Permeability of Poly-L-leucine and Polyglutamic Acid Ester Membranes to Oxygen Dissolved in Water

INTRODUCTION

The permeability of the synthetic poly(α-amino acid) membranes to gases and water vapor has been studied,[1-3] and an experimental method for measuring permeation of dissolved oxygen in water through the membranes has been developed.[4] The possibility of the use of synthetic poly(α-amino acid) as membrane material for biomedical materials has also been examined.[5,6] The development of membranes with large permeability of dissolved oxygen and good mechanical properties under wet conditions is anticipated.[7] In general, hydrophilic polymers are very weak in tensile strength under wet conditions though they have a large permeability to dissolved oxygen.

In this work, we prepared poly-L-leucine and poly(glutamic acid ester) membranes. The permeability of these membranes to oxygen dissolved in water was investigated. Furthermore, the stress–strain behavior of these membranes was investigated in the wet condition.

EXPERIMENTAL

Materials

Poly-L-leucine (PLL) was prepared by the polymerization of N-carboxyamino acid anhydride in benzene using triethylamine as an initiator at room temperature. PLL membranes were prepared by casting diluted polymerization solutions onto glass plates.

Poly(glutamic acid esters), that is, the polymers of n-amyl (PALG), n-heptyl (PHLG), chloroethyl (PCELG), and hexahydrobenzyl glutamate (PHBLG), were prepared by ester exchange reaction of poly(γ-methyl L-glutamate) (PMLG) supplied by Kyowa Hakko K. K. (Japan).[2] The NMR spectra of the polymers in trifluoroacetic acid were observed with a Varian EM360 spectrometer. It was confirmed that the ester exchange reaction was accomplished almost completely. These membranes were prepared by casting from the corresponding 1,2-dichloroethane solution onto glass plate or mercury surface.

All the membranes prepared were confirmed to have α-helical structures on the basis of the infrared absorption spectra.[8] The densities of the membranes were examined by a flotation method using an aqueous calcium chloride solution at 20°C.

The degree of hydration of the membrane, listed in Table I, is the volume fraction of water of the water-swollen membrane and was determined as follows: The membrane was swollen, blotted, and weighed repeatedly until constant weight of the swollen membrane was obtained within experimental error at 20°C. The membrane was then dried to constant weight under vacuum at 80°C.

Procedure

The permeation measurement of dissolved oxygen through the membranes was done by using an oxygen electrode. The experimental method has been reported in detail.[4] The membranes were laminated to polystyrene membranes to avoid membrane degradation during the measurement as described previously. The permeability coefficient P [cm^3 (STP) cm/cm^2 sec cm Hg] was calculated from the steady-state current of the permeation curve.

Prior to measurement, the membranes were immersed in distilled water for about one month. Sorption equilibrium with respect to water is assumed.

Stress–strain measurements were made using an Autograph DSS-100 (Shimadzu Seisakusho, Japan). The crosshead speed was 10 mm/min in all the experiments. The stress–strain measurements were made at 20°C under wet conditions by storing the precut samples in distilled water.

TABLE I
Samples and Activation Energy of Permeation of Dissolved Oxygen

Polymer	Polymer side chain	Casting solvent	Degree of hydration	Activation energy, kcal/ mole
PLL	$-CH_2-CH-(CH_3)_2$	benzene	0.020	3.4
PMLG	$-(CH_2)_2-CO_2-CH_3$	DCE[a]	0.109[b]	8.3[b]
PALG	$-(CH_2)_2-CO_2-(CH_2)_4-CH_3$	DCE	0.018	5.1
PHLG	$-(CH_2)_2-CO_2-(CH_2)_6-CH_3$	DCE	0.018	5.1
PCELG	$-(CH_2)_2-CO_2-(CH_2)_2-Cl$	DCE	0.023	10.9
PHBLG	$-(CH_2)_2-CO_2-CH_2-\langle H \rangle$	DCE	0.023	8.5
PBLG	$-(CH_2)_2-CO_2-CH_2-\langle \rangle$	DCM[c]	0.021[b]	9.5[b]

[a] 1,2-Dichloroethane.
[b] Data from previous study.[4]
[c] Dichloromethane.

RESULTS AND DISCUSSION

Permeability of Poly-L-leucine Membrane

The permeability coefficients of PLL membranes are plotted against the inverse temperature in Figure 1. The permeability coefficients of PLL membrane are larger than those of the poly(α-amino acid) membranes already reported.[4]

In the previous report,[4] in order to elucidate the effect of water on the oxygen permeation of polymers, comparisons between the permeability of oxygen dissolved in water, P_w, and the permeability of gaseous oxygen obtained by the high-vacuum method, P_g, were made. In the case of PLL, the permeability of gaseous oxygen, P_g, was 1.25×10^{-9} cm³ (STP) cm/cm² sec cm Hg at 20°C,[9] so the value of the ratio P_w/P_g is 1.0 at 20°C. This means that the oxygen permeation through PLL membranes is not influenced by water.
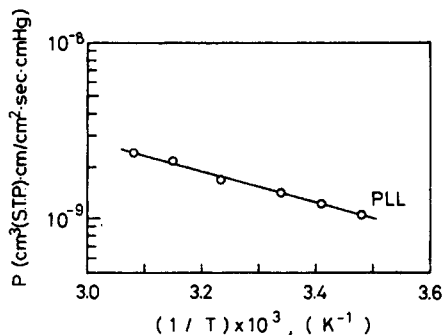

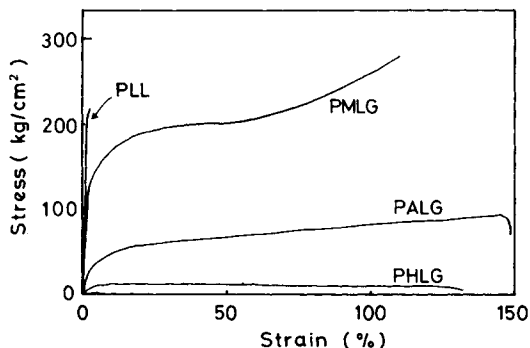Fig. 1. Temperature dependence of permeability coefficients for PLL membrane.

Fig. 2. Stress–strain curves under wet condition at 20°C.

Mechanical property of the membrane was measured under wet conditions, and the stress–strain curve is shown in Figure 2. The PLL membrane is brittle and breaks at very low elongation.

Permeability of Poly(glutamic Acid Ester) Membrane

It has been elucidated that the diffusion of small molecules in poly(α-amino acid) with α-helical structure occurs through the side chain region between the helices.[1-4] The chemical structure of the side chain influences the permeation property of small molecules.[1] It is interesting to modify PMLG by the ester exchange reaction. The permeability coefficients of poly(glutamic acid ester) membranes are plotted against the inverse temperature in Figure 3. The permeability data of PMLG and poly(γ-benzyl L-glutamate) (PBLG) membranes[4] are included in Figure 3 for comparison. As can be seen in the figure, the permeability is largely dependent on the chemical structure of the side chain of the polymers. The permeability of the poly(glutamic acid esters) with linear long side chain, that is, PALG and PHLG, was larger than that of PMLG, while the permeability of the poly(glutamic acid esters) with a bulky group at the end of the side chains, that is, PHBLG, PCELG, and PBLG, was smaller than that of PMLG.

The apparent activation energies of permeation of dissolved oxygen were calculated from Figure 3 and are listed in Table I. The activation energy of polymers with a linear, long side chain was
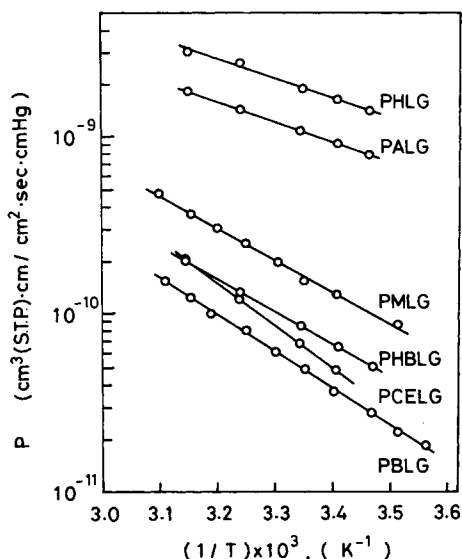

Fig. 3. Temperature dependence of permeability coefficients for poly(glutamic acid ester) membrane.
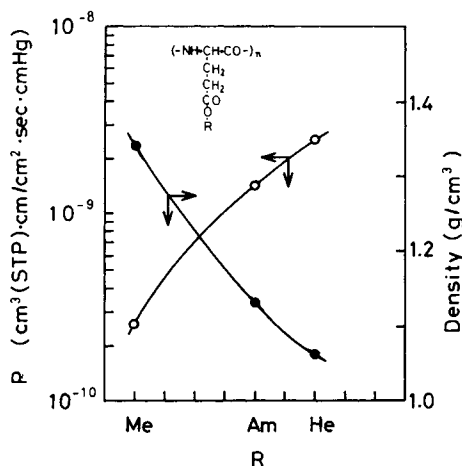
Fig. 4. Permeability coefficient at 35°C and density of membrane at 20°C vs. n-alkyl group of the side chain of poly(glutamic acid ester).

smaller than that of PMLG, while the activation energy of polymers with a bulky group at the end of the side chains was larger than that of PMLG.

It is well known that permeability of dissolved oxygen is highly influenced by the degree of hydration of the membrane.[4] In this case the degree of hydration of the polymers with linear, long side chains was comparable with that of the polymers with bulky groups at the end of the side chains (Table I). The large difference between the permeability of the polymers with linear, long side chains and that of the polymers with bulky groups at the end of the side chains is attributed to the difference of the mobility of the side chains.

The permeability coefficients of poly(n-alkyl glutamate) at 35°C and the densities of these membranes at 20°C are plotted against the carbon number of the n-alkyl group in the side chain of the corresponding polymer in Figure 4. The permeability coefficients increased with increasing the side chain length, while the densities of these membranes decreased. This behavior indicates the increase in the free volume of the side chain region. Thus, the longer the side chain length, the larger the permeability coefficients are expected to become. However, long side chains can move easily in any direction, and this makes them fill up the spaces between the helices evenly. So, the tendency of the increase in the permeability coefficient with side chain length levels off at the region of longer side chains. Furthermore, the membranes of these polymers become soft and flexible with increase in side chain length.

The stress–strain curve of PMLG, PALG, and PHLG was much different from that of PLL (Fig. 2). The PMLG membrane is tough and quite extensible, breaking only at an elongation of over 100%. As the side chain length of the polymers increases, the tensile strength decreases. This phenomenon may be explained by the slip of the helix and the mobility of the side chains. However, a more detailed explanation of this phenomenon is not possible at present.

Membranes partially modified by ester exchange reaction, that is, n-alkyl glutamate and methyl glutamate copolymer membranes, may be expected to have both larger permeability and better mechanical properties.

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