Permeability of Water Vapor and Carbon Dioxide Gas Through Poly(*n*-Alkyl L-glutamate)

AKIRA TAKIZAWA, TOSHIHIRO HAMADA, HIROSHI OKADA, SYUSAKU KADOTA, and HIROSHI NONOYMA, *Department of Fiber and Polymer Technology, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan*

Synopsis

To elucidate the permeation mechanism in polypeptide membranes, permeation of water vapor and carbon dioxide gas through a series of poly(*n*-alkyl L-glutamate) (polymers of methyl, ethyl, propyl, butyl, amyl, hexyl, and octyl glutamate) were studied. It was confirmed that diffusion of small molecular substances in polypeptides takes place through the side chain region between helices. The diffusion coefficient of carbon dioxide gas increases with increase in side chain length. As for water vapor, the diffusion coefficient is highest with poly(*n*-butyl glutamate), and the clustering effect of water may contribute to the diffusion coefficient with increase in the hydrophobic nature of the polymer.

INTRODUCTION

In previous papers,[1,2] the authors have elucidated that the diffusion of small molecular substances through poly(γ-methyl glutamate) would take place where the volume expansion would be promoted by the molecular motion of side chains, namely, at the aperture between the helices.

In the present paper, for the purpose of elucidating the above permeation mechanism in more detail, the influence of side chain length of polypeptides on diffusion phenomena is studied, namely, the permeation of water and carbon dioxide gas through a series of poly(*n*-alkyl L-glutamate) (polymers of methyl, ethyl, propyl, butyl, amyl, hexyl, and octyl glutamates) is examined.

EXPERIMENTAL

Materials

Poly(γ-methyl L-glutamate)(PMLG) supplied by Kyowa Hakko K. K. (Japan) has been obtained by the polymerization of N-carboxyamino acid. The viscosity-average degree of polymerization is 1100–1200, which was determined by the intrinsic viscosity of dichloroacetic acid solution at 25°C.

Poly(n-alkyl L-glutamates), except poly(ethyl glutamate), are prepared by ester exchange reaction of PMLG. Namely, 3 g PMLG, n-alcohol (which is required for exchanging 50-to-1 residue of glutamate), 50 cc dichloroethane, and 1 cc concentrated sulfuric acid as catalyst are mixed in the reaction flask at 70°C. As the reaction proceeds, the reaction mass becomes transparent gradually, and after about two days the completely transparent product is poured into a large amount of methanol, and then the precipitant is filtered and washed thoroughly with methanol. By the nuclear magnetic resonance observation of the trifluoroacetic acid solution,[3,4] the ester exchange reaction is not accomplished by one reaction, but two or three repetitions are necessary for complete ester exchange. As for the poly(ethyl glutamate), many more repetitions will be required by the above method; so the polymer polymerized by the NCA method is used ($[\eta] = 2.0$ in dichloroacetic acid, supplied by Ajinomoto K.K.).

The membranes of poly(n-alkyl L-glutamates) are prepared by dissolving the 5% polymer in dichloroethane and by air drying of the thin layer of the above solution on a mercury surface, and finally by vacuum drying at 50°C for a day. The thickness is 0.10–0.20 mm. All of the membranes prepared have α-helical structures as confirmed, by infrared absorption spectrum observation.[5]

Each alcohol used as penetrant is of extrapure grade.

Permeation and Sorption Experiments

Permeation experiment is performed by Rouse's apparatus.[6] Accordingly, the pressure of the lower-pressure side of the membrane is always zero. The amount permeated, $Q(t)$, is expressed by the volume at the standard state per unit area of the membrane (cc STP/cm^2). The example of the permeation curve, $Q(t)$ versus time t, is shown in Figure 1 for the poly(γ-butyl L-glutamate)–water system. The linear portion of the permeation curve corresponds to the stationary state of permeation, from whose slope the permeation coefficient $\bar{P}$ (cc STP·cm/cm^2·sec·cm Hg) is determined. Dividing $\bar{P}$ by the solubility coefficient S (cc STP/cm^3·cm Hg) of penetrant to the polymer, the stationary state diffusion coefficient $\bar{D}$ is obtained. S is determined by the sorption isotherms. Intercept of the extrapolation of the above linear portion of the permeation curve with the time axis corresponds to the time lag θ, from which the nonsteady-state diffusion coefficient $\bar{D}_\theta$ is calculated. Bars on P and D denote concentration averages.

In the case of water vapor, 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 vaccum system. In the case of introduction of carbon dioxide gas to the higher-pressure side of the membrane, Dry Ice is placed in a flask in the vaccum line, and the path from the flask to the next trap is cooled with a Dry Ice–methanol mixture. Being cooled while passing, water is removed from the carbon dioxide gas. The carbon dioxide gas is then trapped into
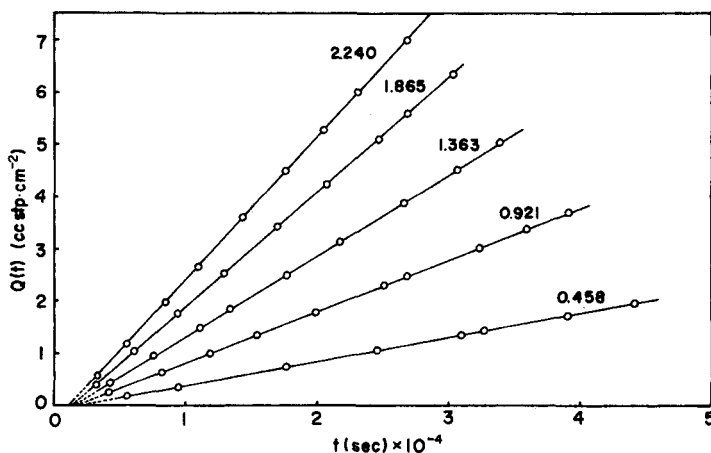
Fig. 1. Permeation curves (amount permeated, $Q(t)$, vs. time t) of poly(n-butyl L-glutamate–water system. Numbers on curves show the applied pressures in cm Hg. Membrane thickness is 0.195 mm.

a trap cooled with liquid nitrogen, and by evacuation nitrogen and oxygen are removed. Thus, purified carbon dioxide gas is introduced into the higher-pressure region of the membrane.

The sorption experiment of water is performed by the usual gravimetric method using a quartz spiral balance. As for carbon dioxide gas, the sorption behavior is observed with a Cahn electromicrobalance (Cahn Instrument Co., Calif., U.S.A.).

Both of the permeation and sorption measurements are done at 25°C.

RESULTS AND DISCUSSION

The sorption isotherms of water on polymers of methyl, butyl, and octyl glutamate are shown in Figure 2. The sorption amount (vertical axis) is
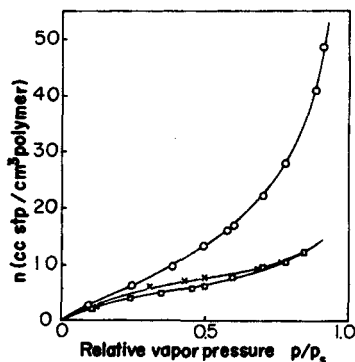

Fig. 2. Sorption isotherms (amount sorbed, n, vs. relative vapor pressure p/p_s) of poly(n-alkyl L-glutamate)–water systems: (O), (X), and (□) denote polymers of methyl, butyl, and octyl glutamate.

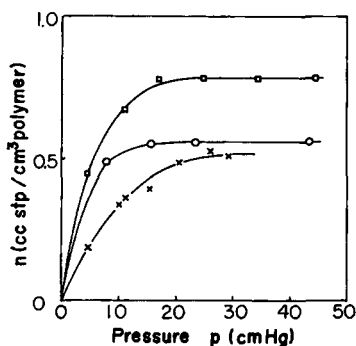|	Poly(γ-methyl L-glutamate)	Poly(n-butyl L-glutamate)	Poly(n-octyl L-glutamate)
Permeability coefficient, cc STP/cm·sec·cm Hg	2.98×10^{-9}	1.98×10^{-8}	2.68×10^{-8}
Solubility coefficient, cc STP/ cm³·cm Hg	4.8×10^{-2}	3.2×10^{-2}	6.1×10^{-2}
Diffusion coefficient, cm²/sec	6.2×10^{-8}	6.2×10^{-7}	4.4×10^{-7}

Fig. 3. Sorption isotherms of poly(n-alkyl L-glutamate)–carbon dioxide gas systems. For legend, see Fig. 2.

expressed by cc STP/cm³ which is directly related to the numbers of molecules which are sorbed. The sorptive ability decreases with increase in side chain length, which shows the effect of the hydrophobic nature of the chain. The amount sorbed divided by vapor pressure corresponds to the solubility coefficient S.

The sorption isotherms of carbon dioxide gas on the above three polymers are shown in Figure 3. The effect of loosening the side chain region with increase in side chain length may exceed the effect of decreasing polarity.

The permeability coefficient $\bar{P}$ and diffusion coefficient $\bar{D}$ of carbon dioxide gas through three kinds of poly(n-alkyl L-glutamate) at 25°C were obtained, and are shown in Table I. It is noted that the permeation and diffusion coefficients increase with increase in side chain length, and that the tendency levels off at the region of longer side chain.

Referring to this, the densities of polymers are determined using calcium chloride aqueous solution (Fig. 4). Though the density decreases gradually with increase inside chain length, the tendency slows down at the region of longer chains. This tendency indicates the increase in free volume of the side chain region. Furthermore, the membranes of these polymers become soft and flexible with increase in side chain length. According to the viscoelastic measurement of poly(n-alkyl L-glutamate),[7] the side chain dispersion
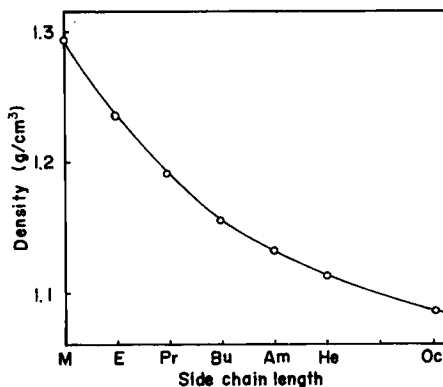
Fig. 4. Density of poly(*n*-alkyl L-glutamate): M, E, Pr, Bu, Am, He, and Oc denote polymers of methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, and *n*-octyl glutamate, respectively.
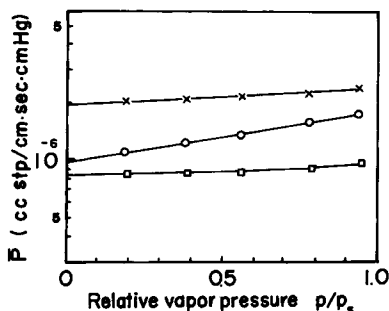

Fig. 5. Water vapor permeability $\bar{P}$ of poly(*n*-alkyl glutamate) vs. relative vapor pressure of water: (O) poly(methyl L-glutamate); (×) poly(*n*-butyl L-glutamate); (□) poly(*n*-octyl L-glutamate).

temperature decreases monotonously with the length of side chain. These results can be explained by the increase in free volume with side chain length.

Thus, the longer the side chain length, the higher the diffusion and permeation coefficients are expected to become, with increase in free volume and motional activity of the side chain region. The permeability and density results, however, cannot be explained only by the molecular motion of the side chain. Long side chains can move easily in any direction, and this makes them fill up the spaces between helices evenly. Thus, the increasing tendency of pore size effective for diffusion may slow down on the region of longer side chains.

The water vapor permeabilities of poly(methyl glutamate), poly(butyl glutamate), and poly(octyl glutamate) are shown against relative vapor pressure of water in Figure 5. In the case of poly(methyl glutamate), the plasticization effect of water is apparent, but with increase in side chain length, the effect becomes less clear. Extrapolation of the curves in Figure
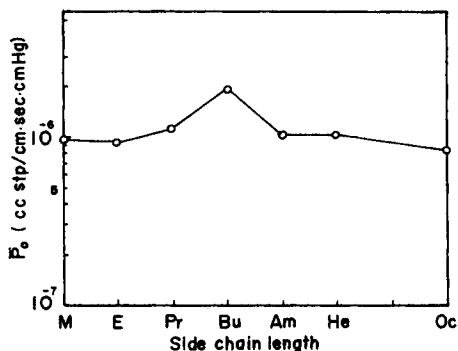
Fig. 6. Extrapolated permeability coefficient P_0 of water through various poly(n-alkyl
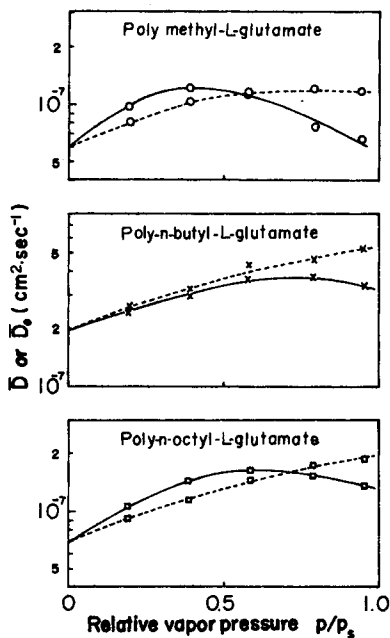L-glutamates). For legend, see Fig. 4.

Fig. 7. Steady-state diffusion coefficient $\bar{D}$ (solid line) and nonsteady-state diffusion
coefficient $\bar{D}_\theta$ (broken line) vs. applied relative water vapor pressure. For legend, see
Fig. 2.

5 to zero water vapor pressure gives the relation between $\bar{P}_0$ (permeability
at zero concentration) and side chain length (Fig. 6). The permeability
of poly(n-butyl L-glutamate) is the highest.

Both the steady-state diffusion coefficient $\bar{D}$ and the nonsteady-state
diffusion coefficient $\bar{D}_\theta$ are shown in Figure 7 against relative water vapor
pressure for three poly(n-alkyl L-glutamates). Generally, $\bar{D}$ is slightly
higher than $\bar{D}_\theta$ in the lower-pressure region, and the relation becomes re-
verse in the higher-pressure region. This can be explained by the con-
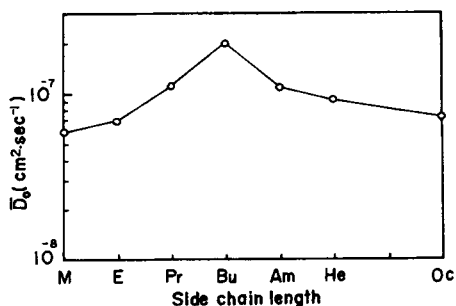
Fig. 8. Extrapolated diffusion coefficient of water, $\bar{D}_o$, in poly(n-alkyl-L-glutamates). For legend, see Fig. 4.

centration dependence of diffusion coefficient, which in the low-concentration region increases with water concentration by plasticization effect, and passes a maximum and then decreases in the high-concentration region by clustering effect.[1] $\bar{D}$ and $\bar{D}_\theta$, however, approach almost the same extrapolated value at zero water vapor pressure.

The extrapolated diffusion coefficient to zero water concentration, $\bar{D}_0$, thus obtained is shown in Figure 8 against the carbon numbers of the alkyl groups of poly(alkyl glutamate). Though the diffusion coefficient increases from poly(methyl glutamate) to poly(n-butyl glutamate) as expected, the group having longer side chains than poly(n-amyl glutamate) shows a decreasing tendency of diffusion coefficient with increase in chain length.

The results cannot be explained by the filling effect described in the case of carbon dioxide. In addition to such factors of the polymer, the contribution of water as penetrant is considered. It was reported in the previous paper that the cluster of four to five water molecules could diffuse in the PMDG.[1] Since the clustering tendency of water molecules increases with the hydrophobic nature of the polymer,[8] it is expected that the clustering is strengthened with increase in length of the hydrophobic side chain. Accordingly, the diffusion of rather larger molecules than usual occurs, and the diffusion coefficient decreases with chain length.

Thus, the diffusion behavior of the poly(n-alkyl glutamate)–water system becomes complicated because of the contribution of the hydrophobic nature of the polymer. To proceed in the study relating the diffusion phenomena with polypeptide structure, it is desirable to follow the diffusion behavior of carbon dioxide in more detail, which has the appropriate size and no clustering tendency; this would be significant, especially for the study of temperature dependency.

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