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Separation of Ethane/Ethylene and Propane/Propylene Systems with a Carbonized BPDA–pp'ODA Polyimide Membrane

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A BPDA–pp'ODA polyimide film was formed on the outer surface of a porous alumina support tube (outside diameter, 2.4 mm; inside diameter, 1.8 mm; void fraction, 0.48; and average pore size, 140 nm) and was then carbonized at an optimized temperature of 700 °C. Membranes prepared by repeating this process two and three times respectively exhibited permeances of approximately $1 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ for C_2H_4 and $2 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ for C_2H_6 at 100 °C. Permeances to C_3H_6 and C_3H_8 at 100 °C were 4×10^{-9} and $1 \times 10^{-10} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, respectively. The selectivities were 4–5 for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ systems and 25–29 for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ systems. When the permeation temperature was decreased to 65 and 35 °C, permeances decreased and selectivities increased to 5–7 for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ systems and 33–56 for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ systems. The permeance and selectivity for an equimolar mixture of C_3H_6 and C_3H_8 were nearly the same as those for the single-component gases.

Introduction

Separation of hydrocarbon gases using membrane technology represents an attractive energy-saving process which includes no phase transformation steps (Eldridge, 1993). Various types of polyimide membranes have recently been developed, and a considerable body of data has been collected (Robeson, 1991; Stern, 1994; Koros, 1995) relative to membrane permeability and permselectivity. Figure 1 shows some typical polyimide structures from which membranes can be prepared. Membranes based on 2,2-bis(3,4-decarboxyphenyl)hexafluoropropane dianhydride (6FDA) are capable of achieving both high selectivity and permeability as a result of the bulky structure of the $-\text{C}(\text{CF}_3)_2-$ substituent group. Matsumoto and Xu (1993a) prepared 6FDA-based asymmetric membranes using phase separation techniques. Membranes prepared by them exhibited an O_2/N_2 permselectivity of 5–6 and an O_2 permeance on the order of $10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. Rezac et al. (1994) modified glassy polymer membranes using a variety of reagents, but the permeance to O_2 was less than $10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ when the O_2/N_2 selectivity was higher than 5–6. The separation of propylene (C_3H_6) and propane (C_3H_8) was investigated by Ito and Hwang (1989), who employed a cellulosic membrane, but the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ permselectivity was less than 4. Lee and Hwang (1992) used a polyimide membrane, which exhibited a $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity of approximately 10. Ilinitch et al. (1992) prepared copolymer membranes of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(2,6-diphenyl-1,4-phenylene oxide) and reported high permselectivities for alkene/alkane separation. The relationship between gas permeabilities and physical properties of polymers has been investigated by a number of investigators (Kim et al., 1988; Stern et al.,

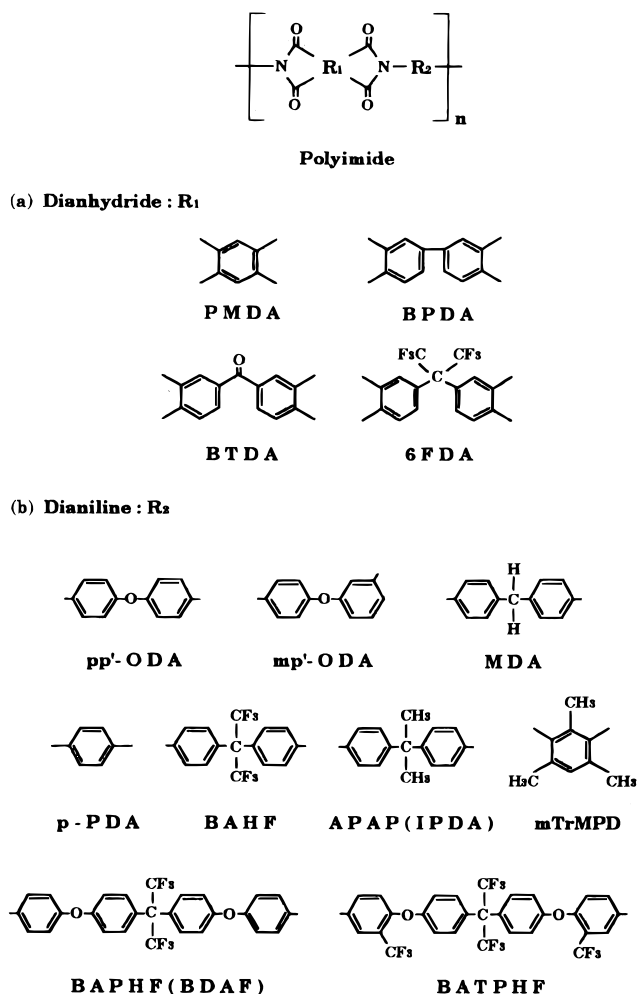


Figure 1. Chemical structures of polyimide compounds.

1989; Yamamoto et al., 1990; Tanaka et al., 1992a,b; Matsumoto et al., 1993a,b; Stern, 1994). Polyimide membranes are permselective below the glass transition temperature, which is usually lower than 300 °C.

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On the other hand, silica-based inorganic membranes are usable at elevated temperatures and are mainly used to separate hydrogen from other gases (Yan et al., 1994; Morooka et al., 1995, 1996; Jiang et al., 1995). Raman and Brinker (1995) reported that silica membranes, modified with monomeric tetraethylorthosilicate (TEOS), exhibited a CH_4/CO_2 selectivity of 36–71 at a CO_2 permeance of $10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$. Except for Asaeda et al. (1995), no workers have reported on the applicability of silica membranes to the separation of alkene and alkane samples which contain the same number of carbon atoms. Zeolite membranes are capable of separating hydrocarbon isomers, such as *i*-butane and *n*-butane, based on differences in molecular size (Jia et al., 1993; Vroon et al., 1995; Yan et al., 1995; Kusakabe et al., 1996), but no information is available on alkene/alkane separations.

It is also known that carbonization of polymer films such as polyimide and poly(furfulyl alcohol) leads to carbon membranes capable of functioning as molecular sieves (Koresch and Soffer, 1983; Jones and Koros, 1995a,b). Hayashi et al. (1995) coated a poly(amic acid) film synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) on the outer surface of a porous alumina support tube. The film was imidized to a polyimide membrane (BPDA-pp'ODA), which was then carbonized at 500–900 °C. Carbonization above 600 °C significantly increased permeance to He, CO_2 , CH_4 , N_2 , and C_2H_6 . Permeance to CO_2 and CO_2/CH_4 permselectivity of the carbonized membrane at 30 °C were $10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ and 100, respectively. The carbonization temperature constituted an important factor in the production of carbon molecular sieves, and the pore structure was further controlled by chemical vapor deposition of carbonaceous matter (Hayashi et al., 1996). Selectivities obtained with carbonized membranes are generally much higher than those of polymeric membranes (Koresch and Soffer, 1983; Jones and Koros, 1995a,b; Hayashi et al., 1996). Since carbon membranes involve high production costs, however, permeability and permselectivity of carbonized membranes require further refinements and improvements before they can be used on a large industrial scale.

In this study, BPDA-pp'ODA polyimide was coated on a porous ceramic hollow tube and carbonized at 700 °C. A process of coating, imidization, and carbonization was repeated, and permeance and permselectivity of small molecules through the membranes were determined. Separation of gases from equimolar mixtures of ethylene/ethane ($\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$) and propylene/propane ($\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$) systems was also investigated.

Experimental Section

Preparation of the Carbonized Polyimide Membrane. The procedure used for the membrane is shown in Figure 2. Powdered samples of BPDA and ODA (15 mmol each) were separately suspended in 30–40 mL of *N,N*-dimethylacetamide (DMAc) which was distilled prior to use. The suspension of BPDA was then added dropwise to the ODA in an inert atmosphere. The resulting solution was stirred at 15 °C for 1 h and at 25 °C for a further 3 h. A homogeneous poly(amic acid) solution was thus obtained. The weight concentration of poly(amic acid) was 8–9%.

A porous α -alumina tube manufactured by NOK Corp., Japan, was used as the support to give the membrane mechanical strength (Yan et al., 1994). The dimensions of the support tube were as follows: outside

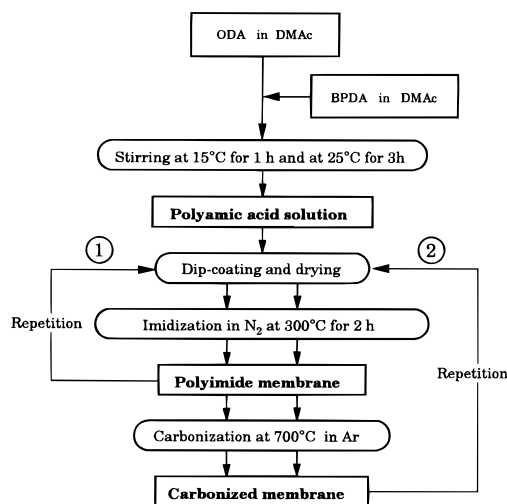


Figure 2. Membrane preparation procedures.

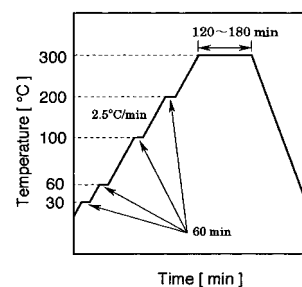


Figure 3. Temperature program for imidization.

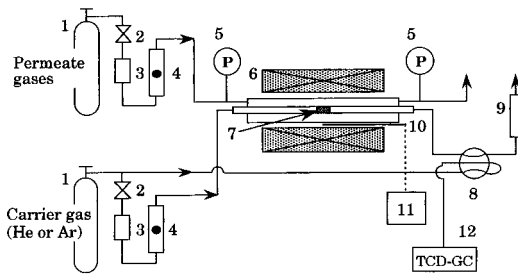


Figure 4. Schematic diagram of the experimental apparatus: (1) gas cylinder; (2) stop valve; (3) mass flow controller; (4) flowmeter; (5) pressure gauge; (6) furnace; (7) membrane; (8) six-way valve; (9) soap-film flowmeter; (10) thermocouple; (11) thermoregulator; (12) gas chromatograph.

diameter, 2.4 mm; inside diameter, 1.8 mm; void fraction, 0.48; and average pore size, 140 nm. The BPDA-pp'ODA polyimide membrane was prepared by dip-coating. The support tube, one end of which was capped with silicone rubber, was dipped in the poly(amic acid) solution for 5 min at 25 °C. The tube was then pulled out of the solution at a rate of ca. 8 mm/s. After air-drying at 25 °C for 12 h, the poly(amic acid) film formed on the outer surface of the support tube was imidized in nitrogen using the multistep heating procedure shown in Figure 3. Carbonized membranes were formed by two procedures by using the reactor system shown in Figure 4. In the first procedure, the coating-imidization cycle was repeated three times, resulting in a pinhole-free BPDA-pp'ODA membrane. The membrane was carbonized in a deoxygenated argon stream at a heating rate of 5 °C/min to 700 °C with no isothermal period and then allowed to cool down to ambient temperature. This membrane is hereafter referred to as 3I-1C. In the second procedure, the coating-imidization-carbonization process was repeated two or three times. These membranes are

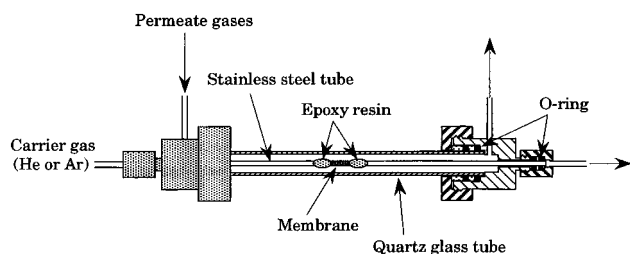


Figure 5. Details of membrane sealing.

referred to as 2(I-C) and 3(I-C), respectively. Hayashi et al. (1995) found that carbonization at temperatures lower than 500 °C had little effect on the permeance of the membrane but that, at 600–700 °C, permeance increased drastically. Permeance to He was 100–500 times larger than that of the initial polyimide membrane. The membrane carbonized at 700 °C exhibited permeances higher than the membrane carbonized at 750 °C, while the permselectivities were not greatly changed. Based on these results, the carbonization temperature in the present study was fixed at 700 °C. The morphologies of the support tube and membranes were observed with a scanning electron microscope (Hitachi S-900).

Characterization of Membranes. Permeation of the *i*-component gas through a membrane is described as follows:

$$q(i) = P(i) [p_H(i) - p_L(i)] \quad (1)$$

where $q(i)$ and $P(i)$ are the flux and permeance of the *i*-component, respectively. $p_H(i)$ and $p_L(i)$ are the partial pressure of the *i*-component at the feed and permeate sides, respectively, and are obtained by logarithmically averaging the partial pressures at the inlet and outlet of each side. When the membrane is symmetrical with a thickness of δ , the permeability $P(i)$ is given by the following equation.

$$P(i) = P'(i) \delta \quad (2)$$

In the present study, δ was defined as the thickness of the carbon film. The permselectivity of the *i*-component relative to the *j*-component is calculated from

$$\alpha(i/j) = P(i)/P(j) = P'(i)/P'(j) \quad (3)$$

The permselectivity is constant in a narrow pressure range. Permeance to single-component penetrants; He, CO₂, O₂, N₂, CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ was measured at 35, 65, and 100 °C. Permeance to each component in mixtures of C₂H₄/C₂H₆ and C₃H₆/C₃H₈ systems was also determined. As indicated in Figure 5, each end of the membrane tube was connected to a stainless steel tube with an epoxy resin. The length of the membrane was about 10 mm. Penetrant gas was introduced without dilution into the feed side (outside of the tube), and helium or argon was fed to the permeate side (inside of the tube) as the carrier. Flow rates on the feed and permeate sides were measured with soap film flowmeters. The total pressure on both sides of the membrane was maintained at 101.3 kPa throughout the experiment, and the effect of the total pressure on permeance was not determined. The concentration of the penetrant gas on the permeate side was determined with a TCD-GC (Shimadzu GC-8A) and was maintained in the range of 0.1–1 vol % by varying

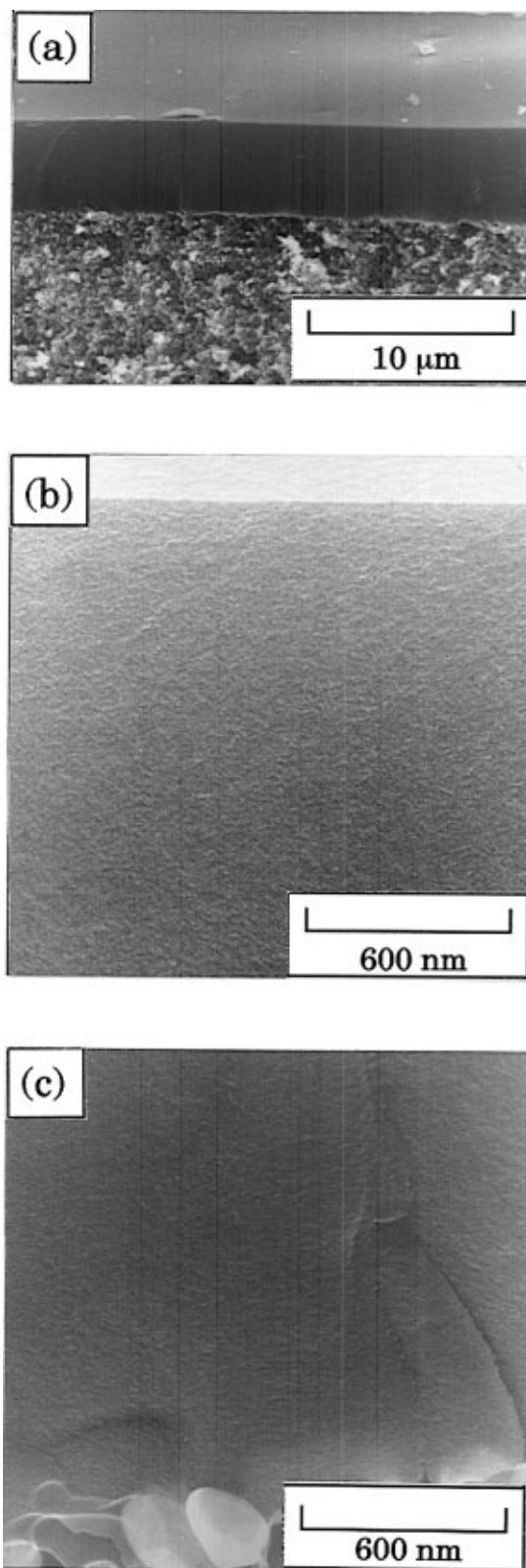


Figure 6. Scanning electron microscope images of 3(I-C) membrane: (a) overview of fractured section; (b) fractured section near the top surface; (c) fractured section near the support.

the carrier flow rate. The permeance was unaffected by the carrier flow rate under the test conditions.

Results and Discussion

Membrane Structure and Permeance. Figure 6 shows the fractured sections of the carbonized membrane 3(I-C). The top surface was very smooth without pinholes, and the thickness was 5–6 μm. A single

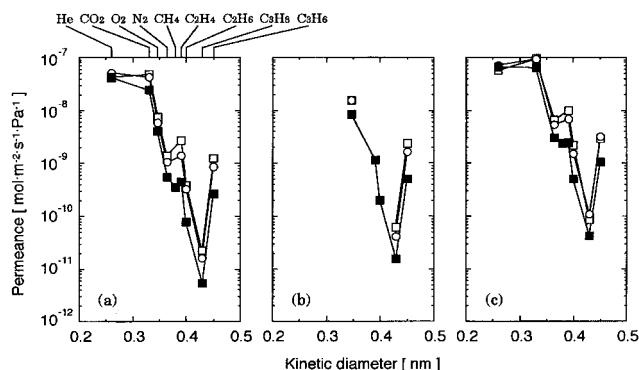


Figure 7. Effect of the membrane preparation process on the relationship between permeance and kinetic diameter of permeates. Preparation process: ■, 3I-1C; ○, 2(I-C); □, 3(I-C). Permeation temperature: (a) 35, (b) 65, (c) 100 °C.

Table 1. Activation Energy for Permeance to a Single-Component Gas

membrane	activation energy (kJ·mol ⁻¹)							
	He	CO ₂	O ₂	N ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
3I-1C	6.3	14	21	25	25	28	20	30
2(I-C)	5.0	11	28	24	23	23	19	28
3(I-C)	4.6	10	22	23	19	26	17	26

carbonized layer was observed, even though the coating-imidization process was repeated three times. This suggests that BPDA–pp'ODA was partially dissolved in DMAc after imidization. The micropore volume of the membrane carbonized at 700 °C was determined by a molecular probe method which had been described by Hayashi et al. (1995). The micropore volume for CO₂ was increased to $2.5 \times 10^{-4} \text{ m}^3 \cdot \text{kg}^{-1}$ by carbonization from $1.4 \times 10^{-5} \text{ m}^3 \cdot \text{kg}^{-1}$ of the initial polyimide.

In Figure 7, permeance to single-component gases at 35, 65, and 100 °C is plotted against the kinetic diameter of permeating molecules (Breck, 1974). The permeance of the 3I-1C membrane was smaller than that of the 2(I-C) and 3(I-C) membranes. The difference between permeances of the 2(I-C) and 3(I-C) membranes was within experimental error. The order for the permeances is not in agreement with the order of the kinetic diameters. The alkenes C₂H₄ and C₃H₆ moved faster than the corresponding alkanes C₂H₆ and C₃H₈.

Table 1 reveals the activation energy for permeation. The activation energy increased with increasing size of the permeating molecules. If the permeation rate is dominated by the sorption equilibrium of the permeating gas in the membrane, the activation energy of gas moving at a faster permeation rate is smaller and normally negative. As listed in Table 1, the alkenes showed activation energies comparable to those of the other gases. This suggests that permeation was controlled by an activated diffusion mechanism rather than a surface diffusion mechanism. The dimensions of the alkene and alkane molecules were calculated from a DREIDING force field (Mayo et al., 1990). The smallest dimensions of a rectangular box which just contains molecules of C₂H₆ and C₂H₄ are 0.41 and 0.37 nm, while those for C₃H₈ and C₃H₆ are 0.43 and 0.40 nm, respectively. Since polyimides are easily graphitized without pressurization (Inagaki et al., 1991), carbonized membranes formed from polyimides possibly possess, to some extent, a graphite structure and recognize molecules by their smallest dimension. These may be the reasons why alkenes are more permeable than corresponding alkanes. Permeation of C₂H₄ or C₂H₆ is faster than C₃H₆ or C₃H₈ because C₃ molecules are longer than C₂ ones.

Table 2. Permselectivity of Carbonized Membranes for Single-Component Systems

membrane	permeation temp (°C)	selectivity	
		C ₂ H ₄ /C ₂ H ₆	C ₃ H ₆ /C ₃ H ₈
3I-1C	100	4.8	25
	65	5.7	33
	35	5.9	49
2(I-C)	100	4.5	29
	35	4.4	54
3(I-C)	100	4.5	29
	35	6.9	56

Table 3. Permeance and Permselectivity of a 2(I-C) Membrane for Mixed-Component Systems^a

permeation temp (°C)	C ₃ H ₆ permeance (mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹)	C ₃ H ₆ /C ₃ H ₈ selectivity
100	2.9×10^{-9} (3.1×10^{-9})	33 (29)
65	1.5×10^{-9} (1.7×10^{-9})	38 (40)
35	7.9×10^{-10} (8.7×10^{-10})	46 (54)

^a Numerals in the parentheses were obtained for single-component systems.

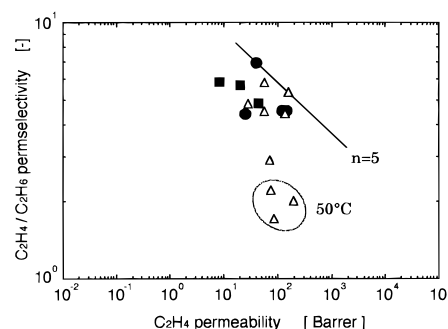


Figure 8. Relationship between C₂H₄/C₂H₆ selectivity and C₂H₄ permeability: Δ, Ilmitch et al. (1992), PPO and PPO copolymers, $T = 20\text{--}50$ °C; ■, 3I-1C membrane, $T = 35\text{--}100$ °C; ●, 2(I-C) and 3(I-C) membranes, $T = 35\text{--}100$ °C.

Table 2 shows permselectivities of the carbonized membranes for the C₂ and C₃ hydrocarbons. At 35 °C, the membranes exhibited a C₂H₄/C₂H₆ selectivity of 5–7 and a C₃H₆/C₃H₈ selectivity of 49–56. The selectivities for the C₂H₄/C₂H₆ and C₃H₆/C₃H₈ systems decreased with increasing permeation temperature but were as high as 4–5 and 25–29, respectively, at 100 °C. The membrane formed by repeating the coating-imidization-carbonization process three times was more permselective than that prepared by repeating the coating-imidization process three times and by a final carbonization. Table 3 shows the relationship between C₃H₆ permeance and C₃H₆/C₃H₈ permselectivity for the 2(I-C) membrane. Both permeance and selectivity for the equimolar mixtures were approximately equal to those for the single-component systems.

Selectivity-Permeability Relationship. Figure 8 reveals the relationship between C₂H₄/C₂H₆ selectivity and C₂H₄ permeability. In the figure caption, T is the permeation temperature. To compare permeation rates of carbonized membranes to those of polyimide membranes, the permeance was converted to the permeability that is often adopted for polymeric membranes. Since the carbonized membrane prepared in the present study was about 5.5 μm thickness, $1 \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ corresponds to 1.6×10^{10} barrer ($1 \text{ barrer} = 3.4 \times 10^{-16} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$). Poly(phenylene oxide) and copolymer membranes prepared by Ilmitch et al. (1992) exhibited a C₂H₄/C₂H₆ selectivity of 5.8 at 20 °C. However, this selectivity decreased to 1.7 at 50 °C. Poly(phenylene oxide) shows the glass transition at 220 °C (Toi et al., 1982). Thus, their membranes would be

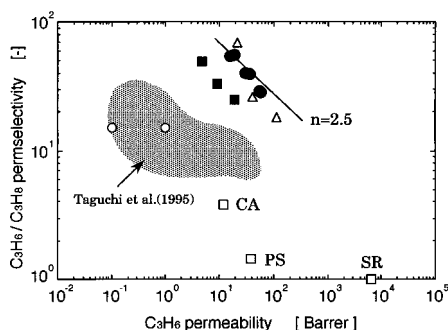


Figure 9. Relationship between C_3H_6/C_3H_8 selectivity and C_3H_6 permeability: \square , Ito and Hwang (1989), cellulose acetate (CA), polysulfone (PS), and silicon rubber (SR), $T = 40^\circ\text{C}$; \circ , Lee and Hwang (1992), polyimide, $T = 30\text{--}70^\circ\text{C}$; Δ , Ilinitch et al. (1992), PPO and PPO copolymers, $T = 20\text{--}50^\circ\text{C}$; dotted zone, Taguchi et al. (1995), 6FDA-based polyimides, $T = 50^\circ\text{C}$; \blacksquare , 3(I-C) membrane, $T = 35\text{--}100^\circ\text{C}$; \bullet , 2(I-C) and 3(I-C) membranes, $T = 35\text{--}100^\circ\text{C}$.

expected to be permselective at low temperatures. The selectivities and permeabilities obtained at $35\text{--}100^\circ\text{C}$ with the carbonized membranes in the present study are, thus far, the best among heat-resisting polymeric membranes. It should be noted that the performance of the carbonized membranes was maintained at a temperature as high as 100°C .

As indicated by Stern (1994) and Koros (1995), there is a trade-off in the relationship between selectivity $\alpha(i/j)$ and permeability P_i . The trade-off line is described as

$$\alpha(i/j) = P_i^{-1/n} \quad (4)$$

For separation of O_2/N_2 systems with polyimide membranes, the selectivity is 10 at most and the n -value is 5–7. On the other hand, for separation of CO_2/CH_4 systems with polyimide membranes, the selectivity is 100 at most and the n -value is 2.5. Although the trade-off relationship is not definite for the C_2H_4/C_2H_6 systems because of the limited number of data, the n -value appears to be 4–5. Thus, an increase in selectivity by 1 order of magnitude corresponds to a decrease in permeability of 4–5 orders.

Figure 9 shows the relationship between C_3H_6/C_3H_8 selectivity and C_3H_6 permeability. The polysulfone and silicon rubber membranes used by Ito and Hwang (1989) showed selectivities of 3.5 and 1.2, respectively, for the C_3H_6/C_3H_8 system. Their cellulose acetate membrane exhibited relatively high selectivities but was not usable at elevated temperatures. The unspecified polyimide membrane used by Lee and Hwang (1992) exhibited a C_3H_6/C_3H_8 selectivity above 10, but the permeability was low. The carbonized membranes prepared in the present study and the PPO-based membranes of Ilinitch et al. (1992) gave high C_3H_6/C_3H_8 selectivities at high C_3H_6 permeabilities. However, the durability of the PPO-based membranes has not been determined. Taguchi et al. (1995) prepared and tested various 6FDA-based polyimide membranes. The performance of their membranes is indicated by the dotted area in Figure 9.

In order to compare the utility and efficiency of the membranes prepared in the present study to those of membranes reported in the literature, the relationship between CO_2/N_2 selectivity and CO_2 permeability was examined, largely because abundant data are available for that system. Permselectivity of CO_2 to CH_4 is normally higher than that of CO_2 to N_2 . Figure 10 reveals major experimental data, and Table 4 shows the conditions for obtaining these data. The trade-off relationship between permeability and permselectivity

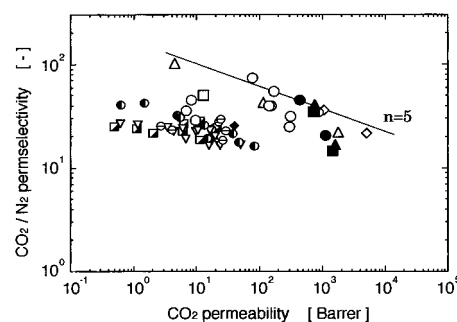


Figure 10. Relationship between CO_2/N_2 selectivity and CO_2 permeability. Keys and conditions are listed in Table 4.

Table 4. Conditions of Carbonized and Polyimide Membranes

investigator	membrane (precursor)	key in Figure 10
Carbonized Membrane		
Koresh and Soffer (1983)	not given	\diamond
Hatori et al. (1992)	(PMDA-ODA)	\square
Suda et al. (1995)	(PMDA-ODA)	Δ
Hayashi et al. (1995)	(BPDA-pp'ODA)	\circ
this study		
3I-1C	(BPDA-pp'ODA)	\bullet
2(I-C)	(BPDA-pp'ODA)	\blacktriangle
3(I-C)	(BPDA-pp'ODA)	\blacksquare
Uncarbonized Polyimide Membrane		
Kim et al. (1988)	6FDA-based	\ominus
Stern et al. (1989)	PMDA- and 6FDA-based	\blacksquare
Tanaka et al. (1992b)	BPDA-, BTDA-, and 6FDA-based	∇
Matsumoto et al. (1993a)	6FDA-pPDA	\blacklozenge
Kita et al. (1994)	BTDA-TrMPD and BTDA/6FDA-TrMPD	\bullet

of polyimide membranes is much improved when polyimide is carbonized under optimized conditions. A carbonized BPDA-pp'ODA polyimide membrane by Hayashi et al. (1995) exhibited a CO_2/N_2 selectivity of 29–55 at 30°C . When the carbonized membrane was modified by chemical vapor deposition with propylene as the carbon source, the CO_2/N_2 selectivity was further increased to 73.4 at 35°C (Hayashi et al., 1996). This suggests that CVD modification is effective and serves to narrow the micropores of the membrane. The CO_2/N_2 selectivity of carbonized membranes shown in Figure 10 is quite high, compared to CO_2/N_2 selectivity of polyimide membranes in the literature. The repetition of coating-imidization-carbonization served to increase the membrane performance for CO_2/N_2 systems. As shown in Figure 7, the CO_2 permeance reached $10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ at 100°C , and the CO_2/N_2 selectivity was 35 at 35°C and 15 at 100°C . The relationship between CO_2/CH_4 selectivity and CO_2 permeance for the carbonized membranes formed in the present study was comparable to that for the TEOS-modified silica membrane prepared by Raman and Brinker (1995).

Conclusions

A BPDA-pp'ODA polyimide membrane was formed on a porous α -alumina support tube and carbonized at 700°C in an inert atmosphere. The resulting membrane was pinhole-free and $5\text{--}6 \mu\text{m}$ thick. The permeances of C_2H_4 and C_2H_6 at 100°C were approximately 1×10^{-8} and $2 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$, respectively. Those of C_3H_6 and C_3H_8 at 100°C were approximately 4×10^{-9} and $1 \times 10^{-10} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$, respectively. Carbonization under optimum conditions shifted the trade-off relationship of the BPDA-pp'ODA

polyimide membrane toward the direction of higher selectivity and permeability.

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