Transport Properties of Synthetic Membranes Having Hydrophilic and Hydrophobic Structures.

Part I. Copolymer Membranes Composed of *N*-vinyl Pyrrolidone and Alkyl Methacrylates

Tsutomu Nakagawa and Yutaka Sugisaki

Department of Industrial Chemistry, Meiji University
Higashi-mita, Tama-ku, Kawasaki 214 Japan

親水性および疎水性構造を有する合成膜の透過性

その1 *N*-ビニルピロリドンとアルキルメタクリレートからなる共重合体膜

仲川 勤・杉崎 裕

明治大学理工学部工業化学科 ☎ 214 川崎市多摩区東三田

In order to clarify the effect of hydrophobic structures on the hydrophilicity of membranes copolymer membranes composed of a hydrophilic monomer and a hydrophobic monomer. 28 copolymer membranes composed of *N*-vinyl pyrrolidone (NVP) as a hydrophilic monomer and methyl methacrylate (MMA), ethyl methacrylate (EMA) and iso-butyl methacrylate (IBM) were synthesized. For these copolymer membranes the effect of the side chains of methacrylates on the water content and permeability of oxygen dissolved in water, and solutes was investigated.

Key words : oxygen permeability, solute permeability, copolymer membrane.

Introduction

Permeability of oxygen dissolved in water, solutes and biological active substances is an important property for membranes for artificial lungs, solid state membrane electrodes, membranes for artificial kidneys and systems for controlled-release. Also, comparison of the state of water contained in synthetic polymers with that in natural polymers seems to be useful to estimate the morphology of the hydrophilic structure of synthetic membranes.

There have been reports which have dealt with the state of water in polymers¹⁾, the transport of

solutes through crosslinked poly (2-hydroxyethyl methacrylate) and its water structure²⁾, the relationship between diffusivity of solutes in hydrogels and their water content³⁾. The explanation of their behavior by free volume model was done and a good agreement was found between the theory and experimental results of solute permeability^{4, 5)}. Hosaka and Tanzawa⁶⁾ reported the oxygen permeability of crosslinked poly (*N*-vinyl pyrrolidone) (NVP) hydrogels membranes and concluded that the oxygen permeability of hydrogels depends on the water content below about 60%. Higuchi and Iijima^{7, 8)} studied gas permeation through poly (vinyl alcohol-co-itaconic acid) membranes and

Table 1 Composition of copolymer membranes and water content at 25°C

Copolymer	NVP, mol-%	Water content, wt-%	Copolymer	NVP, mol-%	Water content, wt-%
NVP-MMA-1	3.44	0.0	NVP-EMA-3	18.1	8.62
NVP-MMA-2	6.84	0.2	NVP-EMA-4	19.3	10.2
NVP-MMA-3	8.10	4.2	NVP-EMA-5	25.7	16.0
NVP-MMA-4	10.5	7.20	NVP-EMA-6	21.3	13.5
NVP-MMA-5	19.2	14.5	NVP-EMA-7	45.2	103
NVP-MMA-6	23.7	18.5	NVP-EMA-8	48.4	—
NVP-MMA-7	30.5	19.0	NVP-IBM-1	6.99	0.0
NVP-MMA-8	31.5	20.5	NVP-IBM-2	8.56	0.60
NVP-MMA-9	33.7	24.5	NVP-IBM-3	18.8	2.90
NVP-MMA-10	38.5	30.5	NVP-IBM-4	21.3	2.40
NVP-MMA-11	45.0	51.0	NVP-IBM-5	25.7	1.30
NVP-MMA-12	47.4	60.0	NVP-IBM-6	41.8	15.1
NVP-EMA-1	7.8	0.54	NVP-IBM-7	43.9	105
NVP-EMA-2	11.4	1.4	NVP-IBM-8	54.9	156

NVP : N-vinyl pyrrolidone, MMA : Methyl methacrylate, EMA : Ethyl methacrylate, IBM : iso-butyl methacrylate

their solute permeability. Reinhart and Peppas⁹⁾ reported the structure of the network of swollen membranes, the diffusivity of solutes, and the effect of the crosslinking of poly (vinyl alcohol) membranes¹⁰⁾.

Although the hydrophilic structures are of importance for the water content and the permeability of solute, hydrophobic structures on the permeability of membranes of copolymers composed of both hydrophilic and hydrophobic monomers are also important. In this report, 28 membranes of copolymers composed of NVP as a hydrophilic monomer and methyl, ethyl and iso-butyl methacrylates as hydrophobic monomers were synthesized. The effect of the side chains of methacrylates on the permeability of oxygen dissolved in water and solutes has been studied.

Experimental

Synthesis of copolymers

All copolymers were synthesized by a radical polymerization technique with AIBN as an initia-

tor. Copolymerization of NVP with methyl methacrylate (MMA), ethyl methacrylate (EMA) and iso-butyl methacrylate (IBM) was carried out in the benzene solution at 50°C. Copolymers were reprecipitated with petroleum ether and purified by precipitation method. Then the products were washed with distilled water at 60°C for 72 hrs to remove a water soluble portion and dried under vacuum. The molar fraction of NVP in copolymers was calculated from the nitrogen content. The composition of copolymers is summarized in Table 1.

Preparation of membranes

The membranes were prepared by casting the polymer solution onto a smooth surface of glass plate and removing the solvent by evaporation. Benzene was used as a solvent for NVP-MMA-1~4, NVP-EMA-1~6, and NVP-IBM-1~6 and DMF was used as a solvent for NVP-MMA-5~12, NVP-EMA-7, 8 and NVP-IBM-7,8. All the membranes were transparent and stable in the mechanical property. NVP-EMA-7,8 and NVP-IBM-7,8 mem-

Figure 1. Schematic diagram of experimental apparatus for permeability measurement of oxygen dissolved in water

H: N₂ or O₂ inlet, J: electrode, K: thermometer, L: glass equipment, M: distilled water, N: magnetic stirrer, O: microammeter, P: voltmeter, Q: dry cell, R: recorder, A: poly (styrene) film or poly (4-methyl pentene-1) film, S: sample.

branes, however, became opaque or translucent, when these membranes were equilibrated in water. Such phenomena suggest that these membranes under swelling are heterogeneous.

The thickness of the membranes, which were equilibrated in water ranged between 0.02 and 0.10 mm.

Method of the oxygen permeation measurement

The permeability of oxygen dissolved in water through membranes was measured with an oxygen electrode. A detailed explanation for the apparatus has been published previously¹¹⁾. The schematic diagram of the experiment is shown in Fig. 1. In this method, normally a sample was directly contacted to the cathode in a 0.5 N KCl solution. To prevent this, the sample was laminated between a thin poly (styrene) or poly (4-methyl pentene-1) film for which the permeability coefficient of oxygen were known. This method has already been reported to be useful for the membranes which contain functional groups such as poly(α -amino acid) membranes¹¹⁾. This method will be called "a laminated method" from now. The permeability coefficient of the laminated membrane, P_{121} , can be calculated by the following equation :

$$\frac{L_{121}}{P_{121}} = \frac{2L_1}{P_1} + \frac{L_2}{P_2}$$

Here, L_{121} is the thickness of the laminated membrane, L_1 and L_2 are the thickness of the poly (styrene) film or poly (4-methyl pentene-1) film and a sample, respectively. P_1 and P_2 are the permeability coefficients of poly (styrene) or poly (4-methyl pentene-1) and the sample. Therefore, P_2 is easily obtained from the above equation.

Method of the solute permeability measurement

Solute permeability was measured by a liquid/liquid dialysis method. A permeation cell was composed of two equal volume compartments which were filled with a distilled water and a solution, respectively. The concentration change of the permeated solute was measured with the differential refractometer and the UV spectrophotometer. The amount of the solute at the equilibrium sorption in the sample was determined as follows : After equilibrating at the same concentration as that of the solution compartment in the dialysis experiment, the membrane was taken out of the solution and carefully blotted with a filter paper. Then, the membrane was immersed in a distilled water. Thus the solute sorbed in the membrane was desorbed and the concentration of the desorbing solution was determined by the identical way of the dialysis.

Method of the measurement of water content in the membrane

The water content of the membrane was determined as follows : The membrane was swollen, blotted and weighed repeatedly until constant weight of the swollen membrane was obtained within experimental error. The membrane was then dried to constant weight under vacuum. The water content of all samples is given in the following equation :

$$\text{water content (\%)} = \frac{\text{weight of water (g)}}{\text{weight of dry copolymer (g)}} \times 100$$

Figure 2. Effect of NVP in copolymers on water content of membrane at 25°C
(○) NVP-MMA, (△) NVP-EMA, (□) NVP-IBM

Results and discussion

Effect of hydrophilic components in the membrane on the water content

The relationship between the molar content of NVP in NVP-MMA, NVP-EMA, NVP-IBM and the water content of these membranes at 25°C is shown in Fig. 2. In both series of NVP-MMA and NVP-EMA, the alkyl groups of methacrylate are rather small, and the moderate increase in the water content is shown by increasing the molar content of NVP until about 40%, and then abrupt increase above 40%. On the contrary, no increase of the water content was shown in the same condition for the series of NVP-IBM. It should be emphasized that the introduction of the hydrophilic chemical structure does not always increase the water content or hydrophilicity. This might be caused surrounding hydrophilic N—C=O groups with large hydrophobic iso-butyl groups interrupting the permeation of water.

Permeability of oxygen dissolved in water

Characteristics of the hydrophilic polymeric

Figure 3. Effect of water content on oxygen permeability at 25°C
(○) non-laminated method, (●) laminated method.

membranes are high solubility of water, high water vapor transmission rates and high gas permeability by plasticizing effect of water or forming channels of water in the membranes when they are equilibrated with water. Assuming that a thin water membranes and its oxygen permeability obeys the diffusion-solution theory, the permeability coefficient of oxygen, 9.3×10^{-9} [cm^3 (STP) $\cdot$ $\text{cm}/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}$] at 25°C, is calculated from the solubility coefficient of oxygen in water¹³⁾ [3.72×10^{-4} cm^3 (STP)/ $\text{cm}^3 \cdot \text{cmHg}$] and the diffusion coefficient¹⁴⁾ [2.5×10^{-5} cm^2/sec] at 25°C. This value is extremely high, compared with those of the known polymeric membranes. Accordingly, if the water filled between polymer segment in the membrane, "channels of water" would be formed, and the higher oxygen permeability would be expected in such water-swollen membranes. This suggests that the change of the oxygen permeability provides a very sensitive analytical way of investigation for the state of the water in the mem-

Figure 4.
(○) NVP-MMA, (△) NVP-EMA, (□) NVP-IBM.

brane. The effect of the laminated method and the non-laminated method on the oxygen permeability of NVP-MMA membranes is shown in Fig. 3. The differences became more remarkable in the region above 25% of water content. Perhaps, some of the water might come out from the membrane by osmosis phenomenon, because of the contact with electrolyte solution in the electrode. Namely, this is dehydration. This suggests that about 20% of water in NVP-MMA membranes, is rather fixed to the polymer, whereas the water in the highly swollen membrane is easily transferred. Unless otherwise noticed, the data obtained by the laminated method were used. The relationships between the molar content of NVP, the water content and the permeability coefficient of oxygen are shown in Fig. 4 (a) and Fig. 4 (b), respectively. In NVP-MMA membranes, permeability coefficient increased with the increasing of NVP or the water content and the effect of water is conspicuous, suggesting the formation of the channel of water par-

tially. In NVP-EMA membranes, the permeability also increased with NVP or the water content. The ratio of the increase, however, is limited in the range of the plasticizing effect by the dissolved water. On the contrary, in NVP-IBM membranes, the introduction of NVP or the increase of the water content showed even the inclination of the decreasing the oxygen permeability until 15% of the water content. In NVP-IBM membranes, the water which apparently showed the increase might be in the fixed state around the hydrophilic groups which are surrounded by the rather large hydrophobic iso-butyl groups. It is only a hypothesis, but the supposed schematic representation of the state of the water in membranes of NVP-MMA and NVP-IBM is shown in Fig. 5. The effect of temperature on the permeability coefficient of oxygen through NVP-MMA and NVP-IBM membranes is shown in Fig. 6 (a) and (b). The slope of the curves, representing the apparent activation energy for permeation, showed the inclination to

Figure 5. Schematic representation of the state of water in NVP-MMA and NVP-IBM

become gentle slopes by increasing the water content for a series of NVP-MMA membranes, especially for NVP-MMA-12. This phenomenon is inconsistent with the activated diffusion theory for non-porous polymer membranes. Refojo^{1,2)} studied effects of temperature on the permeation of water through hydrogel and showed that the water content decreased with the increasing temperature. In our experiment, the water content of NVP-MMA-12 decreased from 60% at 25°C to 48% at 35°C. It is reasonable that the apparent decrease of the slope in Arrhenius plots was brought about by the dehydration at higher temperature. In the case of a series of NVP-IBM membranes, the phenomenon is quite contrary. The effect of temperature on the

permeation of oxygen became clear with the increasing of NVP content or the water content. Of course, though the water content is not large, it seems that fixed water in the membrane played a part in the activated diffusion step.

Solute permeability

The experiment of the solute permeability was carried out in the temperature range of 20~35°C with NVP-MMA-11, NVP-MMA-12 and cellophane for comparison, which were equilibrated in a distilled water. The permeability of the model solutes such as KCl, NaCl, creatinine and uric acid for these membranes were measured. The results are summarized in Table 2. In the cellophane, the permeability increases with the increasing of temperature. On the other hand, the permeability of NVP-MMA-11 and NVP-MMA-12 decreases with the increasing of temperature. Furthermore, the permeability of the solute of small molecular size was higher than that of large molecular size in the cellophane. Such an effect, however, was small in NVP-MMA membrane. This suggests that the properties of NVP-MMA-11 and NVP-MMA-12 are different from those of cellophane. To make clear this, partition coefficient for creatinine and uric acid at 25°C and 35°C was determined. The partition coefficient of NVP-MMA-12 for creatinine and uric acid was 2.29 and 0.15 at 25°C; 1.41 and 0.13 at 35°C, respectively, whereas that of cellophane was almost constant at both temperatures. Since the solute dissolves only into the water containing hydrophilic region, the change of the partition coefficient seems to be the result of the dehydration of the membrane.

Conclusion

In both the series of NVP-MMA and NVP-EMA membranes, the moderate increase of the water content was shown with the increasing of the molar content of NVP until about 40% and then an abrupt increase above 40%. On the contrary, no increase in the water content was shown in the same

(a) Temperature dependence of permeability of NVP-MMA membranes to oxygen dissolved in water

(○) NVP-MMA-2, (△) NVP-MMA-4,
(●) NVP-MMA-6, (□) NVP-MMA-8,
(▲) NVP-MMA-10, (■) NVP-MMA-12.

(b) Temperature dependence of permeability of NVP-IBM membranes to oxygen dissolved in water

(○) NVP-IBM-2, (△) NVP-IBM-4,
(●) NVP-IBM-6.

Figure 6.

Table 2 Solute permeability of NVP-MMA membrane and cellophane

Membrane	Temp. °C	Permeability coefficient, $\text{cm}^2/\text{sec}, \times 10^6$			
		NaCl (58.44)	KCl (74.56)	Creatinine (113.1)	Uric acid (168.1)
NVP-MMA-11	20	0.13	0.26	0.17	0.10
	25	0.10	0.15	0.21	0.09
	30	0.09	0.12	0.16	0.11
	35	0.05	0.08	0.11	0.08
NVP-MMA-12	20	0.30	0.41	0.35	0.20
	25	0.37	0.36	0.42	0.22
	30	—	0.29	0.27	0.18
	35	0.17	0.30	0.26	0.16
Cellophane	20	0.52	0.76	—	0.24
	25	0.72	0.80	—	0.29
	30	0.86	—	—	0.35
	35	0.88	1.06	—	0.46

condition for the series of NVP-IBM membranes. The permeability coefficient of oxygen through NVP-MMA membranes increased with the increasing of the NVP content or the water content. In the case of NVP-IBM membranes, the introduction of hydrophilic NVP or the increase of the water content showed even the inclination of the decreasing the oxygen permeation until 15% of the water content. In the NVP-IBM membranes, the water might be in the fixed state around the hydrophilic groups which are surrounded by the rather large hydrophobic iso-butyl groups. The solute permeation was carried out and the effect of temperature on the swollen NVP-MMA membrane was discussed.

Acknowledgement

The Authors are very grateful to Messrs. S. Okuyama, K. Hasegawa and T. Sakurada for many helpful experiments in the course of this work, particularly during the preparation of the membranes.

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- (受付 1991年2月14日)