

# The Effect of Casting Solvent on the Sorption and Diffusion of Water Vapor in Poly( $\gamma$ -methyl L-Glutamate)

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## Synopsis

Water vapor permeability of poly( $\gamma$ -methyl L-glutamate) (PMLG) membranes prepared by using dichloroethane, trifluoroacetic acid, and formic acid as solvents was studied. The membranes prepared by casting dichloroethane and trifluoroacetic acid solutions of the polymer, designated as PMLG-DCE and PMLG-TFA, respectively, had  $\alpha$ -helical structures according to infrared absorption spectra, while the membranes prepared by allowing the PMLG-TFA membranes to swell in formic acid, designated as PMLG-FA, had mainly a  $\beta$ -sheet structure. The amounts of water sorbed by PMLG-DCE, PMLG-TFA, and PMLG-FA increased in that order. The isotherms of PMLG-TFA and PMLG-FA were sigmoidal-shaped isotherms, and the heat of sorption for PMLG-TFA and PMLG-FA was larger than that for PMLG-DCE, which suggested the presence of the sorption sites. The diffusion coefficients of water for PMLG-DCE increased and then decreased with increasing concentration. On the other hand, the diffusion coefficients for PMLG-TFA and PMLG-FA increased with concentration. The activation energies of diffusion for PMLG-DCE, PMLG-TFA, and PMLG-FA increased in that order. These results were discussed in connection with the molecular conformations of poly( $\gamma$ -methyl L-glutamate) in the membranes. From these results, it is assumed that the molecular chains in the PMLG-TFA membranes are mainly in  $\alpha$ -helical and partly random-coil conformations.

## INTRODUCTION

The transport properties of small molecules through synthetic polypeptides of  $\alpha$ -helical structures have been studied.<sup>1,2</sup> We found that the permeability of water vapor through poly-L-methionine was of the order of  $10^{-7}$  cm<sup>3</sup>(S.T.P.)-cm/cm<sup>2</sup>-sec-cm Hg and that the large permeability was due to the large diffusion coefficient. The sorption and permeation behavior was hydrophobic. The introduction of a hydrophilic group into the side chain of poly-L-methionine had considerable influence on the sorption and permeation behavior of water vapor. The sorption behavior of benzene onto poly( $\alpha$ -*n*-amyl L-glutamate) was interpreted in terms of the theory of the mixing of the solvent with side chains. The Arrhenius plots of diffusion coefficients of benzene for poly( $\gamma$ -methyl L-glutamate) and poly( $\gamma$ -hexahydrobenzyl L-glutamate) 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 side chain motion. The diffusivity data of benzene for poly( $\gamma$ -*n*-amyl L-glutamate) were interpreted in terms of the free volume theory, and it was suggested that the large diffusion coefficient was due to the ease of the side chain motion of the polymer. These results indicate that the diffusion of small molecules in these polypeptides takes place in the side chain regions between helices.

It is known that when polypeptide membranes are formed by casting from

solutions, different chain conformations result in the membranes obtained, depending on the kind of solvent, temperature, casting velocity, etc. Nakajima et al.<sup>3</sup> reported that poly( $\gamma$ -methyl L-glutamate) exists in the  $\alpha$ -helix form in membranes cast from trifluoroacetic acid solutions but in the  $\beta$ -chain form in membranes swollen in formic acid. Mohadger et al.<sup>4</sup> found that the casting solvent has considerable influence on the material properties of poly( $\gamma$ -methyl D-glutamate).

In this work, we prepared the poly( $\gamma$ -methyl L-glutamate) membranes by using dichloroethane (helical solvent), trifluoroacetic acid (random-coil solvent), and formic acid as solvents. The water vapor permeability of these membranes and the sorption behavior of water vapor onto these membranes were investigated and all discussed in connection with the molecular conformations of poly( $\gamma$ -methyl L-glutamate) in the membranes.

## EXPERIMENTAL

### Materials

Poly( $\gamma$ -methyl L-glutamate) (PMLG) supplied by Kyowa Hakko K. K. (Japan) was 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.

The solvents used were dichloroethane, trifluoroacetic acid, and formic acid of extrapure grade, and they were used without further purification.

Membranes were prepared as follows: The membranes designated as PMLG-DCE (0.050–0.060 mm thick) were prepared by casting the dichloroethane solution of the polymer on a glass plate at 20°C. The membranes designated as PMLG-TFA (0.060–0.070 mm thick) were prepared by casting the trifluoroacetic acid solution by the identical technique as PMLG-DCE. The membranes designated as PMLG-FA (0.020–0.030 mm thick) were prepared from PMLG-TFA by allowing the PMLG-TFA membranes to swell in formic acid at room temperature for one month and then drying the swollen membranes under reduced pressure at about 13°C.<sup>3</sup> All membranes were dried under vacuum at 80°C for a day to remove the casting solvents.

Infrared absorption spectra of these membranes were measured and are shown in Figure 1. In PMLG-DCE membranes, characteristic absorptions of the  $\alpha$ -helix appear at 1650  $\text{cm}^{-1}$  (amide I), 1545  $\text{cm}^{-1}$  (amide II), and 615  $\text{cm}^{-1}$  (amide V). We conclude that these polymer chains exist in the  $\alpha$ -helix form in PMLG-DCE membranes. In PMLG-TFA membranes, absorptions are similar to those in PMLG-DCE membranes, and characteristic absorption of the random coil at about 650  $\text{cm}^{-1}$  does not appear clearly, though PMLG is known to dissolve in the coil form in trifluoroacetic acid. We conclude that these polymer chains exist in the  $\alpha$ -helix form in PMLG-TFA membranes. In PMLG-FA membranes, characteristic absorptions of antiparallel  $\beta$ -conformation<sup>5</sup> appear at 1685, 1630, 1530, and 700  $\text{cm}^{-1}$ . Accordingly, we conclude that these polymer chains exist mainly in the  $\beta$ -form in PMLG-FA membranes.

Although not shown here, x-ray diffraction patterns of PMLG-DCE, PMLG-TFA, and PMLG-FA membranes support the respective conclusions derived from the infrared spectra.

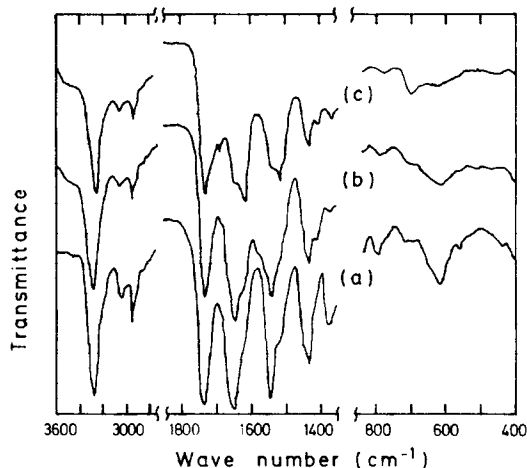


Fig. 1. Infrared absorption spectra of PMLG-DCE (a), PMLG-TFA (b), and PMLG-FA (c).

### Permeation and Sorption Experiments

Permeation measurements were made using Rouse's apparatus.<sup>6</sup> 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 water-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 water at that temperature. The amount of water transferred through the membrane in time  $t$ ,  $Q(t)$ , expressed in volume at standard state per unit area of the membrane [ $\text{cm}^3(\text{S.T.P.})/\text{cm}^2$ ] is plotted versus time  $t$ , as shown in Figure 2 for the PMLG-FA-water system. The linear portions of the permeation curves correspond to steady-state permeation, from whose slopes the permeability coefficients  $\bar{P}$  [ $\text{cm}^3(\text{S.T.P.})\text{cm}/\text{cm}^2\text{sec}(\text{cm Hg})$ ] are determined.

Sorption measurements for water 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 recovery was excellent. The samples used in the sorption experiments were in film form. It took two to five days for sorption equilibrium to be attained. Sorption amounts

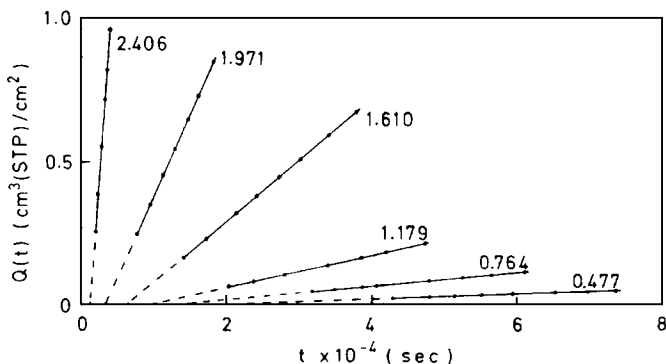


Fig. 2. Permeation curves for PMLG-FA membrane ( $30^\circ\text{C}$ ). Numbers on curves indicate water vapor pressure (cm Hg) of ingoing side.

were expressed in the weight of water per unit weight of dry polymer (g/g). The solubility coefficients  $S$  [ $\text{cm}^3(\text{S.T.P.})/\text{cm}^3\text{-cm Hg}$ ] are calculated by dividing the sorption amount by the vapor pressure.

Steady-state diffusion coefficients  $\bar{D}$  ( $\text{cm}^2/\text{sec}$ ) are obtained by dividing  $\bar{P}$  by  $S$ . The bars on  $P$  and  $D$  denote concentration averages.

## RESULTS AND DISCUSSION

### Permeability Coefficients

The permeability coefficients  $\bar{P}$  of PMLG-DCE, PMLG-TFA, and PMLG-FA membranes at temperatures from 20° to 40°C are plotted against the relative vapor pressure of water in Figure 3. The permeability coefficients of PMLG-DCE and PMLG-TFA membranes increase slightly with relative vapor pressure, while those of PMLG-FA membranes increase steeply with relative vapor pressure. PMLG-TFA and PMLG-FA membranes exhibit smaller permeability than do PMLG-DCE membranes. The permeation behavior of PMLG-DCE membranes is similar to that of poly-L-methionine membranes, which have an  $\alpha$ -helical structure,<sup>1</sup> and the permeability coefficient of PMLG-DCE membranes as a whole is about twice that of poly-L-methionine membranes. The permeation behavior of PMLG-FA membranes is similar to that of nylon 4 membranes,<sup>7</sup> and the permeability coefficient of PMLG-FA membranes is about twice that of nylon 4 membranes.

It was found that the casting solvent has a considerable influence on the permeation behavior.

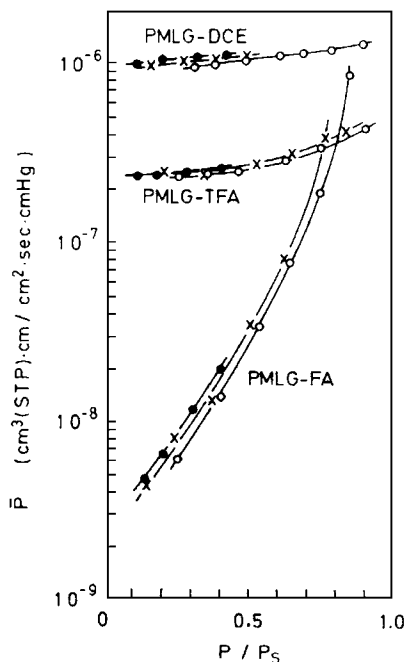


Fig. 3. Permeability coefficients  $\bar{P}$  vs relative vapor pressure of water: (O) 20°C; (X) 30°C; (●) 40°C.

### Sorption

The sorption isotherms of water on PMLG-DCE, PMLG-TFA, and PMLG-FA at temperatures from 20° to 40°C are shown in Figure 4. No hysteresis for these isotherms was observed. The amounts of water sorbed by PMLG-DCE, PMLG-TFA, and PMLG-FA increase in that order. The isotherms of PMLG-TFA and PMLG-FA are sigmoidal-shaped isotherms, and the behavior suggests the presence of sorption sites. The isotherms of PMLG-TFA and PMLG-FA are dependent on temperature, while the isotherms of PMLG-DCE are independent of temperature.

The differential heat of sorption of liquid water,  $Q_L$ , was obtained by means of the Clapeyron-Clausius equation:

$$Q_L = -R \left[ \frac{\partial \ln x}{\partial (1/T)} \right]_C \quad (1)$$

where  $T$  is the temperature,  $R$  is the gas constant, and  $x$  is the relative vapor pressure. The heat of sorption is plotted against the sorption amount of water in Figure 5. For PMLG-DCE, the heat of sorption was about zero. These results suggest that PMLG-TFA and PMLG-FA have strong polar groups which act as the sorption sites of water, while PMLG-DCE does not have such groups.

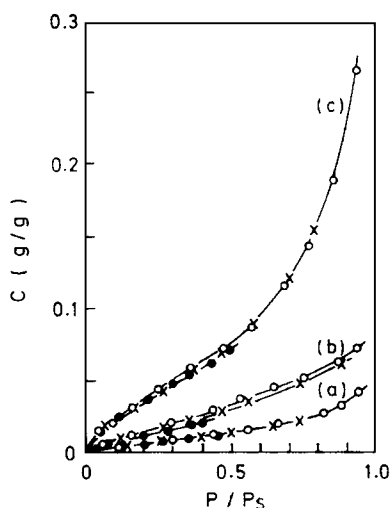


Fig. 4. Sorption isotherms of water on PMLG-DCE (a), PMLG-TFA (b), and PMLG-FA (c): (○) 20°C; (X) 30°C; (●) 40°C.

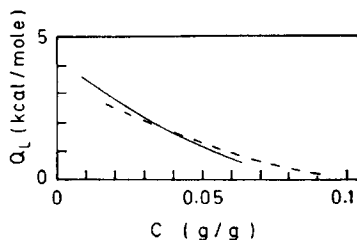


Fig. 5. Differential heat of sorption  $Q_L$  vs sorption amount of water. Solid line represents PMLG-TFA, broken line represents PMLG-FA.

The PMLG-DCE membranes have  $\alpha$ -helical structures, as judged by infrared absorption spectra. PMLG-DCE sorbs more water than does poly-L-methionine, which has an  $\alpha$ -helical structure.<sup>1</sup> The sorption of molecules of low molecular weight onto polypeptides of rod-like,  $\alpha$ -helical structure is reported to be controlled by polymer side chain-solvent mixing.<sup>8,9</sup> In fact, the amounts of water sorbed by PMLG-DCE are about the same as those sorbed by poly(methyl methacrylate), whose molecular structure is similar to the molecular structure of the side chain of PMLG.<sup>10</sup> Accordingly, it is suggested that the peptide groups which form the intramolecular hydrogen bonds do not act as the sorption sites of water.

The PMLG-TFA membranes also have  $\alpha$ -helical structures, as judged by infrared absorption spectra. However, the sorption behavior of PMLG-TFA is different from that of PMLG-DCE; PMLG-TFA sorbs more water than does PMLG-DCE, the isotherms of PMLG-TFA are sigmoidal-shaped isotherms, and the heat of sorption for PMLG-TFA is larger than that for PMLG-DCE, which suggests the presence of sorption sites of water in PMLG-TFA. These sorption phenomena are sensitive to the difference in molecular conformations in the amorphous regions. From these results it may be assumed that molecular chains in the PMLG-TFA membranes are mainly in  $\alpha$ -helical and partly random-coil conformations. It may be assumed that the peptide groups in the region of random structure act as the sorption sites of water.

PMLG-FA membranes have mainly a  $\beta$ -sheet structure as judged by infrared absorption spectra. The amounts of water sorbed by PMLG-FA are much more than those sorbed by PMLG-DCE, and about the same as those sorbed by nylon 4.<sup>7</sup> The heat of sorption for PMLG-FA is larger than that for PMLG-DCE. It is believed that in the case of PMLG-FA the intermolecular hydrogen bonds between the peptide groups are broken by water molecules and that the peptide groups act as the sorption sites of water.

It was found that the casting solvent has a considerable influence on the sorption behavior.

### Diffusion Coefficients

The concentration-average diffusion coefficients  $\bar{D}$  of water in PMLG-DCE, PMLG-TFA, and PMLG-FA at temperatures from 20 to 40°C are plotted against the relative vapor pressure of water in Figures 6, 7, and 8, respectively. The diffusion coefficients for PMLG-DCE increase and then decrease with increasing relative vapor pressure, while those for PMLG-TFA and PMLG-FA increase with relative vapor pressure. Especially the diffusion coefficients for PMLG-FA are greatly dependent on the relative vapor pressure. The diffusion behaviors of PMLG-DCE and PMLG-TFA differ largely. We therefore discuss the concentration dependence of the diffusion coefficient.

From Figures 6, 7, and 8, the concentration-dependent diffusion coefficients  $D(C)$  were calculated as a function of concentration  $C$  of water in the polymer using the equation<sup>11</sup>

$$\bar{D} = \frac{1}{C_1} \int_0^{C_1} D(C) dC \quad (2)$$

The concentration dependence of the diffusion coefficients at 20°C is shown in

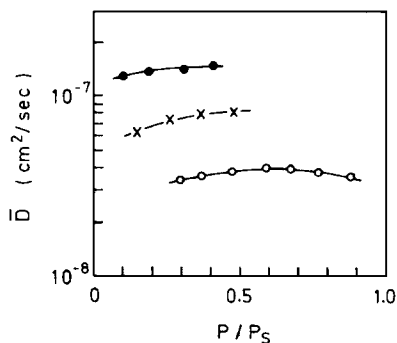


Fig. 6. Average diffusion coefficients  $\bar{D}$  of PMLG-DCE vs relative vapor pressure of water: (O) 20°C; (X) 30°C; (●) 40°C.

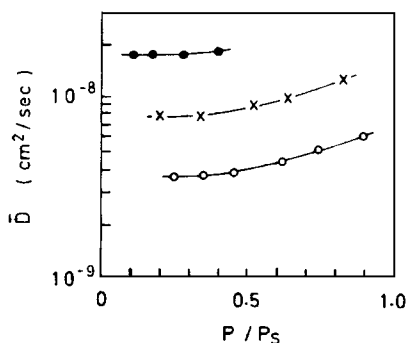


Fig. 7. Average diffusion coefficients  $\bar{D}$  of PMLG-TFA vs relative vapor pressure of water: (O) 20°C; (X) 30°C; (●) 40°C.

Figure 9. For PMLG-TFA and PMLG-FA, the diffusion coefficients increase with concentration; this indicates that the water in PMLG-TFA and PMLG-FA acts as a plasticizer. This behavior seems to be characteristic of water permeation in hydrophilic polymers such as nylon 4.<sup>7</sup> On the other hand, the diffusion coefficient for PMLG-DCE decreases with concentration; this behavior seems to be characteristic of water permeation in hydrophobic polymers.<sup>12</sup> The decrease in the diffusion coefficient for PMLG-DCE is considered to be due to clustering of the water in PMLG-DCE. It is therefore suggested that the molecular chains in the PMLG-TFA membranes are mainly in  $\alpha$ -helical and partly random-coil conformations, as mentioned earlier.

PMLG-TFA and PMLG-FA exhibit smaller diffusibility than does PMLG-DCE.

The temperature dependence of the diffusion behavior in PMLG-DCE, PMLG-TFA, and PMLG-FA was studied. The diffusion coefficients at zero penetrant concentration at each temperature were obtained by extrapolation of the diffusion coefficients to zero penetrant concentration and plotted against the inverse temperature. Since a single straight line for each polymer could easily be drawn through all the points in the range of temperatures studied, the activation energy of diffusion,  $E_D$ , was calculated using the following equation:

$$D(0) = D_0 \exp(-E_D/RT) \quad (3)$$

These data are summarized in Table I. The activation energies of diffusion for

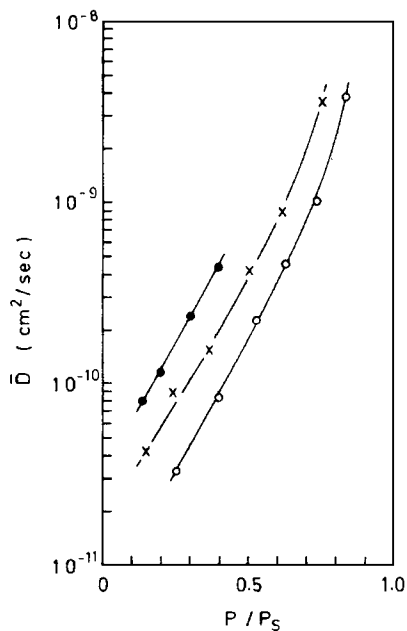


Fig. 8. Average diffusion coefficients  $\bar{D}$  of PMLG-FA vs relative vapor pressure of water: (O) 20°C; (X) 30°C; (●) 40°C.

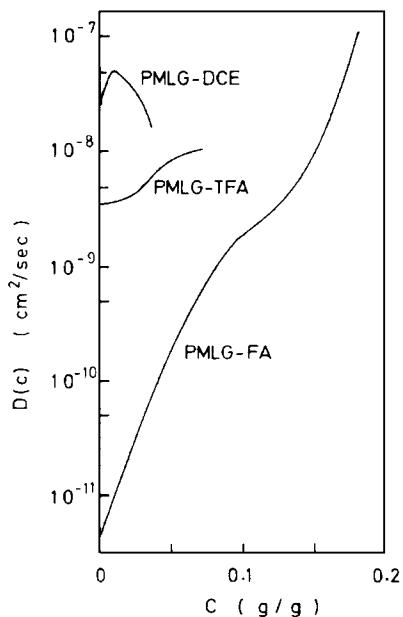


Fig. 9. Concentration dependence of diffusion coefficients of water vapor at 20°C.

PMLG-DCE, PMLG-TFA, and PMLG-FA increase in that order. The activation energy of diffusion for PMLG-DCE with  $\alpha$ -helical structure is about the same as that for poly-L-methionine.<sup>1</sup>

The vast difference in diffusion behavior observed among PMLG-DCE,



TABLE I  
Activation Energy of Diffusion,  $E_D$

	PMLG-DCE	Membrane PMLG-TFA	PMLG-FA
$E_D$ , kcal/mol	13.8	14.5	16.7

PMLG-TFA, and PMLG-FA membranes can be attributed to the difference in the molecular conformations, namely, the type of molecular interaction. In the  $\alpha$ -helical form, the polar groups in the backbone are involved in the formation of intramolecular hydrogen bonds. The diffusion of small molecules in polypeptides with  $\alpha$ -helical structure is reported to occur through the side chain regions between the helices.<sup>1,2,13-15</sup> Accordingly, the mobility of the side chain affects the diffusion properties. In PMLG-TFA, polar groups exist in the backbone which do not take part in the formation of intramolecular hydrogen bonds. The presence of such polar groups affects the diffusion properties: the diffusion behavior of PMLG-TFA is a little more hydrophilic than that of PMLG-DCE. In the case of PMLG-FA, it has been reported that intermolecular hydrogen bonding produces sheet-type structures and that the plane of the sheet is parallel to the surface of the membrane.<sup>3</sup> Accordingly, the smaller diffusion coefficient and the larger activation energy of diffusion are attributed to the lower mobility of the polymer main chain, which is due to the formation of intermolecular hydrogen bonds. Since the intermolecular hydrogen bonds are easily broken by water molecules, the diffusion coefficients largely depend on the concentration of the water.

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