# Hydraulic Permeability of Water in Poly(vinyl Alcohol) Membranes as a Function of the Degree of Hydration

Y. KOJIMA, K. FURUHATA, and K. MIYASAKA, *Tokyo Institute of Technology, Department of Textile and Polymeric Materials, Ookayama, Meguro-ku, Tokyo, Japan*

## Synopsis

Poly(vinyl alcohol) membranes were prepared by solution cast and subsequent annealing. The degree of crystallinity of the membranes at the dry state was not affected by the annealing, whereas the degree of hydration $H$ was markedly changed. This made us assume a double network structure. Hydraulic permeability of water, $K_w$, in PVA membranes was measured to discuss the relation between $H$ and the permeability. $K_w$ increased with increasing $H$ with increasing slope. The linear relation between the reduced permeability $K_w/H$ and $1/H$, expected from a free volume theory, was not obtained in the PVA membranes. This nonlinearity of the relation was confirmed also in various hydrogels reported by other authors. We found that a linear relation between $H$ and logarithm of $K_w/H$, as expected from the Ogston's relation, is achieved in PVA and many other hydrogel membranes with $H$ from 0.4 to 0.9. Under a given degree of hydration, the activation energy of permeation of PVA membrane was larger than that of cellulose, owing to the large amount of bound water in PVA membrane.

## INTRODUCTION

The hydraulic permeability of water has been studied by many authors[1–10] on many kinds of membranes. For example, Yasuda et al.[1] showed that the permeability is well described by the contribution of the free volume of water contained in the membrane. However, we know that many data on the permeability do not always obey the relation derived by Yasuda, which will be shown later in this paper. Generally speaking, the permeability must depend not only on the water content, i.e., the degree of hydration, but also on the geometrical structure of the membrane, which may be characterized by the networks in homogeneous membranes. When we analyze the data on the permeability of water in membranes in relation to the degree of hydration, it is difficult to get enough literature data obtained by the systematic experiments. The purpose of this work is to find experimentally the relation between the permeability and the degree of hydration in the poly(vinyl alcohol) (PVA) membranes which is one of the important hydrogels. The sample membranes were prepared by solution cast, as is usually prepared. In semicrystalline membranes the crystallites play the role as the junction points, and, as a result, they have complicated internal geometrical structures.

## EXPERIMENTAL

### Sample Preparation

PVA (Koso Chem. Co., DP = 2000 and degree of hydrolysis 0.992) was used in this study. The membranes, 200 $\mu$m thick, were cast on PMMA plates from 7% PVA aqueous solution (in open air) at 25°C. In order to obtain membranes of various degrees of hydration (the degree of swelling with water), they were annealed at various temperatures for 10–15 min under vacuum. They were then dipped in water at 25°C for 5 days until the swelling equilibrium was reached, during which water was repeatedly renewed. The weights of the swollen membranes were measured, after being blotted between sheets of paper. They were then dried at 25°C by evacuation, and the weights were measured. The degree of hydration, $H$, was defined as the volume fraction of water in the swollen membrane, and estimated by the equation

$$H = (M_s - M_d)/[(M_s - M_d) + M_d/1.3] \tag{1}$$

where $M_s$ and $M_d$ are the weights of a sample at swollen and dry states, respectively, and 1.0 and 1.3 g/cm$^3$ are used as the densities of water and PVA. Figure 1 shows that the degree of hydration decreases with increasing annealing temperature, as was expected. The decrease in the degree of hydration becomes more remarkable above 110°C which is the second transition point of PVA crystal.[11] The degree of crystallinity of the dry membranes were estimated by the IR, DSC, and wide angle X-ray methods. The crystalline sensitive band at 1146 cm$^{-1}$ [12] was used in the IR method, the heat of fusion of 2.63 kcal/mol[13] was used in the DSC method, and in the X-ray method the diffraction intensity curve of PVA crosslinked with Borax was used as that of the pure amorphous sample. As the value of crystallinity so much depends on the estimation methods, it is difficult to determine which method gives the most reasonable value in this case. It should be, however, noted that the crystallinities from these three methods
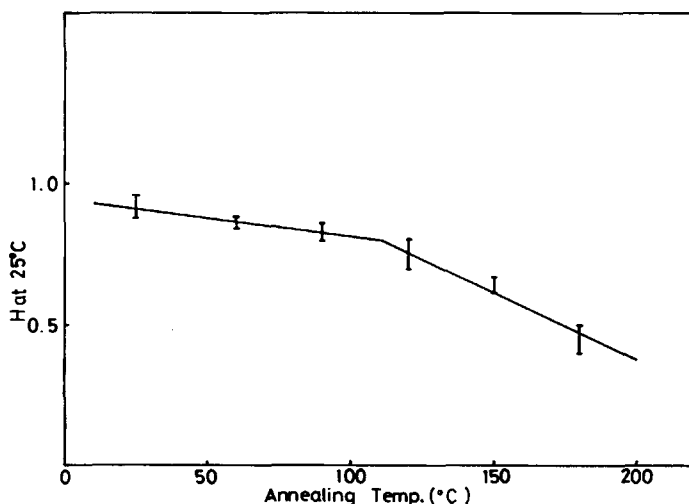


Fig. 1. The degree of hydration of the PVA membrane as a function of annealing temperature.

were found to be independent of the annealing temperature, whereas the degree of hydration markedly depends on it, as shown above. It is widely believed that in semicrystalline polymers a network of amorphous chains is formed with crystallites which act as the junction points. In this sort of amorphous chain network, the degree of swelling depends much on the crystallinity, i.e., the increase in the crystallinity is always accompanied by the decrease in the degree of swelling.[14] However, in the present case, it is difficult to relate the decrease in the degree of swelling with the change in the crystallinity. This made us assume a double network structure, where water is mixed with amorphous chains in each fibril (amorphous chain network) and also with fibrils (fibrillar network). Annealing may cause a great change in the fibrillar network structure without a noticeable increase in the crystallinity. An alternative explanation for the independence of the degree of swelling on the crystallinity is that the crystallinity at the wet state is different (smaller) from that of the dry state. Some researchers[14] insisted that the crystallinity is not changed by wetting, while other researchers[15] reported that the crystallinity decreases with wetting. It seems difficult to assume that the crystallinity does not change by wetting. Then it is natural to suppose that the decrease is more remarkable in the membranes annealed at lower temperature. Even if the second explanation would be more important than the first, we believe that the idea of "double network structure" is important in the semicrystalline membranes.

## Hydraulic Permeability Measurement

Hydraulic permeability of swollen PVA membranes was measured with an apparatus shown in Figure 2. It consists of a high and low pressure compartments 8 cm in diameter, separated by a sample membrane. The high pressure compartment was 6 cm long and 251 $cm^3$ in volume, being equipped with a thermometer and a piston for pressure supply. The low pressure compartment was 6 cm long and 302 $cm^3$ in volume and equipped with a capillary for water flowing out. The volume of permeated water was measured as a function of time. The effective membrane area for the permeation was 12.6 $cm^2$. The sample
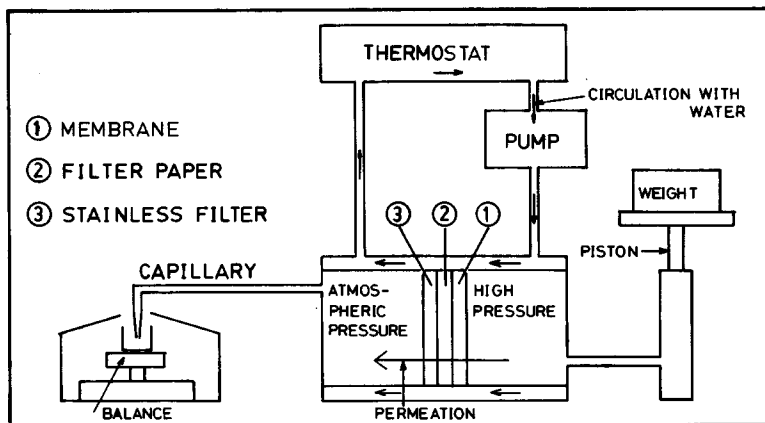


Fig. 2. Schematic diagram of the water permeation cell.

membrane was supported by a sheet of filter paper and a sintered stainless steel filter. The temperature in the cell was controlled to within 0.1°C by circulating water around the cell. The hydraulic permeability $K_w$ was calculated by the following equation:

$$K_w = J_w \Delta X / \Delta P \tag{2}$$

where $J_w$ is the volume flux of water, $\Delta X$ is the thickness of the membrane at the swollen state, and $\Delta P$ is the pressure difference across the membrane.

## RESULTS AND DISCUSSION

Figure 3 shows some examples of the relation between the pressure difference and the water flux. The linear relations, as shown in this figure, were obtained in all cases studied. This means that the permeability does not depend on the pressure difference. The hydraulic permeability $K_w$ is plotted against the degree of hydration, $H$, in Figure 4. $K_w$ increases with increasing $H$, as was expected, and the rate of increase of $K_w$ increases with $H$. According to Yasuda et al.,[1] $K_w$ has the following relation with $H$ at higher than about 0.4:

$$K_w/H = A \exp(-B/HV_{fw}) \tag{3}$$

where $A$ and $B$ are constants and $V_{fw}$ is the free volume fraction of water in the membrane. The data in Figure 4 are replotted in accordance with eq. (3), in Figure 5. The fact that the plot is not linear, as shown in the figure, indicates that eq. (3) is not applicable to this case of PVA hydrogels. This is not only for our case but also for other various hydrogels cited in Figure 6. Instead of eq. (3) we found the linear relation between the logarithm of $K_w/H$ and $H$, i.e.,
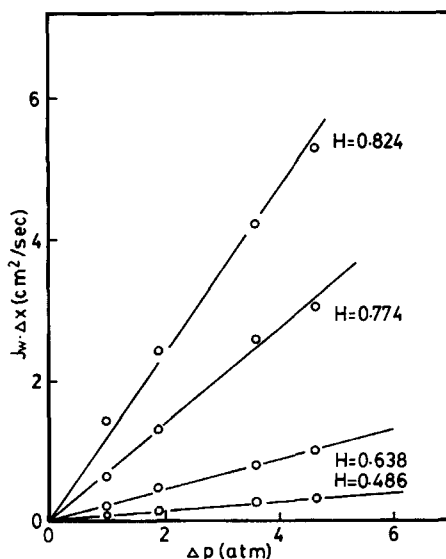
$$\ln(K_w/H) = A + BH \tag{4}$$



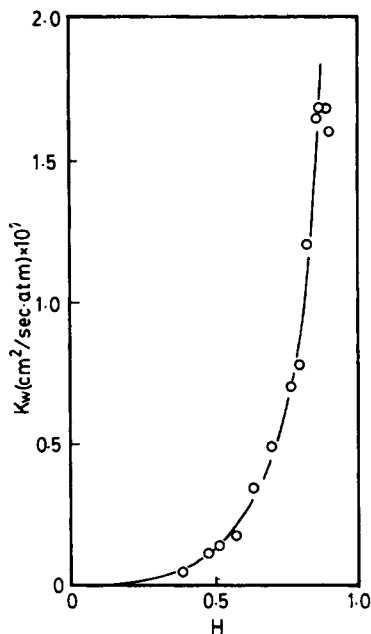Fig. 3. Dependence of water flux on applied pressure at 25°C.

Fig. 4. Dependence of the hydraulic permeability of water at 25°C in PVA membranes on the degree of hydration.

with constants $A$ and $B$. The linearity is satisfied in a range of $H$ from 0.4 to 0.9, and deviates from a linear line at $H$ above 0.9. This relation is achieved in PVA, and many other hydrogel membranes and values $A$ and $B$ are dependent on polymer species. It is interesting to recall Ogston's following work.[16] He showed
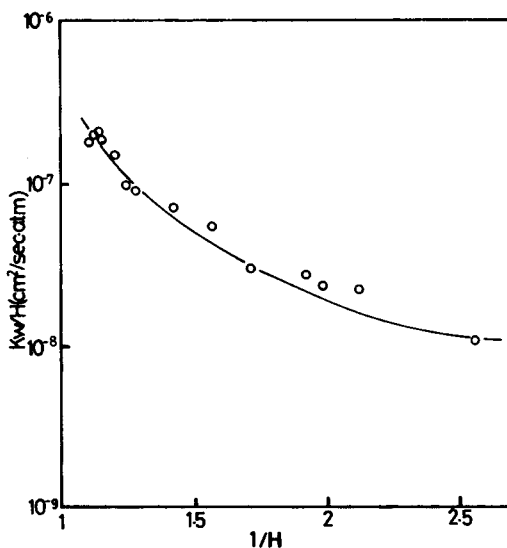


Fig. 5. Relation between the reduced permeability $K_w/H$ of PVA membrane and the reciprocal of the degree of hydration.
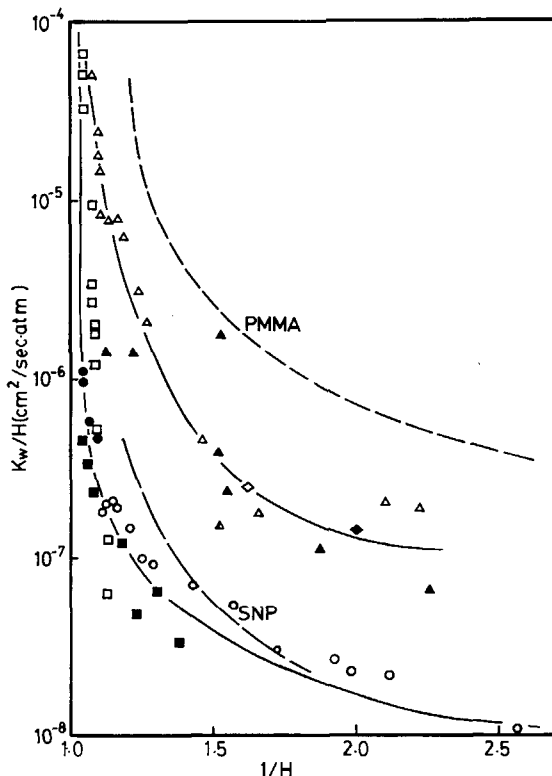
Fig. 6. Relation between the reduced permeability $K_w/H$ of the literature data and the reciprocal of the degree of hydration: (- - -) poly(methyl methacrylate) (PMMA), Ref. 9; (▲) hydrophilic methacrylate polymer (HMP), Ref. 1; (▲) regenerated cellulose (RC), Ref. 1; (△) hydrophilic methacrylate polymer (HMP), Ref. 4; (▲) regenerated cellulose (RC), Ref. 4; (◇) regenerated cellulose (RC), Ref. 5; (◆) regenerated cellulose (RC), Ref. 9; (— —) copolymer of $N$-vinyl pyrrolidone and methyl methacrylate (SNP), Ref. 9; (■) poly(acrylamide) (PAAM), Ref. 2; (□) poly(acrylamide) (PAAM), Ref. 10; (○) PVA, present work.

that the possibility of finding spaces with radius $D$ larger than $r$ in a uniform random suspension of fibrils with length of $L$ and radius of $R$ is given by

$$P(D > r) = \exp[-\pi\nu L(R + r)^2] \qquad (5)$$

with

$$\nu = (1 - H)/\pi L R^2 \qquad (6)$$

where $\nu$ is the number of fibrils in a unit volume of the suspension, $1 - H$ is the volume fraction of fibrils, and $\pi L R^2$ is the volume of a fibril. We may replace the suspension system with a swollen gel by making the fibrils in suspension correspond to the network fibrils, both ends of which are fixed by junction points. If we assume that $r$ is the smallest radius of space that is available for the penetrant (water cluster in this case), the following relation holds to describe the hydraulic permeability:
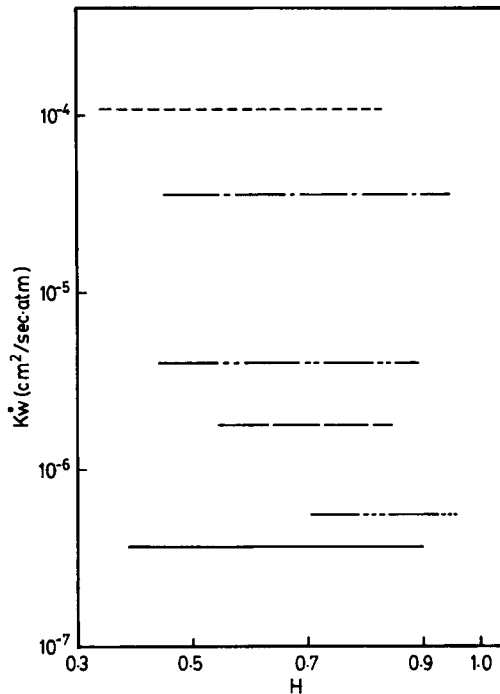
$$K_w/H = K_w^0 P(D > r) \qquad (7)$$

Fig. 7. The value of $K_w^0$ estimated by eq. (8):  (- - - - -) PMMA, Ref. 9; (— - —) HMP, RC, Ref. 4; (— - - —) HMP, RC, Ref. 1; (— — —) SNP, Ref. 9; (— - - - —) PAAM, Ref. 2; (—) PVA, present work.

$K_w^0$ is a reduced permeability of water in hydrogel, and is independent of the geometrical constraint.   Substituting eqs. (5) and (6) into eq. (7), we obtain the relation

$$K_w/H = K_w^0 \exp[-(1 - H)(1 + r/R)^2] \tag{8}$$

$r/R$ depends on polymer species (size of fibrils formed) and penetrant (size of water cluster).   We found the linear relation between logarithm of $K_w/H$ and $1 - H$ in PVA hydrogel and many other hydrogels shown in Figure 6 in a range of $H$ from 0.4 to 0.9, and obtained the values $K_w^0$ and $r/R$ for these hydrogel membranes.   Figures 7 and 8 show thus estimated values of $K_w^0$ and $r/R$, respectively.   $K_w^0$ varies over 2 orders of magnitude among samples.   The smallest value is for our PVA, while the largest is for PMMA hydrogel.   Intermediate values are obtained for cellulosic and hydrophilic methacrylate membranes.   The values of $r/R$ is distributed around about 2, with comparatively small deviation at $H$ below 0.9, and the value for our PVA is the smallest among them.

   The temperature dependency of permeability was studied between 10°C and 25°C.   The linear relation was obtained between $\ln(K_w/H)$ and $1 - H$ at each temperature.   Figure 9 shows some examples of the Arrhenius plots, and Figure 10 shows the apparent activation energy for hydraulic permeation as a function of $H$.   The apparent activation energy increases with decreasing $H$, while the permeability decreased as already described above.   It should be noted that in the vicinity of $H = 1$ the activation energy of permeation approaches the acti-
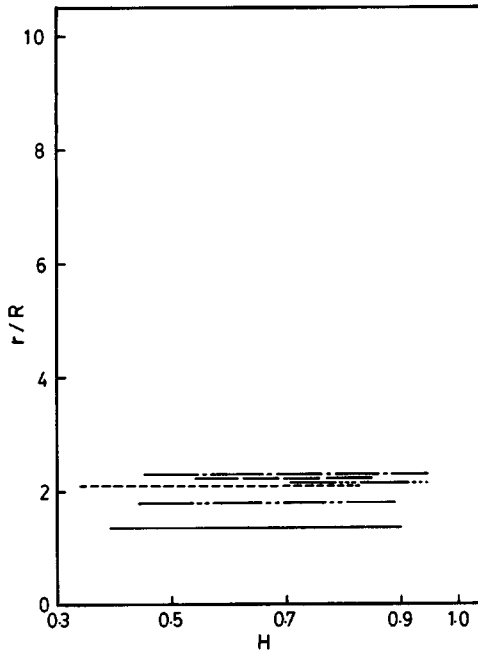
Fig. 8. The value of $r/R$ estimated by eq. (8). Symbols in this figure are the same as those in Figure 7.
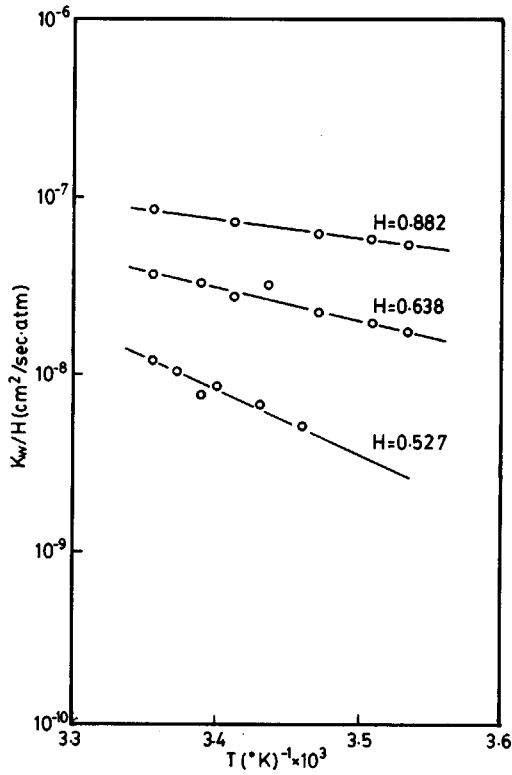


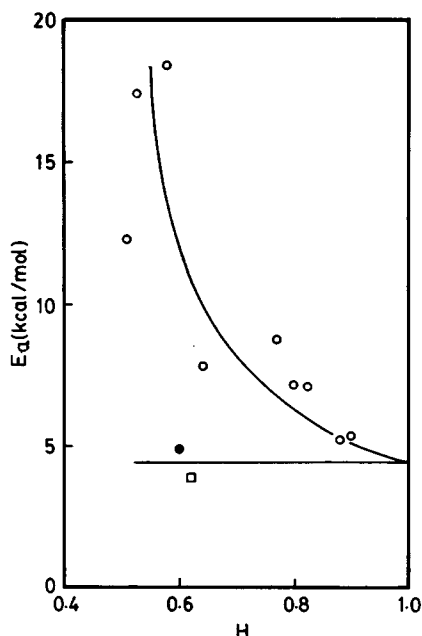Fig. 9. Temperature dependence of $K_w/H$ for PVA membranes.

Fig. 10. Relation between the apparent activation energy $E_a$ of permeation of water and the degree of hydration: (O) present work; (●) cellulose acetate, Ref. 3; (□) regenerated cellulose, Ref. 5.

vation energies of pure water calculated from the temperature dependencies of the viscosity[17] (4.4 kcal/mol) and of the self-diffusion coefficient[18] (4.5 kcal/mol). The activation energies of permeation through cellulosic membranes[3,5] with $H$ of about 0.6 were around 4.5 kcal/mol.

Water molecules in polymer may exist in two or more different states.[19–22] Some of the water molecules are bound to the polymer through hydrogen bonding, sometimes referred to as bound water, whereas the rest of water does not take part in direct hydrogen bonding with the polymer, sometimes referred to as free water, and has a greater degree of mobility. It was shown by Pedley and Tighe[19] that the permeability dramatically increased with the increase in free water content. Hatakeyama and Yamauchi[20] studied the melting behavior of water in PVA hydrogels to show that one repeating unit fixed six water molecules to make bound water (in other words, nonfreezing water). This value corresponds to $H$ of 0.76. Nelson[21] showed that in the case of cellulosic materials the amount of bound water was about 0.24 in $H$, and Lee et al.[22] showed that, in the case of 2-hydroxyethyl methacrylate polymer, 0.25 in $H$ was bound water. Therefore, the smallest $K_w^0$ value for our PVA is considered to be related to the larger amount of bound water in comparison with those for other hydrogel membranes. The $\ln(K_w/H) - (1 - H)$ plot deviates from linearity in a range of $H$ above 0.9. This deviation is probably due to the increase of $K_w^0$ which may be caused by the increasing content of free water. According to Ogiwara et al.,[23] the amount of bound water was almost constant in the temperature range from $-30°C$ up to $40°C$, and the state of bound water was influenced to a considerable extent by a change in temperature; the mobility of bound water decreased with the decrease in temperature and also in $H$. Therefore, the increase in activation

energy at lower $H$ than 0.8 can be related to the large amount of bound water in PVA hydrogels ($H = 0.76$). If a sufficient amount of free water exists, the activation energy of water permeation approaches to that of the self-diffusion of water in bulk, as in the present PVA hydrogel and cellulosic membranes with $H$ of about 0.6.

So far, we have shown that eq. (4) may be better than eq. (3) in describing the relation between the degree of hydration and the water permeability and that eq. (4) can be derived from Ogston's relation [eq. (8)]. However, it should be noted that Ogston's idea might not be the only one that explains eq. (4), although the usefulness of his idea is well recognized.

# References

1. H. Yasuda, C. E. Lamaze, and A. Peterlin, *J. Polym. Sci.*, A-2, **9**, 1117 (1971).
2. M. L. White, *J. Phys. Chem.*, **64**, 1563 (1960).
3. C. M. Gary-Bobo and A. K. Solomon, *J. Gen. Physiol.*, **57**, 610 (1971).
4. M. F. Refojo, *J. Appl. Polym. Sci.*, **9**, 3417 (1965).
5. M. Kawaguchi, T. Taniguchi, K. Tochigi, and A. Takizawa, *J. Appl. Polym. Sci.*, **19**, 2515 (1975).
6. O. M. Ebra-Lima and D. R. Paul, *J. Appl. Polym. Sci.*, **19**, 1381 (1975).
7. N. Lakshminarayanaiah, *J. Appl. Polym. Sci.*, **11**, 1737 (1967).
8. A. Yamauchi, *Tanpakushitsu Kakusan Koso*, **22**, 1418 (1977).
9. H. Tanzawa, *Maku*, **1**, 187 (1976).
10. N. Weiss and A. Silberberg, *Br. Polym. J.*, **9**, 144 (1977).
11. K. Shirakashi, K. Ishikawa, and K. Miyasaka, *Kobunshi Kagaku*, **21**, 588 (1964).
12. E. Nagai, *Poly(vinyl Alcohol)*, I. Sakurada, Ed., Society of Polymer Science, Japan, Tokyo, 1955, p. 245.
13. I. Sakurada, A. Nakajima, and H. Takita, *Kobunshi Kagaku*, **12**, 21 (1955).
14. I. Sakurada, Y. Nukushina, and Y. Sone, *Kobunshi Kagaku*, **12**, 510 (1955).
15. H. Tadokoro, S. Seki, and I. Nitta, *Kobunshi Kagaku*, **13**, 45 (1956).
16. A. G. Ogston, *Trans. Faraday Soc.*, **54**, 1754 (1958).
17. Bingham and Jackson, *Bur. Stds. Bull.*, **14**, 75 (1918).
18. D. E. Gray, Ed., *American Institute of Physics Handbook*, McGraw-Hill, New York , 1963.
19. D. G. Pedley and B. J. Tighe, *Br. Polym. J.*, **11**, 130 (1979).
20. T. Hatakeyama and A. Yamauchi, *Kobunshi to Mizu ni kansuru Toronkai*, Preprint, p. 3 (1980).
21. R. A. Nelson, *J. Appl. Polym. Sci.*, **21**, 645 (1977).
22. H. B. Lee, M. S. Jhon, and J. D. Andrade, *J. Colloid Interface Sci.*, **51**, 225 (1975).
23. Y. Ogiwara, H. Kubota, S. Hayashi, and N. Mitomo, *J. Appl. Polym. Sci.*, **14**, 303 (1970).