

플라즈마 고분자 필름의 기체투과도 : 온도의존성에 관한 연구

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Gas Permeabilities of Plasma Polymerized Films : Temperature Dependence Study

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Abstract : Composite membranes were prepared by the deposition of pentafluoropyridine(PFP) or pentafluorotoluene(PFT) plasma films onto porous Celgard and nonporous poly(dimethylsiloxane) [PDMS] films. Gas permeation measurements for the composite membranes were made in the temperature range of 35°C to 75 °C and the solubilities in plasma polymers were measured using a Cahn Microbalance. The permeability coefficients of plasma polymers obeyed the Arrhenius relationship fairly well. Activation energies for permeation in the plasma films increased with the size of penetrant molecules. The activation energy of plasma polymers was much lower than that of commonly used perfluoropolymers. This difference was proved to be attributable to the much lower heat of solutions of the plasma polymers compared to perfluoropolymers. The diffusion activation energies were comparable with each other.

1. Introduction

Plasma films are very thin, highly crosslinked, and adhere well to variety of substrates. Application of the plasma film to gas separation membranes has several advantages; The thinness of the plasma film increases permeation flux and the crosslinked structure enhances permselectivity of the membrane [1].

The gas permeation properties of plasma films derived from fluorine-rich aromatic monomers were studied in the preceding papers [2,3]. The plasma film deposited on porous Celgard showed CO₂/CH₄ selectivities higher than O₂/N₂ selectivities and comparable to those of commonly used polymers [2].

Composite membranes, of which plasma films were deposited on nonporous PDMS films, showed interfacial resistance to gas permeation. The interfacial resistance is believed to be a result of an interfacial region produced by the interaction between the PDMS and plasma coating layer. The interfacial resistance was great for CH₄ gas, and the resistance was negligible for gases with smaller molecular size (O₂ and N₂) [3]. It was also shown that the gas permeation through the plasma/PDMS composite membrane was affected by the direction of flow for CH₄ gas. The total permeation rate of CH₄ was increased by about 15% when the PDMS side was exposed to the high pressure than when the plasma coating layer was

exposed to the high pressure [3].

The interfacial resistance to permeation of bilayer films is simply estimated using the "series resistance model" as [3]

$$\frac{L_o}{P_o} = \frac{L_A}{P_A} + \frac{L_B}{P_B} + R_{IF} \quad (1)$$

where, P_A and L_A are the permeability coefficient and film thickness of layer A, respectively, and P_B and L_B are for layer B, and P_o and L_o are for the overall composite membrane. R_{IF} represents the interfacial resistance to permeation. If layer A and B represent the substrate and plasma coating layer, respectively, a plot of L_o/P_o versus L_B gives a slope of $1/P_B$ and a y-intercept of $(L_A/P_A + R_{IF})$.

In this work, the temperature dependence of permeability coefficients of plasma polymers was examined. Arrhenius type of plots were made for the permeabilities of composite membranes, and the activation energies for permeation of plasma polymers were compared with those of commonly used perfluoropolymers.

2. Experimental

The plasma polymerization system and experimental procedures are the same as described previously [2]. Porous Celgard (Hoechst Celanese) and non-porous PDMS (Dow Corning Corp.) films were used as substrates for plasma polymerization. The thickness of PDMS used was $0.292\text{mm} \pm 1\%$. Monomers used were pentafluoropyridine (PFP) and pentafluorotoluene (PFT), which were supplied from Aldrich Chemical Co.

The apparatus for permeation measurements was shown previously [2]. Permeant gases used are N_2 , O_2 , CH_4 and CO_2 , all of which were supplied from Linde division of Union Carbide Corp.

3. Results and Discussions

Figures 1 and 2 show the temperature dependence of permeability coefficients of PFP and PFT plasma-polymerized films deposited on Celgard, in the form of semilogarithm plots of the permeability

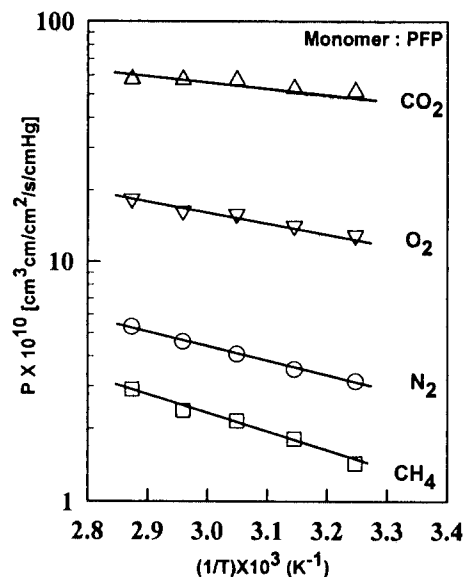


Fig. 1. Temperature dependence of the permeability coefficients of the plasma films deposited on Celgard.

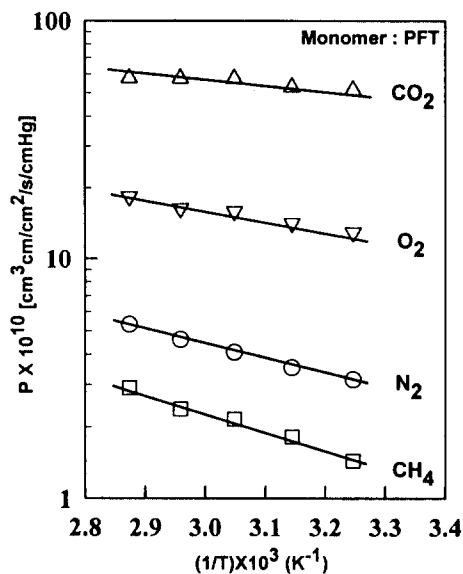


Fig. 2. Temperature dependence of the permeability coefficients of the plasma films deposited on Celgard.

versus the reciprocal of the absolute temperature, $1/T$, in accordance with the Arrhenius equation.

$$P = P_o' \exp \left[\frac{-E_p}{RT} \right] \quad (2)$$

where, P_o' is a constant, and E_p is the activation energy for permeation. The temperature was varied between 35°C and 75°C. In Figures 1 and 2, the permeability coefficients increase with increasing temperature as is usually the case for commonly used polymer membranes. All the data points in the figures fall reasonably on straight lines in the temperature range studied. This implies that the permeability of the plasma films obeys the Arrhenius relationship.

Activation energies for permeation and preexponential factors for the plasma films are presented in Table 1. The plasma films derived from PFP and PFT showed similar activation energies for

Table 1. Permeation parameters in plasma films deposited on Celgard

Gas	Monomer : PFP		Monomer : PFT	
	$P_o' \times 10^{-8}$	E_p	$P_o' \times 10^{-8}$	E_p
N ₂	3.59	2.79	3.03	2.80
CH ₄	3.22	3.45	3.97	3.56
O ₂	4.95	2.13	4.44	2.10
CO ₂	2.18	0.70	1.53	0.66

Units: P_o' [$\text{cm}^3/\text{cm}^2/\text{sec}/\text{cmHg}$] and E_p [Kcal/mol]

the same gases. This result is reasonable since PFP and PFT plasma-polymerized films showed similar gas transport behavior [2]. In Table 1, the activation energy increased as the size of penetrant molecules increased. This suggests that the larger the size of penetrant molecules, the more the energy is required for the penetrant to permeate through the polymer [4]. The activation energies for permeation of the plasma polymers are much lower than those of commonly used polymers [5]. For example, the activation energies of the plasma polymer for O₂ and N₂ are approximately half as high as those of poly(tetrafluoroethylene) [PTFE] for the same gases, and the activation energy for CO₂ is about 4 times lower than that of PTFE (Table 2).

The temperature dependence of permeability

depends on two contributing components: the diffusion coefficient (D) and solubility coefficient (S), of which the temperature dependence is expressed by Arrhenius-type relationships according to the equations, $D = D_o \exp[-E_d/RT]$ and $S = S_o \exp[-\Delta H_s/RT]$. E_d and ΔH_s represent the activation energy for diffusion and the heat of solution, respectively. The activation energy for permeation (E_p) is correlated with E_d and ΔH_s by equation (3), simply applying the relationship $P = DS$.

$$E_p = E_d + \Delta H_s \quad (3)$$

The diffusion activation energy (E_d) of polymers usually has a positive value, and the heat of solution (ΔH_s) has a negative or positive value.

The temperature dependence of solubility coefficients of the plasma polymers was measured using Cahn Microbalance. The heat of solution of PFP and PFT plasma polymers ranged -9 to -9.5 for CO₂ gas as shown in Table 2. For the other gases, precise data were not obtained due to system limitations as described previously [2].

Table 2 compares activation energies and heat of solutions of plasma polymers with those of perfluoropolymers. The data for ΔH_s of the plasma polymer for O₂ and N₂ were taken from literature data for hexafluorobenzene [HFB] plasma films [6], since HFB, PFP and PFT plasma polymerized films showed similar gas transport behavior [2] and they were expected to have similar gas solubilities. In Table 2, the activation energies for diffusion of plasma polymers were obtained using equation (3). The heat of solutions of the plasma polymer were much lower than those of perfluoropolymers, while the activation energies for diffusion were comparable with each other.

Thermodynamically, it has been shown that the heat of solution has a highly negative value when there is specific interactions between solute and solvent in gas-liquid systems [7]. It is likely that much lower ΔH_s of the plasma polymers is due to specific interactions between the sorbed gas and plasma polymer, since plasma polymers have free radicals and active components in the matrices.

Figure 3~5 show the temperature dependence of

Table 2. Gas Transport Parameters in Polymers

Gas	Plasma Polymer			PTFE / FEPb		
	E_p	ΔH_s	E_d	E_p	ΔH_s	E_d
N ₂	2.8	-8.5 ^a	11.3	5.8 / 7.3	-1.3 / -1.9	7.1 / 9.2
O ₂	2.1	-8.5 ^a	10.6	4.5 / 6.1	-1.7 / -2.2	6.3 / 8.3
CH ₄	3.4	-	-	- / 8.3	- / -2.6	- / 10.9
CO ₂	0.7	-9.5	10.2	3.3 / 5.0	-3.5 / -3.8	6.8 / 8.8

^a E and ΔH have a unit of [Kcal/mol]

^{a)} Taken from literature data for hexafluorobenzene plasma polymer.

^{b)} FEP refers to a copolymer of hexafluoropropylene and tetrafluoroethylene

overall permeability coefficients of composite membranes with different coating thicknesses of PFP plasma films deposited on PDMS. CH₄(B) in Figure 5 refers to the permeation when the PDMS side is exposed to the high pressure (backward), while the other cases in Figures 3 and 4 refer to the permeation when the plasma coating layer is exposed to the high pressure (forward). Filled circles in the figures represent the data for untreated PDMS. All the data points fall reasonably on straight lines as shown in the figures. The dense plasma coating decreased the overall permeabilities of the composite membranes with increase in coating thickness. Similar plots were made for composite membranes with PFT plasma coating layers. (The plots are not shown here.)

The permeation activation energies of composite membranes with different coating thickness are presented in Tables 3 and 4. The activation energy of CO₂ in untreated PDMS was negative, i.e., the permeability coefficient of CO₂ decreased with increasing temperature, while the activation energies of the other gases were positive. The same result was obtained for PDMS by Stern et al. [6]. The temperature dependence of permeability depends on both that of diffusion and solubility coefficient. The diffusion coefficient always increases with increasing temperature due to an increase in the chain mobility of polymers, while the solubility coefficient generally decreases with temperature. It seems that the increase in the diffusion coefficient of PDMS for CO₂ with

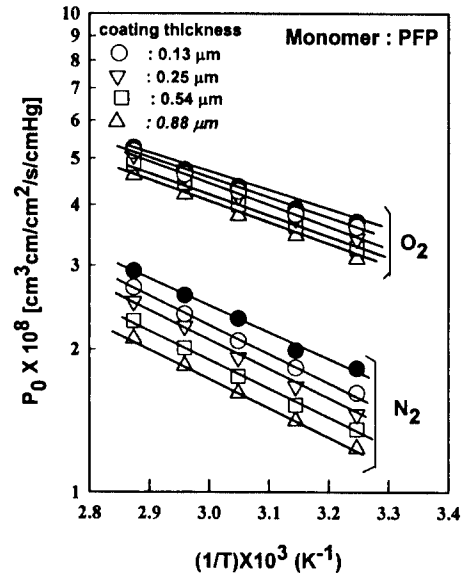


Fig. 3. Temperature dependence of overall permeability coefficients of composite membranes with PDMS substrates: The filled circles represent the data for untreated PDMS.

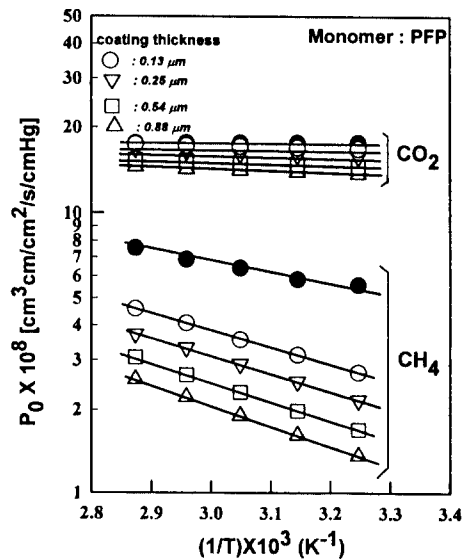


Fig. 4. Temperature dependence of overall permeability coefficients of composite membranes with PDMS substrates: The filled circles represent the data for untreated PDMS.

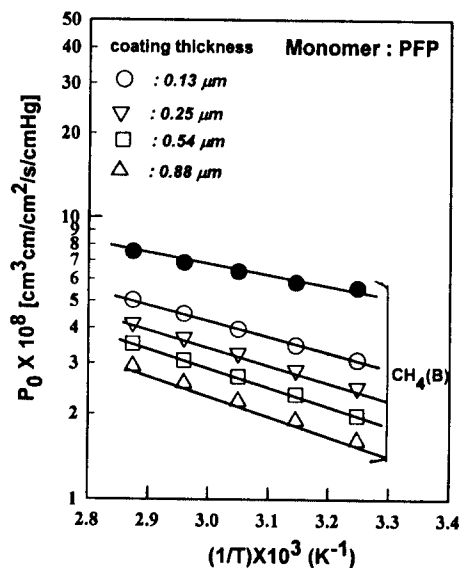


Fig. 5. Temperature dependence of overall permeability coefficients of composite membranes with PDMS substrates: The filled circles represent the data for untreated PDMS.

Table 3. Overall activation energies for permeation in composite membranes with the PFP plasma coating layer and PDMS layer [Kcal/mol]

membrane		N ₂	CH ₄	CH ₄ (B)	O ₂	CO ₂
PDMS(untreated)		2.58	1.63	1.63	1.90	-0.02
Composite membrane	L _B =0.13 μm	2.73	2.79	2.61	2.01	0.18
	L _B =0.25 μm	2.77	2.88	2.74	2.07	0.26
	L _B =0.54 μm	2.79	3.15	3.04	2.10	0.28
	L _B =0.88 μm	2.82	3.34	3.18	2.11	0.33
Composite membrane (Celgard substrate)		2.79	3.45	3.45	2.13	0.70

· L_B refers to the thickness of the plasma coating layer

temperature is smaller than the simultaneous decrease in the corresponding solubility coefficient. This is not the case for the other gases.

In Tables 3 and 4, the overall activation energy for permeation in composite membranes increased with increasing thickness of the plasma coating

Table 4. Overall activation energies for permeation in composite membranes with the PFT plasma coating layer and PDMS layer [Kcal/mol]

membrane		N ₂	CH ₄	CH ₄ (B)	O ₂	CO ₂
PDMS(untreated)		2.58	1.63	1.63	1.90	-0.02
Composite membrane	L _B =0.12 μm	2.74	2.80	2.62	1.98	0.17
	L _B =0.25 μm	2.76	2.86	2.77	2.01	0.26
	L _B =0.50 μm	2.80	3.08	2.93	2.03	0.28
	L _B =0.80 μm	2.82	3.25	3.16	2.06	0.30
Composite membrane (Celgard substrate)		2.80	3.56	3.56	2.10	0.66

· L_B refers to the thickness of the plasma coating layer

layer for each gas, in the range between the activation energy of PDMS and that of the same plasma film deposited on Celgard (Permeation through plasma films deposited on Celgard are assumed not to be affected by the direction of flow, and the CH₄ activation energies of the plasma film on Celgard are the same for both directions in Tables 3 and 4). It was also found that the larger the size of penetrant molecules, the activation energy was more affected by the coating layer thickness. Similar results were obtained by Spencer et. al. [8]. They investigated the temperature dependence of overall permeabilities of hydrogen (d=2.89Å) and methane (d=3.8Å) in composite membranes with cyanogen bromide plasma coating layers deposited on poly (phenyleneoxide). Their result showed that the plasma coating layer affected the activation energy for CH₄ permeation (4.1 increased to 10.4 Kcal/gmol) much more than it affected the activation energy for H₂ permeation (1.7 increased to 3.9 Kcal/gmol) through the composite membrane.

To consider the temperature dependence of the permeability coefficients of the coating layer and interfacial region in composite membranes with PDMS substrate, the plots of L_o/P_o versus the coating thickness are made at every temperatures, based on equation (1), and presented in Figures 6 to 8. In the figures, straight lines were obtained by least-square fits of data points. The slopes of the

lines for each gas show decreasing gradient as temperature increase for all the gases, which implies that the permeabilities of the coating layer increase with increasing temperature.

Figure 9 shows the temperature dependence of the gas permeabilities of the PFP plasma coating layer, estimated from the slopes of the lines in Figures 6 through 8. Figure 10 shows the temperature dependence of the apparent permeation rates of the interfacial region for CH₄ gas, which showed directional dependence of permeation and the greatest interfacial resistance to permeation [3]. The apparent permeation rate is taken as the reciprocal of the interfacial resistance, 1/R_{IF}, which has the same unit as (P/L). All the data points for the coating layer and interfacial layer fall on straight lines fairly well.

Table 5 shows the activation energies for permeation of the plasma coating layer and interfacial layer in composite membranes. The activation energy for permeation of the plasma coating layer deposited on PDMS was comparable to those of the same plasma film deposited on Celgard for the same gases. Comparing the

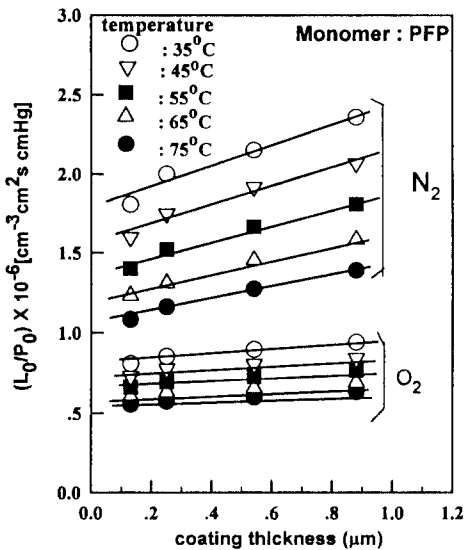


Fig. 6. Plot of L_0/P_0 versus coating layer thickness for composite membranes composed of plasma and PDMS layers.

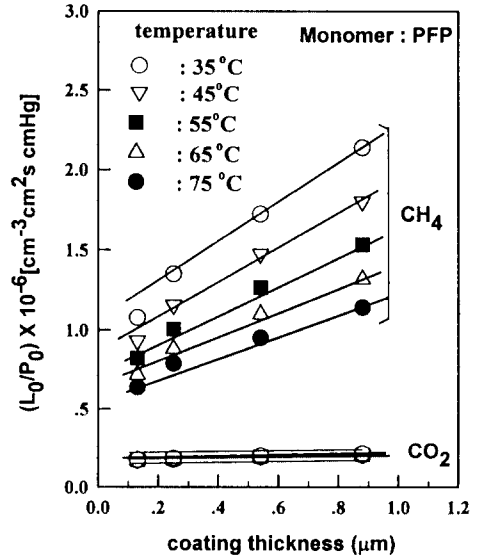


Fig. 7. Plot of L_0/P_0 versus coating layer thickness for composite membranes composed of plasma and PDMS layers.

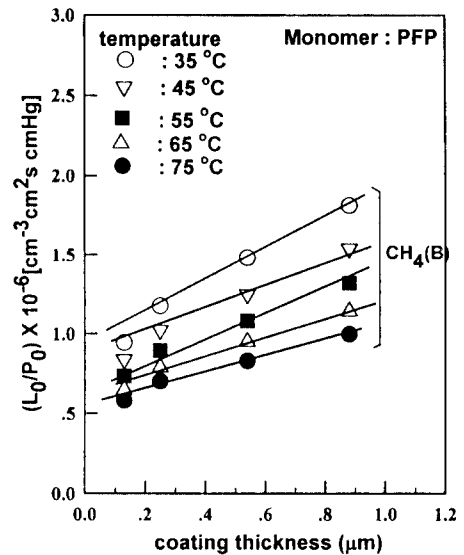


Fig. 8. Plot of L_0/P_0 versus coating layer thickness for composite membranes composed of plasma and PDMS layers.

activation energies for CH₄ permeation in the interfacial layer with those in the plasma coating

layer (Table 5) and PDMS layer (Table 3), it appears that the gas permeation properties of the interfacial layer are more similar to those of the coating layer rather than PDMS layer, suggesting that the interfacial region has crosslinking structure (with PDMS/plasma bondings) similar to the plasma coating layer.

It was previously discussed that the directional dependence of permeation through the composite membrane may be due to the difference in the activation energies of the interfacial region [3]. The change in activation energies for CH₄ of the interfacial layer for different directions of flow was almost negligible in Table 5. Simply applying equation (2) to the interfacial layer,

$$\begin{aligned} \frac{(P_{IF})_{f(ward)}}{(P_{IF})_{b(ackward)}} &= \frac{\left(\frac{1}{R_{IF}}\right)_f}{\left(\frac{1}{R_{IF}}\right)_b} \\ &= \frac{P_o' \exp[-E_p/RT]_f}{P_o \exp[-E_p/RT]_b} \\ &= \frac{(P_o')_f}{(P_o)_b} \exp\left[\frac{-[(E_p)_f - (E_p)_b]}{RT}\right] \end{aligned} \quad (4)$$

Inserting R_{IF} values into equation (4), the ratio of apparent permeation rate, (1/R_{IF})_f/(1/R_{IF})_b, is about

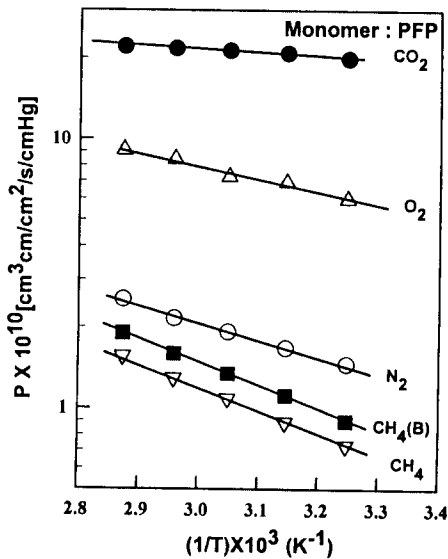


Fig. 9. Temperature dependence of the permeability coefficient of PFP plasma coating layer.

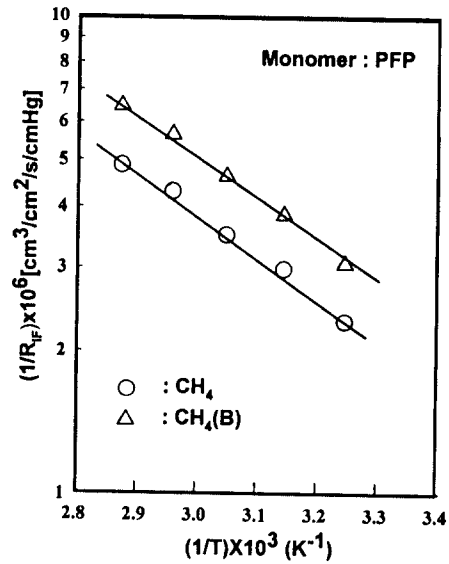


Fig. 10. Temperature dependence of the apparent permeation rate for CH₄ in the interfacial layer of the composite membrane.

Table 5. Activation Energies for permeation of the plasma coating and interfacial layer in composite membranes.

Gas	[Kcal/mol]					
	Coating layer (PDMS)		Interface		Plasma film (Celgard)	
	PFP	PFT	PFP	PFT	PFP	PFT
N ₂	2.87	2.95	-	-	2.79	2.80
CH ₄	4.03	3.90	3.96	4.17	3.45	3.56
CH ₄ (B)	3.96	3.87	4.01	4.01	3.45	3.56
O ₂	2.19	2.56	-	-	2.12	2.10
CO ₂	0.52	0.38	-	-	0.85	0.66

0.7 for CH₄ at 35°C. Assuming that (P_{o'})_f/(P_{o'})_b=1, the difference in activation energies, (E_p)_f-(E_p)_b, is about 0.2 Kcal/mol at 35°C. This difference is within error limits of the activation energy.

Table 6 shows the temperature dependence of the selectivities of PFP plasma polymers deposited on PDMS and Celgard. The selectivity for CO₂ to CH₄ in the plasma polymers deposited on PDMS was estimated, based on the CH₄ permeability when the plasma coating layer was exposed to the

high pressure. The selectivity for O_2 to N_2 and CO_2 to CH_4 decreased as temperature increased for all the cases. It seems to be due to a decrease in the diffusivity selectivity. Chain mobility of polymers increases with temperature. Increase in mobility increases the possibility for larger penetrant molecules to pass through the polymer, and therefore decreases the diffusivity selectivity [9]. Solubility selectivity is known to decrease with temperature in most polymers.

Table 6. Temperature Dependence of the Ideal Selectivity of PFP Plasma Polymers

Temperature (°C)	Coating layer (PDMS)		Plasma film (Celgard)	
	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$
35	4.1	27.3	4.1	46.2
45	3.9	23.5	3.9	41.7
55	3.8	19.6	3.8	37.2
65	3.7	16.7	3.7	33.8
75	3.5	14.0	3.6	27.8

4. Conclusions

Through the temperature dependence study in gas permeation through composite membranes, the following conclusions were made:

- (1) The permeability coefficients of fluorine-rich plasma polymers obeyed the Arrhenius relationship. The activation energy for permeation was dependent on the molecular size of penetrant gases — the larger the molecular size, the higher the activation energy.
- (2) The activation energies for permeation of the plasma polymers were lower than those of commonly used perfluoropolymers. This difference is attributable to be much lower heat of solutions of the plasma polymers compared to perfluoropolymers. The diffusion activation energies were comparable with each other.
- (3) The activation energy for CH_4 permeation of the interfacial layer in PDMS/plasma com

posite membranes was similar to that of the plasma coating layer. This suggests that the interfacial layer would show similar gas transport behavior as the plasma polymer.

Nomenclature

- L : membrane thickness [m]
 P : permeability coefficient [$cm^3(STP)cm/cm^2/sec/cmHg$]
 RIF : interfacial resistance to gas permeation [$cm^3(STP)/cm^2/sec/cmHg$]⁻¹
 Ep : activation energy for permeation [Kcal/mol]
 Ed : activation energy for diffusion [Kcal/mol]
 ΔH_s : heat of solution [Kcal/mol]

Subscripts

- o : overall composite membrane
 1 : layer 1 (PDMS layer) in the composite membrane
 2 : layer 2 (plasma coating layer) in the composite membrane

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