

Gas Transport in Poly(vinyl Cyclohexanecarboxylate)

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Synopsis

Low-pressure gas permeation measurements were performed on poly(vinyl cyclohexanecarboxylate) to evaluate its transport characteristics. The transport data of CO₂, O₂, N₂, He, and Ar, were presented as a function of temperature ranging from 15 to 85°C. The apparent transport parameters were determined by the time lag method above and below the glass transition temperature and they were compared with other polymers of similar chemical structures. The side chain of the polymer has a bulky cyclohexyl group, which seemed to increase gas diffusivity. The activation energy for diffusion seemed to be related with the polarity of side chain. The relationships between gas diffusivity, physical properties, and chemical structure were qualitatively discussed in comparison with the data on poly(vinyl benzoate) and poly(vinyl acetate).

INTRODUCTION

Gas separation by polymer membranes is a very interesting and important problem not only scientifically but also technologically. Many polymers and composite membranes with high permeabilities and/or durability have been developed and, in fact, some of them are useful industrially.¹⁻³ Further development and improvement of new polymers make it necessary to know the relationships between the gas permeability and the chemical structure or physical properties of a polymer. Several studies have been reported on the subject.⁴⁻⁷ For example, Allen et al. have systematically studied some related polymers and discussed the transport of noble gases considering such properties of polymer as free volume, fluctuating free volume, density, chain stiffness, dipole-dipole interaction, and so on.⁷ However, discussion of the gas transport behavior especially gas diffusivity, is still difficult, and further systematic research seems to be necessary.

Previously we reported the transport parameters for several gases of poly(vinyl benzoate) (PVB) and compared with poly(vinyl acetate) (PVAc), which has a similar structure to PVB.⁸ From the discussion in the paper, it seems possible to increase the gas permeability of polymer when the size of side groups is increased. We chose poly(vinyl cyclohexanecarboxylate) (PVCH), whose side group is bulkier than that of PVB, as the next polymer for investigation of this expectation. To study the transport of gases in the polymer, the time lag method was used in this work. First, the transport parameters of CO₂ were compared with the sorption parameters determined by the dual-mode sorption model.⁹ Comparing the data of the three related polymers measured by the similar method, the relationships between the gas

diffusivity and the chemical structure and physical properties of polymers will be discussed qualitatively.

EXPERIMENTAL

Materials

The preparation and the properties of PVCH were described in the preceding paper.⁹

The gases, CO₂, O₂, N₂, He, and Ar, were at least greater than 99.99% pure and no further purification was performed.

Apparatus and Procedure

Permeation measurements were made using facilities and procedures described previously.⁸ Ingoing pressures were usually from 24 to 55 cmHg and varied from 5 to 78 cmHg when the pressure dependence was examined for

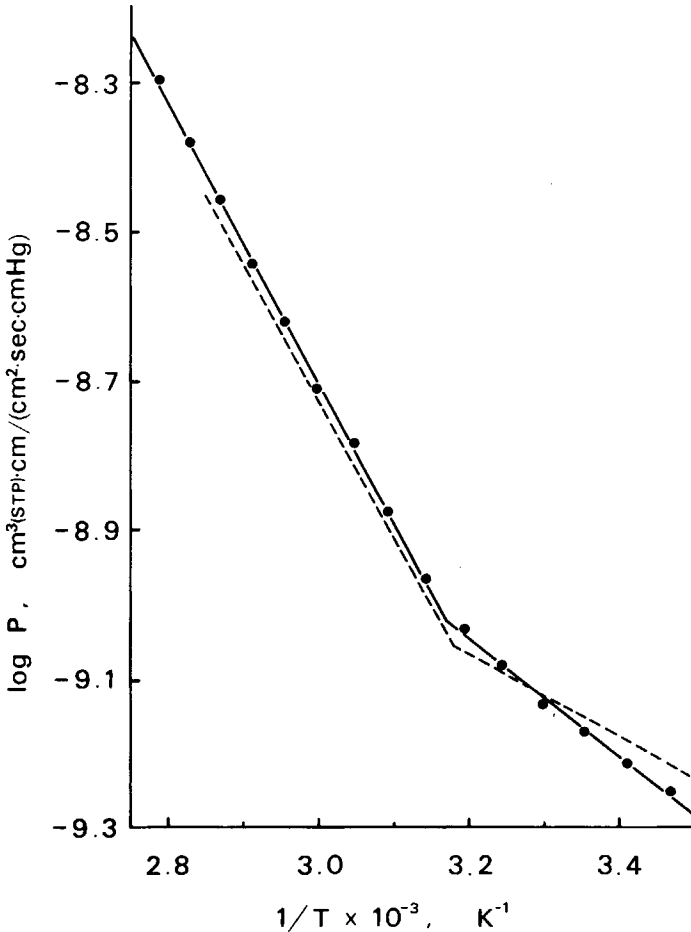


Fig. 1. Temperature dependence of the permeability coefficients for CO₂ in PVCH. (---), Data calculated from the sorption parameters (see text).

CO₂ and O₂. The films were thermally well conditioned at about 85°C before the measurements.

RESULTS AND DISCUSSION

The temperature dependence of the permeability coefficient, P , is presented in Figure 1 in the form of Arrhenius plot for CO₂ in PVCH. The plot shows the change of slope at about 42°C. The temperature dependences of the apparent diffusion, D , and solubility, S , coefficients are presented in Figures 2 and 3, respectively. D was obtained from the time lag, θ , by Eq. (1) and S was calculated by Eq. (2).

$$D = l^2/6\theta \quad (1)$$

$$P = D \cdot S \quad (2)$$

where l is the film thickness. Usually gas sorption process in glassy polymers ($T < T_g$) is more complex than in rubbery polymers ($T > T_g$) because of their unequilibrium states. That is, the gas solubilities do not obey Henry's law and the dual-mode sorption model has been proposed and applied to describe that

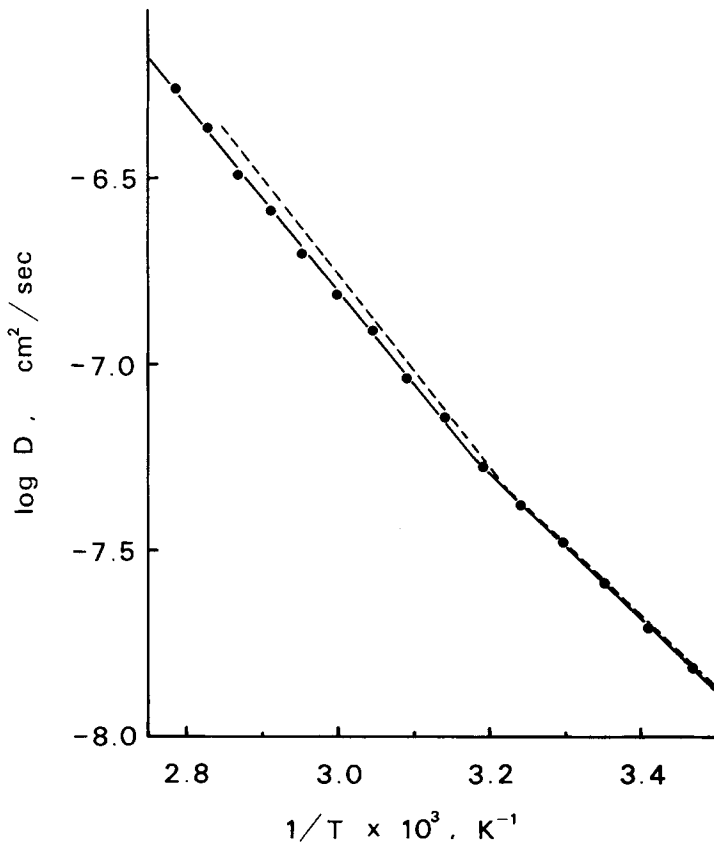


Fig. 2. Temperature dependence of the apparent diffusion coefficients for CO₂ in PVCH. (---), Data measured by the sorption measurements (see text).

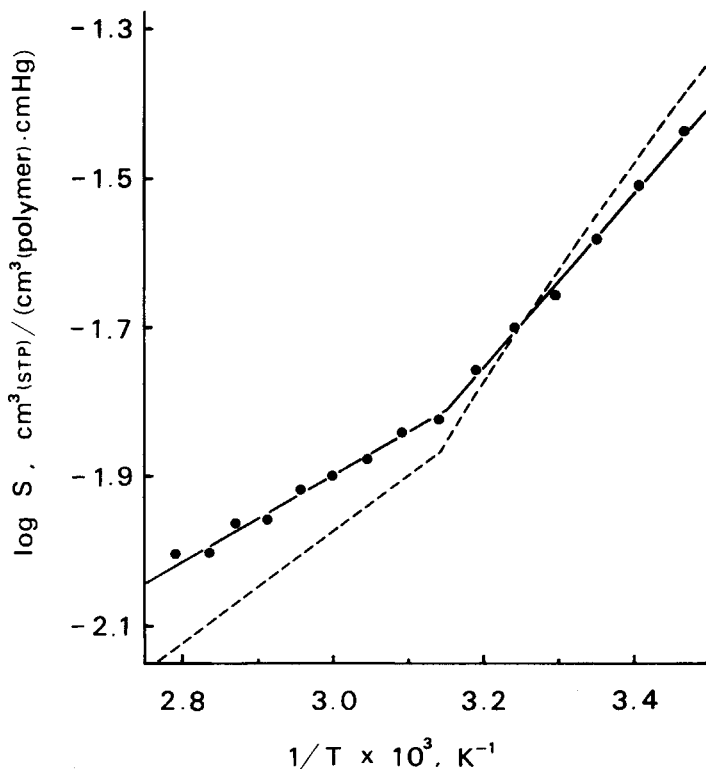


Fig. 3. van 't Hoff plot of the apparent solubility coefficients for CO_2 in PVCH. (---), Data calculated from the sorption parameters (see text).

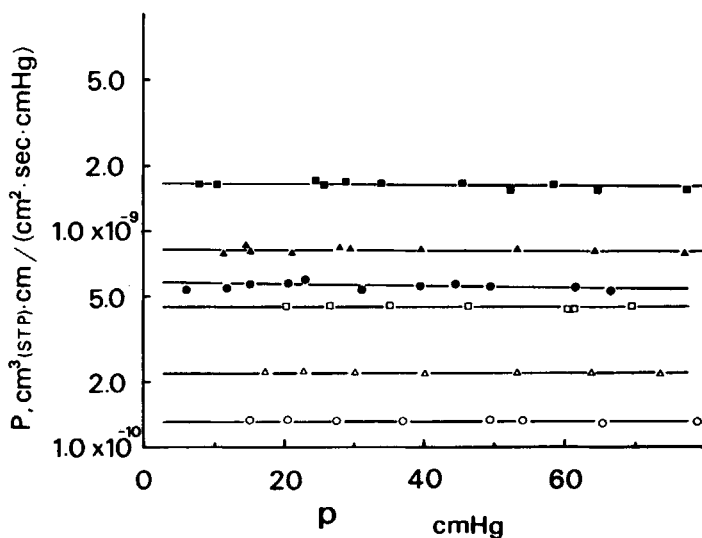


Fig. 4. Pressure dependence of the permeability coefficients for CO_2 and O_2 in PVCH. CO_2 : (●) 15°C ; (▲) 35°C ; (■) 55°C . O_2 : (○) 15°C ; (△) 35°C ; (□) 55°C .

process by many workers. The diffusion process should be complicated by the nature of glasses. According to this, D and S obtained by Eqs. (1) and (2) are not good enough to describe the transport behavior. From the results discussed in the following paragraphs, however, the Fick's and Henry's laws are assumed to be valid in the analysis of the present permeation data.

From the high-pressure sorption measurement, it is well known that thermal annealing reduces microvoids.¹⁰ Therefore, if the polymers are annealed very well, D and S will not be so complex even for glassy polymers. The films used here were conditioned well as noted in the Experimental section. There is no doubt that there were fewer microvoids than in the sample used for sorption measurements, which was exposed to 50 atm of CO_2 before measurement.⁹ The sorption parameters showed that there were only a few microvoids left in PVCH even after high-pressure CO_2 exposure. In Figures 1-3, P , D , and S are compared to the parameters determined by the sorption measurements. k_D and $k_D + C'_H b$ determined by the dual-mode sorption model were divided by 76 cmHg/atm for a units conversion from atmosphere to cmHg, where k_D , C'_H , and b are the Henry's law, the hole saturation, and the affinity constant, respectively. They are plotted by a dashed line as the apparent solubility coefficients in Figure 2. D determined from the sorption process are also plotted by a dashed line as the diffusion coefficients in Figure 3. For convenience, their products are also presented by a dashed line in Figure 1. As shown in the figures, the parameters determined by the different measurements are in good agreement with each other. The agreement confirms that the films used for permeation experiment had, at most, as many microvoids as the sample used for sorption measurements.

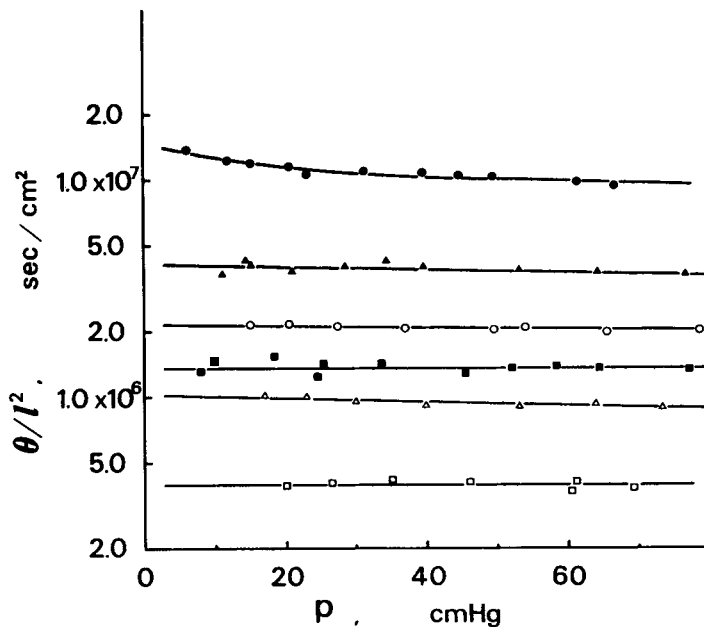


Fig. 5. Pressure dependence of the time lags for CO_2 and O_2 in PVCH. CO_2 : (●) 15°C; (▲) 35°C; (■) 55°C. O_2 : (○) 15°C; (△) 35°C; (□) 55°C.

It is expected that P and D shown in Figures 1 and 2 will be affected only slightly by a few microvoids. The pressure dependences of P and θ shown in Figures 4 and 5 confirm this. They were measured at pressures ranging from about 0.1 to 1 atm. To remove the effect of film thickness, θ was divided by l^2 . The pressure dependence of P is only 10% and that of θ is about 20% at 15°C. As expected, the dependences are decreased with the increase of temperature. Toi et al. reported similar pressure dependences of P and D on CO_2 -PVAc system.¹¹ They calculated the dual-mode parameters from the pressure dependence of D and reported small values of C'_H , which are very close to the values determined on PVCH by the low-pressure sorption measurement.⁹

For less-soluble gases such as O_2 and N_2 , it is plausible to assume that the complexity in permeation in glassy polymers is less than for CO_2 . In sorption isotherms the character of curvature is usually much less, and the parameters of C'_H and b are smaller. In fact, less pressure dependence of P is observed for

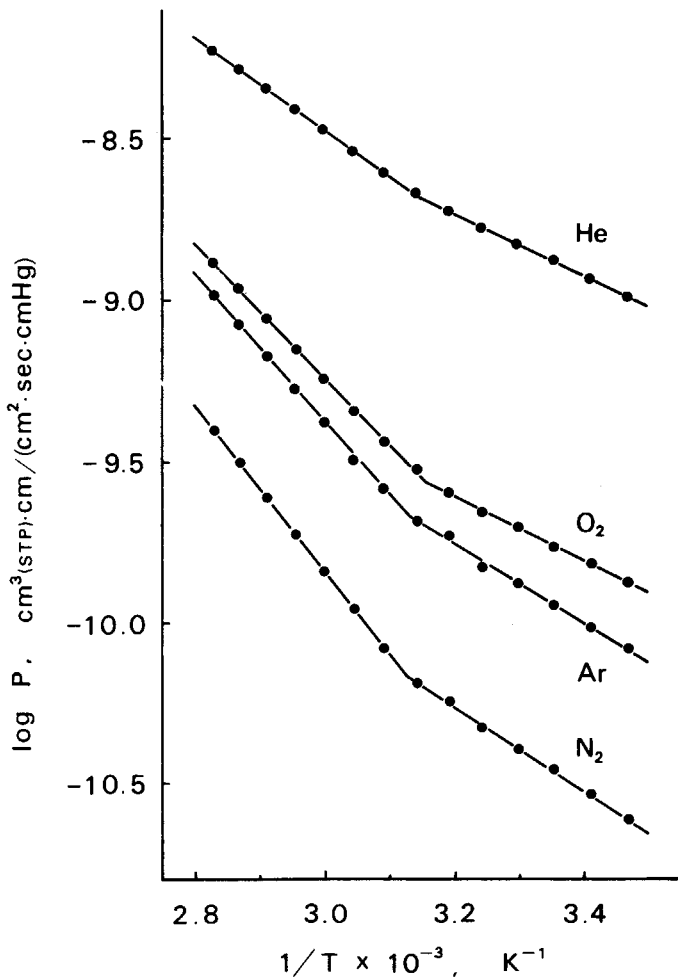


Fig. 6. Temperature dependence of the permeability coefficients for O_2 , N_2 , He, and Ar in PVCH.

O_2 as shown in Figure 4. Even at $15^\circ C$, the pressure dependence of θ is no more than 10%, as shown in Figure 5, and no dependence is observed for either P or θ at $55^\circ C$ as in the case of CO_2 . Taking into account the Results and Discussion sections, Eqs. (1) and (2) are used in the present study on permeation at pressures below 1 atm.

The temperature dependence of P is presented for four gases in PVCH in Figure 6. Every plot has a change of slope at about $45^\circ C$, which corresponds to the sorption data very well and is fairly close to T_g determined by the dilatometry.⁹ D is also presented in the form of Arrhenius plot in Figure 7 and the van 't Hoff plot of S is presented in Figure 8. Each recorded value is the mean of at least three experiments at different upstream pressures. The permeation parameters for all gases are listed in Tables I and II below and above T_g , respectively. Energy diffusions (E_d) are plotted against the squares

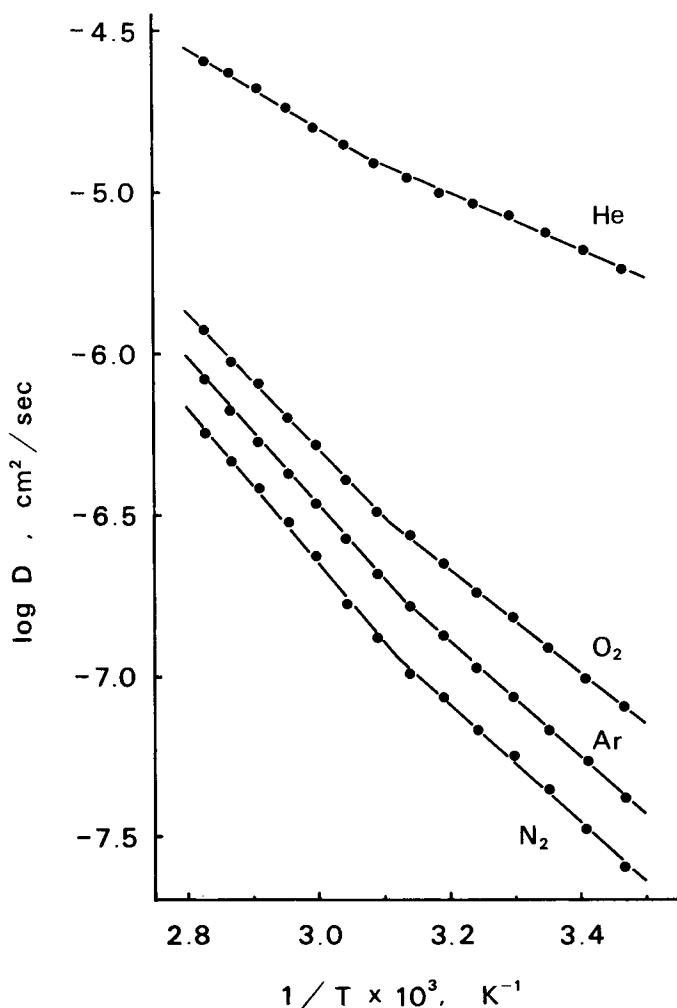


Fig. 7. Temperature dependence of the apparent diffusion coefficients for O_2 , N_2 , He, and Ar in PVCH.

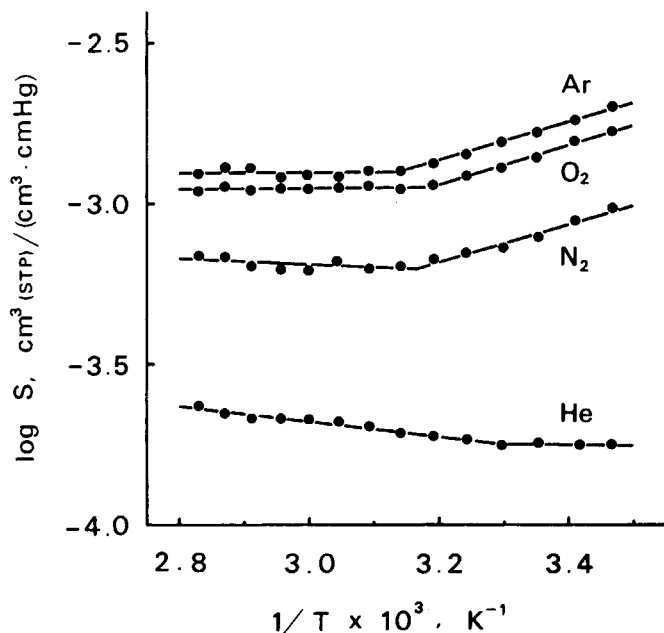


Fig. 8. van 't Hoff plot of the apparent solubility coefficients for O₂, N₂, He, and Ar in PVCH.

TABLE I
Gas Transport Parameters for Carbon Dioxide, Oxygen, Nitrogen,
Argon, and Helium in PVCH Below T_g^a

Gas	P_0	E_p	D_0	E_d	S_0	ΔH_s
CO ₂	3.10×10^{-7}	3.63	9.49×10^{-2}	8.96	3.29×10^{-6}	-5.33
O ₂	4.03×10^{-7}	4.59	3.21×10^{-2}	7.39	1.29×10^{-5}	-2.79
N ₂	9.20×10^{-7}	6.04	7.23×10^{-2}	8.50	9.08×10^{-6}	-2.66
Ar	1.53×10^{-6}	5.63	7.80×10^{-2}	8.27	1.89×10^{-5}	-2.66
He	2.11×10^{-6}	4.38	5.23×10^{-3}	3.89	1.97×10^{-4}	0.0593

^aUnits: $P_0 = \text{cm}^3 (\text{STP}) \cdot \text{cm}/(\text{cm}^2 \cdot \text{s} \cdot \text{cmHg})$; $E_p = \text{kcal/mol}$; $D_0 = \text{cm}^2/\text{s}$; $E_d = \text{kcal/mol}$; $S_0 = \text{cm}^3 (\text{STP})/(\text{cm}^3 (\text{polymer}) \cdot \text{cmHg})$; $\Delta H_s = \text{kcal/mol}$.

TABLE II
Gas Transport Parameters for Carbon Dioxide, Oxygen, Nitrogen,
Argon, and Helium in PVCH Above T_g^a

Gas	P_0	E_p	D_0	E_d	S_0	ΔH_s
CO ₂	8.91×10^{-4}	8.62	4.97	11.4	1.83×10^{-4}	-2.80
O ₂	9.68×10^{-4}	9.49	1.38	9.81	9.89×10^{-4}	-0.0809
N ₂	8.05×10^{-3}	11.8	5.06	11.2	1.23×10^{-3}	0.428
Ar	2.69×10^{-3}	10.4	2.42	10.4	1.24×10^{-3}	-0.00271
He	7.29×10^{-5}	6.61	8.20×10^{-2}	5.66	1.05×10^{-3}	1.06

^aUnits: see Table I.

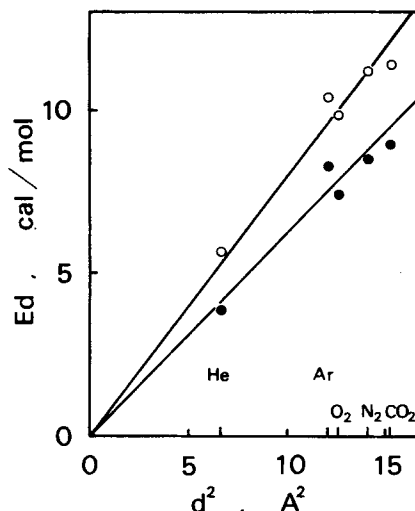


Fig. 9. Activation energies for diffusion in PVCH vs. d^2 (the Lennard-Jones diameter of the gas molecule) (○) above and (●) below T_g .

of the Lennard-Jones diameters¹² in Figure 9 and fairly linear relationships are obtained as Meares observed.¹³ But from our previous results,⁸ data on larger gases such as Kr and Xe would be necessary to confidently establish this correlation.

Some physical properties of PVCH are listed in Table III with those of PVB and PVAc. There seems to be no relationship between the formula weight of the repeating unit and T_g . The interaction between phenyl rings, the π - π interaction, in PVB seems to cause higher T_g and density compared to the other two polymers. The coefficients of cubic thermal expansion, α , below and above T_g were determined by the usual mercurial dilatometry.⁹ In this study, volume at 0°C was used to calculate each to compare to the literature value of PVAc.¹⁴ The π - π interaction also seems to be the cause of the comparatively small α and the higher density of PVB. The solubility parameters were calculated by Small's method.¹⁵ The difference of the solubility parameters between the polymers is small, since the structures, for the most part, the main chain, and the ester linkage, are the same. These properties will

TABLE III
Physical Properties of PVCH, PVB, and PVAc

Polymer	Formula weight of repeating unit	T_g (°C)	d^{25} (g/cm ³)	$\alpha \times 10^4$ (deg ⁻¹)		$\Delta \alpha \times 10^4$ (deg ⁻¹)	δ^c ((cal/cm ³) ^{1/2})
				$T > T_g$	$T < T_g$		
PVCH	154	52	1.119	6.74	2.93	3.81	9.15-9.22
PVB	148	65	1.214	5.58	2.34	3.24	9.89
PVAc	86	28	1.17	6.94 ^b	2.32 ^b	4.62	9.32-9.48
		-31 ^a	-1.19 ^a				9.4 ^c

^a Refs. 7 and 16.

^b Ref. 14.

^c Ref. 15.

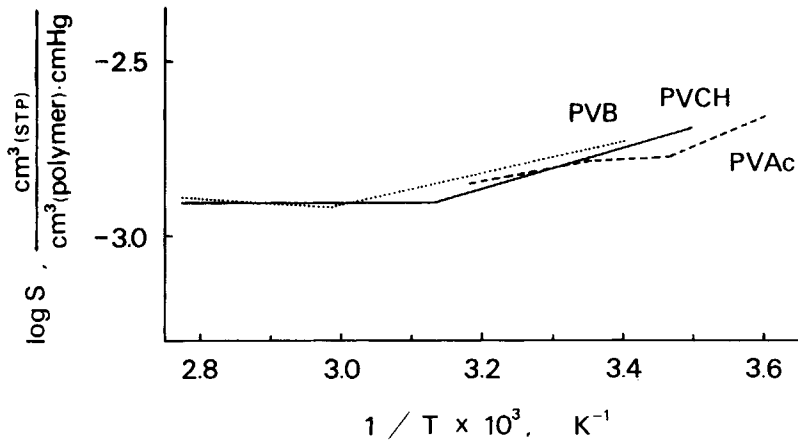


Fig. 10. van 't Hoff plot of the apparent solubility coefficients for Ar in PVCH, PVB,⁸ and PVAc.¹³

be referred to in the following discussion on the transport behaviors of the polymers.

Assuming that Eq. (2) is valid, the gas transport behavior should be discussed in terms of gas diffusivity and solubility. In connection with gas solubility behavior, however, Allen et al. proposed that the solubility of inert gases is rather independent of the nature of the polymer.⁷ In this study, the S values for Ar of the polymers are also very close, as shown in Figure 10, and there were no clear tendencies observed for other gases. Though affinity between polymer and gas is expected to determine solubility, the solubility parameter is not available to the present data.

The activation energies for diffusion for Ar, O₂, and CO₂ in three polymers are listed in Table IV. It is also difficult to compare the gas diffusivity itself and discuss the relationships between diffusion coefficient and polymer structure or properties. Roughly speaking, however, the difference of E_d between above and below T_g seems to be related to $\Delta\alpha$ of the polymer as Pace and Datyner discussed.¹⁷ PVAc shows the largest changes of both α and E_d . Furthermore, we expected that the change of specific volume or α could be directly associated with E_d , at least, in a series of related polymers. That is, the more polymer segments move, the easier gases diffuse. For PVB and

TABLE IV
Activation Energies for Diffusion for Ar, O₂, and CO₂
in PVCH, PVB, and PVAc

Polymer	Ar E_d (kcal/mol)		O ₂ E_d (kcal/mol)		CO ₂ E_d (kcal/mol)		References
	< T_g	> T_g	< T_g	> T_g	< T_g	> T_g	
PVCH	8.27	10.4	7.39	9.81	8.96	11.4	This study
PVB	7.55	9.09	6.00	7.28	7.87	10.8	Ref. 8
PVAc	11.4, 7.96	16.5	11.1, 6.50	14.5			Ref. 13
	8.1	16.4			7.8	17.8	Ref. 11

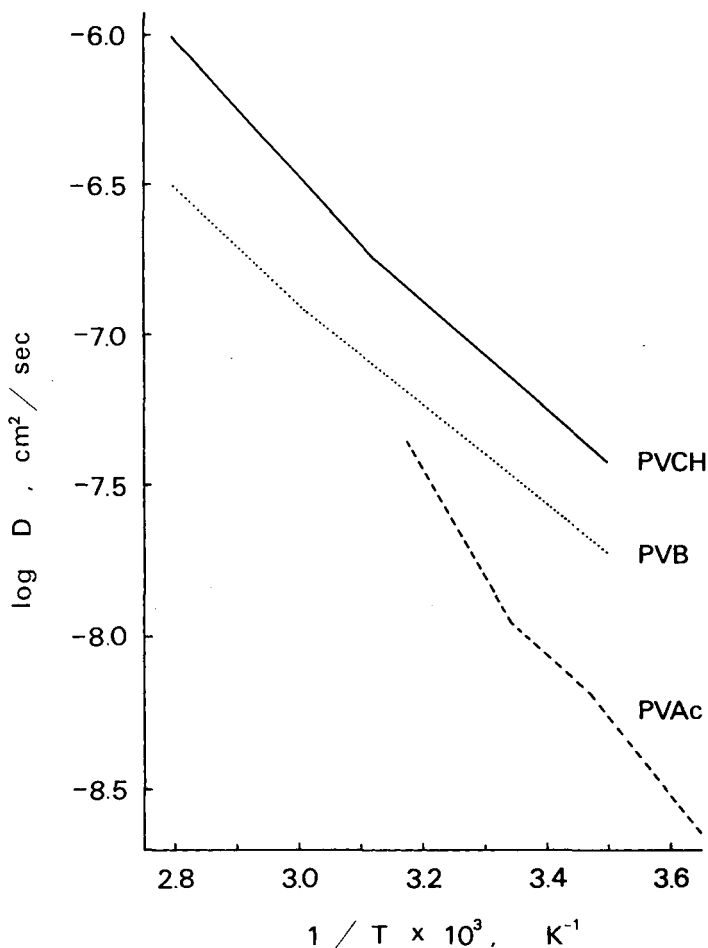


Fig. 11. The temperature dependence of the apparent diffusion coefficients for Ar in PVCH, PVB,⁸ and PVAc.¹³

PVCH, this expectation seems to be true qualitatively. PVB has a smaller α and a smaller E_d , where the π - π interaction is expected to affect strongly and increase the stiffness of polymer. PVCH has bulkier ring structures, not chain structures, than PVB and the side chains work to decrease the stiffness, which is proved by the lowest density in the three. Contrary to phenyl rings, cyclohexyl groups have no interactions based on polarities, therefore, α of PVCH is larger than that of PVB. Consequently PVCH has a higher gas diffusivity than PVB, as shown in Figure 11 for Ar. Even for PVAc, the expectation seems to be applied for the values of Toi et al.¹¹ This polymer has the largest α and E_d above T_g . Meares, however, reported large E_d below the lower T_g (19°C),¹³ where α is small.

The present paper is concerned with a study of gas transport in PVCH and the results are compared with those obtained with PVB and PVAc. From the point of chemical structure, these polymers are only different in the chemical structure of side chain. The cyclohexyl group in PVCH is bulkier than the

methyl group in PVAc and the phenyl in PVB and works to decrease the stiffness of polymer. This seems to account for the highest gas diffusivities for PVCH. Compared to the phenyl group, the cyclohexyl group is less interactive, like the methyl group. This nature of the side groups is expected to explain the larger coefficients of thermal expansion and the higher activation energies for diffusion for PVCH and PVAc than PVB. The present data, however, are insufficient to discuss in more detail and there is no way to describe it quantitatively. Further information on diffusion of gases and physical properties of polymers must be obtained systematically.

References

1. As reviews: H. K. Lonsdale, *J. Membr. Sci.*, **10**, 81 (1982); H. Strathmann, *J. Membr. Sci.*, **9**, 121 (1981).
2. J. M. S. Henis and M. K. Tripodi, *J. Membr. Sci.*, **8**, 232 (1981).
3. T. Masuda, E. Isobe, T. Higashimura, and K. Takada, *J. Am. Chem. Soc.*, **105**, 7473 (1983); T. Higashimura, T. Masuda, and M. Okada, *Polym. Bull.*, **10**, 114 (1983).
4. As a review: V. Stannett, *J. Membr. Sci.*, **3**, 97 (1978).
5. W. H. Burgess, H. B. Hopfenberg, and V. T. Stannett, *J. Macromol. Sci.-Phys.*, **B5**, 23 (1971).
6. M. Fujii, V. Stannett, and H. B. Hopfenberg, *J. Macromol. Sci.-Phys.*, **B15**, 421 (1978).
7. S. M. Allen, V. Stannett, and H. B. Hopfenberg, *Polymer*, **22**, 912 (1981).
8. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **30**, 401 (1985).
9. T. Hirose, K. Mizoguchi, and Y. Kamiya, *J. Appl. Polym. Sci.*, **34**, 000 (1987).
10. A. H. Chan and D. R. Paul, *J. Appl. Polym. Sci.*, **24**, 1539 (1979) and references cited therein.
11. K. Toi, Y. Maeda, and T. Tokuda, *J. Membr. Sci.*, **13**, 15 (1983).
12. M. Trautz, A. Messter, and R. Zink, *Ann. Phys. (Leipz.)*, **7**, 409 (1930); H. L. Johnston and E. R. Grilly, *J. Phys. Chem.*, **46**, 948 (1942).
13. P. Meares, *J. Am. Chem. Soc.*, **76**, 3415 (1954).
14. R. F. Clash and L. M. Rynkiewicz, *Ind. Eng. Chem.*, **36**, 279 (1944).
15. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
16. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., V-51, Wiley, New York, 1975.
17. R. J. Pace and A. Datyner, *J. Polym. Sci.: Polym. Phys. Ed.*, **17**, 465 (1979).

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