The Phase Transition and Shear Modulus of Ionic N-Isopropylacrylamide Gels in Concentrated Salt Solutions

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ABSTRACT: The swelling and mechanical properties of thermally sensitive N-isopropylacrylamide (NIPA) hydrogels containing $0-35$ mM sodium acrylate comonomer have been investigated at room temperature. The swelling medium is an aqueous solution with an NaCl concentration varying from 0 to 3.0M. As the NaCl concentration increases, the ionic NIPA gels shrink. In a dilute sodium chloride solution with NaCl less than 0.1M, the conformational change of the gels is a simple process of osmotic deswelling. As the sodium chloride concentration increases above 0.8M, the gels undergo a shrinkage phase transition. Corresponding to the shrinking of the gels, the shear modulus of the gels gradually increases at the transition point. It is found that the phase transition significantly affects the turbidity of the NIPA gels. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1851–1856, 1997

Key words: N-isopropylacrylamide; gels; volume phase transition; salt solutions

INTRODUCTION

The volume phase transition in polymer gels can be induced by many external stimuli such as temperature, solvent composition, light, electric field, and pH value. Recently, thermal sensitive N-isopropylacrylamide (NIPA) gels have attracted great attention for their scientific interest,[1–4] as well as for their technological potential in a variety of applications including drug delivery[5] and immobilized-enzyme reactors.[6]

Many potential applications of temperature-sensitive gels require the incorporation of fixed ionizable groups in the polymer network. As a result, the ionic gels in salt solutions are of interest. The effect of salt on the phase transition of ionic and nonionic NIPA gels has been reported previously.[7–9] In this article, the swelling equilibria of the neutral and ionic NIPA (NIPA copolymerized by sodium acrylate [SA]) gels are investigated over a wide range of NaCl concentrations in aqueous solutions. It is found that the ionic NIPA gels shrink as the NaCl concentration increases and exhibit a phase transition in the concentrated NaCl solution (above 0.8M) at room temperature. The behaviors of shear modulus and turbidity of the NIPA gels in the shrinking process are investigated to compare with gel swelling properties.

EXPERIMENT

The neutral NIPA gel samples were made by free radical polymerization. A mixture of 690 mM of NIPA (Kodak, Co.), 8.6 mM of methylene-*bis*-acryl-

amide as a crosslinker, and 240 μL of tetra-methyl-ethylene-diamine as an accelerator was dissolved in 100 mL of deionized and distilled water. The ionic NIPA gels were made by incorporating 4, 8, 16, and 35 mM SA into the NIPA pregel solution, respectively. Nitrogen gas was bubbled through the solution to remove dissolved oxygen. Ammonium persulfate (0.169 mM) was added to the solution as an initiator. The pregel solution was then poured into cylindrical glass tubes with diameters from about 5 to 10 mm in a nitrogen environment. After polymerization, the gel samples were taken out of the tubes and extensively washed with deionized and distilled water to remove residual chemicals. It took approximately 10 days for the diameters of the gels to reach the equilibrium value. The diameters and the thicknesses of the gel samples used in the measurement were 8–12 and 10–15 mm in water, respectively.

The dimensions of the gel samples were measured with a caliber with an accuracy of 0.05 mm. In the measurement of swelling ratio, the gel samples were cut into thin strips along the axial direction. The swelling ratio, L/L_e, i.e., the ratio of equilibrium length L in various NaCl concentrations to the length L_e in water at room temperature, was calculated on the basis of the length measurement. The standard deviations of the measured swelling ratio were generally less than 5% of the mean.

The shear modulus was determined by uniaxially compressing a cylindrical gel with a glass plate. This plate was attached to a calibrated digital force gauge. For each displacement of the gel sample, the corresponding force F was recorded. When the volume of the gels is kept constant, one can obtain[10]

$$\frac{F}{S} = G\left(\lambda - \frac{1}{\lambda^2}\right) \qquad (1)$$

where G is the shear modulus, S is the surface area of the undeformed gel, and λ is the z-direction elongation ratio of the gel. By plotting F/S versus $(\lambda - 1/\lambda^2)$, the slope G was obtained. The range of λ varied typically between 1 and 0.8 in the measurement. To reduce the sticky effect of the gel sample near the phase transition, a small amount of vacuum oil was put on the gel surface that contacted with the glass plate. The error of the shear modulus was estimated to be less than 8%. The turbidity of the NIPA gels at various concentrations of sodium chloride solutions was determined by measuring the light transmission at a 555-nm

wavelength with a spectrophotometer (Spectronic 301; Milton Roy Co.) at about 22°C.

RESULTS AND DISCUSSION

Swelling Ratios

Figure 1 shows the swelling behavior of NIPA gels in NaCl solutions (from pure water to 3.0M)
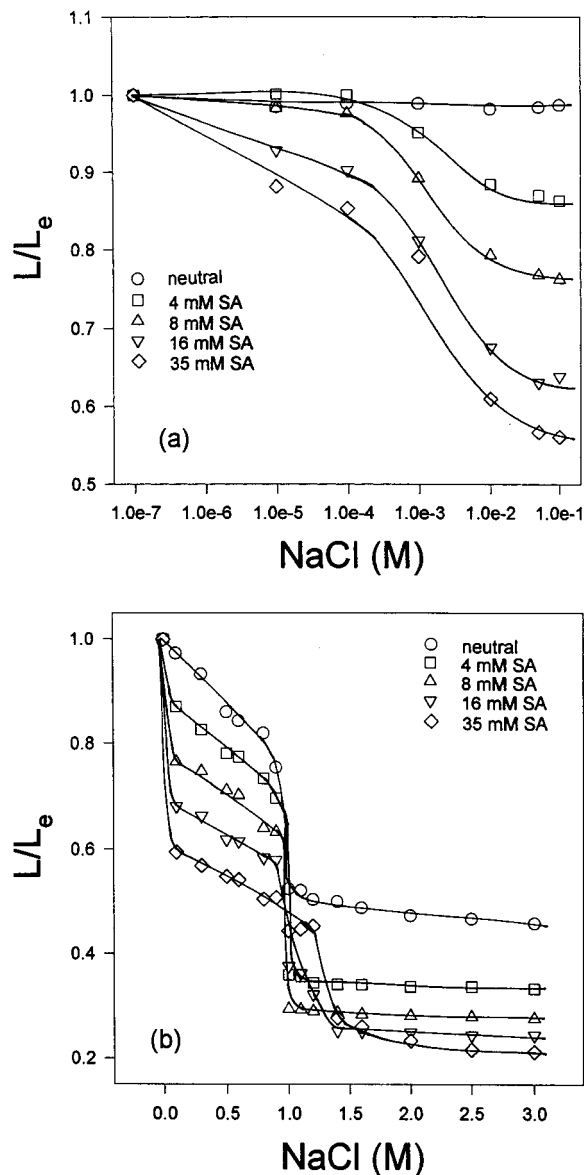
Figure 1 Swelling ratio at 22°C for NIPA/SA copolymer gels as a function of NaCl concentration. The data at $10^{-7}M$ NaCl represent swelling in deionized and distilled water. The solid lines are an aid for the eye. (a) Diluted NaCl solutions, with NaCl concentration from 10^{-7} to $10^{-1}M$; (b) concentrated NaCl solutions, with NaCl concentration from 0 to 3.0M.

at various SA concentrations at about 22°C. Pure water is denoted on Figure 1(a) as $10^{-7}M$ NaCl. The reduced swelling ratios are normalized by the swelling ratio in water. As the salt concentration increases above $10^{-3}M$, the ionic gels shrink rapidly. The degree of deswelling highly depends on the strength of gel ionization (molar number of SA). The shrinking process shown here is continuous and similar to one observed previously.[7] This conformational change is a process of osmotic deswelling and is a result of the competition between the network electrostatic interaction and the Donnan osmotic pressure; it can be explained in terms of the Donnan-equilibria effect.[7,11]

The reduced swelling ratios of NIPA gels in concentrated NaCl solutions are shown in Figure 1(b). When the NaCl concentration approaches about 1.0M, the ionic gels shrink sharply. This sharp shrinkage indicates that there is a volume phase transition in concentrated NaCl solution. Compared with neutral NIPA gel results,[8,9] this figure suggests that the degree of ionization has a strong effect on the phase transition. Because the "salting out" effect produces a gradual and much weaker shrinking change of ionic gels compared with that induced by the volume phase transition, this phase transition cannot be explained in terms of the "salting out" effect.[9] Furthermore, the sharp volume change in the concentrated NaCl solution cannot be explained by the Donnan-equilibria argument,[7,12] because the Donnan effect is screened out by the high NaCl concentration and is much less effective.

Because the ionic NIPA gel exhibits a lower critical solution temperature (LCST), the most probable reason for the observed volume phase transition may be the result of the shift of the LCST of the ionic NIPA gels in the concentrated NaCl solutions. It is known that the LCST of a neutral NIPA gel is shifted to lower temperature, as NaCl molality increases.[8,9] It is believed that this is a result of the disturbance of the water structure by salt ions.[9,13] The shift of an ionic NIPA gel with 8 mM SA as a function of temperature in various NaCl concentrations is shown in Figure 2(a). The transition temperature is clearly related to the NaCl concentration, as shown in Figure 2(b), where the transition temperature T_c corresponds to the point where the maximum change of L/L_e occurs. Analogous to that observed in a neutral NIPA gel in aqueous NaCl solution,[8,9] our results indicate that the concentrated NaCl solution can suppress the LCST of ionic NIPA gels. This phenomenon shows that the driving
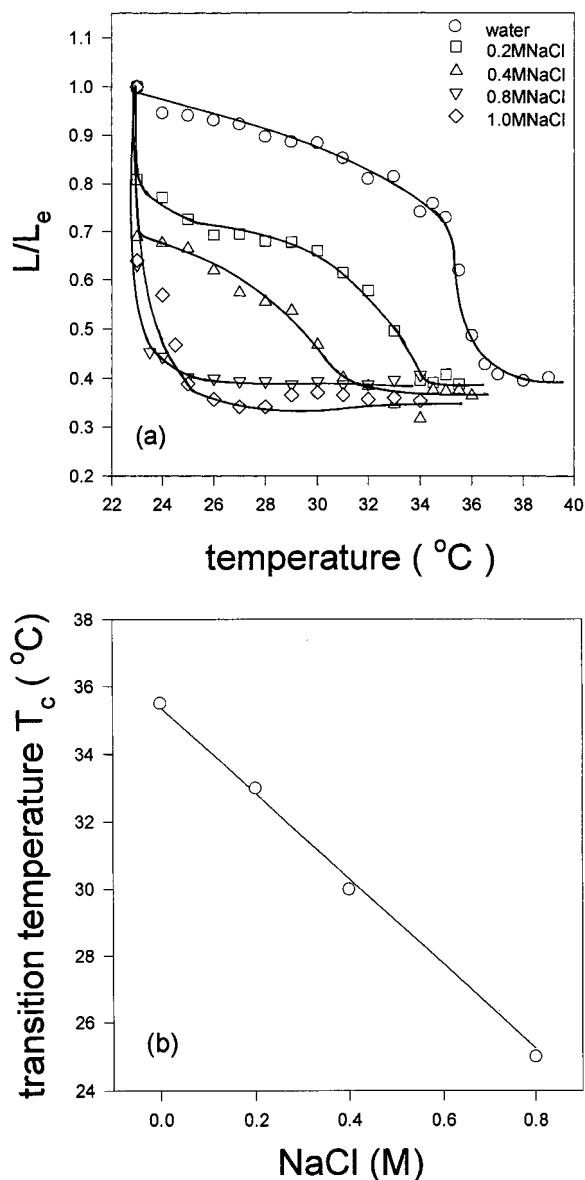
Figure 2 (a) Swelling behavior for 8 mM SA ionic NIPA gel as a function of temperature in aqueous salt solutions with various NaCl concentrations. The solid lines are a guide for the eye. (b) NaCl concentration versus the transition temperature. The solid line is the best least-square fit to the data.

force for the phase transition behavior of the NIPA gels induced by either NaCl or temperature is the same.

The amount of NaCl needed to suppress the phase transition point to room temperature (22°C) is shown in Figure 3 for varying degrees of ionization. To overcome the higher osmotic pressure induced by the higher SA concentration, the transition NaCl concentration has to increase.
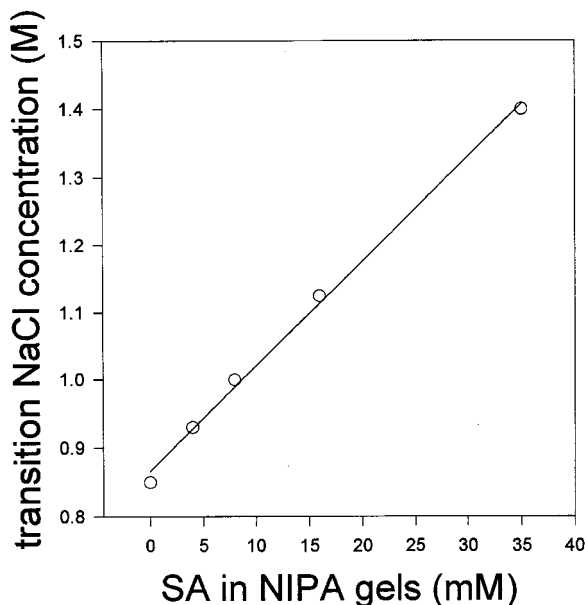
Figure 3 The transition NaCl concentration versus SA concentration in the NIPA gels at room temperature (about 22°C). The solid line is the best least-square fit to the data.

Shear Modulus

Shear modulus plays an important role in the determination of gel properties. Figure 4 shows the shear modulus G_e and the swelling ratio W_e/W_d as a function of SA concentration for the NIPA gels in water at room temperature. W_e and W_d are the weights of the swollen gels in water and dry gels, respectively. The shear modulus G_e decreases with the increase of the SA concentration initially, as predicted by the classic rubber elasticity theory.[15] As the SA concentration increases further, the ionic gels become highly swollen and the values of G_e start to deviate from the prediction of the classic rubber elasticity theory, as suggested by a flat region of G_e in Figure 4. In high swelling limit, the polymer chains in the gels are largely extended and no longer obey Gaussian distribution. As a result, the elasticity of the gels deviates from the classic rubber elasticity theory.[16] The swelling ratio (W_e/W_d), on the other hand, increases monotonically with the SA concentration.

Figure 5 shows the effect of NaCl concentration on the shear modulus G. For clarity, the data have been shifted vertically to different values, as specified in the figure legend. From Figure 5(a), one can see that the shear modulus of the ionic NIPA gels increases gradually because the ionic gels

shrink, while the shear modulus of the neutral NIPA gel remains at about the same value. Figure 5(b) shows that the shear modulus has a significant increase at the phase transition for all gel samples.

It is noted that the shear modulus of the neutral NIPA gel at the phase transition increases about 2.5 times more in a $1.0M$ NaCl aqueous solution than in pure water at room temperature. This result is in good agreement with Hirotsu's observation[17] that shear modulus increases also about 2.5 times near the critical temperature for a neutral NIPA gel in water. The change of the shear modulus near the volume phase transition can be well explained by Flory's phenomenological theory.[17]
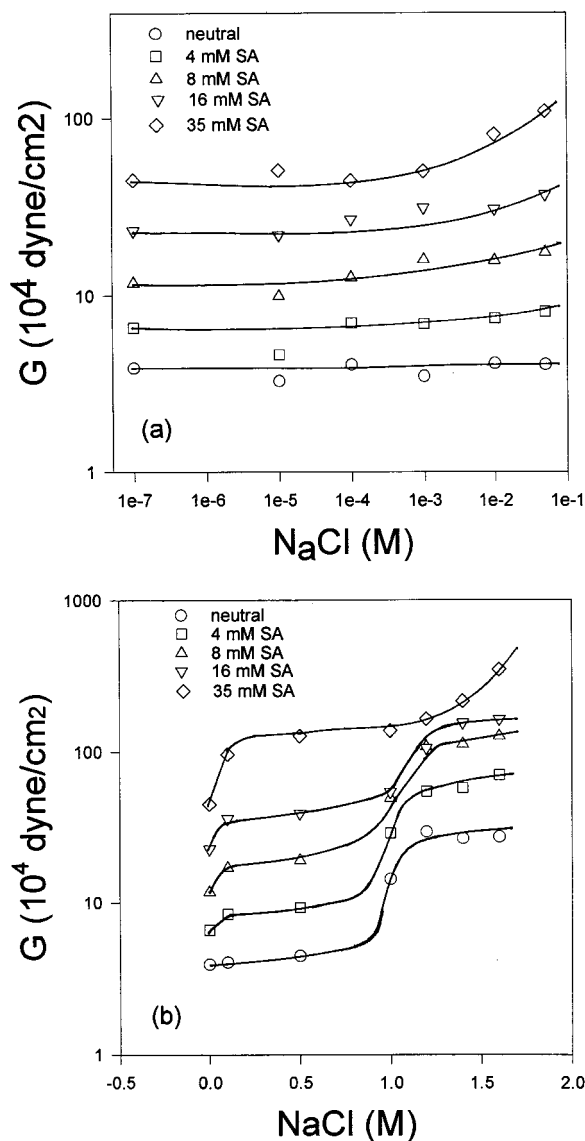
Turbidity Measurement

The turbidity of NIPA gels in NaCl solution is investigated with spectrophotometer. The transmitted light intensity I_t and the incident light intensity I_O are related by the sample turbidity α and the thickness L,[18]

$$I_t = I_O e^{-\alpha L} \tag{2}$$

Therefore, the turbidity of the gels can be obtained from the ratio of the transmitted light intensity to the incident light intensity, $\alpha = -(1/L)\ln(I_t/I_0)$. Figure 6(a) shows the turbidity α of the NIPA gels with various SA concentrations at a wavelength of 555 nm as a function of NaCl
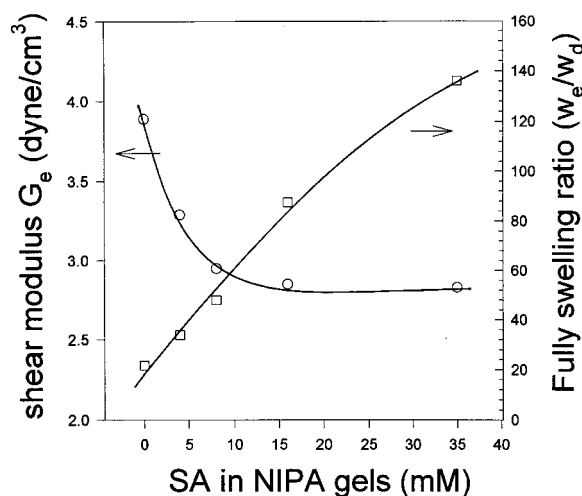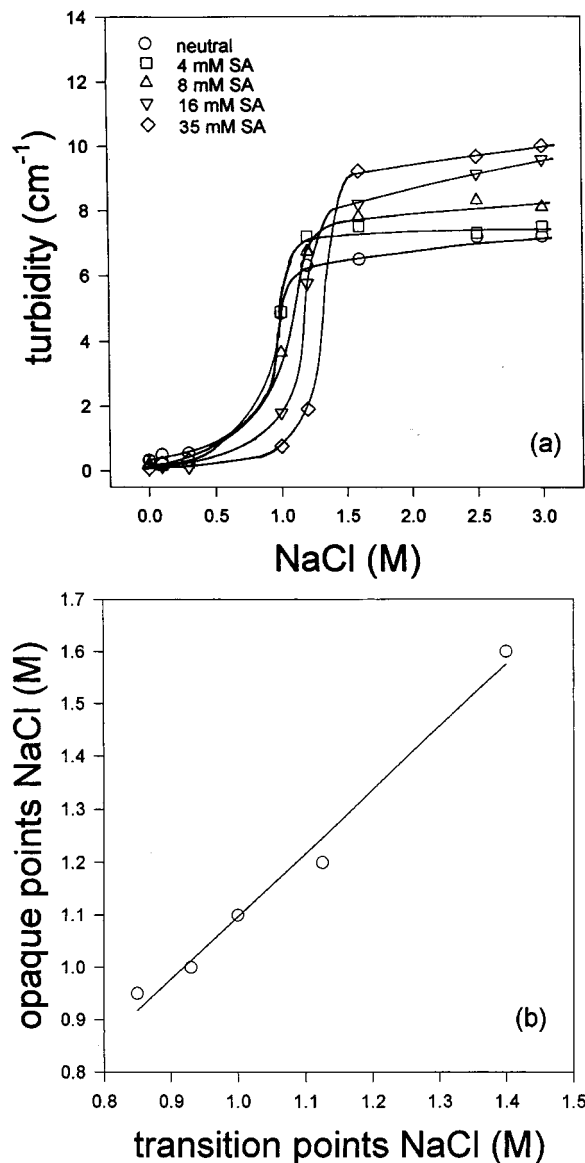

Figure 4 The equilibrium swelling ratio W_e/W_d and the shear modulus G_e of the NIPA gels in water at 22°C as a function of SA concentration.

indicates the existence of the dense and dilute regions, and a stable foam-like structure is formed in the gels.[18] In this experiment, when the turbidity reaches about 4 cm^{-1}, the NIPA gels are defined as in the opaque state. The corresponding NaCl concentration is called the opaque point. Figure 6(b) compares the opaque NaCl concentration and the transition NaCl concentration. This figure further supports the conclusion that the origin of the phase transition in concentrated

Figure 5 The effect of NaCl concentration on the shear modulus of the NIPA/SA copolymer gels with various SA concentrations at 22°C. The solid lines are a guide for the eye. For clarity, the data have been shifted by constant multiplication factors, which are indicated by the number in parentheses. (a) NaCl concentration from 10^{-7} to $10^{-1}M$: neutral (1), 4 mM SA (2), 8 mM SA (4), 16 mM SA (8), 35 mM SA (16). (b) NaCl concentration from 0 to 3.0M: neutral (1), 4 mM SA (2), 8 mM SA (4), 16 mM SA (8), 35 mM SA (16).

concentration. Far away from the transition region, the values of α are very small (less than 0.5 cm^{-1}) and are almost independent of SA concentration. As the gel samples approach the phase transition region, the turbidity increases drastically. Turbidity is related to the spinodal decomposition of the NIPA gels. The high turbidity value

Figure 6 (a) The turbidity of the NIPA gels as a function of NaCl concentration at 22°C. The solid lines are an aid for the eye. (b) The opaque NaCl concentration versus the transition NaCl concentration. The solid line is the best least-square fit to the data.

NaCl solutions is the same as that of the temperature-induced one.

CONCLUSIONS

The experimental results show that there are two shrinking regions in ionic NIPA (NIPA/SA-copolymerized) gels induced by NaCl solutions at room temperature. One is in diluted NaCl solutions (less than $0.1M$) and can be explained by the Donnan-equilibrium argument; the other is in concentrated NaCl solutions (more than $0.8M$), as a result of the suppression of the LCST by NaCl. The shrinking in diluted NaCl solution does not affect the turbidity of the ionic NIPA gel, but the phase transition in concentrated solution can make all NIPA gels opaque. The results shown here may be helpful when developing gel devices such as ionic strength–sensitive biosensors and actuators.[19]

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