

Synthesis and Properties of Fluorine-Containing Polyimides

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ABSTRACT: A series of new fluorine-containing polyimides have been synthesized from the condensation of 2,2-*bis*[4-(4-aminophenoxy)phenyl]propane, 2,2-*bis*[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, or 2,2-*bis*[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane with various aromatic dianhydrides. The dielectric constant at 1 KHz in the fluorine-containing polyimides decreases from 3.51 to 2.72 as fluorine content increases. The poly(amic acid)s had inherent viscosities of 0.52–1.23 dL/g, depending on the diamines and dianhydrides. Most of the resulting polymers showed an amorphous nature and afforded flexible and tough films. The amount of moisture absorption decreases as fluorine content in polyimides increases. The glass transition temperatures of these polyimides were in the range of 287–328°C, and the 10% weight loss temperatures were above 542°C in nitrogen.
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Key words: fluorine-containing polyimides; poly(amic acid); 2,2-*bis*[4-(4-amino-2-trifluoromethylphenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane

INTRODUCTION

Aromatic polyimides are one of the families of high-performance specialty thermoplastics and have been widely applied in the aviation, automobile, aerospace, and electronic fields because of their good thermal stability, chemical resistance, and excellent mechanical and electrical properties. Much attention has been focused recently on the preparation of fluorine-containing aromatic condensation polymers because of their unique properties and high performance.^{1–5} The incorporation of fluorine into polyimide structures has been intensively explored in the past decade with the hope of fine tuning several properties of particular interest. It is known that the increase in solubility, processability, and transparency, and the decrease in water absorption and dielectric

constant, can be achieved by the incorporation of fluorine atoms in the polyimides.^{6–15}

A common synthetic method for aromatic polyimides is the two-stage polyaddition and polycondensation of a dianhydride with a diamine in an aprotic solvent, such as *N,N*-dimethylacetamide, where solution polymerization proceeds under ambient temperature to obtain a soluble poly(amic acid), and then thermal treatment forms polyimides. The precursor poly(amic acid) is initially formed via nucleophilic attack by the diamine at a carbonyl carbon of the dianhydride. The rate of this reaction is largely dependent on the electron-donating potential of the amine and on the electron affinity of the anhydride. Although the ways in which fluorine atoms and trifluoromethyl groups affect the basicity of an amine and the electron affinity of an anhydride carbonyl are complex, it is fair to generalize that the high electronegativity of fluorine acts to reduce the basicity of amines and to increase the electron affinity of anhydrides. In some cases, the steric and electronic characteristics of the fluorinated groups

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may reduce the reactivity of the nucleophilic component in the polycondensation reaction to the point where polymerization is suppressed or effectively precluded.

Although some work has been reported on the fluorine-containing polyimides, no systematic investigation of the effect of fluorine contents on the properties of polyimides has been carried out. In this study, we synthesized a series of diamines with various fluorine contents. From these diamines, a series of new fluorine-containing polyimides could be synthesized by reacting them with various aromatic dianhydrides. The primary aim of this work was to illustrate the effect of fluorine content on the properties of polyimides, such as inherent viscosity, solubility, thermal properties, dielectric constant, and water absorption. The structure/property relationships of the fluorine-containing polyimides, including solubility, crystallinity, and dynamic mechanical properties, were also investigated.

EXPERIMENTAL

Materials

Bisphenol A (from TCI, Tokyo, Japan), *p*-chloronitrobenzene (from TCI), 2,2-*bis*(4-hydroxyphenol)-1,1,1,3,3,3-hexafluoropropane (from Riedel-de Haën Chinosol, Seelze, Germany), 2-chloro-5-nitrobenzotrifluoride (from Aldrich), hydrazine monohydrate (from KATAYAMA, Tokyo, Japan), potassium carbonate (from SHOWA), copper powder (from JANSEN, Geel, Belgium), tetra-*n*-butyl ammonium chloride (TBAC; from Aldrich, Milwaukee, WI, USA), 10% Pd/C (from Ferak), and glacial acetic acid (from ACROS, New Jersey, USA) were used as received. Pyromellitic dianhydride (PMDA; from CHRISKEV, Leawood, KS, USA), 3,3'-4,4'-biphenyltetracarboxylic dianhydride (from CHRISKEV), 3,3'-4,4'-benzophenonetetracarboxylic dianhydride (from CHRISKEV), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA; from Aldrich) were recrystallized from acetic anhydride before use. *N,N*-Dimethylformamide and *N,N*-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

Monomer Synthesis

2,2-*bis*[4-(4-Nitro-2-trifluoromethylphenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (I₃)

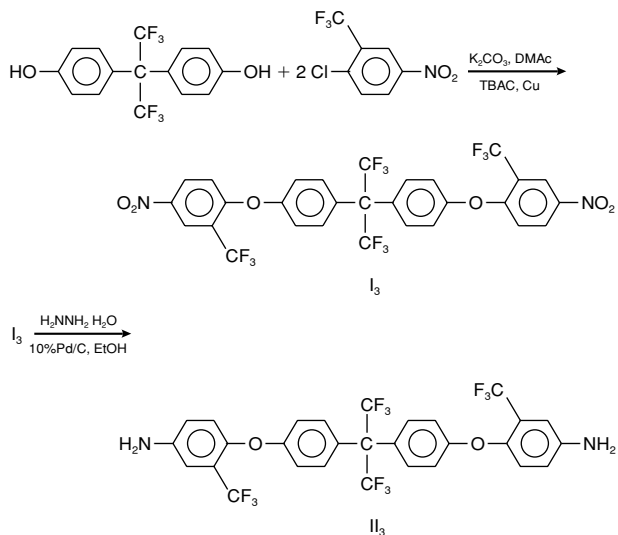
This compound was synthesized by the reaction of 2,2-*bis*(4-hydroxyphenol)-1,1,1,3,3,3-hexafluoropropane (30.60 g, 0.091 mol) and 2-chloro-5-nitrobenzotrifluoride (45.11 g, 0.2 mol) in the presence of potassium carbonate (41.46 g, 0.2 mol), TBAC (0.585 g), copper powder (1.17 g) and DMAc (250 mL) at about 170°C for 42 h. The mixture was then filtered to remove copper powder. The filtered liquid was poured into 400 mL of methanol-water (1 : 1 by volume). The crude was dried in vacuum at 45°C for 2 h. It was stirred with 300 mL of cyclohexane and then isolated by filtration, followed by recrystallization from glacial acetic acid to provide yellow needles (melting point [mp], 173–174°C). The yield was 40.93 g (63.0%). The infrared (IR) spectrum (KBr) exhibited absorptions at 1,510 and 1,345 cm⁻¹ (NO₂), 1,020 and 1,220 cm⁻¹ (C—O—C). Anal. calcd, C₂₉H₁₄F₁₂N₂O₆: C, 48.74%; H, 1.96%; N, 3.92%. Found: C, 48.63%; H, 1.92%, N, 3.85%.

2,2-*bis*[4-(4-Amino-2-trifluoromethylphenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (II₃)

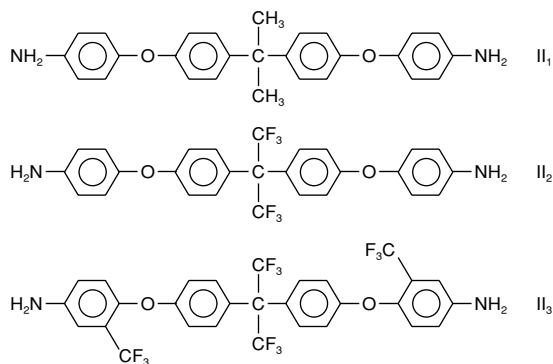
The dinitro compound I₃ (35 g, 0.049 mol), 0.20 g of 10% Pd/C, and 250 mL of ethanol were introduced into the four-neck flask, to which 90 mL of hydrazine monohydrate was added dropwise over a period of 30 min at 86°C. After the addition was completed, the reaction mixture was filtered to remove Pd/C (palladium/charcoal). The crude product was obtained by the removal of excess hydrazine and ethanol and was further recrystallized from ethanol to give white needles (mp, 159–160°C). The yield was 27.6 g (86.1%). The IR spectrum (KBr) showed absorptions at 3,340 and 3,400 cm⁻¹ (N—H) and 1,020 and 1,250 cm⁻¹ (C—O—C). Anal. calcd, for C₂₉H₁₈F₁₂N₂O₂: C, 53.21%; H, 2.75%; N, 4.28%. Found: C, 53.16%; H, 2.74%; N, 4.24%. The reactions are shown in Scheme 1. Scheme 1 also lists various diamines, which were synthesized by procedures similar to those mentioned above.

Polymerization

A typical example of the polycondensation is given below. The reaction is shown in Scheme 2.



Diamines Synthesized:



Scheme 1

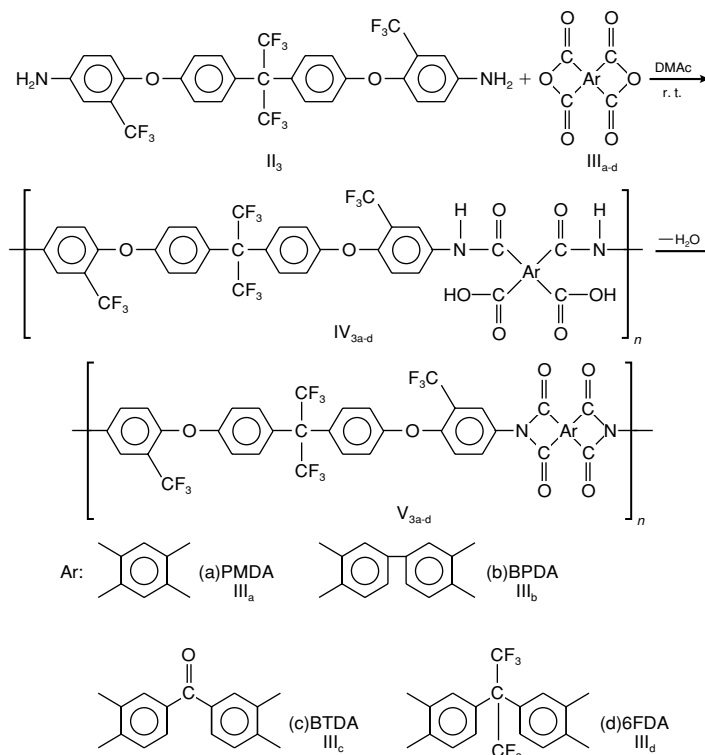
Polyimide V_{3a} Prepared from Diamine II₃ and Dianhydride (PMDA, III_a)

Fluorine-containing diamine II₃ (2.11 g, 0.0322 mol) was dissolved in DMAc (15 mL) to give a clear solution, and PMDA (0.70 g, 0.0322 mol) was then added to the solution with vigorous stirring. The solution was stirred in a dry nitrogen atmosphere at room temperature for 4 h, and the 15 wt % poly(amic acid) IV_{3a} was obtained. The poly(amic acid) solution was trickled into 500 mL of isopropanol-water (1 : 1 by volume), giving rise to a precipitate which was washed thoroughly with isopropanol and water, collected by filtration, and dried. The inherent viscosity of the poly(amic acid) in DMAc was 1.04 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The IR spectrum showing an absorption peak due to carbonyl stretching of the amide group appeared at about 1,725 cm⁻¹ in the poly(amic acid). The poly-

(amic acid) solution thus obtained was cast onto a glass plate, and the solvent was removed at 80°C in a vacuum oven for 2 h. The semidried film was further dried and imidized by sequential heating at 120°C for 30 min, 150°C for 30 min, 180°C for 30 min, and 300°C for 1 h. This treatment promoted imidization and converted poly(amic acid) into polyimide. The resulting polyimide film obtained by the thermal treatment was insoluble in DMAc and other aprotic solvents but soluble in concentrated sulfuric acid. The IR spectrum of the polyimide (film) exhibiting absorption peaks due to carbonyl asymmetric and symmetric stretching of imide groups appeared at 1,725 and 1,780 cm⁻¹ (Fig. 1).

Measurements

The IR spectra were measured with a Jasco VALOR III spectrometer. In a typical experiment, an average of 20 scans per sample was made. The ¹H nuclear magnetic resonance (NMR) spectra were measured with a Bruker WP-100 NMR spectrometer at 200 MHz, using dimethyl-d₆ sulfoxide as a solvent. The ¹H chemical shifts were calibrated by using tetramethylsilane as an internal standard. Elemental analyses were carried out with a Heraeus CHN-Rapid element analyzer. Mass spectrometric analyses were performed on a VG 70-250 S GC/MS spectrometer with a solid inlet. Melting points were obtained on a polarizing microscope (Laboratory Devices MEL-TEMP. II.) melting point apparatus and were uncorrected. The inherent viscosities were measured with a Ubbelohde capillary viscometer (Schott-AVS310). Differential scanning calorimetry (DSC) data were obtained from 8 to 10 mg samples in a nitrogen atmosphere at a flow rate of 30 cm³/min and a heating rate of 20°C/min using a DuPont 910 differential scanning calorimeter. Thermogravimetric analyses (TGA) were performed on a DuPont 951 thermal analyzer using a heating rate of 20°C/min in N₂ at a flow rate of 50 cm³/min. The dielectric constants were measured with a DuPont DEA 2970 (Dielectric Analyzer) at a frequency of 1 KHz and a temperature 30°C in a nitrogen atmosphere at a flow rate of 500 cm³/min by the two parallel plate mode. The specimens were subjected to vacuum pretreatment of 1 Torr at 120°C for 4 h to eliminate absorbed water. Dynamic mechanical analyses (DMA) were made with a Perkin-Elmer DMA 7e. The storage modulus *G'* and tan δ were studied when the sample



Scheme 2

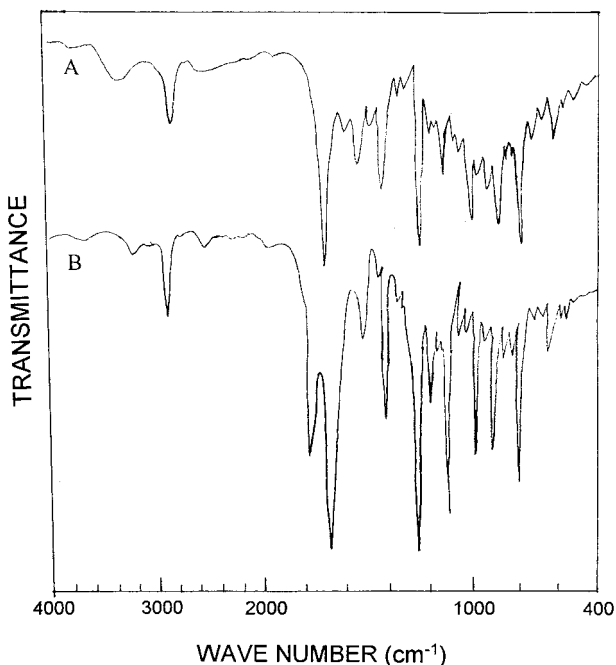


Figure 1 IR spectra of (A) poly(amic acid) IV_{3a} (KBr) and (B) polyimide V_{3a} (film).

was subjected to temperature scan mode at a programmed heating rate of $5^\circ\text{C}/\text{min}$ from ambient to 350°C at a frequency of 1 Hz and an amplitude of 0.2 mm. A sample 10 mm in length, 2 mm in width, and approximately 0.2 mm in thickness was used. The wide-angle X-ray measurements were performed at room temperature with film specimens about 0.2 mm thick on a Rigaku Geiger Flex D-Max IIIa x-ray diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation (40 kV, 15 mA). The scanning rate was $4^\circ/\text{min}$. Qualitative solubility was determined using 0.01 g of polymer in 2 mL of solvent. The water absorption rates were measured. Specimens were immersed in 25°C water, and the weight differences after 3 days were measured.

RESULTS AND DISCUSSION

Synthesis of Monomers

2,2-bis[4-(4-Aminophenoxy)phenyl]propane (II_1) was synthesized in two steps by reducing the dinitro compound obtained by the condensation of 2,2-

bis(4-hydroxyphenyl)propane (bisphenol A) with *p*-chloronitrobenzene. 2,2-*bis*[4-(4-Aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (II₂) was prepared from 2,2-*bis*(4-hydroxyphenol)-1,1,1,3,3,3-hexafluoropropane (bisphenol AF) and *p*-chloronitrobenzene. The synthesis of these two diamines (II₁ and II₂) were according to the reported method.¹⁶ The third diamine, 2,2-*bis*[4-(4-amino-2-trifluoromethyl-phenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (II₃), was synthesized starting from bisphenol AF and 2-chloro-5-nitrobenzotrifluoride, as shown in Scheme 1. It is known that the aryl halides undergo nucleophilic substitution readily if the aromatic ring contains, in addition to halogen, certain electron-withdrawing groups, such as —NO₂, —NO, —CN, or —CF₃, located *ortho* or *para* to halogen. 2-Chloro-5-nitrobenzotrifluoride contains two strong electron-withdrawing groups, —NO₂ at the *para* position and —CF₃ at the *ortho* position to chlorine. Although these two substituents may facilitate nucleophilic attack, however, the bulky trifluoromethyl group sterically hinders the attack of the nucleophilic reagent, bisphenol AF, on the ring to form a carbanion. Therefore, copper powder and TBAC were added as catalysts to promote the reaction.

Preparation of Polymers

Polyimides were synthesized by a conventional two-step polycondensation of a dianhydride and a diamine in an aprotic solvent such as DMAc. In the first step, the ring-opening polyaddition in DMAc at room temperature afforded poly(amic acid)s. Then, the thermal cyclodehydration produced polyimide films. The polyimide films were pale yellow, transparent, and flexible. The pale yellow color of the films is probably attributable to the formation of intermolecular charge transfer complexes between imide and amine moieties for the usual polyimides composed of aromatic dianhydrides and aromatic diamines.¹⁷

The inherent viscosities of poly(amic acid)s and their corresponding polyimides are summarized in Table I. The poly(amic acid)s had inherent viscosities in the range of 0.52–1.23 dL/g. The inherent viscosities of poly(amic acid)s IV_{2a–3d} and polyimides V_{2a–3d} prepared from fluorine-containing diamines are slightly lower than those of IV_{1a–1d} and V_{1a–1d}, which were synthesized from II₁ without a fluorine atom. In addition, the viscosities decrease as fluorine contents increase in polyimides.

Table I Synthesis of Poly(amic acid)s and Polyimides

Poly(amic acid)s		Polyimides	
Code	η_{inh}^a (dL/g)	Code	η_{inh}^b (dL/g)
IV _{1a}	1.23	V _{1a}	0.83
IV _{1b}	0.65	V _{1b}	0.53
IV _{1c}	0.71	V _{1c}	0.51
IV _{1d}	0.61	V _{1d}	0.47
IV _{2a}	1.18	V _{2a}	0.80
IV _{2b}	0.59	V _{2b}	0.55
IV _{2c}	0.65	V _{2c}	0.59
IV _{2d}	0.52	V _{2d}	0.50
IV _{3a}	1.04	V _{3a}	0.79
IV _{3b}	0.55	V _{3b}	0.49
IV _{3c}	0.64	V _{3c}	0.52
IV _{3d}	0.53	V _{3d}	0.45

^a Measured in DMAc at a concentration of 0.5 g/dL at 30°C.

^b Measured in concentrated sulfuric acid at a concentration of 0.5 g/dL at 30°C.

The following two reasons may be responsible for these results. The trifluoromethyl groups have a strong electron-attracting property, which reduces the nucleophilicity of the fluorine-containing diamines II₂ and II₃ and eventually lowers the molecular weight of the poly(amic acid)s IV_{2a–3d}. The bulky trifluoromethyl group especially may sterically hinder the reaction of the adjacent amino group in diamine II₃. Elemental analyses of the polyimides shown in Table II are in good agreement with the calculated values based on the polymer repeating units.

Properties of Polymers

The solubilities of these polyimides are shown in Table III. Polyimides were thoroughly soluble only in concentrated sulfuric acid at room temperature. The poor solubility of polyimides could be attributed to the formation of intermolecular links of poly(amic acid)s during the thermal cyclodehydration process.^{18–20} Polyimide V_{3d}, however, is much more soluble than others. This can be explained by the reduction in chain-chain interaction in polyimide V_{3d}, since fluorine has low intermolecular attractive forces.

The crystallinity of the polyimide films was evaluated by X-ray diffraction analysis with 2 θ ranging from 5 to 35°. As shown in Figure 2, polyimides V_{1a}, V_{2a}, and V_{3a} show crystalline charac-

Table II Elemental Analysis of Polyimides

Polymer	Formula Molecular Weight	Elemental Analysis (%)			
			C	H	N
V _{1a}	(C ₃₇ H ₂₄ N ₂ O ₆) _n (592.61) _n	Calcd:	74.99	4.08	4.73
		Found:	74.68	4.17	4.68
V _{1b}	(C ₄₃ H ₂₈ N ₂ O ₆) _n (668.71) _n	Calcd:	77.23	4.22	4.19
		Found:	76.95	4.28	4.16
V _{1c}	(C ₄₄ H ₂₈ N ₂ O ₇) _n (696.72) _n	Calcd:	75.85	4.05	4.02
		Found:	75.64	4.12	3.98
V _{1d}	(C ₄₆ H ₂₈ F ₆ N ₂ O ₆) _n (818.73) _n	Calcd:	67.48	3.45	3.42
		Found:	67.13	3.53	3.36
V _{2a}	(C ₃₇ H ₁₈ F ₆ N ₂ O ₆) _n (700.55) _n	Calcd:	63.44	2.59	4.00
		Found:	63.25	2.67	3.95
V _{2b}	(C ₄₃ H ₂₂ F ₆ N ₂ O ₆) _n (776.65) _n	Calcd:	66.50	2.86	3.61
		Found:	66.36	2.91	3.58
V _{2c}	(C ₄₄ H ₂₂ F ₆ N ₂ O ₇) _n (804.66) _n	Calcd:	65.68	2.76	3.48
		Found:	65.53	2.85	3.43
V _{2d}	(C ₄₆ H ₂₂ F ₁₂ N ₂ O ₆) _n (926.67) _n	Calcd:	59.62	2.39	3.02
		Found:	59.38	2.43	2.93
V _{3a}	(C ₃₉ H ₁₆ F ₁₂ N ₂ O ₆) _n (836.55) _n	Calcd:	56.00	1.93	3.35
		Found:	55.78	2.01	3.30
V _{3b}	(C ₄₅ H ₂₀ F ₁₂ N ₂ O ₆) _n (912.64) _n	Calcd:	59.22	2.21	3.07
		Found:	58.93	2.25	3.04
V _{3c}	(C ₄₆ H ₂₀ F ₁₂ N ₂ O ₇) _n (940.65) _n	Calcd:	58.74	2.14	2.98
		Found:	58.61	2.21	2.91
V _{3d}	(C ₄₈ H ₂₀ F ₁₈ N ₂ O ₈) _n (1,094.67) _n	Calcd:	52.67	1.84	2.56
		Found:	52.53	1.91	2.50

ter and exhibit two strong peaks around 15 and 20°, which may be due to the more efficient packing of polymer chains containing polypyromelliti-

mide. All of the other polyimides showed amorphous patterns.

The thermal behavior of these polyimides was

Table III Solubility of Polyimides^a

Polymer	Solvent ^b							
	DMAc	DMF	DMSO	NMP	<i>m</i> -Cresol	<i>O</i> -Chlorophenol	Pyridine	Conc. H ₂ SO ₄
V _{1a}	--	--	--	--	--	--	--	++
V _{1b}	--	--	--	--	--	-h	--	++
V _{1c}	--	--	--	-h	--	-h	--	++
V _{1d}	--	--	--	-h	-h	-h	--	++
V _{2a}	--	--	--	--	--	--	--	++
V _{2b}	--	--	--	--	--	-h	--	++
V _{2c}	--	--	--	-h	--	-h	--	++
V _{2d}	-h	-h	-h	-h	-h	+h	-h	++
V _{3a}	--	--	--	--	--	--	--	++
V _{3b}	--	--	--	--	--	--	--	++
V _{3c}	--	--	--	-h	-h	-h	--	++
V _{3d}	-h	-h	-h	-h	-h	+h	-h	++

^a Solubility: (++) soluble at room temperature, (+ h) soluble on heating, (-h) partially soluble on heating, (--) insoluble.

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

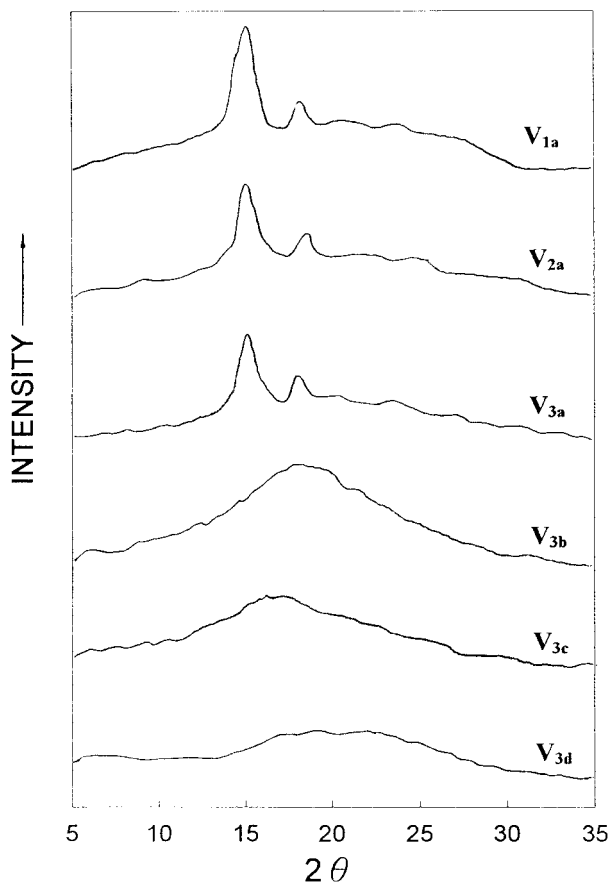


Figure 2 Wide-angle X-ray diffractograms of some polyimides.

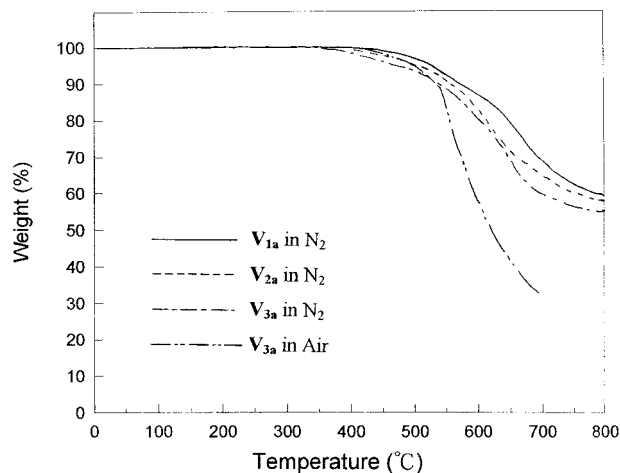


Figure 3 T_G curves for polyimides V_{1a} , V_{2a} , and V_{3a} at a heating rate of $20^\circ\text{C}/\text{min}$.

evaluated by DSC, DMA, and TGA. The results are summarized in Table IV. Representative TGA curves of polyimides V_{1a} , V_{2a} , and V_{3a} are shown in Figure 3. All polyimides show a similar decomposition behavior, characterized by no weight loss below 350°C in air or in nitrogen and the 10% weight loss when temperatures were above 542°C in nitrogen.

Since the residual water or solvent and the history of thermal annealing have sometimes influenced the first heating run of DSC, samples were at first heated to 350°C and the T_g was determined by the second heating. In the DMA measurement,

Table IV Thermal Properties of Polyimides

Polymer	T_g^a ($^\circ\text{C}$)		T_m^b ($^\circ\text{C}$)	Decomposition Temperature ^c ($^\circ\text{C}$)		Char Yield ^d (%)
	DSC	DMA		In N_2	In Air	
V_{1a}	328	329	391	571	565	60.3
V_{1b}	314	314	—	570	563	63.2
V_{1c}	309	311	—	565	556	58.7
V_{1d}	302	312	—	560	555	59.2
V_{2a}	325	327	387	566	559	59.3
V_{2b}	309	312	—	563	558	64.5
V_{2c}	303	308	—	550	540	59.4
V_{2d}	294	297	—	545	539	61.1
V_{3a}	318	318	361	561	553	56.1
V_{3b}	307	309	—	554	546	63.7
V_{3c}	299	301	—	548	541	60.1
V_{3d}	287	290	—	542	537	59.5

^a Glass transition temperature (T_g) measured by DSC and DMA at a heating rate of 20 and $5^\circ\text{C}/\text{min}$, respectively.

^b Melting temperature measured by DSC at a heating rate of $20^\circ\text{C}/\text{min}$.

^c Temperature at 10% weight loss recorded by TGA at a heating rate of $20^\circ\text{C}/\text{min}$.

^d Residual wt % at 800°C in nitrogen.

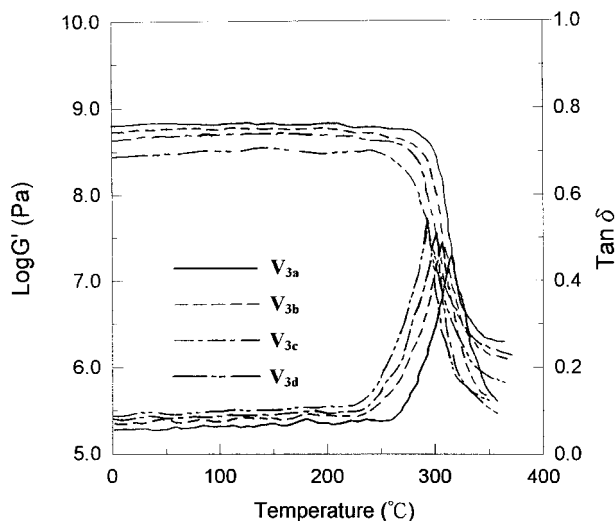


Figure 4 DMA curves for V_{3a-3d} films at a heating rate of $5^{\circ}\text{C}/\text{min}$.

the peak of $\tan \delta$ was identified as the glass transition temperature because a large decrease in G' occurred at this point. The polymers have glass transition temperatures of $287\text{--}328^{\circ}\text{C}$ by DSC and $290\text{--}329^{\circ}\text{C}$ by DMA. The T_g values tend to decrease in the order $V_{3a} > V_{3b} > V_{3c} > V_{3d}$, which is consistent with the decreasing order of stiffness and polarity of the polymer backbone.

The dynamic mechanical properties of the polymers V_{3a-3d} are indicated in Figure 4. The storage moduli tend to decrease in the order $V_{3a} > V_{3b} > V_{3c} > V_{3d}$, and the $\tan \delta$ values tend to increase in the order $V_{3a} < V_{3b} < V_{3c} < V_{3d}$. These results

Table V Dielectric Constant of Polyimides

Polymer	Fluorine Content (%)	Dielectric Constant ^a
V_{1a}	0.0	3.51
V_{1b}	0.0	3.48
V_{1c}	0.0	3.49
V_{1d}	13.9	3.24
V_{2a}	16.3	3.33
V_{2b}	14.7	3.30
V_{2c}	14.2	3.26
V_{2d}	24.7	3.12
V_{3a}	27.3	2.81
V_{3b}	25.0	3.05
V_{3c}	24.2	2.97
V_{3d}	31.2	2.72

^a Measured by DEA at 1 KHz, 30°C (dry dielectric constant).

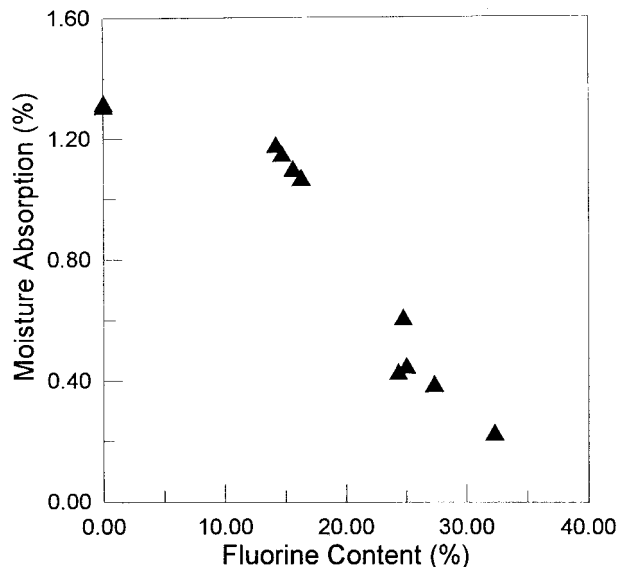


Figure 5 Moisture absorption (%) versus fluorine content (%).

are quite compatible with the decreasing order of stiffness and rigidity of the polymer backbone.

The relationships between dielectric constant and fluorine content in polyimide are shown in Table V. The dielectric constant decreases as fluorine content increases in polyimides. The increase in fluorine content leads to more spacing between polymer molecules and reduces the intermolecular attraction, which reduces the dielectric constant. The polyimides prepared from 6FDA, which contains the bulky 6F group, exhibit lower dielectric constants than those prepared from the other dianhydrides. This can be attributed to the same interaction effect. In addition, fluorine has low electron polarizability, which reduces the dielectric constants of polyimides.

On the other hand, the strong electron-attracting property, resulting from the high electronegativity of the fluorine atom, could produce an additional permanent dipole in the trifluoromethyl group and/or the benzene ring connected to the trifluoromethyl group. These dipoles may increase the polarization and, hence, the dielectric constant. The experimental data on the dielectric constant indicate that the effect of these additional permanent dipoles is smaller than the other effects, that is, the chain-chain interaction and the electronic polarization in polyimide.

The relationship between moisture absorption (%) and fluorine content in polyimides is shown in Figure 5. The moisture absorption (%) de-

creases as the fluorine content increases in polyimides. The lower water absorption characteristics of the fluorine-containing polyimides may be attributed to the hydrophobic trifluoromethyl groups on the surface of the polymer film and also the lower surface activity of the fluorine atoms.

CONCLUSION

Fluorine-containing polyimides have been synthesized from fluorine-containing diamines with various aromatic dianhydrides. It was found that the increase in fluorine content lowers the inherent viscosities, increases the solubility, and decreases the dielectric constant and moisture absorption of the resulting polyimides.

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