2.0 GPa.

The coloration of the polyimide films was elucidated from the yellowness or redness indices observed by a Macbeth color-eye colorimeter. For comparison, the corresponding polyimides (**5'**) without the 3F groups were also prepared and characterized by their color intensity. The color coordinates of these polyimides are given in Table 3. The results shown in Table 4 and Fig. 5 indicate that all the **5** series fluorinated polyimides showed a lower  $b^*$  value (a yellowness index) by contrast with the corresponding nonfluorinated polyimides (the **5'** series). Fig. 5 also shows arrangements of dianhydride moieties in order of the color intensity of polyimides from deep (PMDA) to pale (6FDA) when the diamine structures are fixed. Moreover, the color intensities of the polyimides also can be elucidated from the cut-off wavelength ( $\lambda_0$ ) observed in the UV–visible absorption spectra. Fig. 6 shows the UV–visible spectra of the polyimide films, and the  $\lambda_0$  from these spectra are listed in Table 3. Consistent with the results obtained from colorimeter, all the fluorinated polyimides revealed a lower  $\lambda_0$  than their respective nonfluorinated analogs. The 6FDA and ODPa produce 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 having the 3F groups in their diamine moieties can be explained from the decreased intermolecular interactions.

Table 2  
Solubility behavior of polyimides

Polymer	Solvent <sup>a</sup>									
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Py	Dioxane	THF	$\text{CH}_2\text{Cl}_2$	Acetone
<b>5a</b>	++	++	++	+	+	++	++	++	++	+ -
<b>5b</b>	++	++	+	+	+	++	++	+ -	+ -	S
<b>5c</b>	+	+	+	S	+	++	++	++	+ -	S
<b>5b/c<sup>d</sup></b>	++	++	++	+	+	++	++	++	+ -	S
<b>5d</b>	++	++	+	++	+	++	++	++	++	++
<b>5e</b>	++	++	+	+	+	++	++	++	++	S
<b>5f</b>	++	++	++	+	+	++	++	++	++	++
<b>5a'</b>	-	-	-	-	-	-	-	-	-	-
<b>5b'</b>	+ -	S	-	S	-	-	-	-	-	-
<b>5c'</b>	+	S	S	S	+	-	-	-	-	-
<b>5d'</b>	+	+	S	S	+	-	-	-	-	-
<b>5e'</b>	+	S	S	S	+	+	-	-	-	-
<b>5f'</b>	+	+	+	+	+	+	+	++	+ -	-

Qualitative solubility was determined with 10 mg of polymer in 1 ml of solvent. ++ = Soluble at room temperature; + = soluble on heating; + - = partially soluble on heating; S = swelling; - = insoluble even on heating.

<sup>a</sup> NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; Py, pyridine; THF, tetrahydrofuran.

<sup>b</sup> Copolyimide of diamine **2** with equimolar **3b** and **3c**.

Table 3  
Tensile properties of polyimide films

Polymer <sup>a</sup>	Tensile strength (MPa)	Elongation to break (%)	Tensile modulus (GPa)
<b>5a</b>	94	16	1.6
<b>5b</b>	102	13	2.0
<b>5c</b>	80	8	1.8
<b>5c/b<sup>b</sup></b>	86	8	1.7
<b>5d</b>	84	10	1.7
<b>5e</b>	95	11	1.8
<b>5f</b>	96	13	1.6

<sup>a</sup> All the polyimide films were heated at 300 °C for 1 h prior to tensile test.

<sup>b</sup> Copolyimide of diamine **2** with equimolar BPDA (**3c**) and BTDA (**3b**).

The bulky and electron-withdrawing 3F group in diamine **2** is effective in decreasing CTC formation between polymer chains through steric hindrance and the inductive effect (by decreasing the electron-donating property of diamine moieties). A secondary positive effect of the 3F substituents on the film transparency is the weakened intermolecular cohesive force due to lower polarizability of the C–F bond. The decrease of intermolecular CTC formation is understandable also from the significant solubility of the polyimides prepared from 3F-diamine **2**.

DSC and TGA were used to evaluate the thermal properties of the polyimides. The thermal behavior data of all fluorinated polyimides are presented in Table 5. The  $T_g$  values of these polyimides were in the 312–351 °C range, depending on the dianhydride used. The thermal stability of the polyimides was evaluated by TGA measurements in air and under nitrogen. The temperatures of 10% weight loss ( $T_{10}$ ) in nitrogen and air atmospheres were determined from

Table 4  
Color coordinates and the cut-off wavelength ( $\lambda_0$ ) from UV–visible spectra for both **5** and **5'** series polyimide films

Polymer	Film thickness ( $\mu\text{m}$ )	Color coordinates <sup>a</sup>			$\lambda_0$ (nm)
		$b^*$	$a^*$	$L^*$	
<b>5a</b>	42	78.98	–7.43	93.78	418
<b>5b</b>	40	62.68	–13.64	96.78	409
<b>5c</b>	34	28.31	–9.28	98.79	395
<b>5b/c</b>	33	57.56	–13.07	96.49	405
<b>5d</b>	44	44.27	–12.29	97.90	399
<b>5e</b>	40	21.01	–5.86	98.66	373
<b>5f</b>	47	17.57	–6.61	99.75	373
<b>5a'</b>	28	86.40	0.80	90.38	424
<b>5b'</b>	33	86.92	–6.81	94.10	430
<b>5c'</b>	46	50.27	–14.54	97.86	414
<b>5d'</b>	40	60.03	–14.32	96.81	415
<b>5e'</b>	29	22.15	–8.09	99.07	375
<b>5f'</b>	31	25.59	–10.01	99.37	375
Kapton	38	85.00	0.30	90.00	443

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

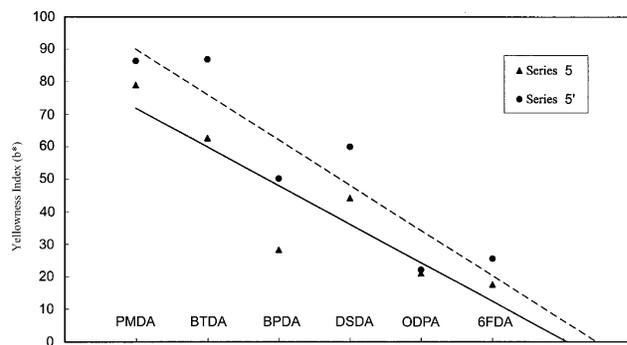


Fig. 5. Comparison of the yellowness index ( $b^*$  value) between the **5** and **5'** series polyimides.

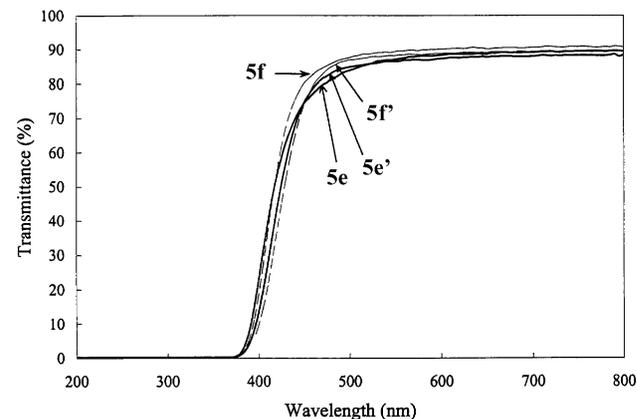
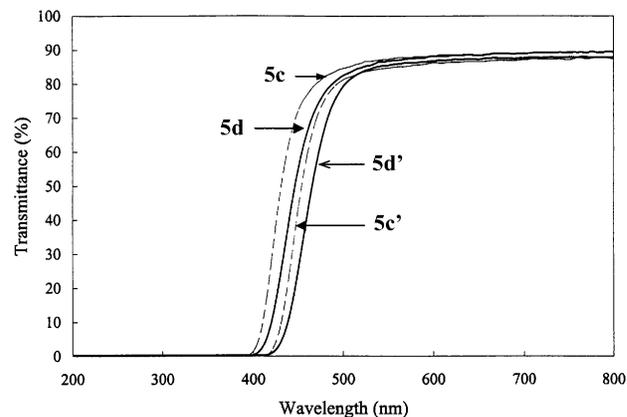
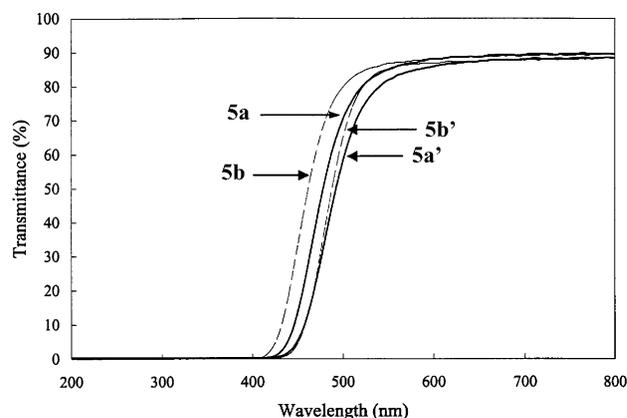


Fig. 6. UV–visible spectra of polyimide films.

Table 5  
Thermal behavior data of polyimides

Polymer	$T_g$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>		Char yield (%) <sup>c</sup>
		In N <sub>2</sub>	In air	
<b>5a</b>	314	513	489	57
<b>5b</b>	313	511	483	59
<b>5c</b>	351	512	491	61
<b>5b/c</b>	338	523	489	61
<b>5d</b>	334	470	460	53
<b>5e</b>	312	494	498	55
<b>5f</b>	326	516	495	54

<sup>a</sup> Midpoint temperature of baseline shift on the second DSC heating trace (scan rate = 20 °C/min) of the sample after quenching from 400 °C.

<sup>b</sup> Temperatures at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

<sup>c</sup> Residual weight (%) at 800 °C in nitrogen.

original TGA thermograms and are also given in Table 5. The  $T_{10}$  values of these polyimides stayed in the range of 470–523 °C in nitrogen and in the range of 460–498 °C in air, respectively. They left more than 53% char yield at 800 °C in nitrogen. The TGA data indicate that these polyimides have fairly high thermal stability.

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. Table 6 shows the results. Polyimides **5a–f** have lower dielectric constants (2.54–3.64 at 10 kHz) compared with standard polyimides such as PMDA/ODA polyimide (3.85). The decreased dielectric constants might be partly attributable to the presence of bulky 3F groups, which result in a less efficient chain packing and an increase in the free volume. In addition, the strong electronegativity of fluorine results in very low polarizability of the C–F bonds, thus decreasing the dielectric constant. Table 6 also presents the moisture absorption of the polyimides, which ranges from 0.1 to 1.1%. In comparison, most of the polyimides **5a–f** exhibited lower moisture absorptions than the corresponding non-fluorinated homologs **5a–f'** and PMDA/ODA polyimide film. Polyimide **5f** exhibited the lowest moisture absorption because of the higher fluorine content in the repeat unit.

#### 4. Conclusions

A novel fluorinated diamine monomer **2** was synthesized via a straightforward, high-yielding two-step procedure, including the Williamson etherification reaction. A series of novel fluorinated polyimides have been obtained from the trifluoromethyl-substituted diamine with different aromatic dianhydrides. The resulting polyimides exhibit high solubility, good film-forming ability, high optical transparency, reasonable thermal stability, high glass transition temperatures ( $T_g > 318$  °C), and good film forming ability together

Table 6  
Moisture absorption and dielectric constants of polyimides

Polyimide	Film thickness (μm)	Moisture absorption (%)	Dielectric constant (dry)		
			1 kHz	10 kHz	1 MHz
<b>5a</b>	42	0.6 (0.6) <sup>a</sup>	2.55	2.54	2.48
<b>5b</b>	40	0.6 (1.0)	3.47	3.47	3.38
<b>5c</b>	34	0.4 (0.7)	2.76	2.75	2.68
<b>5d</b>	44	1.1 (0.7)	3.68	3.64	3.55
<b>5e</b>	40	1.0 (0.6)	3.52	3.52	3.45
<b>5f</b>	47	0.2 (0.2)	2.69	2.66	2.59
Ref <sup>b</sup>	38	2.0	3.89	3.85	3.67

<sup>a</sup> Data in parentheses are those of the corresponding **5'** series polyimides.

<sup>b</sup> A reference polyimide prepared from PMDA and 4,4'-oxydianiline (ODA) ( $\eta_{inh}$  of the poly(amic acid) precursor = 2.90 dl/g).

with low dielectric constants. Thus, this series of polyimides demonstrates a good combination of properties and processability.

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