

Preparation and Properties of Aromatic Polyimides Based on 4,4'-(2,2,2-Trifluoro-1-phenylethylidene)diphthalic Anhydride

DONG-HO LEE,¹ SEUNG-YOUNG KOO,¹ HYUNG-SEOK LEE,¹ WOO SIK KIM,¹ KYUNG EUN MIN,¹ LEE SOON PARK,¹ KWAN HO SEO,¹ INN KYU KANG,¹ HEUNG-JIN CHOI²

¹ Department of Polymer Science, Kyungpook National University, Taegu 702-701, Korea

² Department of Industrial Chemistry, Kyungpook National University, Taegu, Korea

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ABSTRACT: Aromatic polyimides were synthesized from aromatic carboxylic acid dianhydrides, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 4,4'-(2,2,2-trifluoro-1-phenylethylidene)diphthalic anhydride (3FDA), and pyromellitic dianhydride (PMDA), with four typical aromatic diamines. These included polyimide (PI) from 2,2-bis(4-aminophenyl)hexafluoropropane (4BDAP) by two-step procedures; amidation to polyamic acid (PAA), followed by thermal imidization of PAA. The chemical and physical properties of the newly prepared polyimides were compared in terms of their chemical structures, inherent viscosity, thermal property, transmission, dielectric constant, UV cutoff, water absorption, and refractive index. PIs 3FDA/4BDAP and 6FDA/4BDAP were soluble in common organic solvents, whereas others were not. In particular, it was found that the solubility was dependent on the temperature of imidization. The chemical and physical properties of the newly prepared polyimides derived from 3FDA were similar to the polyimides derived from 6FDA. The solubility of polyimide containing an ether functional group in the dianhydride moiety was better than that of the ether functional group in the diamine moiety. The polymers with ether linkage in dianhydride moiety exhibited lower glass transition temperature than their functionality-reversed analogous polymers with ether linkage in diamine moiety. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 38–44, 2002

Key words: aromatic polyimide; thermal imidization; dielectric constant; UV cutoff; solubility; refractive index

INTRODUCTION

The optics and electronics industries have rapidly progressed and new demands are being placed on the materials.^{1–3} Improvements in polyimide properties have been sought by incorporating tri-

fluoromethyl or other perfluoroalkyl groups. Fluorinated polyimides are known to have low dielectric constants^{4,5} and water absorption,^{5,6} but high transparency^{7,8} and solubility⁹ compared to fluorine-free polyimides.

In our previous work,^{10–12} the fluorinated polyetherimides were synthesized from 1,1-bis[4-(3,4-dicarboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride and 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane, which displayed the sound solubility and a high glass transition temperature.

Correspondence to: D. Lee.

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In this work, a new aromatic dianhydride monomer with one trifluoromethyl and one phenyl group, 4,4'-(2,2,2-trifluoro-1-phenylethylidene)diphthalic anhydride, was synthesized. The properties of the newly prepared polyimides were studied in view of their chemical structures, solubility, dielectric constants, viscosity, refractive indices, transparency, water absorption, and thermal properties.

EXPERIMENTAL

Materials

Trifluoroacetophenone (Aldrich Chemical Co., Milwaukee, WI), trifluoromethane sulfonic acid (Aldrich Chemical Co.), *o*-xylene (Junsei Chemical Co., Tokyo, Japan), ethanol (Wako Pure Chemical Co., Osaka, Japan), nitric acid, hydrochloric acid, acetic anhydride (Janssen Chemical, Beerse, Belgium), and acetic acid (BDH Ltd., Poole, England) were used as received.

2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF; Central Glass Co., Tokyo, Japan), 4,4'-diaminodiphenylether (ODA; Fluka Chemical Co., Basel, Switzerland), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP; Chriskev Co. Inc., Leawood, U.S.A), 2,2-bis(4-aminophenyl)hexafluoropropane (4-BDAP; Hoechst, Strasbourg, Germany), pyromellitic dianhydride (PMDA; Chriskev Co.), 2,2-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride (6FDA), and 4,4'-(2,2-trifluoro-1-phenylethylidene)-diphthalic anhydride (3FDA) were purified by sublimation. *N*-Methyl-2-pyrrolidone (NMP; Janssen Chemical) was distilled over phosphorous pentoxide prior to use.

Synthesis of Monomer

4,4'-(2,2,2-Trifluoro-1-phenylethylidene)diphthalic Anhydride

3FDA was synthesized by using a known procedure.¹³ The recrystallized product from the solution (acetic anhydride/acetic acid 4 : 3) yielded 18.5 g (71%) of pale yellow solid. This product was then further purified by sublimation with a melting point (mp) of 201–203°C.

IR (KBr, cm^{-1}): 3070 (aromatic C—H), 1854 and 1782 (C=O anhydride), 1229 (C—F), 899 (one H on aromatic ring), 816 (adjoint H's on aromatic ring), 723, 694 (five adjacent H's on aromatic ring). ¹H-NMR (300 MHz, DMSO-*d*₆), δ : 8.24 (d, $J = 8.7$ Hz, 2H in 3-position to anhydride), 7.82 (d d, $J = 8.7, 1.8$ Hz, 2H in position to anhydride), 7.54 (m, 3H in *meta* and *para* positions on

phenyl group), 7.56 (br d, $J = 1.8$ Hz, 2 h in 5-position to anhydride), 7.14 (m, 2H in *ortho* position on phenyl group).

Synthesis of Polyimides

An equimolar amount of a dianhydride was added to the diamine solution containing 15–20 wt % solids in NMP at room temperature, and the resulting solution was stirred for 24 h at room temperature. The resulting solution of polyamic acid (PAA) was cast onto a glass plate and dried at 60°C under vacuum to produce a transparent PAA film. The dried film was stripped off the glass plates, placed into metal frames, and heated in an air oven for 1 h at 150°C, 30 min at 200°C, 30 min at 250°C, and 1 h at 350°C.³

Measurements

Fourier transformation infrared (FTIR) spectra were obtained with a Nicolet Magma-IRTM 550 FTIR spectrometer, which provided qualitative information on the conversion of PAA to polyimide (PI). In addition, FTIR analysis was utilized to follow the synthesis of 3FDA. H-NMR measurement was performed on a Varian Unity Plus 300 NMR (300 MHz) spectrometer with chemical shifts reported in parts per million.

The water absorption was measured as follows:^{3,14} Specimens were immersed in water at 23°C for 48 h and the weight differences after aging were measured. Inherent viscosities of the soluble PAA were determined in 0.5 g/dL NMP solutions by using a Ubbelohde viscometer at 25°C. Thermal analysis was performed on a DuPont TA 2000 system thermal analyzer. DSC was used to determine the glass transition temperature, and scans were performed at a heating rate of 10°C min⁻¹ to 350°C, 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 the bridge method by using a Hewlett-Packard 4265B.^{3,14} The solubility of the polyimides was investigated by dipping 1 wt % solutions in small capped glass vials for 3 days.¹⁵ Transmission spectra were obtained on 0.013 mm (0.5 mil) thick films at 500 nm, and UV cut-off wavelengths were measured by using a Shimadzu UV-2000. The refractive indices were measured by the wave-guiding method on a Spectra-Physics Model 196-1.¹⁶

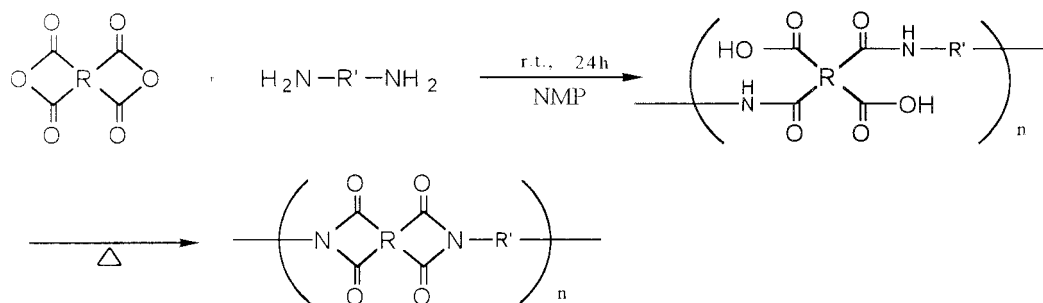


Figure 1 Preparation sequence of polyimide from dianhydride with diamine.

RESULTS AND DISCUSSION

Synthesis of Polymer

The synthesis of PI from three dianhydrides with four diamines was conducted as shown in Figure 1, and the components of the used dianhydride and diamine are shown in Figure 2. The reactive dianhydrides reacted with aromatic diamines even at ambient temperatures, which resulted in PAA with a high degree of polymerization in carefully controlled reaction conditions. Any presence of moisture or monofunctional nucleophilic impurities in the reaction resulted in terminating the extending polymeric chain.

Properties of Polymers

As shown in Table I, the ring opening polyaddition of diamines to anhydrides in NMP afforded PAAs with inherent viscosities between 0.52 and 1.36 dL/g. From the resulting polymer solutions, the transparent and flexible films of the PAAs could be prepared. The PI prepared from most

aromatic diamines used in this study resulted in the satisfactory physical properties and moderate molecular weight to permit casting into a tough film.

Most PIs exhibited high thermal stability and did not decompose below 540°C in nitrogen at a heating rate of 10°C/min. The glass transition temperatures (T_g) of PIs were found to be >260°C by DSC.

The relation between T_g and the structure of PI was as follows: (1) Polymers containing 3FDA had a similar T_g to polymers containing 6FDA. Polymers with 3F-phenylethylene group in the dianhydride moiety had similar T_g within 5°C to the corresponding polymers with 6F-propylene group. Therefore, the 3F-phenylethylene group apparently behaved similarly to the 6F-propylene group in this polymer system. Such trends for thermal properties of polymers were found to be in accordance with previous reports, in which PIs derived from 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane dianhydride with BAPP, BDAF, or 4BDAP and the corresponding polymers from 1,1-bis[4-(3,4-dicar-

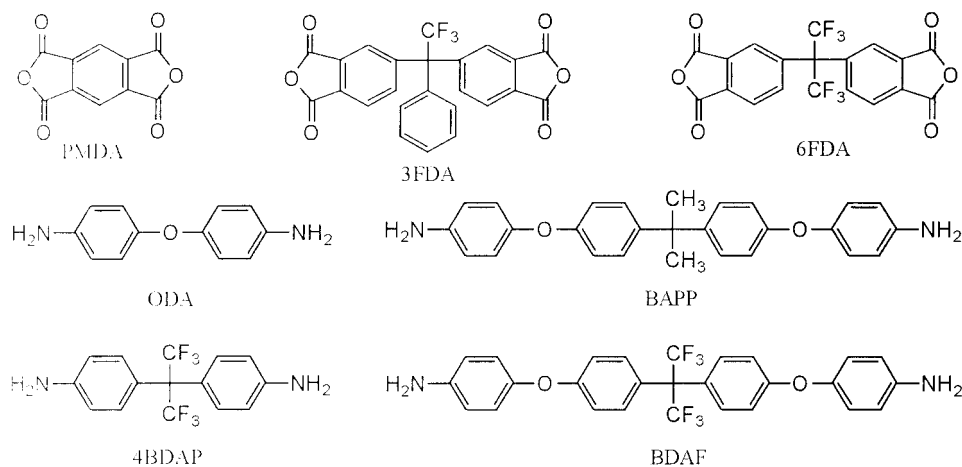


Figure 2 Structures and symbols of aromatic dianhydride and diamine monomers.

Table I Thermal Properties and Viscosities of Polyimides

Polymers	Inh ^a (dL/g)	T_g^b (°C)	Tdi ^c (°C)	Td ₁₀ ^d (°C)	Residue at 900 °C (wt %) ^e
PMDA/BAPP	1.07	322	546	558	50
PMDA/ODA	0.64	>400	599	618	56
PMDA/BDAF	0.78	323	551	581	57
PMDA/4BDAP	0.52	>400	549	561	51
3FDA/BAPP	1.14	262	544	573	58
3FDA/ODA	1.03	308	567	587	63
3FDA/BDAF	1.20	267	557	589	59
3FDA/4BDAP	0.74	316	557	587	57
6FDA/BAPP	1.36	261	555	583	59
6FDA/ODA	1.05	309	572	599	54
6FDA/BDAF	1.14	264	563	588	55
6FDA/4BDAP	0.84	314	570	587	52

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

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

^c Temperatures at which polymer decomposition initiated.

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

^e At 900°C under nitrogen.

boxy-phenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane dianhydride had similar thermal properties.^{10,11} Polymers containing PMDA of rigid structures had much higher T_g over 320°C than those from 3FDA and 6FDA as the dianhydride moiety. (2) Two distinct polymer groups could be classified according to thermal properties of diamine moiety in this polymer system. Polymers synthesized from BAPP or BDAF had similar thermal properties, whereas polymers from ODA or 4BDAP behaved similarly. Polymers 3FDA/BDAF and 6FDA/BDAF containing two more ether linkages in the diamine moiety showed relatively lower T_g (~ 50°C) than polymers 3FDA/4BDAP and 6FDA/4BDAP containing no ether linkage.

However, polymer 6F-BABPA/4BDAP containing two ether linkages in anhydride moiety had a relatively lower T_g than its functionality-reversed analogous polymer 6FDA/BDAF. This observation resulted because the imide functionality in polymer backbone was reversed so that two-ether linkage was in diamine moiety. A similar structural relationship was also observed in the 6F-BABPA/3F-DAM to 3FDA/BDAF. Apparently the polymers with ether linkage in dianhydride moiety had lower T_g than their functionality-reversed analogous polymers with ether linkage in diamine moiety (Fig. 3). (3) Polymer containing the fluorinated polar group $-\text{C}(\text{CF}_3)_2-$ had slightly higher T_g (~ 1–5°C) than the corresponding isomeric polymer with $-\text{C}(\text{CH}_3)_2-$ because the bulky fluorine group decreased the mobility of

main chain.¹⁵ (4) The ether linkage of ODA and the 2,2-bis(trifluoromethyl)propylene group of 4BDAP as diamine moiety in this PI system resulted in similar thermal properties. However, polymers of ODA diamine containing the more flexible ether group had slightly lower T_g (~ 1–5°C) than those of 4BDAP diamine containing the 6F-propylene group similar to $-\text{C}(\text{CF}_3)_2-$.

The qualitative solubility of PI in organic solvent is shown in Table II. Most aromatic PIs were insoluble in most organic solvents. However, the polymer 6FDA/4BDAP with a high fluorine content, 34.1%, was soluble in common solvents such as NMP, DMF, DMAc, pyridine, methylene chloride, and acetone. The superior solubility could apparently be attributed to the combined favorable effects of polar hexafluoroisopropylidene groups both in dianhydride and in diamine moieties. Solubility was found to be dependent on the thermal condition of imidization: PI films cured at 300°C had a little higher solubility than those cured at 350°C. Curing at a higher temperature was much more effective in imidization of PAA to PI. In particular, it was found that the polymer 6F-BABPA/3F-DAM reported previously¹¹ was soluble in most solvents. However, its functionality reversed analogous polymer, 3FDA/BDAF, was not soluble (Table II). Its solubility depended on whether the ether functional group existed in the dianhydride moiety or in the diamine moiety. The solubility of PIs containing an ether func-

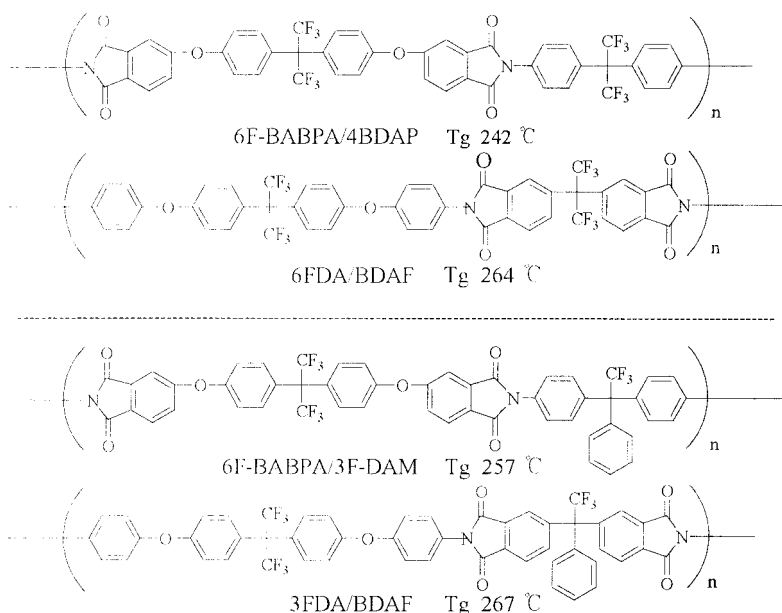


Figure 3 Chemical structures and T_g of functionality reversed analogous PIs: 6F-BABPA/4BDAP to 6FDA/BDAF and 6F-BABPA/3F-DAM to 3FDA/BDAF.

tional group in the dianhydride moiety was better than that of the ether functional group in the diamine moiety.

The UV transmission cutoff and optical transparency were determined on the PI films and given in Table III. The polymer films containing fluorine had excellent optical transparency with a UV cutoff of < 386 nm and $> 90\%$ transmission at 500 nm. Certain trends of UV cutoff were found to decrease with increasing fluorine contents of PIs.

There was a certain relationship between dielectric constant and fluorine weight content in PIs, as shown in Table III. Polymers with high fluorine content had relatively low dielectric constant compared to polymers with low fluorine content. The polymers prepared from 6FDA dianhydride containing six fluorine atoms had dielectric constants as low as 2.5, whereas the polymers from PMDA dianhydride without fluorine had dielectric constants as high as 3.4. These results

Table II Solubility of Polyimide in Various Solvents at Room Temperature

Polymers	NMP		DMF		DMAc		Pyridine		CH ₂ Cl ₂		Acetone	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
PMDA/BAPP	X	X	X	X	△	△	X	X	X	X	X	X
PMDA/ODA	X	X	X	X	X	X	X	X	X	X	X	X
PMDA/BDAF	X	X	X	X	X	△	X	X	X	X	X	X
PMDA/4BDAP	X	X	X	X	○	○	X	△	X	X	X	X
3FDA/BAPP	△	△	△	△	△	△	△	△	△	△	X	X
3FDA/ODA	X	X	△	○	△	△	△	○	△	○	X	X
3FDA/BDAF	△	△	△	△	△	△	△	△	△	△	X	X
3FDA/4BDAP	△	○	○	○	△	○	△	○	△	○	△	△
6FDA/BAPP	△	△	△	△	△	△	△	△	△	△	X	X
6FDA/ODA	X	X	△	△	△	△	△	△	△	△	X	X
6FDA/BDAF	△	○	△	○	△	○	△	△	△	△	△	△
6FDA/4BDAP	○	○	○	○	○	○	○	○	○	○	○	○

○, Soluble; X, insoluble; △, partially soluble.

(a) Final curing temperature at 350°C; (b) final curing temperature at 300°C.

Table III Properties of Polyimide Films

Polymer	Fluorine Content (%)	Transmission at 500 nm (%)	UV Cutoff ^a (nm)	Water Absorption ^b (%)	Dielectric Constant at 1 kHz
PMDA/BAPP	0.0	73	414	1.01	2.9
PMDA/ODA	0.0	71	422	1.42	3.4
PMDA/BDAF	16.3	79	386	0.69	2.7
PMDA/4BDAP	22.1	—	—	—	—
3FDA/BAPP	6.9	88	352	0.70	2.7
3FDA/ODA	9.2	91	360	0.76	2.9
3FDA/BDAF	18.3	90	340	0.53	2.6
3FDA/4BDAP	22.8	91	321	0.28	2.6
6FDA/BAPP	13.9	93	363	0.61	2.6
6FDA/ODA	18.7	92	369	0.64	2.7
6FDA/BDAF	24.6	94	341	0.28	2.5
6FDA/4BDAP	30.7	93	325	0.20	2.5

^a Wavelength of UV cutoff.

^b Measured at 23°C for 2 days.

could be explained by the reduction in chain-chain interaction in fluorinated PIs.⁴ The polymers prepared from 3FDA containing the bulky phenyl group showed approximately similar dielectric constants compared to those of the bulky 6F group, and this result was attributed to the same interaction effect.

The water absorption of PIs decreased with increasing fluorine content because the incorporation of fluorine into the main chain increased the hydrophobicity of PIs.¹⁷ These results were also related to the stability in the dielectric constant of PIs.¹⁴

The refractive index decreased from 1.58 to 1.67 in PIs as fluorine content increased (Table IV). This result demonstrated that the refractive index of PI could be controlled in fluorinated resins because refractive index is governed by electronic polarization.¹⁴ The birefringence of PI films is, in general, defined as the difference of refractive indices of the two polarizations, parallel [$n(\parallel)$] and perpendicular [$n(\perp)$] to the film plane. A very large birefringence between $n(\parallel)$ and $n(\perp)$ of 0.105 was observed for the PMDA/BAPP polymer, whereas the fluorinated polymers containing 3FDA and 6FDA showed relatively small birefringence.

Table IV Refractive Indices of Polyimides

Polymers	Fluorine Content (%)	$n(\parallel)$	$n(\perp)$	Δn^a	N^b
PMDA/BAPP	0.0	1.7050	1.6002	0.1048	1.6700
PMDA/ODA	0.0	1.7290	1.6290	0.1000	1.6960
PMDA/BDAF	16.3	1.6680	1.5818	0.0862	1.6393
PMDA/4BDAP	22.1	1.6170	1.6147	0.0023	1.6162
3FDA/BAPP	6.9	1.6350	1.6342	0.0008	1.6347
3FDA/ODA	9.2	1.6397	1.6394	0.0003	1.6396
3FDA/BDAF	18.3	1.6145	1.6142	0.0003	1.6144
3FDA/4BDAP	22.8	1.6046	1.6043	0.0003	1.6045
6FDA/BAPP	13.9	1.6247	1.6142	0.0105	1.6145
6FDA/ODA	18.7	1.6183	1.6178	0.0005	1.6181
6FDA/BDAF	24.6	1.5952	1.5946	0.0006	1.5950
6FDA/4BDAP	30.7	1.5808	1.5807	0.0001	1.5808

^a Birefringence.

^b Mean value of refractive index: $N = [(n(\parallel) \times 2 + n(\perp))/3]$.

CONCLUSION

The polymers with ether linkage in dianhydride moiety had lower T_g (~ 10 – 20°C) than their functionality-reversed analogous polymers with ether linkage in diamine moiety. Polyimides 3FDA/4BDAP and 6FDA/4BDAP were soluble in common organic solvents, whereas others were not. The polyimide films cured at 300°C had a little higher solubility than those cured at 350°C . The solubility of polyimide containing an ether functional group in the dianhydride moiety was better than that of the ether functional group in the diamine moiety. The chemical and physical properties of the newly prepared polyimides derived from 3FDA were similar to those of the polyimides derived from 6FDA. Polymers with high fluorine content had relatively low dielectric constant and birefringence compared to polymers with low fluorine content.

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