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Effect of salt on the elastic modulus of poly(*N*-isopropylacrylamide) gels

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Abstract

The measurement of tensile modulus of poly(*N*-isopropylacrylamide) (PNIPA) gel in the solution of NaCl, NaI, $LiNO_3$ and $NaNO_3$ was carried out. It was confirmed that the tensile modulus of PNIPA gel in the solution of salt depends on the volume of gel regardless of the kind and concentration of salts. This result leads us to the conclusion that the addition of salt effect only on the mixing contribution to the Flory's type free energy of gel especially in the swollen state. Therefore, our result is in agreement with a recent remarkable discovery that the volume of PNIPA gel depends only on the chemical potential of water in spite of the kind of additives. On the other hand, it was found that on the volume phase transition point and in the deswollen state, the elasticity of PNIPA gel depended on the concentration and kind of the salt because the viscoelasticity emerged due to the shrinkage of polymer network. © 2002 Published by Elsevier Science Ltd.

Keywords: Salt; Volume phase transition; Tensile modulus

1. Introduction

Recently, great many researchers have worked on the polymer gels from both sides of fundamental science and applied science [1]. Above all, it is notable that the experimental discovery of the volume phase transition of gels by Tanaka was one of the most important clues for the current trends of the above-mentioned gels [2]. The volume phase transition of gel was predicted in 1968 by Dušek in the manner of mean field theory [3]. Nowadays, the equilibrium volume change of gel is generally explained by the Flory–Rehner theory [4–6]. Although the original Flory–Rehner theory describes well an essential core of the swelling behaviors from an aspect of the balance of mixing and elastic contribution to the osmotic pressure or free energy of gels, this theory never realizes discontinuous volume change of electrically neutral gel.

However, Hirokawa et al. discovered that neutral gel also exhibits discontinuous volume change in the study of poly(*N*-isopropylacrylamide) (PNIPA) gel [7]. Nowadays, PNIPA gel is well known to exhibit reversible thermal volume phase transition, at $T_t \approx 33.8$ °C. Below T_t, the gel is in the swollen state and the volume shrinks above T_t. After the discovery of discontinuous volume change of PNIPA gel, Erman and Flory had modified their theory [8]. In order to explain the discontinuous volume change of the neutral gel, they had taken account of the dependence of polymer concentration, ϕ, dependence on the interaction parameter, χ, by expansion in terms of ϕ. According to this theory, the continuity of volume change depends principally on the elastic parameters, degree of cross-linkage or number of partial chains between cross-linked points. This numerical prediction had been endorsed by some experiments [9,10].

Moreover, the state of PNIPA gel is altered by many other factors, solvent composition [11], pressure [12,13], etc. It is well known that the addition of salt causes the reduction of volume phase transition temperature of PNIPA gel [14]. On the other hand, it is also well known that the volume change of PNIPA gel becomes continuous by addition of some kinds of salts, e.g. iodide salts. It is thought that the addition of salt effects only on the mixing contribution to free energy of gel not on the elastic contribution according to conventional Flory's theory. However, considering the salt effect, it is possible that the added salts modify the elastic property of PNIPA gel. This contradiction is known as one of the problems of additivity assumption of mixing and elastic contribution to the free energy of gel, which has remained unsettled, especially with respect to the volume phase transition [15–18]. Therefore, it is necessary to make

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certain whether the addition of salts actually changes the elasticity of gel or not. In this report, we try to verify this problem by the measurement of tensile modulus of PNIPA gels in the solutions of various salts.

2. Experimental

First, the NIPA monomer (0.75 g) and *N*,*N*′-methylene-bisacrylamide (BIS: cross-linker, 4.5 mg) were dissolved in latex solutions 0.5 wt% (10 ml) to visualize the sample gels from background of image, secondly, *N*,*N*,*N*′,*N*′-tetramethylenediamine (TEMED; accelerator, 1.25 μl) and ammonium persulfate (APS: initiator, 4.5 mg) were added to the solution. After stirring for a minute, this pre-gel solution was immediately transferred into test tubes with hematocrit tubes (inner diameter, $d_0 = 0.85$ mm). These solutions were stored at about 5 °C for 24 h. After the gelation was complete, the cylindrical gels were put out of the hematocrit tubes by utilizing the temperature-induced shrinkage. These gels were washed in large amounts of distilled water for more than 3 days to remove residual chemicals and monomers. These PNIPA gels were slightly opaque due to latex. It had confirmed that the swelling property and elasticity of PNIPA gel is little affected by such low concentration of latex [19].

In order to check the elasticity of PNIPA gels, they were elongated with uniaxial tension by the following method. Both ends of gels were strapped with thin nylon threads, those diameters were about 0.1 mm, and a brass weight was attached to the bottom side of thread. These gels with the weights were hung into rectangular cell that was filled with solution of NaCl, NaI, $LiNO_3$ and $NaNO_3$ (0–2.0 mol/l) as shown in Fig. 1. The neutral length of gels, that is, the length between both knots without weight, l_0, was set into just 50 mm at 20 °C in the swelling state. The metal weights were prepared in the range of 0–0.25 g. The sample gel behaves ideal elastic body in the range of weight. The tensions, F, were calculated by

$$F = \left(1 - \frac{\rho_0}{\rho}\right)mg \tag{1}$$

where ρ_0 and ρ denotes the density of solution and metal weight, respectively. The density of solution, ρ_0 depends on the concentration and kind of added salt. The density of metal weight (brass), ρ, was 8.57 g/l. The constant, g, is the gravitational acceleration ($g = 9.8$ m/s^2). Length, l and diameter, d of the gels were measured by using available digital camera (CASIO QV300), which takes pictures as bitmap images automatically by intercommunication with a personal computer in response to temperature (accuracy: ±0.05 °C). The temperature was changed slowly, the rate lower than 0.07 °C/h, enough to consider as quasi-static, i.e. equilibrium. Moreover, since we are not concerned with hysteresis of volume change, the measurement was carried out only during heating process.

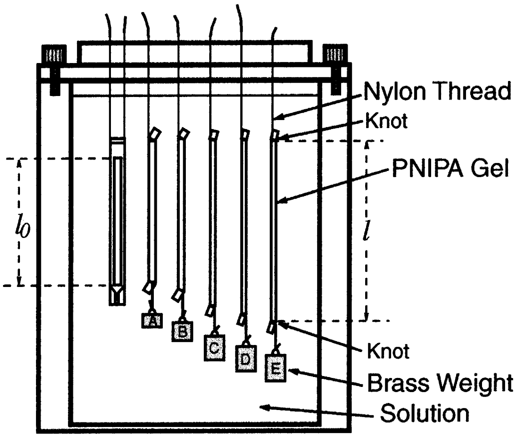

Fig. 1. The experimental setup of the rectangular cell for measurement of tensile modulus of PNIPA gels.

3. Results and discussion

3.1. Swelling ratio

Fig. 2(A)–(D) shows the results of equilibrium swelling curves of PNIPA gels in NaCl, NaI, $LiNO_3$ and $NaNO_3$ solution of various concentrations, respectively. The swelling ratio is defined as a fraction of the volume of PNIPA gel at the present state, V, and the volume at the preparation state, V_0. The volume of the cylindrical gel was calculated by $V = ld^2\pi/4$. It is clear that the volume of PNIPA gel was reduced with increase of salt concentration. Therefore, the volume phase transition temperature, T_t, became lower. As the figures indicate, the continuity of the swelling curve depends on the kind of salt. In the case of NaCl (also NaBr [20]), the discontinuity of volume phase transition was unchanged in spite of the increase of salt

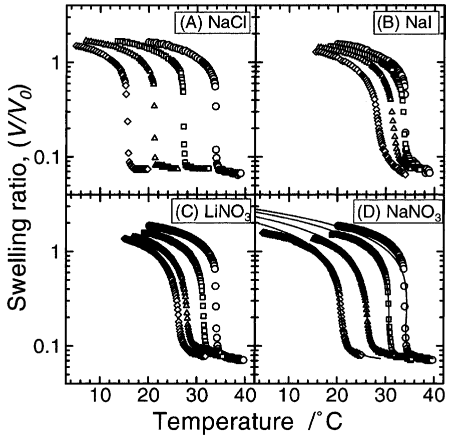

Fig. 2. The swelling ratio of PNIPA gels against temperature in the solution of (A) NaCl, (B) NaI, (C) $LiNO_3$ and (D) $NaNO_3$. The notations represent the concentration of salts, circle; 0 M, rectangle; 0.5 M, triangle; 1 M, and diamond; 1.5 M. The solid lines in figure (D) were drawn by using of Erman–Flory's theory (Eq. (2)).

concentration. On the other hand, the volume change of PNIPA gel becomes gradual (continuous) with increase of concentration of the nitrate salt and NaI. The solid lines in Fig. 2(D) denote results of theoretical calculation by use of the following equation:

$$T_{\Pi=0} = \frac{\left(\frac{1}{2}+\frac{\Delta s}{k}\right)\Theta\phi^2}{\frac{N_c v_1}{N_A V_0}\left(\frac{1}{2}\left(\frac{\phi}{\phi_0}\right)-\left(\frac{\phi}{\phi_0}\right)^{1/3}\right)-\phi-\ln(1-\phi)+\left(\frac{\Delta s}{k}-\chi_2\phi\right)\phi^2} \tag{2}$$

This equation was given by a derivation from the Erman–Flory's free energy of gel under the equilibrium condition of osmotic pressure [8]. N_A and k are Avogadro's number and Boltzmann constant, respectively. The order parameter (ϕ/ϕ_0) is a ratio of volume fraction of polymer at the present state, ϕ, and at the preparation state, ϕ_0. This ratio should have a relation with the swelling ratio as follows, $(V/V_0) \equiv (\phi/\phi_0)$. N_c and v_1 represent the mean number of partial chains between cross-linked points and the molar volume of solvent molecule, respectively. Θ, and Δs are, respectively, the temperature and contribution of entropy for Flory's interaction parameter, χ_1. The relation between Δs and χ_1 is given by

$$\frac{1}{2}-\chi_1=\left(\frac{\Delta s}{k}+\frac{1}{2}\right)\left(1-\frac{\Theta}{T}\right) \tag{3}$$

χ_2 is an extended Flory's interaction parameter about the polymer concentration, ϕ, as follows [8]:

$$\chi=\chi_1+\chi_2\phi+\cdots \tag{4}$$

Although χ_1 has to be a function of temperature, T, as shown in Eq. (3), χ_2 is a constant. Although Eq. (2) describes swelling property of gel qualitatively, it is known that there is a large deviation between the calculation and experiment as in Fig. 2(D). Here, we concentrate on the continuity–discontinuity of volume change of PNIPA gel, and not on the quantitative calculation.

To realize the essential properties of the experimental result through the equilibrium swelling of PNIPA gel in the NaNO$_3$ solution, we had chosen values for the parameters, χ_2 and Θ of Eq. (2), as shown in Fig. 3, where dimensionless constant values, $N_c v_1/N_A V_0$ and ϕ_0, were employed as 0.008 and 0.07, respectively. The volume phase transition temperature, T_t (open circle), was defined as a temperature on the flexion point of the swelling curve of experimental data. On the other hand, Θ should be different from T_t in substance, because Θ is a temperature in the case that the both side of Eq. (3) is equal to 0. However, it seems that these two characteristic temperatures are almost equal in the range of experimental error. It is thought that the reduction of T_t or Θ of PNIPA gel in the change of salt concentration would be caused by reduction of activity of water molecules because of hydration to ions [14,21]. Therefore, in the case of NaNO$_3$, T_t was not proportional to the concentration of salt.

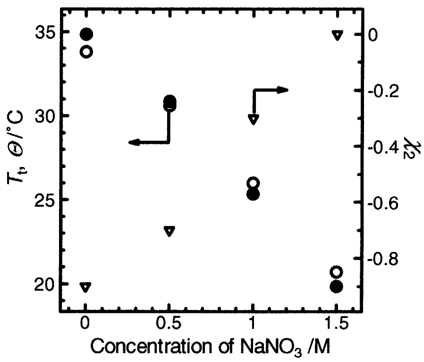

Fig. 3. The variation of parameters, Θ and χ_2, for theoretical calculation in Fig. 2(D). The open circle and filled circle denote the values of T_t and Θ, respectively.

The more continuous the gels change its volume with increase of the concentration of salt, e.g. NaNO$_3$ as shown in Fig. 2(D), larger is the negative value of parameter χ_2. However, it was not clear whether χ_2 was proportional to the concentration of NaNO$_3$ or not. Moreover, it is needless to mention that χ_2 is constant in the case of NaCl, because the outlines of swelling curves are closely congruent independent of the concentration. Although the value of ϕ_0 is stoichiometrically determined by the condition of preparation, the number of partial chain, N_c cannot be determined because of the increment of apparent cross-linked points caused by the entanglement of chains. Thus, the value of N_c was arbitrarily determined to fit the experimental result.

The first thing we notice is that the swelling curves in the swollen state show nearly coincidence with each other by shift along thermal axis. This tendency implies that the value of Δs in Eq. (2) should be constant against change in the concentration of any kind of salt, because it is known that increment of Δs occurs with unexpected decrement of swelling ratio. We did not change the pre-factor of elastic term, $N_c v_1/N_A V_0$ against the concentration of salt in this calculation. Therefore, according to the calculation, it is expected that the addition of salt would not effect on the elastic contribution to free energy of gel. However, the fact is still unknown whether the addition of salt does not really effect on the elasticity of gel. In order to make clear this point, it is essential to measure the elasticity of PNIPA gel in the salt solution.

3.2. Elastic modulus

Tensile modulus (Young's modulus, E) of PNIPA gel in the salt solution was measured. The modulus was calculated with experimental data of tensile strain, $\varepsilon=(l-l_0)/l_0$, and cross-section of stretched gel, S, on the assumption of Hooke's law at each temperature. Where l and l_0 represent the length of gel with strain and without strain, respectively. In this experimental range of weight, the sample gels were

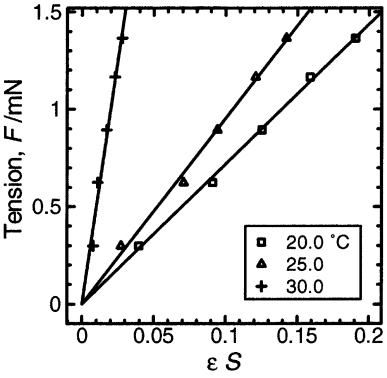

Fig. 4. A plot of tension against the product of tensile strain, ε and cross-section, S of PNIPA gel in 1.0 M $NaNO_3$ solution. The straight lines were drawn by least square method.

elongated as ideal elastic bodies in both of the swollen and the deswollen state. Therefore, the tensile modulus was calculated by linear least squares data fitting method to the Hooke's law,

$$E = F/(S\varepsilon) \tag{5}$$

where F denotes the tension, i.e. weight of metal in the solution.

We have given an example to show that our gels obeyed Hooke's law at this range of weight in Fig. 4. The tension, F, was plotted against products of S and ε of PNIPA gel in 1.0 M solution of $NaNO_3$. Solid, dashed and dotted lines represent calculated result by linear least squares method, for the experimental result at 20.0, 25.0 and 30.0 °C, respectively. Here, the tensile moduli, E, were obtained as slopes of these lines. In the state of swollen and deswollen, each data were in good agreement with Hooke's law.

Fig. 5 shows the tensile modulus of PNIPA gel in the solutions of various kinds of salts in the concentration range 0–2 M against temperature. The tensile modulus of PNIPA gel increased with the shrinkage of gel. The abrupt change of the modulus around the volume phase transition point becomes continuous with increasing of concentration of the salt in the case of nitrate salt and NaI, naturally because the swelling curves also become continuous. Moreover, a downward cusp point was found on the transition temperature in the solution of NaCl or low concentration of nitrate salts and NaI. This phenomenon depends on the gap between the change of length and diameter, i.e. Poisson's ratio that will be examined later.

Additionally, it should be noted that the modulus tends to increase with increasing of salt concentration especially in the deswollen state in the case of some kind of salt, e.g. NaCl, $LiNO_3$, and $NaNO_3$ in Fig. 5. PNIPA gel behave as an ideal elastic body in the swollen state, in contrast it exhibits viscoelastic property in the deswollen state [22]. Thus, it appears that time dependence of the elastic modulus become remarkable in the deswollen state. In our experiment, the heating rates were set 0.1 K/120 min for sodium halide added system and 0.1 K/90 min for nitrate salts added system. In terms of this point, if these gels were heated more slowly enough, the value of tensile modulus in the deswollen state might be invariant in change of the salt concentration.

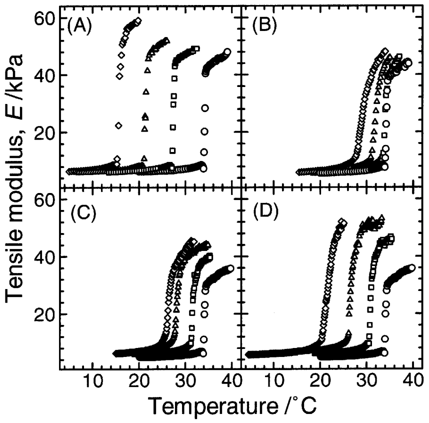

Fig. 5. The tensile modulus (Young's modulus, E) of PNIPA gel in the solution of (A) NaCl, (B) NaI, (C) $LiNO_3$ and (D) $NaNO_3$ in various concentration as a function of temperature. The notations represent the concentration of salts, circle; 0 M, rectangle; 0.5 M, triangle; 1 M, and diamond; 1.5 M.

3.3. Dependence of ϕ on E

Now, in order to check the relation between the concentration (i.e. volume fraction) of PNIPA gel and the modulus, these results were re-plotted in Fig. 6 on the log–log scaled planes. These figures enable us to compare the moduli except for the effect of salt concentration. In the low polymer concentration region, i.e. swollen state, the values of tensile modulus of PNIPA gels almost coincide each other irrespective of variance of the salt concentration. This result clearly shows that the elasticity of PNIPA gel in

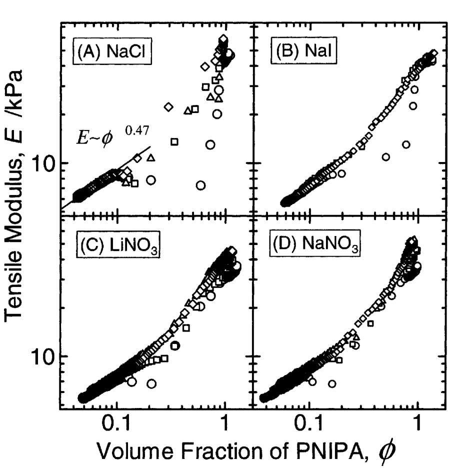

Fig. 6. The tensile modulus (Young's modulus, E) of PNIPA gel in the salt solution of various concentrations as a function of volume fraction of PNIPA ($\phi = \phi_0 V_0/V$). The notations represent the concentration of salts, circle; 0 M, rectangle; 0.5 M, triangle; 1 M, and diamond; 1.5 M.

the swollen state depends on its volume independent of the salt concentration. Moreover, the elasticity of PNIPA gel in the swollen state does not depend only on the concentration of salt, but also on the kinds of salts. Therefore, it is thought that the addition of salt effects only on the mixing contribution to the Flory's type free energy of gel, not effect on the elastic contribution in the swollen state. Recently, Annaka et al. had reported a remarkable result from the other aspect [20,23]. They discovered that the volume of PNIPA gel depended only on the chemical potential of water in spite of kinds of additives. Their result obviously shows that PNIPA gel cannot perceive additives without mediation of water. Taking the hydration of additives into consideration, this phenomenon is explicable. Furthermore, it is reasonable to suppose that the chemical potential of water to PNIPA gel would especially relate to Flory's χ parameter, the contact free energy between polymer and cluster of water molecules. Since χ is an essential parameter of mixing free energy of gel, it is considered that our result is in agreement with their conclusion.

The relation of E and ϕ in the swollen state can be scaled as $E \sim \phi^{\nu}$ [24]. The experimental value of the exponent, ν was determined by linear least square method to be 0.47. The power law of the elastic modulus of neutral gel was estimated by Obukhov et al. in 1994 [25]. They proposed a power relation between shear modulus, G, and volume fraction of polymer, ϕ, where the value of exponent was reported to be $7/12 \approx 0.583$. Ilavsky et al. had determined an exponent of 0.56 for the dependence of concentration on the modulus for polyurethane gel prepared in xylene [26]. Bastide et al. have determined this exponent to be 0.5 for polystylene gels in benzene [27]. In our experiment, the exponent of PNIPA gel was smaller than their results. It is thought that these gaps were caused by the way to measure the elastic modulus. Usually, the shear modulus is converted by an experimental result of the modulus under uniaxial stress, e.g. tensile modulus. Concretely, the tensile modulus related to the shear modulus as follows [28]:

$$E = 2G(\sigma + 1) \tag{6}$$

where σ denotes the aspect ratio against infinitesimal deformation called Poisson's ratio.

$$\sigma = \frac{d - \Delta d}{l + \Delta l} \tag{7}$$

Δd and Δl stand for the decrement of diameter and increment of length of gel, respectively, by infinitesimal elongation. In the case of $\sigma = 0.5$, density of sample never changes by any deformation. One of the typical series of Poisson's ratio of PNIPA gel in the salt solution was shown in Fig. 7. Poisson's ratio of PNIPA gel in the solution of $NaNO_3$ was almost constant value about 0.3 and 0.4 in the swollen state and the deswollen state, respectively. The result, $\sigma \leq 0.5$, denote that the density of PNIPA gel decreases (swells) by elongation. An important point to emphasize is a fact that the value of σ drastically decreased on the volume phase transition point. Especially, in the case of discontinuous volume change, negative Poisson's ratio was observed as same as reported by Hirotsu in 1991 [29].

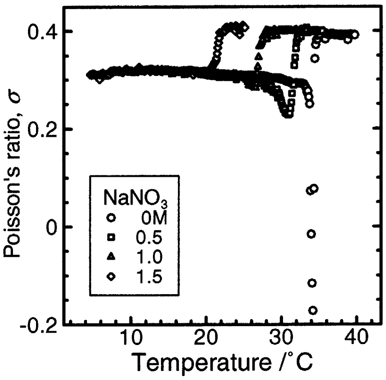

Fig. 7. Poisson's ratio, σ of PNIPA gel in $NaNO_3$ solution of various concentrations against temperature. The notations represent the concentration of salts, circle; 0 M, rectangle; 0.5 M, triangle; 1 M, and diamond; 1.5 M.

We tried to estimate the result by theoretical calculation based on the Flory's theory [6]. According to the theory, shear modulus, G, of gel is given by

$$G = \frac{N_c kT}{2V_0}\left(\frac{V_0}{V}\right)^{-1/3} \tag{8}$$

The value of tensile modulus is also given by Eqs. (6) and (8) and the experimental data of swelling ratio, (V/V_0). The constant values of N_c and V_0 were the same values used for the former calculation for the swelling curve as shown in Fig. 2(D). The calculated value of E in the swollen state was also given by the power relation, $E \sim \phi^{0.48}$. The result clearly shows that swelling behavior of PNIPA in the swollen state can be accounted for by Flory–Rehner's theory regardless of salt content in the solution.

4. Conclusion

The measurement of tensile modulus of PNIPA gel in the solution of various salts was carried out. It was confirmed that the tensile modulus depends on the volume of gel regardless of kind and concentration of salt in the swollen state. On the other hand, on the volume phase transition point and in the deswollen state, the elasticity of PNIPA gel depended on the concentration and kind of the salt, because the viscoelasticity appeared by the shrinkage of polymer network. This result leads us to the conclusion that the addition of salt affect only on the mixing contribution to the Flory's type free energy of gel especially in the swollen state. Further research on the dependence of other kind of additives on the volume change of PNIPA gels would clarify the problem about mixing contribution to the free energy of gel. Moreover, from now on, some comparisons between cross-linked polymer and uncross-linked polymer solution will be necessary to solve this problem.

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