

GAS SORPTION AND TRANSPORT IN POLY (PHENYLENE OXIDE) (PPO) AND ARYL-BROMINATED PPO MEMBRANES

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ABSTRACT

The apparent solubility (S), concentration-average diffusivity (D), and permeability (P), for CO_2 , CH_4 and N_2 through PPO and aryl-brominated PPO at 35°C for pressure ranging from 1 to 26 atm are reported. It is found that P , D , and S of the membranes to all the three gases vary with the extent of bromination. S increases with the increase of the percent of bromine in each case, but D to CO_2 increases remarkably only at higher degree of bromination, and therefore, P to CO_2 is increased by more than 100% over a wide range of pressure in the case. The solubility data are well described by the dual mode sorption model. It is found that the gas molecules sorbed by the Langmuir mode are relatively more immobilized and the contribution of the nonequilibrium character of the polymer to gas permeation increases obviously for CO_2 and is hardly changed for CH_4 with increasing bromine content. These observations are interpreted in terms of changes in specific free volume (SFV) and the cohesive energy density (CED) of the polymers.

INTRODUCTION

Fundamental understanding of sorption and transport of gases in glassy polymers is critical for the logical use of these materials in membrane separation processes and other applications. It is well established for glassy polymers that both sorption and transport involve nonlinear responses to gas pressure and the dual mode model has been developed which accurately describes the non-linearities characteristic of the glassy state^[1-3]. The important goal of the model is to relate the model parameters to polymer structure in a quantitative manner.

Although there is a great number of studies on the preparation of membranes from existing polymers in the literature, systematic investigations on the role of chemical structure of the polymers in determining their transport behavior to gases are still very few. The present paper is concerned with gas sorption and transport in unmodified and aryl-brominated PPO which have been selected because they can be formed into tough membranes and exhibit rather unique gas permeation characteristics^[4] and can be suited for a high-flux, moisture-resistant membrane material^[5]. The another reason for selecting PPO for study is that they can be chemically modified by various reactions, such as halogenation and phosphonylation^[6, 7] and carboxylation^[8].

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But none of the studies has valued the chemical structure in terms of gas permselectivity behaviour until Percec^[9,10], Chern^[11] and Chen^[12] published their works more recently. In this study, bromination on the aromatic ring of PPO backbone by electrophilic substitution reaction was investigated and the features distinguishing modified PPO from unmodified PPO with respect to transport behaviour of CO₂, CH₄ and N₂ were examined.

Gas sorption in polymers

In order to be transported through bulk polymers small molecules must first dissolve in them. It is well known that in rubbery polymers the solution of supercritical gases ($T > T_c$) is accurately described by Henry's law:

$$c = Sp \quad (1)$$

here c is the concentration of gas in equilibrium with the gas phase at partial pressure p , and S is a solubility coefficient. S increases as the gas becomes more condensible, i.e., has a higher Lennard-Jones potential well-depth, ϵ/k , or higher critical temperature (T_c).

In glassy polymers, however, gas sorption is more complex than that in rubbery state. For most glassy polymers the gas sorption isotherms are generally concave to the pressure axis^[13,14], and can be described by a model envisioning dual sorption mechanisms^[1-3]:

$$c = k_D p + C'_H b p / (1 + b p) \quad (2)$$

The first term is simply Henry's law and the second term is of the Langmuir form which is characterized by capacity, C'_H , and affinity, b . The latter mechanism is believed to be resulted from sorption into nonequilibrium regions of free volume existing in the glassy state, and the size of this term increases in proportion to the value of T_g relative to the observation temperature^[4].

Gas transport in polymers

According to the solution-diffusion mechanism the permeability of polymer membrane to gases when the downstream pressure is zero can be written as

$$P = (c/p) \int_0^c D(c') dc' / c = SD \quad (3)$$

where D is the concentration-averaged diffusivity, p is the upstream gas pressure and $D(c')$ is the apparent concentration-dependent diffusivity of the gas.

The intrinsic permselectivity of the polymer to a pair of gases, A and B, without reference to any specific model, can be represented by^[5]

$$\text{Permselectivity} = P_A/P_B = (S_A/S_B) (D_A/D_B) \quad (4)$$

The ratios of S_A/S_B and D_A/D_B are called solubility and mobility selectivity, respectively.

A great deal of research has shown that in rubbery polymers the pressure independent permeability, P , is given by

$$P = k_D D \quad (5)$$

This is inadequate for transport in glassy polymers, because P is dependent on upstream gas pressure in the case. Petropoulos^[15] speculated that the gas molecules sorbed by the Langmuir mode were partially instead of completely immobilization

and proposed a more general form of Fick's law:

$$N = -D_D dc_D/dx - D_H dc_H/dx \quad (6)$$

where c_H is the concentration of gas held in "holes" or the Langmuir part of eq. 2 while D_D and D_H are separate diffusion coefficients applicable to the two species, Henry's and Langmuir's, respectively. Assink's pulsed NMR results have shown that there is a rapid local exchange between gases held by the two modes of sorption and that the Langmuir population has considerably less diffusional mobility than the Henry's law population^[16].

For the boundary condition of the transient permeation experiment the expression for P can be yielded from eq. 6

$$P = k_D D_D (1 + FK/(1 + bp)) \quad (7)$$

here $K = C_H' b/k_D$ and $F = D_H/D_D$. At very large values of bp , P reduces to eq. 5 and at very low values of bp , it becomes

$$P(0) = k_D D_D (1 + FK) \quad (8)$$

$$\text{The ratio} \quad P(0)/P(\infty) = 1 + FK \quad (9)$$

shows that the nonequilibrium character of glassy polymers contributes an additional mechanism to gas permeation in parallel to the normal processes expected from their equilibrium character.

EXPERIMENTAL

Materials

The pristine PPO powder was obtained from GE Co.. Bromination was carried out in chloroform solution by adding chloroform-diluted bromine at 0 °C for 3 hrs without catalyst. The extent of bromination and microstructure of the samples were determined by ¹H NMR. In the following discussion three samples will be designated as PPO, PPOBr (36%) and PPOBr (91%), respectively. The number represents percent of ring-substitution assuming mono-bromination. The density was measured with a NaBr(aq.) density gradient column at 23 °C and T_g was determined by using Perkin Elmer DSC 2 at a 20 °C/min heating rate. Polymer films of roughly 1 mil thick were cast from a 7% (wt.) chloroform solution, devolatilized at room temperature, dried at 80 °C under vacuum for 24 hrs.

Solubility and permeability measurements

A two-transducer pressure-decay cell and a barometric permeation apparatus were used for the solubility and permeability measurements, respectively. Details of the equipment can be found in the literature^[17].

RESULTS AND DISCUSSION

1. Relationship between P , D , S and the nature of the polymers and gases

Table 1 summarized the microstructure and other physical properties of the samples reported in the paper. The glass transition temperatures T_g and the density ρ were experimentally measured as described above. The specific free volume, SFV , was

defined as

$$SFV = Vf/M \quad (10)$$

where M is the average molecular weight in g/mol of repeating unit; Vf is the molar free volume of an amorphous polymer in cm^3/mol and defined as

$$Vf = VM - V_0 = M/\rho - V_0 \quad (11)$$

$$V_0 = 1.3V_w \quad (12)$$

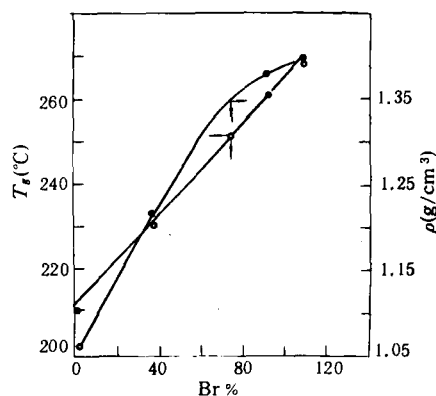


Fig. 1 Glass transition temperature, T_g , and density, ρ as a function of the extent of aryl-bromination in PPO.

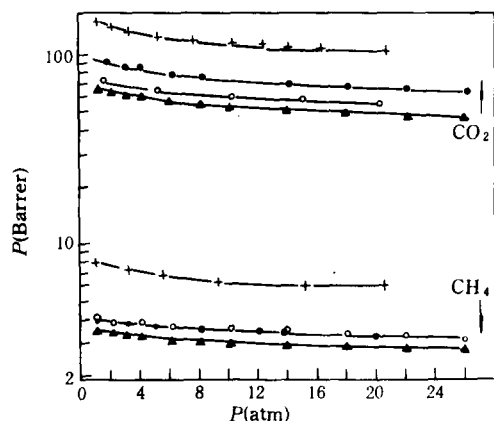


Fig. 2 Pressure dependence of CO_2 and CH_4 permeability in PPO and PPOBr samples.
 $\circ$ PPO; $\blacktriangle$ PPOBr (36%); $\bullet$ PPOBr (91%); $+$ PPOBr (109%)

where V_0 is the zero molar volume in cm^3/mol and V_w is van der Waals volume in cm^3/mol which is estimated using group contribution method^[18]. The solution parameter, δ , is the square root of the cohesive energy density (CED) which is calculated according to van Krevelen^[18]. SFV and δ estimated in this way are listed in Table 1. Figure 1 shows the changes in T_g and ρ with the extent of bromination. Both of them increase linearly with increasing Br%. However, when the percentage of bromine is over 90%, ρ is leveling off. It can be seen from Table 1 that the change in δ is very small (less than 2%). Therefore, the effect of δ on the transport behaviour of the polymers to gases is negligible. However, it is of interest to note that SFV decreases slowly at first and then increases dramatically when the content of bromine in PPO is over 90%.

Table 1 The microstructure and other physical parameters of the PPO samples

Polymer	Substitution (%)		ρ (g/cm^3)	T_g ($^\circ\text{C}$)	M (g/mol)	V_0 (cc/mol)	SFV (cm^3/g)	δ (J/cm^3)
	mono-	di-						
PPO	0	0	1.061	210	120.1	90.12	0.192	19.53
PPOBr (36%)	20.4	7.8	1.203	233	148.6	95.31	0.190	19.65
PPOBr (91%)	73.9	8.5	1.380	262	191.9	102.03	0.193	19.68
PPOBr (109%)	57.9	25.6	1.390	269	206.2	105.86	0.206	19.42

The pressure dependence of the permeabilities of both PPO and PPOBr follows the typical dual mode behavior as shown in Fig. 2. Interestingly, the permeabilities of

PPOBr (36%) to both CO_2 and CH_4 are slightly less than that of PPO while P of PPOBr (91%) to CO_2 is higher than that of PPO and P to CH_4 is almost the same as that of PPO. Therefore, the sample of PPOBr (91%) has higher permselectivity for CO_2 over CH_4 . As to the sample of PPOBr (109%) it has the highest P to CO_2 and the rather more permselectivity for CO_2 over CH_4 than that of PPOBr (36%). It is clear from Table 1 that for the sample of PPOBr (36%) both the higher T_g (lowered chain rotational mobility) and lower SFV lead to reduce the permeabilities to CO_2 and CH_4 , while for the 91% or more bromine-substituted samples, the larger SFV dominated over the effect of chain rotational mobility, leading to the increase of permeability.

Independently measured solubility data of CO_2 , CH_4 and N_2 are presented as sorption isotherms in Fig. 3, which also conform to the typical dual mode shape. The average diffusivity, D , and the apparent solubility coefficient, S , were determined according to eq. 3 from the permeability and sorption data at 20 atm and 35 °C and are listed in Table 2.

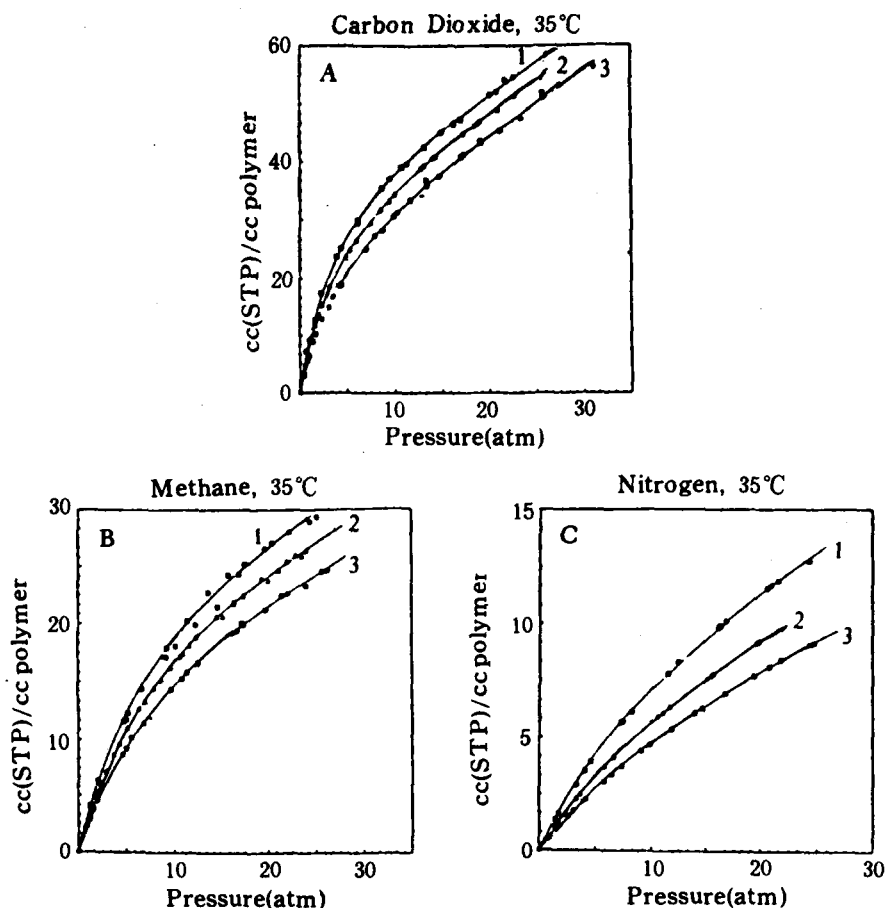


Fig. 3 Sorption isotherms for CO_2 (A), CH_4 (B) and N_2 (C) in PPO and PPOBr samples at 35 °C
1. PPOBr (91%); 2. PPOBr (36%); 3. PPO

From Table 2 it can be seen that the decrease in P of PPOBr (36%) sample to CO_2 and CH_4 arises from the decrease in D pronouncedly and the latter mainly stems from

Table 2 P, D, S and permselectivity of the PPO samples at 20 atm and 35 °C

Polymer	Permeability P (Barrer)*			$\frac{P(\text{CO}_2)}{P(\text{CH}_4)}$	Average diffusivity D (10^{-8} cm ² /sec)			$\frac{D(\text{CO}_2)}{D(\text{CH}_4)}$	Apparent solubility S (cc (STP)/cc-atm)			$\frac{S(\text{CO}_2)}{S(\text{CH}_4)}$
	CO ₂	CH ₄	N ₂		CO ₂	CH ₄	N ₂		CO ₂	CH ₄	N ₂	
PPO	56.8	3.40		16.7	19.4	2.39	/	8.12	2.22	1.08	0.40	2.06
PPOBr (36%)	50.5	3.00	3.10	16.8	15.9	1.90	4.16	8.37	2.41	1.20	0.46	2.01
PPOBr (91%)	68.0	3.40	/	20.0	20.1	1.95	/	10.30	2.57	1.32	0.57	1.95
PPOBr (109%)	107	6.07	/	17.6	/	/	/	/	/	/	/	/

* 1 Barrer = 10^{-10} cc (STP) - cm/cm² - sec - cmHg

the drop in SFV . On the other hand, the increase in P of PPOBr (91%) sample to CO₂ is due to the increase in both D and S , but the increase in permselectivity of CO₂ over CH₄ in the case is due to the increase in mobility selectivity. This is presumably because of the difference in molecular shape and size between the spherical CH₄ and the asymmetric CO₂ and N₂ molecules. Figure 4 shows a correlation of the D and the kinetic diameters $d^{[4,5]}$ of CO₂, CH₄ and N₂ in PPOBr (36%) sample at 35 °C and 20 atm. There is an excellent linear relationship between $\log D$ and d . It shows clearly the extremely strong effect on the penetrant mobility caused by small differences in d . On the other hand, the changes in solubilities for CO₂ and CH₄ in all the three samples are not very large (see Table 2). Especially, the solubility selectivity for CO₂ over CH₄ is basically independent of the extent of bromination. However, the condensability of the penetrants has the strong effect on their solubility in these polymers as shown in Fig. 5 which is the plot of $\log S$ for CO₂, CH₄ and N₂ in PPO and PPOBr at 20 atm and 35 °C against their Lennard-Jones potential well-depth $\epsilon/k^{[4]}$. Obviously, there is an excellent linear relationship between $\log S$ and ϵ/k , and $\log S$ increases sharply with the increase in ϵ/k . It follows that the solubility selectivity

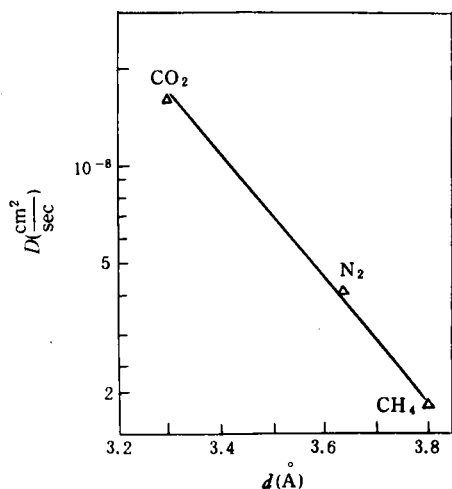


Fig. 4 Correlation of D and the kinetic diameters, d , of CO₂, CH₄ and N₂ in PPOBr (36%) at 20 atm and 35 °C.

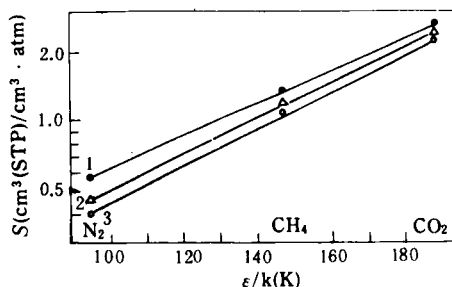


Fig. 5 Correlation of S and the Lennard-Jones potential well-depth parameters, ϵ/k , for CO₂, CH₄ and N₂ in PPOBr (36%) at 20 atm and 35 °C.

1. PPOBr (91%); 2. PPOBr (36%); 3. PPO

mainly depends on the inherent condensability of the respective gases and is relatively insensitive to changes in polymer structure represented by CED .

2. Dual-Mode Model Analysis of The Data

As mentioned above, the pressure dependences of permeability and sorption isotherm in the system of polymer-gas conform the typical dual-mode model, so these data may be better analyzed according to the model. The dual-mode sorption parameter values deduced by a nonlinear regression routine^[19] are summarized in Table 3. It indicates that all the three parameters, k_D , C'_H and b , are larger as the degree of bromination increases. Furthermore, there is a remarkable increase in C'_H for N_2 and in b for CO_2 , as to k_D there is no apparent change in each case. As a result, the composite parameter $K (= C'_H b / k_D)$, the relative magnitude of the Langmuir and Henry's law character of the polymer-gas increases obviously for CO_2 and N_2 , but it is not the case for CH_4 . This is shown in Fig. 6(a). It follows that the aryl-bromination in PPO increased the Langmuir sorption for both CO_2 and N_2 , but hardly changed that for CH_4 . Therefore, this is beneficial to separate CO_2 from CH_4 . However, probably it is not true for enriching oxygen from air.

Table 3 Dual-mode sorption parameters at 35 °C

Polymer		k_D ($\text{cm}^3 \text{ (STP) / cm}^3 \cdot \text{atm}$)	C'_H ($\text{cm}^3 \text{ (STP) / cm}^3$)	b 1/atm	$K = \frac{C'_H b}{k_D}$
PPO	CO_2	0.921	32.74	0.195	6.93
	CH_4	0.321	22.19	0.107	7.40
	N_2	0.153	9.95	0.048	3.12
PPOBr (36%)	CO_2	0.941	35.42	0.244	9.18
	CH_4	0.344	24.93	0.113	8.19
	N_2	0.162	11.83	0.053	3.87
PPOBr (91%)	CO_2	0.969	37.54	0.292	11.31
	CH_4	0.379	26.90	0.120	8.52
	N_2	0.169	15.06	0.057	5.08

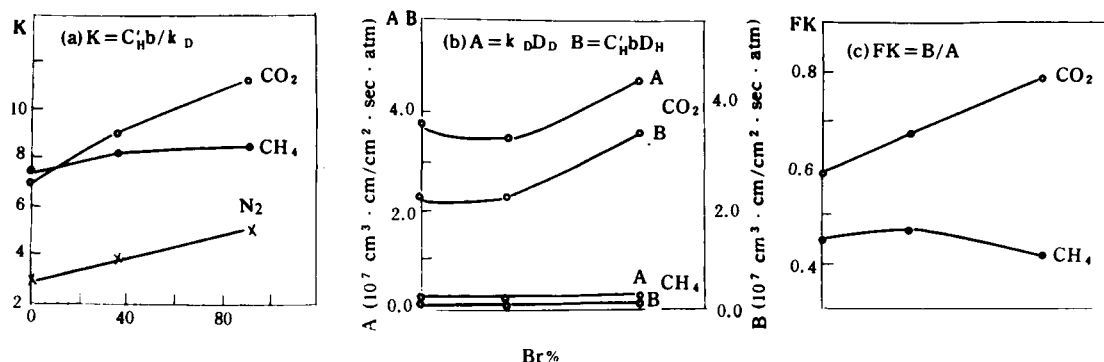


Fig. 6 Composite parameters, $K (= C'_H b / k_D)$ (a), $A (= k_D D_D)$ and $B (= C'_H b D_H)$ (b) and $FK (= B/A)$ (c), as a function of the extent of bromination in PPO.

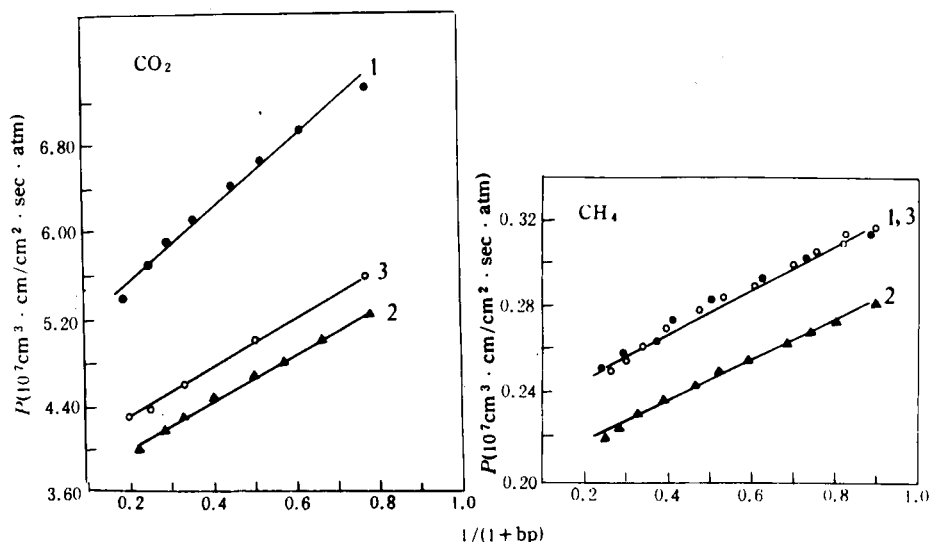


Fig. 7 The steady state permeabilities of CO_2 and CH_4 through PPO (3), PPOBr 36% (2) and PPOBr (91%) (1) samples, as a function of $1/(1+bp)$.

Fig. 7 is the plot of the steady state permeability determined experimentally versus $1/(1+bp)$. Such a good linear relationship between P and $1/(1+bp)$ (the correlation coefficient in each case is more than 0.99) has proved itself to be satisfactory for analyzing the data in question using the dual-mode model represented by eq. 7. The intercept A and slope B of the straight lines in Fig. 7 represent the Henry's law and Langmuir contribution to permeability of gases through the membranes, $k_D D_D$ and $C'_H b D_H$, respectively. The values of A and B are deduced by using linear regression and shown in Fig. 6(b) as a function of bromine content. It is clear from Fig. 6(b) that the Henry's law contribution to total permeability of CO_2 is much larger than Langmuir mode's one and both the two species for CO_2 increase with increasing content of bromine through a minimum at about 20% Br. On the other hand, both the two species for CH_4 are considerably insensitive to aryl-bromination in PPO.

From the linear plots shown in Fig. 7 and the sorption parameters listed in Table 3 the two diffusion coefficients, D_D and D_H and their ratio $F = D_H/D_D$ are deduced for each gas, and the values found are given in Table 4. It is seen from Table 4 that D_D is larger than D_H by more than 10 times in each case, so the ratios F are very small and decrease with the increase of bromine percent. It means that the gas molecules sorbed by the Langmuir mode are relatively more immobilized. The product of F and K , FK , or the ratio of B to A in Fig. 6(b), B/A , which means the contribution of the nonequilibrium character of the polymer to gas permeation, increases obviously for CO_2 and decreases for CH_4 with increasing bromine percent as shown in Fig. 6(c). It follows from discussion above that the increase in CO_2 permeability at higher extent of bromination in PPO arises from the increase in Langmuir sorption and Henry's diffusion mainly.

Table 4 Dual-Mode diffusion coefficients at 35 °C

Polymer	D_D (10^{-8} cm ² /sec)		D_H (10^{-8} cm ² /sec)		$F = D_H/D_D$		FK	
	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄	CO ₂	CH ₄
PPO	41.7	7.1	3.56	0.43	0.085	0.061	0.589	0.451
PPOBr (36%)	36.9	5.8	2.70	0.33	0.073	0.057	0.670	0.467
PPOBr (91%)	48.2	6.1	3.31	0.30	0.069	0.049	0.780	0.417

CONCLUSION

Aryl-bromination in PPO changed the packing state (represented by SFV), intermolecular attraction (represented by CED) and the torsional motion (represented by T_g) of the polymers. In each case the solubility increases with the extent of bromination, but the increase in solubility for CH_4 is larger than that for CO_2 . At higher extent of bromination (e.g., 91% Br), however, there is a large increase in Henry's diffusivity and in Langmuir sorption for CO_2 while the permeability of CH_4 remains roughly the same. As a result, the CO_2 permeability and the selectivity of CO_2 over CH_4 are simultaneously increased by 20% in the case. At even higher extent of bromination (e.g., 109% Br), the CO_2 permeability is increased by 100%.

Keywords:

Poly (Phenylene Oxide) (PPO); Bromination; Membrane; Permeability.

REFERENCES

- [1] Barrer, R.M., *J. Memb. Sci.*, **1984**, 18, 25.
- [2] Vieth, W.R.; Howell, J.M. and Hsieh, H.H., *J. Memb. Sci.*, **1976**, 1, 177.
- [3] Paul, D.R. and Koros, W.J., *J. Polym. Sci., Polym. Phys. Ed.*, **1976**, 14, 675.
- [4] Toi, K. and Paul, D.R., *J. Appl. Polym. Sci.*, **1982**, 27, 2997.
- [5] Chern, R.T.; Koros, W.J.; Hopfenberg, H.B. and Stannett, V.T., ACS Symp. Series 269, American Chemical Society, Washington, DC, **1985**, p. 25.
- [6] Cabasso, I.; Grodzinski, J. and Vofsi, D., *J. Appl. Polym. Sci.*, **1974**, 18, 1969.
- [7] Jauhainen, T.P., *Die Angew. Makromol. Chemie*, **1982**, 104, 117.
- [8] Xie, S.; Macknight, W.J. and Karasz, F.E., *J. Appl. Polym. Sci.*, **1984**, 29, 2679.
- [9] Percec, S., *J. Appl. Polym. Sci.*, **1987**, 33, 191.
- [10] Percec, S. and Li, G., ACS Symp. Series 364, American Chemical Society, **1988**, p. 47.
- [11] Chern, R.T.; Sheu, F.R.; Jia, L.; Stannett, V.T. and Hopfenberg, H.B., *J. Memb. Sci.*, **1987**, 35, 103.
- [12] Chen, G., INPAC 32nd Int. Symp. Macromol. Preprints, 1-6 Aug. **1988**, Kyoto, Japan, p. 861.
- [13] Erb, A.J. and Paul, D.R., *J. Memb. Sci.*, **1981**, 8, 11.
- [14] Barrie, J.A.; Williams, M.L. and Munday, K., *Polym. Eng. Sci.*, **1980**, 20, 20.
- [15] Petropoulos, J.H., *J. Polym. Sci., Pt. A - 2*, **1970**, 8, 1797.
- [16] Assink, R.A., *J. Polym. Sci., Polym. Phys. Ed.*, **1975**, 13, 1665.
- [17] Sanders, E.S.; Koros, W.J.; Hopfenberg, H.B. and Stannett, V.T., *J. Memb. Sci.*, **1983**, 13, 161.
- [18] van Krevelen, D.W. and Hoftyzer, P.J., "Properties of Polymers, Their Estimation and Correlation with Chemical Structure", Elsevier, Amsterdam, **1976**.
- [19] Koros, W.J.; Paul, D.R. and Rocha, A.A., *J. Polym. Sci., Polym. Phys. Ed.*, **1976**, 14, 687.