Gas Transport in Poly(vinyl-*p*-isopropylbenzoate): Comparison and Correlation with Some Other Poly(vinyl esters)

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SYNOPSIS

Gas permeability in poly(vinyl-*p*-isopropylbenzoate) (PV*p-i*-PrB) was determined by a time-lag method. The transport properties were discussed from comparison with the permeability data of other poly(vinyl esters), which were studied previously. All these polymers are structurally related, and the size of a side group or the position of its substituent was changed systematically. The isopropyl group of PV*p-i*-PrB is attached at the *para* position of a phenyl ring and is the largest in size. As a result gas diffusivity and therefore permeability were increased. The effect of the substituent on gas diffusivity was explained as it increases the interchain and intrachain distances. The discussion was supported from the comparison of the density data between PV*p-i*-PrB and other poly(vinyl esters). The diffusion coefficients of six glassy poly(vinyl esters) were correlated at their T_g and good correlations were shown to the free volume and its fraction. On the other hand, gas solubility was little affected by the change of an alkyl group on a phenyl ring. The solubility data of PV*p-i*-PrB and poly(vinyl benzoate) were shown to be clearly correlated with the critical properties of the penetrants. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In previous studies, we have shown that gas permeability in the glassy state of poly(vinyl esters) was largely affected by the structure of the polymer side chain.[1-3] From the comparison between poly(vinyl acetate),[4,5] poly(vinyl benzoate) (PVB),[1] and poly(vinyl cyclohexanecarboxylate) (PVCH),[2] the gas permeability was shown to increase as the side group became larger or bulkier. In addition, from comparison of three isomeric polymers, poly(vinyl methylbenzoates),[3] the position of a methyl group on the phenyl ring also affected the gas permeability; that is, poly(vinyl *p*-methylbenzoate) (PV*p*-MeB) was about two or three times more permeable to gas than poly(vinyl-*o*-methylbenzoate) and poly(vinyl-*m*-methylbenzoate) at ambient temperature.[3] Because the size of the side group was the same, the *para*-methyl group increased

but the *meta*- and *ortho*-methyl groups decreased free volume where penetrant gases diffuse, by changing the interchain and/or intrachain distance or spacing.

Our purpose was to understand the structural factors affecting gas transport properties by systematically examining the effect of the side chain size. The substituent on the phenyl ring of poly(vinyl-*p*-isopropylbenzoate) (PV*p-i*-PrB), an isopropyl group, is the bulkiest and stretches outward from the *para* position of the phenyl ring, that is, from the main chain. According to our previous studies,[1-3] these factors suggested qualitatively that gas diffusivity or permeability of PV*p-i*-PrB is higher than for any other poly(vinyl ester) cited above in the glassy state or at room temperature. For this report, we accumulated the gas permeation data on PV*p-i*-PrB to support our previous discussion. For the latter part of this paper, we attempted to correlate the diffusion and solubility coefficients of PV*p-i*-PrB. Gas diffusivity of PV*p-i*-PrB and five other poly(vinyl esters) were correlated with their fractional free volumes and free volumes. In this

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attempt, we adopted the free volume and its fraction at T_g of each polymer. The correlation of solubility coefficients of PVp-i-PrB and PVB and the critical properties of the penetrant gas was attempted quantitatively, using the equations proposed by Stern et al.[6,7]

EXPERIMENTAL

Materials

Poly(vinyl-p-isopropylbenzoate) was prepared from p-isopropylbenzoic acid chloride and poly(vinyl alcohol) (Wako Pure Chemicals Co., Ltd., Osaka; polymerization degree $n = 2,000$ and 80% hydrolyzed). p-Isopropylbenzoic acid chloride was prepared from the corresponding acid (Wako Pure Chemicals Co., Ltd., Osaka) and thionyl chloride and was distilled before use. These reaction procedures were previously reported.[1-3] The degree of esterification reaction was estimated by elemental analysis for carbon and hydrogen and no nitrogen was detected. The infrared spectra of PVp-i-PrB film also showed no hydroxyl groups remaining. It was concluded that the reaction was practically complete (> 97% esterified).

All solvents and other chemicals were used as received. The gases were greater than 99.9% pure and used as received.

Film Preparation

The films of PVp-i-PrB were prepared by casting a ~ 10% benzene solution onto a glass plate on mercury.[1-3] The films were removed from the glass plate after evaporation of the solvent at room temperature for several days and were further dried under vacuum for several days with increasing temperatures up to 95°C, well above T_g. The thickness of the membranes used for gas permeation experiments was 114.2–153.5 μm [μ-Mate, Sony Magnescale Inc., Tokyo].

Thermal Properties

The specific volume-temperature measurements were performed in a mercury-filled dilatometer with a heating rate of 0.5°C/min as reported previously.[1-3] The thermal expansion coefficients below (α_g) and above (α_r) T_g were determined from the resulting dilatometry and the density at 25°C (d^{25}), respectively, and calculations were based on the

density at 0°C. The thermal properties of other polymers were reported elsewhere.[2,3]

Density

The floating method was applied to determine the polymer density using a KI aqueous solution at 25°C. The density of the KI aqueous solution, which was adjusted to equal that of PVp-i-PrB, was determined by an Anton Paar Density Meter (DMA60).

Permeation Measurements

Permeation measurements were performed as previously reported,[1] with films thermally conditioned above T_g in a permeation cell before all measurements.

BACKGROUND

Permeation Parameters

The permeability coefficient (P) obtained from the steady-state permeation rate, is the product of the average diffusion (D) and solubility (S) coefficients.

$$P = DS \tag{1}$$

We have previously demonstrated that these equations are applicable for a few glassy polymers, as the plasticization effect of gases is negligible below 1 atm and little pressure dependence was observed for P.[8,9] In this treatment, the *apparent* diffusion coefficient below T_g, D_a, can be calculated from the time lag (θ) using eq. (2).[10,11a,11b]

$$D_a = l^2/6\theta \tag{2}$$

where l is the membrane thickness. In this case, the apparent solubility coefficient, S_a, can also be determined from P and D_a by applying eq. (1). Above T_g, D_a and S_a are the true average diffusion and solubility coefficients, respectively. In this report, the apparent coefficients, D_a and S_a, are also used in the Arrhenius plots together with D and S.

Diffusion Coefficient in Free-Volume Model

The gas diffusion phenomenon in polymers has been often explained by the free-volume concept.[11] Free-volume models do not deal with microscopic descriptions or behaviors of a penetrant–polymer system but give a correlation between the diffusion

coefficient and the free volume from statistical considerations.[11] The free-volume model developed by Fujita[12] provides a satisfactory description of the concentration and temperature dependences of diffusion coefficients [eq. (3)] of small molecules in rubbery polymers.[6,7,13-15]

$$D_T = RTA_d\exp(-B_d/v_f)$$ (3)

where D_T is the thermodynamic diffusion coefficient; R and T are the gas constant and the absolute temperature, respectively; A_d and B_d are the characteristic constants of the gas–polymer system, and v_f is the fractional free volume. Although the diffusion coefficient obtained from the time-lag method [eq. (2)] is the mutual diffusion coefficient, it is very close to the thermodynamic diffusion coefficient under the experimental conditions in the present study, that is, when the penetrant concentration is low. In the latter part of this study, eq. (3) is applied for the mutual diffusion coefficient and the fractional free volume at T_g of some poly(vinyl esters).

Correlations of Solubility Coefficients

Several researchers have reported the correlation of gas solubility in rubbery polymers.[6,7,16-19] Stern et al. derived some correlations between the solubility coefficient and the critical properties of the penetrant based on thermodynamic considerations, and recently applied eqs. (4) and (5) for polyethylene[6] and several silicone rubbers.[7]

$$\log S(0) = a(T_c/T)^2 + b$$ (4)

$$\log[S(0)p_c] = a'(T_c/T)^2 + b'$$ (5)

where $S(0)$ is the solubility at the limit of zero pressure of the penetrant, which is very close to S (T > T_g) and S_a ($T < T_g$) obtained under the present experimental conditions. T_c and p_c are the critical temperature and critical pressure of the penetrant, respectively, and a, a', b, and b' are constants. The units of $S(0)$ are $cm^3(STP)/(cm^3(polymer) \cdot atm)$, while T_c and p_c are in units of K and atm, respectively. In this report, we applied these correlations for PVp-i-PrB and PVB to compare their gas solution behaviors.

RESULTS

As in previous reports,[1-3] gas permeation experiments were performed both below and above T_g. The
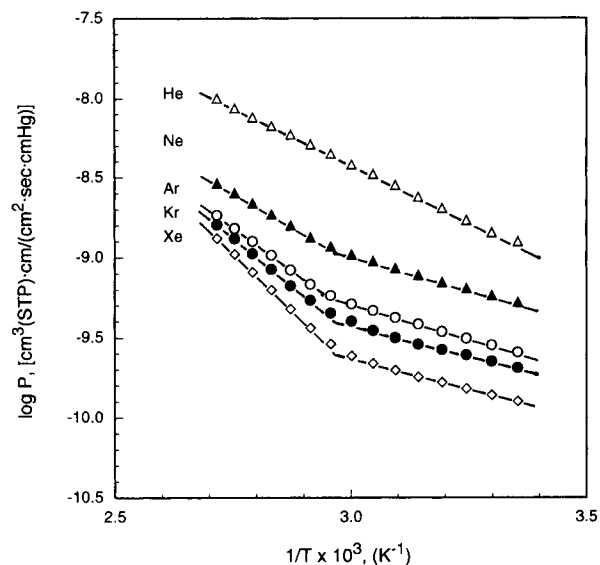
Figure 1 Temperature dependence of the permeability coefficients of noble gases for PVp-i-PrB.

Arrhenius plots of permeability and diffusion coefficients and van't Hoff plots of solubility coefficients are shown for all noble gases in Figures 1–3, respectively. As seen in the figures, the slope changes were observed around T_g, which is usually observed for glassy polymers.[1-5,8,9,16] For other multiatom gases, the same characteristics were also obtained for gas permeation, diffusion, and solution behaviors below and above T_g. Since the effect of T_g on the diffusion of gases is related to both the size of the penetrants and the extent of the change of the polymer matrix, the slope inflection is dependent on the gas–polymer systems.[16] For gas solubility, similar changes are due to the glass transition but the tendency is opposite to that observed for diffusivity. The solubility below T_g is the sum of dual-mode sorption, Henry's law and Langmuir terms,[11a,11b,20] and the latter term disappears at T_g. In addition, the Henry's law constant decreases as the temperature increases, except in quantum gases such as hydrogen and helium.

The permeation parameters for all gases studied are listed in Tables I and II, below and above T_g, respectively. The parameters indicate that the gas permeability of this polymer is rather high in the group of poly(vinyl esters). As an example, PVp-i-PrB was compared with PVB and PVp–MeB for Ar in Figures 4–6. Figure 4 shows that the permeability at 35°C was 500% higher for PVp-i-PrB (introduction of an isopropyl group to PVB) while it increased only 40% for PVp–MeB (introduction of a methyl group). From Figures 5 and 6, it is apparent that the
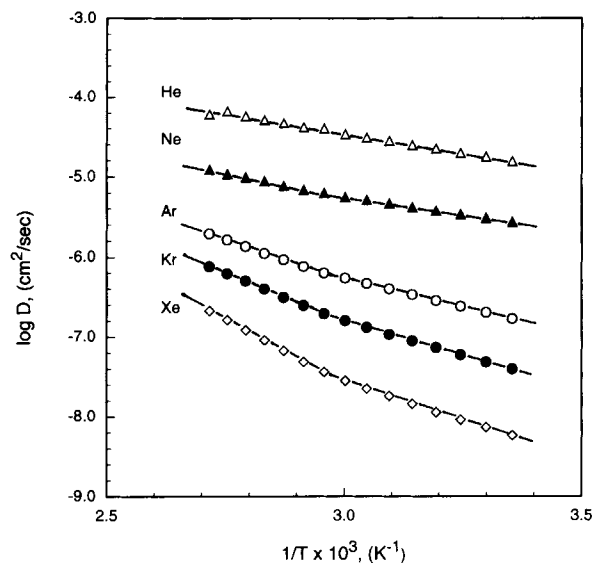
Figure 2 Temperature dependence of the diffusion coefficients of noble gases for PVp-i-PrB.

increase in diffusivity was the cause of the permeability increase. Small changes in both solubility coefficient and temperature dependence were observed. This trend was also observed for other gases. In Table III, three transport coefficients are compared for Ar and CO_2 with some poly(vinyl esters) at 35°C.

DISCUSSION

Effects of the Substituent

The addition of side groups or an increase in side group bulk usually inhibited chain-packing efficiency, making for larger free volume in the polymer matrix and allowing lower density when they are spherical and nonpolar. The thermal properties of five poly(vinyl esters) are listed in Table IV to show the effects of side chain structure or increased bulk. The densities for PVp-i-PrB, PVp–MeB, and PVB increase in this order and show that an isopropyl group and a methyl group in the *para* position decrease chain packing as expected.

Another effect, a bulky side group, was expected to create steric hindrance, reducing polymer chain mobility and raising the T_g. The second column in Table IV indicates that the T_g is raised about 10°C for PVp–MeB by the addition of the methyl group to PVB, that is, a methyl group in the *para* position reduces chain mobility. On the other hand, the substitution increases the free volume in the polymer matrix as described in the previous paragraph. This is the same effect of the *para*-methyl group observed

for poly(p-methylstyrene).[24] The isopropyl group, however, has little effect on the T_g for PVp-i-PrB. This was unexpected because an isopropyl group does not cause the T_g to change but lowers the density more than a methyl group. Presently we believe that the addition of two alkyl carbon—carbon bonds and their geometrical arrangement work to increase the local and segmental chain mobility and cancel the effect of bulkiness on T_g. A similar effect is seen for PVCH ($T_g = \sim 55°C$), which has a bulky but more flexible cyclohexyl group compared to the phenyl group. Puleo et al.[24] have reported the complexity of the T_g data for poly(p-methoxystyrene) in the series of *para*-substituted polystyrenes.

The effect of the *para*-substituent on the density seems rather simple. The discussion, however, would be valid only for the *para*-substituents of the phenyl ring because the substituents at the other positions (*ortho* and *meta* positions) increase the polymer density and reduce the T_g for poly(vinyl methylbenzoate) as reported previously.[3] Permeability data have also shown that introduction of a methyl group causes different effects depending on the phenyl ring position.[3]

The molar volume of polymers and their side groups can be estimated by the group contribution method.[25] According to this method, in the progression from the phenyl group of PVB to the p-isopropylphenyl group of PVp-i-PrB, the size of the substituent increases about 65% at 25°C. As a result, an isopropyl group at the *para* position increases the diffusivity about 450% for Ar and 400% for CO_2 at
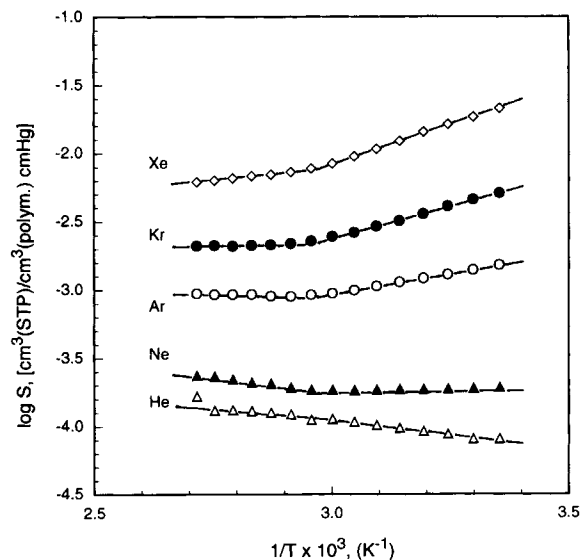
Figure 3 Temperature dependence of the solubility coefficients of noble gases for PVp-i-PrB.

Table I   PVp-i-PrB Gas Transport Parameters Below T_g

Gas	P_o	E_p	D_o	E_d	S_o	ΔH_s
He	7.86×10^{-5}	6.57	2.57×10^{-2}	4.39	3.06×10^{-3}	2.18
Ne	3.34×10^{-7}	3.83	2.72×10^{-3}	4.09	1.23×10^{-4}	-0.27
Ar	1.75×10^{-7}	3.87	1.11×10^{-2}	6.58	1.57×10^{-5}	-2.71
Kr	3.30×10^{-8}	3.30	1.67×10^{-2}	7.68	3.19×10^{-6}	-4.38
Xe	3.85×10^{-10}	3.39	1.24×10^{-2}	8.63	3.10×10^{-6}	-5.25
O_2	2.40×10^{-7}	3.91	1.38×10^{-2}	6.40	1.73×10^{-5}	-2.49
N_2	1.17×10^{-7}	4.27	1.60×10^{-2}	7.00	7.29×10^{-6}	-2.73
CO_2	1.46×10^{-8}	1.15	1.58×10^{-2}	7.25	9.23×10^{-7}	-6.10
CH_4	6.82×10^{-8}	3.53	2.93×10^{-2}	7.91	2.32×10^{-6}	-4.38

Units: $P_o = [cm^3(STP)\ cm]/(cm^2\ s\ cmHg)$, $D_o = cm^2/s$, $S_o = [cm^3(STP)]/[cm^3(polym.)\ cmHg]$, E_p, E_d, ΔH_s = kcal/mol.

35°C, as shown in Table III. A bulky isopropyl group increases the interchain and/or intrachain distance and is responsible for the diffusivity increase and the density decrease mentioned in the previous paragraph. Its effects are in agreement with those of a para-methyl group, which produces about 150% and 20% increases in diffusivity for Ar and CO_2, respectively. Combined with the previous results of PVAc, PVB, and PVCH, it is apparent that gas permeability changes largely by modification of the ester acid. When the ester acid has a ring structure, not only its size but also its additional substituents affect gas permeability, as shown in the previous study.[3] It should be mentioned that the side chain shape is important. All side chains mentioned above are spherical or made up of spherical elements like methyl, phenyl, and cyclohexyl groups. The situation must be different for flexible side chains, for example, n-alkyl groups.

Gas Diffusivity and Free Volume Correlation on Poly(vinyl esters)

In order to achieve our purpose, we systematically investigated the gas permeation behavior of six poly(vinyl esters) which differ in the size of their side chains. We attempted to correlate the diffusion coefficient and the free volume of these polymers. For a similar purpose, Lee[26] and other researchers[27,28] successfully applied this treatment to the permeability-free volume relationships of many polymers. The permeability data of poly(vinyl esters) can also be correlated to the previous work. Considering the similarity of their chemical structures, the permeability coefficients at 35°C were plotted for O_2, N_2, and CO_2 with those of a series of substituted polystyrenes by Puleo et al.[24] As seen in Figure 7, they were well correlated in this scale of specific free volume. This plot is useful from a practical point of view, since it is applicable for the estimation of permeability of a new polymer with a similar chemical structure.

On the other hand, many recent researchers[20,28] have looked into the diffusivity–free volume relationships from the mechanistic point of view. Few studies, however, have discussed the rubbery state of glassy polymers. In our study,[1-3] gas transport behaviors have been determined at temperatures encompassing T_g for all poly(vinyl esters) mentioned in the previous sections. In addition, the

Table II   PVp-i-PrB Gas Transport Parameters Above T_g

Gas	P_o	E_p	D_o	E_d	S_o	ΔH_s
He	7.16×10^{-5}	6.51	1.57×10^{-1}	5.62	4.56×10^{-4}	0.89
Ne	1.45×10^{-4}	7.90	2.56×10^{-2}	5.60	5.67×10^{-3}	2.30
Ar	1.55×10^{-3}	9.98	8.28×10^{-1}	9.48	1.88×10^{-3}	0.50
Kr	5.41×10^{-3}	11.00	3.91	11.30	1.38×10^{-3}	-0.31
Xe	7.13×10^{-2}	13.02	1.14×10^{2}	14.70	6.25×10^{-4}	-1.68
O_2	9.23×10^{-4}	9.28	6.70×10^{-1}	8.94	1.38×10^{-3}	0.34
N_2	2.59×10^{-3}	11.00	1.64	10.13	1.58×10^{-3}	0.86
CO_2	4.76×10^{-4}	8.13	2.00	10.49	2.38×10^{-4}	-2.36
CH_4	7.83×10^{-3}	11.33	6.15	11.48	1.27×10^{-3}	-0.14

Units: See footnote to Table I.
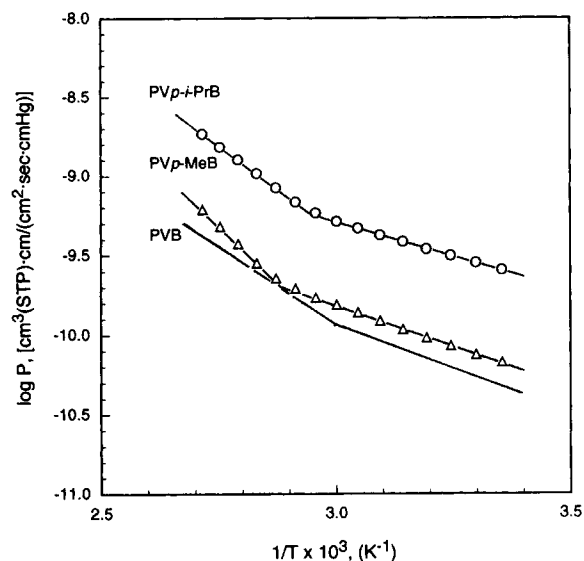
Figure 4 Comparison of Ar permeability coefficients between PVp-i-PrB, PVp-MeB, and PVB.

Figure 5 Comparison of Ar diffusion coefficients between PVp-i-PrB, PVp-MeB, and PVB.

temperature-specific volume relationships were measured for most of them. Therefore it is possible to apply Fujita's equation, eq. (3), for not only their glassy states but also their rubbery states. The latter is the condition for which the equation was originally derived. We applied the diffusion coefficients at T_g to eq. (3) as the data of the rubbery state because it is the temperature at which each polymer becomes a rubber and has almost the same thermal mobility.

The diffusion coefficient term $[D(T)]$ divided by T, eq. (6), is derived from eq. (3).

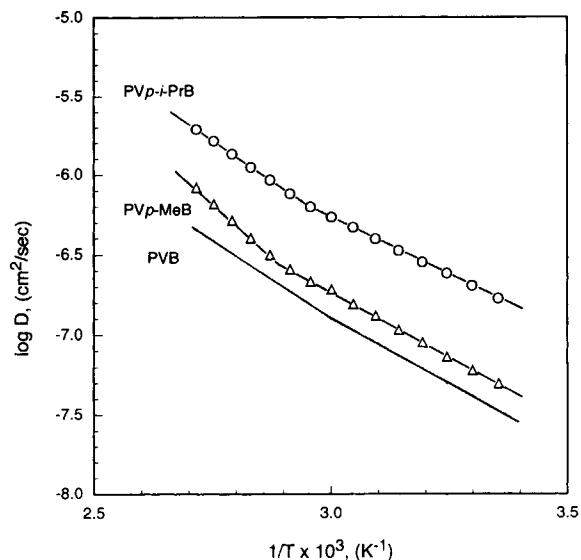$$D(T)/T = RA_d \exp(-B_d/v_f) \qquad (6)$$

We applied the free volume defined by Bondi[29] and calculated it from the measured specific volume at T and an estimated volume at 0 K, V_0, which is obtained in eq. (7) using the group contribution method.[25,29]

$$V_0 = 1.3V_w \qquad (7)$$

where V_w is the van der Waals volume of the polymer. The free volume change caused by the penetrant was ignored because of its low concentration. Therefore the fractional free volume v_f can be given by eq. (8):

$$v_f = (V - V_0)/V \qquad (8)$$

where V is the specific volume of the polymer at a certain temperature and V_0 is the occupied volume
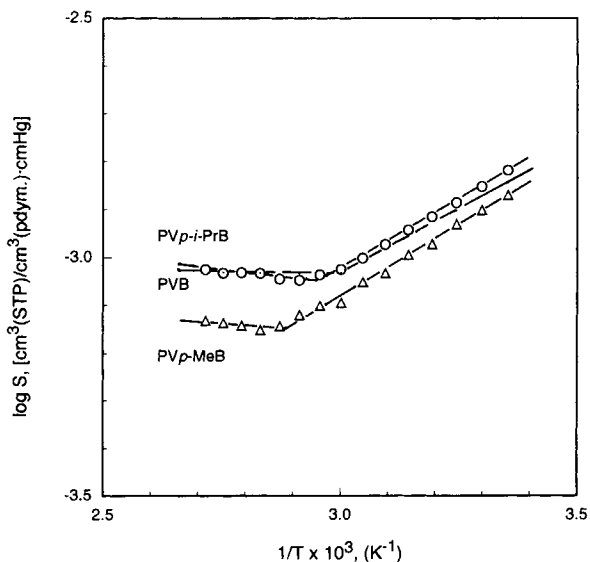
at absolute zero. The difference between V and V_0 $(V - V_0)$ is the specific free volume. Substituting eq. (8) for v_f, eq. (6) at T can be expressed by eq. (9):

$$D(T)/T = A \exp[-BV(T)/(V(T) - V_0)] \qquad (9)$$

where A and B are RA_d and $-B_d$ in eq. (6) at the temperature T, respectively. When the specific free volume is applied to eq. (6) instead of v_f, the correlation can be written as eq. (10):

Figure 6 Comparison of Ar solubility coefficients between PVp-i-PrB, PVp-MeB, and PVB.

**Table III   Permeability, Diffusion, and Solubility Coefficients[a]
for Ar and CO_2 in Some Poly(vinyl esters) at 35°C**

	$P(35°C) \times 10^{10}$		$D(35°C) \times 10^7$		$S(35°C) \times 10^3$	
	Ar	CO_2	Ar	CO_2	Ar	CO_2
PVp-i-PrB	3.15	22.2	2.41	1.14	1.31	19.4
PVCH	1.56	8.26	1.06	0.420	1.46	19.8
PVp–MeB	0.856	6.73	0.738	0.361	1.16	18.7
PVB	0.612	6.32	0.491	0.299	1.24	21.6
PVAc[b]	0.297	—	0.259	—	1.15	—
PVAc[c]	—	2.03	—	0.0747	—	27.2

[a] Units: $P(35°C)$ = [cm^3(STP) cm]/(cm^2 s cmHg), $D(35°C)$ = cm^2/s, $S(35°C)$ = [cm^3(STP)]/[cm^3(polym.) cmHg].
[b] Ref. 4.
[c] Ref. 5.

$$D(T)/T = A'\exp[-B'/(V(T) - V_0)]\quad(10)$$

where A' and B' are also the parameters.

It has been shown that diffusion coefficients[20,28] for a given gas can be correlated reasonably well with free volume of different polymers. We examined eq. (10) for various gases with the diffusion coefficients and the dilatometric data from the six poly(vinyl esters) studied so far. The results at 35°C and T_g are shown in Figures 8 and 9, respectively, for Ne, Ar, and Kr. The data of He and Xe are not seen in the figure because the diffusivity data of He is unreliable due to its short time lag, and the limited number of Xe data are not enough to correlate. It can be seen that the correlation in Figure 9, at T_g, is more linear and therefore fits better with eq. (10) than that of Figure 8. The dashed lines in Figure 9, at T_g, were arbitrarily drawn to show the relation; a rather reasonable tendency was seen, that is, the diffusivity increased as the fractional free volume

increased. As the noble gases are spherical and less interactive with the functional groups of polymer chain than multiatom gases, the results were interpreted in terms of the structural changes in the polymer matrix. Four other gases studied—O_2, N_2, CO_2, and CH_4—also showed similar tendencies. Although eq. (9) was also examined, no better correlation was obtained even for the data at T_g. The present correlation in Figure 9 is rather good, and therefore can be used to obtain an estimate of the diffusivity of a given poly(vinyl ester) with its dilatometric data. The parameters A' and B' determined for seven gases by least-square fitting are given in Table V.

Solubility Relationship

We have reported here that gas solubility in poly(vinyl esters) was almost structure-independent under our experimental conditions because most of
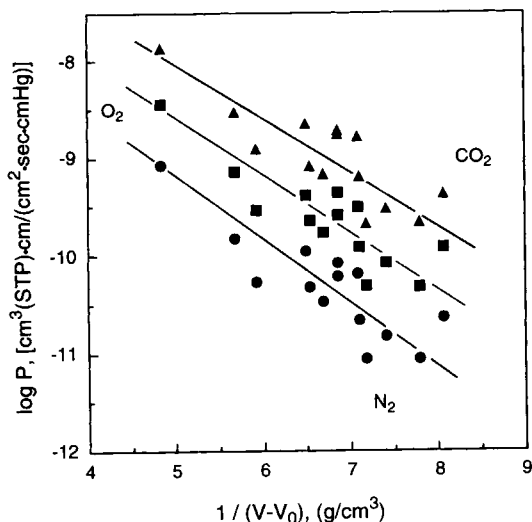
Table IV   Physical Properties of Some Poly(vinyl esters)

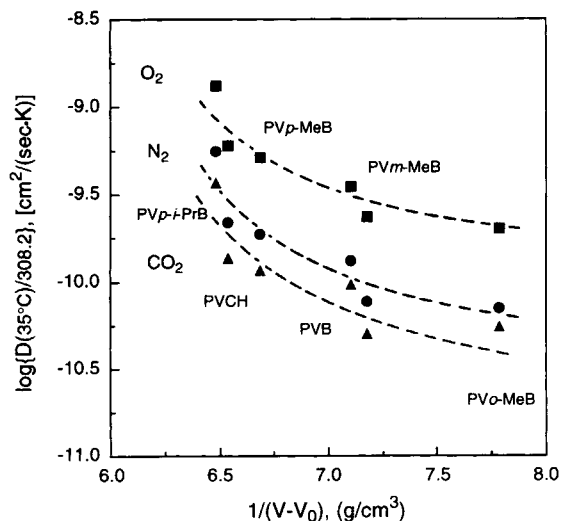| Polymer	d^{25} (g/cm³)	T_g (°C)		$\alpha \times 10^4$ (deg⁻¹)	
		DSC	Dilatometry	α_g ($T < T_g$)	α_r ($T > T_g$)
PVp-i-PrB	1.117	67	66	2.89	6.90
PVp–MeB	1.163	72	75	2.38	6.45
PVB	1.214	—	65	2.34	5.58
PVCH	1.119	55 ~ 56	52	2.93	6.74
PVAc	1.17 ~ 1.19[a]	28 ~ 31[a]	—	2.32[b]	6.94[b]
PVAc[c]	1.176	32	—	—	—

[a] Refs. 21 and 22.
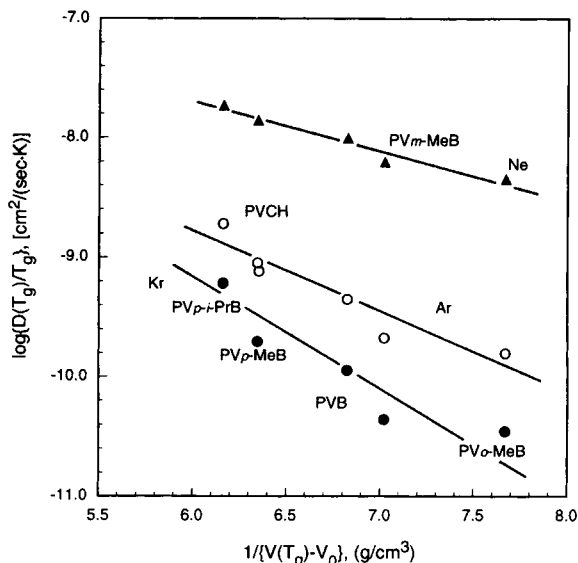[b] Ref. 23.
[c] Ref. 5.

Figure 7 Correlations of CO_2 (▲), O_2 (■), and N_2 (●) permeability coefficients at 35°C with specific free volume for several poly(vinyl esters) and substituted polystyrenes.[24]

their chemical properties, such as polarity and solubility parameter, were quite similar.[1-3] Independent sorption experiments for PVCH and PVB also supported this conclusion.[30,31] It is interesting to question whether the solubilities in *some* polymers can be described by a *single* equation like eq. (4) or eq. (5); that is, if such a correlation of gas solubility were established for some polymers, it should apply to other polymers in the series. The equations were applied for most gases studied (O_2, N_2, CO_2, CH_4, Ar, Kr, and Xe) in PVp-i-PrB and PVB at all ex-


Figure 9 Correlation of Ne, Ar, and Kr diffusion coefficients at T_g with specific free volume for poly(vinyl esters).

perimental temperatures, that is, below and above each T_g. Both equations gave good results for PVp-i-PrB and PVB except for quantum gases such as H_2 and He, and Figure 10 shows the plot of eq. (4). The correlations, eqs. (4) and (5), became

$$\log S(0) = 1.81(T_c/T)^2 - 1.54 \quad (11)$$

$$\log[S(0) \cdot p_c] = 2.09(T_c/T)^2 + 0.04 \quad (12)$$

and their correlation factors (R^2) were 0.96 and 0.95, respectively. Even from the independent correla-

Figure 8 Correlation of Ne, Ar, and Kr diffusion coefficients at 35°C with specific free volume for poly(vinyl esters).
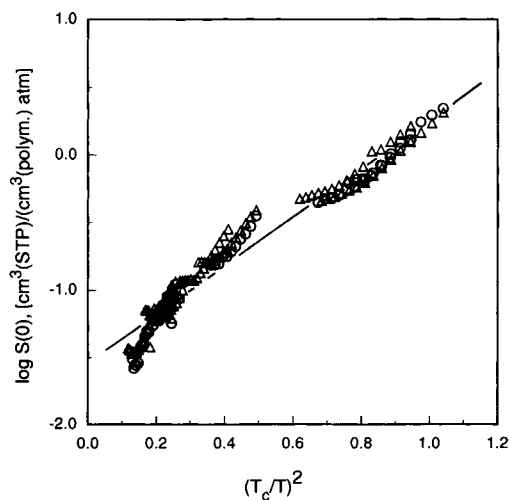
Figure 10 Correlation of the solubility coefficients of seven gases (O_2, N_2, CO_2, CH_4, Ar, Kr, and Xe) with (T_c/T)^2 in PVp-i-PrB (○) and PVB (△). Plots of eq. (4).

Table V Correlation Parameters between Diffusion Coefficient with Specific Free Volume in Eq. (10)

Gas	A'	B'	Correlation Factor (R^2)
Ne	5.01×10^{-6}	0.411	0.95
Ar	1.94×10^{-5}	0.680	0.89
Kr	2.40×10^{-5}	0.781	0.85
O_2	1.14×10^{-5}	0.605	0.85
N_2	8.64×10^{-6}	0.644	0.85
CO_2	3.15×10^{-6}	0.600	0.81
CH_4	3.49×10^{-5}	0.793	0.87

tions of the solubility data below and above T_g, similar results were obtained for both polymers. Considering the correlation factors of eqs. (11) and (12), they are quite good and are applicable for estimating gas solubility of a polymer in a series of poly(vinyl esters) with no strongly polar groups. In addition, it is shown that these equations are practically applicable for both rubbery and glassy states as long as the penetrant concentration is low, even though the equations were originally derived for rubbery polymers.

CONCLUSION

Gas transport properties of PV*p-i*-PrB were determined and compared with those of five poly(vinyl esters). Gas diffusivity of PV*p-i*-PrB was higher than any other poly(vinyl ester) because of the bulky isopropyl group at the *para* position on the phenyl ring. The small change observed in gas solubility was understandable considering that the chemical structures were quite similar. Comparing the diffusion coefficient of each polymer at T_g with specific free volume yielded a rather good correlation. Additionally, a very good relationship was found between the solubility coefficients of PV*p-i*-PrB and PVB and critical properties, T_c and p_c, of the penetrants.

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