

Gas Separation Properties of Polymers Containing Fluorene Moieties

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Polymers containing fluorene moieties are interesting because of their potential applications as photoelectronic materials and as gas separation membranes. In this work, the gas transport properties of two novel poly(arylene ether)s, one containing diphenylfluorene (FBP) and 2,6-bis(trifluoromethylphenylene)pyridine (6FPPr) groups and the other containing FBP and 2,5-bis(3-trifluoromethylphenylene)thiophene (6FPT) groups in the main chain, were investigated. The influence of temperature on permeability, diffusivity, and selectivity is reported at temperatures from 30 to 65 °C. Activation energies of permeation and diffusion for He, H₂, CO₂, O₂, N₂, and CH₄ were obtained for the diphenylfluorene-containing polymers. It was found that the two FBP-containing poly(arylene ether)s studied here show higher gas permeabilities than most of the reported FBP-containing polymer membranes. A comparison revealed that the replacement of the thiophenylidene group with the pyridinylidene has an obvious influence on the gas transport properties of these polymers. The polymer membrane with the pyridinylidene group has gas separation properties superior to that with the thiophenylidene group.

Introduction

Membrane separation of gases has emerged into an important unit operations technique offering specific advantages over more conventional separation procedures (e.g., cryogenic distillation and adsorption).^{1–4} Engineering polymers from the classes of aromatic polysulfones,^{5–8} polycarbonates,^{8–10} polyarylates,^{11–12} poly(aryl ketone)s,¹³ poly(aryl ether)s,¹⁴ polyimides,^{15–19} and polypyrrolones^{20,21} have shown interesting proper-

ties as membranes for gas separation. Several members of these classes of polymers (e.g., polysulfone based on bisphenol A, tetrabromo bisphenol A polycarbonates, and poly(2,6-dimethyl-1,4-phenylene oxide)) have been utilized commercially in gas separation applications. The potential application of a polymer as a separation membrane depends on the possible throughput and the purity of product. This means that both the permeability coefficient for the gas that is transported more rapidly and the selectivity should be as large as possible. Therefore, in the past 20 years, the study of gas permeability and permselectivity of polymer membranes has become a subject of strong research with worldwide participation in both industrial and academic laboratories. Although the main motivation for these works

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was primarily an empirical search for improved materials for gas separation membranes, another aim, which is often present but not always manifested, is the development of rules for prediction of the permeation parameters^{22,23} of polymers that still have not been investigated or even prepared. Such rules, when available, would simplify or significantly facilitate the task of directed synthesis of novel membrane materials with improved properties. However, to achieve such rules, it is necessary to have a good understanding of the relationship between the properties of the polymers and their gas transport behavior.

On the basis of the analysis of gas transport data obtained for a series of poly(ether ketone)s containing bulky indane moieties, a general guideline was suggested by Maier³ for the structure of polymers for further study of the relationship between polymer structure and permselectivity. The polymer chains should incorporate large, bulky structural elements that are linked by "flexible segments". The dimensions of the bulky groups and the length of the flexible chain segments between them should control the distribution of the gap diameters in the free volume. This would bring about the possibility of directly adjusting the fractional free volume that is accessible to gases with different molecular diameters. At the same time, the selectivity should primarily be determined by the length of the flexible segment and its architecture (bond angle, structure) as well as the degree of free rotation around those bonds that form the hinges between the flexible segments and the fixed, bulky groups.

In recent years, polymers containing fluorene moieties have been interesting because of their potential applications as photoelectronic materials.^{24–25} These polymers are also interesting for gas separation. Polysulfone,^{7–8} polycarbonates,⁸ polyacrylates,^{11–12} poly(ether ketone)s,²⁶ and poly(arylene ether ketone)²⁷ derived from 4,4'-(9-fluorenylidene)bisphenol (FBP) have been synthesized and their gas transport properties have been reported. In this work, two poly(arylene ether)s containing fluorene moieties in polymer chains were fabricated into dense membranes and their gas transport properties for He, H₂, CO₂, O₂, N₂, and CH₄ were studied. Similar to the indane-containing poly(ether ketone)s and polyimides reported by Maier, the diphenylfluorene moieties in these two poly(arylene ether)s are large, bulky, and rigid groups. Therefore, the investigation of gas separation properties for such polymers and a comparison between these polymers and those reported in the literature^{7,8,11,26,27} will be interesting.

Experimental

Materials. The synthesis and characterization of these poly(arylene ether)s containing diphenylfluorene were reported in a previous paper.²⁸ The preparation of this new class of semifluorinated polymers relied on the aromatic substitution

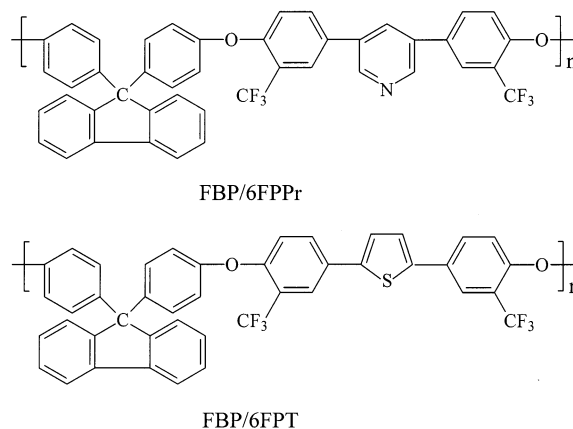


Figure 1. Molecular structure and denotations of the FBP-containing poly(arylene ether) membranes.

polymerization of trifluoromethyl-activated bishalo monomers with different bis(phenols). 4,4'-(9-Fluorenylidene)bisphenol was used for the synthesis of the poly(arylene ether)s. Molecular structures of the poly(arylene ether) membranes studied in this work are presented in Figure 1.

Membrane Preparation. Nonporous planar membranes were prepared by casting the poly(arylene ether)s solution onto glass plates and dried for 24 h at 100 °C under vacuum. The PAE membranes thus-obtained were removed from the glass plates and dried for another 24 h at 100 °C under vacuum. All membranes were treated according to the same procedure. The thickness of the dry membranes used for the permeability and diffusivity coefficient measurements varied from 80 to 110 μm .

Measurements of Gas Separation Properties. Mean permeability coefficients, P , and effective diffusion coefficients, D , were measured at 1 atm for different temperatures between 30 and 65 °C by the time-lag method.²⁹ A cell was employed that was separated into two compartments by the membrane. Both compartments and the membrane were initially vacuumed for 24 h before measurement. To begin the measurement, the input chamber was filled with gas to be studied. The pressure p_1 in the input chamber was kept constant, while an increase in pressure Δp in the permeating chamber was measured. Once the stationary state was achieved, the increase in pressure was linear with time t . The volume of the measurement cell V , the membrane area A , the membrane thickness l , the temperature T , and the pressure p_1 on the input side are all known and constant, so the permeability coefficient can be calculated according to the equation

$$P = \Delta p V l / R T A p_1 t \quad (1)$$

Effective diffusion coefficients can be calculated from the time-lag θ using eq 2:

$$D = \bar{l}^2 / 6\theta \quad (2)$$

The ideal permselectivity of the membranes toward a gas A relative to another gas B were calculated from the individual pure gas permeabilities:

$$\alpha_{A/B} = P_A / P_B \quad (3)$$

where P_A and P_B are the corresponding permeability coefficients of gas A and gas B, respectively.

Results and Discussion

1. Effect of Temperature on Gas Permeabilities, Diffusivities, and Selectivities. Within a tempera-

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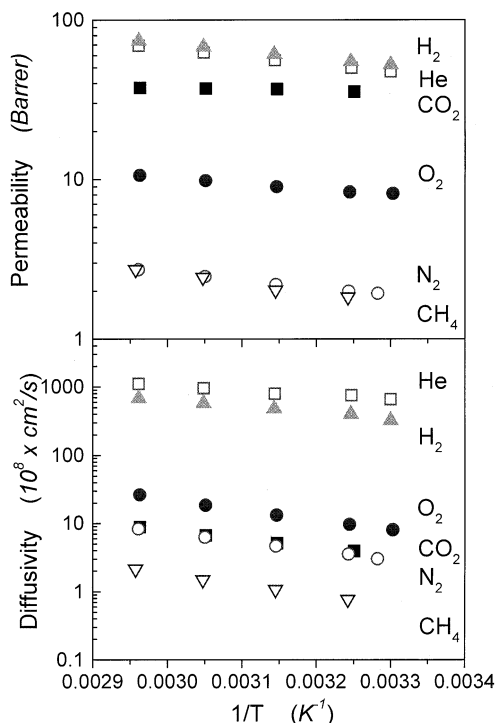


Figure 2. Temperature dependence of gas permeation and diffusion coefficients for the FBP/6FPPr membrane at 1atm.

ture range in which no significant thermal transitions of the polymer occurs, the temperature dependence of permeabilities and diffusivity can be described by two Arrhenius expressions,

$$P = P_0 \exp(-E_p/RT) \quad (4)$$

$$D = D_0 \exp(-E_d/RT) \quad (5)$$

where P_0 and D_0 are pre-exponential factors, E_p is the apparent activation energy for permeation, E_d is the activation energy for diffusion, R is the gas constant, and T is the temperature.

The effect of temperature on permeability and diffusion coefficients for He, H₂, CO₂, O₂, N₂, and CH₄ at 1-atm upstream pressure for these diphenylfluorene (designation FBP, which was reported in the literature, is used in this work to avoid confusion) containing polymer membranes are presented in Figures 2 and 3, respectively. From these figures, it is clear that the temperature dependence of P and D can be described by the Arrhenius equations. Therefore, active energies of gas transport for the two membranes were obtained and are reported in Table 1. These properties can be of interest per se as physicochemical characteristics of energy barriers in mass transport of small molecules through a polymeric matrix. Practical importance of these parameters stems from the fact that they are needed for the calculations of gas permeation and diffusion coefficients at elevated and low temperatures.

The effects of temperature on the permselectivity and diffusion selectivity of the membranes are shown in Figures 4 and 5. It was found that the permselectivity values of the two membranes for CO₂/CH₄ and H₂/CH₄ gas pairs decreased with the increase of temperature. However, the values of the He/N₂ gas pair increased with the temperature increasing for both membranes.

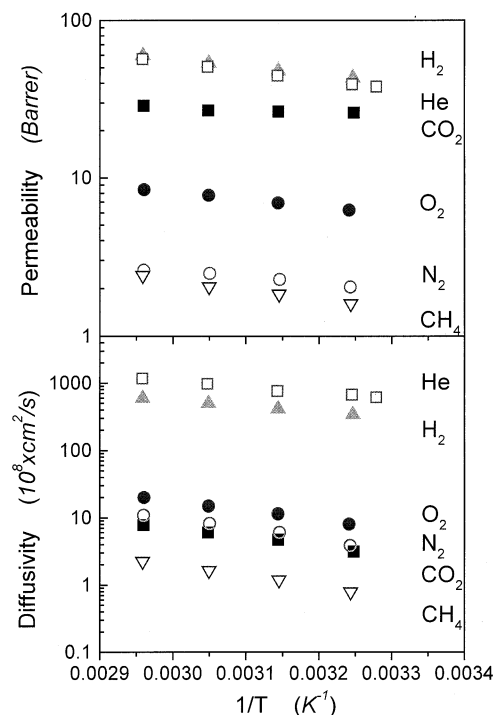


Figure 3. Temperature dependence of gas permeation and diffusion coefficients for the FBP/6FPT membrane at 1atm.

Table 1. Activation Energies for the Permeation and Diffusion

polymer	CO ₂	O ₂	N ₂	CH ₄	He	H ₂
	E_p (kJ/mol)					
FBP/6FPT	2.60	8.78	7.15	11.43	10.39	9.38
FBP/6FPPr	1.49	6.47	8.80	11.74	9.32	8.66
	E_d (kJ/mol)					
FBP/6FPT	24.77	26.07	29.47	29.65	16.42	16.30
FBP/6FPPr	22.95	28.41	25.30	29.08	12.30	15.70

Concerning the O₂/N₂ gas pair, on the other hand, an increase and a decrease in permselectivity for FBP/6FPPr and FBP/6FPT, respectively, were observed. Nevertheless, the diffusion selectivity values decreased with the increase of temperature in most cases corresponding to gas pairs and the two membranes, with an exception of the O₂/N₂ gas pair with respect to the FBP/6FPPr membrane. The reason for these results is not clear at this moment.

2. Overall Pure Gas Transport Properties. Gas permeability coefficients, diffusion coefficients, and selectivity values measured at 1atm and 35 °C are summarized in Tables 2 and 3, respectively. The solubility values calculated from $S = P/D$ and the solubility selectivity values are listed in Table 4. It can be seen from Table 2 that the permeability coefficient and the selectivity value with respect to gas pairs of CO₂/CH₄, O₂/N₂, He/N₂, and H₂/CH₄ are both higher for FBP/6FPPr than for FBP/6FPT. For example, the CO₂ permeability of FBP/6FPPr is 38% larger than that of 6FPT-DPF, while the CO₂/CH₄ selectivity of the former membrane is 22% higher than that of the latter membrane. The He permeability and the He/N₂ selectivity for the FBP/6FPPr membrane are 1.27 and 1.3 times for the FBP/6FPT membrane, respectively. From Tables 3 and 4, it seems that the high gas permeability coefficients for the FBP/6FPPr membrane derive from

Table 2. Permeabilities and Permselectivities for the FBP-Containing Poly(arylene ether)s at 35 °C and 1 atm^a

polymer	P_{CO_2}	P_{O_2}	P_{N_2}	P_{CH_4}	P_{He}	P_{H_2}	$\alpha_{\text{CO}_2/\text{CH}_4}$	$\alpha_{\text{O}_2/\text{N}_2}$	$\alpha_{\text{He}/\text{N}_2}$	$\alpha_{\text{H}_2/\text{CH}_4}$
FBP/6FPT	25.75	6.22	2.06	1.59	39.5	43.2	16.18	3.02	19.2	27.2
FBP/6FPPr	35.65	8.40	1.99	1.80	50.0	55.0	19.82	4.22	25.1	30.6

^a P in barrers, 1 barrer = 10^{-10} cm³(STP)·cm/cm²·s·cmHg.

Table 3. Diffusion Coefficients for the FBP-Containing Poly(arylene ether)s at 35 °C and 1 atm^a

polymer	D_{CO_2}	D_{O_2}	D_{N_2}	D_{CH_4}	D_{He}	D_{H_2}	$D_{\text{CO}_2}/D_{\text{CH}_4}$	$D_{\text{O}_2}/D_{\text{N}_2}$	$D_{\text{He}}/D_{\text{N}_2}$	$D_{\text{H}_2}/D_{\text{CH}_4}$
FBP/6FPT	3.34	8.08	4.00	0.80	654	341	4.20	2.02	164	426
FBP/6FPPr	3.92	9.61	3.40	0.75	715	384	5.21	2.83	210	512

^a D in 10^{-8} cm²/s.

Table 4. Solubilities for the FBP-Containing Poly(arylene ether)s at 35 °C and 1 atm^a

polymer	S_{CO_2}	S_{O_2}	S_{N_2}	S_{CH_4}	S_{He}	S_{H_2}	$S_{\text{CO}_2}/S_{\text{CH}_4}$	$S_{\text{O}_2}/S_{\text{N}_2}$	$S_{\text{He}}/S_{\text{N}_2}$	$S_{\text{H}_2}/S_{\text{CH}_4}$
FBP/6FPT	5.86	0.58	0.39	1.52	0.046	0.096	3.85	1.49	0.12	0.063
FBP/6FPPr	6.91	0.66	0.44	1.82	0.053	0.11	3.80	1.50	0.12	0.060

^a S in cm³(STP)/cm³·atm.

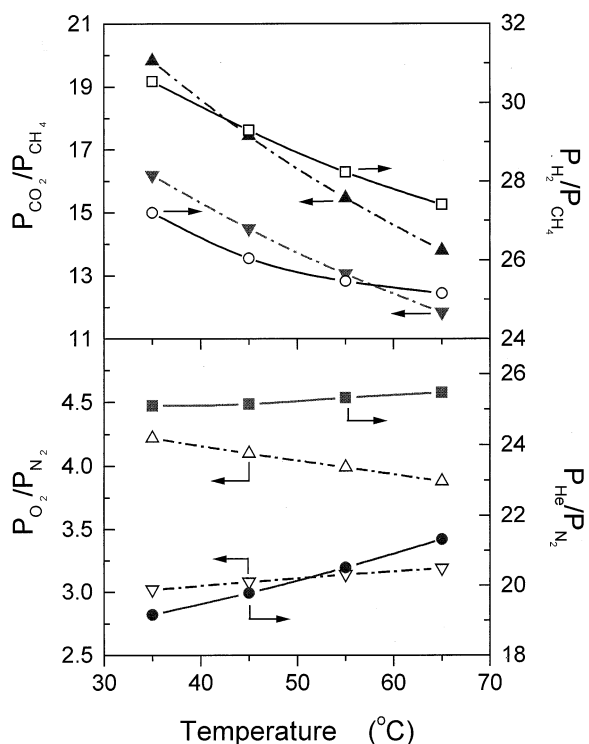


Figure 4. Effect of temperature on the permselectivity values. \blacktriangle , \triangle , \blacksquare , \square : FBP/6FPPr. \blacktriangledown , \triangledown , \bullet , \circ : FBP/6FPT.

both high diffusion coefficients and high solubility values. However, the high selectivity values for this membrane are mainly due to its high diffusion selectivity values. It also can be seen from Tables 2 and 3 that, for the FBP/6FPPr membrane, the gas permeability coefficient decreases following the gas sequence $\text{H}_2 > \text{He} > \text{CO}_2 > \text{O}_2 > \text{N}_2 > \text{CH}_4$, while the diffusion coefficient decreases in the following sequence: $\text{He} > \text{H}_2 > \text{O}_2 > \text{CO}_2 > \text{N}_2 > \text{CH}_4$. For the FBP/6FPT, the gas permeability coefficient shows the same sequence; however, the diffusion coefficient decreases according to $\text{He} > \text{H}_2 > \text{O}_2 > \text{N}_2 > \text{CO}_2 > \text{CH}_4$. All these results imply that the replacement of the thiophenylidene group with the pyridinylidene has an obvious influence on the gas transport properties of these polymers.

3. Comparison of Structurally Related Polymer Membranes. A comparison between these two polymer membranes and the literature reported polymer mem-

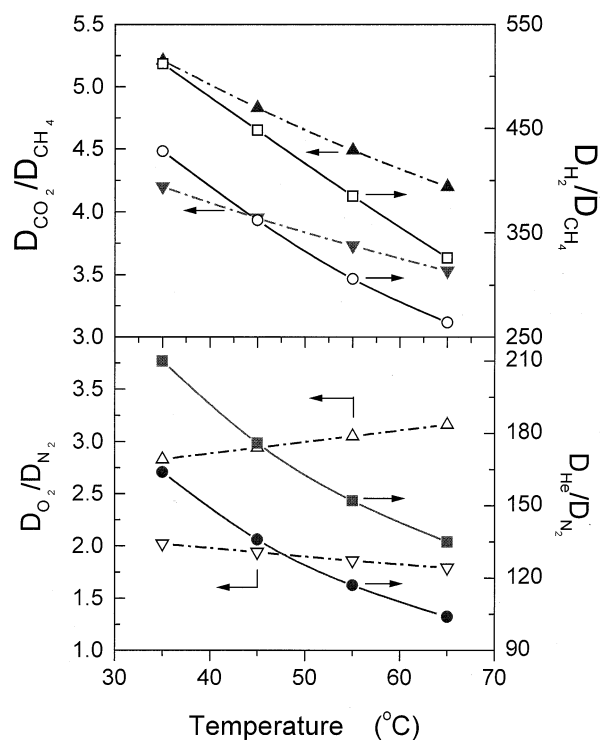
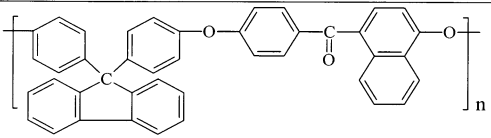
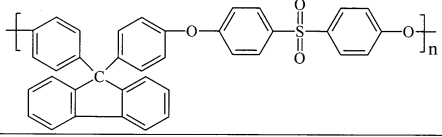
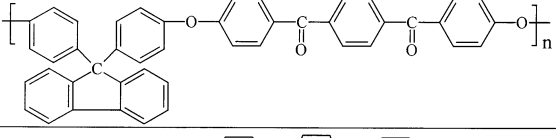
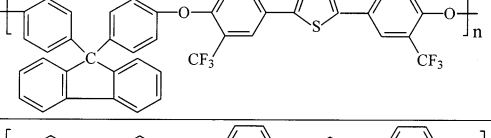
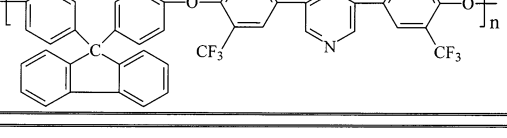
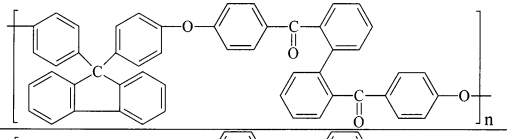
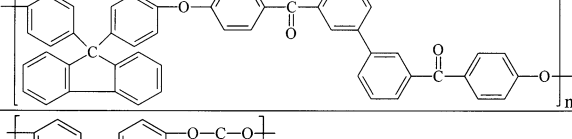
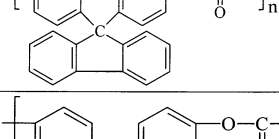
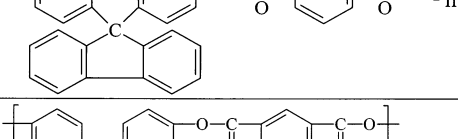
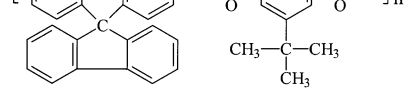


Figure 5. Effect of temperature on the diffusion selectivity values. \blacktriangle , \triangle , \blacksquare , \square : FBP/6FPPr. \blacktriangledown , \triangledown , \bullet , \circ : FBP/6FPT.

branes containing diphenylfluorene moieties would be very interesting. Similar to the indane containing poly(ether ketone)s reported by Maier³, the diphenylfluorene moieties in these polymers are large, bulky, and rigid groups. Therefore, the length of the "flexible segment" and its architecture (bond angle, structure) as well as the degree of free rotation around those bonds that form the hinges between the flexible segments and the fixed, bulky groups should have a great influence on gas permeability and permselectivity.

The effects of the introduction of different flexible segments between the FPB groups in the main chain on the permeabilities as well as permselectivities are compared in Table 5. The length of flexible segments between the FPB groups can be estimated roughly and it decreases according to $\text{FBP}/3,3'\text{-DBBP} > \text{FBP}/2,2'\text{-DBBP} \gg \text{FBP}/\text{PKT} > \text{FBP}/\text{NP} > \text{FBP}/\text{SF} > \text{FBP}/6\text{FPT} \approx \text{FBP}/6\text{FPPr} > \text{FBP}/\text{IA} = \text{FBP}/\text{tBIA} > \text{FBP}/\text{PC}$. As can be

Table 5. Comparison of Gas Transport Properties of Polymers Containing Fluorene Moieties

Designation	Molecular Structure of the Polymer Containing Fluorene Moieties	P _{O2}	P _{N2}	α _{O2/N2}	P _{CO2}	P _{CH4}	α _{CO2/CH4}
FBP/NP		1.42	0.22	6.4	4.97	0.19	25.9
FBPSF		2.76	0.48	5.75	14.0	0.54	26.0
FBPKT		1.68	0.29	5.79	-	-	-
FBP/6FPT		6.22	2.06	3.02	25.7	1.59	16.2
FBP/6FPPr		8.40	1.99	4.22	35.6	1.80	19.8
Designation	Molecular Structure of the Polymer Containing Fluorene Moieties	P _{O2}	P _{N2}	α _{O2/N2}	P _{CO2}	P _{CH4}	α _{CO2/CH4}
FBP/2,2'-DBBP		0.72	0.097	7.4	2.40	0.078	30.8
FBP/3,3'-DBBP		0.53	0.064	8.3	1.87	0.055	34.0
FBPC		3.18	0.59	5.37	15.1	0.058	26.0
FBP/IA		3.03	0.57	5.32	12.4	0.62	20.1
FBP/tBIA		9.55	1.93	4.95	36.8	2.37	15.5

seen from Table 5, with the exception of FBP/6FPT, FBP/6FPPr, and FBP/tBIA, the O₂ permeability decreases in the polymer order FBP/3,3'-DBBP < FBP/2,2'-DBBP < FBP/NP < FBPKT < FBPSF < FBP/IA < FBPC while the CO₂ permeability decreases in the following order: FBP/3,3'-DBBP < FBP/2,2'-DBBP < FBP/NP < FBP/IA < FBPSF < FBPC. It seems that the gas permeability coefficients increase approximately with the decrease of the flexible segments length, not including FBP/6FPT, FBP/6FPPr, and FBP/tBIA. The

FBP/6FPPr, FBP/6FPT, and FBP/tBIA show much higher gas permeabilities than the other FBP-containing polymer membranes. Although the chemical structures of these polymers are different, it could be concluded that substitution with -CF₃ and/or -C(CH₃)₃ on the benzene ring in the flexible segment can increase gas permeability remarkably. For example, the O₂ permeability for FBP/6FPPr is 5 and 3 times for FBPK²⁶ and FBPS,^{7,8} respectively, while the CO₂ permeability of FBP/6FPPr is 154% higher than that of FBPS.

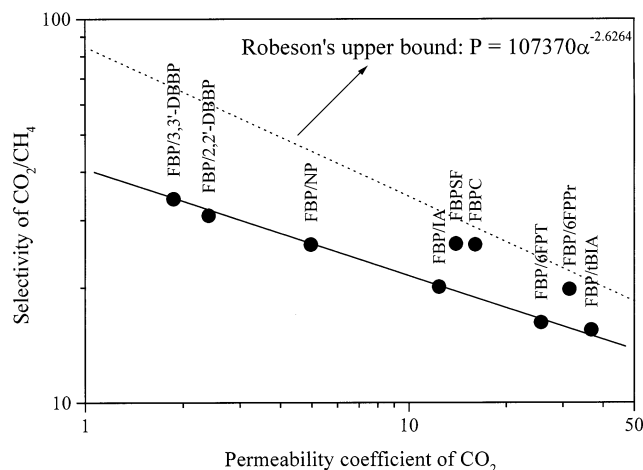


Figure 6. Relationship between O_2/N_2 permselectivity and O_2 permeability for various FBP-containing polymeric membranes.

Figures 6 and 7 show the plots of the permselectivity for O_2/N_2 and CO_2/CH_4 gas pairs versus the permeability of highly permeable gases for polymer membranes listed in Table 5. Linear “tradeoff” relationships were obtained for most of the polymers. As can be seen from Figure 6, the data of FBP/6FPPr investigated here and the reported FBPSF and FBPC⁸ polymers for the CO_2/CH_4 system are above the linear line while the FBP/6FPT is below the linear line for the O_2/N_2 system (Figure 7). This means that the polymer membrane with the pyridinylidene group in the flexible segment has gas separation properties superior to that with the thiophenylidene group. The CO_2/CH_4 and O_2/N_2 performances of these FBP-containing polymer membranes are also compared to the “upper bound” tradeoff line³⁰

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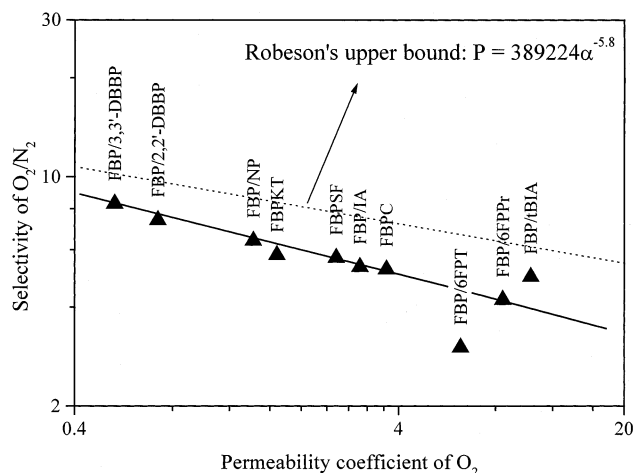


Figure 7. Relationship between CO_2/CH_4 permselectivity and CO_2 permeability for various FBP-containing polymeric membranes.

in Figures 6 and 7. All of the polymers exhibit gas separation performances below the upper bound limit. However, in a comparison of the slope of the linear line for these FBP-containing polymers with that of Robeson's upper bound line, it seems that decreasing the flexible segments length between the FPB groups as well as substitution with $-CF_3$ and/or $-C(CH_3)_3$ on the benzene ring in the flexible segment can improve the separation performance for the CO_2/CH_4 gas pair but depress the O_2/N_2 separation performance.

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