Volume Phase Transition in Neutral Copolymer Gels

Takaharu Okajima and Shunsuke Hirotsu

Department of Life Science, Graduate School of Bioscience and Biotechnology, Tokyo Institute of Technology,
Nagatsuta-cho, Midori-ku, Yokohama 226-8501, Japan
Fax: 81-45-924-5732, e-mail: tokajima@bio.titech.ac.jp, shirotu@bio.titech.ac.jp

A volume phase transition of neutral copolymer gels composed of N-isopropylacrylamide (NIPA) and acrylamide (AA) monomers has been investigated in detail. These gels were polymerized in a buffer solution at pH=7.0 to prevent hydrolyzing a part of the acrylamide groups into acrylic acid groups. It is found that the transition temperature at which the neutral copolymer gels reach a shrunken phase increases with increasing the molar ratio of AA monomer to NIPA monomer C_{AA}/C_{NIPA}. The transition becomes continuous even C_{AA}/C_{NIPA} is as small as 0.7%. On the contrary, the transition temperature of NIPA gels in AA solution decreases with increasing C_{AA}/C_{NIPA}. The copolymer gels used in the present study are useful for studying the phase transition behavior of gels having different polymer-solvent interactions because NIPA and AA have the lower-critical solution temperature and the upper-critical solution temperature, respectively.

Key word: volume phase transition, N-isopropylacrylamide, acrylamide, gels, copolymer

1. INTRODUCTION

Poly-N-isopropylacrylamide (NIPA) gels in pure water undergo the volume phase transition at ~34°C near the critical point. This is a binary system consisting of NIPA network and water solvent. In the case of ternary systems, gels exhibit various behaviors with respect to the phase transition. For example, NIPA gels in binary solvents such as an alcohol-water mixture exhibit a reentrant phase transition in which the gels shrink in the intermediate solvent composition and swell in both water-rich and alcohol-rich compositions.[1-3] Furthermore, ionized gels in which charged monomers such as acrylic acid are substituted for a part of neutral NIPA monomers in chains undergoes large discontinuous volume transition at temperature higher than that in NIPA gels.[1] These phenomena have been semi-quantitatively understood on the basis of a mean-field theory, the so-called Flory-Huggins theory.[1]

On the other hand, other ternary systems have not been fully investigated. One such system is neutral copolymer gels consisting of two different neutral monomers in a single solvent. A swelling equilibrium of this gel could be attained only by satisfying the equilibrium between the osmotic pressures of gels resulting from the mixing free energy and the elastic energy.[4] This situation is essentially different from that in a single gel in binary solvents because in the latter the relative composition of solvent inside the gel is different from the composition of the surrounding solvent.[5]

In the present study, we measured the detailed swelling of neutral copolymer gels composed of NIPA and acrylamide (AA) monomers. The phase diagram on NIPA gels is opposed to that on AA gels, i.e., the former has the lower-critical solution temperature and the latter being the upper-critical solution temperature. Thus, the present copolymer gels (NIPA-co-AA gels) would be useful for studying the phase transition behavior of gels having different polymer-solvent interactions. Swelling of NIPA gels in AA solution was also measured.

2. PREPARATION METHOD

A series of copolymer gels composed of NIPA and AA monomers were prepared by radical polymerization. The NIPA monomer concentration C_{NIPA} and the AA monomer concentration C_{AA} of mM units were varied by keeping the total monomer concentration to be 700mM. N,N'-methylenebisacrylamide (BIS) was used as a cross-linker, the concentration of which was fixed at 8.62mM. The NIPA and AA monomers and BIS were dissolved in a buffer solution (pH7) which consists of 0.1M Tris(hydroxymethyl)aminomethane (Tris) and hydrogen chloride to prevent hydrolyzing a portion of the acrylamide groups into acrylic acid groups. Ammonium persulfate as a initiator and N,N,N',N'-tetramethylethylenediamine (TEMED) as a accelerator were added in the solution for gelation to occur, and the polymerization was initiated in a test tube including capillaries with 1mm i.d. at 5°C.

The resultant copolymer gels were taken from capillaries and washed in a large amount of deionized and distilled water to remove unreacted molecules and electrolyte molecules such as TEMED, Tris and hydrogen chloride in the gels. Then, the washed gels were inserted in thermostated cell surrounding a pure water to measure the swelling equilibrium as a function of temperature.

3. RESULTS AND DISCUSSION

Figure 1 shows the swelling degree d/d_0 of NIPA-co-AA gels as a function of temperature. It is seen that the

Volume Phase Transition in Neutral Copolymer Gels

volume change becomes fairly continuous except poly-NIPA gels. The temperature at which the gels almost collapse increases remarkably with increasing C_{AA}. Note that the discontinuity of the volume change disappears even if AA monomers are slightly substituted for NIPA monomers, $C_{AA}/C_{NIPA}=0.7\%$, which approximately corresponds to one AA monomer in three subchains.

In Fig.2, the swelling degree of NIPA-co-AA gels at different high temperatures is replotted as a function of C_{AA}. The shrunken size of NIPA-co-AA gels seems to be almost independent of C_{AA}. The volume size of AA monomer is smaller than that of NIPA monomer. Thus, the net volume fraction of copolymer gels inherently decreases as the increase of AA monomers included in network. This is one of the reason why the shrunken size of gels having larger C_{AA} is observed to be almost the same as that of gels having smaller C_{AA}. Another possible explanation is that water molecules would be excluded from the shrunken gels as C_{AA} increases. In this stage, however, we cannot describe any further explanation.

Fig.3 Swelling ratio of NIPA gels in AA monomer solution. The AA monomoer concentration C_{AA} are ● :0mM ,○:350mM, ■:700mM.
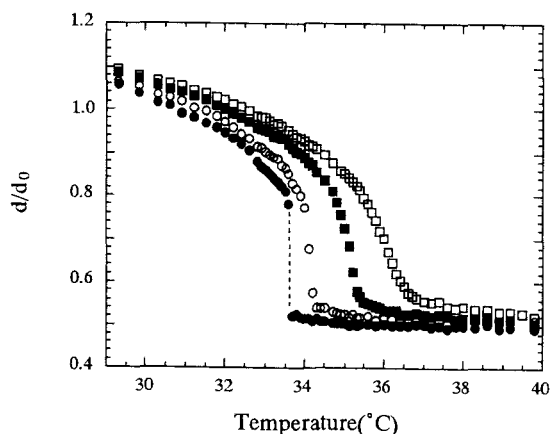

Temperature(°C)
Fig.1 Swelling curves of NIPA-co-AA gels on heating process. Total mount of monomers such as NIPA and AA was fixed at 700mM. The amounts of AA are as follows: ●:0mM, ○:5.0mM, ■:15mM, □:25mM.
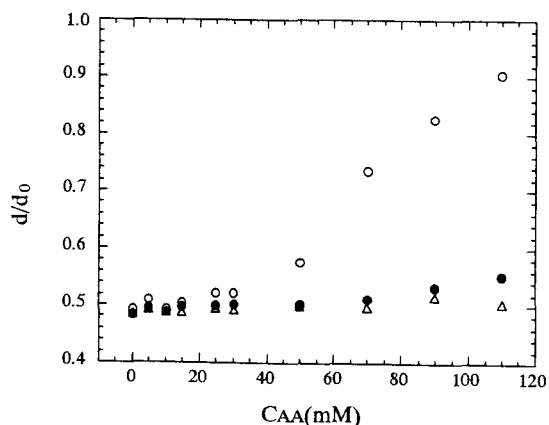

C_{AA}(mM)

Fig.2 Swelling degree of NIPA-co-AA gels as a function of C_{AA} at different temperatures: ○:39.8°C, ●:50.4°C, △:62.4°C.
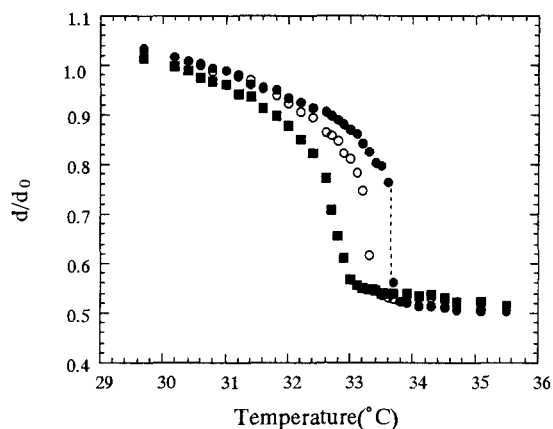
Figure 3 shows the swelling degree of NIPA gels in AA monomer solution as a function of temperature. With increasing C_{AA} in water solvent, the transition temperature of NIPA gels decreases, and the transition becomes apparently continuous. In spite of the large amount of C_{AA} (700mM) the change of transition temperature due to the addition of AA monomer in water was less than 1°C.

In summary, we measured the swelling of gels in two sets of ternary systems consisting of NIPA, AA, and water. One is that the neutral copolymer gels composed of NIPA and AA in a single water solvent, and another is NIPA gels in binary systems composed of AA monomer and water. The effect of the addition of C_{AA} on the volume phase transition of gels is conspicuously observed in the former system as compared with the latter one. The transition temperature increase with increasing C_{AA} in NIPA-co-AA gels in water and vice versa in NIPA gels in AA solution. This contrary feature on the transition might be explained by Flory-Huggins theory. The further considerations are now in progress.

References
[1] For a review, see "Responsive Gels: Volume Phase Transitions I, and II", Ed. K.Dusek , Springer-Verlag, Berlin, Adv.Polym.Sci. Vols. 109 & 110(1993).
[2] S.Hirotsu, J.Phys.Soc.Jpn. 56, 233-42(1987).
[3] T.Amiya, Y.Hirokawa, Y.Hirose, Y.Li, T.Tanaka, J.Chem.Phys. 86, 2375-79(1987).
[4] P.J.Flory, "Principles of Polymer Chemistry , Cornel University Press, N.Y. (1953) pp.541-94.
[5] A.R.Khokhlov in Ref.1.