

Gas Permeability of Copolypeptide Membranes Composed of γ -Methyl L-glutamate and γ -Benzyl L-glutamate

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Synopsis

Membranes of copoly(γ -methyl L-glutamate, γ -benzyl L-glutamate) (PMBLG) as well as the related homopolymer membranes were prepared, and permeabilities of oxygen, nitrogen, argon, and carbon dioxide were measured in the 0–70°C temperature range. The values of permeability coefficients and solubility coefficients of the copolymers were smaller than those of permeability coefficients and solubility coefficients of the two homopolymers for every gas studied. The diffusion coefficients of the gases showed a minimum at around 25 mole % benzyl glutamate. The temperature at a maximum of $\tan \delta$ spectra for the membranes showed a maximum at around 25 mole % benzyl glutamate. The Arrhenius plots of diffusion coefficients and solubility coefficients for PMBLG, which contained 50 and 71 mole % benzyl glutamate, showed a break at about 50 and 40°C, respectively. This permeation behavior is explained by assuming a unique interaction between methyl glutamate and benzyl glutamate side chains.

INTRODUCTION

In previous articles^{1–3} we have reported that the transport behavior of small molecules through homopolypeptide membranes is influenced by the chemical structure of the side chains and the transition temperature which is related to side chain motion. The studies indicate that the sorption and diffusion of small molecules in homopolypeptides occurs through the side chain region between helices.

In the present work, the gas permeability of copoly(γ -methyl L-glutamate, γ -benzyl L-glutamate) membranes was studied. Three copolypeptide membranes with different comonomer ratios as well as their related homopolymer membranes, poly(γ -methyl L-glutamate) and poly(γ -benzyl L-glutamate), were prepared, and the effects of temperature and monomer composition in the copolymer on gas permeability of these membranes were investigated.

EXPERIMENTAL

Materials

Poly(γ -methyl L-glutamate) (PMLG) was supplied by Kyowa Hakko K.K. (Japan). Poly(γ -benzyl L-glutamate) (PBLG) was prepared by the polymerization of *N*-carboxyamino acid anhydride (NCA) in dioxane. Copoly(γ -methyl

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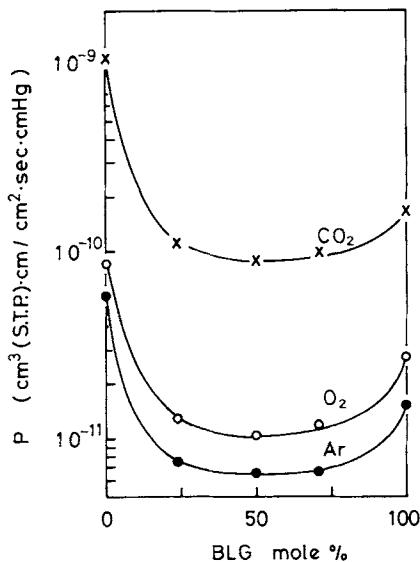


Fig. 1. Permeability coefficients as function of benzyl glutamate composition in copolymers at 20°C.

L-glutamate, γ -benzyl L-glutamate) (PMBLG) was prepared in a mixture of dioxane and 1,2-dichloroethane. Triethylamine was used as an initiator.

Molecular weight was determined by an *N*-terminal titration method. Monomer composition of the copolymers was estimated from high-resolution NMR spectra measured by a 60 MHz spectrometer (Varian EM360) in trifluoroacetic acid. Monomer composition of the copolymer was almost the same as the initial mixing ratio of NCAs. Benzyl glutamate (BLG) mole % in the copolymers are 24 (50,000), 50 (65,000), and 71 (40,000), where the figures in parentheses are molecular weights. The copolymers will be designated PMBLG-XX, where XX is the mole % benzyl content (see Fig. 7, for example, PMBLG-24).

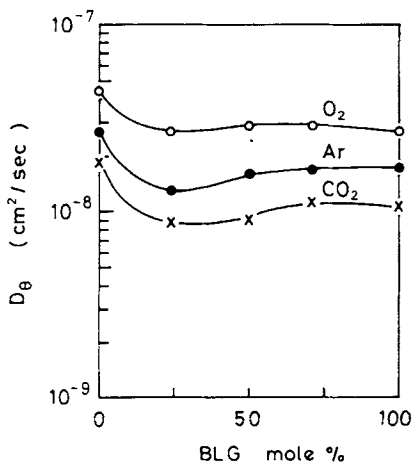


Fig. 2. Diffusion coefficients as function of benzyl glutamate composition in copolymers at 20°C.

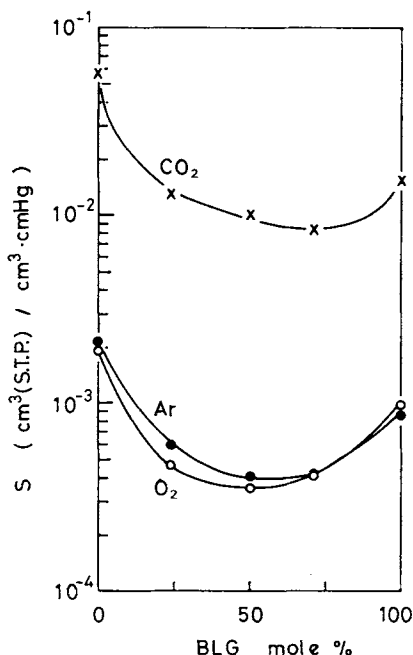


Fig. 3. Solubility coefficients as function of benzyl glutamate composition in copolymers at 20°C.

It should be noted that the product of the monomer reactivity ratios for the copolymerization of methyl L-glutamate and benzyl L-glutamate is very close to unity, i.e., 0.98, which means that the two types of monomers are arranged at random along the chain in relative amounts specified by the composition of the initial monomer mixture.⁴

Membranes were prepared by casting the 1,2-dichloroethane solution of these polymers onto glass plates and by drying in air at 20°C and finally under vacuum at 80°C for a day to remove the dichloroethane. Thicknesses were 0.150–0.200 mm. All of the membranes prepared were confirmed to have α -helical structures on the basis of infrared absorption spectra.⁵ The densities of all the membranes were examined by a flotation method using an aqueous calcium chloride solution at 20°C.

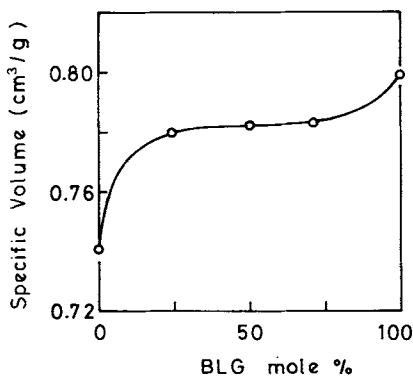


Fig. 4. Specific volume of membranes as function of benzyl glutamate composition in copolymers at 20°C.

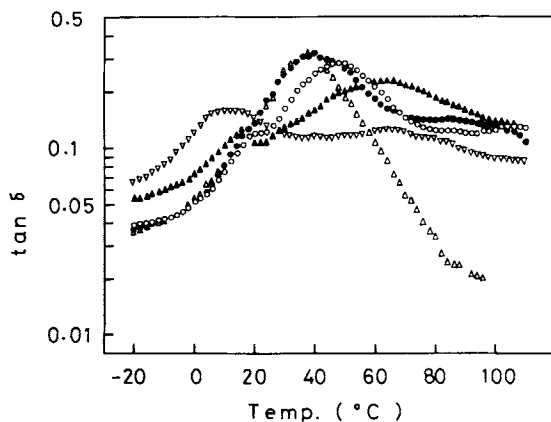


Fig. 5. $\tan \delta$ as a function of temperature: (∇) PMLG; (\blacktriangle) PMBLG-24; (\circ) PMBLG-50; (\bullet) PMBLG-71; (\triangle) PBLG.

Apparatus and Procedure

The general theory of gas transport in polymers and detailed discussions of the methods of measurement and calculation of the permeability, diffusion, and solubility coefficients, P , D_θ , and S , respectively, have been published elsewhere.⁶ The experimental method used in this study was an adaptation of the high-vacuum gas transmission technique described by Stannett and co-workers.⁷ A time lag method was used for the calculation of diffusion coefficients. Solubility coefficients were calculated by $S = P/D_\theta$.

Viscoelastic behaviors were measured at a frequency of 110 Hz and a heating rate of 2°C/min in the temperature range -70–150°C with a Vibron DDV-IIC manufactured by Toyo Baldwin Co. Ltd.

RESULTS AND DISCUSSION

Effect of Monomer Composition in Copolymer on Gas Permeability of Copolypeptide Membranes

The permeability coefficients P [$\text{cm}^3(\text{STP}) \text{ cm}/\text{cm}^2 \text{ sec cm Hg}$], diffusion coefficients D_θ (cm^2/sec), and solubility coefficients S [$\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{cm Hg}$] of CO_2 , O_2 , and Ar at 20°C as a function of benzyl glutamate composition in the

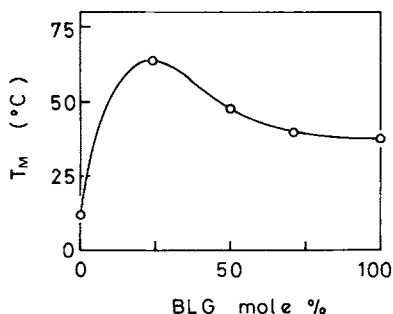


Fig. 6. Temperature of the maximum $\tan \delta$ as function of benzyl glutamate composition in copolymers.

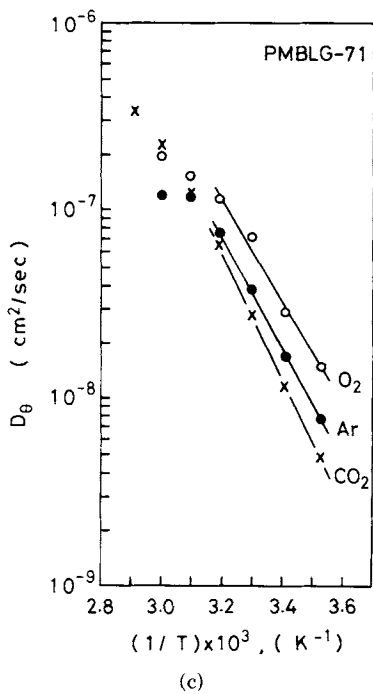
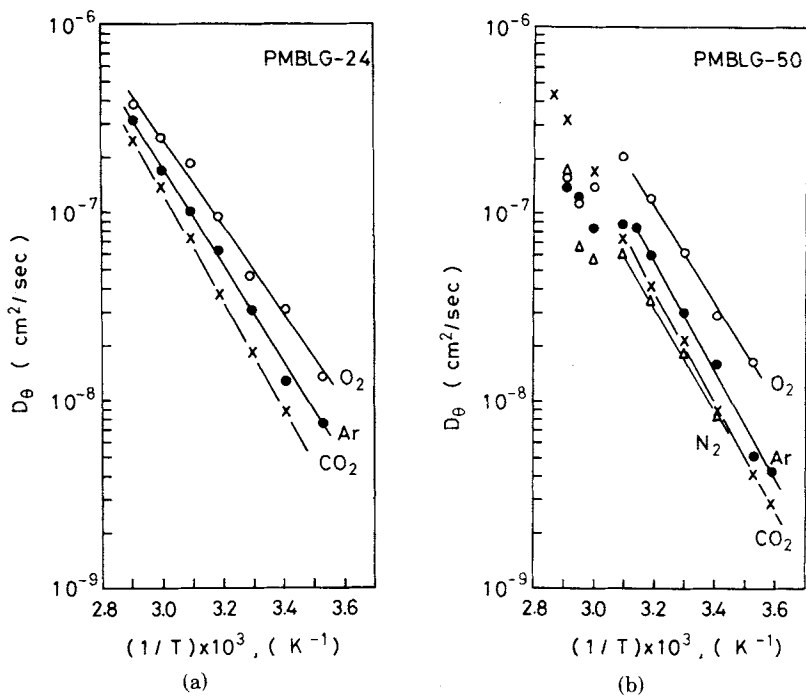


Fig. 7. Temperature dependence of diffusion coefficient.

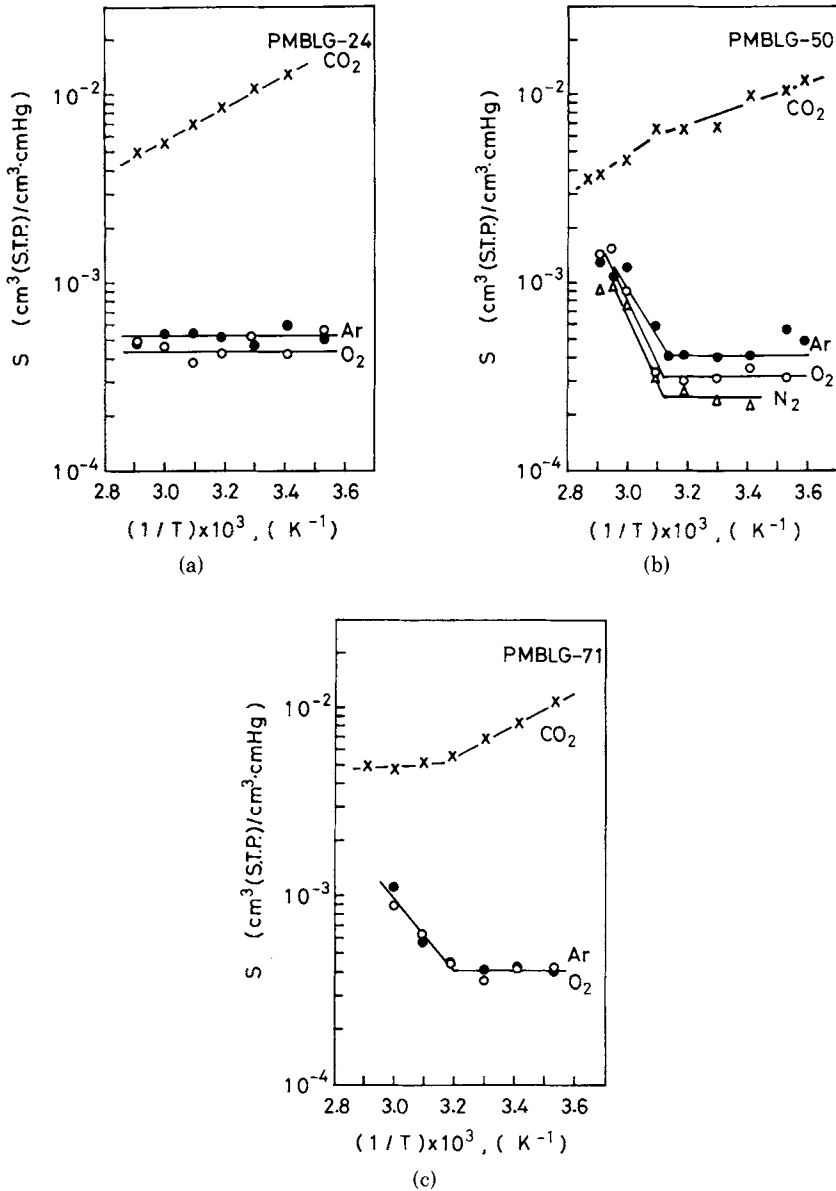


Fig. 8. Temperature dependence of solubility coefficient.

copolymers are shown in Figures 1, 2, and 3, respectively. The values of permeability coefficients and solubility coefficients of the copolymers were smaller than those of permeability coefficients and solubility coefficients of the two homopolymers PMLG and PBLG for every gas studied. The diffusion coefficients for the gases showed a minimum at around 25 mole % benzyl glutamate.

We have suggested that the sorption and diffusion of small molecules in homopolypeptides having α -helical structure take place in the side chain region

between helices.¹⁻³ Therefore, it is expected that the condition of the packing of the side chains may influence the transport property in copolypeptide membranes. In order to examine the condition of the packing of the side chains in the membranes, the specific volumes of the membranes were measured and plotted in Figure 4 as a function of benzyl glutamate composition in the copolymers. The specific volume of the copolymer was not proportional to the benzyl glutamate residue composition but was between those of the homopolymers. From these experimental results, it may be suggested that there is a unique interaction between methyl glutamate and benzyl glutamate side chains.

In order to obtain information on side chain-side chain interaction, the dynamic mechanical relaxation behavior of these copolypeptide membranes was examined. Figure 5 shows the temperature dependence of the loss spectrum, $\tan \delta$. The β peaks, which are attributed to the onset of motion of the side chains, were observed in the temperature range 10–65°C. The temperature of the β peak (T_M) is plotted in Figure 6 as a function of mole % benzyl glutamate component in these copolypeptide membranes. It should be pointed out that the temperature of the β peak was not exactly proportional to the benzyl glutamate residue composition but showed a maximum at around 25 mole % benzyl glutamate. It is noteworthy that the value of this point coincided with the minimum value of the diffusion coefficient (Fig. 2).

Tsutsumi et al.⁸ have investigated the relaxation phenomena of copoly(γ -methyl L-glutamate, γ -benzyl L-glutamate) in the solid state by means of dielectric relaxation measurements. They have reported that the temperature of the maximum dielectric loss showed a maximum at around 30 mole % benzyl glutamate.

This behavior should be attributed to the influence of the unique effect of the side chain-side chain interaction. If we consider such interactions in the α -helix conformation of polypeptides, there is a strong packing of the side chain in homopolypeptides; while in these copolymers, the condition of the packing of the side chain is highly modified by the unique side chain-side chain interaction. In this case, there seems to be a unique interaction between methyl glutamate and benzyl glutamate side chains. The condition of the packing of these side chains may be an important factor in determining the solubility of gases in polypeptides. Such side group interactions may play an important role in the side group mobility, and this seems to have a pronounced effect on the relaxation behavior of the copolypeptides and also the diffusion behavior in membranes.

Effect of Temperature on Gas Permeability of Copolypeptide Membranes

The diffusion coefficients and the solubility coefficients of PMBLG-24, PMBLG-50, and PMBLG-71 membranes are plotted against inverse temperature in Figures 7 and 8, respectively. Both PMBLG-50 and PMBLG-71 showed a break at about 50 and 40°C for PMBLG-50 and PMBLG-71, respectively. It should be pointed out that the breaking point temperatures for PMBLG-50 and PMBLG-71 are in approximate agreement with the β -peak temperatures for the corresponding copolymers (Fig. 6). Accordingly, it is suggested that these breaks are due to the cooperative motion of the two types of side chains caused by the unique interaction in PMBLG-50 and PMBLG-71. It is assumed that in

PMBLG-24 the β -peak temperature was so high that the diffusion coefficient did not show a break in the temperature range studied. From the result, it appears that the permeability of the copolypeptide membranes is influenced by side chain-side chain interaction.

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