NOTES

Effects of Trifluoromethyl Side Groups on Gas Permeability and Permselectivity in Polyimides

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Polyimides are interesting in application for gas separation membranes. The relationship between chemical structure and gas permeability has been extensively investigated.^{1–6} In general, polymeric membranes with higher permeability tend to exhibit lower permselectivity. However, the introduction of hexafluoroisopropylidene $-\text{C}(\text{CF}_3)_2-$ linkage in polymer chain of polyimide increases gas permeability without significant loss of permselectivity for CO_2/CH_4 separation.^{1,4,5} The polyimide prepared from 4,4'-hexafluoroisopropylidene phthalic anhydride (6FDA) and 2,2'-bis(aminophenyl)hexafluoropropane (BAHF), which has two $-\text{C}(\text{CF}_3)_2-$ linkages in the repeat unit, is excellent for CO_2/CH_4 separation.⁵

The CF_3 groups in the $-\text{C}(\text{CF}_3)_2-$ linkages cause less-efficient packing of polymer chains due to reduced molecular interaction and steric hindrance. Reduction of the chain packing increases diffusion coefficients of gases and decreases the diffusivity selectivity. Simultaneously, the CF_3 groups restrict internal rotation of the phenylene rings adjacent to the linkages and reduce local mobility of the polymer chain. In the glassy state, restriction of the local motion of polymer chains tends to

reduce diffusion coefficients of gases and increase the diffusivity selectivity. Thus, CF_3 groups have two opposite effects. In general, the former effect is larger than the latter. Therefore, for the gas separation system such as H_2/CH_4 , where there is a large difference in molecular size between the gas pair (effective diameter: 0.29 nm for H_2 , 0.38 nm for CH_4), the introduction of $-\text{C}(\text{CF}_3)_2-$ linkage causes considerable increase in diffusion coefficients with a large decrease in the diffusivity selectivity. For the CO_2/CH_4 system, where there is small difference in molecular size (effective diameter: 0.35 nm for CO_2) and large difference in molecular shape between the gas pair, the former effect on diffusivity selectivity is rather small because of the small difference in molecular size and is canceled out by the latter effect. This is the reason that the introduction of $-\text{C}(\text{CF}_3)_2-$ linkage causes a large increase in permeability without a significant loss of permselectivity for the CO_2/CH_4 separation.

In this study, polyimides with trifluoromethyl side groups (CF_3) on phenylene rings in polymer chain were prepared, and permeation properties of H_2 , CO , CO_2 , and CH_4 were measured to investigate the effects of the CF_3 side groups on the gas permeability and

permselectivity.

EXPERIMENTAL

A diamine used was 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB). Tetracarboxylic dianhydrides used were 1-(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P3FDA), pyromellitic dianhydride (PMDA), and 6FDA. The chemical structures of polyimides prepared are shown in Figure 1 together with those of related polyimides. Polymerization and film preparation of the polyimides were described in previous papers.^{7,8} The films used were 20–30 μm thick. The characterization experiments were carried out by methods described elsewhere.³ A vacuum time-lag method was used to measure permeability coefficient P . A Sartorius S3D-P model electronic microbalance was used to measure the solubility coefficient S . P and S were measured at 10 atm and 35°C. Average diffusion coefficient $\bar{D}$ was evaluated by equation $\bar{D} = P/S$.

RESULTS AND DISCUSSION

Characterization results of the polyimides are listed in Table I together with those of the related polyimides from BAHF,⁵ 2,2',4,4'-tetramethyldiaminobenzidine (TMBZ),⁹ and

4,4'-oxydianiline (pp' ODA).⁵ Fraction of "free space" V_F refers to the ratio of the so-called "expansion volume"¹⁰ to the observed volume and were calculated from eq 1

$$V_F = (V_T - V_0)/V_T \quad (1)$$

where V_T and V_0 are specific molar volumes at temperature T and 0 K, respectively. V_T was

Figure 1. Chemical structures of polyimides.

Table I. Characterization of polyimide films^a

Polyimides	T_g °C	Density g cm ⁻³	V_F (—)	δ (J cm ⁻³) ^{1/2}	[F]
6FDA-TFDB	335	1.477	0.190	24.6	24
6FDA-TMBZ ^b	346	1.355	0.146	25.9	13
6FDA-BAHF ^c	305	1.480	0.182	24.1	24
6FDA- pp' ODA ^c	299	1.432	0.165	27.2	14
PMDA-TFDB	> 400	1.489	0.160	28.7	18
PMDA- pp' ODA ^c	(420)	1.395	0.129	34.6	0
P3FDA-TFDB	322	1.590	0.142	26.8	25

^a [F] is the fluorine content, in [10⁻³ mol cm⁻³].

^b Reference 9.

^c Reference 5.

Table II. Permeability, diffusion and solubility coefficients and ratios of coefficients for CO₂/CH₄ system in polyimides at 35°C and 10 atm^a

Polyimides	P_{CO_2}	$\bar{D}_{\text{CO}_2}$	S_{CO_2}	P_{CH_4}	$\bar{D}_{\text{CH}_4}$	S_{CH_4}	$P_{\text{CO}_2}/P_{\text{CH}_4}$	$\bar{D}_{\text{CO}_2}/\bar{D}_{\text{CH}_4}$	$S_{\text{CO}_2}/S_{\text{CH}_4}$
6FDA-TFDB	56	11	5.3	1.7	1.1	1.6	34	10	3.4
6FDA-TMBZ ^b	50	—	—	1.4	—	—	35	—	—
6FDA-BAHF ^c	51	8.1	6.3	1.3	0.66	2.0	38	12	3.1
6FDA- <i>pp'</i> ODA ^c	17	3.1	5.4	0.34	0.22	1.6	49	14	3.4
PMDA-TFDB	14	3.2	4.4	0.37	0.30	1.3	37	11	3.5
PMDA- <i>pp'</i> ODA ^c	3.6	0.80	4.5	0.094	0.079	1.2	38	10	3.8
P3FDA-TFDB	1.7	0.66	2.6	0.022	0.034	0.69	76	19	3.9

^a P is in $10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$, $\bar{D}$ is in $\text{cm}^2 \text{ s}^{-1}$, and S is in $10^{-2} \text{ cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ cmHg}^{-1}$.^b Reference 9.^c Reference 5.

calculated from density data, V_0 was estimated to be 1.3 times¹¹ the van der Waals volume calculated by the group-contribution method of Bondi.¹² The solubility parameter δ was calculated by the group-contribution method of van Krevelen.¹¹

Permeation data for the CO₂/CH₄ system are listed in Table II. $\bar{D}$ varied by a factor of 30, while S varied by a factor of 2 with changing the chemical structure. The differences in P_{CO_2} and $P_{\text{CO}_2}/P_{\text{CH}_4}$ were mainly attributed to differences in $\bar{D}_{\text{CO}_2}$ and $\bar{D}_{\text{CO}_2}/\bar{D}_{\text{CH}_4}$, respectively. $S_{\text{CO}_2}/S_{\text{CH}_4}$ was almost constant around 3.5. Permeation data for the H₂/CO and H₂/CH₄ systems are listed in Table III. For these systems, differences in P and P ratios are considered due to those in the $\bar{D}$ and $\bar{D}$ ratios, respectively.

The permeability and permselectivity for 6FDA-TFDB polyimide were similar with those for 6FDA-BAHF. The CF₃ groups in TFDB moiety which cause less-efficient packing of polymer chains seem to result in high permeability. Molecular model examination using a Stuart type model showed that two CF₃ side groups on ortho positions to the single bond of biphenyl in TFDB moiety restrict the internal rotation of biphenyl by the steric hindrance and reduce local motion of the polymer chains. This situation was similar to that for -C(CF₃)₂- linkage mentioned above. It is noted that the permeability and perm-

Table III. Permeability coefficients and permeability coefficient ratios for H₂/CO, H₂/CH₄ systems in polyimides at 35°C and 10 atm^a

Polyimides	P_{H_2}	$P_{\text{H}_2}/P_{\text{CO}}$	$P_{\text{H}_2}/P_{\text{CH}_4}$
6FDA-TFDB	120	26	73
6FDA-TMBZ ^b	100	—	75
6FDA-BAHF ^c	108	26	81
6FDA- <i>pp'</i> ODA ^c	41	35	120
PMDA-TFDB	34	33	90
PMDA- <i>pp'</i> ODA ^c	11	39	110
P3FDA-TFDB	8.5	66	380

^a P is in $10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} \text{ cmHg}^{-1}$.^b Reference 9.^c Reference 5.

selectivity of 6FDA-TMBZ polyimide are also similar with those of 6FDA-TFDB and 6FDA-BAHF polyimides. This indicates that the four CH₃ groups on ortho positions to single bond of biphenyl and two CF₃ groups have similar effects on the restriction of both efficient polymer chain packing and internal rotation of biphenyl.

In spite of higher content of fluorine, P3FDA-TFDB polyimide had smaller V_F , lower P as compared with PMDA-TFDB. This indicates that CF₃ substitution of benzene ring in PMDA moiety causes efficient packing of the polymer chains and results in reductions in both P and $\bar{D}$. These variations are contrary to the above-mentioned effects of the CF₃ groups in the -C(CF₃)₂-linkage. The reason is

considered to be as follows. Charge transfer (CT) interaction takes an important part in polymer chain-chain interactions in aromatic polyimides.¹³ The magnitude of CT interaction depends on the electron affinity of the acid dianhydride moiety and electron ionization potential of the diamine moiety. The color of the polyimide films is attributed mainly to CT absorption.¹⁴ The P3FDA-TFDB polyimide films are yellow, whereas PMDA-TFDB and 6FDA-TFDB polyimide films are pale yellow and colorless, respectively. In the electronic absorption spectra of the films (20 μ m thick), absorbance of 0.3 was observed at 470, 425, 375 nm for P3FDA, PMDA, and 6FDA. This indicates that the magnitude of CT interaction is in the order P3FDA-TFDB > PMDA-TFDB > 6FDA-TFDB. The -C(CF₃)₂-groups in 6FDA and BAHF reduce electron-accepting and electron-donating ability of the moiety, respectively by interruption of the π -electron conjugation, resulting in significant reduction in CT interaction. As a result, 6FDA- and/or BAHF-based polyimide films are less-colored. The reduced molecular interaction is one reason why polyimides having -C(CF₃)₂- groups have large V_F . The introduction of an electron-attracting substituent such as CF₃ on the benzene ring in the diamine increases the ionization potential and therefore reduces CT interaction. The introduction of electron-attracting substituents into the dianhydride increases the electron affinity and therefore enhances CT interaction. The stronger molecular interactions of polymer chains in P3FDA-TFDB polyimide result in smaller V_F and lower P and $\bar{D}$, compared with PMDA-TFDB polyimide.

There is a general trend for every gas separation system that polymers having higher

P exhibit lower P ratios. Robeson reported an upper bound line for membrane performance of polymers in the plots of logarithm of P ratio for each gas pair *versus* logarithm of P of the more permeable gas.¹⁵ The plots for 6FDA-TFDB, 6FDA-TMBZ, and 6FDA-BAHF polyimides for H₂/CH₄ and CO₂/CH₄ systems were on upper bound lines. The plot for P3FDA-TFDB polyimide for H₂/CH₄ system was slightly below the upper bound line.

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