

Preparation and Properties of Novel Soluble Aromatic Polyetherimides from 1,1'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane Dianhydride and Aromatic Diamines

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SYNOPSIS

New aromatic polyetherimides containing the 1,1'-bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride unit were prepared by a conventional two-step method from 1,1'-bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride and several diamines. This procedure yielded high molecular weight polyetherimides with inherent viscosities of 0.22–1.29 dL/g. Most of the corresponding polyetherimides were soluble in organic solvents such as *N*-methyl-2-pyrrolidone, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and methylene chloride under ambient temperature. The glass transition temperatures (T_g) of these polymers were in the range of 207–264°C and the temperatures of 10% weight loss were over 520°C at a heating rate 20°C/min in nitrogen. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Generally, linear aromatic polyimides are well recognized as highly thermally stable engineering plastics and have been widely used as reliable materials. However, the applications of polyimides are somewhat limited by processing difficulties due to insolubility in organic solvents and their high glass transition or melting temperatures.^{1,2}

A number of successful approaches to increase solubility and processability of polyimides without sacrificing their high thermal stability employ the introduction of flexible or nonsymmetrical linkages in the polymer backbone or the incorporation of bulky substituents as pendant phenyl groups and ether linkages into the polymer backbone.^{3–7} Some organic-soluble aromatic polyimides using highly phenylated tetracarboxylic dianhydrides have been demonstrated. Our present studies also reveal that

the highly phenylated aromatic tetracarboxylic dianhydride containing fluorine such as 1,1'-bis[4-(3,4-dicarboxyphenoxy)-phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride could be used for the preparation of soluble high-temperature aromatic polyetherimides.

The present article deals with the synthesis of novel soluble aromatic polyetherimides containing the 1,1'-bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride unit by the polymerization of 3F-BABPA with aromatic diamines through a conventional two-step method. The characteristics of polyetherimides such as solubility and thermal behavior are also discussed.

EXPERIMENTAL

Monomer Synthesis

N-Phenyl-4-nitrophthalimide

N-Phenyl-4-nitrophthalimide was synthesized in 94% yield from 4-nitrophthalic anhydride by a

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known method.⁸ 4-Nitrophthalic anhydride⁹ was synthesized by a known method from 4-nitrophthalic acid¹⁰ that was prepared from 4-nitrophthalimide (Tokyo Kasei Chemical Co., Japan): IR (KBr) 3114 (Ar—), 1779 (C=O), 1718 (C=O), 1536 (Ar—NO₂), 1493 (Ar—NO₂), 1378, 1345, 1099 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 8.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.61 (dd, *J* = 2.4, 0.6 Hz, 1H), 8.22 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.60–7.40 (m, 5H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 165.7, 165.4, 151.7, 136.5, 133.2, 131.8, 130.0, 129.2, 128.6, 127.5, 125.1, 118.3; mp 192–194°C.

1,1'-Bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane

1,1'-Bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane was synthesized by a known method⁷: yield 80%; IR (KBr) 3261 (—OH), 1612, 1598, 1513, 1443, 1379, 1254, 1225, 1145, 829 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 7.36 (br m, 3H, Ar), 7.09 (br m, 2H, Ar), 6.85 (d, *J* = 8.4 Hz, 4H), 6.77 (d, *J* = 8.4 Hz, 4H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 156.9, 140.6, 130.7, 130.2, 129.5, 128.4, 127.8, 115.2, 63.5 (F₃C—C—, ²*J*_{C-F} = 23.4 Hz, q); mp 228–229°C.

1,1'-Bis[*N*-phenyl-4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3F-diimide)

1,1'-Bis[*N*-phenyl-4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3F-diimide) was synthesized from *N*-phenyl-4-nitrophthalimide and the disodium phenoxide salt of 1,1'-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (3F-sodium salt) by a known method.⁸ A mixture of 1,1'-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (20.6 g, 0.06 mol) and 50% sodium hydroxide solution (9.6 g, 0.12 mol) 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. This trap was then replaced with a recirculating trap packed with calcium hydride, and then the condensed distillate was passed through the trap. The mixture was further heated until no hydrogen evolution took place in the calcium hydride packing. 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 mixture was added 1.2*N* hydrochloric acid. The precipitate was collected by filtration and dried to give

white solid (42.9 g, 91%): mp 220–237°C; IR (KBr) 3068 (Ar), 1773 (C=O), 1718 (C=O), 1599, 1504, 1478, 1373, 1273, 1240, 1148 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.6–7.4 (m, 17H), 7.3–7.1 (m, 10H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 166.5, 166.3, 162.0, 154.9, 139.3, 135.8, 134.4, 132.0, 131.7, 129.4, 129.0, 128.8, 128.4, 128.2, 127.4, 126.12, 126.09, 123.7, 119.7, 112.8, 64.0 (F₃C—C—, ²*J*_{C-F} = 23.4 Hz, q).

1,1'-Bis[4-(3,4-dicarboxylic acid phenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (3F-tetra-acid)

3F-Tetra-acid was prepared from 3F-diimide (41.7 g, 0.053 mol) by hydrolysis with aqueous NaOH (19.1 g, 0.477 mol, 10%) under reflux for 24 h and then the mixture was allowed to cool slowly. To the cooled mixture was added 1.2*N* hydrochloric acid. The precipitate was isolated by filtration. The product was dissolved in a minimum amount of hot water and then extracted with ethyl ether. The extract was dried over anhydrous magnesium sulfate and concentrated to dryness *in vacuo* to give a white solid (32.7 g, 94%); IR (KBr) 3436 (—OH), 3071 (Ar), 1709 (C=O), 1596, 1505, 1237, 1147, 834 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.40 (br, m, 4H), 7.21 (s, 2H), 7.3–7.1 (m, 11H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 168.3, 167.6, 158.4, 155.3, 139.5, 136.9, 135.3, 132.5, 131.6, 129.5, 128.8, 128.4, 127.5, 119.8, 119.3, 118.5, 64.0 (F₃C—C—, ²*J*_{C-F} = 23.4 Hz, q).

1,1'-Bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride (3F-BABPA)

A mixture of the above 3F-tetra-acid 31.5 g (0.04 mol) and acetic anhydride 50.0 g (0.480 mol) was heated at reflux for 1 h. The dianhydride product was obtained by removing acetic anhydride from the reaction mixture *in vacuo* as a yellowish solid (22.9 g, 93%); mp 98–107°C; IR (KBr) 3074 (Ar), 1853 (C=O), 1778 (C=O), 1599, 1505, 1482, 1279, 1232, 1152, 893, 739 cm⁻¹; ¹H-NMR (300 MHz, DMSO-*d*₆) δ 8.10 (d, *J* = 9.0, 2H), 7.64 (m, 4H), 7.43 (m, 4H), 7.30–7.10 (m, 9H); ¹³C-NMR (75 MHz, DMSO-*d*₆) δ 163.2, 162.6, 162.5, 154.2, 139.2, 136.2, 134.2, 131.8, 131.5, 129.4, 128.8, 128.4, 128.0, 125.4, 125.3, 120.0, 119.3, 113.7, 63.9 (F₃C—C—, ²*J*_{C-F} = 23.4 Hz, q).

ANAL: Calcd for C₃₆H₁₉O₈F₃: C, 67.93%; H, 3.01%. Found: C, 68.02%; H, 3.23%.

Materials

4-Nitrophthalimide, 2,2,2-trifluoroacetophenone, trifluoromethane sulfonic acid, phenol, aniline, sodium hydroxide, acetic anhydride, acetic acid, dimethyl sulfoxide, and toluene was used as received. Benzidine (BZ; Fluka Chemical Co., Switzerland), 1,4-phenylenediamine (4-PDA; Aldrich Chemical Co., U.S.A.), 1,3-phenylenediamine (3-PDA; Aldrich), 4,4'-diaminodiphenylether (ODA; Fluka), 4,4'-methylenedianiline (MDA; Aldrich), bis(4-aminophenoxy)biphenyl (BAPB; Chriskev Co., U.S.A.), 1,4-bis(4-aminophenoxy)benzene (TPE-Q; Chriskev), 4-(4-aminobenzyl)cyclohexylamine (ABCHA; Air Products and Chemicals, Inc., U.S.A.), 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF; Central Glass Co., Japan), 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP; Chriskev), 2,2'-bis[3-(4-aminophenyl)hexafluoropropane (3BDAP; Hoechst, Germany), 1,3-bis(4-aminophenoxy)benzene (TPE-R; Chriskev), and 2,2'-bis[4-(4-aminophenyl)hexafluoropropane (4-BDAP; Hoechst) were purified by sublimation. *N*-Methyl-2-pyrrolidone was distilled over phosphorus pentoxide before use.

Polymer Synthesis

Polyamic acid resins were prepared in solution containing 15–20 wt % solids in *N*-methyl-2-pyrrolidone (NMP) by first dissolving the diamines at room temperature. An equimolar amount of a dianhydride was then added and the solutions were stirred for 8–24 h. The solutions were cast onto a glass plate. The polyamic acid films were thermally converted to the corresponding polyetherimide by heating in an air oven for 1 h each at 100, 200, and 300°C.

Measurements

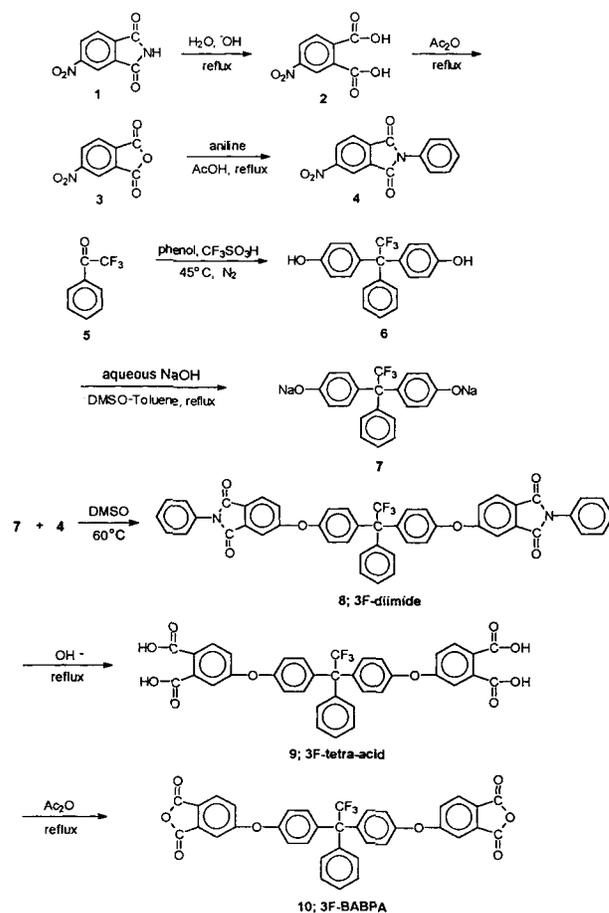
IR spectra were recorded on a Nicolet Magma-IRTM 550 Fourier transform infrared spectrophotometer. ¹H-NMR and ¹³C-NMR spectra were measured on a Varian Unity +300 spectrometer. Melting points were determined on a Buchi 510 apparatus in open capillaries and are uncorrected. Elemental analysis was carried out by Leco CHNS-932. Inherent viscosities of the polyamic acids and polyetherimides were determined at 25°C using 0.5 g/dL solutions in DMAc. Thermal properties were carried out at a heating rate 20°C/min using a DuPont differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TGA), attached to a DuPont TA 2000 system. 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).

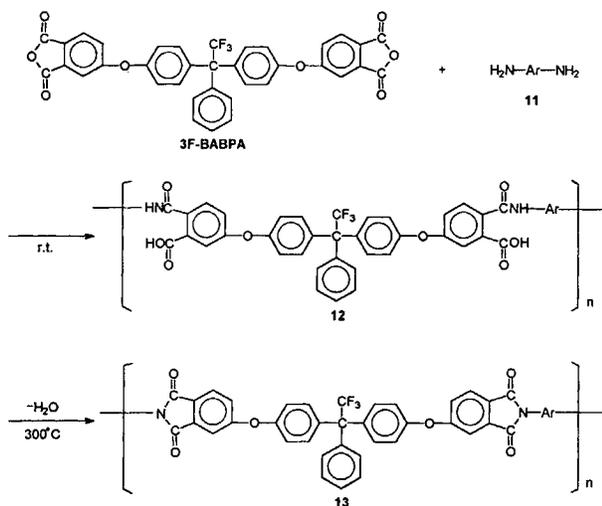
RESULTS AND DISCUSSION

Monomer Synthesis

Synthesis of a new polymer-forming monomer, 1,1'-bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride (3F-BABPA **10**), was prepared by reactions of eight steps as shown in Scheme 1. The 4-nitrophthalic anhydride **3** was prepared in-house from hydrolysis of pure 4-nitrophthalimide **1** in aqueous sodium hydroxide¹⁰ and cyclodehydration of 4-nitrophthalic acid **2**.⁹ Because the commercial 4-nitrophthalic anhydride was contaminated with 5–8% 3-nitrophthalic anhydride, it was necessary to prepare purer *N*-phenyl-4-nitrophthalimide **4**. The *N*-phenyl-4-nitrophthalimide **4**



Scheme 1



Scheme 2

was synthesized by reacting 4-nitrophthalic anhydride **3** and aniline.⁸ 1,1'-Bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane **6** was prepared by reacting 2,2,2-trifluoroacetophenone **5** and phenol.

The reaction was carried out in a three-neck round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, drying tube, and liquid addition funnel.⁷ Disodium phenoxide salt of 1,1'-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (3F-sodium salt **7**) was prepared by reacting 1,1'-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane **6** and 50% NaOH solution in DMSO-toluene (1 : 1).⁸ The method using aqueous NaOH rather than sodium methoxide as a base was beneficial for the industrial production of 3F-sodium salt **7**. In general,⁸ 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 did the chloro derivative in the phthalimide. 1,1'-Bis[*N*-phenyl-4-(3,4-dicarboxyphenoxy)-phenyl]-1-phenyl-2,2,2-trifluoroethane (3F-diimide **8**) was synthesized by reacting *N*-phenyl-4-nitrophthalimide **4** and 3F-sodium salt **9**. The reaction between 3F-sodium salt **7** and the substituted *N*-phenyl-4-nitrophthalimide **4** proceeds quantitatively in either DMF or DMSO at 25–60°C. 1,1'-Bis[4-(3,4-dicarboxylic acid phenoxy)phenyl]-1-

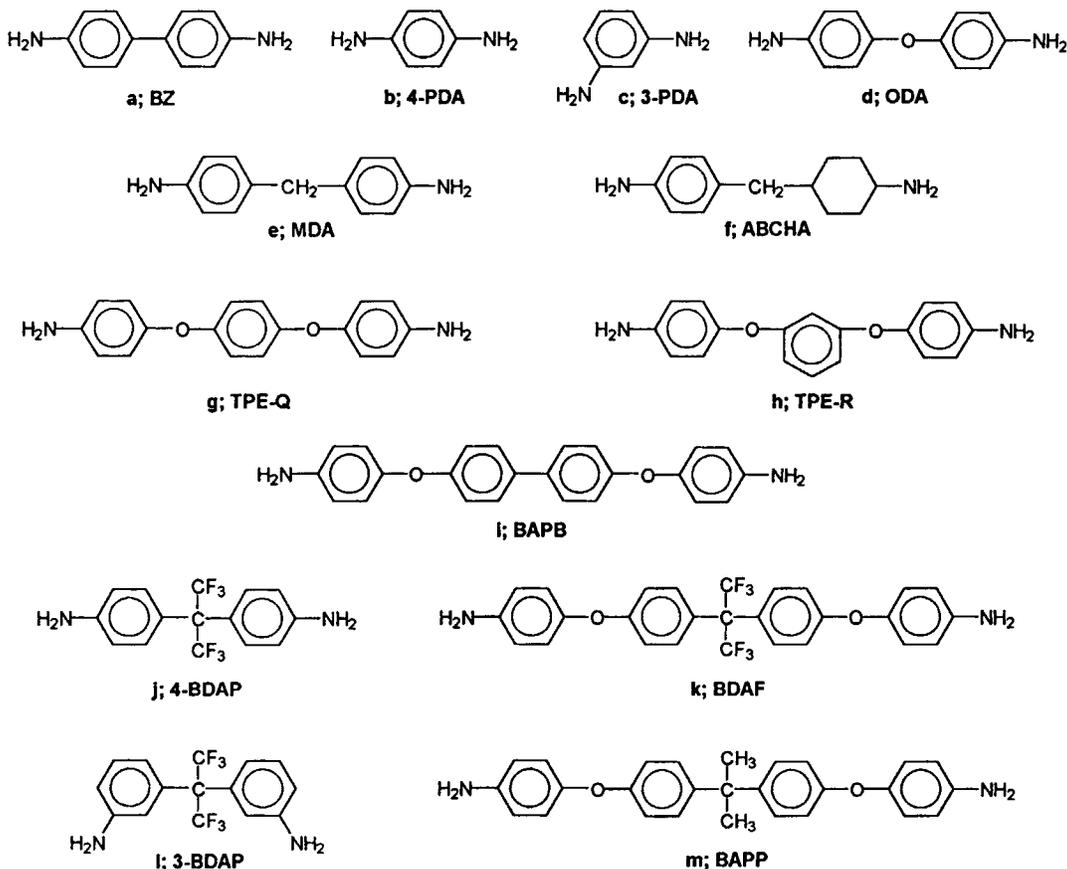


Figure 1 Structures and common symbols of aromatic diamine monomers.

phenyl-2,2,2-trifluoroethane dianhydride (3F-tetra-acid **9**) was prepared by the hydrolysis of 3F-diimide **8** in the NaOH solution. The free tetra-acid **9** was isolated from the reaction mixture after acidifying below pH 1. The new polymer-forming monomer, 3F-BABPA **10**, was prepared by the cyclodehydration of 3F-tetra-acid **9** in acetic anhydride. The IR spectrum of the dianhydride 3F-BABPA **10** exhibited characteristic absorption of C=O group stretching at 1853 and 1778 cm^{-1} .

All aromatic protons of 3F-BABPA, which has only aromatic protons, were not well resolved in the region of 7.0–8.2 ppm in $^1\text{H-NMR}$, but relative intensities of each group of the same kind protons, against a resolved doublet ($J = 9.0$ Hz) at 8.10 ppm for 3,3'-dihydrogens of phthalic anhydride moieties, was matched with the expected value. Two kinds of chemical shifts of C=O groups of anhydride functionality were clearly observed at 162.6 and 162.5 ppm in $^{13}\text{C-NMR}$, whereas due to the free carboxylic acid groups of the corresponding tetra-acid **9**, the resonances were observed at 167.0 and 167.5 ppm in $^{13}\text{C-NMR}$.

Properties of Polymers

The polyetherimides from 3F-BABPA and various diamines were prepared as shown in Scheme 2. Generally, the physical and chemical properties of polyimide polymers are dependent on the chemical structure of monomers in the polyimide backbone.⁶ Target polyetherimides on a specific dianhydride monomer were prepared with structurally different aromatic diamines **11**, which have various bridges and functionalities, i.e., (1) *para*- and *meta*-phenylene, (2) 6H-propyl [$-\text{C}(\text{CH}_3)_2-$] and 6F-isopropyl [$-\text{C}(\text{CF}_3)_2-$], (3) phenyl and cyclohexyl, and (4) ether and methylene linkages. The chemical structures and common symbols of the monomeric aromatic diamines used in the polyetherimide synthesis are shown in Figure 1.

The inherent viscosities of polyamic acids **12a–12m** and polyetherimides **13a–13m** are shown in Table I. The ring-opening polyaddition of diamines to anhydrides in NMP at room temperature affords polyamic acids with inherent viscosities between 0.70 and 1.99 dL/g, suggesting the formation of high molecular weight polymers. From the resultant polymer solutions, transparent and flexible films of the polyamic acids could be obtained by casting. The thermal conversion to polyetherimides was carried out by successive heating of the polyamic acids films for 1 h each at 100, 200, and 300°C under air. The resultant polyetherimides had inherent viscosities

Table I Inherent Viscosities of Polyamic Acids and Polyetherimides Using 3F-BABPA with Various Diamines

Dimine	Inherent Viscosity ^a (dL/g)	
	Polyamic Acid	Polyetherimides
a	1.18	0.60
b	0.73	—
c	0.88	—
d	1.09	0.82
e	1.20	0.95
f	0.86	0.66
g	1.99	0.65
h	1.73	0.88
i	1.35	1.29
j	0.46	0.32
k	1.10	0.48
l	0.70	0.22
m	1.26	0.59

^a Measured at 25°C at a concentration of 0.5 g/dL in NMP.

of 0.22–1.29 dL/g in NMP. The inherent viscosities of polyetherimides were lower than those of polyamic acids. The polyetherimides prepared from most aromatic diamines used in this study resulted in satisfactory physical properties and high molecular weight to permit casting tough films.¹¹ However, the polyetherimides **13j** and **13l** had low molecular weight and were brittle. The diamines 4-BDAP (**j**) and 3-BDAP (**l**) containing the hexafluoroisopropylidene moiety did not give a high molecular weight polymer with 3F-BABPA dianhydride. The diamines 4-BDAP (**j**) and 3-BDAP (**l**) might be differentiated from the other aromatic diamine monomers based on the chemical reactivity toward the dianhydride monomers. These amines have a strong electron-withdrawing group, the hexafluoroisopropylidene moiety, connecting both sides of the aromatic amine. Probably, the nucleophilicity of these two amines are comparatively lower than that of the other aromatic diamine monomers. The steric effect is not applicable to explain the results, because, e.g., diamines BZ (**a**), 4-PDA (**b**), and 3-PDA (**c**) would have a similar steric effect and more rigidity.

The formation of polyetherimides was confirmed by IR spectroscopy. In the IR spectra, the polyetherimides exhibited characteristic imide absorptions at 1780, 1720, 1370, and 720 cm^{-1} . The thermal behavior of the polyetherimides was evaluated by DSC and TGA techniques. The DSC curves of polyetherimides **13a**, **13d**, **13h**, **13i**, and **13k** are shown in Figure 2.

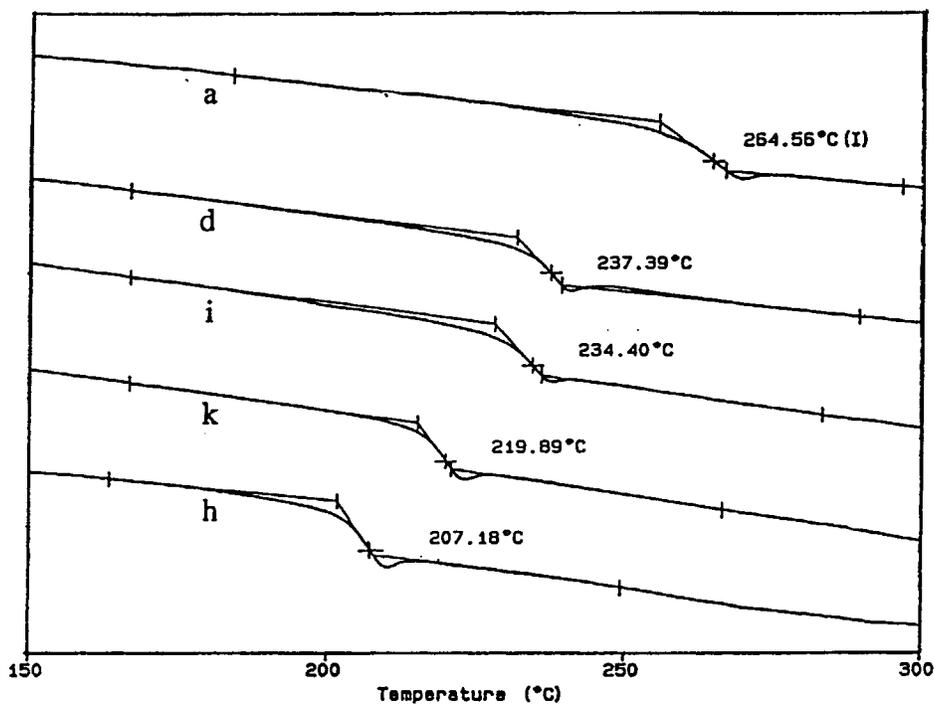


Figure 2 DSC curves for polyetherimides of 13a, 13d, 13h, 13i, and 13k at heating rate 20°C/min in nitrogen.

The thermal properties of the polyetherimides are summarized in Table II. Most of polyetherimides showed high thermal stability and did not decompose below 560°C in nitrogen and below 500°C in air at

heating rate of 20°C/min. The lower thermal stability in air than in nitrogen is common. These aromatic polyetherimides also revealed slightly lower decomposition temperatures in air than in nitrogen.

Table II Thermal Properties of Polyetherimides Using 3F-BABPA with Various Diamines

Polymer	T_g^a (°C)	Decomposition Temperature ^b (°C)		Residue ^c (wt %)
		In Air	In Nitrogen	
13a	264	625	635	60.6
13b	254	—	625	60.0
13c	239	—	580	61.4
13j	244	—	—	—
13d	237	—	580	65.5
13e	235	—	565	60.9
13i	234	560	570	61.2
13g	225	—	580	51.8
13f	223	475	520	25.9
13k	220	—	580	61.1
13m	217	535	565	52.1
13l	216	—	580	61.6
13h	207	—	580	57.9

^a Determined by DSC at a heating rate of 20°C/min in nitrogen.

^b Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20°C/min.

^c At 900°C in nitrogen.

Table III Solubility of Polyetherimide Used 3F-BABPA with Various Solvents at Room Temperature

	NMP	DMF	DMAc	Pyridine	CH ₂ Cl ₂
13a	++	—	++	++	—
13b	++	++	++	+	+
13c	—	++	—	++	++
13d	—	++	—	++	++
13e	++	—	—	—	++
13f	++	+	++	++	++
13g	++	++	—	++	++
13h	++	+	++	++	++
13i	++	++	++	++	++
13j	++	++	++	++	++
13k	++	++	++	++	++
13l	++	++	++	++	++
13m	++	++	++	++	++

++: Soluble, —: insoluble, +: partially soluble.

Generally, the thermal stability of polyimides including a methylene moiety and a cyclohexyl moiety in the backbone was found to be relatively low.⁶ **13e** and **13f** polymers had thermally flexible methylene groups ($-\text{CH}_2-$) and cyclohexane units in the polymer backbone, respectively. The glass transition temperatures (T_g) of the polyetherimides were found to be 207–264°C by DSC. The relation between T_g and the structure of diamines used was as follows: (a) Polymers linked with the biphenyl moiety, **13a** and **13i**, showed a higher transition temperature than that of polymers linked with the phenylene moiety, **13b** and **13g**. (b) Polymers linked with the *para*-phenylene moiety, **13b**, **13g**, and **13j**, showed a higher glass transition temperature than that of analogous polymers linked with the *meta*-phenylene moiety, **13c**, **13h**, and **13l**, respectively. (c) Polymers **13g**, **13i**, and **13k** containing two ether linkages in the diamine monomer showed relatively lower glass transition temperatures than those of polymers **13d**, **13a**, and **13j** containing the same bridges in the polymer backbone. (d) Polymer **13f** containing the cyclohexyl group in the backbone had a lower thermal stability than that containing the phenyl group **13e**. (e) Polymer **13k** containing the polar group $-\text{C}(\text{CF}_3)_2-$ had a higher T_g than that of the alkyl group like $-\text{C}(\text{CH}_3)_2-$ in **13m**.

The qualitative solubility of the polyetherimides in various solvents is shown in Table III. Most aromatic polyetherimides prepared from dianhydride 3F-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. Polymers **13a**, **13b**, **13c**, **13d**,

and **13e** had somewhat limited solubility. However, polymers **13g**, **13h**, **13i**, and **13m** containing two ether linkages and **13j**, **13k**, and **13l** incorporating fluorine atoms had good solubility. This may be due to the effect of the flexible ether linkage and a polar group. Polymer **13f** with the cyclohexyl structure had also good solubility. All the polymers are insoluble in common solvents such as acetone. The superior solubility can be apparently attributed to the combined favorable effects of polar group as hexafluoroisopropylidene and the bulky pendant group of 3F-BABPA and aromatic ether linkages in the polyetherimide backbone. Thus, these good solubilities for these polymers might be derived from 3F-BABPA dianhydride monomer.

The tensile properties of the polyetherimide films are summarized in Table IV. The films had a tensile

Table IV Tensile Properties of Polyetherimide Films

Polymer	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
13a	65	5	2.1
13b	80	7	2.5
13c	108	10	2.5
13d	110	22	1.7
13e	77	9	1.7
13g	96	18	1.9
13h	96	70	2.0
13k	88	17	1.6
13m	92	11	1.7

strength of 65–110 MPa, elongation to break of 4–70%, and tensile modulus of 1.6–2.5 Gpa. All the polymers listed in Table IV behave as ductile materials with good tensile strengths and moderate elongation to break except for the brittle behavior of polymers **13f**, **13j**, and **13l**.

CONCLUSION

Thermally stable aromatic polyetherimides were successfully prepared from newly synthesized anhydride monomer 3F-BABPA and various aromatic diamine monomers. The introduction of the bulky 3F-BABPA unit into the polyetherimide backbone brought about soluble aromatic polyetherimides with high T_g and good thermal stability. Thus, the present novel polyetherimides are considered as new, promising, processable high-temperature polymeric materials.

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