

# Salt Effect on Elastic Properties of Shrunken *N*-Isopropylacrylamide Gel

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The tensile moduli of poly(*N*-isopropylacrylamide) gels in salt-free and NaCl solutions were measured by changing the temperature. A partition of NaCl between the gel and the solution outside the gel was examined. It was found that the tensile force relaxed after elongation and that the relaxation moduli depended on the temperature  $T$  and NaCl concentration  $C_s$ . The relaxation of the tensile modulus,  $Y(t)$ , for the shrunken gel was fitted to  $Y(t) = (Y_i - Y_e)(1 + t/\tau)^{-\beta} + Y_e$ , where  $t$  is the time after elongation. The  $\beta$  and  $\tau$  values were found to be independent of  $C_s$ . The moduli at initiation,  $Y_i$ , and at equilibrium,  $Y_e$ , increased with  $T$  in the salt-free and NaCl solutions. The transitional changes of these moduli were observed at the temperatures at which the volumes of the gels changed transitionally.  $Y_i$  and  $Y_e$  of the shrunken gel increased with  $C_s$ , whereas those of the swollen gel were insensitive to  $C_s$ . The NaCl concentration was approximately a 300th part of the concentration of monomeric units of the NIPA chain in the shrunken gel. This suggests that a small amount of NaCl molecules changes the structure of the clustered water molecules surrounding the chains to restrict chain freedom and increases the moduli. The effect of NaCl molecules on the state of the clustered water molecules was detected as a change in the transition enthalpy, which was obtained by differential scanning calorimetry measurements.

## 1. Introduction

The *N*-isopropylacrylamide (NIPA) gel, which exhibits a temperature-induced volume phase transition, has been intensively investigated.<sup>1</sup> The combination of dehydration of the chains (divesting the hydrophobic isopropyl group of the clustered water molecules) and the entropic force of the chains induces the volume phase transition.<sup>2</sup> The dehydration is induced by destabilization of the clustered water molecules surrounding the isopropyl group when their chemical potentials exceed that of the bulk water. The volume phase transition behavior of the NIPA gel induced by the addition of salt<sup>3,4</sup> or saccharide<sup>5</sup> molecules has been explained by the dehydration mechanism mentioned above.<sup>6</sup> Our interest here is the physicochemical properties of the shrunken gel, which is composed of mostly dehydrated chains.

The gel in the swollen state can be considered similar to a semidilute polymer solution in a good solvent. In the shrunken gel, where most of the water molecules are repelled from the gel, the cross-linked and dangling chains are highly entangled with each other. As reported elsewhere,<sup>7</sup> the tensile force responding to the elongation of the shrunken NIPA gel relaxes according, approximately, to the power function of time  $t$  after the elongation, such that  $Y(t) = (Y_i - Y_e)(1 + t/\tau)^{-\beta} + Y_e$ . Here,  $Y_i$  and  $Y_e$  are the moduli at initiation and at equilibrium, respectively. The power function of  $t$  is interpreted as the relaxation of the constraint of the entangled dangling chains in the network.<sup>7–9</sup>  $\tau$  is the primary reptation time of an entangled chain. The value of  $\beta$  decreases with the increase in density of the cross-linked chains. The  $\tau$ ,  $\beta$ , and  $Y_e$  values can be good measures for looking into the interaction among the chains and

small molecules in the shrunken gel, which is regarded as a solidlike but soft complex of highly entangled chains and solvent molecules.

The addition of NaCl molecules to water reduces the dimension of the clustered bulk water and decreases the chemical potential of the water molecules to destabilize the hydrated state of the NIPA chain, which decreases the transition temperature.<sup>6</sup> The high free energy of NaCl molecules in the hydrophobic condition of the shrunken gel is considered to result in the low partition of NaCl into the shrunken gel, as has been indicated in our former experiment.<sup>10</sup> It is important to point out that even a small amount of NaCl molecules changes the properties of the shrunken gel. The purpose of the present experiment was to clarify the effects of NaCl on the elastic properties of the shrunken gel. It was found that the  $Y_e$  and  $Y_i$  values of the shrunken gel in the NaCl solution were larger than those in the salt-free solution and that the  $\tau$  and  $\beta$  values changed little as the NaCl concentration increased. In the present study, the NaCl concentration dependent enthalpy change due to the hydration-dehydration of NIPA chains was also examined to reveal the effect of NaCl molecules on the clustered state of water molecules in the collapsed chains.

## 2. Experimental Section

A rodlike NIPA gel was prepared in a glass tube (inner diameter = 0.3 mm) by radical copolymerization in an aqueous solution of 1M NIPA monomer and 0.01 M *N,N'*-methylenebis(acrylamide) for 24 h at 5 °C. A plate gel was synthesized in a container made of two glasses separated by a spacer, which was 1 mm in thickness. Polymerization was initiated by ammonium persulfate and accelerated by *N,N,N',N'*-tetramethylethylenediamine. The synthesized gels were taken out, rinsed thoroughly with water and dried. The NIPA monomer was purified by

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recrystallization from the mixture of *n*-hexane and toluene. All chemicals used were of reagent grade.

The partition of NaCl molecules was determined as follows. A dry gel of weight  $W_{\text{dry}}$  was placed in 2 mL of a NaCl aqueous solution, the concentration of which was  $C_{\text{NaCl}}$  ( $\text{mol dm}^{-3}$ ), and then the gel stood at a given temperature for a period longer than two weeks. The gel/solution partition coefficient  $K_p$  is defined as  $K_p = C_{\text{gel}}/C_{\text{sol}}$ , where  $C_{\text{gel}}$  and  $C_{\text{sol}}$  are the NaCl concentrations inside and outside the gel ( $\text{mol kg}^{-1}$ ), respectively.  $C_{\text{sol}}$  was evaluated from the electric conductance of the solution.  $C_{\text{gel}}$  was estimated by using the relationship  $C_{\text{gel}}(W_{\text{gel}} - W_{\text{dry}}) + C_{\text{sol}}(W_{\text{tot}} - W_{\text{gel}}) = 2 \times 10^{-3} C_{\text{NaCl}}$ , where  $W_{\text{gel}}$  is the weight of the gel and  $W_{\text{tot}}$  is the weight of the entire system (gel + solution). The degree of swelling,  $S_d$ , is defined as  $S_d = (d/d_0)^3$ , where  $d$  is the size of the gel in the NaCl solution and  $d_0$  is the size of the shrunken gel in the salt-free solution.

Details of the apparatus for the tensile force measurement of a rod gel are described elsewhere.<sup>7</sup> The electric resistance of a strain gage (AE-801 Capto Co., Norway) was transformed into electric voltage, which was monitored with a computer-aided instrument. A force of 0.1–2000 dynes could be monitored with a time resolution of 0.1 ms using this computer-aided instrument. A rod gel was inserted into two platinum rings, each of which was connected by a platinum wire to the sensor and translational stage. For embedding the gel between the rings during measurements, stoppers made of silk strings were carefully wound around the gel at each end. A series of tensile force measurements were carried out for one gel by exchanging the solution outside the gel. The elongation length of the gel was adjusted to an accuracy of 10  $\mu\text{m}$  by sliding the translational stage. The gel was elongated after equilibrating the solution. The tensile force after elongation was recorded with the computer-aided instrument. In the 0.75M NaCl solution, it took one week to reach equilibration in the change from the swollen to the shrunken state, although the equilibration time to achieve the shrunken gel in the salt-free solution was a few hours. The temperature of the solution was controlled to within 0.1  $^{\circ}\text{C}$ . The gel was elongated by a given distance (typically a few hundred  $\mu\text{m}$ ) within 0.2 s. The force decayed to a time-independent value,  $F_e$ , during a period of about 500 s after elongation. During measurement, the gel was immersed in the solution. The natural length of the gel,  $l_0$ , was obtained from an inflection point in a plot of  $F_e$  and the distance  $l$  between the rings. A linear relationship between  $l_0$  and the radii of the tensile-force-free gel,  $r_0$ , at various temperatures was shown to pass through the origin. Young's moduli at initiation,  $Y_i$ , and at equilibrium,  $Y_e$ , are given as follows:

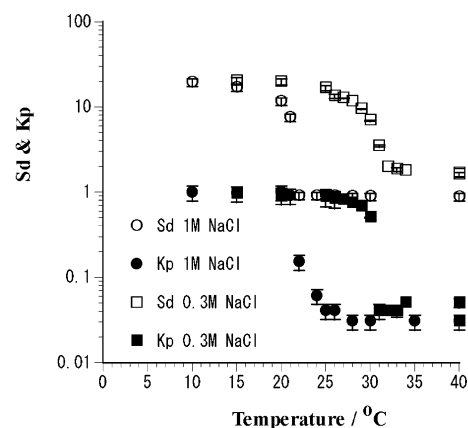
$$Y_i = \frac{\lambda F_i}{\pi r_0^2 (\lambda - 1)} \quad (1)$$

and

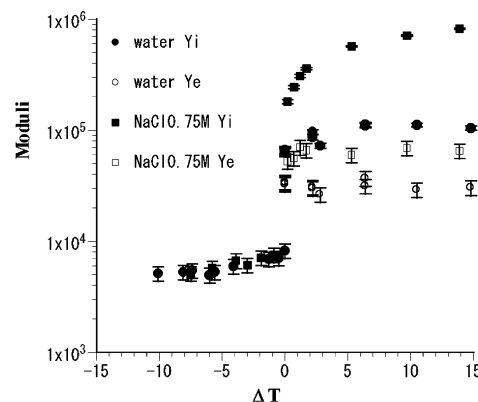
$$Y_e = \frac{\lambda F_e}{\pi r_0^2 (\lambda - 1)} \quad (2)$$

Here,  $\lambda$  is the elongation ratio defined as  $\lambda = l/l_0$ . The typical  $\lambda$  value was about 1.1 in this experiment.

Measurements of the differential scanning calorimetry (DSC) were made with a DSC3100 calorimeter (MacScience Co., Ltd.) from 5 to 45  $^{\circ}\text{C}$  (at a heating rate of 1  $^{\circ}\text{C}/\text{min}$ ). A small amount of the NaCl solution was adsorbed with the dried gel of known weight  $W_g$ . The gel remained in a sealed glass container to reach the equilibrating swollen state and was transferred to a seal-



**Figure 1.** Temperature dependence of the degree of swelling,  $S_d$ , and the partition coefficient of NaCl into the gel,  $K_p$ .



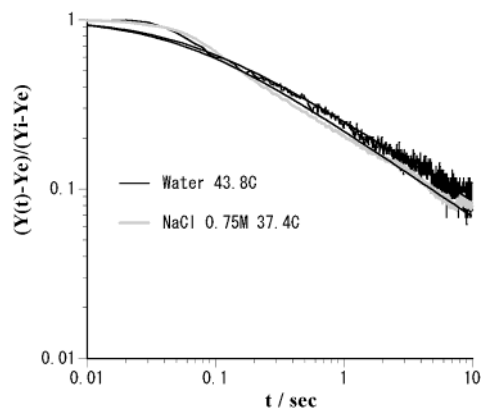
**Figure 2.** Young's moduli at initiation,  $Y_i$ , and at equilibrium,  $Y_e$ , as functions of the temperature difference from the volume phase transition temperature,  $\Delta T$ . The closed and open symbols represent  $Y_i$  and  $Y_e$ , respectively.

type aluminum pan for the DSC measurement. No change in the total weight of the wet gel,  $W_t$ , was detected before and after the measurement. A total mole of the wet gel,  $N_t$ , was defined as  $N_t = \{(W_t - W_g)/\{M_0\} + \{W_g\}/\{M_1\}$ , where  $M_0$  and  $M_1$  were the molecular weights of the water molecule and a monomeric unit of NIPA, respectively. A mole fraction of the water molecules in the gel system,  $W$ , was given by  $W = \{(W_t - W_g)/\{N_t M_0\}$ . The amount of NaCl molecules inside the gel was so small that it could be neglected in the estimation described above.

### 3. Results

Figure 1 shows the degree of swelling,  $S_d$ , and the partition of NaCl into the gel,  $K_p$ , plotted against the temperature. Both the  $S_d$  and  $K_p$  values decrease with an increase in temperature and transitionally drop at transition temperatures. The transition temperature decreases with the increase in NaCl concentration. The  $K_p$  values of the shrunken gel obtained in the present experiment were smaller than previously reported values.<sup>10</sup> The present result is more reliable, because electric conductance is more sensitive to concentration than osmolality, which has been previously used to evaluate NaCl concentration. The present experiment confirms that NaCl tends to be excluded from the shrunken NIPA gel.

Figure 2 shows  $Y_i$  and  $Y_e$  plotted against the temperature difference  $\Delta T$  from the volume phase transition temperature. The moduli of the swollen gels increase monotonically with temperature. It should be mentioned that the moduli of the swollen gels are a function of  $\Delta T$  irrespective of the existence



**Figure 3.** Comparison between the normalized relaxation moduli,  $\Delta Y(t)/\Delta Y(0)$ , of the shrunken gels in the NaCl-free and 0.75 M NaCl aqueous solutions. The solid lines represent the function of  $(1 + t/\tau)^{-\beta}$ , the  $\tau$  and  $\beta$  values of which are described in Table 1.

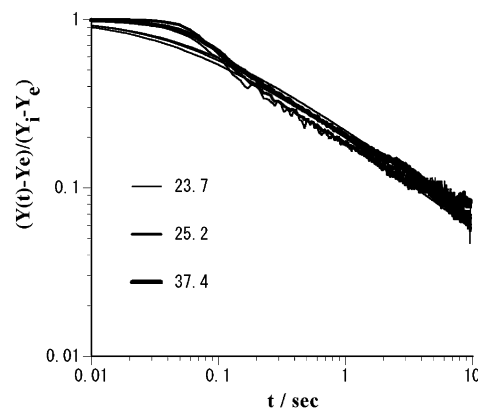
of NaCl molecules. The chemical potential of the bulk water molecules<sup>6</sup> is a monotonically decreasing function of temperature and the NaCl concentration of the solution. A decrease in the chemical potential of the bulk water molecules destabilizes the cluster structure of the water molecules surrounding the isopropyl group of the NIPA gel. This causes an increase in the degree of dehydration of the chains, which leads to a decrease in the end-to-end distance of the cross-linked chains to shrink the gel. The decrease in the chain dimension increases the entropy of the chains and the elasticity. Thus, the elasticity of the gel increases with rising temperatures. The moduli increase transitionally at the volume phase transition points of the gels, as shown in Figure 2. The transition in the moduli reflects the transition in the degree of dehydration of the chains. The  $Y_i$  value of the shrunken gel increases with  $\Delta T$  until about  $\Delta T = 10$  °C and then levels off above that, whereas the changes in the  $Y_e$  value of the shrunken gel due to temperature are very small, as shown in Figure 2.

The decaying function  $Y(t)$  from  $Y_i$  to  $Y_e$  of the shrunken gel differs from that of the swollen gel. As reported before,<sup>7</sup> the time dependence of the normalized relaxation modulus,  $\Delta Y(t)/\Delta Y(0)$ , of the swollen gel looks like an exponential function of  $t$ , where  $\Delta Y(t) = Y(t) - Y_e$  and  $\Delta Y(0) = Y_i - Y_e$ . Figure 3 shows the log-log plot of  $\Delta Y(t)/\Delta Y(0)$  of the shrunken gels with respect to time  $t$  after elongation. The relaxing elastic forces of the shrunken gels in the NaCl-free and NaCl solutions decay according to the same type of power function of  $t$  as follows:

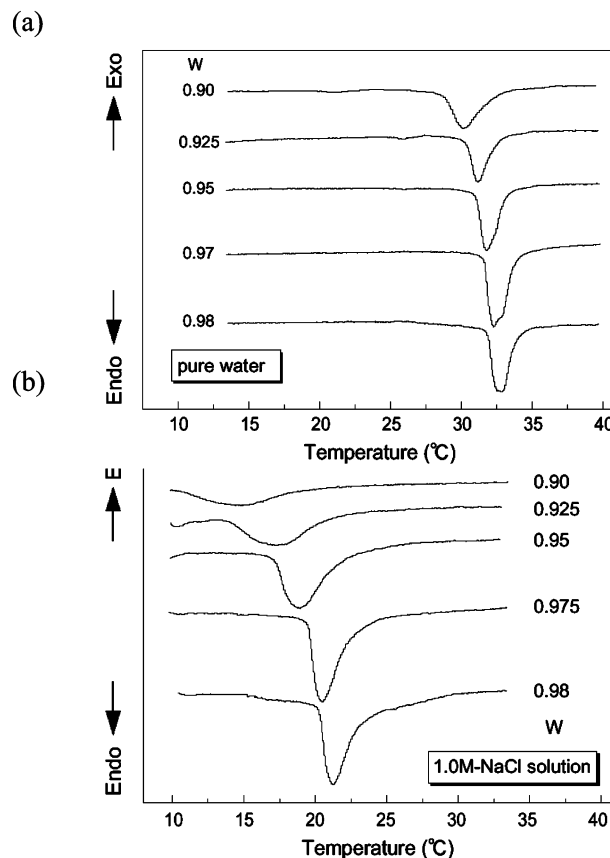
$$\Delta Y(t)/\Delta Y(0) = (1 + t/\tau)^{-\beta} \quad (3)$$

The decaying behavior of the shrunken gels in the 0.75 M NaCl solution is insensitive to temperature, as shown in the log-log plot of Figure 4. The power function of  $t$  can be explained by the elastic relaxation of the dangling chain ends in the cross-linking networks with topological constraints. According to the theory,<sup>7-9</sup>  $\tau$  is the primary reptation time of an entangled chain and  $\beta$  is  $q/\alpha$ , where  $q$  is the cross-linking degree of the network and  $\alpha$  is the characteristic density of the constraining mesh for dangling chains. The  $\tau$  and  $\beta$  values of least-squares fits to eq 1 are shown in Table 1. It can be said that the  $\tau$  and  $\beta$  values are independent of temperature and NaCl concentration. This indicates that the primary time for entangled chains and the constraining mesh density for dangling chains are little affected by temperature and NaCl concentration.

The DSC curves shown in Figure 5 demonstrate that transition enthalpy  $\Delta H_{tra}$  decreases with a decrease in the mole fraction



**Figure 4.** Temperature dependence of the normalized relaxation moduli,  $\Delta Y(t)/\Delta Y(0)$ , of the shrunken gels in 0.75 M NaCl aqueous solutions. The solid lines represent the function of  $(1 + t/\tau)^{-\beta}$ , the  $\tau$  and  $\beta$  values of which are described in Table 1.

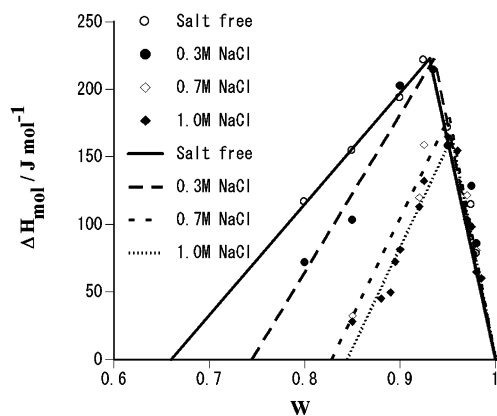


**Figure 5.** DSC thermograms of the NIPA gels in NaCl-free (a) and 1 M NaCl (b) aqueous solutions.

**TABLE 1:  $\tau$  and  $\beta$  Values of Least Square Fits to the Function of  $(1 + t/\tau)^{-\beta}$  for the Data Shown in Figures 3 and 4**

$C_s$ (M)	temp (°C)	$\tau$ (sec)	$\beta$
0	43.8	$5.7 \pm 0.5 \times 10^{-2}$	$0.48 \pm 0.02$
0.75	23.7	$3.9 \pm 0.4$	$0.49 \pm 0.02$
0.75	25.2	$5.7 \pm 0.5$	$0.55 \pm 0.03$
0.75	37.4	$5.6 \pm 0.5$	$0.52 \pm 0.03$

of water molecules in the gel  $W$ . It can be presumed that the decrease in the amount of dehydrated water molecules results in the decrease in  $\Delta H_{tra}$ , because  $W$  changes from about 0.96 to about 0.66 with the change from the swollen to the shrunken state in the salt-free solution.<sup>11</sup> Figure 5 also shows that the decreasing of  $W$  lowers the transition temperatures of gels in



**Figure 6.** Molar transition enthalpy of the system,  $\Delta H_{\text{mol}}$ , as functions of the mole fraction of the water molecule.

**TABLE 2:**  $n_0$ ,  $n_1$ ,  $(n_1 - n_0)$ ,  $\Delta H_1$ , and  $\Delta H_{\text{NIPA}}$  Values of Least Square Fits to Equations 4 and 5 for the Data Shown in Figure 6

$C_s$ (M)	$n_0$	$n_1$	$n_1 - n_0$	$\Delta H_1$ (J mol <sup>-1</sup> )	$\Delta H_{\text{NIPA}}$ (J mol <sup>-1</sup> )
0	2.0 ± 0.1	13.5 ± 0.1	11.5 ± 0.2	280 ± 10	3,230 ± 160
0.3	2.9 ± 0.3	14.5 ± 0.1	11.6 ± 0.4	300 ± 20	3,450 ± 390
0.7	4.8 ± 0.4	19.5 ± 0.1	14.7 ± 0.5	250 ± 20	3,700 ± 400
1.0	5.4 ± 0.4	20.6 ± 0.1	15.2 ± 0.5	230 ± 20	3,550 ± 380

both the NaCl and salt-free solutions. The transition of the gel, the  $W$  value of which is between the upper and the lower transition boundaries, occurs in the hysteresis loop. The transition temperature within the hysteresis loop has a U-shape function of  $W$ . That is, the transition temperature lowers with  $W$  up to a certain value of  $W$ , above which it rises with  $W$ . The former  $W$  dependence of the transition temperature is shown in Figure 5. Figure 6 shows the  $W$  dependence of the molar transition enthalpy,  $\Delta H_{\text{mol}} = \Delta H_{\text{tra}}/N_t$ , which can be approximately described by the following relationships:

$$\Delta H_{\text{mol}} = \Delta H_1(n_1 - n_0)(1 - W); \quad n_1/(1 + n_1) < W < 1 \quad (4)$$

$$\Delta H_{\text{mol}} = \Delta H_1\{W(1 + n_0) - n_0\}; \quad n_0/(1 + n_0) < W < n_1/(1 + n_1) \quad (5)$$

$\Delta H_1$  is the enthalpy change for one molar water molecule in the transfer from the hydrophobic hydration state to the bulk state. Here,  $n_0$ , and  $n_1$  are the numbers of water molecules hydrated with a monomeric unit of the chain in the shrunken and swollen states at the transition, respectively, and  $n_1 - n_0$  is the number of water molecules dissociating from hydrophobic hydration. Therefore, the enthalpy change per NIPA monomeric unit,  $\Delta H_{\text{NIPA}}$ , can be given by  $\Delta H_{\text{NIPA}} = \Delta H_1(n_1 - n_0)$ . The  $n_0$ ,  $n_1$ ,  $(n_1 - n_0)$ ,  $\Delta H_1$ , and  $\Delta H_{\text{NIPA}}$  values of least-squares fits to eqs 4–5 are shown in Table 2. The NaCl molecules increase the hydration numbers ( $n_0$ ,  $n_1$ ) and the transition enthalpy of NIPA ( $\Delta H_{\text{NIPA}}$ ), but decrease the hydration enthalpy of one water molecule ( $\Delta H_1$ ).

#### 4. Discussions

It is expected that the partition of NaCl into the shrunken gel is much lower than the partition into the swollen gel, because the NaCl molecules tend to expel from hydrophobic conditions. The important finding of the present partition experiment is that NaCl molecules are distributed in the shrunken gel, even though their amount is very small. This has not been clarified in an experiment reported previously.<sup>10</sup> The experiment could not

deny the possibility of the null partition into the shrunken gel because the partition value was of the same order as the experimental error. The  $K_p$  value of the shrunken gel in the 1 M NaCl solution decreases up to 28 °C and then levels off. This indicates that the degree of dehydration of the shrunken gel chains increases with the rise in temperature at temperatures above the transition point, 22 °C. A decrease in the chemical potential of water molecules with the increase in temperature shifts the hydration-dehydration equilibrium to increase the dehydrated unit of the chains.<sup>2</sup> The hydrated parts of the chains in the shrunken gel at the transition dehydrate above the transition temperature, up to 28 °C.<sup>2</sup> The weak temperature dependence of the  $K_p$  value of the shrunken gel in the 0.3 M NaCl, shown in Figure 1, is due to a lack of accuracy of the experimental data.

The existence of NaCl in the shrunken gel increases the  $Y_i$  and  $Y_e$  values, as shown in Figure 2. The molar ratio of the monomeric unit to the NaCl molecule in the shrunken gel in the 0.75 M NaCl aqueous solution is about 300, which is estimated from the  $K_p$  being 0.04 and the size of the shrunken gel being about half of that of the synthesized gel. It is astonishing that such a small amount of NaCl causes so much of an increase in the moduli of the shrunken gel,  $Y_e$  and  $Y_i$ , as shown in Figure 2. The increase in the moduli of the gel can be explained by the decrease in the configurational freedom of the chains, as follows. The hydrated water molecules surrounding the  $\text{Na}^+$  and  $\text{Cl}^-$  ions form hydrogen bonding with each other<sup>12</sup> because of their strong electric field. In the shrunken gel, parts of the water molecules are considered to bind to the amide group. The hydrogen bonds forming among water molecules bound to the amide groups act as the constraint force for the chains to increase the moduli. Because of the long-range nature of an electric field in a medium with a low dielectric constant,<sup>13</sup> such a small amount of NaCl could promote the hydrogen-bond formation to increase the moduli, as shown in Figure 2. This is rather speculative explanation for the increases of  $Y_e$  and  $Y_i$  values due to NaCl.

The  $Y_e$  values of the shrunken gel in the NaCl and NaCl-free solutions are rather temperature-independent, as shown Figure 2. However, the temperature dependence of  $Y_i$  of the shrunken gel is greatly enhanced by the addition of NaCl. The increase in temperature makes the hydrated parts of the chain dehydrated, as described above. The changing of the chain from the hydrated to the dehydrated state is inferred to be very small, because the change in the size of the shrunken gel due to temperature is very small. Therefore, rising temperatures produce little change in the  $Y_e$  modulus, which is affected by the entropy force of the cross-linking network in the shrunken gel. However,  $Y_i$  of the shrunken gel in the NaCl-free solution significantly increases with rising temperatures. This indicates that the stress of the dangling chains,  $\Delta Y(0)$ , is very sensitive to the degree of chain dehydration and is dependent on temperature. An increase in the degree of dehydration reduces the dielectric constant of the gel to strengthen the hydrogen-bonding force. The water molecules cluster and partly form the hydrogen bonds with amide groups to bridge the chains in the shrunken gel. The difference in temperature sensitivity between  $\Delta Y(0)$  and  $Y_e$  indicates that the water bridges constrain the freedom of the dangling chains more than the freedom of the cross-linking chains. It is plausible that the free dangling chains are more constrained by the bridges than the cross-linking chains. The increase in  $\Delta Y(0)$  with the increase in the degree of dehydration or temperature is enhanced, as shown in Figure 2, by the



existence of a small amount of NaCl, which strengthens the water bridge by the mechanism mentioned before.

The NaCl-mediating hydrogen-bond formation mentioned above is also indicated by the significant increases in  $n_0$  and  $n_1$  with the concentration of NaCl, as shown in Table 2. The  $\Delta H_1$  decreases with the decrease in the changing number of hydrogen bonds per one water molecule in transferring it from the hydrophobic hydration layer to the bulk, which is the result of a structural change in the cluster of water molecules. It is inferred from the decrease in  $\Delta H_1$  with  $C_S$ , as shown in Table 2, that  $\text{Na}^+$  and  $\text{Cl}^-$  ions change the clustered structures of water molecules in the shrunken gel. However, further experiments are needed to clarify how the structure changes.

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## References and Notes

- (1) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379–6380.
- (2) Sasaki, S.; Maeda, H. *Phys. Rev. E* **1996**, *54*, 2761–2765.
- (3) Park, T. G.; Hoffman, A. S. *Macromolecules* **1993**, *26*, 5045–5048.
- (4) Suzuki, A. *Adv. Polym. Sci.* **1993**, 199–240.
- (5) Kawasaki, H.; Sasaki, S.; Maeda, H.; Mihara, S.; Tokita, M.; Komai, T. *J. Phys. Chem.* **1996**, *100*, 16282–16284.
- (6) Sasaki, S.; Kawasaki, H.; Maeda, H. *Macromolecules* **1997**, *30*, 1847–1848.
- (7) Sasaki, S.; Koga, S. *Macromolecules* **2002**, *35*, 857.
- (8) Curro, J. G.; Pincus, P. *Macromolecules* **1983**, *16*, 559–562.
- (9) De Gennes, P. G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979; p 230.
- (10) Kawasaki, H.; Mitou, T.; Sasaki, S.; Maeda, H. *Langmuir* **2000**, *16*, 1444.
- (11) Shibayama, M.; Mizutani, S.; Nomura, S. *Macromolecules* **1996**, *29*, 2019.
- (12) Annaka, H.; Motokawa, K.; Sasaki, S.; Nakahira, T.; Kawasaki, H.; Maeda, H.; Amo, Y.; Tominaga, Y. *J. Chem. Phys.* **2000**, *113*, 5980.
- (13) Sasaki, S.; Koga, S.; Maeda, H. *Macromolecules* **1999**, *32*, 4619.