

Effect of Introduced Electric Charge on the Volume Phase Transition of *N*-Isopropylacrylamide Gels

Hideya Kawasaki, Shigeo Sasaki, and Hiroshi Maeda*

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka, 812 Japan

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We report the temperature-induced volume phase transition behavior of a copolymer gel of *N*-isopropylacrylamide and sodium acrylate (NIPA-AA) at pH 9.5 in the range of low mole fraction of the acrylate x ($x < 0.01$), either in salt-free aqueous solution or NaCl aqueous solutions. Introduction of electric charges into the network switched the temperature-induced volume change of the gel from a discontinuous to a continuous type in salt-free aqueous solutions. The switching of the regime took place within a very narrow range of x around a very small value of 0.002. The continuous volume change in salt-free aqueous solution was transformed into the discontinuous one in NaCl aqueous solutions of 0.1 and 0.3 M. Effects of the two factors, the charged monomer fraction and the ionic strength, were explained in a unified manner in terms of the Donnan osmotic pressure. We found that the continuous or the discontinuous regime of NIPA-AA gel was well characterized, respectively, by the high or low osmotic pressure. Similar results were obtained with NIPA–sodium poly(styrene sulfonate) copolymer gels.

Introduction

Polymer gels are known to exist in two phases, the swollen and the shrunken state. Some gels transform between the two states discontinuously according to a variation in external conditions: temperature, solvent composition, or pH.^{1–9} The behavior is known as the volume phase transition of gels.^{2,10}

For the temperature-induced volume phase transition, *N*-isopropylacrylamide (NIPA) gel has been reported to exhibit a discontinuous volume change with temperature.¹¹ Hirotsu et al. have reported the temperature-induced phase transition behavior for copolymer gels of *N*-isopropylacrylamide and sodium acrylate (NIPA-AA).¹² The introduction of charges to NIPA chains enhanced the discontinuity of the volume transition: the transition temperature and the width of transition both increased with the amount of acrylic acid component in the network. The increase in the discontinuity was explained by increased Donnan osmotic pressure of counterions on the basis of the Flory–Huggins theory combined with the ideal Donnan osmotic pressure.¹² Another theory also has reproduced the volume phase transition of ionic gels.¹³ Prausnitz et al., however, have reported experimentally that the volume change behavior of NIPA-AA gel including pure NIPA gel is continuous and the volume change becomes smoother as the gel ionization is increased by changing solution pH.¹⁴ Different behaviors of the temperature-induced volume phase transition of NIPA-AA gel with the ionization have not been clarified.

Recently, we have found that the discontinuity of the volume transition of NIPA-AA gel increased with the amount of uncharged carboxyl groups at pH < 6.3, but the volume change behavior became continuous at pH > 7.5 as the content of ionized carboxyl groups increased.¹⁵ The potentiometric titration for NIPA-AA gel has revealed that the dissociation constant of carboxyl groups in NIPA-AA gel decreases with increasing temperature above 34 °C. The discontinuous volume change at pH < 6.3 was correlated with the decrease in the carboxyl ionization of NIPA-AA gel, and a significant fraction of the carboxyl group in the shrunken gel was unionized. On the other

hand, for NIPA-AA gels at pH > 7.5 which undergo the continuous volume change, almost all the carboxyl groups were ionized even at high temperature. Our results suggest that an introduction of electric charge into the NIPA chains alters the discontinuous volume change of NIPA gel to the continuous one. It was also suggested that the decrease in the ionization with increasing temperature, which reduced the corresponding Donnan osmotic pressure of counterions, played an essential role in the discontinuous volume change of NIPA-AA gel.

In this study, we are concerned with the effect of electric charge on the volume phase transition of NIPA gel since charged groups on the gel network have been considered to play an essential role in the discontinuous volume change of gels.^{2,4,12,13} An understanding of the role of electric charge in the gel swelling is important to a complete description of the volume phase transition of the gel.

In NIPA-AA gel at pH < 6.3, we need to consider the change of the carboxyl ionization in the temperature-induced volume phase transition as mentioned above, which is quite complex when trying to examine the effect of electric charge on the volume phase transition. In order to avoid this complexity, we carry out the swelling measurement of the gel using NIPA-AA gel at pH 9.5, where all carboxyl groups are dissociated. The introduction of ionized groups into the gel network yields the Donnan swelling osmotic pressure due to counterions within the gel. A correlation between the Donnan osmotic pressure and the swelling behavior of NIPA-AA gel will be examined by changing the composition of acrylate in the gel and the ion strength. The volume change of ionic copolymer NIPA gels containing sodium styrenesulfonate residues (NIPA-NaPSS) in water will be also examined. The ionic groups in this copolymer gel are completely dissociated at any pH.

Experimental Section

NIPA-AA gels were prepared by radical copolymerization in aqueous solutions of *N*-isopropylacrylamide, sodium acrylate or sodium styrenesulfonate, and *N,N'*-methylenebis(acrylamide) (3.5 mM). The total residue concentration of NIPA-AA gel was fixed to be 700 mM. The polymerization was initiated by

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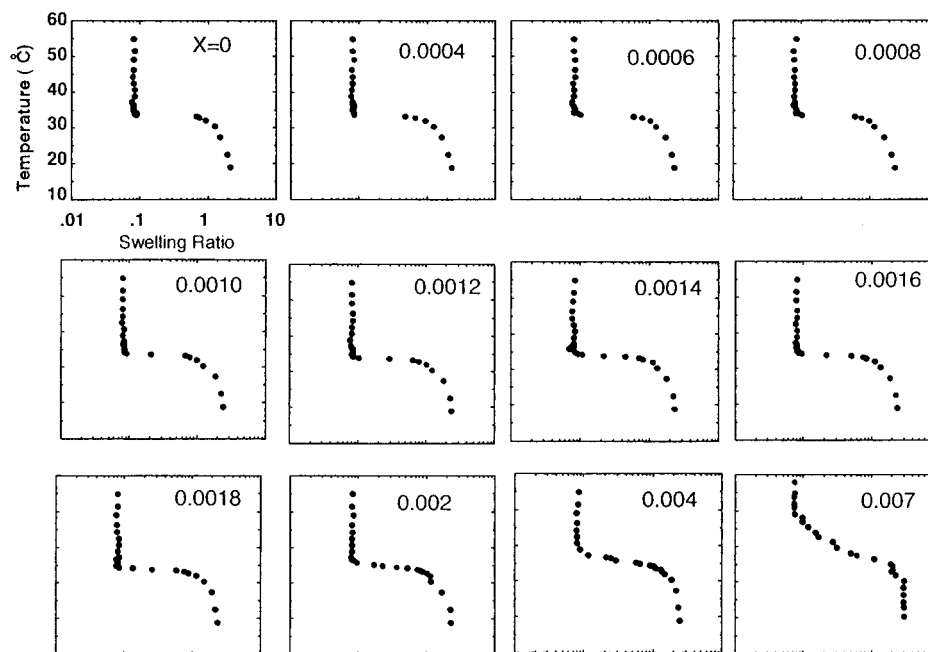


Figure 1. Temperature dependence of the swelling ratios for NIPA-AA gels with various compositions at pH 9.5 in salt-free polyelectrolyte buffer solution. The mole fraction of acrylate x is shown in the figure.

ammonium persulfate (APS), accelerated by N,N',N',N' -tetramethylethylenediamine (TEMED), and carried out at 5 °C for 24 h. Gels with a mole fraction of the acrylate x in pregelation solution are denoted as NIPA-AA(x). We carried out hydrogen ion titration on two NIPA-AA copolymer samples ($x = 0.010$ and 0.035) and found the acrylate mole fractions as 0.0085 and 0.030, respectively. We expect similar relationship for the copolymer gels. NIPA-NaPSS gels were prepared in the same way as that employed for the preparation of NIPA-AA gels. The gel synthesized in a capillary (0.296 mm diameter) was cut into a rod form (20 mm length) and rinsed thoroughly with distilled water and then was dried gently. For NIPA-AA gel, the dried gel fixed in a sample holder was immersed into the solution, the pH of which was well stabilized as described below. For NIPA-NaPSS gel, it was immersed into pure water.

Gel volume, V , was determined from the diameter of rod-shaped gels, d , measured by using the optical microscope. The swelling ratio was defined as $V/V_0 = (d/d_0)^3$, where d_0 was the diameter of the capillary in which the gel was synthesized. The pH of the gel was kept at 9.5 ± 0.2 by equilibrating the gel with the 5 mM polyacrylate (PAA) solution. To avoid the salt effect on the volume phase transition behavior of gels,^{7,16} the polyacrylate buffer was used in this study instead of the buffer of low molecular weight electrolytes. The molecular weight of PAA was more than 1×10^6 according to the supplier (Wako Chemicals Co. Ltd.). The temperature in the gel swelling experiment was controlled within ± 0.1 °C.

Results and Discussion

The temperature dependence of the swelling ratios of NIPA-AA gels in the course of raising the temperature at pH 9.5 in salt-free polyelectrolyte buffer is shown in Figure 1. The volume change behavior of NIPA-AA gels changes from a discontinuous type of nonionic NIPA gel ($x = 0$) to a continuous one, as the acrylate content x increases. We extended the swelling measurement to copolymer gels consisting of strong-electrolyte-type comonomer. The temperature dependence of the swelling ratios of NIPA-NaPSS gels under increasing temperature in water is shown in Figure 2. NIPA-NaPSS gels show

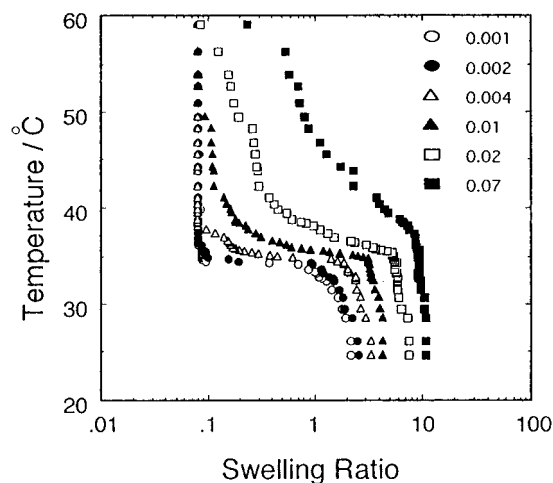


Figure 2. Temperature dependence of the swelling ratios for NIPA-NaPSS gels with various compositions in water. The mole fraction of acrylate, x is shown in the figure.

continuous volume changes, which is similar to that of positively ionized NIPA gels such as copolymer gels of *N*-isopropylacrylamide and {[methacrylamido]propyl}trimethylammonium chloride (MAPTAC).¹⁷ These results obtained here indicate that an introduction of charges into the network switches the temperature-induced volume change of NIPA gel from the discontinuous type to the continuous one. This is different from the result¹² that the ionization of NIPA gel chains enhances the discontinuity of the volume phase transition. This discrepancy between our result and that reported by Hirotsu et al.¹² is most probably due to the difference of pH used in the experiments.¹⁵ We confirmed that the continuous volume changes shown in Figures 1 and 2 were reversible: identical for both warming up and cooling down.

Generally, a hysteresis in the phase transition as well as the direct observations of the discontinuous volume change can be regarded as evidence of the discontinuous transition.^{11,18,19} The hysteresis of the volume change in nonionic NIPA gel was observed in the present study, which was also reported by Hirokawa et al.¹¹ The areas associated with a hysteresis

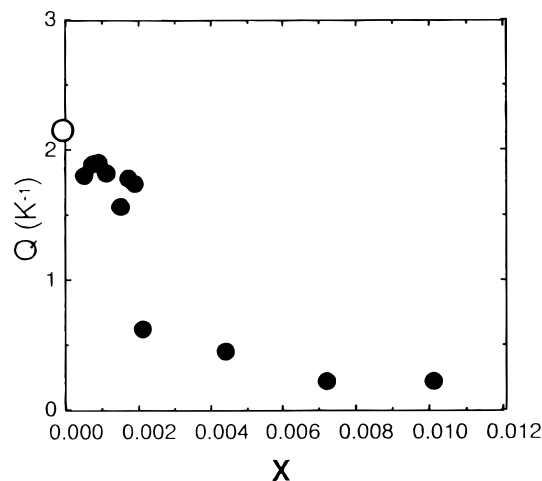


Figure 3. Maximum values of the derivative $[-d \log(V/V_0)/dT]$, Q , for NIPA-AA gel as a function of the mole fraction of acrylate, x . The Q value for NIPA gel ($x = 0$) is also shown as reference.

loop were too small for copolymer gels to be reliably detected at $x > 0.001$.

To understand the physicochemical mechanism of the observed switch of the transition type, it is important to see whether a critical x value exists or not, at which the volume change behavior of the gel switches from a discontinuous to a continuous type. However, it was difficult to determine the critical x value on the basis of the observation of the hysteresis. To decide the critical x value, we calculated derivatives $[-d \log(V/V_0)/dT]$ for each of the swelling curves of NIPA-AA gels shown in Figure 1 and took the maximum value Q of the derivative as a measure of the sensitivity of the conversion between the swollen and the shrunken state for a given swelling curve. Figure 3 shows the dependence of Q on x for the NIPA-AA gels. The Q value for NIPA gel ($x = 0$) is also shown as a reference. It is obvious that Q changes sharply in a very narrow range of x between 0.0018 and 0.0020. The Q values for NIPA-AA gels of less than $x = 0.0018$ fall in a range between 1.5 and 2 K^{-1} and are close to the Q value for NIPA gel ($x = 0$) that shows a discontinuous volume change. This indicates that the discontinuous change at $x = 0.0018$ switches to a continuous one at $x = 0.0020$. A small amount of charge is sufficient for the regime change.

Figure 4 shows the temperature dependence of the NIPA-AA ($x = 0.007$) gel in NaCl solutions of various concentrations. The continuous behavior in the absence of NaCl is transformed into a discontinuous one in the presence of 0.1 and 0.3 M NaCl. The transition temperature at 0.3 M NaCl was slightly lower than that of pure nonionic NIPA gel, which was consistent with the reported salt effect on NIPA gel.¹⁶

It was demonstrated that the volume change behavior of NIPA-AA gel depended on both the mole fractions of charged acrylate x and NaCl concentration (ionic strength). The Donnan osmotic pressure increases with x and decreases with an increase in the ion strength. We present a phenomenological approach in terms of the Donnan osmotic pressure to see the effects of the two factors, x and ionic strength, on the volume change behavior. The Donnan pressure Π/RT in the present copolymer gels is given as follows, since the charge contents of gels were very low (ideal Donnan) and the gels were immersed in the 5 mM polyacrylate solution.

$$\Pi/RT = C_e + 2C_s - (\phi_p C_e' + 2C_s') \quad (1)$$

In eq 1, the additivity of the osmotic pressure^{20–22} for the external polyelectrolyte solution is assumed. C_e and C_e' (=5

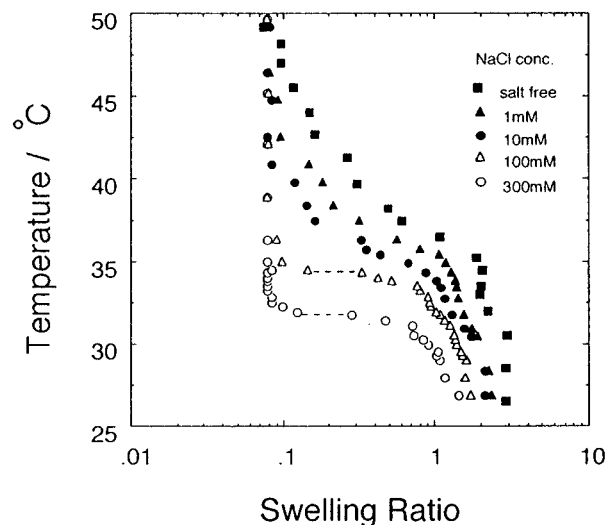


Figure 4. Temperature dependence of the swelling ratios for NIPA-AA gels ($x = 0.0071$) in NaCl solutions of various concentrations. NaCl concentrations are shown in the figure.

mM) refer to the carboxylate concentrations of the gel and the external polyacrylate solution, respectively. C_s and C_s' denote NaCl concentrations inside and outside the gel, respectively. ϕ_p (=0.14) refers to the osmotic coefficient of the polyacrylate in salt-free solutions.²³ The Donnan equilibrium is given according to the eq 2 to a good approximation in the present study.

$$(C_e + C_s)C_s = (\gamma' \pm)^2 (C_e' + C_s')C_s' \quad (2)$$

In eq 2, $\gamma' \pm$ was evaluated according to Manning's limiting law.²² When salt is not present in the external solution ($C_s' = 0$), eq 1 reduces to $\Pi/RT = C_e - \phi_p C_e'$. It is to be pointed out that significant differences between the nominal and the actual values of x cause little or no change in the calculated Π values. Although both C_e and C_s in eqs 1 and 2 should be modified, their sum ($C_e + 2C_s$) or ($C_e + C_s$) remains essentially unchanged. Figure 5 shows the Q values as a function of the swelling pressure Π/RT for NIPA-AA gels in salt-free aqueous solution and NaCl aqueous solutions. The Q values for NIPA-NaPSS gel are also shown with open squares. In this case, $\Pi/RT = C_e$. For both gels, Π/RT was evaluated at the completely deswollen state ($V/V_0 = 0.08$). As shown in Figure 5, a good correlation was found between the Π/RT and the sensitivity of the conversion Q for NIPA-AA gel, irrespective of whether the perturbation was made by x at a constant C_s ($=0$) or by C_s at a constant x . At low swelling pressures the discontinuous regime prevails, while the continuous regime becomes dominant at high swelling pressures. The Donnan osmotic pressure given by eq 1 provides us a unified picture of the effect of charges and the salt on the volume phase transition of the gels. This indicates that the continuous and the discontinuous regimes of NIPA-AA gels are well characterized by high and low swelling pressures.

The volume change behavior of NIPA-NaPSS gel changes from the discontinuous type to the continuous one as x increases, which is similar to that of NIPA-AA gel at pH 9.5, as seen in Figures 1 and 2. The switching for NIPA-NaPSS gel, however, takes place in a higher range of Donnan pressure than that for the NIPA-AA gel, as shown in Figure 5. This may be partly because the polymer–polymer affinity of NIPA-NaPSS gel at high temperature is stronger than that of NIPA-AA gels due to the hydrophobic aromatic groups on the side chains in NIPA-NaPSS gel.

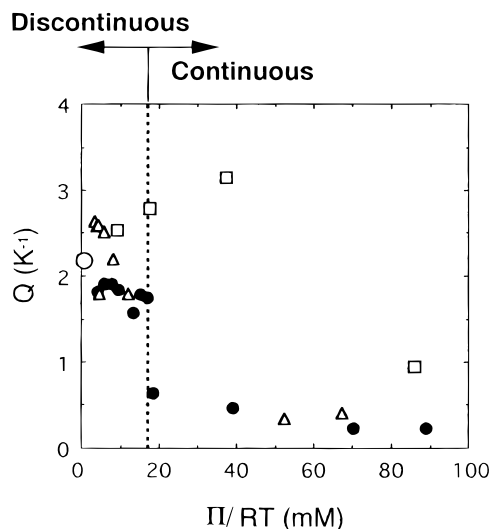


Figure 5. Maximum values of the derivative $[-d \log(V/V_0)/dT]$, Q , as a function of the ion swelling pressure Π/RT for NIPA-AA gels in salt-free polyelectrolyte buffer or NaCl aqueous solutions and for NIPA-NaPSS gels in water. Π/RT was evaluated at the completely deswollen state ($V/V_0 = 0.08$). Solid circles and open triangles refer to NIPA-AA gels in salt-free polyelectrolyte buffer and in NaCl aqueous solutions, respectively. Open squares represent those for NIPA-NaPSS gels in water. The Q value for nonionic NIPA gel (open circle) is also shown at $\Pi = 0$, while the exact value is -0.7 . A broken line is tentatively drawn to indicate a border between the two regimes of the continuous and the discontinuous volume change for NIPA-AA gels.

Any significant effect of polyacrylate buffer solution was not noted. We observed a continuous volume change for a copolymer NIPA gel ($x = 0.04$) in water by adjusting pH with NaOH. All the results on NIPA-NaPSS gels were obtained in water without polyacrylate buffer. For pure NIPA gels, polyacrylate buffer outside the gel exerts osmotic compression on the gel, leading to a lowering of the transition temperature, T_c . However, this lowering of T_c was not detected simply because of a small osmotic pressure ($\Pi/RT = 7 \times 10^{-4}$ M). For NIPA gels, crossover of the transition type (continuous or discontinuous) has been reported to depend on the cross-linker concentration²⁴ as well as on other factors. The discontinuous volume change in the present study is consistent with this proposed category.

The existence of a shrunken phase for a charged network requires strong polymer–polymer affinity (i.e., the Flory–Huggins parameter χ is a large positive). The χ parameter of NIPA gels has been suggested to increase with temperature due

to the hydrophobic interaction between NIPA side chains, and the discontinuous volume change of NIPA-AA gel has been considered to occur since the attractive force due to the hydrophobic interaction overwhelms the repulsive force of the Donnan osmotic pressure at high temperature. The continuous volume change of NIPA-AA gel observed in the present study suggests that the hydrophobic interaction of NIPA chains is not strong enough, even at high temperatures, to overcome the increased Donnan osmotic pressure. The volume changes of NIPA-AA gel at pH 9.5 and NIPA-NaPSS gel probably become continuous as a result of the increased Donnan pressure. It is worth noting that an introduction of a small amount of charge into the NIPA gel chains ($x = 0.002$) changes the discontinuous volume change to a continuous one. This may suggest that the transition of NIPA gel is close to the critical point.

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