

Reentrant Swelling Behavior of Poly(N-isopropylacrylamide) Gel

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The equilibrium swelling curves of poly(N-isopropylacrylamide) gel are measured in four binary mixed solvent systems of water and organic alcohols. The organic alcohols chosen here are methanol, ethanol, 1-propanol, and 2-propanol, respectively. The re-entrant equilibrium swelling curves are obtained in these four binary mixed solvent systems of water and alcohols. The gel collapses into compact state when the concentration of alcohol is increased from water. The gel, then, swells again if the concentration of alcohol is increased further. The collapse transition of the gel occurs at the mole fraction of organic alcohol of $X_o = 0.04$ except for the system of methanol and water in which the collapse transition of the gel occurs at $X_o = 0.14$. We find that the re-swelling processes of the gel, in these binary mixed solvent systems, strongly depend on the species of the organic alcohols used.

Key words: reentrant volume phase transition, thermo-sensitive gel, water

1. INTRODUCTION

Gel is a state of matter that consists of the polymer network that swollen by the fluid. The physical properties of gel are affected by the interactions between the polymer network and the gel fluid. According to the various interactions between the polymer network and the gel fluid, the gel shows fascinating phenomena. Among others, the volume phase transition of the gel is one of the characteristic properties of the gel where the gel shows the transition between the collapsed and the swollen states. The transition is either continuous or discontinuous that depends on the composition of the gel. It has been reported by many researchers that the transition between these two states are caused by changing the external environment in which the gel is exposed to. The typical variables that control the swelling of the gel are the composition of the solvent, the temperature, pH, and so forth [1, 2]. Among others, the volume phase transition of the gel in the binary mixed solvent system is one of the fundamental properties that reflect the quality of the solvent against the polymer chain of the polymer network of the gel. The polymer chains of the polymer network collapse into the compact state when they are exposed to the poor solvent. On the other hand, if the polymer network is filled with the good solvent, the chains will expand. As a results, the gel either collapses and swells in response to the quality of the solvent. The interaction between the polymer chain of the gel and the solvent, thus, can be evaluated by measuring the swelling ratio of the gel alone.

Recently, we reported the swelling behaviors of the non-ionic poly(acrylamide) gel in the binary mixed solvent systems of water and six organic solvents. We find that the swelling curves of non-ionic

poly(acrylamide) gel can be superposable onto a single master-swelling curve. The swelling curves are, then, analyzed in terms of the mean field theory. It is found that the experimental results are well explained by the mean field theory of the swelling of the gel. These results indicate that only the average polarizability of the mixed solvent determines the swelling behaviors of poly(acrylamide) gel [3]. The results further indicate that the mole fraction of the mixed solvent is a relevant variable to describe the swelling curves of the gel.

In this report, we extend the research to the poly(N-isopropylacrylamide) gel systems. The swelling behaviors of poly(N-isopropylacrylamide) gel in the binary mixed solvent systems have been studied two decades ago [4]. After their pioneering work, however, detailed study has yet to be made until now. In this study, we study the swelling behaviors of poly(N-isopropylacrylamide) gel taking into account the following points. First of all, we measured the swelling ratio of the gel as a function of the mole fraction of the mixed solvent since the mole fraction is a relevant variable that describe the swelling curve of the gel. Besides, the gel is prepared by the photo-polymerization method by which totally non-ionic gel can be prepared, and hence we are safely neglecting the effects of the ionic groups. The experimental results, then, are analyzed in terms of the equation of state of the gel [5, 6].

2. EXPERIMENTAL

The sample gels are synthesized by the photo-polymerization method to avoid the ionization of the gel [7]. The non-ionic photo-initiator used here is 2,2'-azobis[2-methylene-N-(2-hydroxyethyl)propionamide], which is kindly supplied from Wako Chemicals Co.. This initiator does not contain ionic group, and hence the gels synthesized by this initiator are totally non-ionic.

The main-chain component, *N*-isopropylacrylamide, is kindly supplied from Kohjin Co. and is used after re-crystallization by the standard method. The cross-linker, *N,N'*-methylene-bis-acrylamide, is purchased from BioRad Co. and used without further purification.

The total amount of the gel is fixed at 700mM while the mole fraction of cross-linker is fixed at 0.01. The monomer, the cross-linker, and the initiator are dissolved into the distilled and de-ionized water, which is prepared by Mili-Q system. The solution is de-gassed for 30min and then is shone by UV light at a wavelength of 360nm. The sample gels are polymerized in capillaries of the inner diameter of $d_0 = 141\mu\text{m}$. The gel is taken out of the capillary and then extensively washed by distilled and de-ionized water. The solvent systems used here are the binary mixed solvent systems of water and four organic alcohols: methanol, ethanol, 1-propanol, and 2-propanol (reagent grade). These alcohols are purchased from Wako Chemical Co. and used without further purification.

The swelling ratio of the gel is measured by a measuring system that consists of a microscope (Diaphoto TMD, Nikon) and a video scaler (Nikon Instech). The details of the system have been reported elsewhere [8]. By using this measuring system, the swelling curves of the gel can be determined using only single piece of the gel sample. The temperature is controlled to 20.0°C to an accuracy better than 0.01°C.

3. RESULTS

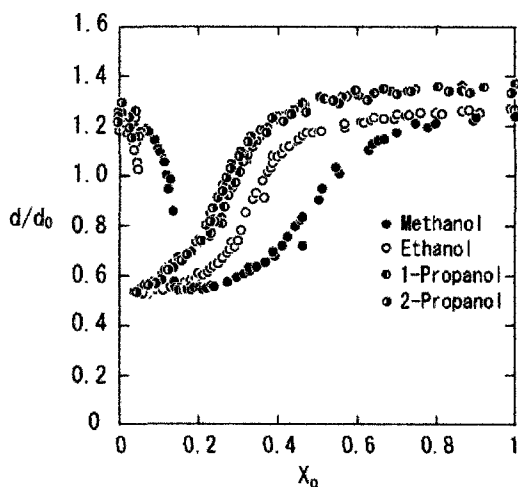


Figure 1. The equilibrium swelling curves of poly(*N*-isopropylacrylamide) gel in four binary mixed solvent systems of water and the organic alcohols. The mole fraction of the organic alcohol in the mixed solvent is represented by X_0 .

Figure 1 shows the swelling curves of non-ionic poly(*N*-isopropylacrylamide) gel. The results are plotted as a function of the mole fraction of the organic alcohol in the binary mixed solvent with water. Firstly, the gel that is swollen in water gradually collapses when the concentration of the organic alcohol is increased. Then, the volume of the gel decreases discontinuously. The discontinuous volume phase transition occurs at the mole fraction of the organic alcohols of about 0.04 for ethanol,

1-propanol, and 2-propanol. It is clear from these results that the discontinuous volume phase transition point of the gel is shifted to higher mole fraction of about 0.14 in the case of the mixed solvent of water and methanol.

At above the discontinuous volume phase transition point, the gel swells with the increase of the organic alcohol component in the mixed solvent systems. In this region, the swelling processes of the gel are continuous. In addition to this, the concentration of the re-swelling point depends strongly on the species of the organic alcohol used. For instance, the gel swells quickly in the mixed solvent of water and 2-propanol. In contrast, the swelling of the gel is slow in the mixed solvent of water and methanol. The swelling curve is, thus, shifted to higher concentration region of alcohol in the case of the mixed solvent of water and methanol than other alcohols. The re-swelling point of the gel increases in the order of 2-propanol, 1-propanol, ethanol, and methanol. The transition points of the re-swelling processes, which is determined from the middle point of the swelling curves, are 0.49 for methanol, 0.33 for ethanol, 0.28 for 1-propanol, and 0.26 for 2-propanol. The swelling ratio of the gel in pure alcohols becomes larger in the same order given above. It is found that the swelling behavior of the gel is reversible except in the vicinity of the discontinuous volume phase transition region. We observed a very weak hysteresis around the immediate vicinity of the discontinuous volume phase transition point.

4. DISCUSSION

Poly(*N*-isopropylacrylamide) is known to show the volume phase transition in water in response to the temperature change. The gel collapses into compact state when temperature is raised above 34°C. The gel is, therefore, sometime called as the "thermo-sensitive" gel. This characteristic swelling behavior is thought as the results of the hydrophobic interaction between water and *N*-isopropyl groups in the side chain. Although the thermo-reversible volume phase transition of poly(*N*-isopropylacrylamide) gel has been studied extensively, the re-entrant volume phase transition in the binary mixed solvent systems has yet to be studied in detail. The results shown in Fig. 1 indicate a typical feature of the re-entrant volume phase transition of poly(*N*-isopropylacrylamide) gel.

The results shown in Fig. 1 is similar with the one obtained in the previous study [4]. The details are, however, different from previous results. For instance, the transition points are almost the same for ethanol, 1-propanol, and 2-propanol if the concentration is expressed by the mole fraction of the organic alcohol in the mixed solvent. Besides, the concentration of the collapse transition point is very low that is about 0.004 for these three mixed solvent systems. The only exception is the mixed solvent system of water and methanol. In this binary mixed solvent system, the concentration of the discontinuous transition point is shifted to higher mole fraction of organic component of about 0.14. These swelling behaviors of poly(*N*-isopropylacrylamide) gel in the mixed solvent systems of water and organic alcohols are qualitatively the same with poly(acrylamide) gel systems [3]. In the

case of poly(acrylamide) gel, the collapse transition of the gel is thought to be related to the disruption of the dynamic cluster of water molecules that is created around the polymer chains of the gel. The results obtained here, hence, also suggest that the collapse of poly(N-isopropylacrylamide) gel at lower concentrations of the organic component may be caused by the extinction of the dynamic cluster structure of water molecules around the hydrophobic side group. These results are in good agreement with the dielectric studies of the binary mixtures of water and organic alcohols [9]. The results obtained here are, however, quantitatively different from the poly(acrylamide) gel system. In the case of poly(acrylamide) gel, the transition point is same for most solvent systems, and hence, the swelling curves of the gel are expressed by a single master curve. The total swelling curves of poly(N-isopropylacrylamide) gel obtained here, however, could not be superposed onto a master swelling curve. It strongly suggests that the interaction between N-isopropylacrylamide and the organic alcohols plays essential roles in this system especially at higher concentration region of the organic alcohols.

The gel swells in the good solvents. Hence, the larger the swelling ratio, the better the quality of the solvent. The swelling ratio of the gel in the pure alcohols increases in the order of methanol, ethanol, 1-propanol, and 2-propanol. The results indicate that the quality of the solvent becomes better as the hydrophobic nature of the solvent increases. The transition point of the re-swelling process of the gel in each mixed solvent is consistent with above results.

The results obtained here seem to suggest that the swelling curves of poly(N-isopropylacrylamide) gel can be divided into two regions. One region is the swollen region below the discontinuous collapse transition point. In this region, the swelling of the gel is only determined by the formation of the dynamic clusters of water molecule in the solvent. Poly(N-isopropylacrylamide) is known as the hydrophobic polymer, which is essentially insoluble in water. However, the cage structure of water is formed around the hydrophobic side groups that help the polymer to dissolve into water. When the cage structure of water is disrupted, either by heating or the addition of the organic solvent, the polymer chain segregate from the solution. In the case of the gel, the segregation of the polymer chain leads the gel to collapse. Since the extinction of the cluster structure is determined only by the concentration of the organic component in the mixed solvent, the collapse transition of the gel occurs at the same mole fraction of the mixed solvent. The only exception is the system of water and methanol in which the disruption of the dynamic cluster structure of water molecules occurs at rather higher concentration region of methanol. The results obtained here quantitatively agree with the dielectric studies of the mixtures of water and alcohols [9]. The second region is the region where the gel shows the re-swelling behavior, that is, the higher concentration region of the organic components. In this region, the swelling of poly(N-isopropylacrylamide) gel strongly depends on the species of organic alcohol used. The quality of the organic solvent against the polymer chain directly determines the entire swelling behaviors of poly(N-isopropylacrylamide) gel in this region. The

swelling ratios of the gel in pure alcohols as well as the transition point of the re-swelling process indicate that the quality of these alcohols as the solvent for poly(N-isopropylacrylamide) becomes better in hydrophobic alcohols than the hydrophilic one. The continuous swelling of the gel in this region indicates that the interaction parameter between the polymer and the solvent is a smooth function of the mixing ratio of the solvent. The results are confirmed by the measurements of the composition of the mixed solvent "in the gel" and "the external solvent" [10]. It indicates that the specific interaction such as the characteristic adsorption of the solvent can be negligible at higher concentration region of the organic alcohols. It further suggests that the single solvent approximation is not too worth in this region. It is, however, suggested by this study that the characteristic adsorption becomes dominant in the discontinuous volume phase transition point of the gel. The three body interaction between N-isopropylacrylamide, the organic alcohol and water should be taking into account in this region.

It may be, thus, of interest to analyze by the re-swelling curves of the gel in terms of the mean field theory at the higher concentration region of the organic alcohols. In Fig. 2, we show the preliminary fitting results of the swelling curves using the mean field theory of the swelling of gel given as follows.

$$\begin{aligned} \tau &= 1 - \frac{\Delta F}{kT} \\ &= -\frac{\nu v}{N_A \phi_0^2} \left[(2f+1) \left(\frac{\phi}{\phi_0} \right) - 2 \left(\frac{\phi}{\phi_0} \right)^{1/3} \right] + \frac{2}{\phi} + \frac{2 \ln(1-\phi)}{\phi^2} + 1 \end{aligned}$$

Here, τ , N_A , k , and T are the reduced temperature, Avogadro's number, Boltzmann constant, and the temperature. The free energy of interaction between polymers and the polymer and the solvent is expressed by ΔF and ν the molar volume of the solvent. ϕ_0 and ϕ are the volume fraction of the polymer network at the random configuration and that of the equilibrium state. Since the gel is totally non-ionic, f is chosen as 0. The value of ϕ_0 can be determined accurately from the composition of the pre-gel solution to $\phi_0 = 0.090 \pm 0.005$. The molar volume of the solvent is assumed to be the same with that of water. The swelling ratio of the gel is related to the volume fraction of the polymer network as $(d/d_0)^3 = \phi_0/\phi$. Under these conditions, the best fitting parameters of ΔF and ν are determined. The results are given in Fig. 2. The fitting is not better at higher concentration region of the organic alcohols. It, however, reproduces the swelling behaviors of the gel in the re-swelling region rather well. Further detailed analyses of the results are required for the full understanding of the re-entrant volume phase transition of poly(N-isopropylacrylamide) gel. Such studies are now under way and will be reported elsewhere.

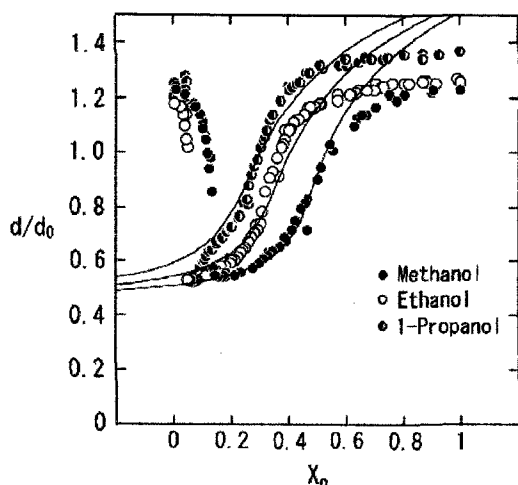


Figure 2. Preliminary fitting results of the swelling curves of poly(*N*-isopropylacrylamide) gel.

5. CONCLUSION

The re-entrant volume phase transition of poly(*N*-isopropylacrylamide) gel in the binary mixed solvent systems of water and the organic alcohols. By measuring the swelling curve of the gel as a function of the mole fraction of the organic alcohol in the mixed solvent, we find that the collapse transition of the gel occurs at the same mole fraction of the mixed solvent. The only exception is the mixed solvent of water and methanol in which the gel collapses into compact state at rather higher concentration of methanol. We also find that

the swelling ratio of the gel increases monotonically at higher concentrations of the organic alcohols. The results suggest that the quality of the mixed solvent changes monotonically with the mixing ratio. It is, however, suggested that the swelling of the gel in the higher concentration region of the organic alcohols strongly depends on the species of alcohol used. The results, thus, suggest that the interaction between the *N*-isopropylacrylamide and the organic alcohols plays essential roles in the swelling of poly(*N*-isopropylacrylamide) gel in this region.

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