The Transport Phenomena of Some Model Solutes through Postcrosslinked Poly(2-Hydroxyethyl Methacrylate) Membranes with Different Tactic Precursors

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Synopsis

Two series of membranes of various degree of hydration have been prepared by postcrosslinking highly syndiotactic and isotactic poly(2-hydroxyethyl methacrylate) [P(HEMA)] with various amounts of hexamethylene diisocyanate (HMDIC). The equilibrium water content, the partition coefficient, and the permeability of the model solutes such as urea, acetamide, NaCl, 2-propanol, and isobutanol for these membranes were measured. In addition, differential scanning calorimetry (DSC) study for the membranes was performed. The membranes of the isotactic precursor are more hydrated at 25°C compared to the ones of its syndiotactic counterpart. This may be due to the more hydrophobic nature of syndiotactic P(HEMA). The partition coefficient data show that the solutes of urea, acetamide, and NaCl are partitioned only into the water-containing region, whereas the alcohol solutes are preferentially sorbed on to polymer matrix. The permselectivity data of urea to NaCl reveal that the permselectivity of crosslinked isotactic P(HEMA), (ISO) membranes increases as the amount of HMDIC is increased from 2.5 to 10 mol %, while the trend is reversed for crosslinked syndiotactic P(HEMA), (SYN) membranes. The apparent diffusivity order of urea, acetamide, and NaCl is not the same in those two characteristic membranes: the order is urea > NaCl > acetamide for highly crosslinked ISO membranes, and NaCl > urea > acetamide for all SYN membranes, which was compared with the free diffusion data in aqueous solution and interpreted in terms of the water-structural orderliness within membranes.

INTRODUCTION

Since Wichterle and Lim[1] emphasized crosslinked poly(2-hydroxyethyl methacrylate) P(HEMA) hydrogel as a biomedically important material, many studies about this hydrogel[2] have been accomplished. Among of them, especially, the study of transport phenomena in these hydrogel membranes[3–8] has received new impetus in recent years because of the potential use in hemodialysis membranes. But all these studies have, so far, referred to solution- or bulk-polymerized P(HEMA) in the presence of diester crosslinker, which is relatively atactic in triad tacticity.

Light-scattering and rheooptical measurement data[9] of water-swollen gels based on atatic P(HEMA) show that, though these gels appear to be optically quite homogeneous, there are regions having a higher degree of order composed of secondary structural domains of hydrophobic and hydrogen-bonded portions.[10] Therefore, it is presumed that the preparation of highly tactic P(HEMA) accompanies the change of microheterogeneity and equilibrium water content of this hydrogel.

Recently Gregonis et al.[11] have prepared highly syndiotactic and isotactic

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P(HEMA) by UV photolysis and coordination polymerization, respectively, and measured the equilibrium water swelling properties of these hydrogels. Their data show that these two types of hydrogel have different swelling behaviors with temperature. Also, we have prepared tactic P(HEMA) in a similar manner to theirs and determined the water-structural orderliness within these hydrogels by a dilatometric technique.[12] From that dilatometric hysteresis, data has confirmed the change of the structural orderliness of water with different tactic precursors.

Above swelling, dilatometric data allow us to investigate the transport properties of some model solutes through these hydrogel membranes, and to characterize them. Low-molecular-weight model solutes in this study are NaCl, urea, acetamide, 2-propanol, and isobutanol.

EXPERIMENTAL

Materials

Highly pure HEMA monomer of low diester content (<0.02%) was purchased from Hydron Laboratories, Inc., and was used without further purification. The crosslinker, hexamethylene diisocyanate (HMDIC), was obtained from Polyscience, Inc. All the solutes in this study were of reagent grade purity and used as received from E. Merck Co.

Preparation of Linear Tactic Polymers

The preparative method of highly syndiotactic and highly isotactic P(HEMA) can be found elsewhere.[11] The initiator, azobis(methyl isobutyrate) was prepared by the method of Mortimer[13] and used in photopolymerization of HEMA at −50°C. Utilizing a photoreactor designed by us, syndiotactic P(HEMA) was obtained after 6 h of photolysis of methanolic monomer solution in the presence of the modified azo initiator, using Rayonet low-pressure mercury arc as a irradiating UV (254 nm) source.

The hydrolysis process of isotactic poly(benzoxyethyl methacrylate) was somewhat different from Gregonis et al.'s.[11] The synthesized isotactic poly(benzoxyethyl methacrylate) was hydrolyzed in the cosolvent of acetone, *N*,*N*-dimethyl formamide (DMF), and methanol (volume ratio 3:2:2) with aqueous potassium hydroxide for 30 min at 50°C. The reaction mixture was cooled to room temperature and neutralized, and then the hydrolyzed product was precipitated in water. All the polymers obtained were redissolved and reprecipitated three times.

Polymer Characterization

The ^{13}C NMR spectra of predominately syndiotactic and isotactic P(HEMA) were obtained by a Varian FT-80A NMR spectrometer. The data show that isotactic P(HEMA) has more than 80% isotactic content and syndiotactic P(HEMA) has 85% syndiotactic content.[11] The infrared spectra (Fig. 1) were obtained on a Perkin-Elmer 267 Grating Infrared Spectrophotometer. The following Mark–Houwink equation[14] was used for the crude estimation of the molecular weight of linear tactic P(HEMA) in DMF at 25°C:

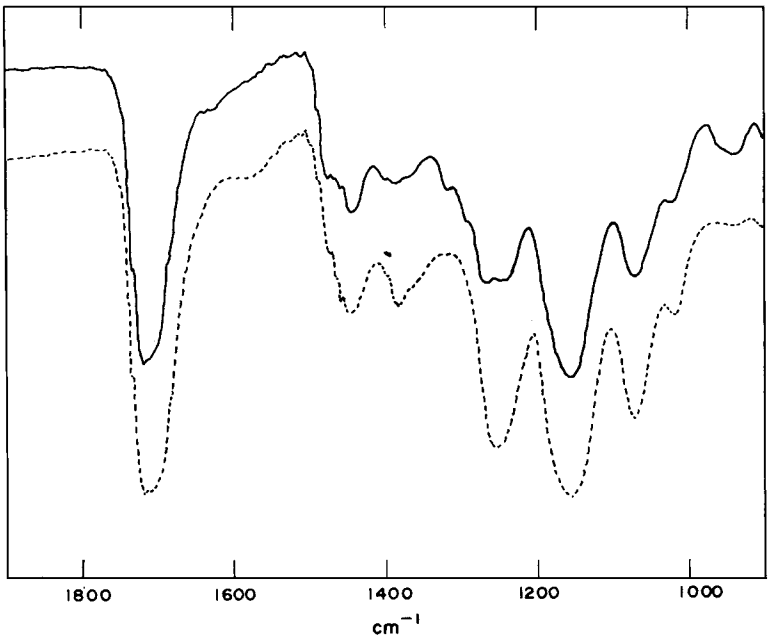


Fig. 1. The infrared spectra of syndiotactic (—) and isotactic (- - -) P(HEMA).

$$[\eta] = 8.90 \times 10^{-5} M_v^{0.72} \quad (1)$$

The viscosity measurements show that both syndiotactic and isotactic P(HEMA) have similar molecular weight:

$M_v = 5.32 \times 10^5$ for isotactic P(HEMA)
$M_v = 4.97 \times 10^5$ for syndiotactic P(HEMA)

Membrane Preparation

The crosslinked P(HEMA) membranes with different tactic precursors were obtained as follows. The vacuum dried tactic polymer was dissolved in dry *N*,*N*-dimethyl acetamide. The dissolved polymer solution mixed well with the desired molar amount of HMDIC, and the catalyst[15] (dibutyltin dilaurate 6.6 $\times 10^{-5}$ mol/L) was poured onto a polypropylene mold. The mold was placed in a closed oven at room temperature for 24 h under dry nitrogen atmosphere, and, then, the solvent was slowly evaporated in a stream of clean air for 24 h. The polypropylene sheet to which the dried membrane stuck was placed under vacuum for 10 h and dipped into distilled water for 12 h. This was partially dehydrated under vacuum for 5 h, and, then, the membrane was slowly drawn apart from polypropylene sheet. In this way, 2.5, 5, 7.5, and 10 mol % crosslinked dense P(HEMA) membranes with different tactic precursors were obtained. Hereafter, the membrane of syndiotactic P(HEMA) with no crosslinker is abbreviated to SYN 0. All other membranes are labelled in the same manner. All the membranes were equilibrated in distilled water for at least 1 month, during which the water was frequently replaced. The thickness of these water swollen membranes ranged from 0.08 to 0.13 mm.

Electron Microscopy

Membrane samples equilibrated in distilled water were freeze-fractured in liquid nitrogen and freeze-dried overnight. And then, the samples were coated with gold and examined at ambient temperature with a JEOL scanning electron microscope (SEM) at an angle of 45°.

Permeability

A permeation cell was designed, as shown in Figure 2, in a conventional batch type, which has two compartments of equal volume (200 ml). Each chamber was magnetically stirred at 750 rpm to eliminate boundary layer resistance and was connected to a circulating thermostat (Lauda K-2/R) for temperature control. All measurements were made at 25°C ± 0.1 in this study. The solute permeability coefficient P is calculated from the following equation which is obtained from mass balance equations[16]:

$$P = \frac{-d}{A(1/V' + 1/V'')t} \ln \left[\left(1 + \frac{V'}{V''}\right) \frac{C_t}{C_0} - \frac{V'}{V''} \right] \tag{2}$$

where V', V'', A, d, C_0, and C_t are the volumes of the concentrate and the diluent compartment, membrane area (7.1 cm^2) and the thickness, and the concentrations of the concentrate compartment at time $t = 0$ and $t = t$, respectively. Concentration changes were measured with a Brice-Phoenix differential refractometer. The concentration C_0 of initial charging solution was 0.17 mol/L for salts and 25 mL/L for alcohol solutes.

Partition Coefficient

The appropriately blotted sample was equilibrated at 25°C for 2 days in the solution of known volume of the same concentration as that of the solution of concentrate compartment in the dialysis experiments. Triply distilled water was used in this experiment. To increase the reproducibility of the K_D value of less-partitioned solid solute, the two-step sorption and desorption technique[17] was employed for NaCl, urea, and acetamide solutes. Here, the partition coefficient K_{D_2} is defined as follows:

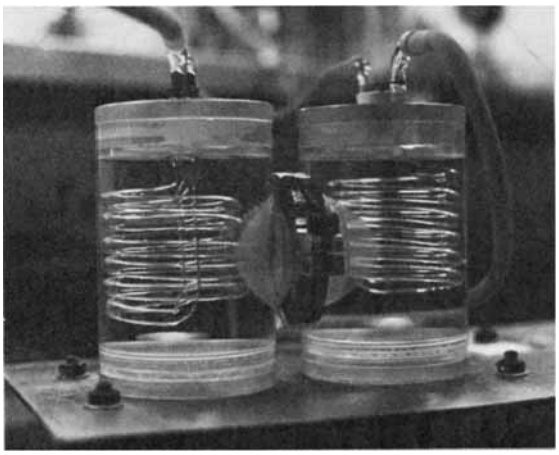


Fig. 2. The dialysis cell for measuring solute permeability.

$$K_{D_2} = \frac{V_s^0}{V^m}\left(\frac{C_{s2}^s}{C_{s1}^s - C_{s2}^s}\right) \tag{3}$$

where V^m = swollen membrane volume, V_s^0 = solution volume which is equal in both sorption and desorption experiments, C_{s1}^s = concentration of external solution after sorption, and C_{s2}^s = concentration of external solution after desorption.

In the case of volatile organic solutes such as 2-propanol, isobutanol, and cyclohexanol, the partition coefficients K_{D_1} were determined by the one-step sorption technique. K_{D_1} is defined as follows:

$$K_{D_1} = \frac{V_s^0}{V^m}\left(\frac{C_{s1}^0 - C_{s1}^s}{C_{s1}^s}\right) \tag{4}$$

where C_{s1}^0 is the initial concentration of external solution.

Differential Scanning Calorimetry (DSC)

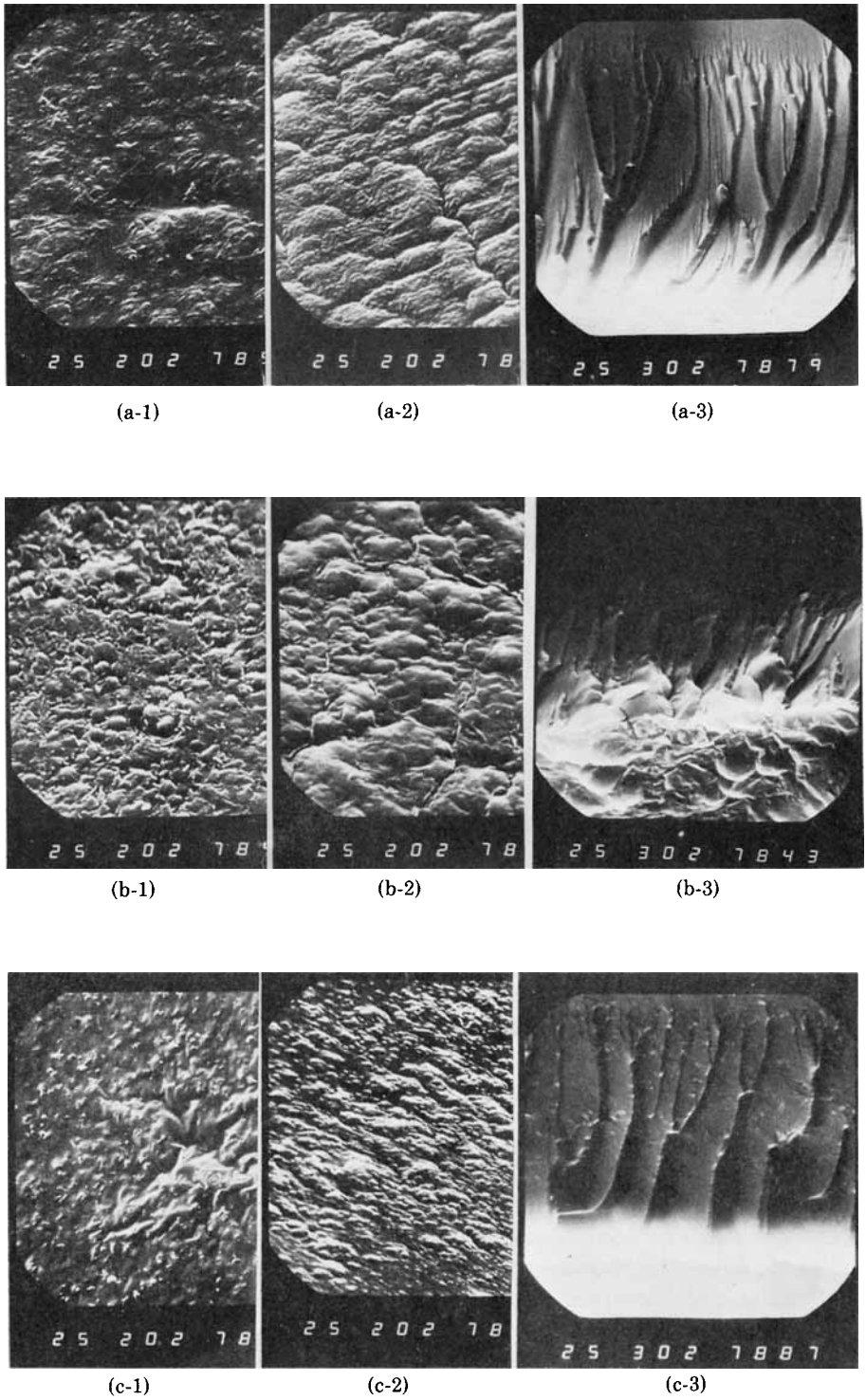
A DuPont 990 thermal analyzer and cell base was used for all the melting measurements. The DSC was calibrated by using indium and distilled water as standards. An about 6–15 mg membrane sample equilibrated at 25°C was sealed in a aluminum pan and cooled down with liquid nitrogen to −70°C in the DSC cell. The cell was slowly heated in a stream of nitrogen gas at a program rate of 5°C/min up to 20°C. The area of the melting peak was measured with a mechanical planimeter.

RESULTS AND DISCUSSION

Membrane Structure and Water Content

All membranes prepared are permanently translucent except SYN 0, ISO 2.5, and ISO 5 membrane, and the opaqueness increases with crosslinker content. This optical heterogeneity may derive from the surface roughness of the membranes, as can be seen from SEM data in Figure 3. The size and number of spherical hump on the air-dried surface of SYN membrane increases with the crosslink density, but the cause of occurrence of these humps cannot be known clearly yet. None of the optically transparent membranes do show any irregular surface. The cross sections of all membranes do not reveal any porous structures, magnified up to 10^4, and show the layered structures which always develop in the neighborhood of compressed side when fracturing the membrane. In the solution copolymerization of HEMA with diester crosslinker, the formation of optically heterogeneous gel, which is caused by micro- and macrosyneresis effect,[18] is possible by an increase in the degree of crosslinking or by changes in polymer–diluent interactions. This loose-structured gel has a highly porous structure of a high content of voids and retains more water compared to the homogeneous gel.[19] The SEM data show that the nature of optical heterogeneity of the postcrosslinked gel in this study is different from that of the diluent induced heterogeneity.[2]

The equilibrium water contents in the postcrosslinked gel membranes of tactic P(HEMA) at 25°C are plotted against the added crosslinker mol % in Figure 4, along with Jadwin et al.'s data,[5] in which the crosslinking was effected by ethylene



(a-1) (a-2) (a-3)

(b-1) (b-2) (b-3)

(c-1) (c-2) (c-3)

Fig. 3. The scanning electron micrographs of membranes; (a), (b), and (c) are for SYN 2.5, SYN 7.5, and ISO 7.5 membranes, respectively; (1) and (2) are for the surfaces of air-dried and mold side, respectively; (3) is for the cross section near the surface of each membrane.

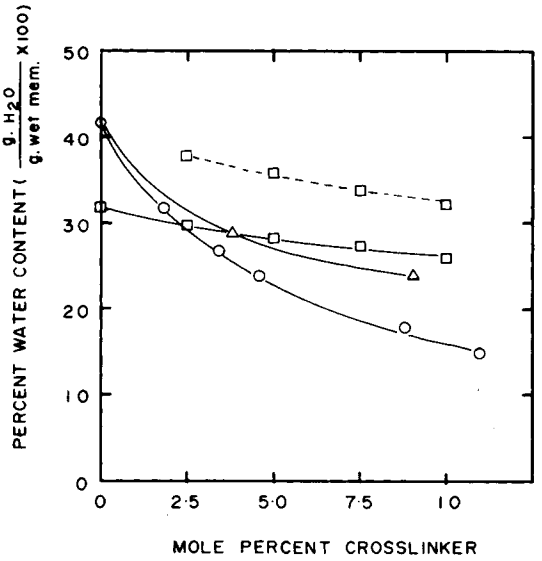


Fig. 4. The equilibrium water content of HEMA membranes as a function of crosslinker content; (△) and (○) EGDMA and TPT crosslinked, respectively, redrawn after Ref. 5; (□) HMDIC; (- - □ - -, — □ —) the data at 25°C for ISO and SYN membranes, respectively.

glycol dimethacrylate (EGDMA) and trimethylol propane trimethacrylate (TPT) and the membranes are all optically homogeneous. When crosslinked with HMDIC, the hydroxyl group of HEMA monomer unit is replaced with —OCONH—, but it is expected that this replaced group does not have a deleterious effect on the hydration of crosslinked P(HEMA) because of the similar absorptive affinity[20] of the —OH and —CONH— groups for water. It is evident that HMDIC is less effective in reducing water content than EGDMA and TPT for a given amount of crosslinker, as expected from the crosslinked molecular forms: HMDIC of a relatively long chain forms two urethane linkages at two ends of it between two pendant hydroxyl groups of polymer chains, while EGDMA and TPT of a short chain link the backbones of polymer chains. It is noticeable that the uncrosslinked syndiotactic P(HEMA) membrane has a fairly lower water content than the solution-polymerized HEMA membrane without having the crosslinker (Jadwin et al.[5]). The latter, in fact, contains slight diester crosslinks and is atactic in triad tacticity.[11] This lowered swelling may be due to the effective chain packing of highly syndiotactic P(HEMA).

As is seen in Figure 4, ISO membranes are far more hydrated than SYN membranes. The chain end effect on the hydration can be neglected because the molecular weight of two linear precursors of tactic polymers is similar. The hydration difference between these two types of membranes can be explained in terms of Russell et al.'s CPK® space-filling molecular models[21] of tactic P(HEMA). In isotactic P(HEMA) the hydrophilic pendant groups are all displaced outward in gauche conformations along the helix of polymer backbone chain, but the syndiotactic chain is composed of repeated $T_+ T_- T_+ G$ conformation along the backbone, which results in the intramolecular hydrogen bond between adjacent hydroxyl groups of every TGT sequence, and the characteristic ratio of the latter are smaller than that of the isotactic chain. Consequently, ISO membranes take up more water than SYN membranes.

Partition Coefficient

All the values of K_{D_2} show a good reproducibility with the standard deviation of 6–10%. The measured molar partition coefficients (K_{D_2}) of urea, acetamide, and NaCl are linearly correlated with the equilibrium water content of membranes at 25°C (Fig. 5). This may be reasonable because of the use of relatively long chain crosslinker of HMDIC. The linear correlation indicates that the partition of these salts occurs only into the water-containing region, which is all interconnected. The order of affinity for these HEMA hydrogel membranes is urea > acetamide > NaCl independent of the two precursors. It was reported that, in aqueous solution, hydrogen bonding does not significantly influence the dextran gel–solute association[22] and the interaction between model peptide groups.[23] In HEMA hydrogel membrane–ureas and amide solute system,[24] the good linear correlation of K_{D_2} with apparent polarization of the solutes in aqueous solution suggests the existence of a van der Waals–London type interaction with the gel. Therefore, the higher affinity of urea over acetamide for water-swollen P(HEMA) is mainly governed by the dispersion force, not by the hydrogen bonding.

The partition coefficients K_{D_1} of 2-propanol, isobutanol, and cyclohexanol are plotted against the water contents in each membrane in Figure 6. By contrast with the K_{D_2} of salts, the K_{D_1} of these alcohols do not have linear correlation over the whole water content ranges. All three alcohols under the investigation prefer the SYN membranes having more hydrophobic nature to the ISO membranes having more hydrophilic nature. The partition of lower alcohol (e.g., 2-propanol) into the membranes is less favored with decreasing the water content in both SYN and ISO membranes, but the absorption of isobutanol and cyclohexanol increases with decreasing the water content in SYN membranes. Hydrophobicity is, generally, a controlling factor on the preferential sorption of alcohols on the polymer matrix in the water-containing system: the magnitude of this effect increases with the decreasing polarity of the compound sorbed,[22,25] as can be seen in Figure 6.

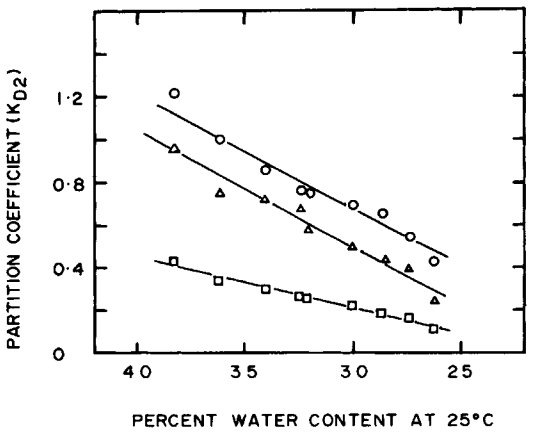


Fig. 5. The partition coefficient of salt solutes of HEMA membranes as a function of equilibrium water content of membranes at 25°C: (○) urea; (△) acetamide; (□) NaCl.

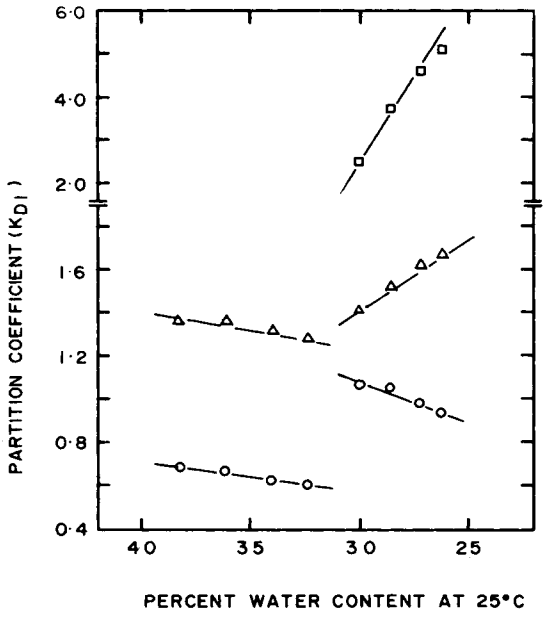


Fig. 6. The partition coefficient of alcohol solutes of HEMA membranes as a function of equilibrium water content of membranes at 25°C: (○) 2-propanol; (△) isobutanol; (□) cyclohexanol.

Permeability and Permselectivity

Using the membranes equilibrated in distilled water at 10°C for 2 days, the permeability coefficients show a good reproducibility within the standard deviations of 3–5%. The calculated permeability coefficients (P) from eq. (2) are plotted against mol % crosslinker content in Figures 7 and 8. All the measurements were carried out in the initial steady state at 25°C, using the membranes equilibrated in distilled water. Although the membranes are asymmetric in both

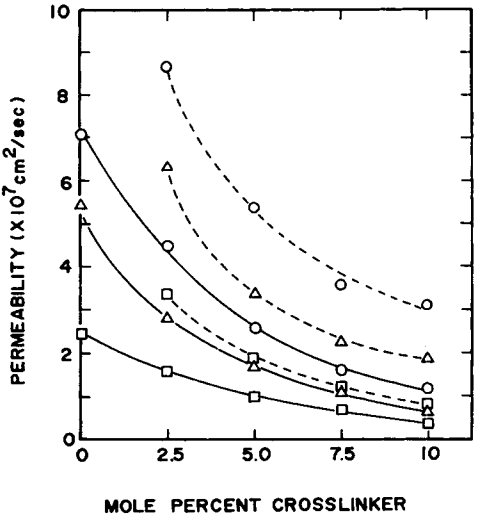


Fig. 7. The permeability of salt solutes through HEMA membranes as a function of crosslinker content at 25°C: (---) ISO membranes; (—) SYN membranes; (○) urea; (△) acetamide; (□) NaCl.

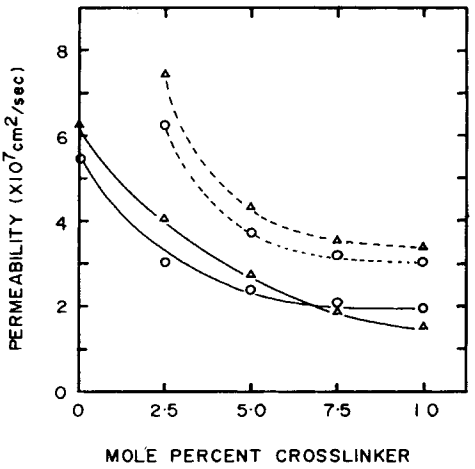


Fig. 8. The permeability of alcohol solutes through HEMA membranes as a function of crosslinker content at 25°C; (---) ISO membranes; (—) SYN membranes; (○) 2-propanol; (△) isobutanol.

of the two surfaces of the air-dried and mold sides, as indicated in SEM data, the directionality effect was not observed within experimental error in the permeability measurements. The permeability data show the higher permeability to ISO membranes of higher water content than to SYN membranes. The permeability decreases monotonously with increasing HMDIC content. In the light of a similar molecular weight (about 60) of three salt solutes, it can be seen that the higher the affinity, the faster the permeation rate and, therefore, that the order of permeability of these solutes is the same as that of affinity in both two types of membranes. It can be suggested that the variation of conformation of polymer chain does not effectively alter the extent of interaction of these three salts with the polymer matrix in this gel system as expected in K_{D_2} data, and that the conformational variation of polymer simply results in the overall change of permeability and partition coefficient due to the alteration of water content.

It is noticeable that isobutanol, having larger size, permeates more rapidly than 2-propanol does due to the higher affinity of isobutanol, but there occurs a size effect in the highly crosslinked SYN membranes (Fig. 8).

In such delicate systems as mentioned above, it is convenient to consider the permselectivity, the ratio of permeability of one solute to another, to see the effect of conformational change of polymer and crosslinker content on the permeability of solutes. The permselectivity data (Table I) of urea to NaCl show that the permselectivity of ISO membranes increases with the HMDIC content, while the trend is reversed for SYN membranes. As can be seen in Table I, the

TABLE I
Dialysis Permselectivity of Urea to NaCl at 25°C

HMDIC (mol %)	P_{urea}/P_{NaCl}		$K_{D_2}{}^{urea}/K_{D_2}{}^{NaCl}$		$D_{AM}^{urea}/D_{AM}^{NaCl}$	
	SYN	ISO	SYN	ISO	SYN	ISO
0	2.84		3.06		0.93	
2.5	2.81	2.56	3.10	2.80	0.91	0.91
5.0	2.60	2.95	3.59	2.97	0.70	1.02
7.5	2.30	3.00	3.24	2.87	0.70	1.05
10	2.52	3.94	3.98	2.85	0.78	1.44

permselectivity of urea to NaCl is mainly controlled by the kinetic (diffusivity) effect rather than by the solubility effect. The ratio $K_{D_2}^{urea}/K_{D_2}^{NaCl}$ for SYN membranes of lower water content rises as the crosslink density is increased, but the ratio for ISO membranes of higher water content is relatively constant and lower than that for SYN membranes. This means that the increase of water content due to the conformational change of polymer reduces the sorptive selectivity of urea to NaCl. The kinetic effect by the increase of crosslink density is dissimilar in both two types of membranes. There is some direct or indirect evidence for the existence of supramolecular ordering[4,5,9,10] of hydrophobic and hydrogen-bonded portions for transparent gels from atactic P(HEMA). If this supramolecularly ordered region is assumed, the number of water molecules per hydroxyl group loses physical significance and, therefore, the existence of water pockets of clustered water should be assumed, considering the total water content within the gel. From the dissimilarity in the kinetic effect of dialysis, it can be inferred that the size and number of those segregated regions might be changed differently in the two membranes as the crosslink density is varied, though the micromorphological nature of these two types of gel is not yet known in the literature.

The permselectivity relationship between these solutes may arise from the inaccessibility[26,27] of NaCl to the lower dielectric region containing bound water. Since these salts of similar molecular weight are imbibed only into the water-containing hydrophilic regions, the structural orderliness of water within the water-swollen polymer matrix plays an important role in the permeation of salts. The various states of water within water-swollen polymers have been suggested differently by many authors. Among of them, the existence of bound water is commonly accepted, but this nonfreezing water in the water-swollen polymer system should not be identified with strongly bound immobilized water.[28,29] This bound water is believed to be of importance in many separations of aqueous salt solutions.[27]

Recently we have determined the bound water content of water swollen tactic P(HEMA) crosslinked with 5 mol % HMDIC by a dilatometric technique[12] under the assumption of the existence of three states of water,[30-35] X, Y, and Z waters, where X water is ordinary bulk waterlike, Y water is intermediate waterlike which melts below the melting point of X water, and Z water is bound waterlike that does not exhibit phase transitions. The result is shown in Table II. As is indicated in Table I, ISO membranes have higher permselectivity than SYN membranes. This may be due to the larger amounts of bound plus intermediate water in water pockets,[5] as shown in Table II. The increase of permselectivity of ISO

TABLE II
Approximate Contribution of X, Y, and Z Water in 5 mol % HMDIC Crosslinked Gel

	g/g Wet gel		g/g Dry polymer		Percentage in total water content	
	SYN	ISO	SYN	ISO	SYN	ISO
X	0.064	0.07	0.093	0.11	21	18
Y	0.056	0.10	0.081	0.16	18	26
Z	0.19	0.21	0.28	0.34	61	55
W[a]	0.31	0.38	0.45	0.61	100	100

[a] W = total water fraction in gel.

membranes means the increase of bound water with HMDIC content. A more detailed discussion is given in the next subsection.

Diffusion Coefficient and Water Structure

The apparent diffusion coefficient D_{AM} of a permeant, which is a criterion for its mobility within membrane phases, is obtained from

$$P = K_D D_{AM} \tag{5}$$

where P and K_D have been previously defined. The diffusion coefficients of urea, acetamide, and NaCl for ISO membranes are plotted against crosslinker content (Fig. 9), and those for SYN membranes are plotted against the equilibrium water content at 10°C of the membranes in Figure 10. The calculated values show the reproducibility of the standard deviation of maximum 10% at high crosslinker density. The diffusion coefficients of each solute for SYN membranes show a good linear dependence on the total water content, while those for ISO membranes do not. The mobility within the SYN 0 membrane is larger than that within ISO 2.5 membrane of higher water content. Therefore, it may be deduced that the polymer chain segments around a junction effectively impede the diffusion of a permeant. It is interesting to note that the apparent diffusion coefficient of NaCl for SYN and ISO membranes is almost the same at the same level of crosslinking. This means that, assuming the bound water content as a main factor to the resistance to the diffusion of NaCl, the water pockets,[5] if they exist, within SYN and ISO membranes available for the diffusion of NaCl, have the same ratio of bound to freezable water. But, in the case of urea and acetamide, the situation is rather complicated because of their possible accessibility to the region of polymer plus bound water. The deviation between the diffusion coefficients for SYN and ISO membranes is more and more pronounced with increasing the crosslinker concentration.

All the DSC melting thermograms for SYN and ISO membranes, equilibrated in distilled water for 5 days at 25°C, are shown in Figures 11 and 12, respectively. All the endothermic peaks confirm the existence of two types of freezing water

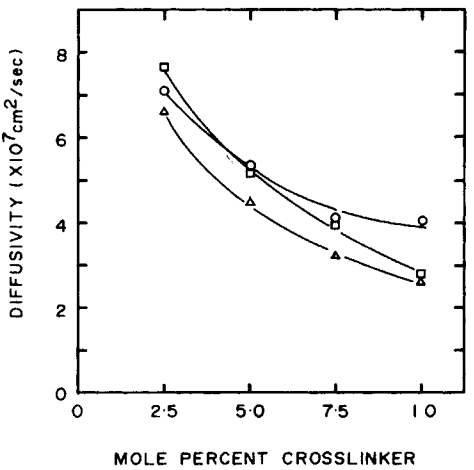


Fig. 9. The diffusivity of salt solutes within ISO membranes as a function of crosslinker content at 25°C: (○) urea; (△) acetamide; (□) NaCl.

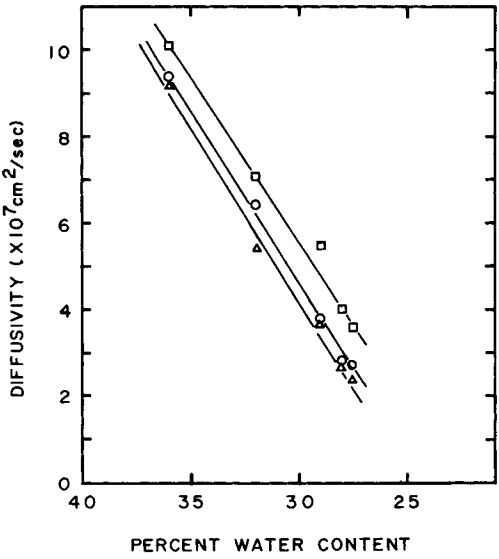


Fig. 10. The diffusivity of salt solutes, at 25°C, within SYN membranes as a function of equilibrium water content: (□) NaCl; (○) urea; (△) acetamide.

of X and Y water. X water has a freezing point $T_X = -5 \pm 1$°C. As can be seen in Figures 11 and 12, the thermograms indicate that X water mainly contributes to the freezable water in SYN membranes, and that the peak broadening[33,34] below T_X of ISO membranes may be ascribed to the excess of Y water, all of which is supported by previous dilatometric data.[12]

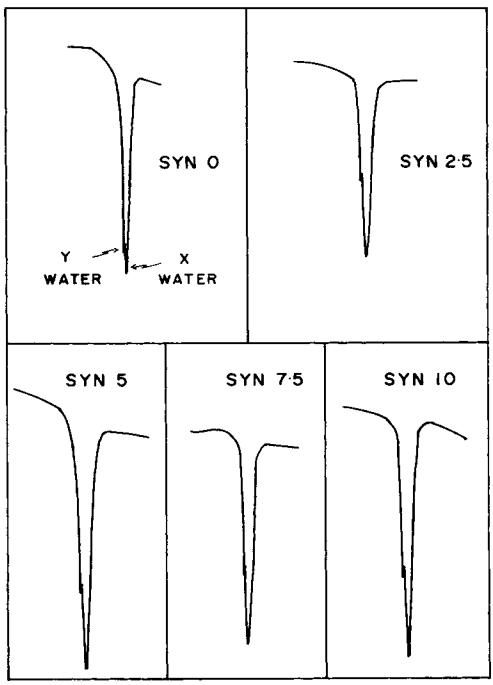


Fig. 11. The DSC melting thermograms for SYN membranes equilibrated in distilled water at 25°C.

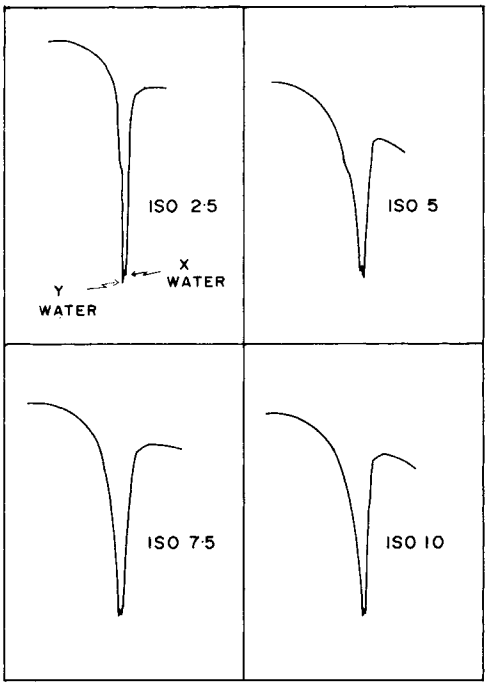


Fig. 12. The DSC melting thermograms for ISO membranes equilibrated in distilled water at 25°C.

There are some controversies about what causes the deficit in the heat effect of the water in macromolecular gels: Pouchly et al.[29] suggested that the deficit might be due to the heat of mixing or the heat of dilution, while some authors[12,31,33,34,36] believe that this may be due to the structuring of water in the gel network, which was indirectly verified by the studies such as dilatometry,[12,31,32] specific conductivity,[12,31,32] dielectric measurement,[32] and pulse NMR.[33]

The amount of bound water in the membrane was approximately estimated from the equation[34]

$$W_z = W_t - Q_{endo}/Q_f \tag{6}$$

where W_z and W_t are the weight fractions of bound and total water in the membrane, respectively, Q_{endo} is the observed endothermic heat (cal/g wet membrane), and Q_f is the heat of fusion of ice (79.7 cal/g). It was recently reported that the heat of fusion for X water in the HEMA hydrogel is almost identical to that of pure ice.[33] The observed overall endothermic heat (Q_{endo}) originates from X and Y water. Therefore, the use of the above equation might produce slightly erroneous results for the estimation of bound water in ISO membranes where there exists a larger amount of Y water. Though exact deconvolution of ice melting peaks for ISO membranes is impossible, none of the peak shapes show any great change of the ratio of X and Y water with HMDIC content and are reproducible from sample to sample under the same running condition.[33] It is expected, therefore, that the estimated bound water contents from eq. (6) are systematic for the membranes from the same precursor. The area of the melting peaks were within ±5% on repeated runs. The calculated

approximate bound water contents are tabulated in Table III. As is shown in Table III, the bound water fraction of SYN membranes is relatively constant throughout the whole crosslinker content range in this study, whereas that of ISO membranes increases with HMDIC content. It is well known that both the dilatometric technique and the integral heat method of DSC give almost consistent values of bound water content.[12,31] The calculated W_z of 0.22 of the SYN membrane is comparable to the measured value by a dilatometric method, but that of the ISO membrane is smaller than the dilatometrically measured value (Table II) as expected, due to the higher amount of Y water. At any rate, from Table I and Figure 9, it is expected that the excess of Y water and the increase of Z water with the crosslinker content of ISO membranes might induce the increase of the permselectivity and the lower mobility of NaCl than urea in the highly crosslinked regions. That is, though urea and acetamide containing the water structure breaking group of $-NH_2$[37,38] are closely accessible to a polymer chain through some possible interactions such as dipole–dipole, H bonding, etc., an ion lacking specific interaction[39] cannot closely approach such a low dielectric region[27] of the polymer chain surrounded by bound water.

For the effect of crosslinker concentration on the water structural orderliness within membranes, our bound water content data for the postcrosslinked HEMA membranes have somewhat different tendency from Jadwin et al.'s data[5] for TPT-crosslinked HEMA membranes. They found that in the TPT-crosslinked system, the ratio of primary (bound) to secondary (intermediate plus bulk) water is not affected by the increase of crosslink density, based on the constancy of the molal distribution coefficient (K*) of NaCl under the assumption of no sorption of salt into primary water. The chain of TPT crosslinker is too short to accommodate any water molecules in the neighborhood of the crosslinking point. Consequently, TPT crosslinking results in the effective reduction of total water content and the simultaneous reduction of primary and secondary water. In the case of HMDIC of relatively long spacer crosslinker, the water molecule might exist in the junctured regions, at least in the form of bound water, which is self-explanatory for no decrease of bound water fraction (W_z) with crosslinker concentration. When we calculated the molal partition coefficient (K^*) of NaCl from the molar partition coefficient (K_D), the results supported the change of the ratio of primary to secondary water or, consequently, the increase of bound water content in total water.

In spite of the increase of percentage of bound water in total water content with HMDIC content, as is seen in Figure 10, the order of diffusivity of salts for all SYN membranes is the same as that in aqueous solution (Table IV). According to DSC thermograms (Fig. 11) and dilatometric data (Table II), there are larger amounts of X water than Y water in all SYN membranes. All the

TABLE III
Calculated Bound Water Fraction in Membranes from DSC Results Using Eq. (6)

Membrane	W_t	Q_{endo}/Q_f	W_z	Membrane	W_t	Q_{endo}/Q_f	W_z
SYN 0	0.322	0.102	0.22				
SYN 2.5	0.300	0.094	0.21	ISO 2.5	0.382	0.238	0.14
SYN 5.0	0.285	0.068	0.22	ISO 5.0	0.361	0.207	0.15
SYN 7.5	0.272	0.056	0.22	ISO 7.5	0.340	0.178	0.16
SYN 10	0.262	0.037	0.23	ISO 10	0.324	0.155	0.17

TABLE IV
Diffusion Coefficient (D) of Solutes in Pure Water at 25°C

Solute	Molecular wt	$D \times 10^5$ cm^2/s
NaCl	58.44	1.479[a]
Urea	60.06	1.382[b]
Acetamide	59.07	1.252[b]

[a] R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Academic, New York, 1959.
[b] L. G. Longsworth, *J. Phys. Chem.*, **67**, 689 (1963).

diffusion coefficients of salts for SYN membranes are linearly correlated with the total water content within membranes, though the bound water fraction (W_z) is constant in all membranes. Especially for SYN membranes, the permselectivity of urea and acetamide to NaCl decreases with increasing crosslinker content.

All the above-observed facts for SYN membranes strongly imply the existence of segregated regions of polymer and water. It is well known[9] that, though it is visually transparent, low crosslinked P(HEMA) gel prepared by a traditional method has some structural order probably imposed by inhomogeneous crosslinking as well as by specific diluent–polymer interactions dictated by the amphiphilic nature of the polymer. The P(HEMA) radically initiated at 50–60°C has the tacticity of 58% syndiotacticity and 42% heterotacticity.[11] Therefore, at low crosslinker density, the tendency of segregation might be enhanced by introducing high syndiotacticity into P(HEMA) because of the more hydrophobic nature of syndiotactic chain. Russell et al.'s CPK® molecular models of tactic P(HEMA)[21] indicate that the syndiotactic chain is less extended than its isotactic counterpart. Accordingly, the probability of intrachain crosslinking might be higher in syndiotactic P(HEMA), which is partly reflected in the equilibrium water content data[24] at 10°C: The change of crosslinker content of 2.5 to 10 mol % causes the water content drop of 12% for the ISO membrane, while only 4.5% water content variation occurs for the SYN membrane. Also, the lower water content drop with crosslinker content and the surface morphology, as seen in Figure 3, might be some clues to the more inhomogeneous crosslinking of syndiotactic P(HEMA).

Considering all the facts, it might be concluded for the SYN membrane that the size of water pockets, at least, does not decrease with increasing HMDIC content, but their concentrations decrease, which results in the same order of diffusivity as in aqueous solution, for the whole crosslinker concentration range in this study.

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