

The Transport Properties of CO₂ and CH₄ for Brominated Polysulfone Membrane

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(Received 10 December 1998 • accepted 25 March 1999)

Abstract- The sorption and permeation properties of CO₂ and CH₄ for synthesized brominated polysulfone, BPSf (bromobisphenol A polysulfone) were measured, and compared with the values for PSf (bisphenol A polysulfone), MPSf (bisphenol A methylated polysulfone) and TMSPSf (bisphenol A trimethylsilylated polysulfone) to investigate the structure-property relationships. Especially, the effect of polarity of substituents on the transport properties was studied. The effect of operating pressure on the permeation properties of polysulfones was examined. The permeation properties for a mixture of CO₂ and CH₄ were also measured, and these results were compared with those obtained from the experiments of pure gases. The sorbed concentrations and permeability coefficients are well fitted to the dual mode model. The permeability coefficients of each gas of a binary mixture are less than those of pure gases, and the extent of reduction in permeability coefficient is larger for less permeable polymer. The ideal separation factor for four polysulfones increases in the following order: TMSPSf < PSf < BPSf < MPSf. The ideal separation factor for BPSf is higher than other polysulfones having similar permeability coefficients of CO₂ with BPSf. It can be explained that the strong polarity of bromine in BPSf increases cohesive energy density of polymer, and reduces the chain packing-inhibiting ability. The ranking of permeability coefficient correlates well with fractional free volume. The variation of d-spacing is not consistent with the permeability coefficient.

Key words : Bromination, Polysulfone, Sorption, Permeation, Mixed Gas

INTRODUCTION

New materials with higher permeability and selectivity are required to advance the membrane technology in many gas separation applications [Stern, 1994; Koros and Fleming, 1993; Bae et al., 1998; Kim et al., 1996]. Careful molecular design of polymer structure can lead to noble materials that enhance the gas transport properties. Recent studies have focused on the systematic variation of polymer structures to increase permeability and selectivity, with attempts made to introduce bulky substituents into polymer membrane [McHattie et al., 1991a, b, 1992; Ghosal et al., 1996; Pixton and Paul, 1995; Kim et al., 1988; Aitken et al., 1992]. Our previous study also described results for gas permeation measurements in methyl and trimethylsilyl substituted polysulfone membranes, respectively [Kim and Hong, 1997a, b]. In general, the transport properties for polymer membranes depend on intermolecular packing distance, chain stiffness, polymer-polymer interaction and polymer-penetrant interaction. The polymer-polymer interaction of those factors is affected by the presence of the polar side groups, and the increase in polymer-polymer interaction leads to the higher selectivity. Considering this fact, this work involves the synthesis of bromobisphenol A polysulfone (BPSf), in which phenyl rings of bisphenol units in polysulfone are substituted with bromine atoms. Bisphenol A polysulfone (PSf) has been used commercially as a gas separation membrane material, and it has a stable aro-

matic backbone that is amenable to bromination. The gas pair chosen for this study is the CO₂/CH₄ system. The separation of these gases is of interest in oil recovery, the treatment of landfill gases and sweetening of natural gases [Bhide and Stern, 1993; Bollinger et al., 1982; Rautenbach and Welsch, 1994]. The purpose of this study is to investigate the effect of bromine atoms on CO₂ and CH₄ transport properties. In addition, we evaluate brominated polymer as a potential membrane material for gas separations. The present work is a part of a study of a family of polysulfone in which systematic structural modifications are made. Further studies deal with the substitution of bromine atoms into bisphenol A trimethylsilylated polysulfone (TMSPSf). The previous results described that TMSPSf is several times more permeable than PSf, but shows a lower value of selectivity [Kim and Hong, 1997b].

EXPERIMENTAL

1. Materials

Bisphenol A polysulfone (PSf, Udel® P-3500) was obtained from Amoco Chemical Co. The reagents for synthesis were purchased commercially and used as received without further purification. The procedure described by Guiver et al. [1989] was used for the synthesis of BPSf. PSf (0.075 mol, 33.15 g) was dissolved in chloroform (180 mL), and bromine (12 mL) was added to a stirred solution at room temperature. White clouds of HBr soon evolved. The mixture was stirred at room temperature for 24 hr and then precipitated into methanol. The recovered brominated polysulfone was reprecipitated sev-

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eral times using THF and methanol to leach out residual free bromine, then filtered and dried in a vacuum oven.

2. Characterization

¹H-NMR spectrum was recorded on a Bruker DRX-500 spectrophotometer. Elemental analysis was performed by Cario-Erba EA 1108 analyzer. The glass transition temperature (T_g) for each material was measured using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 °C/min. Polymer density was measured using a density gradient column filled with aqueous solutions of calcium nitrate at 23 °C. Fractional free volume (FFV) of the polymers was calculated by the group contribution method proposed by Bondi [1964; Van Krevelen, 1990]. The wide-angle X-ray diffraction (WAXD) measurements were carried out using a Rigaku WAXD-D/MAX III X-ray diffractometer with Cu K α radiation with wavelength of 1.54 Å. The average intersegmental distances or "d-spacings" were calculated from the Bragg equation [Balta-calleja and Vonk, 1989], $n\lambda = 2d \sin\theta$, at the angle of maximum peak of scan. Cohesive energy density (CED) was estimated by the group contributions published by Fedors [Van Krevelen, 1990].

3. Membrane Preparation

The membrane was cast from 10 wt% solution in chloroform on a clean glass plate at room temperature. The membrane was dried under atmosphere for 24 hr, during which time the rate of solvent removal was decreased by covering the glass plate with aluminum foil. After drying, the membrane was lifted from the glass plate and completely dried in a vacuum oven at 150 °C for several days.

4. Gas Sorption and Permeation

Pure gas sorption measurements were made for CO₂ and CH₄ up to 25 atm and at 30 °C. Equilibrium sorption was measured in a two-volume pressure decay type of sorption cell. The sorption apparatus is described in detail in an earlier paper [Kim and Hong, 1997a].

Permeability measurements were also made for pure CO₂ and CH₄ and their binary mixture using the variable volume method employed in our laboratory [Kim and Hong, 1997a]. The volumetric flow rate through the membrane to the downstream side was determined by observing the displacement of 1-propanol in the capillary tube connected to the downstream side. In this work, the effective membrane area is 9.6 cm². The permeability coefficients were calculated by Eq. (1) and (2). Permeation runs were carried out 30 °C and up to 25 atm.

$$P = \bar{D} \cdot \bar{S} = \frac{J_s L}{p_1 - p_2} \quad (1)$$

$$J_s = \frac{\pi d^2}{4A} \frac{273.15 p_b}{76T} \frac{dh}{dt} \quad (2)$$

where P [Barrer, cm³(STP)cm/cm² s cmHg] is the mean permeability coefficient, \bar{D} [cm²/s] is the apparent diffusion coefficient, and \bar{S} [cm³(STP)/cm³ cmHg] is the apparent solubility coefficient. J_s [cm³(STP)/cm² s] is the steady-state rate of gas permeation through unit area when the constant gas pressures p_1 and p_2 are maintained at the membrane interface, and L [cm] is the effective membrane thickness. d [cm] is the diameter of capillary, A [cm²] is the membrane permeation area, p_b

[cmHg] is the barometric pressure, T [K] is the experimental temperature, and dh/dt is the displacement rate of propanol in the capillary. The permeation rates for the components of binary gas mixture of CO₂ and CH₄ (CO₂/CH₄=57.5/42.5 vol%) were determined by the volumetric flow rate of gas mixture and the concentration of each component on the upstream and downstream side. The concentrations of the components were determined by Gas Chromatograph (Shimadzu 8A) with a column packed with Porapak Q.

RESULTS AND DISCUSSION

1. Synthesis

Fig. 1 shows the chemical structure of synthesized BPSf. The reactive substitution position is situated ortho to the aryl ether linkage in the bisphenol unit. This position is the most favorable site because it is electrophilically activated by oxygen atom. The degree of substitution (DS) was calculated by peak area of ¹H NMR spectrum and the result of elemental analysis. The DS was almost 100 %. Fig. 2 shows the ¹H-NMR spectrum of BPSf.

Elemental Analysis--Calculated ; C=53.97 %, H=3.35 %, O=10.66 %, S=5.39 %, Br=26.62 %, Found ; C=53.53 %, H=3.37 %, O=10.71 %, S=5.97 %, Br=26.41 %

¹H-NMR (CDCl₃) δ (ppm) ; 7.84 (4H, -C₆H₄SO₂-), 7.49 (2H, -C₆H₃Br-C(CH₃)₂-), 7.13 (2H, -C₆H₃Br-C(CH₃)₂-), 6.96 (2H,

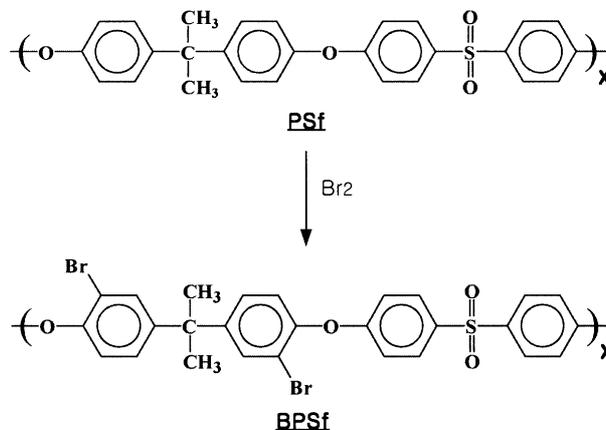


Fig. 1. The chemical structure of BPSf.

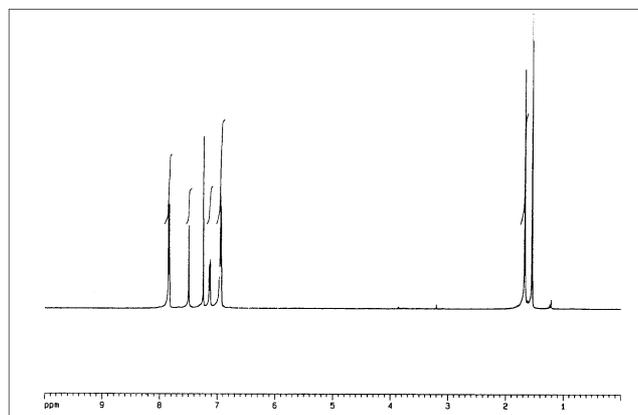


Fig. 2. Sorption isotherms for CO₂ and CH₄ in BPSf at 30 °C.

-C₆H₃-Br-C(CH₃)₂-, 6.93 (4H, -C₆H₄SO₂-), 1.67 (6H, -C₆H₃Br-C(CH₃)₂-)

2. Pure Gas Sorption and Permeation-Dual Mode Model

Sorption isotherms for CO₂ and CH₄ in BPSf are shown in Fig. 3. The pure gas sorption isotherms show concave to the pressure axis, and can be described by a "dual sorption model" [Vieth et al., 1966]. According to the dual sorption model, the equilibrium concentration of sorbed gas in glassy polymers can be described as a function of pressure.

$$C = C_D + C_H$$

$$C = k_D p + \frac{C'_H b p}{1 + b p} \quad (3)$$

where, C [cm³(STP)/cm³] is the equilibrium concentration of the sorbed gas, and C_D and C_H represent Henry's law mode sorption and Langmuir mode sorption, respectively. The parameter, k_D [cm³(STP)/cm³ atm] is the Henry's law solubility constant, C'_H [cm³(STP)/cm³] is the Langmuir sorption capacity, and b [atm⁻¹] is the Langmuir affinity constant. These sorption parameters can be obtained by nonlinear least-square regression, and

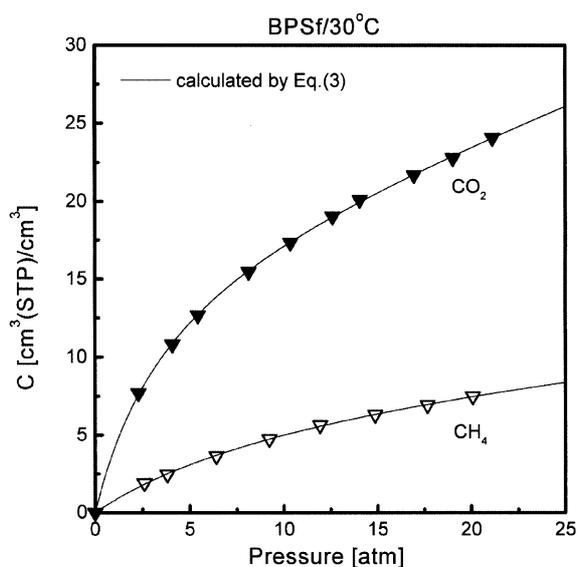


Fig. 3. Pressure dependency of permeability coefficients of CO₂ and CH₄ for BPSf at 30 °C.

are listed in Table 1. The solid curves in Fig. 3 represent the dual mode fits of the actual data, substituting the values of sorption parameters given in Table 1. It is shown that the sorption of pure CO₂ and CH₄ is well fitted by the dual sorption model.

The permeability coefficients of pure gases for BPSf are shown as a function of upstream pressure in Fig. 4. The permeability coefficients of CO₂ and CH₄ decrease with increasing upstream pressure, which is consistent with other glassy polymers [Koros and Chern, 1987; Bae et al., 1994]. This pressure-dependency of permeability coefficients has been generally described as "dual mobility model" (or "partial immobilization model") proposed by Paul and Koros [1976]. According to the dual mobility model, the populations in each of the sorptions can be assigned separate diffusion coefficients D_D and D_H; the permeability coefficient of pure gas can be written as:

$$P = k_D D_D \left[1 + \frac{FK}{(1 + b p_1)(1 + b p_2)} \right] \quad (4)$$

where, $K = \frac{C'_H b}{k_D}$ and $F = \frac{D_H}{D_D}$

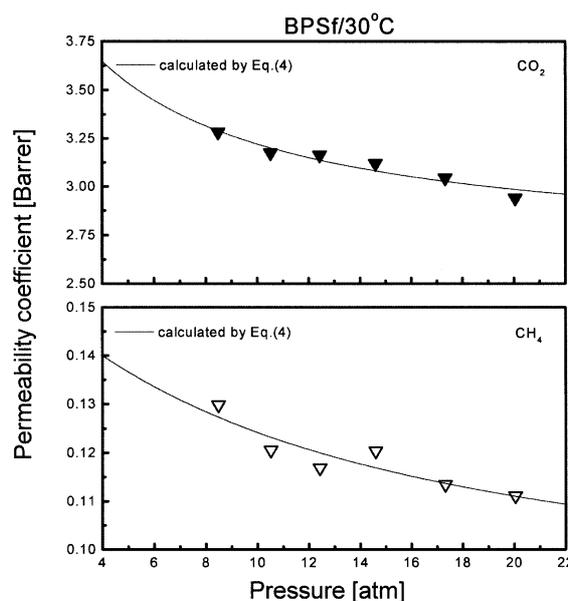


Fig. 4. Permeability coefficients of CO₂ for PSf, MPSf, TMSPSf and BPSf at 30 °C.

Table 1. Dual mode parameters^a for BPSf, PSf^b, MPSf^b, and TMSPSf^c at 30 °C

Polymer	Gas	k _D	C' _H	b	D _D	D _H
BPSf	CO ₂	0.429	17.70	0.261	4.718	0.674
	CH ₄	0.096	8.81	0.084	0.652	0.082
PSf	CO ₂	0.630	16.50	0.356	4.799	0.581
	CH ₄	0.167	9.04	0.118	0.692	0.106
MPSf	CO ₂	0.482	12.17	0.287	2.846	0.452
	CH ₄	0.078	7.35	0.108	0.520	0.051
TMSPSf	CO ₂	0.324	20.719	0.155	30.973	1.202
	CH ₄	0.199	8.299	0.090	3.521	0.221

^aUnits : k_D [cm³(STP)/cm³ atm] ; C'_H [cm³(STP)/cm³] ; b[atm⁻¹] ; D_D×10(cm²/s) ; D_H×10 (cm²/s)

^bData from Kim and Hong, 1997a

^cData from Kim and Hong, 1997b

The diffusion coefficients, D_D and D_H are calculated from the slope and intercept of the plot of experimental permeability coefficient versus $1/(1+bp_1)(1+bp_2)$. The diffusion coefficients obtained by this analysis are also listed in Table 1. The solid curves in Fig. 4, which are calculated by Eq. (4) using parameters given in Table 1, show that the permeability coefficient is well fitted to the dual mobility model over the entire pressure range.

3. The Effect of Substituents on Transport Properties

The comparison of the permeability coefficients of CO_2 and CH_4 and ideal separation factors for modified polysulfones are shown in Figs. 5-7, and those values at 10 atm are listed in Table 2. The ideal separation factor was calculated from the ratio of the pure component permeability coefficients, i.e., $P_{\text{CO}_2}/P_{\text{CH}_4}$. In Figs. 5-7 and Table 2, MPSf and TMSPSf are the polymers in which ortho sites of sulfone unit in PSf have been

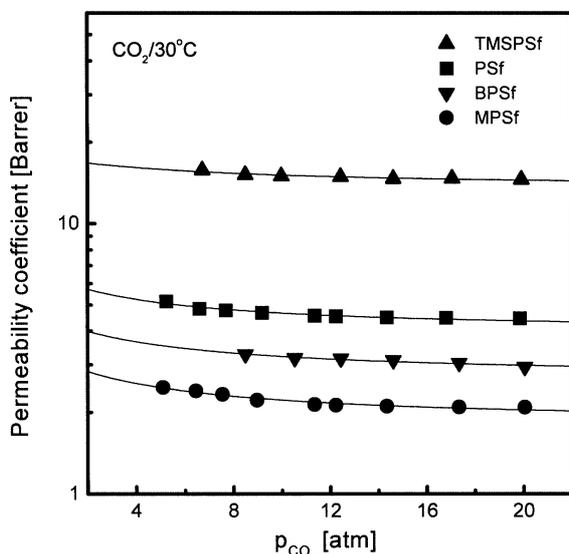


Fig. 5. Permeability coefficients of CH_4 for PSf, MPSf, TMSPSf and BPSf at 30 °C.

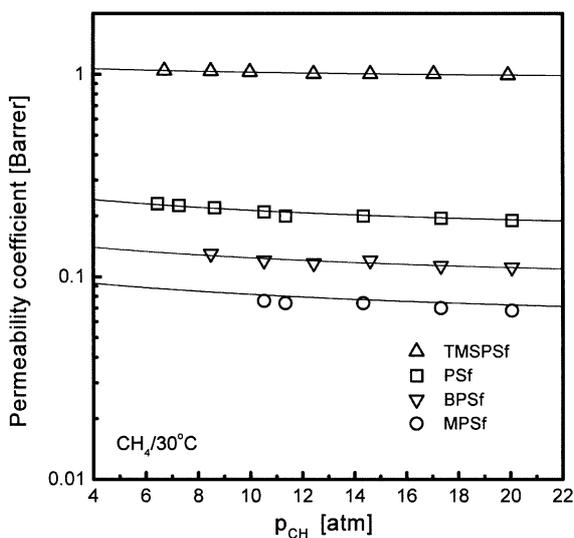


Fig. 6. Ideal separation factors of CO_2 and CH_4 for PSf, MPSf, TMSPSf and BPSf at 30 °C.

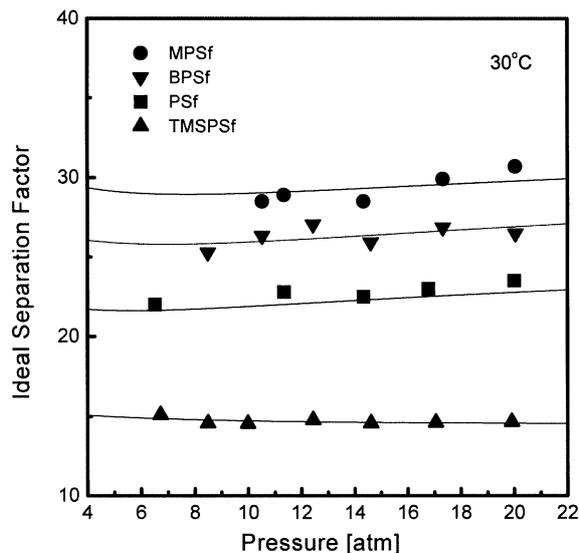


Fig. 7. Correlation of ideal separation factor with permeability coefficient for CO_2 at 10 atm and 30 °C.

Table 2. Transport properties^a of CO_2 and CH_4 for BPSf, PSf^b, MPSf^c, and TMSPSf^c at 30 °C and 10 atm

Polymer	P_{CO_2}	$a_{\text{CO}_2/\text{CH}_4}$	S_{CO_2}	$S_{\text{CO}_2/\text{CH}_4}$	D_{CO_2}	$D_{\text{CO}_2/\text{CH}_4}$
BPSf	3.2	27	1.7	3.4	1.9	7.9
PSf	4.6	22	2.4	2.8	1.9	7.8
MPSf	2.2	29	1.8	3.0	1.2	9.6
TMSPSf	15.1	16	2.1	2.7	7.2	5.5

^aUnits : $P \times 10^{10}$ [$\text{cm}^3(\text{STP}) \text{ cm/s cm}^2 \text{ cmHg}$]; $D \times 10^8$ (cm^2/s); $S \times 10^7$ [$\text{cm}^3(\text{STP})/\text{cm}^3 \text{ cmHg}$].

^bData from Kim and Hong, 1997a.

^cData from Kim and Hong, 1997b.

replaced with methyl and trimethylsilyl groups, respectively. In this study, the ideal separation factor of four polysulfones increases in the following order, TMSPSf < PSf < BPSf < MPSf, and the permeability coefficients are in the opposite order. The ideal separation factor for BPSf is increased by above 20% than that for PSf, and is higher than other polysulfones having the similar permeability coefficients of CO_2 with BPSf. Fig. 8 describes the correlation of ideal separation factors with permeability coefficients of CO_2 . Open symbols in Fig. 8 represent the results of polysulfones substituted with other functional groups [Ghosal and Chern, 1992; Ghosal et al., 1996]. As mentioned above, in general, the permeation properties depend on intermolecular packing distance, chain stiffness, and polymer-polymer interaction if polymer-penetrant interaction is very small. These factors are related to fractional free volume, d-spacing, glass transition temperature, and solubility parameter, so these physical properties are listed in Table 3. Intermolecular packing distance is determined from fractional free volume (FFV) or d-spacing. The fractional free volume, given in Table 3, is calculated by Eq. (5). The group contribution method of Bondi [1964; Van Krevelen, 1990] is used to calculate V_o , the hypothetical specific volume of the polymer at 0 K, and V , the specific volume of the polymer at T, is determined from the polymer density.

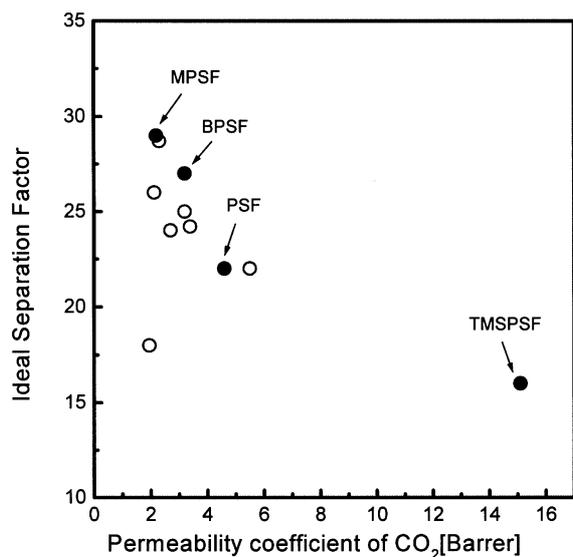


Fig. 8. Correlation of permeability coefficients at 10 atm and 30 °C with inverse fractional free volume; A=TMSPSF, B=PSf, C=BPSf, and D=MPSf.

Table 3. Physical properties for BPSf, PSf^a, MPSf^a, and TMSPSF^b

Polymer	T _g (°C)	r (g/cm ³)	d-spacing (Å)	d (cal/cm ³) ^{1/2}	FFV
BPSf	190.9	1.514	4.7	12.9	0.156
PSf	190.3	1.243	5.2	12.4	0.158
MPSf	177.6	1.213	5.2	12.1	0.151
TMSPSF	164.0	1.126	5.6	11.0	0.167

^aData from Kim and Hong, 1997a

^bData from Kim and Hong, 1997b

$$FFV = \frac{V - V_o}{V} \quad (5)$$

As shown in Tables 2 and 3, the ranking of permeability coefficient correlates well with FFV. Fig. 9 represents the correlation of permeability coefficients with 1/FFV for CO₂ and CH₄. BPSf shows a lower value of both permeability coefficient and FFV than PSf. It can be explained that the interchain interaction increased by induced dipole, so the interchain distance is decreased. TMSPSF has the highest FFV and permeability coefficient, and MPSf has the lowest values. This result is discussed in detail in previous papers [Kim and Hong, 1997a, b]. The variation of d-spacing is not consistent with permeability coefficient. Jacobson [1991] suggested that d-spacing might not be sensitive to intermolecular packing in the presence of strong polar chain interaction.

Cohesive energy density (CED) is also an important factor for the prediction of structure-selectivity relationships. The higher the CED, the higher the attractive forces between polymer chains. This means that the permselectivity will tend to be higher for polar polymers than nonpolar polymers. Cohesive energy density is usually expressed in terms of solubility parameter d [(cal/cm³)^{1/2}], where $d = (CED)^{1/2}$, and the values of solubility parameter are listed in Table 3. The higher ideal separation factor of BPSf than PSf is due to the polarity of bromine. The strong

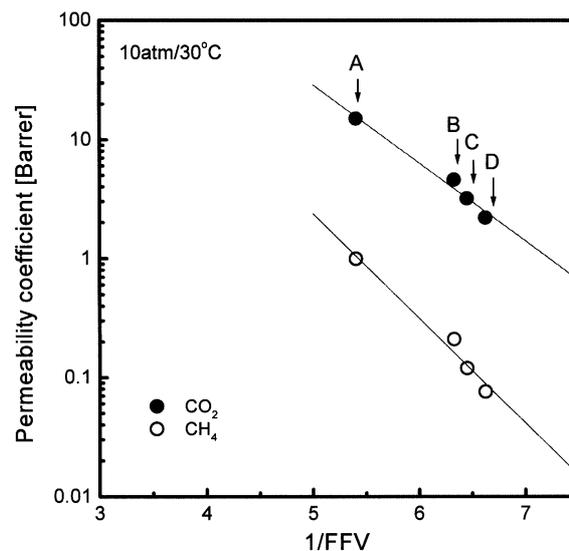


Fig. 9. Permeability coefficients for CO₂ in a binary mixture for BPSf at 30 °C.

polarity of bromine may act to reduce the chain packing-inhibiting ability, and enhance the molecular-sieving effect. For the polymers in this study, the polysulfone with higher d has the higher ideal separation factor, with the exception of MPSf. For MPSf, the deviation can be explained by the fact that the methyl groups of MPSf are accommodated between the polymer chains without forcing about them.

4. Mixed Gas Permeation

The gas transport and separation property studies have been especially focused on glassy polymers because of their superior gas selectivities in comparison to rubbery polymers. The presence of unrelaxed volume in a glassy polymer plays an important role in controlling the gas permeation rate and, thereby, the separation of two or more components [Dhingra and Marand, 1998]. However the use of single gas permeation data to estimate the separation properties of such a membrane can lead to erroneous results. In this study the permeation properties for a mixture of CO₂ and CH₄ were measured, and these results were compared with those obtained from the experiments of pure gases. The permeability coefficients of CO₂ and CH₄ in a binary mixture through BPSf membranes are shown in Fig. 10. The dashed curves in Fig. 10 represent the values calculated from pure gas data by Eq. (4) based on the respective partial pressures, and which is to compare mixed gas permeabilities with the values of pure gases at the same partial pressure. In Fig. 10, mixed gas permeability coefficients are lower than the respective pure component values. Such a reduction in permeability coefficient in a binary mixture is commonly observed in other polymers [Ghosal et al., 1996; Chern et al., 1984]. Based on the dual mode model for pure gas, Koros [1980] extended the model to the case of gas mixtures in glassy polymers. For cases involving only weak penetrant-penetrant and penetrant-polymer interactions, Koros [1980] assumed that the primary effect for a mixture is competition by the various penetrants for the fixed unrelaxed volume in the polymer, and that diffusivity of a penetrant in the polymer is not much changed by introducing the second component.

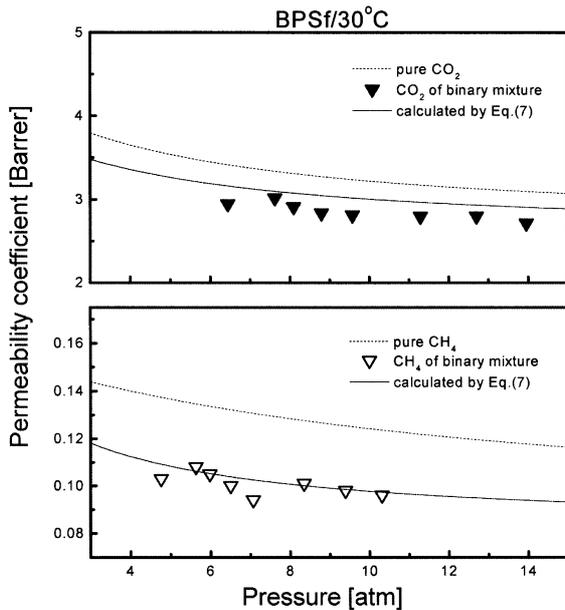


Fig. 10. Separation factors for CO₂ and CH₄ in a binary mixture for PSf, MPSf, TMSPSf, and BPSf at 30 °C.

For component A in a binary mixture, the concentration of sorbed gas and permeability coefficient can be written as Eq. (6) and (7), respectively.

$$C_A = k_{DA}P_A + \frac{C'_{HA}b_A P_A}{1 + b_A P_A + b_B P_B} \quad (6)$$

$$P_A = k_{DA}D_{DA} \left[1 + F_A K_A \frac{1 + \frac{(b_B P_{A1} P_{B2} - b_B P_{A2} P_{B1})}{P_{A1} - P_{A2}}}{(1 + b_A P_{A1} + b_B P_{B1})(1 + b_A P_{A2} + b_B P_{B2})} \right] \quad (7)$$

where, subscripts A and B represent components A and B, and all the parameters are obtained by pure gas experiment. The solid curves in Fig. 10 represent the values calculated from pure gas data by Eq. (7), and show that the permeability coefficient in a binary mixture is reasonably well fitted to the dual mobility model for a binary gas mixture, Eq. (7). According to the above assumption and Eq. (6) and (7), the permeability depressions in Fig. 10 are due to the solubility effect, and result from the competition between CO₂ and CH₄ for the Langmuir sites in glassy polymers. When A and B are relatively noninteracting components, component B fills some of the Langmuir sites previously available to A in the absence of B. The lowering of the concentration driving force of A lowers its flux through the membrane. Therefore, the permeability of A in the binary mixture is lower than that of pure A [Kesting and Fritsche, 1993].

The separation factor, α is defined as Eq. (8)

$$\alpha_{(A/B)} \equiv \frac{y_A/y_B}{x_A/x_B} \quad (8)$$

where y_i 's and x_i 's are the mole fraction of the components in the downstream and upstream, respectively. When the pressure of the downstream is very small compared with the upstream pressure, the separation factor will be approximately equal to the ratio of permeabilities, P_A/P_B . Fig. 11 represents the separation factors of CO₂ and CH₄ in a binary mixture for PSf, MPSf, TMSPSf and BPSf at 30 °C.

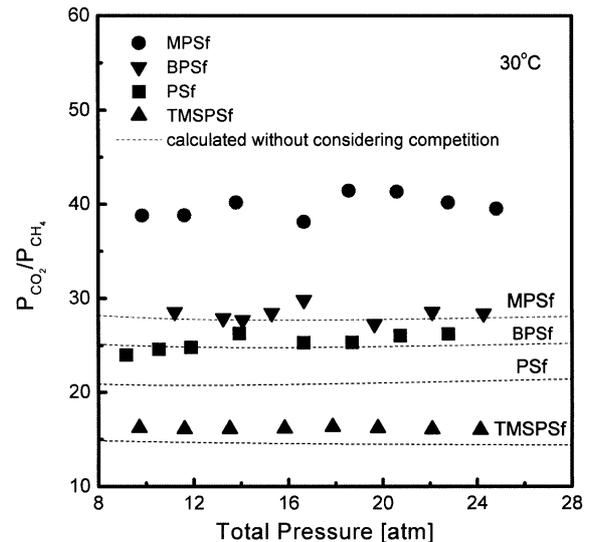


Fig. 11. Separation factors of CO₂ and CH₄ in a binary mixture for PSf, MPSf, TMSPSf and BPSf at 30 °C. (Dashed lines represent calculated values without considering competition effect)

ration factors obtained by the ratio of mixed gas permeabilities. The data for PSf, MPSf and TMSPSf are also included for comparison. The dashed lines in Fig. 11 correspond to calculated values by Eq. (4), without considering the competition effect. The mixed gas permselectivity is higher than the pure gas value, which also shows the competition effect between each component. For each polymer, the value of Langmuir affinity constant, b , for CO₂ is higher than for CH₄, so the depression of permeability coefficient of CH₄ in a binary gas mixture is higher than that of CO₂, as expected by Eq. (6). Therefore, the separation factor of mixed gas is higher than the value without considering competition effect.

CONCLUSIONS

Bromobisphenol A polysulfone (BPSf) was synthesized, and the effect of the substitution of bromine atoms on the transport properties was investigated. The substitutions of polar substituents show a strong effect on chain packing distance. The replacement of phenylene hydrogens of PSf with bromine atoms results in higher chain interaction, judged by the value of cohesive energy density, and lower fractional free volume. The strong polarity of bromine increases interchain packing ability. As a consequence, BPSf is more than 20 % selective than PSf, and has a higher value of separation factor than other modified polysulfones with similar value of permeability coefficient.

The permeability coefficients of each gas in a binary mixture are lower than the respective values of pure gases, which shows the competition effect between each component. The extent of such a depression is larger for less permeable polymer for each gas. For each polymer, the depression of permeability coefficient of CH₄ is larger than that of CO₂ having the higher Langmuir affinity constant.

NOMENCLATURE

A	: membrane permeation area [cm ²]
b	: Langmuir affinity constant [atm ⁻¹]
C	: equilibrium concentration of the sorbed gas [cm ³ (STP)/cm ³]
C' _H	: Langmuir capacity constant [cm ³ (STP)/cm ³]
D	: diffusion coefficient [cm ² /s]
d	: diameter of capillary tube [cm]
h	: height of capillary tube [cm]
J	: diffusion flux [cm ³ (STP)/cm ² s]
k _D	: Henry's law solubility constant [cm ³ (STP)/cm ³ atm]
L	: membrane thickness [cm]
P	: permeability coefficient [cm ³ (STP) cm/cm ² s cmHg]
p	: pressure [cmHg]
p _b	: barometric pressure [cmHg]
S	: solubility coefficient [cm ³ (STP)/cm ³ cmHg]
T	: temperature [K]
t	: time [s]
V	: specific volume
x	: mole fraction of upstream of the membrane
y	: mole fraction of downstream of the membrane

Greek Letters

a	: separation factor
d	: solubility parameter [(cal/cm ³) ^{1/2}]

Subscripts

A	: component A
B	: component B
D	: Henry's law mode
H	: Langmuir mode
S	: steady state
1	: upstream of the membrane
2	: downstream of the membrane

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