

Preparation and Properties of Soluble Aromatic Polyetherimides Based on 2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride

DONG-HO LEE,¹ SEUNG-YOUNG KOO,² DAE-YONG KIM,¹ HEUNG-JIN CHOI³

¹ Department of Polymer Science, Kyungpook National University, Taegu, Korea

² Department of Industrial Chemistry, Kyungil University, Kyungsan, Korea

³ Department of Industrial Chemistry, Kyungpook National University, Taegu, Korea

Received 12 May 1999; accepted 10 July 1999

ABSTRACT: Aromatic polyetherimides were synthesized from a fluorine containing aromatic carboxylic acid dianhydride, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (6F-BABPA) and five typical aromatic diamines including 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3F-DAM) by two-step procedures—amidation to polyamic acids (PAA), followed by thermal imidization of PAA. The chemical and physical properties of the newly prepared polyetherimides (PEI) were compared in terms of their chemical structures, inherent viscosities, mechanical, and thermal properties. All polyetherimides were well soluble in common organic solvents such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), pyridine, and methylene chloride. A PEI prepared from 6F-BABPA/3F-DAM was especially easily dissolved in NMP. The glass transition temperature (T_g) range of the obtained PEI was 209–257°C. The dielectric constants and refractive index were 2.8–3.2 and 1.61–1.56, respectively. The polyetherimide, 6F-BABPA/BAPP, with a low fluorine content (11.4% fluorine content), has 0.99% water absorption, whereas the polyetherimide, 6F-BABPA/4-BDAP, having a high fluorine content (26.0% fluorine content) showed 0.35% of water absorption. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 249–257, 2000

Key words: aromatic polyetherimide; thermal imidization; aromatic carboxylic acid dianhydride; fluorine containing polyetherimide; dielectric constant

INTRODUCTION

Optics and electronics industry have been rapidly progressed; therefore, new demands are being placed on the materials.^{1–3} Improvements in polyimide properties have been sought by incorporating trifluoromethyl or other perfluoroalkyl groups. Fluorinated polyimides are known to have low

dielectric constants,^{4,5} low water absorption,^{5,6} high transparency,^{7,8} and high solubility⁹ compared to fluorine-free polyimides.

In previous work,¹⁰ we synthesized the fluorinated polyetherimides (PEIs) from 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride and aromatic diamines, which showed good solubilities and high glass transition temperature. In this work to enhance the properties of PEIs, a new aromatic dianhydride monomer with two trifluoromethyl groups, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexa-

Correspondence to: D.-H. Lee.

Journal of Applied Polymer Science, Vol. 76, 249–257 (2000)
© 2000 John Wiley & Sons, Inc.

fluoropropane (6F-BABPA) was synthesized. With five aromatic diamine monomers having fluorinated alkyl and phenyl groups, the dianhydride 6F-BABPA polymerized to yield new fluorine-containing PEIs.

The properties of the newly prepared polyimides were studied in view of their chemical structures, solubility, dielectric constant, viscosity, refractive indices, transparency, water absorption, thermal, and mechanical properties.

EXPERIMENTAL

Materials

2,2-Bis(4-hydroxyphenyl)hexafluoropropane (Bisphenol 6F; Riedel Haen, Germany), trifluoromethanesulfonic acid (Aldrich Chemical Co., Milwaukee, WI), sodium hydroxide, acetic anhydride, acetic acid, dimethyl sulfoxide, aniline hydrochloride (Junsei Chemical Co., Japan), aniline, and toluene were used as received. 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF; Central Glass Co., Japan), 4,4'-diaminodiphenylether (ODA; Fluka Chemical Co., Switzerland), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP; Chriskev Co. Inc., USA), and 2,2-bis(4-aminophenyl)hexafluoropropane (4-BDAP; Hoechst, Germany) were purified by sublimation. 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3F-DAM)¹¹ and *N*-phenyl-4-nitrophthalimide¹⁰ were prepared by the known methods. *N*-Methyl-2-pyrrolidone (NMP; Janssen Chemica, Belgium) was distilled over phosphorous pentoxide prior to use.

Synthesis

2,2-Bis[*N*-phenyl-4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane (6F-Diimide)^{10,11}

A mixture of 2,2-bis(4-hydroxyphenyl)hexafluoropropane (20.2 g, 60 mmol) and 50% NaOH (9.6 g, 0.12 mol) solution in 400 mL of dimethyl sulfoxide-toluene (1 : 1) was heated with stirring at reflux under nitrogen atmosphere until no visible trace of water could be seen in the Dean-Stark trap. After the reaction was done, toluene was removed from the mixture by distillation and then the mixture was cooled to room temperature. To the mixture was added *N*-phenyl-4-nitrophthalimide (32.2 g, 0.12 mol). The reaction mixture was further heated with stirring at 60°C for 5 h, and then cooled to room temperature. To the mix-

ture was added 1.2 *N* hydrochloric acid (2 L) with vigorous stirring. The precipitate was collected by filtration and dried to give white solid (42.0 g, 87%): m.p. 204–205°C; IR (KBr) 3074 (Ar), 1773 (C=O), 1724 (C=O), 1598, 1504, 1478, 1373, 1273, 1247, 1179 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 8.02 (d, *J* = .1 Hz, 2 H), 7.6–7.4 (m, 18 H), 7.31 (d, *J* = .7 Hz, 4 H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 166.4, 166.3, 161.5, 156.2, 134.5, 132.1, 132.0, 129.0, 128.4, 128.3, 127.5, 126.6, 126.2, 124.3, 119.7, 113.4.

2,2-Bis[4-(3,4-dicarboxylic acid phenoxy)phenyl]hexafluoropropane (6F-Tetraacid)^{10,11}

A mixture of 6F-diimide (41.2 g, 53 mmol) and NaOH (19.1 g, 0.48 mol) in 172 mL of water was heated at reflux for 24 h, and then was cooled to room temperature.

To the cooled mixture was added 2 *N* HNO₃ (2 L) with vigorous stirring. The precipitate was isolated by filtration. The product was dissolved in a minimum amount of hot water and then extracted with ethyl ether. The combined extract was dried over anhydrous magnesium sulfate and concentrated to dryness *in vacuo* to give white solid (32.7 g, 93%): m.p. 225–227°C; IR (KBr) 3433 (—OH), 3081 (Ar), 1712 (C=O), 1599, 1509, 1244, 1205, 1176 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 7.93 (d, *J* = .4 Hz, 2 H), 7.40 (br m, 6 H), 7.20 (br m, 6 H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 168.1, 167.6, 157.7, 156.7, 137.0, 132.7, 131.9, 128.2, 127.7, 120.5, 119.4, 119.1.

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (6F-BABPA)^{10,11}

A mixture of the above 6F-tetraacid (32 g, 48 mmol) and acetic anhydride (60 g) was heated at reflux for 1 h. The dianhydride product was obtained by removing acetic anhydride from the reaction mixture *in vacuo* as white solid (26.5 g, 88%): m.p. 226–228°C; IR (KBr) 3078 (Ar), 1854 (C=O), 1779 (C=O), 1602, 1509, 1482, 1279, 1259, 1240, 1175, 894, 738 cm⁻¹; ¹H-NMR (400 MHz, DMSO-*d*₆) δ 8.13 (d, *J* = .52 Hz, 2 H), 7.65 (m, 4 H), 7.53 (d, *J* = 8.60 Hz, 4H), 7.33 (d, *J* = 8.60 Hz, 4 H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ 163.0, 162.8, 162.7, 155.8, 134.5, 132.4, 129.1, 128.3, 126.18, 125.9, 120.3, 114.4 (two carbon atoms of hexafluoroisopropylene group are not seen due to fluorine-coupled splitting); Anal. Calcd for

$C_{31}H_{14}F_6$: C, 59.25; H, 2.25. Found: C, 59.21; H, 2.27.

1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3F-DAM)¹²

A mixture of trifluoroacetophenone (10 g, 0.057 mol), aniline (35 g, 0.37 mol), and aniline hydrochloride (15 g, 0.12 mol) was heated at reflux for 24 h. At the end of the reflux period, sodium bicarbonate (10 g) was added and the mixture was steam distilled until the distillate was clear. The aqueous solution was cooled and the solid, dark-blue residue was broken up and collected by filtration. The residue was dissolved in benzene and dried over anhydrous magnesium sulfate. The benzene was removed by a rotary evaporator, and the remaining solid was recrystallized from benzene–petroleum ether (petroleum ether was added to a hot benzene solution). The recrystallized purplish 3F-DAM was sublimed to give 16.7 g (85% from the ketone) of white crystals: m.p. 216°C; IR (KBr) 3486 and 3385 (NH_2), 1142 (C—F), 828 (*para*-disubstituted Ar), 760 and 710 cm^{-1} (*mono*-substituted Ar); 1H -NMR (300 MHz, DMSO- d_6) δ 7.3 (m, 3 H), 7.1 (m, 2 H), 6.6 (d, 4 H, $J = .7$ Hz), 6.5 (d, 4 H, $J = .7$ Hz), 5.1 (br s, 4 H); ^{13}C -NMR (75 MHz, DMSO- d_6) δ 147.7, 141.0, 129.9, 129.3, 127.9, 127.2, 126.7, 113.1, 63.1 (F_3C-C- , $^2J_{C-F} = 22.8$ Hz, q). Anal. Calcd for $C_{20}H_{17}N_2F_3$: C, 70.17; H, 5.01; N, 8.18. Found: C, 70.34; H, 5.02; N, 8.20.

Synthesis of Polyetherimides

To the diamine solution containing 15–20 wt % solids in NMP at room temperature was added an equimolar amount of a dianhydride. The resulting solution was stirred for 8–24 h at room temperature. The resulting solution of polyamic acids was cast onto a glass plate and dried at 60°C under vacuum to produce a transparent polyamic acid (PAA) film. The dried film was stripped off, placed into metal frames, and heated in an air oven for 1 h at 150°C, for 30 min at 200°C, for 30 min at 250°C, and for 1 h at 300°C.³

Measurements

Fourier transformed infrared (FTIR) spectra were obtained with a Nicolet Magma-IRTM 550 FTIR spectrometer that provided qualitative information describing the conversion of PAA to the PEI. Also, FTIR analysis was utilized to follow the

synthesis of 6F-BABPA dianhydride and 3F-DAM diamine.

1H -NMR and ^{13}C -NMR studies were performed on a Varian Unity plus 300 NMR (300 MHz) and a Bruker Avance Digital 400 NMR (400 MHz) spectrometer with chemical shifts reported in ppm.

Elemental analysis was carried out by Leco CHNS-932.

The water absorption was measured as follows:^{3,13} specimens were immersed in 23°C water for 48 h, and the weight differences after aging were measured.

Inherent viscosities of the soluble polyetherimides were determined in 0.5-g/dL NMP solutions by using Ubbelode viscometer at 25°C.

Thermal analysis was performed on a Du Pont TA 2000 system thermal analyzer. DSC was used to determine T_g . Scans were performed at a heating rate 10°C min^{-1} to 350°C, and cooled rapidly to room temperature, and then at a heating rate 10°C min^{-1} to 350°C under a nitrogen atmosphere.

The dielectric constants were measured at 1 KHz by bridge method using an Hewlett-Packard 4265B.^{3,13}

The solubility of the fluorinated polyetherimides was investigated by dipping 1 wt % solutions in small capped glass vials for 3 days.¹⁴

Transmission spectra were obtained on 0.013 mm (0.5 mil) thick films at 500 nm, and UV cutoff wavelengths were measured using a Shimadzu UV-2000.

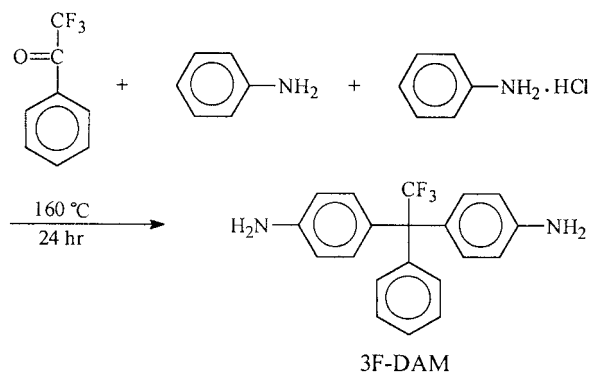
The refractive indices were measured by waveguiding method on a Spectra-physics Model 196-1.¹⁵

Tensile properties were determined from stress–strain curves obtained with a Shimadzu AGS-500A at an elongation rate of 10 mm/min. The measurements were performed at room temperature using solution-cast film specimens (ca. 60 μm thick, 1 cm wide, and 3 cm gauge length).

RESULTS AND DISCUSSION

Synthesis of Monomer

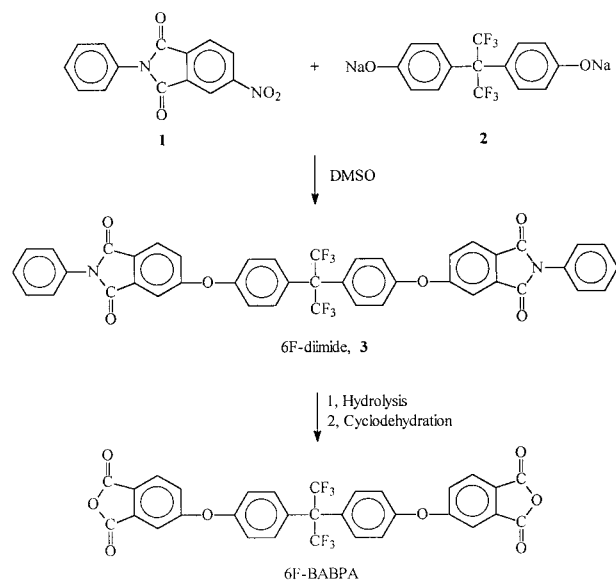
A fluorinated polymer-forming diamine monomer 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3F-DAM) was utilized for preparing fluorinated polyetherimide polymers. The diamine 3F-DAM was prepared by a reaction of trifluoro-



Scheme 1

acetophenone, aniline, and aniline hydrochloride, as shown in Scheme I.¹²

This aromatic substitution and condensation of trifluoroacetophenone with aniline requires aniline hydrochloride as an acid catalyst. This weak acid activates the electrophilicity of carbonyl carbon, which is activated with electron-withdrawing behavior of the trifluoromethyl group, but also accelerates dehydration of the intermediate carbinol to a carbocation and subsequent aromatic substitution. The amount of aniline hydrochloride is not critical to complete the reaction, but affects the reaction rate and the formation of uncharacterized blue impurities. With the modified reaction condition we could obtain the product 3F-DAM in 85% yield reproducibly.



Scheme 2

2,2-Bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride (6F-BABPA) has been utilized for preparing fluorinated PEIs as a fluorinated polymer-forming dianhydride monomer. The dianhydride 6F-BABPA had been synthesized by aromatic nucleophilic substitution on 4-fluorophthalic anhydride with 2,2-bis-(4-hydroxyphenyl)hexafluoropropane (Bisphenol AF).¹⁶ However, we have synthesized 6F-BABPA from *N*-phenyl-4-nitrophthalimide **1** and disodium salt

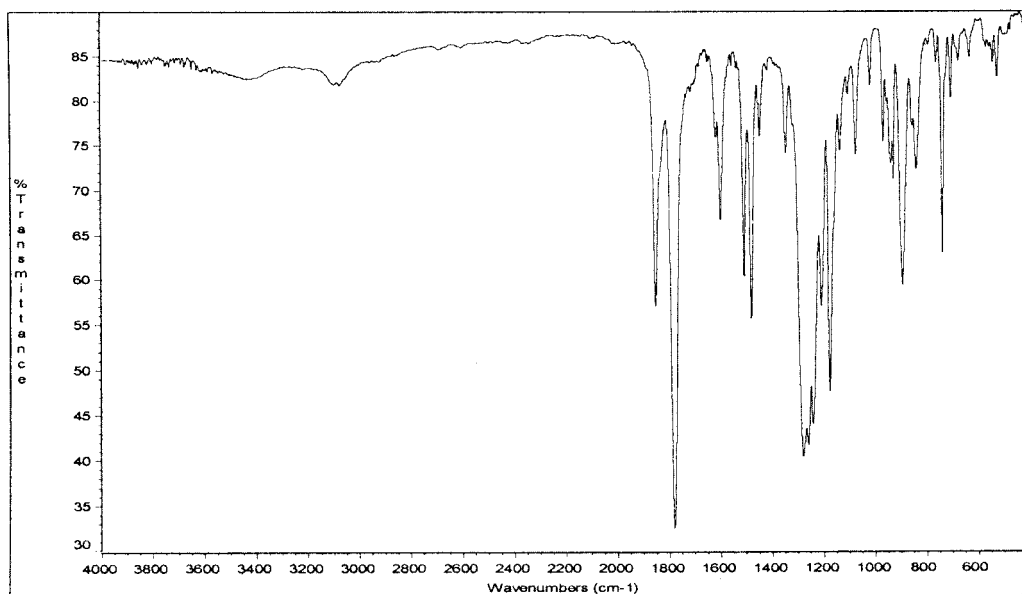


Figure 1 IR spectrum of 6F-BABPA dianhydride.

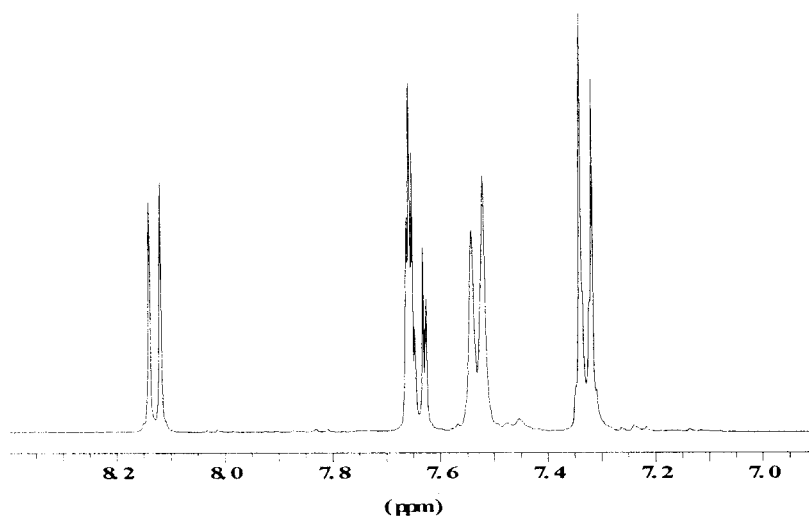


Figure 2 ^1H -NMR spectrum of 6F-BABPA dianhydride in DMSO.

of Bisphenol AF (6F-sodium salt **2**), as shown in Scheme II. The *N*-phenyl-4-nitrophthalimide was synthesized by reacting 4-nitrophthalic anhydride and aniline. The 4-nitrophthalic anhydride was prepared in house from hydrolysis of pure 4-nitrophthalimide in aqueous sodium hydroxide and cyclodehydration of 4-nitrophthalic acid. Because the commercial 4-nitrophthalic anhydride was contaminated with 5–8% 3-nitrophthalic anhydride, it was needed to prepare the purer *N*-phenyl-4-nitrophthalimide **1**. 6F-Sodium salt **2** was prepared by reacting 2,2-bis(4-hydroxyphenyl)hexafluoropropane and 50% NaOH solution in DMSO-toluene (1 : 1). The method using aqueous NaOH rather than sodium methoxide as the base was beneficial from the industrial produc-

tion of 6F-sodium salt. In general,¹⁷ the nitro groups in 4-nitrophthalimides are displaced by phenoxide about six and nine times faster than the corresponding fluorine, which reacted approximately four times faster than the chloro derivative in the phthalimide. 2,2-Bis[*N*-phenyl-4-(3,4-dicarboxyphenoxy)phenyl] hexafluoropropane (6F-diimide **3**) was synthesized by reacting *N*-phenyl-4-nitrophthalimide **1** and 6F-sodium salt **2**. The reaction between 6F-sodium salt **2** and the substituted *N*-phenyl-4-nitrophthalimide **1** proceeds quantitatively in either DMF or DMSO at 25–60°C. Hydrolysis of **3**, followed by dehydration, afforded the dianhydride monomer 6F-BABPA in a 72% overall yield, as shown in Scheme II.

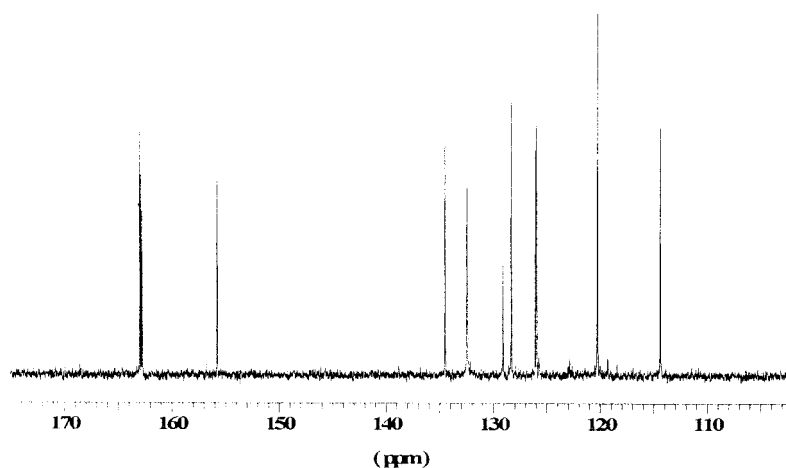


Figure 3 ^{13}C -NMR spectrum of 6F-BABPA dianhydride in DMSO.

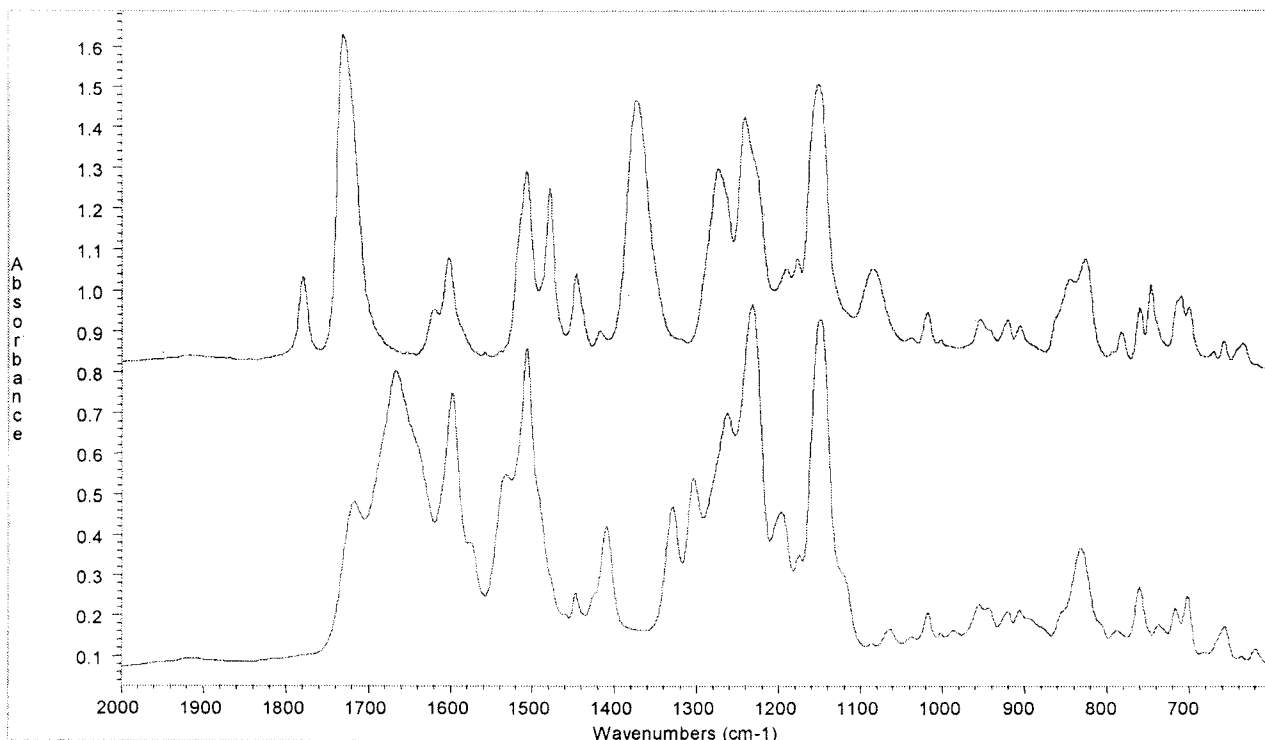


Figure 4 IR Spectra of 6F-BABPA/3F-DAM obtained by thermal imidization: bottom; PAA, upper; PEI.

The chemical structure of prepared 6F-BABPA was confirmed by its IR, ^1H -, ^{13}C -NMR, elemental analysis, and melting (Figs. 1–4).¹⁶

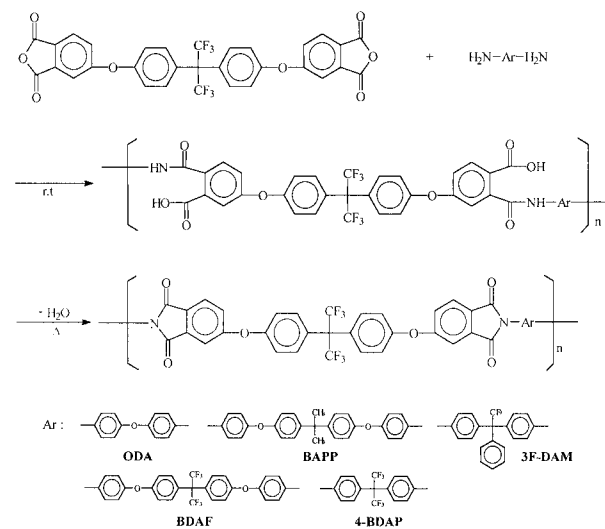
The IR spectrum of dianhydride 6F-BABPA exhibited the two characteristic C=O stretching bands at 1854 and 1800 cm^{-1} , and C—F stretching band at 1176 cm^{-1} .

All five kinds of aromatic protons of 6F-BABPA are observed in 7.3–8.2 ppm in ^1H -NMR. Two kinds of AA'BB' protons of 4-phenoxy moiety are seen as doublet of doublets. Aromatic protons of phthalic anhydride moieties were not well resolved in the region of 7.6–8.2 ppm in ^1H -NMR, but relative intensities of each group of same kind protons against a resolved doublet ($J=8.52$ Hz) at 8.12 ppm for 3-H protons of phthalic anhydride moieties were matched with the expected value. Two kinds of chemical shifts of C=O groups of anhydride functionality was clearly observed at 163.0 and 162.8 ppm in ^{13}C -NMR, whereas due to the free carboxylic acid groups of the corresponding tetraacid, the resonances was observed at 168.1 and 167.6 ppm in ^{13}C -NMR. Two carbon atoms, trifluoromethyl and tertiary, of the hexafluoroisopropylidene group are not seen due to fluorine-coupled splitting in $^{13}\text{C}\{^1\text{H}\}$ spectrum.

The purity and elemental composition are confirmed by microanalysis.

Synthesis of Polymers

The synthesis of PEIs from 6F-BABPA and five diamines were conducted as shown in Scheme III.



Scheme 3

Table I Thermal Properties and Viscosities of Polyetherimides

Polymers	Inh ^a dL/g	Inh ^b dL/g	T_g^d (°C)	T_{di}^e (°C)	$T_{d_{10}}^f$ (°C)	Residue at 900°C (wt %) ^g
6F-BABPA/BAPP	1.08	0.43	211	553	566	49.3
6F-BABPA/ODA	1.28	0.64 ^c	230	562	578	49.5
6F-BABPA/3F-DAM	1.18	0.59	257	549	569	49.2
6F-BABPA/BDAF	1.14	0.58	216	550	579	43.8
6F-BABPA/4-BDAP	0.96	0.52	242	551	574	53.3

^a Inherent viscosities were determined in 0.5 g/dL NMP solutions at 25°C for PAA.

^b Inherent viscosities were determined in 0.5 g/dL NMP solutions at 25°C for PEI.

^c Inherent viscosity was determined in 0.5 g/dL DMAc solution at 25°C for PEI.

^d Determined by DSC at a heating rate of 10°C/min in nitrogen.

^e Temperatures at which polymer decomposition initiate.

^f Temperatures at which 10% weight loss was recorded by TGA at heating rate of 10°C/min.

^g At 900°C under nitrogen.

The reactive dianhydride 6F-BABPA reacted with aromatic diamines even at ambient temperature resulted in polyamic acid with a high degree of polymerization in a carefully controlled reaction condition. Any presence of moisture or monofunctional nucleophilic impurities in the reaction resulted in terminating the extending polymeric chain.

Properties of Polymers

Generally, the physical and chemical properties of polyetherimide polymers are dependent on the chemical structure of monomers in the polyimide backbone.¹⁸ Target polyetherimides on a specific dianhydride monomer were prepared with structurally different aromatic diamines, which have various molecular skeletons and functionalities, i.e., (1) 6H-isopropylene ($-\text{C}(\text{CH}_3)_2-$), (2) 6F-isopropylene ($-\text{C}(\text{CF}_3)_2-$), (3) 3F-phenylethylene, and (4) ether linkages.

Infrared spectra provided qualitative information describing the conversion of PAA to the PEI. The bands at 1780 and 1730 cm^{-1} , the two coupled stretching of the imide carbonyl functionality

in the PEI, is normally monitored for following the progress of the imidization reaction. The band near 1670 cm^{-1} due to C=O stretching of carboxylic acid gradually disappeared by heating of the polyamic acids. The band near 1150 cm^{-1} is a characteristic stretching vibration of the C—F bonds (see Fig. 1).

The inherent viscosities of PAA and polyetherimides are shown in Table I. In this study, the ring-opening polyaddition of diamines to anhydrides in NMP afforded polyamic acids with inherent viscosities between 0.96–1.28 dL/g. From the resulting polymer solutions, transparent and flexible films of the polyamic acids could be prepared. The thermal conversion to polyetherimides was carried out by successive heating of the polyamic acids films in air. The resulting polyetherimides showed inherent viscosities of 0.43–0.59 dL/g in NMP.

The inherent viscosities of polyetherimides were lower than those of the corresponding polyamic acids. The polyetherimides prepared from most aromatic diamines used in this study resulted in satisfactory physical properties and

Table II Solubility of Polyetherimide with Various Solvents at Room Temperature

Polymer	NMP	DMF	DMAc	Pyridine	CH_2Cl_2	Acetone
6F-BABPA/BAPP	++	++	++	++	++	–
6F-BABPA/ODA	–	+	++	–	++	–
6F-BABPA/3F-DAM	++	++	++	++	++	+
6F-BABPA/BDAF	++	++	++	++	++	+
6F-BABPA/4-BDAP	++	++	++	++	++	+

++: Soluble, +: Partially soluble, –: Insoluble.

Table III Properties of Polyetherimide Films Containing 6F-BABPA

Polymer	Fluorine Content (%)	Transmission at 500 nm (%)	UV Cutoff ^a (nm)	Water Absorption ^b (%)	Dielectric Constant at 1 kHz
6F-BABPA/BAPP	11.4	89	356	0.99	3.0
6F-BABPA/ODA	14.4	—	—	—	3.2
6F-BABPA/3F-DAM	18.3	90	355	0.48	2.8
6F-BABPA/BDAF	20.5	90	350	0.41	2.8
6F-BABPA/4-BDAP	26.0	90	329	0.35	2.8

^a Wavelength of UV cutoff.^b Measured at 23°C for 2 days.

moderate molecular weight to permit casting tough films. Most of polyetherimides showed high thermal stability, and did not decompose below 560°C in nitrogen at a heating rate of 10°C/min. The glass transition temperatures (T_g) of the polyetherimides were found to be 211–257°C by DSC. The relation between T_g and the structure of diamines was as follows: (a) Polymer 6F-BABPA/BDAF, containing more than two ether linkages in the diamine monomer, showed relatively lower glass transition temperatures than those of polymers 6F-BABPA/4-BDAP containing the same bridges in the polymer backbone. (b) Polymer 6F-BABPA/3F-DAM, containing the 3F-phenylethylene group in the backbone, had higher thermal stability than that containing the 6F-propylene group. (c) Polymer 6F-BABPA/BDAF, containing the polar group like $-\text{C}(\text{CF}_3)_2-$, had higher T_g than that of the alkyl group like $-\text{C}(\text{CH}_3)_2-$ in 6F-BABPA/BAPP.

The qualitative solubility of the polyetherimides in organic solvents is shown in Table II. Most aromatic polyetherimides prepared from dianhydride 6F-BABPA were soluble in aprotic polar solvents such as NMP, DMF, and DMAc, and even in less polar solvents like pyridine, and methylene chloride at room temperature. The polymers 6F-BABPA/ODA, and 6F-BABPA/BAPP containing lower fluorine relatively are insoluble in common solvents such as acetone. The superior solubility can be apparently attributed to the combined favorable effects of polar group like hexafluoroisopropylidene, bulky pendant group of 3F-DAM, and aromatic ether linkages in the polyetherimide backbone. Thus, these good solubilities for these polymers might be derived from 6F-BABPA dianhydride monomer.

The UV transmission cutoff and optical transparency were determined on the PEI films. As

seen in Table III, the polymer films containing 6F-BABPA had excellent optical transparency, with a UV cutoff of 329 nm and 90% transmission at 500 nm. However, certain trends of the UV cutoff were found to decrease with increasing the fluorine contents of PEIs.

The relationship between the dielectric constant and the fluorine weight content in PEIs is showed in Table III. The dielectric constant decreases as fluorine content increases in PEIs, with polymer 6F-BABPA/ODA being the highest at 3.2, and polymers 6F-BABPA/3F-DAM, 6F-BABPA/BDAF, and 6F-BABPA/4-BDAP being the lowest at 2.8. These results can be explained by the reduction in chain–chain interaction in fluorinated PEIs.¹⁹ The polymer prepared from 3F-

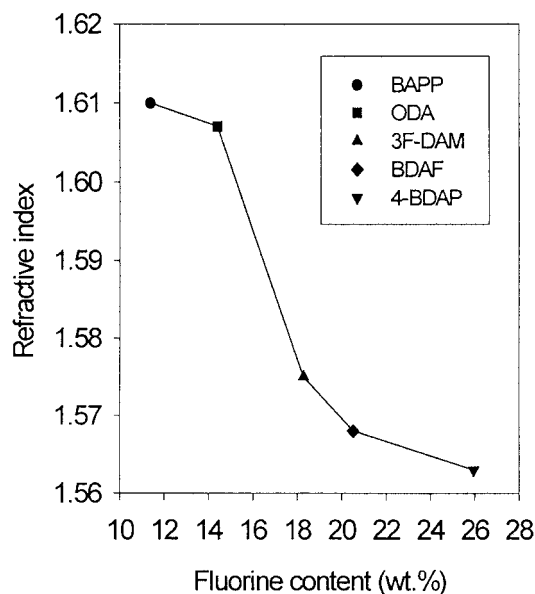
**Figure 5** Relationship between refractive index and fluorine content in PEIs.

Table IV Tensile Properties of Polyetherimide Films

Polymer	Yield Point (kg _f /cm ²)	Tensile Strength (kg _f /cm ²)	Elongation (%)	[η] (dL/g)
6F-BABPA/BAPP	851	791	20	0.43
6F-BABPA/BDAF	801	724	14	0.58
6F-BABPA/4-BDAP	827	827	7	0.52
6F-BABPA/3F-DAM	747	745	6	0.59

DAM, which contains the bulky phenyl group, shows approximately similar dielectric constant compared with that of the bulky 6F group. This can be attributed to the same interaction effect.

The water absorption of PEIs decreases with increasing fluorine content because the incorporation of fluorine into the main chain increased the hydrophobicity of PEIs.²⁰ These results are related to the stability in the dielectric constant of PEIs.¹³

The refractive index decreases from 1.59 to 1.54 in PEIs as the fluorine content increases (Fig. 5). It is demonstrated that the refractive index of PEI can be controlled as in the fluorinated resins, because the orientation polarization can be neglected in the refractive index, and the refractive index is governed by electronic polarization.¹³

The tensile properties shown in Table IV were determined at room temperature. The films had a tensile strength of 724–827 kg_f/cm², and an elongation at break of 6–20%. The polymers 6F-BABPA/BAPP, and 6F-BABPA/BDAF that contain a double ether linkage in the diamine monomer, failed at 14–20% elongation, resulting in a greater toughness than the polymers 6F-BABPA/4-BDAP and 6F-BABPA/3F-DAM. Polymer 6FDA/BDAF was reported as a flexible material,²¹ whereas 6F-BABPA/4-BDAP was observed as stiff and brittle materials.

REFERENCES

- Denton, D. D.; Day, D. R.; Priore, D. F.; Senturia, S. D.; Anolick, E. S.; Scheider, D. J *Electron Mater* 1985, 14, 119.
- Burggraf, P. *Semiconduct Int* 1988, March, 58.
- Matsuura, T.; Yamada, N. *Macromolecules* 1991, 24, 5001.
- St. Clair, A. K.; St. Clair, T. L. *PMSE* 1988, 59, 28.
- Goff, D. L.; Yuan, E. L. In *Polymeric Materials for Electronics Packaging and Interconnection*; Lupinski, J. H.; Moore, R. S., Eds.; American Chemical Society, Washington, DC, 1989, p. 93.
- Mercer, F. W.; McKenzie, M. T. *High Perform Polym* 1993, 5, 97.
- St. Clair, A. K. In *Proceedings of the 2nd International Conference on Polyimides*; Weber, W. D.; Gupta, M. R., Eds.; Society of Plastic Engineers: Brookfield, 1987, p. 16.
- St. Clair, A. K., et al., *Polym Mater Sci Eng Proc* 1984, 51, 62.
- Harris, F. W.; Norris, S. O. *Polyimides: Synthesis, Characterization and Application*; Mittal, K. L., Ed.; Plenum: New York, 1984, p. 3.
- Koo, S.-Y.; Lee, D.-h.; Choi, H. J.; Choi, K.-Y. *J Appl Polym Sci* 1996, 61, 1197.
- Koo, S.-Y.; Lee, D.-H.; Choi, H.-J.; Choi, K.-Y.; Koo, K.-M.; Jeon, I. L. *Polymer (Korea)* 1996, 20, 664.
- Kray, W. D.; Rosser, R. W. *J Org Chem* 1977, 42, 1186.
- Ichino, T.; Sasaki, S.; Matsuura, T.; Nishi, S. *J Polym Sci Part A Polym Chem* 1990, 28, 323.
- Brink, M. H. *Polymer* 1994, 35, 5018.
- Russell, T. P.; Gugger, H. *J Polym Sci Polym Phys Ed* 1983, 21, 1745.
- Stoakley, D. M.; St. Clair, A. K.; Croall, C. I. *J Appl Polym Sci* 1994, 59, 1479.
- Williams, F. J.; Doahue, P. E. *J Org Chem* 1977, 42, 3414.
- Wilson, D.; Stengenberger, H. D.; Hergenrother, P. M. *Polyimide*; Chapman and Hall: New York, 1990, p. 79.
- St. Clair, A. K., et al. *Polym Mater Sci Eng Proc* 1988, 59, 28.
- Hougham, G.; Tesoro, G. *Macromolecules* 1994, 27, 5964.
- Rojstaczer, S.; Ree, M.; Yoon, D. Y.; Volkens, W. *J Polym Sci Part B Polym Phys* 1992, 30, 133.