

## Gas Separation Properties of 6FDA-Based Polyimide Membranes with a Polar Group

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**Abstract:** 6FDA-based polyimides were prepared from the thermal imidization reaction of 6FDA with diamines of BAPAF, DAP, and DABA having a polar group of hydroxyl or carboxyl. Properties of the dense polyimide membranes were characterized and their gas permeation properties for H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> were investigated. Permeabilities, diffusion coefficients and diffusivity selectivities of polar group-containing polyimide membranes including 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA polymer for the gases did not change largely. The separation properties of 6FDA-TrMPD polyimide membrane used as a reference polymer were compared with those of the polyimide membranes mentioned above. It was found that the polyimides of 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA, which were soluble in alcohol or/and 2-methoxyethanol, could be applicable to the preparation of a dense composite membrane by dip-coating method.

**Keywords:** 6FDA, polyimide membrane, gas separation, polar group, separation properties.

### Introduction

The application of membranes to gas separation has grown up rapidly since the installation of the first industrial plant in the early 1980s.<sup>1</sup> An advantage of polymeric composite membranes is that their gas permeability and selectivity can be controlled by the combination of various polymer components.<sup>2,3</sup> Polyimides are prepared by the imidization of polyamic acids obtained from dianhydride and diamine. In the preparation of a polyimide membrane for gas separation, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) is well known as an anhydride component of the membrane which exhibits both high selectivity and permeability compared to common glassy polymers.<sup>4,5</sup>

In the preparation of 6FDA-based polyimides, various amines have been used. Based on CO<sub>2</sub> separation, the gas permeability of 6FDA-based polyimide membranes has been reported in the range of 2 to 440 Barrers [ $10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$ ].<sup>4,15</sup> The polyimide membranes with diamines of oxydianiline (ODA), phenylenediamine (PDA), 2,2-bis-(aminophenoxyphenyl)hexafluoropropane (BDAF), methylenedianiline (MDA), 2,7-diaminofluorene (DAF), 3,6-diaminocarbazole (CDA), 2,7-diaminofluorenone (DAFO), 3,5-diaminobenzotrifluoride (DBTF), etc. showed the relatively low CO<sub>2</sub> permeability below 25 Barrers. On the

other hand, 6FDA polyimide membranes with phenylene-diamine having over 3 methyl group, such as 2,4,6-trimethyl-1,3-phenylene-diamine (TrMPD), 2,3,5,6-tetramethyl-1,4-phenylenediamine (TeMPD) exhibited the high flux of up to 440 Barrers for CO<sub>2</sub>.<sup>8</sup> These 6FDA-based polyimides mentioned above were prepared in form of dense membranes using tetrahydrofuran (THF) or a aprotic solvent such as 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), and dimethylformamide (DMF) since the polymers were not easily soluble in another solvent such as alcohol and glycol ether. The solubility limitation of 6FDA-based polyimide to such solvents could not lead to the fabrication of a composite membrane by dip-coating method. In order to prepare a dense and composite membrane it is necessary to use a 6FDA-based polyimide, which can be soluble in alcohol or glycol ether.

Diamine moieties, used for preparation of 6FDA-based polyimide, play an important role in the control of a selectivity and permeability of gases through polyimide membranes. In particular the chemical structure and functional group of diamine can determine a packing density and local mobility of polymer chains and then affect the membrane separation performance, i.e., permeability and selectivity. To our knowledge, 6FDA-based polyimide dense membranes with a polar group of hydroxyl or carboxyl among diamines have not been reported systematically.

In this study 6FDA-based polyimide dense membranes having a polar group of hydroxyl and carboxyl in a diamine

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moiety were prepared and gas permeation properties of the membranes were compared with a 6FDA-TrMPD polyimide membrane.

## Experimental

**Preparation of Polyimide Membranes.** 6FDA as a dianhydride was obtained from Daikin Co.(Japan). Diamines including 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAPAF), 2,4-diaminophenol dihydrochloride (DAP), 3,5-diaminobenzoic acid (DABA), and TrMPD were purchased from Aldrich Co.. TrMPD was recrystallized with hexane. Other chemicals were used without further purification.

The polyimides were prepared by polycondensation with equimolar amounts of the dianhydride and diamines followed by a cyclodehydration reaction. In the initial reaction step, the polycondensation reaction was carried out at room temperature to form a poly(amic acid) in NMP. Thermal imidization at 200°C with continuous removal of water by xylene azeotrope was employed for the polymer. Dry NMP was used for the synthesis solvent. The resultant polymers of 6FDA-DAP, 6FDA-DABA, and 6FDA-TrMPD polyimides were precipitated in methanol and dried under vacuum at 150°C. However, the precipitation of 6FDA-BAPAF polyimide, which could be soluble in methanol, was done in water.

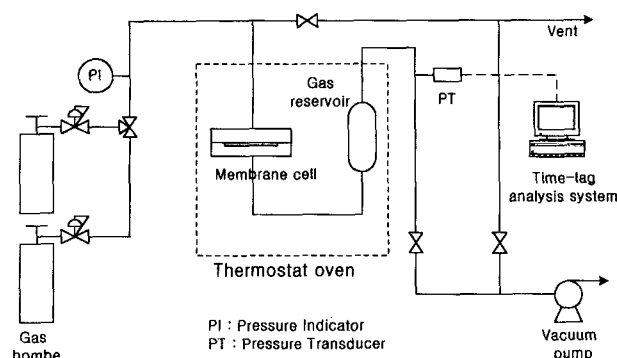
Dense membranes were prepared by casting 15 wt% 6FDA-based polyimide solution in NMP onto a glass plate and dried for 6 hrs at 90°C and for additional 10 hrs at 150°C under reduced pressure. The thickness of the 6FDA-based polyimide membranes was in the range of 80 to 100  $\mu\text{m}$ .

**Membrane Characterization.**  $^1\text{H-NMR}$ (300 MHz) spectra of 6FDA-based polyimides were measured with Bruker AM300 using dimethylsulfoxide- $d_6$  as a solvent obtained from Aldrich. Glass-transition temperature,  $T_g$  of the polymer was determined at a heating rate of 10°C/min under nitrogen atmosphere by DSC method (Dupont 2910). Density of polymer was determined by Archimedes principle using a micro-balance system. The wide-angle X-ray diffraction was performed on a Rigaku D/Max-III B utilizing  $\text{CuK}\alpha$ ( $\lambda = 1.54 \text{ \AA}$ ) radiation.

**Gas Permeation.** Hydrogen, oxygen, nitrogen, carbon dioxide, and methane were applied to gas permeation for 6FDA-based polyimide membranes prepared. Gas permeability measurements were done at 25°C using the vacuum apparatus equipped with an accurate pressure transducer as shown in Figure 1. The upstream pressure was 5 kg/cm $^2$  and downstream pressure was always 10 torr or less.

Permeation parameters were calculated from the so-called time-lag methods using the following equation :

$$D = l^2/6\theta \quad (1)$$



**Figure 1.** Schematic diagram of gas permeation apparatus.

where  $D$  is the diffusion coefficient,  $l$  the membrane thickness, and  $\theta$  the time lag. Solubility coefficient,  $S$  was obtained by dividing permeability coefficient,  $P$  by  $D$ . According to a solution-diffusion mechanism,  $P$  is the product of  $D$  and  $S$ , i.e.  $P = D \times S$ .

A Selectivity or an ideal separation factor,  $\alpha_{A/B}$  is defined as

$$\alpha_{A/B} = P_A/P_B = (D_A/D_B)(S_A/S_B) \quad (2)$$

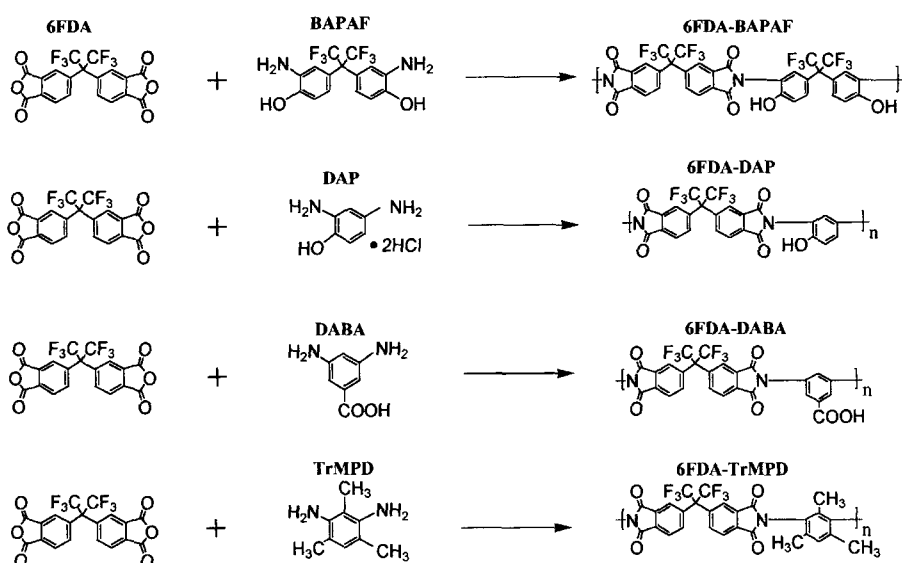
The subscript,  $A$  or  $B$  denotes each penetrant across the membrane.

## Results and Discussion

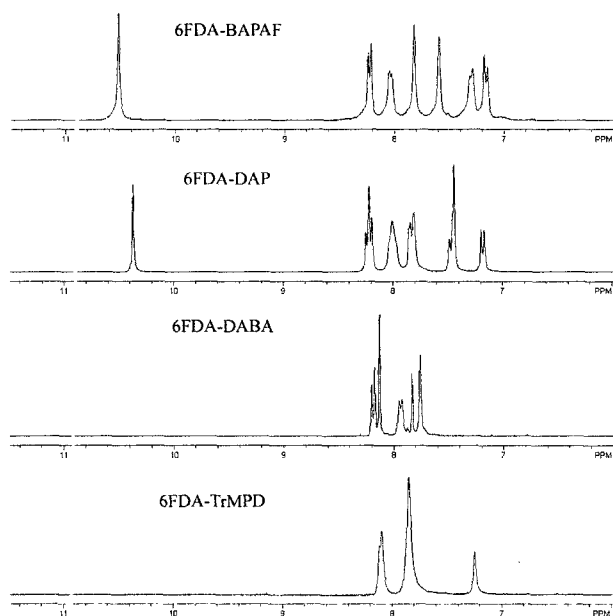
**Preparation of 6FDA-Based Polyimide with a Polar Group.** 6FDA-based polyimides with a polar group of hydroxyl or carboxyl were prepared as shown in Figure 2. 6FDA-TrMPD polyimide as a reference polymer was also synthesized. The structures of 6FDA-based polyimides were verified by the  $^1\text{H-NMR}$  and FT-IR analysis. In Figure 3, peaks at 10.5 and 10.4 ppm were due to a proton of hydroxyl group of 6FDA-BAPAF and 6FDA-DAP, respectively; peaks at 7.1 to 8.3 ppm due to a proton of condensed aromatic ring of each polyimide.  $^1\text{H}$  Chemical shifts of benzoic acid group in 6FDA-DABA polyimide are exhibited in the range of 7.2 to 8.2 ppm. The polyimide of 6FDA-TrMPD, which did not contain a hydroxyl and carboxyl group, showed different  $^1\text{H}$  chemical shifts compared with other polyimide used. Fluorine( $\text{CF}_3$ ) and imide( $\text{C-N str.}$ ) groups of 6FDA-based polyimides were shown in the range of 1350~1200 and 1300~900  $\text{cm}^{-1}$  in Figure 4, respectively. From results of  $^1\text{H-NMR}$  and FT-IR spectra, the imidization of 6FDA-based polyimides in Figure 2 was confirmed.

The solubility of 6FDA-based polyimides in alcohol and glycol ether was listed in the literature<sup>16</sup>. 6FDA-BAPAF polyimide was well soluble in both alcohol and glycol ether. However, 6FDA-DAP and 6FDA-DABA polyimides were soluble only 2-methoxyethanol even though 6FDA-DAP polymer was partially soluble in 2-ethoxyethanol. This indi-

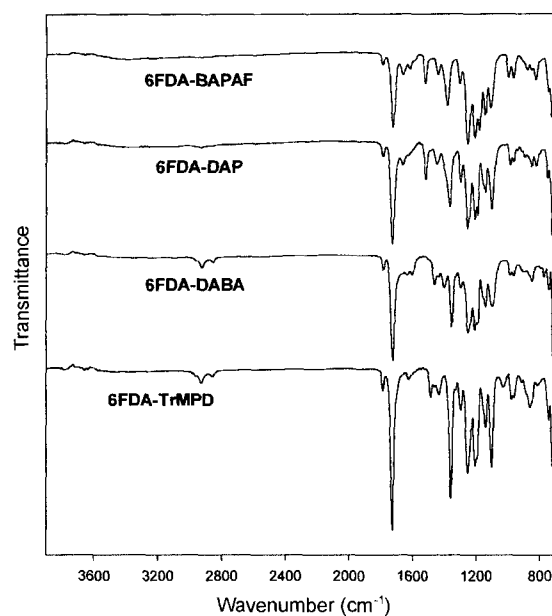
## 6FDA-Based Polyimide Membrane



**Figure 2.** Reaction scheme of the synthesis of 6FDA-based polyimides.



**Figure 3.**  $^1\text{H-NMR}$  spectra of 6FDA-based polyimides.



**Figure 4.** FT-IR spectra of 6FDA-based polyimides.

cates that the dense membrane of polar group-containing 6FDA-based polyimides can be prepared using alcohol and 2-methoxyethanol as well as aprotic solvents or THF. Also it is possible to prepare a composite membrane by dip-coating method since alcohol and glycol ether as a coating solvent is appropriate. The fabrication of a composite membrane using the 6FDA-based polyimides with a polar group is reported in another paper.<sup>16</sup>

**Membrane Properties.** Properties of 6FDA-based polyimide membranes used are listed in Table I. Molar fraction of free volume,  $V_f$  and cohesive energy density, CED were

calculated by the group contribution method of Bondi<sup>17</sup> and van Krevelen,<sup>18</sup> respectively. The equation of  $V_f$  is defined as follows:

$$V_f = (V_T - V_0) / V_T \quad (3)$$

where  $V_T$  and  $V_0$  are specific molar volumes at temperature,  $T$  and 0 K, respectively.  $V_T$  is estimated from density data, and  $V_0$  is estimated to be 1.3 times the van der Waals volume calculated by the group-contribution method of Bondi.

In Table I, 6FDA-based polyimides with a hydroxyl or

**Table I. Properties of 6FDA-Based Polyimide Membranes**

Polyimide	$T_g^a$ (°C)	Density (g/cm <sup>3</sup> )	d-spacing <sup>b</sup> (Å)	$V_f$ (-)	CED (J/cm <sup>3</sup> )
6FDA-BAPAF	312	1.503	5.1742	0.2013	1,026
6FDA-DAP	344	1.404	5.3770	0.2547	759
6FDA-DABA	348	1.511	5.3720	0.1751	786
6FDA-TrMPD	377	1.322	5.6230	0.2061	697

<sup>a</sup>Glass-transition temperature determined using DSC.

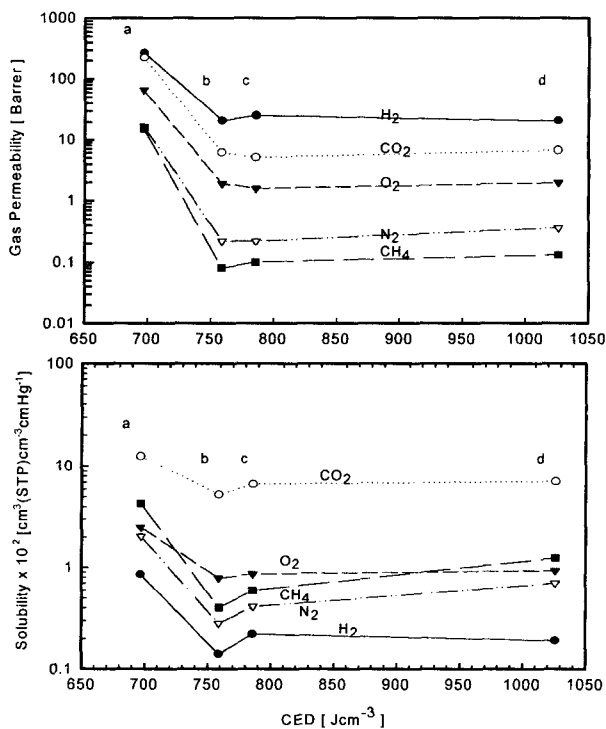
<sup>b</sup>Mean interchain spacing, determined using a wide-angle X-ray diffraction and calculated from Bragg's equation,  $n\lambda = 2d\sin\theta$ .  
Barrer =  $10^{-10}$  cm<sup>3</sup>(STP) · cm · cm<sup>-2</sup> · s<sup>-1</sup> · cmHg<sup>-1</sup>.

carboxyl group, i.e. 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA exhibited relatively high density, low d-spacing, and high CED compared with the 6FDA-TrMPD polyimide without a polar group. Such properties of the polar group-containing polyimides determine a packing density, local mobility of polymer chains, and interaction between a penetrant and the polymer, and then affect the permeation performances.

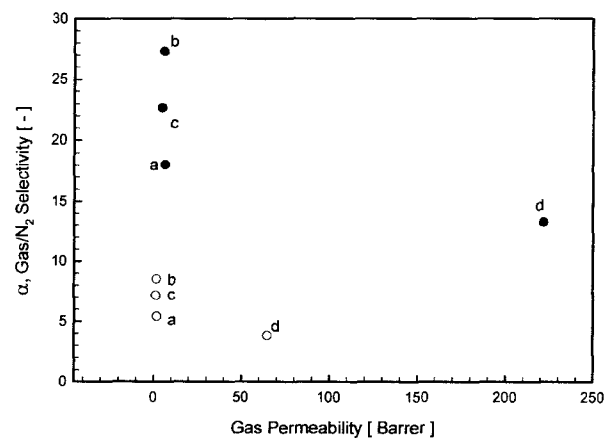
**Gas Permeability and Selectivity.** Figure 5 illustrates the relationship between CED and gas permeability and solubility. In the figure gas permeability values at the same CED increased with an inverse order of the kinetic molecular diameter, i.e.  $H_2 > CO_2 > O_2 > N_2 > CH_4$ . Among the gases,  $CO_2$  showed the highest solubility value and  $H_2$  the lowest solubility value, calculated from permeability and diffusivity coefficient. The high permeabilities of two gases

are attributed to the high solubility of  $CO_2$  in the polymer and the high diffusivity of  $H_2$  in the polymer structure as shown in the Figures 5 and 9, respectively. There were significant difference between the gas permeability of 6FDA-TrMPD and that of polar group-containing polyimides of 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA having relatively low values. The gas permeabilities for polar group-containing polyimides did not change with an increase in CED. This result means that a variation of CED of the polyimides did not affect the permeability of each gas. The CED is a measure of the cohesive force between molecules. In general the polymer chains pack together more closely if this value becomes larger. Thus, the apparent diffusion coefficients become small and the permeation fluxes decrease. The discrepancy between our results and such a general rule seems to be due to a nature of polar group-containing polyimides.

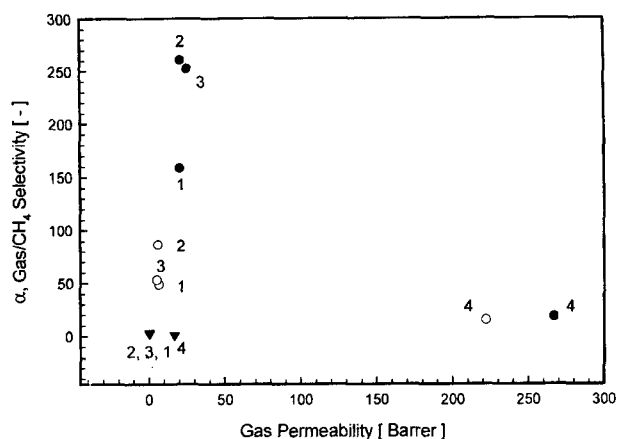
Figures 6 and 7 show plots of gas permeability and selectivity over  $N_2$  and  $CH_4$ , respectively. In the Figure 6,  $CO_2/N_2$  separation selectivity for 6FDA-based polyimides was higher than  $O_2/N_2$  selectivity. This results is an inverse order compared with the diffusivity selectivity order of  $D_{O_2}/D_{N_2} > D_{CO_2}/D_{N_2}$  in Figure 8. It suggests that for  $CO_2$  permeation the solution over diffusion was prevailed throughout the solution-diffusion model. The fact was proven by high solubility coefficients of  $CO_2$  in the Figure 5.



**Figure 5.** Effect of cohesive energy density on gas permeability and solubility for 6FDA-based polyimides: (a) 6FDA-TrMPD; (b) 6FDA-DAP; (c) 6FDA-DABA; (d) 6FDA-BAPAF.



**Figure 6.** Relation between gas/ $N_2$  selectivity and permeability. ●  $CO_2$ ; ○  $O_2$ ; (a) 6FDA-BAPAF; (b) 6FDA-DAP; (c) 6FDA-DABA; (d) 6FDA-TrMPD.



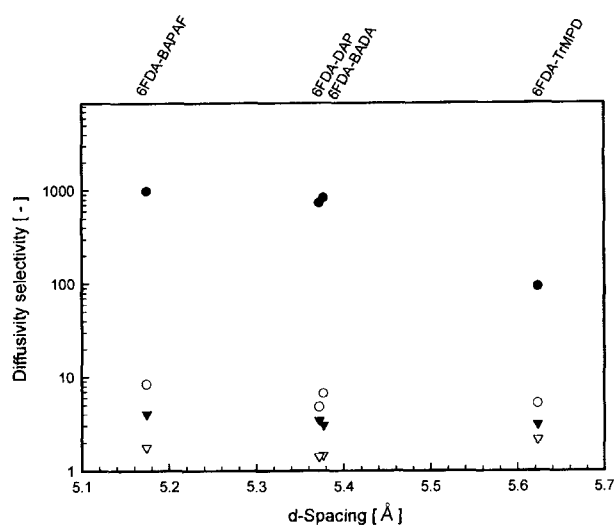
**Figure 7.** Gas/CH<sub>4</sub> selectivity vs permeability. (●) H<sub>2</sub>; (○) CO<sub>2</sub>; (▼) N<sub>2</sub>; (1) 6FDA-BAPAF; (2) 6FDA-DAP; (3) 6FDA-DABA; (4) 6FDA-TrMPD.

In Figure 7 gas/CH<sub>4</sub> separation selectivities were ranked in the following order:  $\alpha_{\text{H}_2/\text{CH}_4} > \alpha_{\text{CO}_2/\text{CH}_4} > \alpha_{\text{N}_2/\text{CH}_4}$ . Polar group-containing polyimides of 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA showed high CO<sub>2</sub>/CH<sub>4</sub> separation selectivity of 48 to 86 while they exhibited relatively low CO<sub>2</sub> permeability of 5 to 7 Barrers, compared with 6FDA-TrMPD polyimide having low CO<sub>2</sub>/CH<sub>4</sub> separation selectivity and high CO<sub>2</sub> permeability of over 200 Barrers.

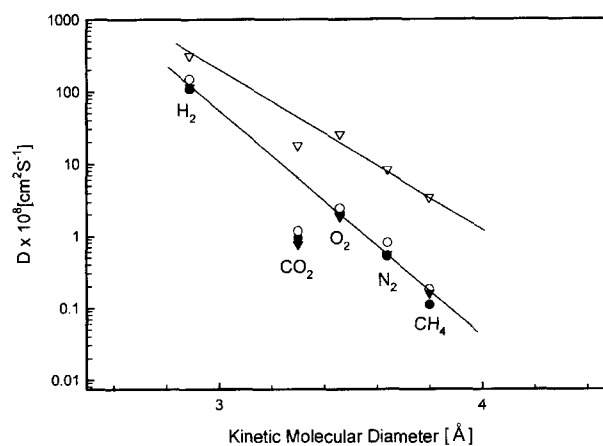
This phenomenon of high permeation for the 6FDA-TrMPD polyimide membrane has been reported in the literature.<sup>8,15</sup> Tanaka *et al.*<sup>8</sup> explained that it is the reason why for 6FDA-TrMPD polymer the rigidity and non planar structure of the polymer chain, and the bulkiness of methyl groups make chain packing inefficient, resulting in increase in both diffusion and solubility coefficients of gas.

**Diffusivity Behavior.** Figure 8 shows relationship between diffusivity selectivities of each gas pair and d-spacing of 6FDA-based polyimides in Table I. The diffusivity selectivities of 6FDA-based polyimides with a polar group decreased slightly with increasing d-spacing of the polymers.  $D_{\text{H}_2}/D_{\text{CH}_4}$  diffusivity selectivity of polar group-containing polyimides was much higher than that of the 6FDA-TrMPD polymer. These results may be caused by differences in space filling by bulky side groups such as C(CF<sub>3</sub>)- and -C(CH<sub>3</sub>)-. Diffusions for 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA polyimides are considered to be affected by the diamine moiety with a polar group. When compared, values of diffusivity selectivity for gas pair at the same d-spacing were ranked in the following order:  $D_{\text{H}_2}/D_{\text{CH}_4} > D_{\text{CO}_2}/D_{\text{CH}_4} > D_{\text{O}_2}/D_{\text{N}_2} > D_{\text{CO}_2}/D_{\text{N}_2}$ .

Figure 9 exhibits dependence of kinetic molecular diameter of gases on diffusion coefficients. Diffusion coefficients decreased with increasing kinetic molecular diameter of gases. The diffusion coefficients of 6FDA-TrMPD at the same gas were much higher than those of polar group-con-



**Figure 8.** Diffusivity selectivity of gases vs. d-spacing of 6FDA-based polyimides. (●)  $D_{\text{H}_2}/D_{\text{CH}_4}$ ; (○)  $D_{\text{CO}_2}/D_{\text{CH}_4}$ ; (▼)  $D_{\text{O}_2}/D_{\text{N}_2}$ ; (▽)  $D_{\text{CO}_2}/D_{\text{N}_2}$ .



**Figure 9.** Correlation of diffusion coefficient with kinetic molecular diameter. (●) 6FDA-BAPAF; (○) 6FDA-DAP; (▼) 6FDA-DABA; (▽) 6FDA-TrMPD.

taining polyimides. Higher diffusion coefficients of the 6FDA-TrMPD membrane seem to be related to the rigidity and inefficient packing of the polyimide mentioned above. The diffusion coefficients of CO<sub>2</sub> for 6FDA-based polyimides were smaller than those of O<sub>2</sub> despite the kinetic diameter of CO<sub>2</sub> smaller than that of O<sub>2</sub>, and were deviated from the lineation of experimental data. This anomalous behavior is in agreement with the literatures.<sup>8,14</sup> The coefficients of our solubility (Figure 5) and Zimmerman's sorption<sup>14</sup> of CO<sub>2</sub> were much higher than those of O<sub>2</sub>. The polymer structure saturated by CO<sub>2</sub> sorption can retard a little the passage of the gas across a membrane due to interaction between gas molecule and polymer segment.

## Conclusions

The dense membranes of 6FDA-based polyimides having a polar group of hydroxyl or carboxyl were prepared and applied to their gas separation of H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>. Polar group-containing polyimides of 6FDA-BAPAF, 6FDA-DAP, and 6FDA-DABA showed high separation selectivity of 18 to 27 and 48 to 86 for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>, respectively, and low CO<sub>2</sub> permeability of 5 to 7 Barrers while 6FDA-TrMPD polyimide exhibited relatively low selectivity and high permeability of CO<sub>2</sub>. Gas permeabilities and diffusion coefficients for the polar group-containing polyimide membranes did not vary largely due to the nature of the polymers. Values of diffusivity selectivity for 6FDA-based polyimide membranes at the same d-spacing were ranked in the following order:  $D_{H_2}/D_{CH_4} > D_{CO_2}/D_{CH_4} > D_{O_2}/D_{N_2} > D_{CO_2}/D_{N_2}$ . 6FDA-based polyimides with a polar group, which are soluble in alcohol or/and glycol ether, are applicable to fabrication of a composite membrane by dip-coating method as well as preparation of a dense membrane.

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