

Water Vapor Sorption and Permeability of Polyglutamic Acid

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Equilibrium water vapor sorption on polyglutamic acid and diffusion behavior of water vapor in the polymer is studied. The result is as follows:

(1) Water vapor sorptive capacity of polyglutamic acid is the order of 1/10 of that of polyglutamic acid sodium salt and several times that of poly- γ -methyl-D-glutamate (PMDG). This reflects the influence of chemical structure of the polymer.

(2) Steady state permeation coefficient \bar{P} of polyglutamic acid—water system shows remarkable concentration dependency, and this is explained by plasticization effect of water to the polymer. The \bar{P} is the order of 1/10~1/100 of PMDG and is slightly higher than that of cellophane in the high pressure range.

(3) Steady state diffusion coefficient \bar{D} also shows marked concentration dependency and is order of 1/10~1/1000 of PMDG. With plasticization by water, the diffusion in the side chain region becomes more easily as in the case of PMDG.

(4) Sorption process and non-steady state permeation process are non-Fickian. This is due to the restriction of side chain motion owing to the α -helical structure of the polymer and the interaction between side chains.

1. Introduction

In order to investigate the relation between the sorption and diffusion of small molecular substances and the unique higher order structure of synthetic polypeptides, the authors elucidated that (1) the permeability of water vapor through poly- γ -methyl-D-glutamate (PMDG) was as high as the order of 10^{-6} cc stp/cm \cdot sec \cdot cmHg at 25°C, which owed to the high diffusion coefficient¹⁾, (2) the diffusion of small molecular substances would take place in the side chain region between helices by the study of permeation of alcohols of various molecular size²⁾ (3) hence, water vapor and CO₂ gas permeability through a series of poly-n-alkylglutamate was affected remarkably by the conformation of side chain region, and in the case of water vapor the clustering effect of water molecule might contribute to the diffusion behavior²⁾, and that (4) the sorption of the penetrant on polypeptide took place in the side chain region, and the swelling effect of side chain had to be considered³⁾.

As the higher order structure of polyglutamic acid contains not only intramolecular hydrogen bond which constitutes the α -helix, but also the intermolecular interaction between carboxylic acid groups, the sorption and diffusion phenomena may become more complex comparing with the above polyglutamic acid ester. In the present paper the influence of the intermolecular interaction on water sorption and permeability of the polymer is examined.

2. Experimental

2.1. Materials

Poly-L-glutamic acid membrane was supplied by Tokyo Cellophane K.K. (Japan). The density of the film is determined to be 1.359 by the floatation method using toluene-carbon tetrachloride mixture. The membrane thickness is 4.93×10^{-3} cm. Infrared absorption spectrum observation shows the absorption relating to the stretching of C=O (1645 cm^{-1}) and deformation of NH (1543 cm^{-1}) which form hydrogen bond in α -helix, and stretching of NH (3290 cm^{-1}) which forms hydrogen bond. This con-

firms that the substantial structure of the polymer is α -Helix. Using the dilatometry the second order transition temperature of the polymer is 29°C which reflects the molecular motion of the side chains. This is confirmed by the viscoelastic measurement⁴⁾, broad line NMR observation⁵⁾ and X-ray analysis⁶⁾.

2.2. Sorption and Permeation Apparatus

The sorption experiment of water vapor is performed by the two-series sorption apparatus which is capable of gravimetric and volumetric observation simultaneously⁷⁾. Sorption amount is expressed in terms of $n(\text{g/g polymer})$, but in the case of calculating the solubility coefficient

S described later, n must be expressed in terms of cc stp/cm^3 polymer. At first, the equilibrium sorption isotherm is obtained. With this isotherm, the desired increase of water vapor pressure necessary for a constant increase of sorption amount is determined. According to the differential sorption method⁸⁾, the water vapor pressure is increased succeedingly by the amount determined above, and the sorption processes are followed until equilibria are attained.

For the permeation of water vapor, the Barrer and Barrie's apparatus⁹⁾ is modified. Fig.1 shows the schematic diagram. B denotes

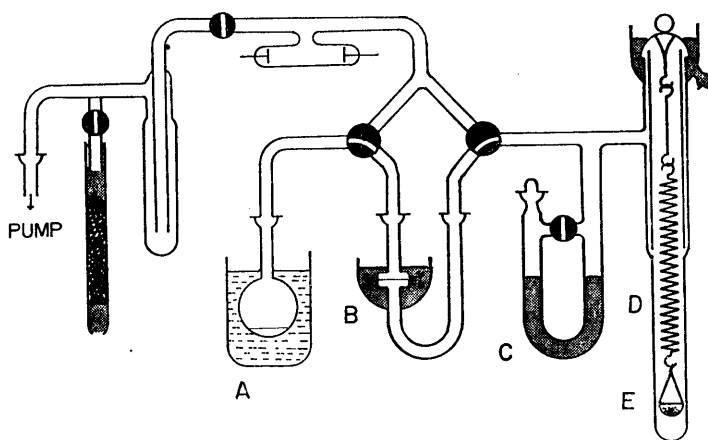


Fig.1. Schematic diagram of permeation apparatus: A, storing flask for vapor generation; B, permeation cell; C, manometer; D, quartz helical balance; E, molecular sieve

the permeation cell, in which the polymer membrane is set. Vapor pressure of the higher pressure region of the membrane is supplied by saturated vapor of A flask, which contains distilled water, and the temperature is controlled by the bath. The cell is mercury sealed, and the area of membrane for permeation is 10.17 cm^2 . The water vapor permeated the membrane is adsorbed on the molecular sieve (Linde Co. 13X) E which is suspended from the quartz helical balance D. Hence, the vapor pressure of the lower pressure region is essentially zero, and the permeation amount $Q(t)$ (cc stp/cm^2) at time t is determined by elongation of the balance. The manometer C is set for check of the vapor pressure of the lower pressure region. The whole apparatus is under the temperature control by air. Further, the part of cell is temperature controlled by circulating

water within $\pm 0.1^\circ\text{C}$.

The observation is carried out at 25°C.

3. Results and Discussion

3.1. Equilibrium Sorption and Sorption Kinetics of Water Vapor on Polyglutamic Acid

Fig.2 shows the equilibrium sorption isotherm of water on polyglutamic acid at 25°C. For comparison, the isotherms of polyglutamic acid sodium salt¹⁰⁾ and PMDG¹⁾ are also shown in the Figure. As for the polypeptide-penetrant systems, it is known that the penetrant molecules are mixed randomly with side chains of the polypeptide^{11,12,3)}. Since the polarity of the side chain of polyglutamic acid is larger than that of PMDG, it becomes the strong localized site for adsorption and S-shape adsorption mechanism is more evident in the case

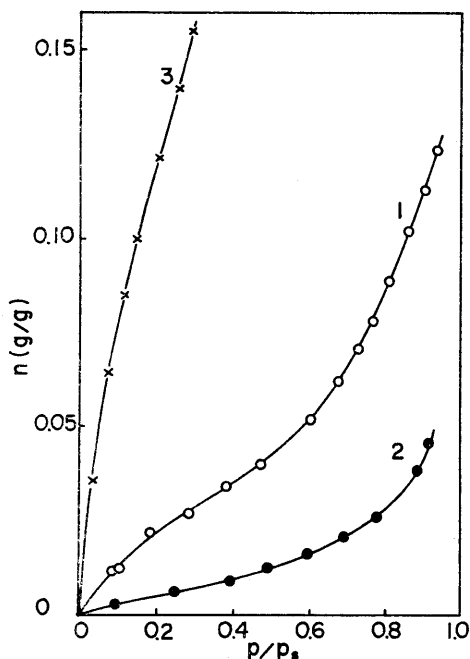


Fig. 2. Equilibrium sorption isotherm (amount sorbed n vs. relative vapor pressure P/P_s relation) of water on polyglutamic acid (1), poly- γ -methyl-D-glutamate (2) and polyglutamic acid sodium salt (3) at 25°C.

of polyglutamic acid. Because of the hydration effect of the carboxylic acid group, the water sorption amount is almost three times that of PMDG in general. Naturally, comparing with extremely high sorption amount of polysodium glutamate (a polyelectrolyte), the water sorption amount of polyglutamic acid is low. The application of BET's adsorption theory to the polymer-water system, in which the polymer structure changes with the sorption of water, is improper and undesirable¹³⁾. In this case, too, BET plot shows the curve which is concave upwards, and the isotherm is not explained by the adsorption theory quantitatively.

According to this equilibrium sorption isotherm, water vapor pressure is increased stepwise so as to increase the sorption amount by 0.01 g/g polymer, and the sorption process is followed with differential method succeedingly (Fig. 3). In the case of the low vapor pressure, two-stage sorption behavior⁸⁾ is evident, and up to the saturated vapor pressure, sorption process shows complex behavior which is generally S-shape. This shows that the sorption

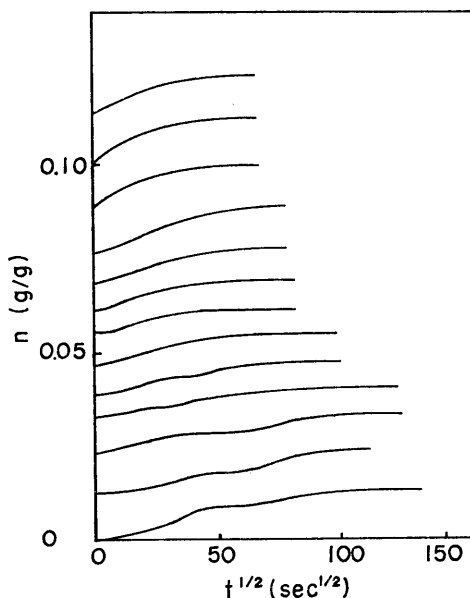


Fig. 3. Differential sorption process of polyglutamic acid-water system at 25°C

process is essentially non-Fickian. As is stated previously, the dry polymer has the side chain dispersion temperature at 29°C, which corresponds the glass transition temperature of usual polymer¹⁴⁾. The fact that the experiment is performed at 25°C, which is lower than the transition temperature, may contribute to the non-Fickian behavior. In other words, the process does not satisfy the Fickian conditions¹⁵⁾ that the surface concentration of the membrane is always constant, or that the diffusion coefficient is not time dependent. By plasticizing effect of water, the transition temperature may be reduced to some degree, and in fact, the sorption curve near saturated vapor pressure (the uppermost curve) shows the pseudo-Fickian behavior. For reference, from the curve, the reduced sorption curve ($\Delta n(t)/\Delta n(\infty) \sim t^{1/2}/L$ relation, where $\Delta n(t)$ is the increase of sorption amount at time t , $\Delta n(\infty)$ is that of the equilibrium, and L is the film thickness) is derived, and using the equation

$$\Delta n(t)/\Delta n(\infty) = 4(Dt/L^2)^{1/2} \left[\pi^{-1/2} + \sum_{m=1}^{\infty} (-1)^m \operatorname{ierfc} \left\{ mL/(Dt)^{1/2} \right\} \right]$$

the diffusion coefficient D is calculated with the initial slope of the reduced sorption curve¹⁶⁾. The D value thus determined is $4.6 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$ and almost the same as nonsteady state

diffusion coefficient of permeation described later. However, it is still lower than the steady state diffusion coefficient of permeation, and this shows clearly that the sorption process is yet in the region of non-Fickian behavior.

3.2. Water Vapor Permeability through Polyglutamic Acid Membrane

The permeation curves (the amount permeated $Q(t)$ (cc stp/cm²) vs. time t (sec) relationships) at 25°C with applied vapor pressure of 0.213, 0.458, 0.861, 1.279, 1.548 and 2.238 cmHg are shown in Fig.4. The linear portion of the permeation curve corresponds to the

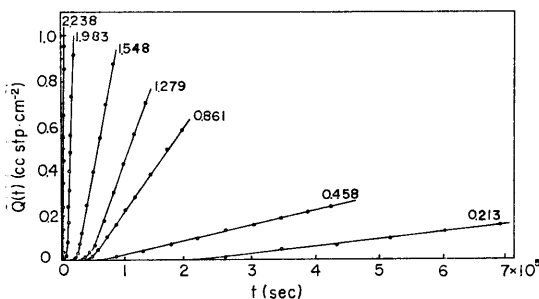


Fig. 4. Permeation curves (amount permeated $Q(t)$ vs. time t relations) of polyglutamic acid-water system. Numbers on the curves show the applied pressures in cmHg.

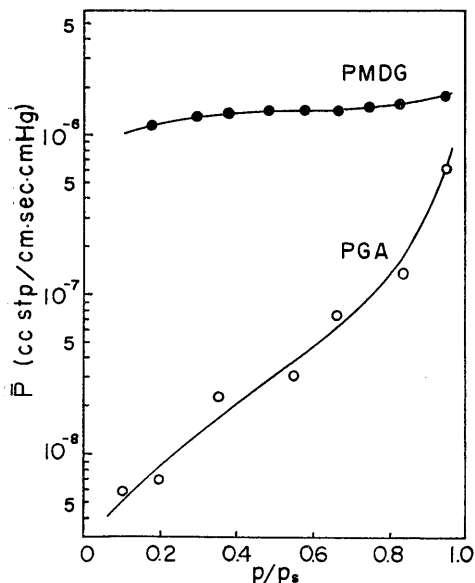


Fig. 5. Relation between water permeability coefficient at 25°C and applied relative vapor pressure of water: ○, polyglutamic acid; ●, poly- γ -methyl-D-glutamate

steady state of permeation, from whose slope the permeation coefficient \bar{P} (cc stp/cm².cmHg=the slope \times membrane thickness/applied pressure; bar denotes the concentration average) is determined and shown in Fig.5. The \bar{P} increases with water vapor pressure (water concentration in polymer) remarkably, and this is related to the plasticization of the polymer by water. This behavior is typical for the lyophilic polymer¹⁷⁾. For comparison, \bar{P} of PMDG is also shown in the Figure. \bar{P} of this lyophobic polymer is almost independent on water concentration. \bar{P} of polyglutamic acid is lower than that of PMDG by almost one figure at the high pressure region and by two figures at the low pressure region, and is slightly higher than cellophane¹⁷⁾ at the high pressure region. Dividing \bar{P} with solubility coefficient of water to the polymer S (cc stp/cm³.cmHg, the slope of the sorption isotherm) stationary state diffusion coefficient \bar{D} is obtained and shown in Fig.6. In the Figure, non-steady state diffusion coefficient \bar{D}_θ ($\bar{D}_\theta = L^2/6\theta$, time lag θ is the intercept of the extrapolation of the linear portion

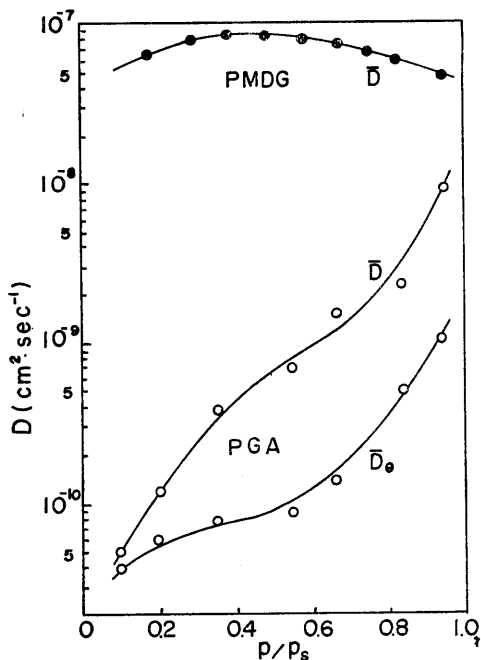


Fig. 6. Relations between steady state diffusion coefficient \bar{D} , non-steady state diffusion coefficient \bar{D}_θ at 25°C and applied relative vapor pressure of water: ○, polyglutamic acid; ●, poly- γ -methyl-D-glutamate

of the permeation curve with the time axis) is also shown. Though the absolute values of \bar{D} and \bar{D}_θ are fairly different on the same condition, both show the marked concentration dependency, and this is explained by the relaxation of polymer structure by the plasticizing effect of water. The difference between \bar{D} and \bar{D}_θ indicates that the permeation of the non-steady state is non-Fickian, namely that the surface concentration of membrane does not become constant instantaneously^{2, 15)}. On the steady state, the surface concentration of the membrane becomes constant because the long time has been passed, and thus the diffusion coefficient of the steady state is the correct one. The difference between \bar{D} and \bar{D}_θ becomes small in the low water concentration range, which is the same behavior as that of the usual polymer¹⁸⁾. This may be due to the fact that the constitution of equilibrium surface concentration takes place within a relatively short time interval. For comparison, steady state diffusion coefficient \bar{D} of PMDG is also shown in Fig. 6. The \bar{D} value shows the slight concentration dependency, and the clustering effect of water molecule^{1, 2)} is evident on the high pressure range. The fact that \bar{D} of polyglutamic acid is lower than that of PMDG by one to three figures is due to the interference of mobility of side chain by the interaction between side chains. With increase of water concentration in the polymer, the interaction between the side chains are gradually disrupted, and the \bar{D} of polyglutamic acid approaches to that of PMDG which shows the characteristic diffusion within the side chain region between the helices.

That the \bar{D}_θ value and the diffusion coefficient calculated from the sorption kinetics agree with each other is due to that the relaxation of polymer surface required the similar time interval for both cases. The non-Fickian behavior of the polyglutamic acid-water system is related to the α -helical structure of the polymer which inhibits the side chain motion at its root and to the restriction of side chain motion by the interaction between them.

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