

Gas Transport Properties of a Series of Cardo Polyarylethers

ZHONGGANG WANG,^{1,*} TIANLU CHEN,² JIPING XU²

¹ Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, P. R. China

² Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

Received 6 November 2000; accepted 7 May 2001

ABSTRACT: Gas transport of H₂, CO₂, O₂, N₂, and CH₄ in a series of cardo polyarylethers were examined over a temperature range of 30 ~ 100°C. These polymers include three poly(aryletherketone)s, two poly(arylethersulfone)s, and one poly(aryletherketoneketone). It was found that the large length/diameter ratio of the polymer repeat unit for cardo polyaryletherketoneketone (PEKK-C) and strong intermolecular interaction in hydrogen-bonded polyarylethersulfone (PES-H) and hydrogen-bonded polyaryletherketone (PEK-H) resulted in a considerable increase in gas permselectivity. Alkyl-substituted polyaryletherketone (PEK-A), bearing a pendant bulky propyl group on the cardo ring, simultaneously exhibited 62.5% higher H₂ permeability and 59.8% higher H₂/N₂ permselectivity than unmodified poly(aryletherketone) (PEK-C). The causes of the trend were interpreted in terms of chain packing density, segmental motion ability, steric factor, and intermolecular interaction of polymers, together with gas kinetic diameter and critical temperature data. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 791–801, 2002

Key words: poly(aryletherketone); poly(arylethersulfone); membrane; gas separation

INTRODUCTION

Gas separation with polymer membranes has been proven to be very successful in a variety of industrial applications, including hydrogen recovery from reactor purge gas, nitrogen, and oxygen enrichment, and stripping of carbon dioxide from natural gas, etc.^{1,2} New polymeric membrane materials with high gas permeability and permselectivity are constantly required to continually advance the development of gas separation technology.

Recent studies indicate that separation of smaller molecules such as hydrogen from larger molecules such as nitrogen with polymer membranes is mainly affected by the packing density and segmental motion ability of the polymer chain. High permeability is primarily caused by more free volume, while significant increase in gas permselectivity may be due to restricted segmental motion.^{3–6} On the basis of these facts, one can design new polymers to combine the two favorable factors, and thus synthesized polymers should have both high gas permeability and high permselectivity.

Poly(aryletherketone) (PEK-C) and poly(arylethersulfone) (PES-C), obtained from phenolphthalein with bis(4-nitrophenyl)ketone and bis(4-chlorophenyl)sulfone, respectively, have been noted for their excellent mechanical tough-

Correspondence to: Z. Wang (wangzhonggang@hotmail.com).

* Present address: Institute of Polymer Research Dresden e. V, D-01069, Germany.

Journal of Applied Polymer Science, Vol. 83, 791–801 (2002)
© 2002 John Wiley & Sons, Inc.

ness, electrical/insulating, thermo-oxidative stability as well as high glass transition temperature (218 and 256°C, respectively).⁷ In contrast to hydroquinone-based polyetheretherketone (PEEK), which is insoluble even in polar aprotic solvents, PEK-C and PES-C are soluble in a few polar solvents such as *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and chloroform. These characteristics enable PEK-C and PES-C to possibly serve not only as structural resins but also as functional materials used in ultrafiltration, reverse osmosis and gas separation.

The present paper mainly dealt with the gas permeability through a series of newly prepared polyarylether membranes over a temperature range from 30 to 100°C. The systematic variations in chemical structure were expected to result in interesting and unique variation in physical properties, e.g., packing density and segmental motion of the polymer chain, and thus should significantly affect the gas permeation behavior in polymer membranes. The effects of polymer structure on gas transport properties were investigated through differential scanning calorimetry, wide angle X-ray diffraction (WAXD), and density measurement methods.

EXPERIMENTAL

Materials

Phenolphthalein was purchased from Beijing Chemical Works, and purified by recrystallization from 50:50 (v/v) mixed solvent of ethanol and water, mp 262 ~ 263°C; bis(4-chlorophenyl)sulfone (DCDPS) was purchased from Beijing Chemical plant, and purified by recrystallization from ethanol two times; dimethyl sulfoxide (DMSO) and DMF were purified by vacuum distillation just before use; anhydrous potassium carbonate was finely powdered prior to use; 1,4-bis(4-fluorobenzoyl)benzene (FBB), 3,3'-bis(4-hydroxyphenyl)-isobenzopyrrolidone (HPP), and *N*-propyl-3,3'-bis(4-hydroxyphenyl)-isobenzopyrrolidone (APP) were prepared in our laboratory according to refs. 8 and 9.

All the polyarylethers studied here were prepared via nucleophilic polycondensation from the corresponding bisphenols with dihalides in DMSO using K_2CO_3 as catalyst. A typical procedure for cardo polyaryletherketoneketone (PEKK-C) as follows: to a solution of 4.1462 g (0.03mol) anhydrous K_2CO_3 , 12 mL toluene and 11.8 mL

DMSO, 4.8052 g (0.015mol) phenolphthalein and 4.8348 g (0.015mol) 1,4-bis(4-fluorobenzoyl)benzene were added. A slow stream of nitrogen was maintained throughout the whole reaction. The temperature was raised to 140°C to remove water formed by azeotropic distillation with toluene for about 2 h; then the toluene was distilled out and temperature was raised gradually to 175°C, allowed to react at this temperature for additional 2 h and finally a viscous solution was obtained. After cooling, it was diluted with DMF and settled overnight. The supernatant liquid was coagulated in mixed precipitant of ethanol and water to separate the white polymer. The polymer was washed successively with boiling water to remove the inorganic salt and dried in air at 100°C for 12 h. Other polymers were synthesized in a similar procedure as described above. Their chemical structures as well as reduced viscosity and density data are presented in Table I.

Dense Film Preparation

The polymer samples were dissolved in DMF to form a solution of 8 wt %, which was cast onto a clean glass plate at 60°C in an oven for 8 h. After most solvent evaporated, the film was stripped from glass plate and transferred to vacuum oven and dried further at 200°C and 10 mm Hg for 48 h. Films thick were 35 ~ 40 μm .

Measurements

Reduced viscosities were measured using an Ubbelohde Viscometer at a concentration of 0.5% (w/v) in DMF at $25 \pm 0.01^\circ\text{C}$.

Polymer densities were determined in film sample in a density gradient column containing an aqueous solution of calcium nitrate at 30°C.

Glass transition temperatures (T_g s) were determined on Perkin-Elmer DSC-7, over a temperature interval of 100 ~ 400°C at a heating rate of 20°C/min. T_g s were read at the middle of the change in the heat capacity.

Free volume (V_F) of each of the polymers is given by the equation below:

$$V_F = V_T - V_0 \quad (1)$$

where V_T is specific volume, which can be calculated from the polymer density determined; V_0 is the polymer occupied volume at 0 K, and was obtained according to the group contribution method of Sugden.¹⁰

Table I Chemical Structure of the Polyarylethers

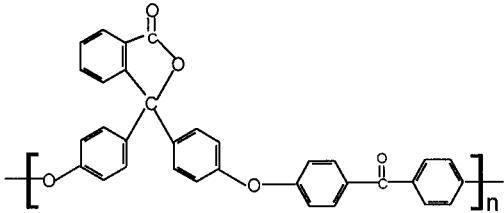
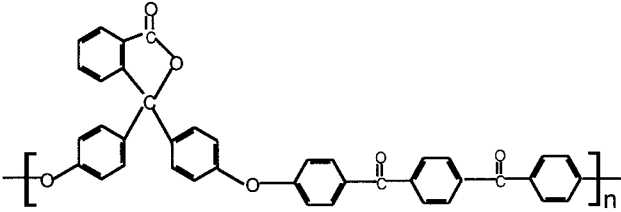
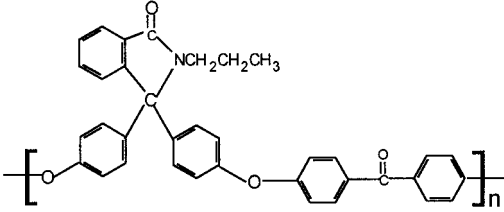
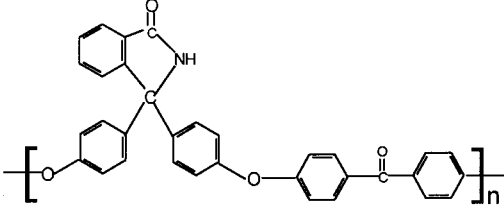
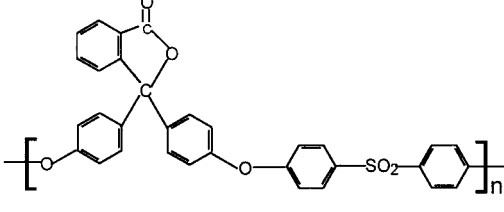
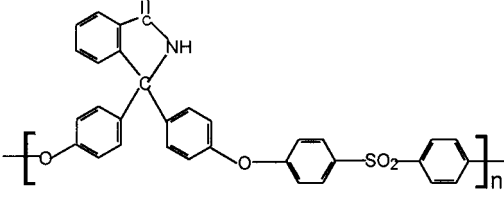
Chemical Structure	Abbreviation	$\eta_{RV}(\text{dL/g})$	$\rho(\text{g/cm}^3)$
	PEK-C	0.663	1.249
	PEKK-C	0.625	1.256
	PEK-A	0.695	1.185
	PEK-H	0.518	1.250
	PES-C	0.663	1.307
	PES-H	0.592	1.310

Table II Gas Transport Properties of Polymers at 30°C

Polymers	<i>P</i> (barrer)			α		
	H ₂	O ₂	CO ₂	H ₂ /N ₂	O ₂ /N ₂	CO ₂ /CH ₄
PEK-C	11.7	0.951	2.73	75.6	6.22	33.2
PEKK-C	7.51	0.634	2.17	103	8.71	38.5
PEK-A	16.9	1.42	4.46	72.2	6.07	28.6
PEK-H	9.91	0.663	2.36	108	7.21	34.2
PES-C	12.1	0.939	5.74	72.6	5.63	40.1
PES-H	9.05	0.651	3.71	105	7.95	54.3
PSF ¹⁴	10.4	1.24	4.42	49.8	5.93	23.1

P: barrer, 1 barrer = 10⁻¹⁰ × cm³ (STP) cm/cm² cmHg.

WAXD measurements were performed on a D/Max-B X-ray diffractometer with Cu K α radiation having a wavelength of 1.54 Å. The inter-chain distance, or *d*-spacing can be calculated with Bragg's equation:

$$\lambda = 2d \sin \theta \quad (2)$$

where θ refers to the angle of the peak maxima.

Pure gas permeability coefficients over the temperature interval of 25–100°C for H₂, O₂, N₂, CO₂, and CH₄ were measured using an apparatus described in the literature.¹¹ The permeation cell temperature was controlled within $\pm 0.2^\circ\text{C}$, and was measured by a calibrated Cu-constantan thermocouple inserted just above the membrane in the permeation cell. In order to eliminate the CO₂ plastification effect, CO₂ was determined finally after the other gases. All the gases used here were at least 99.99% in purity. The permeability coefficient (*P*) was obtained from the slope of pressure–time plots after a steady state has been reached. The apparent diffusion coefficients (*D*_{app}) were determined using the time lag method according to the relation:

$$D_{\text{app}} = l^2/6L \quad (3)$$

where *L* is the time lag and *l* is the thickness of the membrane. The solubility coefficient (*S*) of the gases in each polymer membrane can be calculated by the relation $S = P/D$. The ideal separation factor ($\alpha_{A/B}$) of gas *A* through a polymer membrane over another gas *B* is given by the relation

$$\alpha_{A/B} = P_A/P_B = D_A/D_B \times S_A/S_B \quad (4)$$

where *P*_A and *P*_B are the permeability coefficients for gases *A* and *B*, *D*_A and *D*_B are diffusivity coefficients, *S*_A and *S*_B are solubility coefficients, and the ratio *D*_A/*D*_B and *S*_A/*S*_B are known as the diffusivity selectivity and the solubility selectivity, respectively.

RESULTS AND DISCUSSION

Gas Permeability, Diffusivity, and Solubility

Permeability and selectivity coefficients of five gases are summarized in Table II. In each polymer, the permeability of H₂ was the highest, and was followed sequentially by CO₂, O₂, N₂, and CH₄, which was the same as the order of the gas kinetic diameter— σ_{H_2} (2.80 Å) < σ_{CO_2} (3.30 Å) < σ_{O_2} (3.46 Å) < σ_{N_2} (3.64 Å) < σ_{CH_4} (3.80 Å)¹²—but different from the tendency of critical temperature— $T_{c(\text{CO}_2)}$ (304.2 K) > $T_{c(\text{CH}_4)}$ (190.6 K) > $T_{c(\text{O}_2)}$ (154.6 K) > $T_{c(\text{N}_2)}$ (126.2 K) > $T_{c(\text{H}_2)}$ (33.2 K).¹³ Therefore, the gas permeabilities in this series of polymers were primarily correlated with the kinetic factors.

All the polymers in this study had H₂ permeability of about 10 barrers, similar to that of commercial bisphenol-A polysulfone (PSF), but showed significantly higher H₂/N₂ permeability selectivity. Among them, the H₂/N₂ selectivity coefficients of PEKK-C, hydrogen-bonded polyaryletherketone (PEK-H) and hydrogen-bonded polyarylethersulfone (PES-H), were more than twice as high as that of PSF. In comparison with PEK-C and PES-C, hydrogen-bonded PEK-H and PES-H displayed greatly increased gas permselectivity and decreased permeability. Some results in this series of polymers were interestingly

Table III Diffusivity and Solubility of CO₂ and CH₄ Gases

Polymers	Diffusivity		Solubility			
	CO ₂	CH ₄	CO ₂	CH ₄	$D_{\text{CO}_2}/D_{\text{CH}_4}$	$S_{\text{CO}_2}/S_{\text{CH}_4}$
PEK-C	0.746	0.0959	2.78	0.651	7.78	4.27
PEK-H	0.554	0.0594	3.24	0.883	9.33	3.67
PEK-A	1.16	0.144	2.91	0.823	8.02	3.55
PES-C	1.23	0.132	3.55	0.824	9.31	4.31
PES-H	0.662	0.0583	4.27	1.08	11.3	3.95

Diffusivity: 10^{-8} cm²/s; solubility: cm³ (STP)/cm³ atm.

found to run counter to the so-called gas permeability and permselectivity trade-off rule. Compared to PEK-C, alkyl-substituted polyaryletherketone (PEK-A), which had a pendant n-propyl group on the cardo ring, simultaneously exhibited higher gas permeabilities and higher permselectivities. For example, its permeability of H₂ and selectivity of H₂/N₂ increased by 62.5 and 59.8%, respectively. In addition, PES-C also exhibited higher performance both in CO₂ permeability and CO₂/CH₄ permselectivity.

The data of gas diffusivity and diffusivity selectivity, with the gas solubility and solubility selectivity for the polymers is presented in Tables III and IV. The relationship plots of diffusivity coefficients as a function of gas kinetic diameter are given in Figure 1. For O₂, N₂, and CH₄, which had similar critical temperature, gas diffusivities were observed to linearly decrease with the increase of penetrant size, as in the case of gas permeabilities. However, for CO₂, the high solubility or sorption ability on the polymer chain might appear disadvantageous for its diffusion. In spite of CO₂'s smaller molecule size, its diffusion coefficient was smaller than that of O₂.

Structure-Property Relationship

All the six polymers in this study contain the rigid bulky cardo group, endowing them with specific physical properties such as high glass transition temperature and excellent solubility in moderate organic solvents. Flexible and tough free-standing films could be easily cast from their solutions. PES-H and PEK-H had lactam groups instead of lactone groups of PES-C and PEK-C. The strong intermolecular hydrogen bonds between lactam groups severely inhibited PES-H and PEK-H segmental motion ability. As a measure of the rigidity of polymer chain, the glass transition temperature (T_g) of PES-H was 32°C higher than that of PES-C, and T_g of PEK-H was also 45°C higher than that of PEK-C. On the other hand, the measured free volume (V_f) of PEK-H decreased from 0.124 cm³/g of PEK-C to 0.115 cm³/g, and a similar result was also observed for PES-H, indicating that the intermolecular hydrogen bonds resulted in PES-H and PEK-H having denser chain packing density. Both tight chain packing and restricted segmental motion were unfavorable for the gas diffusion through polymer membranes. Especially, the dif-

Table IV Diffusivity and Solubility of O₂ and N₂ Gases

Polymers	Diffusivity		Solubility			
	O ₂	N ₂	O ₂	N ₂	$D_{\text{O}_2}/D_{\text{N}_2}$	$S_{\text{O}_2}/S_{\text{N}_2}$
PEK-C	2.15	0.488	0.336	0.238	3.48	1.41
PEK-H	1.65	0.274	0.296	0.202	6.02	1.45
PEK-A	4.05	0.815	0.268	0.209	4.98	1.28
PES-C	3.24	0.685	0.220	0.185	4.73	1.19
PES-H	1.51	0.301	0.328	0.218	5.02	1.51

Diffusivity: 10^{-8} cm²/s; solubility: cm³ (STP)/cm³ atm.

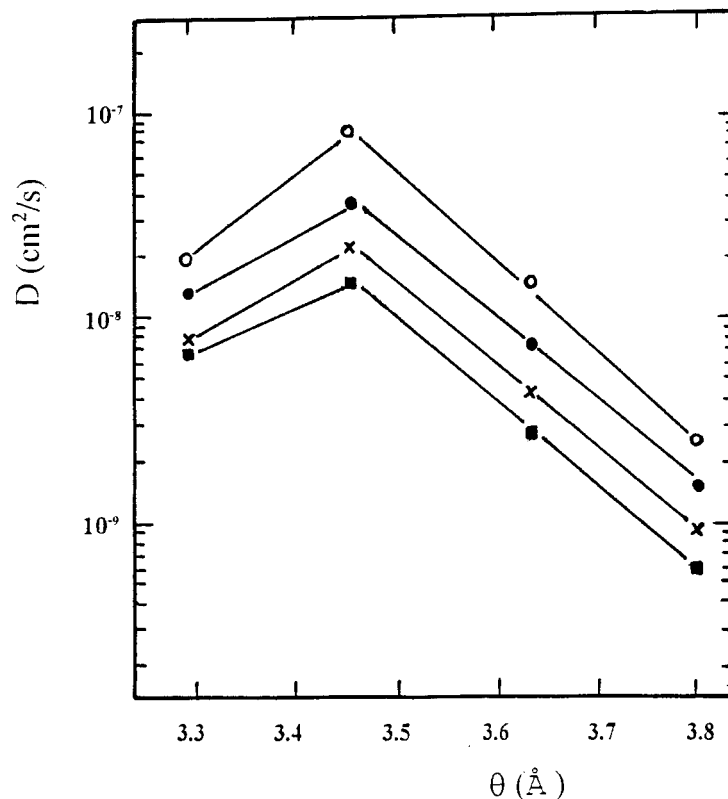


Figure 1 Plots of $\text{Log}D$ vs penetrant size (θ) for these polymers. (\times) PEK-C; (\bullet) PES-C; (\blacksquare) PES-H; (\circ) PEK-A ($\times 2$).

fusion coefficients of larger gas molecules, such as nitrogen and methane, decreased more rapidly than the smaller gas molecules. As a result, PES-H and PEK-H exhibited significantly higher gas permselectivities with decreased gas permeabilities.

After the hydrogen atom in lactam ring of PEK-H was replaced with the n-propyl group, intermolecular hydrogen bonds disappeared, and the resultant PEK-A had a more flexible polymer chain, demonstrated by its 39°C lower T_g than that of PEK-H. Nevertheless, PEK-A still displayed slightly higher T_g than PEK-C due to the steric effect of the bulky propyl group. As shown from the WAXD patterns for PEK-C, PEK-A, and PEKK-C in Figure 2, relative to PEK-C, the diffraction halo of PEK-A shifted toward a smaller diffraction angle (2θ). The calculated d -spacing of PEK-A was 5.21 \AA , while it was 4.83 \AA for PEK-C. Correspondingly, The free volume of PEK-A was also 5.6% larger than that of PEK-C, indicating that the pendant propyl group was effective to open the polymer chain of PEK-A. Consequently, the O_2 diffusion coefficient of PEK-A was nearly twice that of PEK-C due to its high free volume, while its O_2/N_2 diffusion selectivity also increased

by 43% owing to its hindered segmental motion. This was why PEK-A simultaneously possessed higher gas permeabilities and permselectivities than PEK-C.

Cardo polyaryletherketoneketone (PEKK-C) was achieved by extending the repeat unit of PEK-C with the $-\text{CO}-\text{C}_6\text{H}_4-$ group. The rigid and relatively symmetric phenyl ketone group could enhance the length/diameter ratio, and this was responsible for PEKK-C having a higher glass transition temperature and denser chain packing. The T_g of PEKK-C increased from 218°C of PEK-C to 233°C , and the V_f and d -spacing of PEKK-C decreased by 8.1 and 10.6%, respectively. As a result, the PEKK-C membrane displayed high gas permselectivity.

For the O_2/N_2 gas pair, the data in Table II revealed that the gas permeabilities of the six polymers ranked in the following order: PEKK-C < PES-H < PEK-H < PEK-C < PES-C < PEK-A, which was the same as that of gas diffusivities. Furthermore, as shown in Table IV, the O_2/N_2 diffusivity selectivities in this series of polymers ranged from 3.48 to 5.68, whereas the solubility

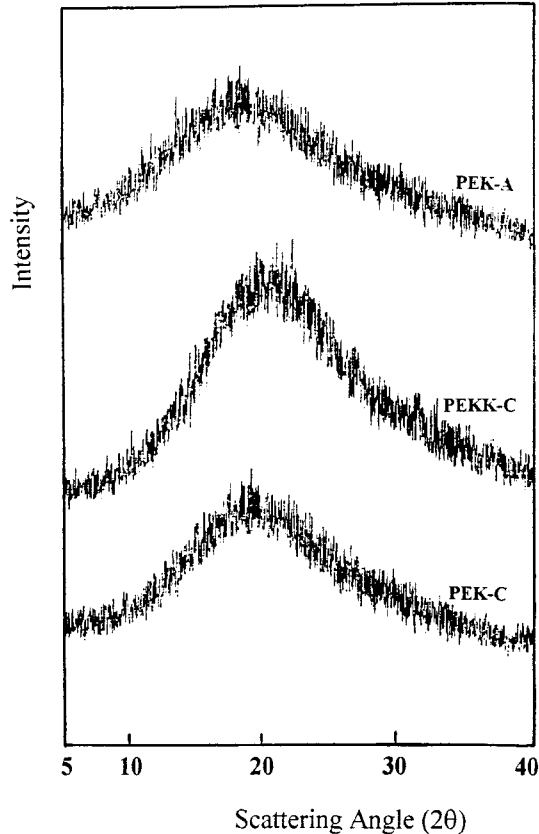


Figure 2 Wide-angle X-ray diffraction patterns of polymers.

selectivities were only about 1.4. So the difference of gas permeabilities of polymers in this study were determined mainly by variation in the gas diffusivities, as in the case of most glassy polymer membrane materials.¹⁵⁻¹⁸

The curve of gas solubilities (S) in polymers as a function of gas critical temperature (T_c) is illustrated representatively for PES-H in Figure 3. In each polymer, gases with high T_c tended to have high S . Carbon dioxide, which had the highest T_c among the five gases, exhibited the highest solubility. The solubility coefficient of CO_2 was found to be higher than N_2 by a factor of 11 ~ 23. Hence, for the CO_2/CH_4 gas pair, thermodynamic factors should be considered in order to understand their gas permeation behavior.

The effects of polymer structure on solubility for a specific condensable gas can be investigated through the polymeric solubility parameter, which is equal to the square root of polymer cohesive energy density (CED). CED data calculated by the group contribution method¹⁹ are given in Table V. The existence of lactam groups increased PES-H and PEK-H CED; as a result, they exhibited higher solubility coefficients for CO_2 and CH_4 . The solubility selectivities of CO_2/CH_4 for this series of polymers were quite high, varying from 3.55 to 4.31. In comparison with

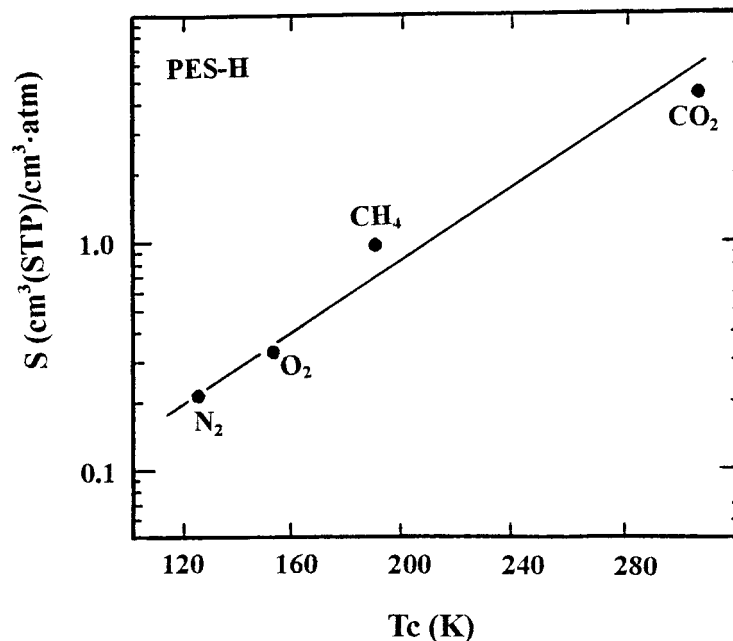


Figure 3 Relationship of $\text{Log}S$ vs T_c in PES-H.

Table V Some Physical Properties of Polymers

Polymers	ρ	T_g	$V_{30^\circ\text{C}}$	V_0	V_f	$1/V_f$	CED
PEK-C	1.249	218	0.801	0.673	0.124	8.07	458.4
PEKK-C	1.256	233	0.796	0.682	0.114	8.77	470.4
PEK-A	1.185	224	0.844	0.713	0.131	7.63	607.7
PEK-H	1.250	263	0.800	0.685	0.115	8.70	501.0
PES-C	1.307	256	0.765	0.647	0.115	8.70	495.6
PES-H	1.310	289	0.763	0.658	0.105	9.52	673.0

ρ : g/cm³; T_g : °C; V : cm³/g; CED : KJ/cm³.

that of O₂/N₂ of only about 1.4, for the separation of CO₂ from CH₄, the contribution coming from solubility and solubility selectivity played a significant role on the overall gas permeability and permselectivity.

Previous reports have shown that gas permeability coefficients for a given gas in different polymers can be correlated well with the free volume of the polymer according to the following relation^{20–22}:

$$P = Ae^{-B/VF} \quad (5)$$

in which the parameters A and B depend on the type of gas.

For noncondensable gases, such as N₂, as shown in Figure 4, the relationship of P_{N_2} and $1/V_F$ was found to be quite consistent with the

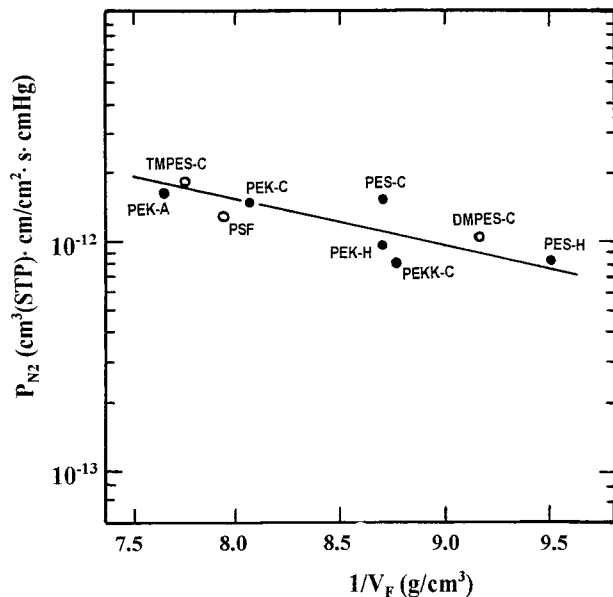


Figure 4 Correlation between P_{N_2} and $1/V_F$ of polymers. PSF: bisphenol-A polysulfone¹⁴; DMPES-C: dimethyl-substituted PES-C¹⁴; TMPES-C: tetramethyl-substituted PES-C.¹⁴

above equation. The polymer with more free volume tended to have high gas permeability. But, for condensable CO₂ gas, things were different. The polymers in this study can be approximately classified into two categories, i.e., poly(aryletherketone)s and poly(arylethersulfone)s. Within the same series of polymers, the correlation of P_{CO_2} with free volume was rather successful (see Fig. 5). The reason that CO₂ permeabilities in polyarylethersulfones were found to be evidently higher than that in polyaryletherketones might be attributed to the stronger interaction between CO₂ molecule and SO₂ group.

Temperature Dependence

In the temperature range of 30–100°C, the relationships between gas permeability and diffusivity with temperature for all the polymers studied here were consistent with the Arrhenius equation:

$$P = P_0 e^{-E_p/RT} \quad (6)$$

$$D = D_0 e^{-E_D/RT} \quad (7)$$

$$S = S_0 e^{-H_S/RT} \quad (8)$$

where P_0 , D_0 , and S_0 are preexponential factors, R is gas constant, while E_p and E_D are the appar-

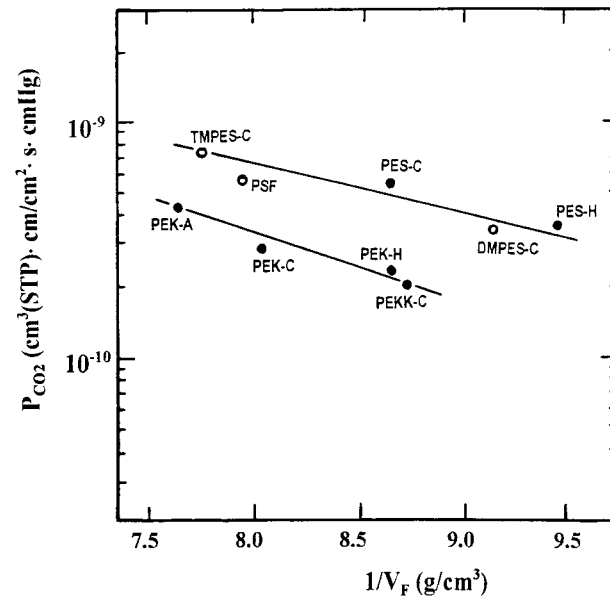


Figure 5 Correlation between P_{CO_2} and $1/V_F$ of polymers. PSF: bisphenol-A polysulfone¹⁴; DMPES-C: dimethyl-substituted PES-C¹⁴; TMPES-C: tetramethyl-substituted PES-C.¹⁴

ent activation energy and H_s is solution heat. E_p , E_D , and H_s can be used as a measure of temperature dependency of gas permeation, diffusion, and solution.

Typical curves of $\text{Log}P$ vs $1/T$, $\text{Log}D$ vs $1/T$, and $\text{Log}S$ vs $1/T$ for PES-H are illustrated in Figures 6–8. Other polymers gave similar behaviors. It was observed from the above figures that the gas permeation and diffusion coefficients increased with temperature, whereas gas solution coefficients decreased with temperature. The results also supported the fact that the gas permeabilities in this series of polymers were controlled by the gas diffusivities other than solubilities. $E_{p,s}$, $E_{D,s}$, and H_s for CH_4 , N_2 , O_2 , and CO_2 , calculated from the slope of plots, are listed in Table VI. For the four gases, $E_{p,s}$ were in the order of $\text{CH}_4 > \text{N}_2 > \text{O}_2 > \text{CO}_2$. Among the four gases, CH_4 exhibited the highest permeation activation energy because of its largest molecule kinetic diameter (θ), whereas the lowest E_p of CO_2 was due to its very low solution heat. The $E_{p,s}$ in this series of polymers are listed in the same order of $\text{PEKK-C} > \text{PES-H} > \text{PEK-H}$

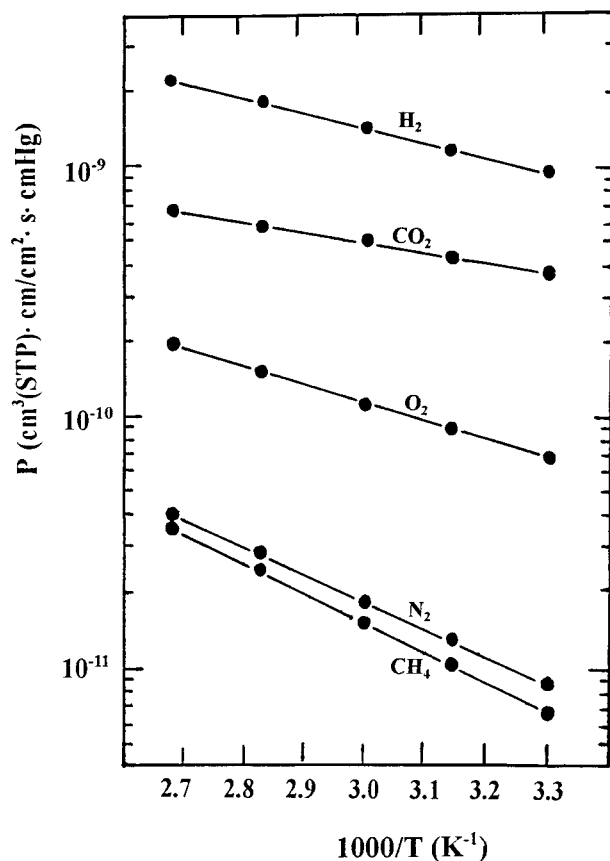


Figure 6 Plots of gas permeability as a function of temperature in PES-H.

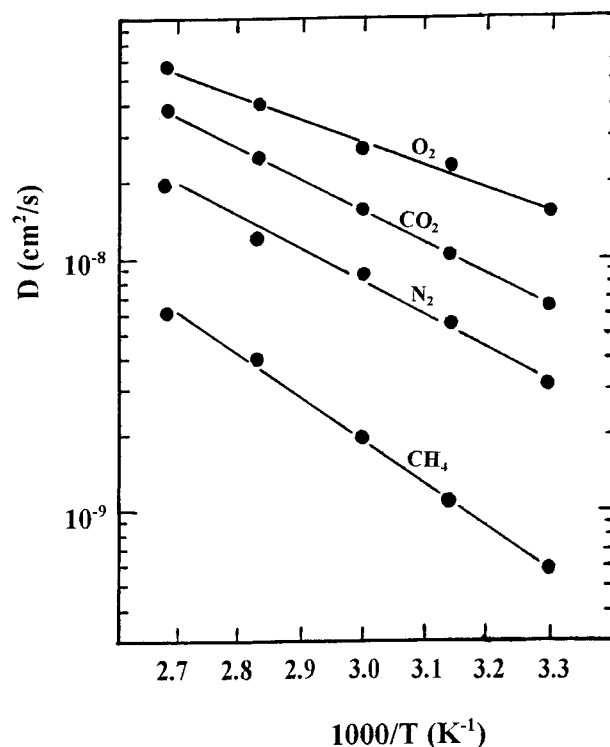


Figure 7 Plots of gas diffusivity as a function of temperature in PES-H.

$> \text{PEK-C} > \text{PES-C} > \text{PEK-A}$, which is inversely related to the gas permeabilities.

According to Meares's gas diffusion hypothesis,²³ E_D was equated to the product of cohesive energy density (CED) and the volume of the diffusional cylinder as below:

$$E_D = (\pi/4)\delta^2\lambda(\text{CED}) \quad (9)$$

where δ is the diameter of the cylinder and λ is the diffusional length. The term $(\pi/4)\delta^2\lambda$ is the required somewhat cylindrical volume for gas diffusion, which is mainly related to size of permeable gas molecules, while CED can be used as the indicator of interaction of polymer chains and mainly determine the ability in segmental motion of polymer chain.

Densely packed polymers have less unoccupied "free" space, and require larger segmental motions to open a sufficient passageway for diffusion. Consequently, the dense chain packing and strong interchain interacting PES-H and PEK-H exhibited higher cohesive energy density, and reasonably had high diffusion activity energy. On the contrary, packing-inhibited chain structure led to PEK-A lower diffusion activity energy.

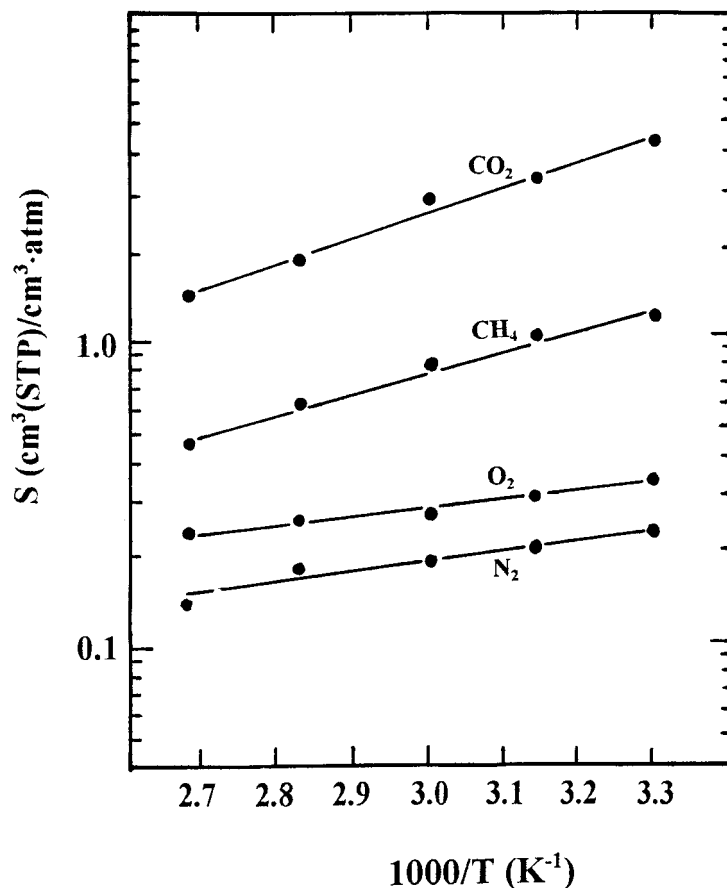


Figure 8 Plots of gas solubility as a function of temperature in PES-H.

For the gas pair to be separated, since the E_p s of larger penetrant (such as N_2) was usually bigger than that of smaller one (such as H_2 and O_2), the permeability coefficients of larger penetrants appeared to grow more rapidly with the rise of temperature. As a result, the increase in gas permeability with temperature was always accompanied by a great loss in gas selectivity. As shown in Table VII, among the six polymers, PEKK-C still

maintained high H_2/N_2 selectivity in 65.8 and O_2/N_2 selectivity in 6.03, exhibiting potential use as high temperature gas separation membrane material.

CONCLUSIONS

The above results demonstrate that subtle variations in chemical structure can yield evident effects

Table VI Apparent Activation Energies of CO_2 , CH_4 , O_2 , and N_2

Polymers	CO_2			CH_4			O_2			N_2		
	E_P	E_D	H_S	E_P	E_D	H_S	E_P	E_D	H_S	E_P	E_D	H_S
PEK-C	5.43	19.5	-14.1	22.9	30.1	-7.15	14.9	17.6	-2.70	19.3	22.4	-3.14
PEK-H	6.19	23.1	-16.9	24.2	35.3	-11.1	—	—	—	—	—	—
PEKK-C	—	—	—	—	—	—	15.3	18.4	-3.13	20.2	24.7	-4.46
PEK-A	4.64	18.4	-13.8	21.0	28.3	-7.34	10.5	15.1	-4.59	16.3	19.5	-3.17
PES-C	8.07	21.9	-13.8	21.4	30.5	-9.12	12.5	15.8	-3.27	18.6	22.8	-4.21
PES-H	8.11	23.7	-15.6	22.1	32.2	-10.3	13.9	18.2	-4.32	21.0	25.6	-4.55

Unit: kJ/mol.

Table VII Gas Transport Properties of Polymers at 60 and 100°C

Polymers	60°C				100°C			
	P_{H_2}	α_{H_2/N_2}	P_{O_2}	α_{O_2/N_2}	P_{H_2}	α_{H_2/N_2}	P_{O_2}	α_{O_2/N_2}
PEK-C	18.8	57.6	1.62	5.08	31.5	48.9	2.88	4.48
PEKK-C	12.8	85.3	1.09	7.27	21.5	65.8	1.98	6.03
PEK-A	23.6	56.3	2.06	4.92	31.2	39.7	3.10	3.94
PEK-H	15.9	79.1	1.17	5.82	26.5	56.5	2.17	4.62
PES-C	19.2	59.3	1.77	5.22	26.4	46.7	2.52	4.43
PES-H	13.4	73.0	1.07	5.84	20.4	49.5	1.83	4.44

P: barrer; 1 barrer = $10^{-10} \times \text{cm}^3$ (STP) $\text{cm}/\text{cm}^2 \text{cmHg}$.

on the polymeric segmental mobility, chain packing density, and interchain interaction, so as to considerably change gas transport properties in polymer membranes. For noncondensable gases, such as H_2 , O_2 , and N_2 , the gas permeabilities were correlated well with the free volume of polymers. However, for the condensable CO_2 gas, the good correlation between gas permeability and free volume could only be obtained within the same series of polymers, i.e., either poly(aryletherketone)s or poly(arylethersulfone)s in this study. The possible reason may be due to CO_2 molecule stronger interaction with SO_2 group in poly(arylethersulfone)s.

Similar to most glassy polymers, the gas permeability behavior in the six polymers was primarily governed by the gas diffusivity other than solubility factor. The effects of polymer structural variations on gas permeabilities were attributed to polymer chain rigidity, length/diameter ratio, steric hindrance, and intermolecular interaction. For example, the increased length/diameter ratio of polymer repeat unit and strong intermolecular hydrogen bonds led to PEKK-C, PEK-H, and PES-H low gas permeability and extremely high permselectivity. The bulky and rigid propyl group in PEK-A could enhance both its gas permeability and permselectivity.

The gas permeability temperature dependencies were studied according to the gas permeation apparent activation energy, diffusion activation, and solution heat. The results revealed that the solution heat was mainly determined by the gas critical temperature and the diffusion activation energy was dependent on the free volume, segmental mobility as well as gas molecule size. The combination of high glass transition temperature and fairly high gas selectivity coefficients made PEKK-C a promising candidate used as high temperature gas membrane separation material.

REFERENCES

1. Spillman, R. W. *Chem Eng Prog* 1989, 85, 41.
2. Mazur, W. H.; Chan, M. C. *Chem Eng Prog* 1982, 78, 38.
3. Usenko, K. A.; Springer, J.; Privalko, V. *J Polym Sci, Polym Phys Ed* 1999, 37, 2183.
4. Dorkenoo, K. D.; Pfromm, P. H.; Rezac, M. E. *J Polym Sci, Polym Phys Ed* 1998, 36, 797.
5. Shigetoshi, M.; Hiroki, S.; Tsutomu, N. *J Membr Sci* 1998, 141, 21.
6. Pixton, M. R.; Paul, D. R. *Macromolecules* 1995, 28, 8277.
7. Chen, T. L.; Yuan, Y. G.; Xu, J. P. *Chinese Patent* 1,038,098, 1988.
8. Ji, X. L.; Zhang, W. J. *Chinese J Appl Chem* 1993, 10, 106.
9. Baeyer, A. *Annales de Chemie* 1980, 202, 80.
10. Sugden, S. *J Chem Soc* 1927, 1786.
11. Liu, W. Y.; Chen, T. L.; Xu, J. P. *J Membr Sci* 1990, 53, 203.
12. Breck, D. W. *Zeolite Molecular Sieves*; John Wiley & Sons: New York, 1994; p 636.
13. Jeans, J. *An Introduction to the Kinetic Theory of Gases*; Cambridge University Press: London, 1982; p 183.
14. Wang, Z. G. *Doctoral thesis, Changchun Institute of Chemistry, Chinese Academy of Sciences*, 1996.
15. McHattie, J. S.; Koros, W. J.; Paul, D. R. *Polymer* 1991, 32, 840.
16. Koros, W. J.; Fleming, G. K.; Jordan, S. M. *Prog Polym Sci* 1988, 13, 339.
17. Hellums, M. W.; Koros, W. J.; Husk, G. R.; Paul, D. R. *J Membr Sci* 1989, 46, 93.
18. Aitken, C. L.; Koros, W. J.; Paul, D. R. *Macromolecules* 1992, 25, 3424.
19. Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers*, 3rd ed.; Elsevier: New York, 1992.
20. Fujita, H. *Diffusion in Polymers*; Academic Press: New York, 1968.
21. Lee, W. M. *Polym Eng Sci* 1980, 20, 65.
22. Maeda, Y.; Paul, D. R. *J Polym Sci, Polym Phys Ed* 1987, 25, 1005.
23. Meares, P. *J Am Chem Soc* 1954, 76, 3415.