

# Incorporation Effects of Fluorinated Side Groups into Polyimide Membranes on Their Physical and Gas Permeation Properties

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**ABSTRACT:** The effects of incorporation of fluorinated alkyl side groups into polyimide membranes were investigated in terms of their physical and gas permeation properties. Four polyimides with fluorinated side groups and four polyimides without the side groups were prepared by polycondensation of 2-(perfluorohexyl)ethyl-3, 5-diamino benzoate (PFDA) and *m*-PDA with four aromatic dianhydrides (6FDA, OPA, BTDA, and PMDA), respectively. It was found that the incorporation of fluorinated side groups into the polyimide membranes decreased their surface free energies ( $T_{gs}$ ), solubility parameters, and fractional free volume (FFV)s and therefore, enhanced the permeabilities for CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> gases but reduced the selectivities for CO<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub> gas pairs depending upon the structure of dianhydride monomers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2756–2767, 2000

**Key words:** fluorinated polyimides; membrane; gas separation; 2-(perfluorohexyl)ethyl-3,5-diaminobenzoate; amorphous polymer; solubility parameter; surface free energy; fractional free volume

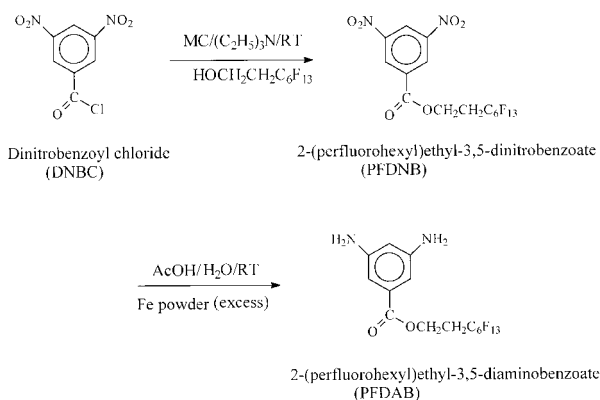
## INTRODUCTION

Aromatic polyimides have been studied intensively as prospective membrane materials because of their good gas permeation properties as well as excellent thermal and mechanical properties.<sup>1–4</sup> A lot of studies have been carried out using these polyimides,<sup>5–7</sup> and their gas permeation properties could be highly improved by modification of their chemical structure with various diamines and dianhydrides monomers as well as introduction of specific functional groups into polymer main chains.<sup>8</sup>

Polyimides with fluorinated side groups are expected to be the good candidate materials with both high permeability and high selectivity for gas separation because of their unique hydrophobic and bulky characteristics: they can affect significantly the affinity or solubility of gases to membranes, their chain rigidity, internal rotation of the bonds, molecular distances, and free volume between the polymer chains. Such properties are important factors enhancing permeability and selectivity of glassy polymer. 6FDA (hexafluoroisopropylidene-diphthalic anhydride)-based polyimides seem to be good examples.<sup>9–13</sup> In spite of these unique characteristics, the gas separation studies with these polyimides except a series of hexafluoroisopropylidene(-C(CF<sub>3</sub>)<sub>2</sub>-)-based polyimides have been rarely reported.<sup>14</sup> Systematic studies have not been carried out

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**Scheme 1.** Synthetic route of PFDAB.

to investigate the incorporation effect of fluorinated alkyl side groups into polyimides on their physical properties and their relationship with the gas separation properties.

In this study, four polyimide membranes with fluorinated side groups were prepared by polycondensation of 2-(perfluorohexyl)ethyl-3,5-diaminobenzoate (PFDAB) with four aromatic dianhydrides in *N*-methyl-2-pyrrolidone, respectively. As reference materials that do not have fluorinated side groups, four polyimide membranes were also prepared by polycondensation of *m*-phenylene diamine (*m*-PDA) with the same aromatic dianhydrides, respectively. The fluorinated diamine, PFDAB was synthesized according to Scheme 1.

## EXPERIMENTAL

### Reagents

2-Perfluorohexylethanol (PFOH:  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}_2\text{OH}$ ) was purchased from Hoechst Co. (Frankfurt, Germany). Methylene dichloride (MC), hexane, ethyl acetate (EA), acetic acid (AA), triethyl amine (TEA), Fe powder, and 3,5-dinitrobenzoyl chloride (DNBC) were purchased from Aldrich Chemical Co. (Milwaukee, Wisconsin, U.S.A.). They were all used for the preparation of the fluorinated diamine, PFDAB, without further purification. *m*-PDA, purchased from Aldrich, was purified by vacuum distillation before use. Hexafluoroisopropylidenediphthalic anhydride (6FDA), oxydiphthalic dianhydride (ODPA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) were purchased from Aldrich. 6FDA was vacuum-dried at 15°C for

24 h before use. ODPA, BTDA, and PMDA were recrystallized from acetic anhydride before use. Anhydrous *N*-methyl-2-pyrrolidone (NMP), obtained from Aldrich, was used as a solvent for the preparation of polyimides.

### Synthesis of 2-(perfluorohexyl)ethyl-3,5-dinitrobenzoate (PFDNB)

The synthetic route of PFDAB is outlined in Scheme 1. In a 250-mL, three-necked round flask equipped with a nitrogen inlet, a magnetic stirrer, a dropping funnel, and an ice water bath, 10 g (0.0047 mol : 1.0 equiv) of DNBC was dissolved in 94 mL of MC and stirred vigorously at ambient temperature. In a 200-mL one-necked flask, 12.53 mL (0.056 mol : 1.2 equiv) of PFOH and 9.2 mL (0.066 mol : 1.4 equiv) of TEA were also dissolved in 113 mL of MC. With the aid of dropping funnel, the mixed PFOH solution was added slowly for 1 h to the three-necked flask containing DNBC solution with vigorous stirring under dry  $\text{N}_2$  purge. After an additional 2 h, the solution was transferred to 500 mL of separating funnel, followed by three times washing of 100 mL of  $\text{NaHCO}_3$  aqueous solution. By evaporation of the reaction solution under vacuum, the crude product was obtained and recrystallized from EA/hexane to give the fluorinated dinitro compound, PFDNB (19.0 g, 73.2 wt %).

MW,  $\text{C}_{15}\text{H}_7\text{F}_{13}\text{N}_2\text{O}_6$ , 558.20 (calc.), 558 (Mass anal.); MP, 117.4°C (by differential scanning calorimetry, DSC) and 117°C (by Thomas-Hoover (6427-F10) apparatus); IR(KBr), 3094 (C=C-H str., aromatic), 1736 (C=O str., ester), 1629 (C=C str., aromatic), 1545 (C-N str.,  $\text{NO}_2$ ), 1350 (C-N str.,  $\text{NO}_2$ ),  $^1\text{H-NMR}$ (DMSO- $d_6$ , ppm); 4 peaks,  $\text{CH}_2\text{CF}_2$ (3.00–2.87, t-t, 2H),  $\text{CH}_2\text{-O}$ (4.71, t, 2H), Ar-H(8.92, s, 2H ; 9.05, s, 1H),  $^{13}\text{C-NMR}$ ( $\text{CDCl}_3$ - $d_3$ , ppm); 7 peaks, 30.5(t, 1H, fluorine-carbon coupling), 58.5 (s, 1H), 122.7 (s, 1H), 128.4 (s, 2H), 133.3 (s, 1H), 148.8 (s, 2H), 162.1 (s, 1H);  $(\text{CF}_2)_6\text{CF}_3$  (disappeared due to fluorine-carbon coupling).

### Synthesis of PFDAB

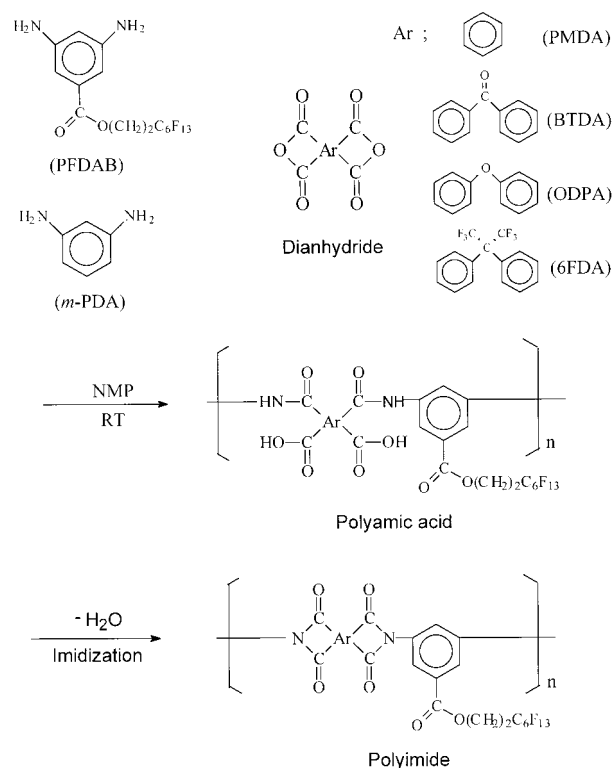
Twenty-two grams (0.0394 mol : 1 equiv) of the PFDNB was dissolved in 120 mL of glacial acetic acid and 8 mL of water in a 500-mL, three-necked flask equipped with a reflux condenser, an efficient magnetic stirrer, and a  $\text{N}_2$  gas inlet. With vigorous stirring, 26 g (0.4654 mol : 11.8 eqv) of Fe powder (100 mesh) was added in a small portion

over a period of 0.5 h and the temperature of the reaction mixture was maintained at 25°C. After all Fe powder was added, the mixture was stirred for an additional 2 h. The product was washed with EA/hexane and then filtered through Cellite. The filtrate was washed with water and aqueous NaHCO<sub>3</sub> and then evaporated under vacuum. The crude product was purified by recrystallization from EA/hexane to give the fluorinated diamino compound, PFDAB. (11.10 g, 56.6%).

MW, C<sub>15</sub>H<sub>7</sub>F<sub>13</sub>N<sub>2</sub>O<sub>6</sub>, 498.24 (calc.), 498 (Mass anal.); MP, 122.37 deg; C (by DSC), 122°C (by Thomas Hoover apparatus); IR(KBr), 3455 and 3357 cm<sup>-1</sup> (N-H str. amine), 1736 cm<sup>-1</sup> (C=O str. ester), 1366 cm<sup>-1</sup> (C-N str. amine); <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, ppm); 5 peaks, CH<sub>2</sub>CF<sub>2</sub> (2.64–2.81, t-t, 2H), CH<sub>2</sub>-O(4.49–4.45, t (fluorine-proton coupling), 2H). NH<sub>2</sub> (5.02, s, 4H), Ar-H (6.04–6.02, t, 2H(o); 6.42 and 6.41, d, 1H(p)); <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>, ppm); 7 peaks, 29.74–29.20(t, 1H, fluorine-carbon coupling), 56.3 (s, 1H), 103.6 (s, 2H), 103.92 (s, 1H), 130.2 (s, 1H), 149.4 (s, 2H), 166.5 (s, 1H); (CF<sub>2</sub>)<sub>6</sub>CF<sub>3</sub> (disappeared due to fluorine-carbon coupling).

### Polymerization and Membrane Preparation

Chemical structures of the monomers and the synthetic route of the eight polyimides are shown in Scheme 2. Polyimide membranes were prepared by direct (one-pot) imidization or two-step thermal imidization method. In a 50-mL, four-necked round flask equipped with a N<sub>2</sub> gas inlet, a magnetic stirrer, a thermometer, and a reflux condenser, a prescribed amount of diamine was dissolved in NMP at room temperature for 1 h. After the addition of stoichiometric amount of a dianhydride, the solution was stirred for 2 h to yield a viscous poly(amic acid) (PAA) solution. The total concentration of diamine/dianhydride mixture in NMP was maintained at 15 wt %. In the case of ODPA-, BTDA-, and PMDA-based polyimides, PAA solutions were precipitated during the heating process (one-pot imidization). Accordingly, the polyimide membranes were prepared from 15 wt % of PAA in NMP solution through thermal imidization. The PAA solution was cast onto the glass plate to predetermined thickness. The glass plate was then heated at 80°C in vacuum oven for 12 h and then heated at 250°C for 2 h to yield the polyimide membranes. In the case of ODPA-*m*-PDA, BTDA-*m*-PDA, and PMDA-*m*-PDA systems, the final imidization temperature used was 300°C.



**Scheme 2.** Synthetic route of the polyimides used in this study.

In the case of 6FDA-PFDAB and 6FDA-*m*-PDA systems, 15 wt % PAA solutions were heated at 200°C for 24 h to yield homogeneous polyimide solutions (one-pot imidization system). This solution was poured into a large amount of methanol with vigorous stirring with the aid of homomixer. The yellow precipitate of fine powder form was washed twice with methanol and with hot water, respectively, and dried under vacuum at room temperature. 6FDA-PFDAB and 6FDA-*m*-PDA membranes were prepared with the casting solutions of 15 wt % of the polyimides in NMP solutions. The glass plate was then heated at 80°C in vacuum oven for 12 h and then heated at 250°C for 2 h to yield the polyimide membranes.

### Spectroscopic Analysis

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were obtained with a Bruker DRX300 and AMX500, respectively, using tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained from Micromass (Model: Autospec) mass spectrometer. Fourier transform infrared (FTIR) and attenuated total reflection (ATR) spectra were obtained with Bio-Rad and Digilab FTS-80, respectively.

### Thermal Analysis

Melting point of monomer was determined with Thomas-Hoover apparatus and DSC analyzer. Thermal properties of polymers were examined with DSC analyzer system (TA 2910) and thermogravimetric analysis (TGA) thermal analyzer system (TA 2950) at a heating rate of 10°C/min in N<sub>2</sub> atmosphere

### Viscosity Measurement

Intrinsic viscosity ( $\eta_{\text{int}}$ ) of PAAs was determined at 30°C in NMP with a concentration of 0.5 g/dL<sup>-1</sup> by using Cannon-Fenske viscometer.  $\eta_{\text{int}}$  is calculated from the following equation:

$$\eta_{\text{int}} = \frac{\sqrt{2(\eta_{\text{sp}} - \ln \eta_{\text{rel}})}}{C}$$

where  $C$  is 0.5 g/dL and  $\eta_{\text{sp}}$  and  $\eta_{\text{rel}}$  represent the specific viscosity and relative viscosity, respectively.

### X-ray Diffractometry

Wide-angle X-ray diffractograms were recorded on a X-ray diffractometer (Model D/MAX IIIB Rigaku) using nickel-filtered CuK $\alpha$  radiation with wavelength of 1.54 Å. The scanning speed was 2°/min.

### Density and Fractional Free Volume Measurement

Density of polymer was determined with buoyancy technique. The force of buoyancy was measured with a micro-balance system. Volume of the sample can be calculated from the weight difference of the sample by applying Archimedean principle. From the weight in air and the volume of the sample, the density can be obtained. Fractional free volume (FFV) was calculated from the following equation:

$$FFV = \frac{V - V_0}{V}$$

where  $V$  is the specific molar volume at temperature  $T$  and  $V_0$  is the molar volume occupied by the molecules at 0°K per mole of repeating unit of the polymer.  $V_0$  is estimated as 1.3 times of the van der Waals volume ( $V_0 = 1.3 V_w$ ), which was calculated from the group contribution data reported by Bondi and van Krevelen.<sup>15,16</sup>

### Measurement of Surface Free Energy

Surface tension or surface free energy of polymer,  $\gamma_{\text{SV}}$ , can be divided into a dispersive component  $\gamma_{\text{SV}}^d$  and a polar component  $\gamma_{\text{SV}}^p$  ( $\gamma_{\text{SV}} = \gamma_{\text{SV}}^d + \gamma_{\text{SV}}^p$ ). The surface free energy  $\gamma_{\text{SV}}$  was calculated by applying the contact angle  $\theta$  to the Young-Wu equation<sup>17</sup>:

$$\gamma_{\text{LV}}(1 + \cos \theta) = \frac{4\gamma_{\text{SV}}^d\gamma_{\text{LV}}^d}{\gamma_{\text{SV}}^d + \gamma_{\text{LV}}^d} + \frac{4\gamma_{\text{SV}}^p\gamma_{\text{LV}}^p}{\gamma_{\text{SV}}^p + \gamma_{\text{LV}}^p}$$

where  $\gamma_{\text{LV}}$  is surface tension of contacting liquid and  $\gamma_{\text{LV}}^d$  and  $\gamma_{\text{LV}}^p$  are a dispersive component and a polar component of the surface tension of  $\gamma_{\text{LV}}$ , respectively. Contact angles were measured using the sessile drop method on a Rame-Hart goniometer. Wetting liquids used for contact angle measurements were methylene iodide and water.<sup>18</sup> They were used for the calculations of surface free energies of polymer surfaces. The surface tensions of the wetting liquids was confirmed by measuring with a dynamic contact angle analyzer (Cahn, DCA-322).

### Measurement of Solubility Parameter

Solubility parameter of polymers can not be determined directly because most polymers cannot be vaporized without decomposition. It can be calculated simply and conveniently by using molar attraction constants. Solubility parameter can be divided into three components corresponding to the three types of interaction forces: the contribution of dispersion force,  $\delta_d$ , polar force,  $\delta_p$ , and hydrogen bonding force,  $\delta_h$ . From molar attraction constants and molar volume of repeating unit of polymer,  $V$ , three solubility parameter components of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  can be calculated. It is necessary to know exactly the density of polymer. Molar attraction constants of  $F_{di}$ ,  $F_{pi}$ , and  $F_{hi}$  for dispersion, polar and hydrogen bonding forces for a number of structural groups are given by van Krevelen.<sup>16</sup> Hansen's data of polytetrafluoroethylene (PTFE) were used for the calculation of three molar attraction constants of -CF<sub>2</sub>CF<sub>2</sub>- group of fluorinated polyimides.<sup>19</sup> The values of three components of  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  and total solubility parameter,  $\delta_t$ , for the polymers are calculated using the following Hoftyzer-van Krevelen's methods<sup>16</sup>:

$$\delta_d = \frac{\sum F_{di}}{V}, \quad \delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V}, \quad \delta_h = \frac{\sqrt{\sum E_{hi}}}{V},$$

$$\delta_1 = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$$

### Measurement of Solubility

Solubility of polymer for various organic solvents was measured visually by immersing the polyimide membranes in an organic solvent at 30°C or at elevated temperatures for 48 h.

### Gas Permeation Test

Pure gas permeabilities for CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> gases were measured using the laboratory-made high vacuum apparatus by applying the time-lag technique. The downstream volume was about 60 cm<sup>3</sup>. The gas permeability was measured at 5 atm of feed pressure. The permeation cell was maintained at 25°C. Gas permeabilities were measured in the sequence CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>. Ideal selectivity ( $\alpha_{A/B}$ ) was calculated from the following equation:

$$\alpha_{A/B} = P_A/P_B$$

where  $P_A$  and  $P_B$  are the permeabilities of pure gas  $A$  and  $B$ , respectively. This ideal selectivity can provide a useful estimation of the separation performances for the actual mixed gas.

## RESULTS AND DISCUSSION

### Synthesis of Monomer PFDAB

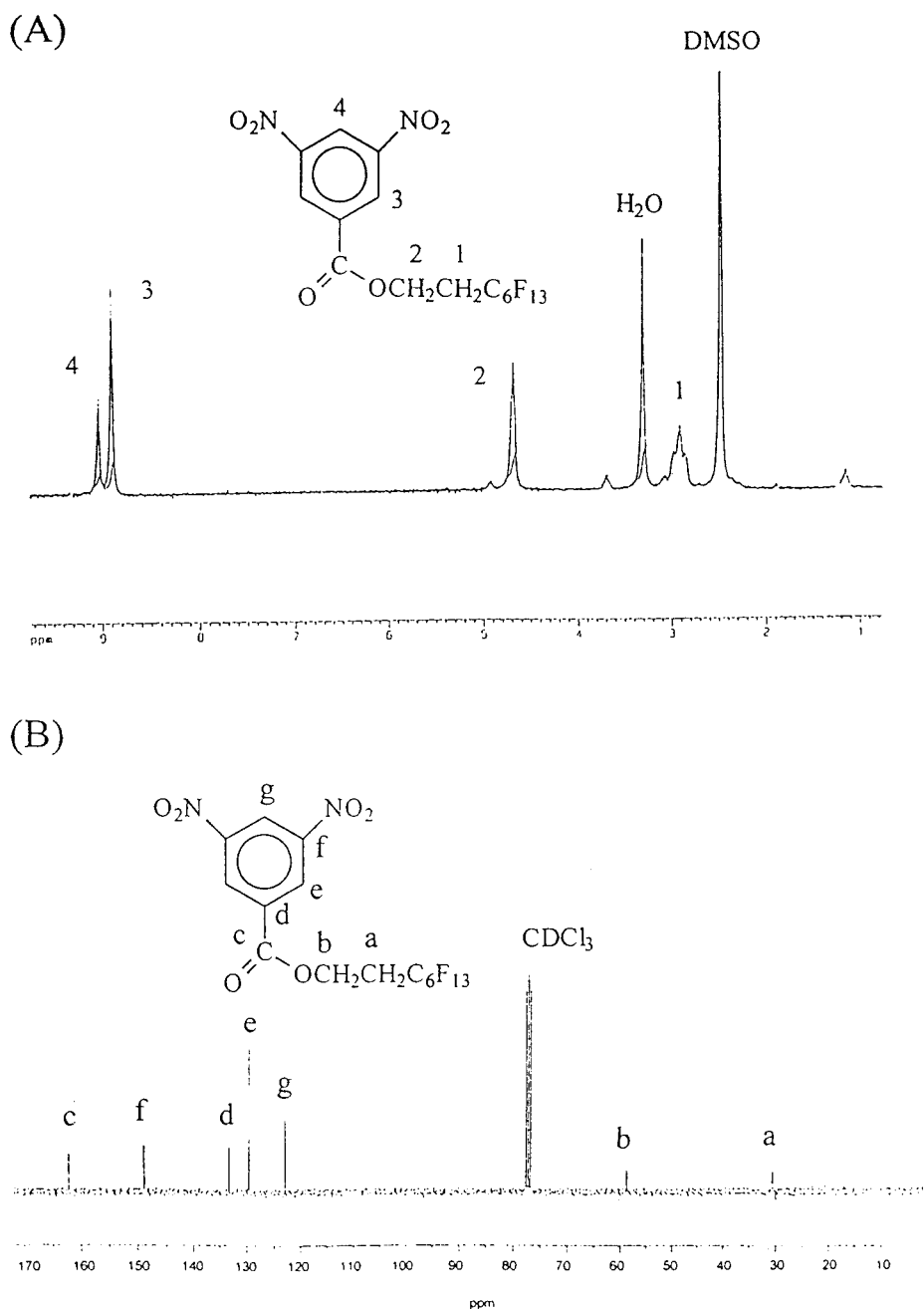
The fluorinated diamino compound, PFDAB was synthesized through two-step reactions: esterification of DNBC with PFOH to give fluorinated dinitro compound, PFDNB, and reduction of PFDNB with Fe powder in acetic acid/water to give the PFDAB. Synthesis of the PFDNB and PFDAB was confirmed by spectroscopic and mass analysis. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of PFDNB are shown in Figure 1. <sup>1</sup>H-NMR spectrum shows the triplet-triplet peaks at 3.00–2.87 ppm corresponding to the two equivalent protons of CH<sub>2</sub>CF<sub>2</sub> unit. The peak at 4.70 ppm is the peak of two protons of CH<sub>2</sub>-O unit. The peak of 8.92 ppm and the singlet peak at 9.05 ppm are corresponding to the two protons of ortho position and one proton of para position of ring, respectively. <sup>13</sup>C-NMR spectrum exhibits 7 characteristic peaks in the range of 31–183 ppm. The peaks of 6 carbons of perfluorohexyl group disappeared due to the carbon-fluorine coupling effect. IR spectrum shows the absorption band at 1736 cm<sup>-1</sup> corresponding to the stretching of C=O of ester group and the

characteristic two absorption band at 1545cm<sup>-1</sup> and 1350 cm<sup>-1</sup> corresponding to the asymmetric stretching of NO<sub>2</sub>. Mass spectrum shows molecular weight of molecular ion of PFDNB is 558, which corresponds to the calculated molecular weight of PFDNB(C<sub>15</sub>H<sub>7</sub>F<sub>13</sub>N<sub>2</sub>O<sub>6</sub>; 558). These results confirm that PFDNB was successfully synthesized.

PFDAB was synthesized from PFDNB. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of PFDAB are shown in Figure 2. <sup>1</sup>H-NMR spectrum shows the triplet-triplet peaks at 2.64–2.81 ppm corresponding to the two equivalent protons of CH<sub>2</sub>CF<sub>2</sub> unit. The triplet peak at 4.49–4.45 ppm is the peak of the two protons of CH<sub>2</sub>-O unit. They show characteristic fluorine-proton coupling pattern. The singlet peak at 5.02 ppm comes from the four protons of diamine. The peak at 6.04–6.03 ppm and the peaks at 6.42 ppm and 6.41 ppm are corresponding to the two protons of ortho position and one proton of para position of the ring, respectively. The <sup>13</sup>C-NMR spectrum exhibits 7 characteristic peaks in the range of 28–166 ppm. The peaks of 6 carbons of perfluorohexyl group also disappeared due to the carbon-fluorine coupling effect. IR spectrum shows the absorption band at 3455 and 3357 cm<sup>-1</sup> corresponding to characteristic N-H stretching bands of diamine and the absorption band at 1736 cm<sup>-1</sup> corresponding to the stretching of C=O of ester group. The absorption band at 1366 cm<sup>-1</sup> is the C-N stretching band of amine. Mass spectrum shows the molecular weight of the molecular ion of PFDAB is 498 (calculated molecular weight of PFDAB(C<sub>15</sub>H<sub>11</sub>F<sub>13</sub>N<sub>2</sub>O<sub>2</sub> is 498.24). The above results of <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FTIR, and mass analysis confirm that PFDAB was successfully synthesized.

### Preparation and Characterization of Polyimide Membranes

Four polyimides membranes with the fluorinated side groups and four polyimide membranes without the side groups were prepared from two aromatic diamines of PFDAB and *m*-PDA with four aromatic dianhydrides of 6FDA, OPA, BTDA, and PMDA in NMP, respectively. Because physical properties and permeation properties of polyimide membranes are largely influenced by imidization degree, the exact estimation of degree of imidization should be made before analyzing physical properties of polyimides. Imidizations of polyimides were monitored by ATR/IR spectroscopy and DSC/TGA thermal analysis. PAA spec-

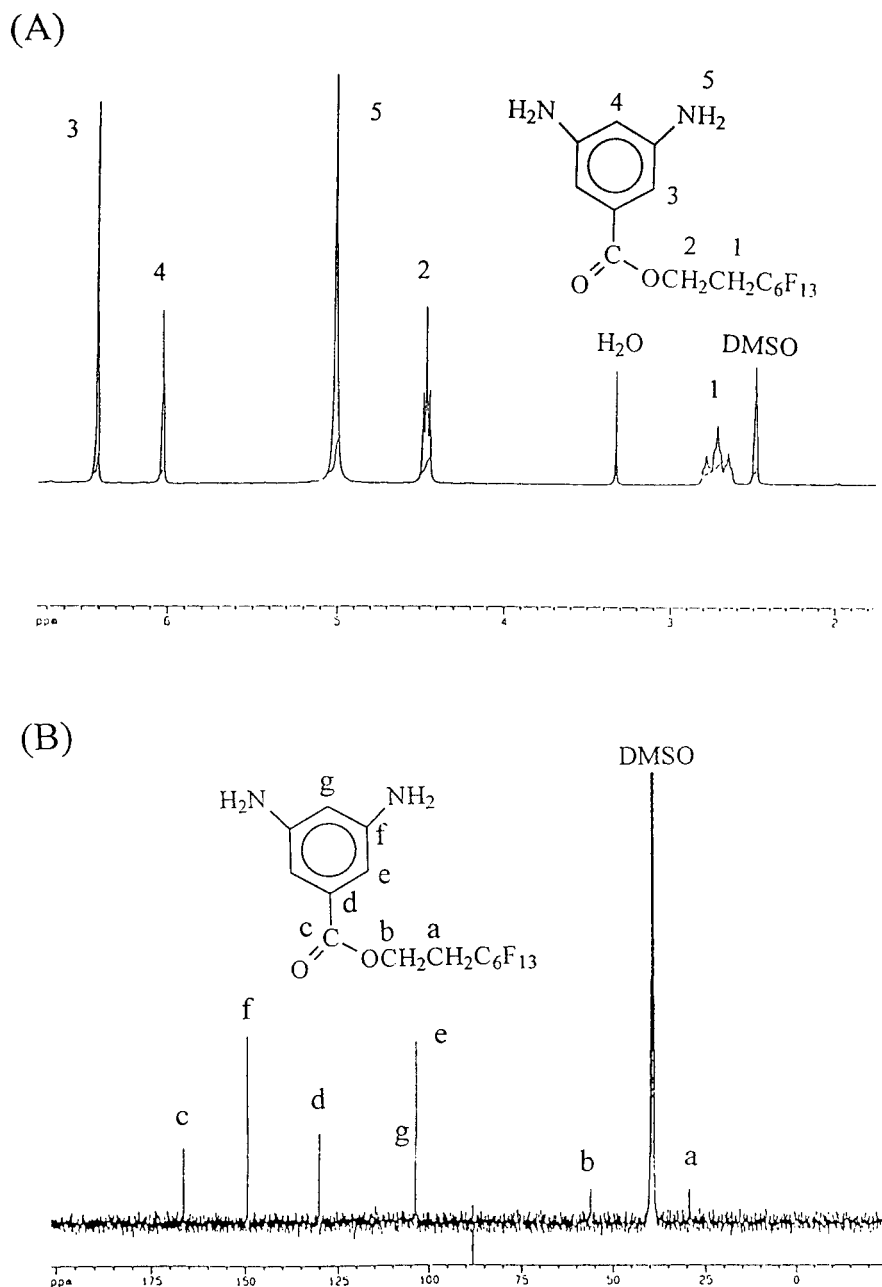


**Figure 1** NMR spectra of the fluorinated dinitro compound, PFDNB. (A)  $^1\text{H}$ -NMR spectrum and (B)  $^{13}\text{C}$ -NMR spectrum.

trum showed the characteristic peak of amide absorption at  $1650\text{ cm}^{-1}$  (amide I) and  $1545\text{ cm}^{-1}$  (amide II). Two amide peaks almost disappeared and the characteristic peaks of imide ring at  $1777\text{ cm}^{-1}$  (C=O),  $1718\text{ cm}^{-1}$  (C=O),  $1375\text{ cm}^{-1}$  (C-N), and  $720\text{ cm}^{-1}$  (C-N) were observed in the ATR-IR spectra of PFDAB-6FDA and the other polyimide membranes. The polyimide films that showed full imidization by ATR-IR spectra did not

show any transitions corresponding to imidization during DSC/TGA analysis. The IR spectra and DSC/TGA analysis indicated that all the PAAs were fully converted into polyimides under our imidization conditions.

Intrinsic viscosities of PAAs, thermal properties and film qualities of the polyimides are summarized in Table I. In all cases, intrinsic viscosities of PAAs are greater than  $0.43\text{ dL/g}$ , and seem



**Figure 2** NMR spectra of the fluorinated diamino compound, PFDAB. (A)  $^1\text{H}$ -NMR spectrum and (B)  $^{13}\text{C}$ -NMR spectrum.

to be high enough to cast flexible and tough membranes. In all cases, tough polyimide membranes were obtained except PMDA-based polyimide membrane, which were somewhat brittle. The brittleness of PMDA-based polyimides may be attributed to rigid structure of PMDA-*m*-PDA main chain. The glass transition temperature ( $T_g$ )s of the polyimides from PFDAB are much lower than those of the polyimides with *m*-PDA. Such behav-

ior can be explained in terms of incorporation of fluorinated side groups with hydrophobicity and bulkiness, i.e., fluorinated side groups lowers cohesive energy and reduces the molecular interaction or chain rigidity, which can increase free volumes of the polymers.  $T_g$ s of the polyimides from PFDAB decrease in the following dianhydride order: PMDA > BTDA > 6FDA > ODPA. Structural rigidity originated from PMDA and

**Table I** Intrinsic Viscosities of Poly(amic acid)s, Thermal Properties, and Film Qualities of the Polyimides

Monomer Pair (Diamine-Dianhydride)	$[\eta]^a$ (dL/g)	$T_g^b$ (°C)		$T_d^c$ (°C)		Film Quality
		Experimental Value	Literature Value <sup>2,20</sup>	1st	2nd	
6FDA-PFDAB	0.61	205	—	368	550	Flexible and tough
6FDA- <i>m</i> -PDA	0.64	290	297	—	547	Flexible and tough
ODPA-PFDAB	0.54	200	—	365	580	Flexible and tough
ODPA- <i>m</i> -PDA	0.58	301	305	—	540	Flexible and tough
BTDA-PFDAB	0.43	208	—	364	582	Tough
BTDA- <i>m</i> -PDA	0.64	—	320	—	—	Tough
PMDA-PFDAB	0.53	256	—	370	604	Somewhat brittle
PMDA- <i>m</i> -PDA	0.61	—	290,340	—	570 <sup>d</sup>	Somewhat brittle

<sup>a</sup>Intrinsic viscosity of PAA measured in 0.5 g/dL NMP solution at 30°C.

<sup>b</sup>Determined by DSC method at a heating rate of 10°C/min in N<sub>2</sub> atmosphere.

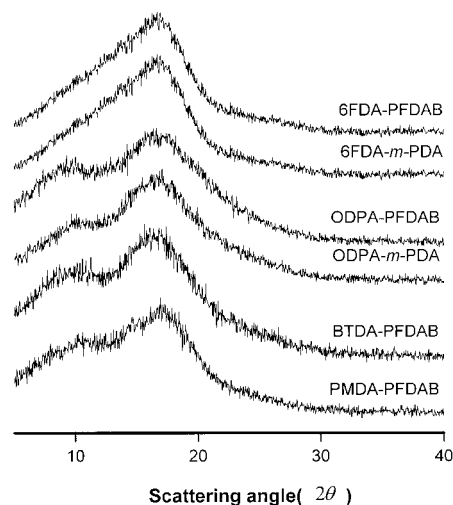
<sup>c</sup>Onset temperature of decomposition determined by TGA method at a heating rate of 10°C/min in N<sub>2</sub> atmosphere.

<sup>d</sup>Determined from the TGA thermogram in the literature.<sup>2</sup>

BTDA may restrict glass transition of the polyimides, and increase their  $T_g$ s. TGA data of six polyimides show that decomposition of these polyimides from PFDAB occurred in two steps. The first decomposition starts at 364–370°C and the second at 540–604°C. But the decomposition of polyimides from *m*-PDA proceeds through one step and initiated at 547–570°C. Apparently the first decomposition of the polyimides occurs from the ester groups of the PFDAB.

Gas diffusion through a polymer is largely influenced by chain packing density and local mobility of polymer chains that are related to physical properties such as crystallinity, d-spacing, density,  $T_g$ , and FFV. Wide-angle X-ray diffractograms of the polyimides are shown in Figure 3. They are all broad and structureless, indicating that they are all amorphous. One broad peak is observed in two soluble 6FDA-based polyimides; whereas two broad peaks are observed in the other four nonsoluble polyimides (see the solubility data in Table III). The  $2\theta$  values (or d-spacings) of PFDAB-based polyimides seems to be the same as those of *m*-PDA-based polyimides having the same dianhydrides, though d-spacings often are taken as the average interchain spacings and related to the FFVs, the d-spacing value of these polyimides were not significantly changed by the incorporation of fluorinated side group in spite of their hydrophobicity and bulkiness. Densities and FFVs of the polyimides are shown in Table II, which includes the literature values of the density of BTDA-*m*-PDA and PMDA-*m*-PDA polyimides.

The polyimides from PFDAB have higher density than the polyimides from *m*-PDA because of high fluorine content. However, the FFVs of PFDAB-based polyimides are significantly higher than those of the *m*-PDA-based polyimides. The reciprocal value of FFV has been taken by some investigators as measures of chain packing density and membrane diffusivity. The higher values of FFV of fluorinated polyimides are originated from incorporation of fluorinated side groups, for their hydrophobic and bulky characters disturb their chain packing. This phenomenon is well consistent with  $T_g$  behaviors as expected. The FFVs of

**Figure 3** Wide-angle X-ray diffractograms of the polyimide membranes.



**Table II Densities and FFVs of the Polyimide Membranes**

Monomer Pair (Dianhydride- Diamine)	Formula of Repeating Unit	Molecular Weight of Repeating Unit (Dalton)	Density ( $\rho$ ) <sup>a</sup> (g/cm <sup>3</sup> )		FFV <sup>b</sup>	
			Experimental Value	Literature Value <sup>20</sup>	Experimental Value	Literature Value <sup>20</sup>
6FDA-PFDAB	C <sub>34</sub> H <sub>13</sub> N <sub>2</sub> O <sub>6</sub> F <sub>19</sub>	906.09	1.60	—	0.183	—
6FDA- <i>m</i> -PDA	C <sub>25</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> F <sub>6</sub>	516.15	1.50	1.47	0.160	0.162
ODPA-PFDAB	C <sub>31</sub> H <sub>13</sub> N <sub>2</sub> O <sub>7</sub> F <sub>13</sub>	772.12	1.55	—	0.174	—
ODPA- <i>m</i> -PDA	C <sub>22</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub>	382.22	1.41	1.41	0.109	0.102
BTDA-PFDAB	C <sub>32</sub> H <sub>13</sub> N <sub>2</sub> O <sub>7</sub> F <sub>13</sub>	784.12	1.57	—	0.160	—
BTDA- <i>m</i> -PDA	C <sub>23</sub> H <sub>10</sub> N <sub>2</sub> O <sub>5</sub>	394.34	—	1.40	—	0.112
PMDA-PFDAB	C <sub>25</sub> H <sub>9</sub> N <sub>2</sub> O <sub>6</sub> F <sub>13</sub>	680.06	1.68	—	0.135	—
PMDA- <i>m</i> -PDA	C <sub>16</sub> H <sub>6</sub> N <sub>2</sub> O <sub>4</sub>	290.24	—	1.43	—	0.117

<sup>a</sup>Determined by buoyancy method at 25°C.

<sup>b</sup>Calculated from the equation  $(V - V_0)/V$  and group contribution method by Bondi and van Krevelen.<sup>15,16</sup>

the polyimides with PFDAB decrease in the following dianhydride order: 6FDA < ODPA < BTDA < PMDA, which is the same order of decreasing the solubility parameter of the polyimides. The reason for the relatively low FFV of PMDA-PFDAB polyimide may be originated from their high packing due to rigid-flat configuration of PMDA-*m*-PDA structure.

Surface free energy and solubility parameter of polymers are directly related with FFVs of polymeric membranes. Contact angles, surface free energies and solubility parameters for the polyimides are summarized in Table III. The fluorinated polyimides shows higher contact angles for

both water and methylene iodide than the non-fluorinated polyimides. The higher contact angle values of the fluorinated polyimides for both water and methylene iodide are attributed to the low surface free energy due to the fluorinated surface. The extremely low values of polar components ( $\gamma_{SV}^p$ ) were observed in the polyimide membranes from PFDAB in spite of their high content of polar carbonyl groups (see the relatively large values of two solubility parameter components,  $\delta_p$  and  $\delta_h$ ). The reason is that when the polyimide membranes are prepared under the vacuum, the linear hydrophobic perfluorohexylethyl groups can be favorably arranged in air side with low surface

**Table III Contact Angles, Surface Free Energies, and Solubility Parameters of Polyimide Membranes**

Monomer Pair (Dianhydride-Diamine)	Fluorine Content (wt %)	Contact Angle <sup>a</sup> (Deg)		Surface Energy <sup>b</sup> (Dyne/cm)			Solubility Parameter <sup>c</sup> (MPa) <sup>1/2</sup>			
		Water	Methylene Iodide	$\gamma^d$	$\gamma^p$	$\gamma^t$	$\delta_d$	$\delta_p$	$\delta_h$	$\delta_t$
6FDA-PFDAB	39.8	114	74	21.1	0.0	21.1	16.2	3.5	6.7	17.9
6FDA- <i>m</i> -PDA	22.1	97	62	26.2	1.3	27.5	17.7	5.6	7.2	19.9
ODPA-PFDAB	32.0	96	58	28.6	1.1	29.7	16.5	4.1	7.5	18.6
ODPA- <i>m</i> -PDA	0.0	76	43	36.4	5.7	42.1	18.8	7.2	8.8	22.0
BTDA-PFDAB	31.5	98	58	30.0	0.8	30.8	16.8	4.3	7.4	18.9
BTDA- <i>m</i> -PDA <sup>d</sup>	0.0	—	—	—	—	—	18.8	7.3	8.4	21.8
PMDA-PFDAB	36.3	94	94	67	2.7	25.3	17.2	4.9	7.9	19.3
PMDA- <i>m</i> -PDA <sup>d</sup>	0	—	—	—	—	—	18.4	9.4	9.4	22.7

<sup>a</sup>Measured using the sessile drop method on a Rame-Hart goniometer.

<sup>b</sup>Calculated from Young-Wu equation.<sup>17</sup>

<sup>c</sup>Calculated from molar attraction constants given by Hoftzer-Van Krevelen.<sup>16</sup>

<sup>d</sup>Solubility parameter data of these polymers calculated using the density data of literature.<sup>20</sup>

**Table IV Solubilities of the Polyimide Membranes**

Monomer Pair (Dianhydride-Diamine)	Solubility <sup>a</sup> in Organic Solvents												
	NMP	DMA	DMF	DMSO	THF	AC	CF	MEK	EA	MC	AA	IPA	TOL
6FDA-PFDAB	+	+	+	+	++	++	++	++	++	++	-	-	-
6FDA- <i>m</i> -PDA	++	++	++	++	++	++	++	++	++	++	-	-	-
ODPA-PFDAB													
BTDA-PFDAB	-	-	-	-	-	-	-	-	-	-	-	-	-
PMDA-PFDAB													
ODPA- <i>m</i> -PDA													
BTDA- <i>m</i> -PDA	-	-	-	-	-	-	-	-	-	-	-	-	-
PMDA- <i>m</i> -PDA													

<sup>a</sup>Solubility: (++) soluble at room temperature; (+) swelling at room temperature but wholly soluble at elevated temperature; (-) insoluble even on heating.

Abbreviations: NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran; AC, acetone; CF, chloroform; MEK, methylethyl ketone; EA, ethyl acetate; MC, methylene dichloride; AA, acetic acid; IPA, isopropyl alcohol; TOL, toluene.

energy, which has been found frequently in perfluoroalkyl group-containing acrylated polymers.<sup>21</sup> However, the surface free energy of the polyimides from PFDAB decreases in the following dianhydride order: BTDA > ODPA > PMDA > 6FDA, which indicates that the polyimides with higher fluorine content exhibit lower surface free energy. Incorporation of fluorinated side groups lowers the surface free energy and increases hydrophobicity of polyimide surface. Three-component solubility parameters ( $\delta_d$ ,  $\delta_p$ ,  $\delta_h$ ) and total solubility parameters ( $\delta_t$ ) of the polyimides were calculated using Hoftyzer-van Krevelen's molar attraction constants.<sup>16</sup> The polyimides from PFDAB have lower the values of three-component and total solubility parameters than the polyimides from *m*-PDA, presumably because incorporation of fluorinated group reduce molecular interaction or cohesive energy of polymer segments, and makes them more hydrophobic. Unlike the trend of surface free energy versus fluorine contents of the polyimides from PFDAB, their solubility parameter decreases in the following dianhydride order: PMDA > BTDA > ODPA > 6FDA, which agrees well with their polar groups (C=O) contents and FFV order in Table II. In order to estimate their FFVs, the solubility parameter of these fluorinated polyimides might be a good indicator than the surface free energy because of the surface alignment of perfluoro-hexylethyl groups.

Solubilities of the six polyimides in organic solvents are summarized in Table IV. Two 6FDA-based polyimide membranes are soluble in ace-

tone, MEK, EA, and MC, whereas the other four polyimide membranes are insoluble in all organic solvents. Generally, aromatic polyimides are insoluble because of rigid, fused ring structure of their main chain. Solubility of 6FDA-based polyimides is attributed to hexafluoroisopropylidene (-C(CF<sub>3</sub>)<sub>2</sub>-) group, that separate the aromatic ring, and hinder the interaction between neighboring molecules (i.e., charge transfer complex formation). 6FDA-*m*-PDA polyimide is soluble in polar aprotic solvents such as DMSO, DMAc, DMF, and NMP at the room temperature, but 6FDA-PFDAB polyimide is soluble at elevated temperature.

### Gas Transport Properties

Table V show that the permeabilities and selectivities for three polyimide membranes from PFDAB and three membranes from *m*-PDA. In this study, the permeabilities of two PMDA based polyimide membranes could not be obtained because of their brittleness. The permeabilities and selectivities of 6FDA-*m*-PDA membranes available in the literature are:  $P(\text{CO}_2) = 9.20$ ,  $P(\text{O}_2) = 3.01$ ,  $P(\text{N}_2) = 0.447$ ,  $P(\text{CH}_4) = 0.160$  (in Barrer =  $10^{-10}[\text{cm} \cdot \text{cm}^3 (\text{STP}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$ ).<sup>22</sup> The deviations with our permeability data are within 5–25 %, which seems to be originated from different manufacturing history. In Table V, the permeabilities of the polyimide membranes decrease in the following order:

$$P(\text{CO}_2) > P(\text{O}_2) > P(\text{N}_2) > P(\text{CH}_4)$$

This is the order of increasing kinetic diameters or van der Waals volume of the penetrant mole-

**Table V Pure Gas Permeabilities and Ideal Selectivities of the Polyimide Membranes at 25°C at 5 atm**

Monomer Pair (Dianhydride-Diamine)	Pure Gas Permeabilities (Barrer)				Ideal Selectivities ( $\alpha_{A/B}$ )		
	P <sub>CO<sub>2</sub></sub>	P <sub>O<sub>2</sub></sub>	P <sub>N<sub>2</sub></sub>	P <sub>CH<sub>4</sub></sub>	P <sub>CO<sub>2</sub></sub> /P <sub>CH<sub>4</sub></sub>	P <sub>CO<sub>2</sub></sub> /P <sub>N<sub>2</sub></sub>	P <sub>O<sub>2</sub></sub> /P <sub>N<sub>2</sub></sub>
6FDA-PFDAB	17.77	4.74	0.74	0.44	40.4	24.0	6.4
6FDA- <i>m</i> -PDA	9.73	2.55	0.38	0.21	46.3	25.6	6.7
ODPA-PFDAB	11.03	2.61	0.56	0.36	30.6	19.7	4.9
ODPA- <i>m</i> -PDA	0.301	0.081	0.012	0.0064	47.3	25.1	6.8
BTDA-PFDAB	10.10	2.20	0.48	0.29	34.8	21.0	4.6
BTDA- <i>m</i> -PDA	0.428	0.112	0.016	0.0086	49.8	26.8	7.0

cules. It can be said that the permeability and selectivity of these polyimides are predominantly determined by the size of the permeants, i.e., the smaller gas permeate faster than the larger ones. In Table V, the polyimide membranes from PFDAB show highly enhanced permeability for CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> gases and moderately reduced selectivity for CO<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/N<sub>2</sub> gas pairs compared with those of the polyimides from *m*-PDA. The results are consistent with the commonly observed "trade-off" between permeability and selectivity, that is, more permeable polymers tend to exhibit lower selectivities and vice versa. ODPA-PFDAB and BTDA-PFDAB polyimide membranes show large increase in permeability and large decrease in selectivity compared with their *m*-PDA-based membranes, as expected in their enhanced FFVs. Permeability and selectivity of 6FDA-PFDAB membranes changed a little compared with the changes of BTDA- and ODPA-based polyimides. From the values listed in Tables II and V, the permeability order of these polyimides is well consistent with the increasing order of calculated FFV values: 6FDA-PFDAB > ODPA-PFDAB > BTDA-PFDAB  $\cong$  6FDA-*m*-PDA >> BTDA-*m*-PDA > ODPA-*m*-PDA. As many investigators have pointed out that the gas permeabilities of glassy polymers are reasonably correlated with their FFV, this result also shows the similar behavior. The high permeability of the PFDAB-based membranes seems to be originated from the enhanced FFVs due to the incorporation of fluorinated side groups. 6FDA-PFDAB membrane shows excellent gas permeability and selectivity for four gases. Its high permeability and high selectivity might be explained due to the 6FDA ability of optimum distribution of polymer free volume and packing disruption.

## CONCLUSIONS

Four polyimide membranes with fluorinated alkyl side groups and four polyimides without the side groups were successfully prepared by polycondensation of 2-(perfluorohexyl)ethyl-3, 5-diamino benzoate (PFDAB) and *m*-PDA with four aromatic dianhydrides (6FDA, ODPA, BTDA, and PMDA) in NMP, respectively. The fluorinated diamine, PFDAB, was synthesized through esterification of DNBC with PFOH to give 2-(perfluorohexyl)ethyl-3,5-dinitrobenzoate (PFDNB), followed by reduction of the nitro compounds with Fe powder in acetic acid/water.

FTIR/ATR/NMR/Mass spectra confirmed that PFDAB and the resulting polyimides were successfully synthesized. X-ray diffractograms showed that all the polyimides prepared were amorphous. The incorporation of fluorinated side groups into polyimide membranes decreased their  $T_g$ , low surface free energy and solubility parameter (i.e., cohesive energy) and highly increased their fractional free volume (FFV) and therefore, the polyimide membranes with fluorinated groups exhibited higher permeability for CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> gases but lower selectivity for CO<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub> gas pairs than the polyimides without the side groups. The gas permeabilities of these membranes were highly influenced by their FFVs and kinetic diameter of gases.

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