Permeability of Polyglutamic Acid Ester Membranes to Benzene Vapor

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Synopsis

Permeability of poly(γ-methyl L-glutamate)(PMLG), poly(γ-hexahydrobenzyl L-glutamate)-(PHBLG), and poly(γ-*n*-amyl L-glutamate)(PALG) membrane to benzene vapor was studied. Permeability coefficients of all the membranes were large, of the order of 10^{-9}–10^{-6} cm^3(STP) cm/cm^2 sec cm Hg, and increased markedly with increasing relative vapor pressure and temperature. The large permeability was due to the large diffusion coefficient. The sorption behavior of the PALG–benzene system was interpreted in terms of the theory of the mixing of solvent with side chains. The Arrhenius plots of diffusion coefficients for PMLG and PHBLG showed a break at about 29 and 40°C, respectively, where the volume-expansion curves of each polymer also showed a break, which is thought to be related to the side-chain motion. The diffusivity data for PALG were examined in terms of Fujita's free-volume theory, and it was found that the value of the average free-volume fraction in the pure polymer for PALG was much larger than that for vinyl polymers. This means that the side-chain motion of PALG is easy and is the reason that the diffusion coefficients for PALG are large. These results indicate that the diffusion of benzene in these polypeptides takes place in the side-chain regions between helices.

INTRODUCTION

A few papers[1–4] on the transport properties of small molecules through synthetic polypeptides of rodlike, α-helical structure have been published. Vapor sorption onto polypeptides is reported to be controlled by polymer side chain–solvent mixing,[5–7] whereas the diffusion of small molecules in polypeptides is reported to occur through the side-chain region between helices.[1–3]

The purpose of this study is to provide information on the mechanism of permeation of organic vapors through polypeptides. Namely, the permeability of poly(γ-methyl L-glutamate), poly(γ-hexahydrobenzyl L-glutamate), and poly(γ-*n*-amyl L-glutamate) membranes to benzene vapor and the sorption behavior of benzene onto these polymers are studied, and then the diffusibility of benzene in these polymers is considered.

EXPERIMENTAL

Materials

Poly(γ-methyl L-glutamate)(PMLG) supplied by Kyowa Hakko K.K. (Japan) has been prepared by the polymerization of *N*-carboxyamino acid anhydride. The viscosity-average molecular weight is about 60,000, which was determined by the intrinsic viscosity of dichloroacetic acid solution at 25°C.

Poly(γ-hexahydrobenzyl L-glutamate)(PHBLG) and poly(γ-*n*-amyl L-glutamate)(PALG) were prepared by ester exchange reaction of PMLG.[8] Namely,

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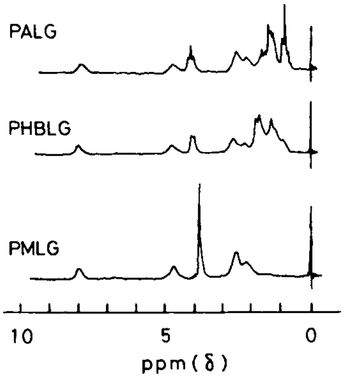


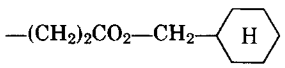
Fig. 1. Expansion curves of PMLG, PHBLG, and PALG.

PMLG, alcohol of 25-fold molar quantity per residue of glutamate, dichloroethane as solvent, and concentrated sulfuric acid as catalyst were mixed in the reaction flask at 70°C. After 5 hr, the reaction was continued for a further 15 hr under reduced pressure as the methanol yielded was removed from the reaction mixture. The reaction solution was poured into a large amount of methanol, and then the precipitant was filtered, washed thoroughly with methanol to remove the acid, and dried under vacuum. The nmr spectra of the polymers in trifluoroacetic acid were observed with a Varian EM360 Spectrometer (Fig. 1). For both PHBLG and PALG, the resonance peak at 3.9 ppm attributed to the $-COOCH_3$ group for PMLG disappeared. Accordingly, we believe that the ester exchange reaction is accomplished almost completely.

The membranes of PMLG, PHBLG, and PALG were prepared by casting the corresponding 2–3% dichloroethane solutions onto glass plates and by drying in air and finally under vacuum at 80°C for a day to perfectly remove the dichloroethane. The thickness was 0.050–0.070 mm. All of the membranes prepared were confirmed to have α-helical structures on the basis of the infrared absorption spectra.[9] The densities of all the membranes were examined by a flotation method using an aqueous calcium chloride solution at 20°C and summarized in Table I.

Dilatometric measurements on PMLG, PHBLG, and PALG were carried out, and the mercury head as a function of temperature is shown in Fig. 2. As seen in the figure, all of the polymers show a break in the curve. These breakpoint temperatures are summarized in Table I. Poly(γ-methyl L-glutamate) and poly(γ-benzyl L-glutamate) have been reported to have a breakpoint in the specific volume–temperature curves in the vicinity of room temperature,[10,11] where both polymers have been found to show mechanical and dielectric relax-

TABLE I
Properties of Samples

Polymer	Polymer side chain	Density, g/cm^3	Breakpoint temperature, °C
PMLG	$-(CH_2)_2CO_2-CH_3$	1.35	26
PHBLG	 $-(CH_2)_2CO_2-CH_2-$ H	1.12	36
PALG	$-(CH_2)_2CO_2-(CH_2)_4-CH_3$	1.12	−2

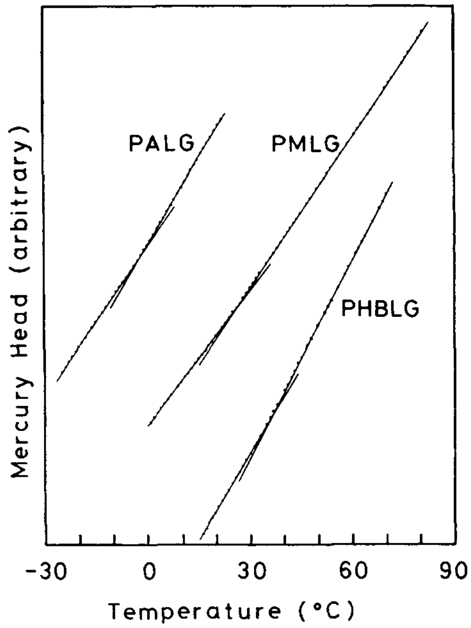


Fig. 2. Dilatometric measurements on PMLG, PHBLG and PALG.

ations due to side-chain motion.[12] So this break is considered to be manifestation of the glass transition, which is related to the onset of side-chain motion.

The benzene used as penetrant was of extrapure grade.

Permeation and Sorption Experiments

Permeation measurements were made using Rouse's apparatus[13]; accordingly, the pressure of the lower pressure side of the membrane is always near zero, and the pressure of the higher pressure side of the membrane is set up by controlling the temperature of the benzene-filled flask, which is connected to the higher pressure side of the membrane in the vacuum system; and so the pressure corresponds to the saturated vapor pressure of the benzene at that temperature. The amount of benzene transferred through the membrane in time t, $Q(t)$, expressed in the volume at the standard state per unit area of the membrane [cm^3(STP)/cm^2], is plotted vs time t in Fig. 3 for the PMLG–benzene system. The linear portions of the permeation curves correspond to steady-state permeation, from whose slopes the permeability coefficients, $\bar{P}$[cm^3(STP) cm/cm^2 sec cm Hg], are determined.

Sorption measurements for benzene vapor were carried out by the gravimetric method using the usual quartz spiral balance. The sensitivity of a quartz spring was about 1 mm/mg. The spring obeyed Hook's law, and its reversibility was excellent. The samples used in sorption experiments were in film form. Sorption amounts were expressed in the volume at the standard state per unit volume of polymer [cm^3(STP)/cm^3]. Solubility coefficients, S[cm^3(STP)/cm^3 cm Hg], are calculated by dividing the sorption amount by vapor pressure.

Steady-state diffusion coefficients, $\bar{D}$ (cm^2/sec), are obtained by dividing $\bar{P}$ by S.

The bars on P and D denote concentration averages.

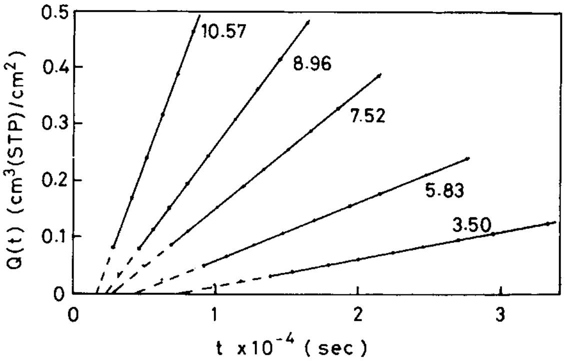


Fig. 3. Permeation curves of the PMLG-benzene system (35°C). Numbers on curves show the applied pressures in cm Hg.

RESULTS AND DISCUSSION

Permeability Coefficients

The permeability coefficients, $\bar{P}$, of PMLG, PHBLG, and PALG membrane are plotted against the relative vapor pressure of benzene in Figs. 4, 5, and 6, respectively. The permeability coefficients of all the membranes depend on the relative vapor pressure and temperature. The permeability coefficients of PALG, PHBLG, and PMLG membrane decrease in that order. However, the permeability coefficients of all the membranes are very large compared with those of vinyl polymers.

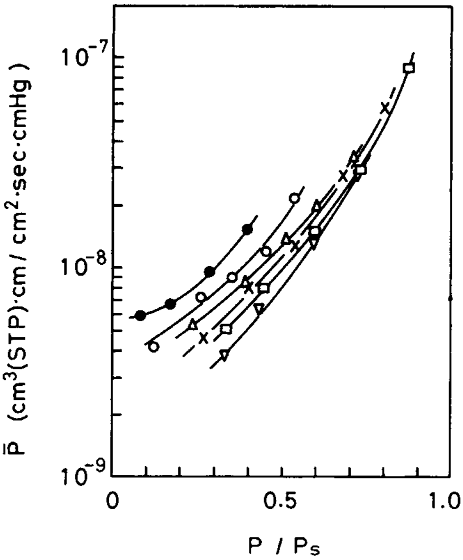


Fig. 4. Permeability coefficients $\bar{P}$ of PMLG membrane vs relative vapor pressure of benzene: ▽, 20°C; □, 25°C; ×, 30°C; △, 35°C; ○, 40°C; ●, 50°C.

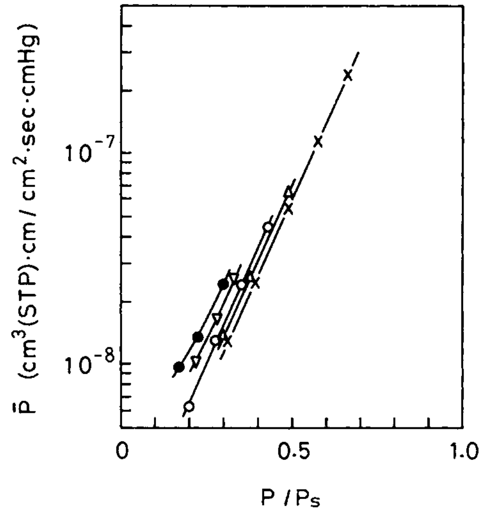


Fig. 5. Permeability coefficients $\bar{P}$ of PHBLG membrane vs relative vapor pressure of benzene: ×, 30°C; △, 35°C; ○, 40°C; ▽, 45°C; ●, 50°C.

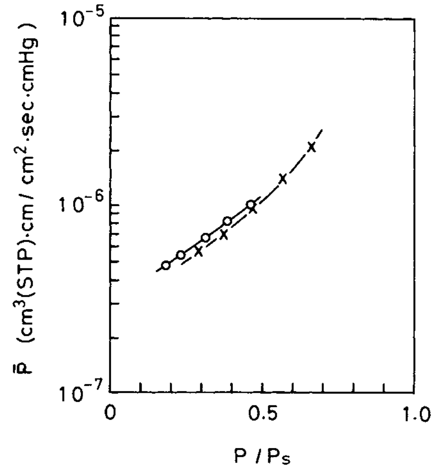


Fig. 6. Permeability coefficients $\bar{P}$ of PALG membrane vs relative vapor pressure of benzene: ×, 30°C; ○, 40°C.

Sorption

The sorption isotherms of benzene on PMLG, PHBLG, and PALG are shown in Figs. 7, 8, and 9, respectively. No hysteresis for these isotherms was observed. The isotherms of PMLG are dependent on the temperature, whereas the isotherms of PHBLG and PALG are independent of the temperature over the entire range of relative pressures studied. The isotherms of PMLG are the sigmoidal-shape isotherms, and the behavior suggests the presence of the sorption sites, whereas the isotherms of PHBLG and PALG are the solution-shape isotherms. The amounts of benzene sorbed by PALG, PHBLG, and PMLG decrease in that order.

Vapor sorption onto polypeptides of rodlike, α-helical structure is reported to be controlled by polymer side-chain–solvent mixing.[5,6] PALG has α-helical structure as judged by infrared absorption spectra. Since the temperature of

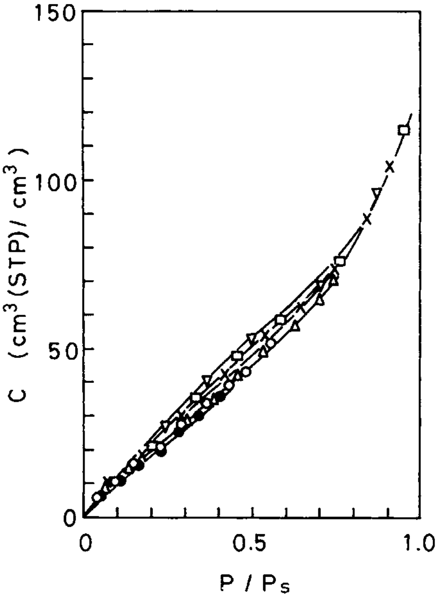


Fig. 7. Sorption isotherms of benzene on PMLG: ▽, 20°C; □, 25°C; ×, 30°C; △, 35°C; ○, 40°; ●, 50°C.

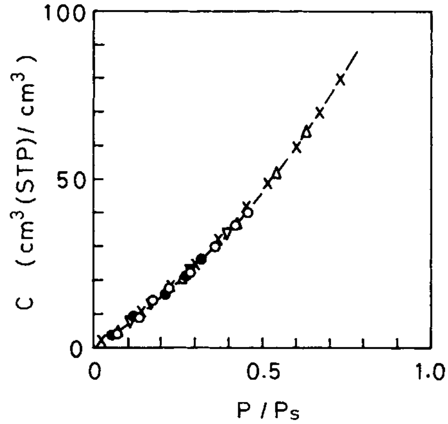


Fig. 8. Sorption isotherms of benzene on PHBLG: ×, 30°C; △, 35°C; ○, 40°C; ▽, 45°C; ●, 50°C.

sorption experiment for PALG was higher than the glass-transition temperature, which was related to the onset of side-chain motion, the rotational motion of the side chain of PALG was probably well done at the experimental temperature. Accordingly, the random-mixing model of polymer solution may be applicable to the PALG–benzene system.

The volume fraction of benzene sorbed is plotted as a function of activity of benzene in Fig. 10. In the calculated curve by Flory's theory of solutions of impenetrable, rodlike particles,[14] the volume fraction of benzene increased gradually and then steeply with the activity of benzene. It was found that the observed behavior was not explicable in terms of the theory.

Next, the theory of the mixing of solvent with side chains of α-helical solute particles was applied to PALG–benzene system. The equation derived by Flory and Leonard[5] was

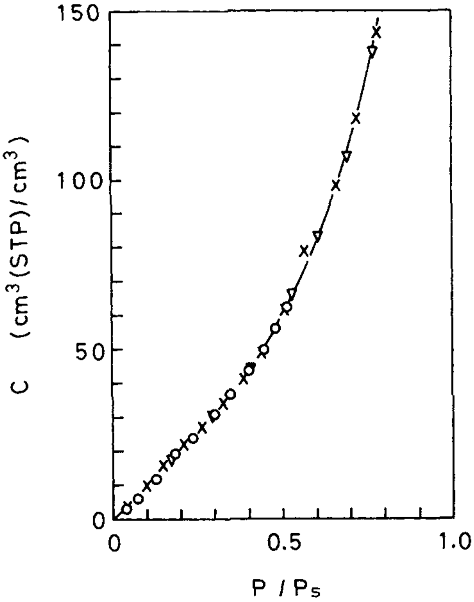


Fig. 9. Sorption isotherms of benzene on PALG: ▽, 20°C; ×, 30°C; ○, 40°C.

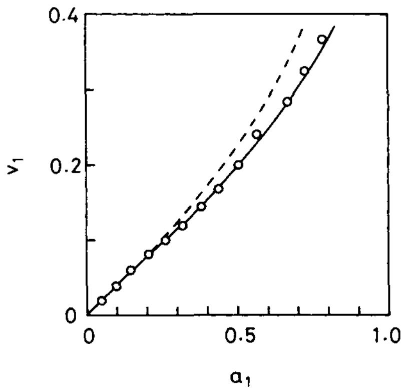


Fig. 10. Observed and calculated sorption isotherms of benzene on PALG: ○, observed value; – – –, calculated curve according to eq. (1) with $\chi_1 = -0.31$; —, calculated curve according to eq. (3) with $\chi_1 = -0.31$ and $x = 1.9$.

$$\ln a_1 = \ln v_1' + v_2' + \chi_1(v_2')^2 \qquad (1)$$

where a_1 is the activity of solvent, χ_1 is the thermodynamic interaction parameter, and $v_1' = 1 - v_2'$ is the volume fraction of solvent calculated on the basis of mixing being confined to the side chains. The relationship of v_1' and v_2' to the volume fraction of solvent, v_1, and of solute, v_2, of the entire system is given by

$$v_2'/v_1' = (M_s/M_u)(v_2/v_1) \qquad (2)$$

where M_s and M_u are, respectively, the molecular weights of the side chain and of the entire peptide unit. The broken line in Fig. 10 was calculated from eq. (1) for χ_1 value of -0.31 chosen to fit the experimental data at low activities. The discrepancy between the calculated curve and present experimental data can be seen at high activities. The discrepancy has been noted for the results examined by Flory et al.[5] and Rai et al.[6]

Takizawa[7] reported that the discrepancy at high activities was due to the effect of the elastic force of the side chain developed in opposition to the swelling process and derived the following equation:

$$\ln a_1 = \ln v_1' + v_2' + \chi_1 \cdot (v_2')^2 + \frac{(v_2')^{1/3} - v_2'}{x} \tag{3}$$

where x is the number of segments of the side chain. The difference between eq. (1) and the experimental data corresponds to the fourth term of the right-hand side of eq. (3). The solid line in Fig. 10 was calculated from eq. (3) for $\chi_1 = -0.31$ and $x = 1.9$. Since the ratio of the molar volume of the side chain to that of benzene is 1.8, the value of x is reasonable.

Accordingly, these results suggest that the sorption of benzene onto PALG may take place in the side-chain region. If it is assumed that the sorption of low molecules onto polypeptides of rodlike, α-helical structure takes place in the side-chain region, it is thought that the diffusion of low molecules in polypeptides may occur in the side-chain region between helices.

Diffusion Coefficients

The diffusion coefficients, $\bar{D}$, of benzene in PMLG, PHBLG, and PALG are plotted against the relative vapor pressure of benzene in Figs. 11, 12, and 13, respectively. The diffusion coefficients of all the membranes depend on the relative vapor pressure. Especially the strong concentration dependence of the diffusion coefficients in PHBLG is considered to be due to the plasticization effect of benzene, as PHBLG has a bulky cyclohexyl group in the side chain. The diffusion coefficients of PALG, PHBLG, and PMLG decrease in that order. The diffusion coefficients of all the membranes are very large compared with those of vinyl polymers, and the large permeability is due to the large diffusion coefficient.

The temperature dependence of diffusion behavior in PMLG and PHBLG was studied. The comparison of the diffusion coefficients should be done with the diffusion coefficients at zero penetrant concentration at each temperature.

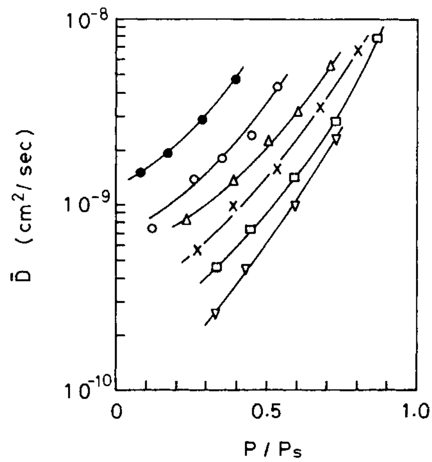


Fig. 11. Diffusion coefficients $\bar{D}$ of PMLG membrane vs relative vapor pressure of benzene: ▽, 20°C; □, 25°C; ×, 30°C; △, 35°C; ○, 40°C; ●, 50°C.

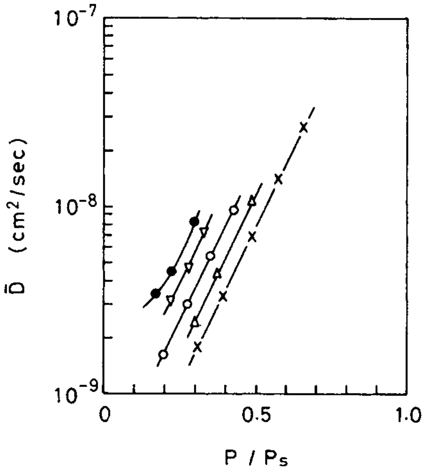


Fig. 12. Diffusion coefficients $\bar{D}$ of PHBLG membrane vs relative vapor pressure of benzene: ×, 30°C; △, 35°C; ○, 40°C; ▽, 45°C; ●, 50°C.

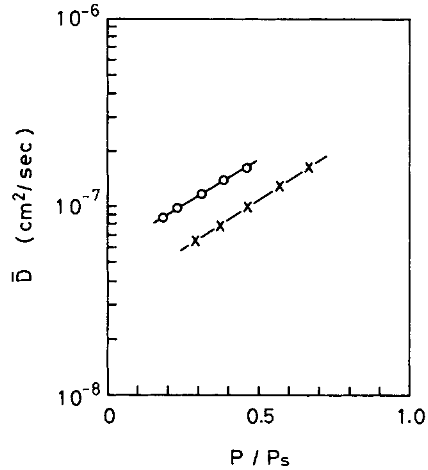


Fig. 13. Diffusion coefficients $\bar{D}$ of PALG membrane vs relative vapor pressure of benzene: ×, 30°C; ○, 40°C.

However, in order to avoid the ambiguous extrapolation to zero penetrant concentration, we compared the diffusion coefficients with those at the same concentrations that cause the same degree of plasticization; the diffusion coefficients at the concentration of benzene, 36 cm^3(STP)/cm^3 for PMLG and 25 cm^3(STP)/cm^3 for PHBLG, at each temperature are plotted against the inverse temperature in Fig. 14. As seen in the figure, both PMLG and PHBLG show a break at 29 and 40°C for PMLG and PHBLG, respectively. These breakpoint temperatures are in approximate agreement with those observed in the dilatometric measurements and reflect the motion of the side chain. In general, the second-order transition temperature of polymers is depressed when solvents are mixed with polymers. In the case of the diffusion of solvents in polymers, breakpoint temperatures in the Arrhenius plots of diffusion coefficients are reported to be depressed in the presence of solvents.[15] However, for both PMLG and PHBLG the effect of benzene on the depression of the breakpoint temperature is small.

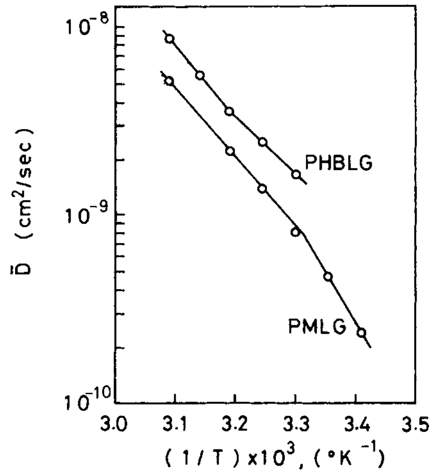


Fig. 14. Temperature dependence of diffusion coefficient.

The mechanism of permeation of benzene vapor through the polypeptides was studied. Concentration-dependent diffusion coefficients, $D(C)$, were calculated as a function of the concentration C of benzene in the polymer using the equation[16]

$$\bar{D} = \frac{1}{C_1} \int_0^{C_1} D(C)\, dC \tag{4}$$

When the concentration-dependent diffusion coefficients obtained above were expressed in D_1^0, mutual diffusion coefficients, D_v, and intrinsic diffusion coefficients, $\mathcal{D}$, were obtained from the relations[16]

$$D_v = D_1^0/(1 - v_1)^2 \tag{5}$$

$$\mathcal{D} = D_v/(1 - v_1) \tag{6}$$

where v_1 is the volume fraction of benzene corresponding to the concentration C_1. Mutual and intrinsic diffusion coefficients for the PALG–benzene system are plotted as a function of volume fraction of benzene in Fig. 15 and are seen to increase with increasing volume fraction of benzene. This behavior is analogous to that of amorphous polymer–solvent systems, such as the poly(methyl acrylate)–ethyl acetate system.[17]

Backbone chains of PMLG, PHBLG, and PALG are all known to be rigid α-helices in the solid state. However, side chains of these polymers are long and flexible, and a transition that is very analogous to the glass transition occurs in the side-chain regions as described previously. In the vicinity of the transition temperature that is related to the onset of side-chain motion, the Arrhenius plot of diffusion coefficients has a breakpoint (Fig. 14), and this behavior is analogous to that for vinyl polymers in the glass-transition temperature. Furthermore, it is reported[12] that the side-chain relaxation in α-helical polypeptides is well described by the William-Landel-Ferry (WLF) equation,[18] which is usually applied to the relaxation associated with the glass transition of amorphous polymers, and that the side chains of these polymers are almost amorphous.

The diffusion of penetrants in amorphous polymers above the glass-transition temperature has been interpreted in terms of the free-volume theory. However, it is of interest to examine whether the diffusion of penetrants in polypeptides is interpreted, in terms of the free-volume theory above the glass-transition

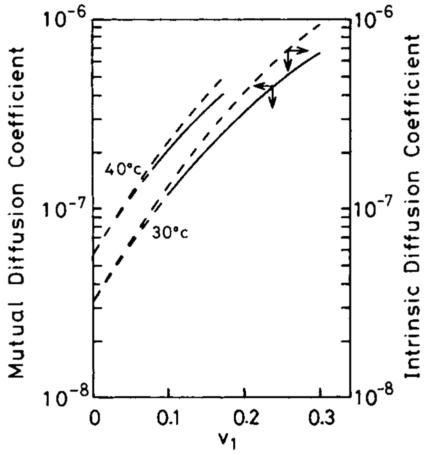


Fig. 15. Mutual and intrinsic diffusion coefficients vs volume fraction of benzene.

temperature, is related to the onset of side-chain motion.

The free-volume theory proposed by Fujita[19] will be used to examine the present diffusivity measurements. Fujita has derived the following relation:

$$\left[\ln \frac{D_T}{D(0)}\right]^{-1} = \frac{f(0,T)}{B_d} + \frac{[f(0,T)]^2}{B_d \beta(T)} \frac{1}{v_1} \tag{7}$$

where D_T is the thermodynamic diffusion coefficient, $D(0)$ is the limiting value of D_T at zero penetrant concentration, $f(0,T)$ is the average free-volume fraction in the pure polymer, B_d is related to the minimum hole size required for the displacement of given penetrant molecule in the polymer, and $\beta(T)$ is the difference between the average free-volume fraction in the pure penetrant, $\gamma(T)$, and $f(0,T)$. It is assumed that B_d is independent of both temperature and concentration.

The thermodynamic diffusion coefficient D_T is obtained from the relation[19]

$$D_T = \mathcal{D} \left(\frac{d \ln v_1}{d \ln a_1}\right) \tag{8}$$

where $(d \ln v_1/d \ln a_1)$ is obtained from the sorption isotherm.

According to eq. (7), a plot of $[\ln (D_T/D(0))]^{-1}$ vs $1/v_1$ should be linear for a given penetrant–polymer system and have a slope of $[f(0,T)]^2/B_d{\cdot}\beta(T)$ and an intercept of $f(0,T)/B_d$ at $(1/v_1) = 0$. Such plots are shown in Fig. 16 for PALG and are seen to be linear over the entire range of $1/v_1$ values investigated. The free-volume parameters B_d, $\gamma(T)$, $f(0,T)$, and $\beta(T)$ can be calculated from the slope and intercept in Fig. 16 and the expression for the free volume of the pure liquid:

$$f(1,T) = f(0,T) + \beta(T) \tag{9}$$

The difference in the free volume of the pure liquid at temperatures T_1 and T_2 is equal to the volumetric expansion of the liquid times the temperature difference. These parameters are summarized in Table II.

It is interesting to note that the values of $f(0,T)$ for PALG are much larger than those for poly(ethyl acrylate)[19] and polyethylene,[20] and the same order as those of $\gamma(T)$. Since the backbone chains of PALG are known to be rigid α-helices, the larger free volume for PALG is considered to arise mainly from the side-chain

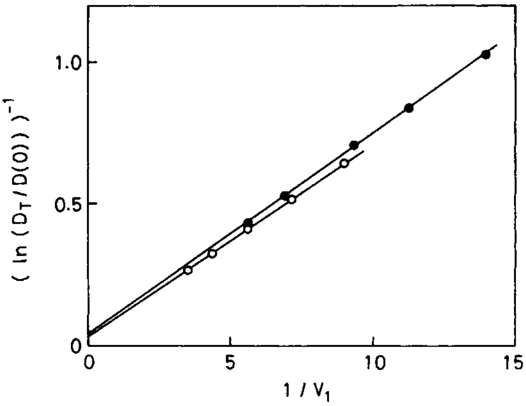


Fig. 16. Dependence of $[\ln (D_T/D(0))]^{-1}$ on v_1^{-1}: ○, 30°C; ●, 40°C.

TABLE II

Free-Volume Parameters for the PALG–Benzene System

Temperature, °C	$f(0,T)$	$\beta(T)$	$\gamma(T)$	B_d
30	0.15	0.074	0.224	4.7
40	0.16	0.078	0.238	4.7

regions. Accordingly, it is suggested that the side-chain motion of PALG is easy. It may be concluded that the larger diffusion coefficients of PALG than those of vinyl polymers are due to the ease of the side-chain motion of PALG.

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