Notes

Swelling Behaviors of Poly(*N*-isopropylacrylamide) Gel in Poly(ethylene glycol)–Water Mixtures

Toru Ishidao,* Masaaki Akagi, Hiroshi Sugimoto, Yoshio Iwai, and Yasuhiko Arai

Department of Chemical Engineering, Kyushu University, Fukuoka, 812 Japan

Received July 13, 1993
Revised Manuscript Received October 1, 1993

1. Introduction

It has been shown that some gels undergo discontinuous volume changes depending on external conditions (e.g., temperature[1–5]). Several gels [in particular, poly(*N*-isopropylacrylamide) (NIPA) gel] are expected to be applied as a size-selective extraction solvent.[6] Recently, it is reported that the NIPA gel with an entrapped enzyme shows a discontinuous volume change according to both substrate and product composition changes within the gel phase.[7] To apply the gel as an extractor or biochemical sensor, we should study on fundamentals such as (1) volume change of the gel in binary mixtures (i.e., low molecular weight solvent–water, oligomer–water, or polymer–water) and (2) concentrations inside and outside the gel. Furthermore, fundamental knowledge on mesh sizes of the gel network and interaction between the network and solvents become very important. Some researchers have reported a variety of results in reference to hydrophobic interaction in the thermoshrinking gel,[2,3] composition of solvents uptaken in the gel,[8–10] and deswelling of the gel in polymer solution.[11,12] These mechanisms of swelling behavior have become gradually clear by these considerable contributions.

In this paper, the swelling behaviors of NIPA gel in PEG200–water, PEG1000–water, PEG6000–water, PEG20000–water, and PEG50000–water mixtures are measured and discussed.

2. Experimental Section

Materials. *N*-Isopropylacrylamide (NIPA; main-chain monomer) purchased from Eastman Kodak Co., Ltd., was recrystallized from a benzene–hexane mixture (27 vol % of benzene) at room temperature and dried under vacuum at room temperature for 1 day. *N,N'*-Methylenebisacrylamide (BIS; cross-linker), ammonium peroxodisulfate (AP; initiator), *N,N,N',N'*-tetramethylethylenediamine (TEMED; accelerator), and 2-propanol were purchased from Nakarai Chemical, Ltd. These reagents were all special grade and used without further purification. Their purities are believed to be more than 98%, 98%, and 99.5% for AP, TEMED, and 2-propanol, respectively. Reagent-grade poly(ethylene glycol)s (PEG200, PEG1000, PEG6000, PEG20000, and PEG50000) were purchased from Wako Pure Chemical Industries, Ltd. The weight-average molecular weights (M_w) of PEG1000, PEG6000, PEG20000, and PEG50000 measured by gel permeation chromatography are 1000 (M_w/M_n = 1.11), 8800 (M_w/M_n = 1.02), 21 400 (M_w/M_n = 1.08), and 37 100 (M_w/M_n = 1.31), respectively, where M_n is the number-average molecular weight. PEG200 was used without further purification, and its purity is believed to be more than 99.9%. The other PEGs were purified under vacuum at room temperature for 1 day. Water was distilled, degassed, and deionized using a Millipore Milli-Q water purification system.

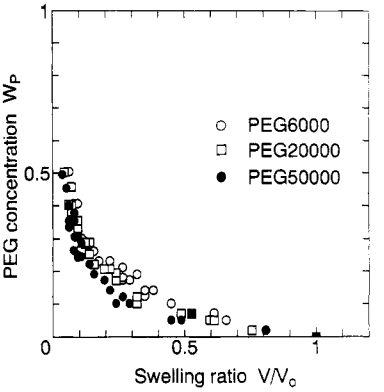

Figure 1. Swelling ratio V/V_0 of the NIPA gels in PEG6000–water, PEG20000–water, and PEG50000–water mixtures with PEG mass fraction W_P at 25 °C: (○) PEG6000; (□) PEG20000; (●) PEG50000.

Synthesis. NIPA gels were prepared by free-radical polymerization in water at 0 °C, according to the method reported by Otake et al.[3] NIPA monomer (150 mmol) and BIS (1.5 mmol) were dissolved in 125 mL of water, while AP (0.8 mmol) was dissolved in another 125 mL of water. The two solutions were cooled to 0 °C and then mixed. Further, TEMED (0.2 mL) was added to the mixture. After 30 min, this mixture was transferred into glass tubes (0.85 mm in inner diameter and 50 mm in length) for gelation. After 1 day, the cylindrical gel samples were taken out of the glass tubes using hydraulic pressure. The gels were immersed in a 3 vol % 2-propanol aqueous solution for 1 week to wash away any residual chemicals. The swollen gel was cut, and about 5-mm-length chips were obtained. These chips were soaked in an excess amount of pure water (about 500 mL) to elute 2-propanol.

Measurement of Gel Volume. The NIPA gel samples (about 5-mm-length chips) were immersed in vials (100 mL) filled with a PEG–water solution. The volume of solution in the vial was much larger than the gel volume (about 10 000 times) so that the concentration of the solution was practically unchanged. The vials were then set in a temperature-controlled water bath (25 ± 0.1 °C) at least for 3 days. The diameter of the gels, D, was measured by a calibrated microscope at swelling equilibrium condition. Assuming that the gel swells isotropically, the swelling ratio of the gel was calculated as $V/V_0 = (D/D_0)^3$, where V and V_0 are the volumes of gel at equilibrium and reference conditions, respectively. There are various standards in evaluation of V_0. Sometimes, V_0 at the preparation condition and dry state are adopted. In this study, V_0 is given as the swelling equilibrium volume in pure water at 25 °C. The volumes of swelling gel are considered to be accurate within 10% judging from the reproducibility.

3. Experimental Results

Figure 1 shows the concentration dependence of the swelling ratios for various aqueous PEG solutions: PEG6000–water, PEG20000–water, and PEG50000–water mixtures. Measurement in the range $W_P > 0.5$ could not be carried out because PEGs were not dissoluble. The present gels deswell in the whole concentration range measured. The degree of deswelling becomes large in the high external PEG concentrations. As the molecular weight of PEG increases, the swelling ratio becomes smaller at the same W_P.

0024-9297/93/2226-7361$04.00/0

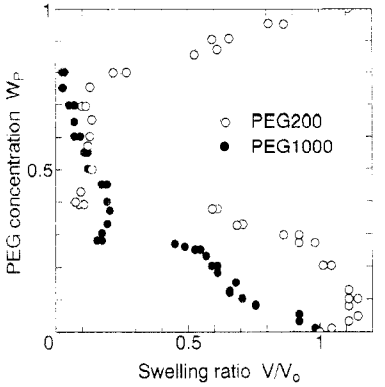

Figure 2. Swelling ratio V/V_0 of the NIPA gels in PEG200–water and PEG1000–water mixtures with PEG mass fraction W_P at 25 °C: (○) PEG200; (●) PEG1000.

Figure 2 shows the swelling ratios of the NIPA gels in PEG200–water and PEG1000–water mixtures. In the PEG1000–water mixture, discontinuous-volume phase transition was observed at $W_P = 0.27$. The gel was slightly reswollen from $W_P = 0.27$ to 0.4, and deswelling behavior was again observed in the range $W_P > 0.4$. A similar swelling behavior was observed in the PEG200–water mixture up to $W_P = 0.7$, and volume phase transition was observed at $W_P = 0.39$. However, the gel was reswollen in the range $W_P > 0.7$; that is, reentrant swelling behavior is shown. Further, slight swelling was observed in the range $W_P = 0.0$–0.07.

4. Discussion

In the PEG6000–water, PEG20000–water, and PEG-50000–water mixtures, as shown in Figure 1, the NIPA gels exhibited continuous deswelling behavior. A large amount of PEG could hardly penetrate into the gel network because PEG chains are long enough. This fact is supposed from the result of measurements by Bastide et al.[11] In fact, a small amount of linear polymer (lower molecular weight PEG) penetrates into the network.

In the PEG1000–water mixture as shown in Figure 2, the degree of deswelling up to the transition point is much smaller than that in the PEG6000–water mixture shown in Figure 1. It can be considered that a significant number of PEG1000 chains may penetrate into the network. The osmotic pressure generally depends on the amount of PEG in solution. For the same concentration W_P, therefore, the osmotic pressure of the PEG1000–water mixture is larger than that of the PEG6000–water mixture. On the contrary, the gel in the PEG1000–water mixture swells much more compared with the gel in the PEG6000–water mixture, because of penetration of PEG1000 into the gel network. Freitas et al.[6] have reported water absorption efficiencies of the NIPA gel for extraction of aqueous PEG solutions. The results for dilute feeds of PEG show that the efficiencies for PEG400, -3400, -8000 and -18500 are 10, 30, 56, and 80%, respectively. Consequently, the gels absorb low molecular weight PEGs but exclude high molecular weight PEGs. This result coincides with the present work.

A considerable deswelling accompanying volume phase transition at $W_P = 0.27$ is observed in the PEG1000–water mixture. This swelling behavior is similar to the results by Mukae et al.[8] They suggested that the swelling of the NIPA gel in water may be caused by a strong hydration around amide groups in polymer networks. Therefore, by addition of a small amount of organic solvent into water, the hydration shell is partly destroyed, and then dehydrated polymer chains associate to form a collapsed structure. Though the PEG chain used in this work is much longer than that of solvents (methanol, ethanol, 1-propanol, and 2-methyl-2-propanol) used by them, it can be considered that the same phenomena arises inside the gel. Slightly reswollen behavior shown in the range $W_P = 0.27$–0.4 should be discussed by further experimentation on PEG1000 distribution inside and outside the gel.

The NIPA gel shows the reentrant phenomenon in the PEG200–water mixture. This swelling behavior is quite similar to the results on the NIPA gel in low molecular weight solvent–water mixtures.[1,2,8] The deswelling of the polymer network is a jumpwise first-order phase transition ($W_P < 0.5$), and the reswelling is realized ($W_P > 0.5$). This reswelling behavior may be due to the adsorption of PEG200 molecules upon the collapsed gel network, which is supposed by Mukae et al.[8]

5. Conclusions

The deswelling of the NIPA gel in PEG6000–water, PEG20000–water, and PEG50000–water mixtures depends mainly on the osmotic pressure of the solution outside the gel. A jumpwise volume phase transition observed in the PEG1000–water mixture can be considered to be caused by dehydration of water from the network. The reswelling in the PEG200–water mixture may be due to the adsorption of PEG200 molecules upon the collapsed gel network. These suppositions should be examined by further experimentation on PEG distribution inside and outside the gel. The results for the PEG distribution will be presented in a forthcoming paper.

Acknowledgment. We gratefully acknowledge the financial support provided by the Grant-in-Aid for Scientific Research of the Ministry of Education, Science and Culture, Japan (B-05453096; 1993).

References and Notes

(1) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *87*, 1392.
(2) Hirotsu, S. *J. Phys. Soc. Jpn.* **1987**, *56*, 233.
(3) Otake, K.; Inomata, H.; Konno, M.; Saito, S. *Macromolecules* **1990**, *23*, 283.
(4) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(5) Wada, N.; Yagi, Y.; Inomata, H.; Saito, S. *Macromolecules* **1992**, *25*, 7220.
(6) Freitas, R. F. S.; Cussler, E. L. *Chem. Eng. Sci.* **1987**, *42*, 97.
(7) Kokufuta, E.; Tanaka, T. *Macromolecules* **1991**, *24*, 1605.
(8) Mukae, K.; Sakurai, M.; Sawamura, S.; Makino, K.; Kim, S. W.; Shirahama, K. *J. Phys. Chem.* **1993**, *97*, 737.
(9) Ishidao, T.; Mishima, K.; Iwai, Y.; Watanabe, T.; Arai, Y. *J. Assoc. Mater. Eng. Resour. Jpn.* **1989**, *2*, 53.
(10) Ishidao, T.; Iwai, Y.; Hashimoto, Y.; Arai, Y. *Polym. Eng. Sci.*, in press.
(11) Bastide, J.; Candau, S.; Leibler, L. *Macromolecules* **1981**, *14*, 719.
(12) Vasilevskaya, V. V.; Khokhlov, A. R. *Macromolecules* **1992**, *25*, 384.