Self-Diffusion of THO within Tactic Poly(2-hydroxyethyl methacrylate) Membranes

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The self-diffusion experiment of water was performed across two series of tactic poly(2-hydroxyethyl methacrylate), P (HEMA) membranes prepared by crosslinking with various amount of hexamethylene diisocyanate (HMDIC). The tagging material was tritium hydroxide (THO) and the efflux of THO was counted on a Liquid Scintillation Counter. The transport data of THO show that the permeability decreases as the amount of HMDIC increased from 2.5 to 10 mole% and the self-diffusions coefficient shows a parallel trend with it. The diffusivity data was discussed in terms of the change of water structural orderliness within membranes. Using the relation between viscosities and diffusivities derived from Eyring's absolute rate theory, the corresponding viscosities of water within two series of tactic P(HEMA) membranes were obtained. From this, it is seen that the viscosity of water within tactic P(HEMA) membranes may have the same values with those of supercooling water whose temperature ranges from −28 to −36 °C.

Introduction

The transport phenomena through some P(HEMA) membranes have been studied by many authors.[1-4] Among of them, Yasuda et al.[1] have derived the permeability of homogeneous polymer membranes on the basis of the free volume concept of diffusion. According to them, no fixed pores or channels are assumed in the homogeneously swollen polymer and the diffusion of water is determined by the total free volume. Ratner and Miller[2] suggested that P(HEMA) membranes have a high permeability to urea due to a strong interaction between the polymer and urea. They confirmed the pore flow model in which solute transport takes place through the water filled regions essentially unaffected by the surrounding polymer matrix.

The P(HEMA) membrane which have been studied above is relatively atactic in a triad tacticity. Recently, Gregonis *et al.*[5] have made highly syndiotactic and isotactic P(HEMA) by U. V. photolysis and anionic polymerization, respectively and determined the water swelling properties of tactic P(HEMA) membranes crosslinked with HMDIC as functions of temperature and crosslinker concentration. They proposed that the stereochemistry of the polymer chain is a factor in determining swelling behavior of the hydrophilic gel.

Recently, Alexandrowicz[6] performed double traced self-diffusion of water across a series of membranes of different pore sizes and chemical constitution by using T and ^{18}O simultaneously. They suggested the observed self-diffusion ratio T/O as means to detect changes in the state of water in membranes and in solutions. But the state of water in pores or interstices of membranes is not unequivocal,[7,8] even though measurements of viscous flow, diffusion and ionic mobility as well as electron microscopy have been used for this purpose on membranes with relatively large, well-defined pores.

In this study, the self-diffusion coefficients within syndiotactic and isotactic P(HEMA) membranes are measured by using THO as a tracer and the corresponding viscosities are calculated from the diffusivity data by using Eyring's relationship.[9,10] From this, it will be discussed that the difference of water state in pores between syndiotactic and isotactic P(HEMA) membrane with crosslinker content in terms of the viscosity and molecular conformation. Following this, the corresponding temperatures of the water within tactic P(HEMA) membrane to those of bulk water are obtained from the viscosity data.

Experimental Methods

Materials. Highly pure 2-hydroxyethyl methacrylate (HEMA) monomer of low diester content (<0.02 %) was obtained from Hydron Laboratories Inc., and used it without any other purifications. Hexamethylene diisocyanate (HMDIC), using as a crosslinker, was obtained from Polyscience Inc.. Labeled compound, tritiated water(THO) was supplied by New England Nuclear Company and its specific activity is 25 mCi/mole.

Synthesis of P(HEMA). Syndiotactic and isotactic P(HEMA) with high tacticity was synthesized by Gregonis *et al.*[5] Syndiotactic P(HEMA) was obtained after 6 hrs. of U. V. (254 nm) photolysis of methanolic monomer solution at −40 °C using the initiator, azobis (methyl isobutyrate), which was prepared by Mortimer[11] previously. The obtained syndiotactic P(HEMA) has 85 % tacticity which is taken from C^{13} n.m.r. spectra. The production of isotactic P(HEMA) requires the use of a suitable blocking group, such as benzoyl group on the free hydroxyl of HEMA, then benzoxyethyl methacrylate(BEMA) is produced. The anionic initiator for BEMA polymerization is *n*-butyllithium and copper iodide complex, $Li(nBu)_2Cu$. The hydrolysis process[12] of isotactic P(HEMA) was slightly different from the method of Gregonis *et al.*[5] Isotactic P(HEMA) was hydrolysed in the cosolvent of acetone, N, N-dimethyl formamide(DMF), and methanol (its volume ratio 3:2:2) with aqueous potassium hydroxide(KOH) for 30 min. at 50°C. After reacting sufficiently, the mixture was cooled to the room temperature and neutralized with aqueous hydrochloric acid, after that, the hydrolysed product, isotactic P(HEMA) was precipitated in

water. It has more than 80 % isotactic content.

Membrane preparation. After dissolving the vacuum dried tactic P(HEMA) in dry N,N-dimethyl acetamide throughly, desired amount of crosslinking agent, HMDIC, and the catalyst[13], dibutyltin dilaurate (6.6×10^{-5} mole/*l*), was mixed well with it. The mixture was poured on a polypropylene mold which was placed in a closed reactor for 24 hrs. under the dry nitrogen atmosphere. The preliminary membrane was dried in the clean air, then dried in vacuum for 10 hrs. to remove solvent completely. The dried membrane stuck was dipped into distilled water for 12 hrs. This was partially dehydrated under vacuum for 2 hrs., then the membrane was slowly drawn apart from polypropylene sheet. The preparative membranes were dipped into distilled water for 4 weeks with daily exchange of water, then used for experiment.

Isotactic and syndiotactic P(HEMA) membranes of 2.5, 5.0, 7.5 and 10 mole % crosslinked with HMDIC was prepared. Hereafter, isotactic P(HEMA) membrane of 2.5 mole % crosslinker is abbreviated to ISO 2.5. All other membranes are labelled in the same manner.

Permeability. The equation used to obtain permeability P was derived[14] from the mass balance equation;

$$\ln\left(1-2\frac{C_t}{C_0}\right)=-\left(\frac{1}{V_1}+\frac{1}{V_2}\right)A\cdot\frac{P}{d}\cdot t \qquad (1)$$

where V_1 is the volume of the concentrated compartment, V_2 is the volume of the diluent compartment, A is membrane area, d is membrane thickness, C_0 is the count of THO at time o in the concentrated compartment, C_t is the count of THO at time t in the diluent compartment, respectively.

A permeation cell was designed in our laboratory,[12] a batch type, and has two compartments of equal volume (200 m*l*). Before the permeation experiment, the membrane was equilibrated in triply distilled water at 25 °C for 2 days. Initially, one compartment (compartment I) was charged with the THO aqueous solution whose concentration was 40 $\mu l/l$ and the other (compartment II) with triply distilled water. Each compartment was connected to a circulating thermostat (Lauda K-2/R) to keep the constant temperature and stirred at 750 r.p.m. to eliminate the bound layer effect.

All experiments were performed at 25°C. The characteristic of our permeation cell is; S=7.1 cm, and the thickness of preparative membranes are in the range of 0.08–0.13 mm. The thickness was measured by the micrometer (Model 549, Testing Machines, Inc.).

At time t, 50 μl of the sample was taken from compartment I and transferred into plastic vials (capacity 20 m*l*) into which 10 m*l* of sicntillation solution were previously introduced. Scintillation solution was prepared with PPO(2, 5-diphenyloxazole), POPOP[1, 4-bis(5-phenyloxazol-2-yl)-benzene] and naphthalene in distilled dioxane. The sample were anlyzed in Liquid Scintillation Counter (Beckman, LS-3133T). All permeation experiment was ended, when approximately 10 % of the initial amount of tracer had crossed the membrane.

The plot of $\ln(1-2C_t/C_0)$ versus time yield a straight line with slope $=-(1/V_1+1/V_2)\,A\cdot P/d$. Substituting the measured values of V_1, V_2, A and d, we obtain permeability p(cm²/sec).

Partition coefficient. The partition coefficient(K_D) is defined as the ratio of the concentration of THO in the membrane phase to its concentration in the solution phase, the two phases being in equilibrium.

To increase the reproducibility of K_D value, two-step sorption and desorption technique[15] was used. Here, K_{D_2} is defined as follows;

$$K_{D_2}=\frac{V_s^0}{V^m}\left(\frac{C^s_{s_2}}{C^s_{s_1}-C^s_{s_2}}\right) \qquad (2)$$

where V_s^0, V^m, $C^s_{s_i}$ are the volume of the surrounding solution, the volume of the swollen membrane which is equal in both sorption and desorption experiments, the THO count of surrounding solution after sorption and that after desorption, respectively. The swollen membrane volume was obtained from multiplying the membrane thickness by the membrane area, where the thickness was measured with the micrometer (Model 549) and the area with the calipers.

Presoacked membranes at 25°C were surface dried between damp filter paper and placed in the toppered bottle containing 10 m*l* of aqueous solution of known concentration. The membranes were equilibrated for 24 hrs. at 25 °C, then removed, surface dried and placed in a bottle containing 10 m*l* of pure water for 24 hrs. at 25°C. From first equilibrium, we obtained $C_{s_1}{}^s$ and at second equilibrium $C_{s_2}{}^s$ was obtained. The sample was analyzed by Liquid Scintillation Counter.

Results and Discussion

All membranes prepared are translucent except ISO 2.5 and ISO 5 membrane, and the opaqueness increases with the crosslinker content. It was seen from Scanning Electron Microscope (SEM) data[12] that the optical heterogeneity might be derived from the surface roughness of the membrane. The water content of tactic P(HEMA) membrane at 25°C are listed in Table 1. It shows that the water content decrease gradually as the crosslinker content increase and ISO membranes are more hydrated than SYN membranes. The difference of hydration between these two types of membranes can be explained in terms of Russell[16] *et al*'s CPK^R space-filling molecular models. The conformational difference between isotactic P(HEMA) and syndiotactic P(HEMA) are all displaced outward from the helix backbone, but for

TABLE 1: The Water Content and Calculated Bound Water Fraction in Membranes from DSC Results

Membrane		W_t	W_x
SYN	2.5	0.300	0.21
	5.0	0.285	0.22
	7.5	0.272	0.22
	10	0.262	0.22
ISO	2.5	0.382	0.14
	5.0	0.361	0.15
	7.5	0.340	0.16
	10	0.324	0.17

W_t : total water content

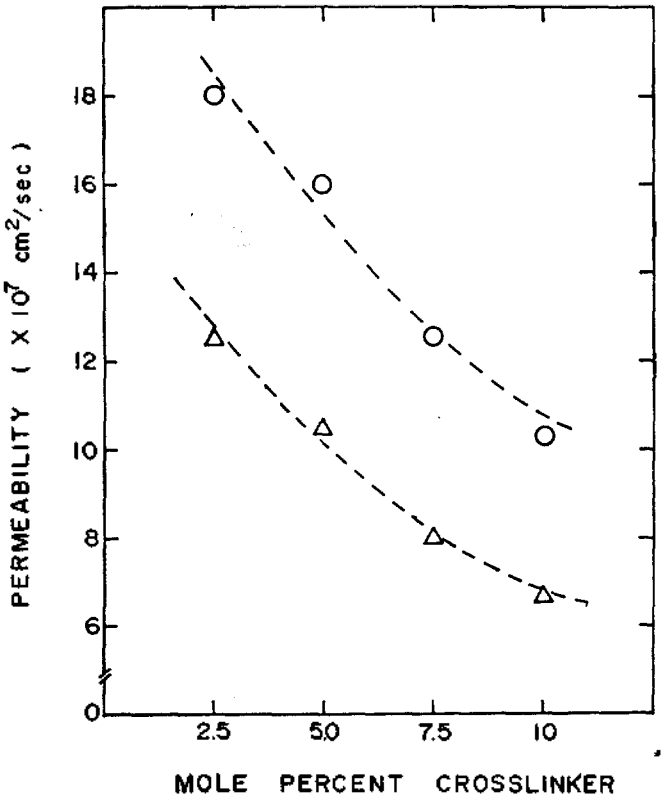

Figure 1. The permeability of THO through tactic P(HEMA) membranes as a function of crosslinker content at 25 °C; (O), ISO membrane; (△), SYN membrane.

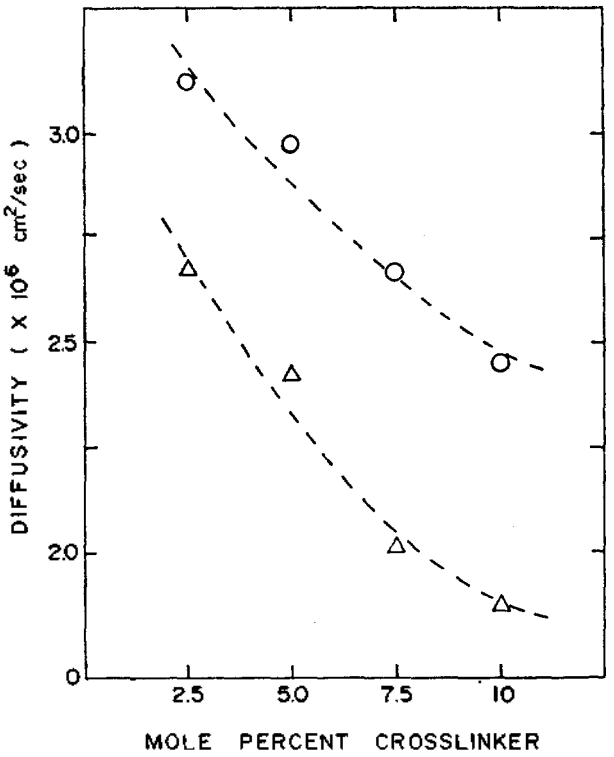

Figure 2. The partition coeffcient of THO within tactic P(HEMA) membranes as a function of crosslinker content at 25°C; (O), ISO membrane; (△) SYN membrane.

syndiotactic P(HEMA), the polar and apolar groups are interspersed along the helix backbone. This fact may give an account, in part, of the difference observed in the swelling

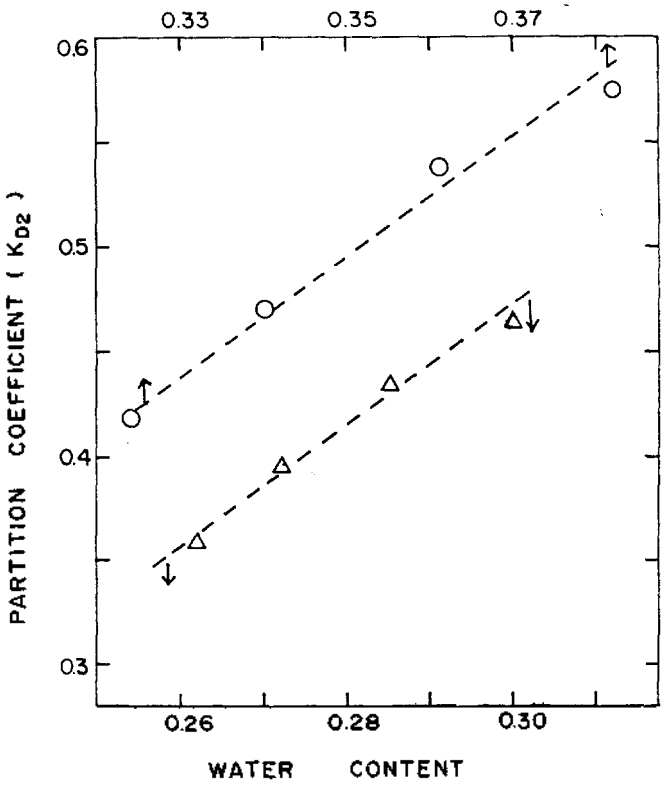

Figure 3. The diffusivity of THO within tactic P(HEMA) membranes as a function of crosslinker content at 25 °C; (O), ISO membrane; (△), SYN membrane.

behavior of these two counterpart.

Using the membranes equilibrated in distilled water at 25 C for 2 days, the permeability data were obtained within the standard deviation of 3–5 %. Figure 1 illustrates the permeability coefficient versus crosslinker content of tactic P(HEMA) membranes. It can be seen that the permeability of THO decrease with the increases of crosslinker content and show the higher value to ISO membranes than to SYN membranes. Thus, it is assumed that the permeability values are proportional to the water content because the permeation process may occur through water-containing region. The results of permeation experiment are consistent with the trend of water contents.

The partition coefficient of THO obtained from two-step sorption and desorption technique are shown in Figure 2 within the standard deviation of 7–10 %. The partition coefficient (K_D) are linearly correlated with the equilibrium water content in membranes. From this linear correlation, one sees that the distribution of THO in membranes occurrs only into the watercontaining region.

Diffusivity of THO, as the criterion for its mobility within the membrane phase, is obtained from following relationship

$$P = K_D \cdot D \tag{3}$$

where P and K_D are previously defined. The obtained diffusivity data are plotted in Figure 3 within standard deviation of of 10–15 %. Wang *et al.*[17] measured the self-diffusion of pure water by capillary method with the value of 2.44×10 cm²/sec at 25 °C. The self-diffusion of bulk water measured

nowadays have the scattered values which range between 1.91×10 cm^2/sec and 2.6×10 cm^2/sec.[18] No matter what the self-diffusion coefficient of pure water is, that of the water within tactic P(HEMA) exhibits about ten times higher value than bulk water. The diffusivity data for two series of tactic P(HEMA) membranes show a parallel trend with the permeability results.

The relation between diffusion coefficient and viscosity was obtained by Eyring and Ree,[9] and was improved by Eyring and Jhon[10] assuming hexagonal packing system. Thus the following equation is used to calculate the viscosity.

$$D=\frac{kT}{6\left(\frac{\sqrt{2}\,V_s}{N}\right)^{1/3}\eta} \tag{4}$$

where V_s, N, k and T are the solid-like volume of water, Avogadro number, Boltzmann constant and absolute temperature, respectively. Above equation was applied to our system and the viscosity of water within tactic P(HEMA) membrane was calculated using the obtained diffusivity data. The calculated visocisty and its corresponding temperature for bulk water are listed in Table 2. The corresponding temperature to viscosity was obtained by Korson *et al's*[19] method.

From Table 2, it may be suggested that the water in ISO membrane phase have the same viscosity as the bulk water whose temperature range from -28.5 to -32.4 °C. It can be explained that SYN membranes have the smaller water content than ISO membranes, thus the water in SYN membrane phase is more viscous.

The various states of water within water-swollen polymers have been suggested differently by many authors.[20-22] Among of them, the existence of bound water is commonly accepted, and recently the bound water content of water-swollen tactic P(HEMA) crosslinked with 5 mole % HMDIC was obtained by dilatometric technique[23] under the assumption of the existence of three states of water, *X*, *Y*, and *Z* water, where *X* water is ordinary bulk water-like, *Y* water is intermediate water-like which melts below the melting point of *X* water, and *Z* water is bound water-like that does not exhibit phase transitions. The result is shown in Table 3. It can be seen that the percentage of *Z* water in total water content is larger for SYN membranes than ISO membranes. This fact is consistent with the difference of visocosity data of water within ISO and SYN membranes. From this, it is presumed that the bound water content is a main factor of the resistance for the self-diffusion processes.

It can be assumed that the increase of the crosslinker content induces the increase of viscosity. Recently, the bound water fraction in tactic P(HEMA) membranes were calculated[12] from DSC results, which is listed in Table 1. The calculated W_Z of SYN membrane is comparable to the measured value by a dilatometric method, but W_Z of ISO membrane is smaller than the dilatometrically measured value due to the higher amount of *Y* water. Even though W_Z is almost constant for each tactic P(HEMA) membrane, the percentage of *Z* water among the total water content increase monotonously with the crosslinker content. Thus, the decrease of water content, that is, the increase of bound water percentage by increasing crosslinker concentractions gives a main effect on the viscous property.

TABLE 2: The Calculated Viscosity and Corresponding Temperature of Water

Membrane		η (CP)	Temp. (°C)
SYN	2.5	7.43	−31.1
	5.0	8.13	−32.5
	7.5	9.75	−35.1
	10	10.60	−36.3
ISO	2.5	6.35	−28.5
	5.0	6.63	−28.2
	7.5	7.42	−31.1
	10	8.11	−32.4

TABLE 3: The Approximate Contribution of X, Y, and Z Water in 5 mole % HMDIC Crosslinked Gel

	g./g. wet gel		Percentage in total water content	
	SYN	ISO	SYN	ISO
X	0.064	0.07	21	9
Y	0.056	0.10	18	26
Z	0.19	0.21	61	55
W_t	0.31	0.38	100	100

TABLE 4: The permselectivity of THO to NaCl at 25 °C

mole %	P_{THO}/P_{NaCl}	
HMDIC	SYN	ISO
2.5	7.70	5.28
5.0	10.48	9.05
7.5	12.71	10.46
10	17.26	13.24

From the permselectivity defined as the ratio of the permeability of one solute to another, it can be seen that the effect of conformational change of polymer matrix and crosslinker concentration on the permeability of solute. The permselectivity data of THO to NaCl are shown in Table 4. The permeability of NaCl was obtained previously in our laboratory.[12] The permselective relationship may arise from the inaccessibility[24,25] of NaCl to the lower dielectric region containing bound water. The variation of the dielectric constant of the water state within membrane phase was investigated from dielectric relaxation and it was found that the dielectric constant of the bound water was very low.

It can be seen in Table 4 that SYN membranes show the higher permselectivity than ISO membranes under the same level of mole % crosslinker content. This may be due to the smaller amounts of total water content and the higher percentage of Z water within SYN membranes. From the permselectivity data, it may be assumed that the lacal dielectric constant of the region available for the transport of NaCl is lower for SYN membrane than for ISO membrane.

The permselectivity for SYN membranes increase more rapidly than for ISO membranes with the increase of crosslin-

ker content. This means that the size and number of those segregated regions might be changed differently in the two membranes as the crosslinker density is varied, though the micromorphological nature of these two types of gel is not yet known in the literature.

Conclusion

Using THO as a tracer material, the self-diffusion coefficient for two series of tactic P(HEMA) membranes with the variation of the crosslinker, HMDIC content is obtained and shows about ten times higher value than for bulk water. First, permeability and partition coefficient were measured and compared with the water content within water-swollen tactic P(HEAM) membranes. Permeability and partition coefficient data of tactic P(HEMA) membranes decrease monotonously with the increase of crosslinker content and that for isotactic P(HEMA) membranes show the higher value than for syndiotactic P(HEMA) membranes. This trend is consistent with the water contents of water-swollen tactic P(HEMA) membranes.

Eyring's relation was used to calculate the viscosity of water from diffusivity data. The obtained viscosity data for the water within water-swollen isotactic P(HEMA)membranes range 6.4 - 8.1cp. This indicates that the water within water-swollen isotactic P(HEMA) membrane phase have the viscosity corresponding to the bulk water with the temperature range from -28.5 to -32.4 °C. From this, it is assumed that the water within membrane phase exhibits the similar characteristics observed in the supercooling water state.

In the case of syndiotactic P(HEMA) membrane with the smaller water content, it exhibits the lower temperature ranges from -31.1 to -36.3 °C, than isotactic P(HEMA) membrane.

From the permselectivity data of THO to NaCl for tactic P(HEMA) membranes, it can be seen that the permeation on process changes differently in the two series of membranes with the change of crosslinker content due to the conformational dissimilarity between syndiotactic and isotactic P(HEMA).

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