Effects of mechanical stress on the volume phase transition of poly(N-isopropylacrylamide) based polymer gels

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The effects of mechanical stress on the volume phase transition of a poly(N-isopropylacrylamide) (PNIPA) gel as well as a copolymer gel composed of N-isopropylacrylamide (NIPA) and sodium acrylate (SA) were investigated in the relatively low stress region. The PNIPA gel without elongational stress showed the behavior close to the second order phase transition. The character of the first order transition became clear under tension, and the transition temperature increased with increasing applied stress. Similar behavior was observed for the NIPA-SA copolymer gel, but the copolymer gel showed the first order transition in the whole stress range investigated. The thermodynamical linear region, where the transition temperature varies linearly with applied stress, was narrower than the mechanical linear region determined by the stress–strain relation of the gels. The change in the transition behavior by the application of the mechanical stress originated chiefly from the volume change in the gels by the applied mechanical stress. It was found that the curve of the transition temperature against applied stress corresponds to the phase boundary between the swollen and collapsed phases for the gels. On the basis of the experimental data, a phenomenological model describing the volume phase transition of the polymer gels is proposed in the frame of the Landau-type free energy expression. © *2000 American Institute of Physics.* [S0021-9606(00)51341-5]

I. INTRODUCTION

Some polymer gels show a discontinuous volume change responding to an infinitesimal change of an external field such as temperature. The discontinuous change in volume is called the volume phase transition of polymer gels. Many studies[1] have been attempted to clarify the mechanism of the volume phase transition of polymer gels. In most studies, poly(N-isopropylacrylamide) (PNIPA) and PNIPA based copolymer gels have been used. PNIPA gels are electrically neutral but the gels show the discontinuous volume change at a certain temperature around 35 °C if the crosslink density and polymer concentration are low enough. The theory[2] developed by Tanaka *et al.*, which is based on the free energy expression of the Flory type, can describe a basic feature of the volume phase transition of the polymer gels, but the applicability is limited to the polymer gels with higher ion content than the critical value. The origin of the volume phase transition of the neutral PNIPA gels still remains unclear at present. The effects of the application of the mechanical stress have also been investigated to clarify the nature of the phase transition.[3–8] For PNIPA gels as well as PNIPA based copolymer gels, it has been well established that the discontinuous character becomes stronger as the applied stress increases, but the effects of the mechanical stress on the phase transition cannot be still fully understood in the region of small deformation as well as large deformation.

We have shown[9–11] that the application of mechanical work to polymer gels induces the volume change in the polymer gels. The polymer gel under elongation has lower polymer concentration, or larger volume than that at rest, namely, in the nondeformed state. Generally, the effects of the application of the mechanical work on the phase transition behavior cannot be compared directly between the deformed and nondeformed gels, because they are different in polymer concentration and then the difference may affect the phase behavior of the gels in the different way. When the applied strain (or, stress) is so small that the stress–strain relation remains linear, however, the effects of the applied mechanical stimulus may be expected to appear only as a change in volume (polymer concentration) of the gels. The aim of this study is to examine the effects of the application of the smaller elongational stress on the volume phase transition through the change in volume for polymer gels near the critical point for the volume phase transition. The effects of the introduction of ionic groups to network chains on the transition behavior are also investigated. A theoretical model with the Landau-type free energy expression is also proposed on the basis of the experimental results.

II. EXPERIMENT

Two types of polymer gels were prepared by radical polymerization technique in distilled water. One is a PNIPA gel sample-coded as PNS00, and the other is a copolymer gel comprising N-isopropylacrylamide (NIPA) and small amount of sodium acrylate (SA), which is sample-coded as PNS10. In the polymerization, N, N'-methylene-bis(acrylamide) (BIS) and ammonium peroxodisulfate(AP)

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were used as a crosslinker and as initiator, respectively. The agents were dissolved in 100 ml of distilled water. Molar concentrations for PNS00 were 1525 mM (NIPA), 25.4 mM (BIS) and 3.5 mM (AP), and those for PNS10 were 1518 mM (NIPA), 10 mM (SA), 25.5 mM (BIS), and 3.5 mM (AP). As an accelerator, N, N, N', N'-tetramethylethylenediamine (240 μl) was also used for the polymerization of the polymer gels. The total monomer concentration before gelation (namely, in the pregel solution) was fitted to be 15 wt. %. After the pregel solutions were poured into glass tubes, the gelation was performed at 20 °C for 24 h. Then, the gels were removed from the tubes, and were kept in distilled water for 2–3 d to wash out the reaction residues and also to achieve the equilibrium swelling. PNS10 reswelled to a larger extent than PNS00 in the equilibration process. The diameter d and length L of the gels were, respectively, about 300 μm and about 15 mm at 30.0 °C.

The cylindrical gel specimens were fixed in a specially designed water bath. The temperature of the specimens was kept constant by circulating temperature-controlled water in the outer jacket of the apparatus. The accuracy in the measurement of temperature T was ±0.02 °C. Both d and L were monitored by a combination of a charge coupled device camera and a TV monitor through the glass window of the apparatus. Elongation was made by applying metal weights, each of which was 35 mg, to the bottom of the cylindrical specimen with an adhesive. The stress–strain curves for the gels were measured at 30.0 °C in elongational mode. In the measurements, the tension (stress) was varied by changing the number of weights from one to two, and then finally to four. The temperature T dependence of d was investigated on heating and then on cooling in the region of T near the volume phase transition temperature T_{tr}. The temperature was varied at an interval of 0.1 °C and the tension was varied in the same way as in the case of the mechanical tests.

A combination of the true stress σ and engineering strain ϵ was employed for the data analysis. They are defined by

$$\sigma = \frac{f}{S}, \tag{1}$$

$$\epsilon = \frac{L - L_0}{L_0}, \tag{2}$$

where f is the tension and S is the cross-sectional area under elongation, L_0 being the value of L at rest. Specifically, σ and ϵ at 30.0 °C are designated as σ_{30} and ϵ_{30}, respectively.

III. RESULTS AND DISCUSSION

A. Volume phase transition of PNIPA and NIPA-SA copolymer gels

Figure 1 shows a plot of ϵ_{30} against σ_{30} for PNS00 and PNS10. The data points for each gel specimen fall well on a straight line, showing a linear stress–strain relation in this load range. The slope of the line gives the initial Young's modulus at 30.0 °C (E_{30}). The value of E_{30} for PNS00 was 8.5×10^4 Pa and that for PNS10 was 7.7×10^4 Pa, indicating that the modulus decreases by the introduction of ionic

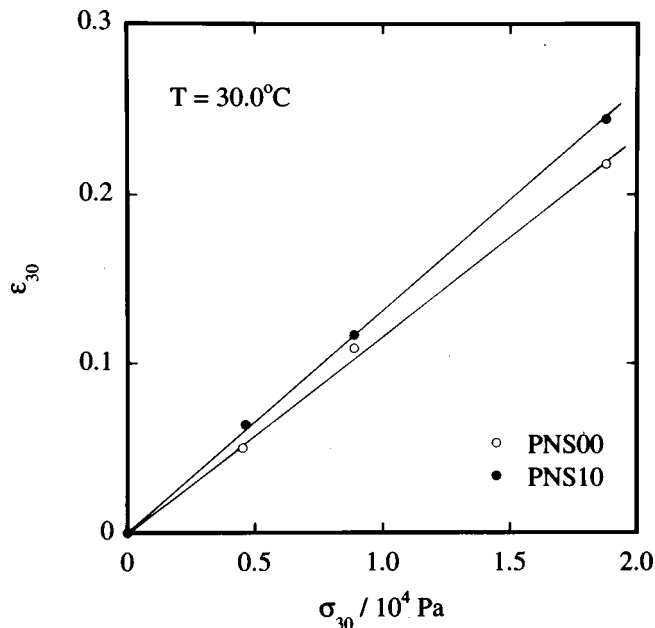FIG. 1. A plot of strain ϵ_{30} against stress σ_{30} for PNS00 and PNS10 at 30.0 °C. The lines were drawn as a guide to the eye.

groups into network chains. As stated in Sec. II, the gels were immersed in distilled water after preparation to wash out the reaction residues, and the gels swelled further in this process. The change in volume was larger for PNS10. This means that the polymer concentration for PNS10 is lower than that for PNS00, although the final concentration for the gels could not be measured with reliable accuracy because the specimens were too small. The results for E_{30}, however, indicate that the polymer concentration decreases by the introduction of ionic groups.

In Fig. 2, the reduced diameter is plotted against T for PNS00. Here, d_{30} is the value of d at 30.0 °C and is also the value in the deformed state for the gels under tension. A discontinuity is observed on all of the four curves, and the transition temperature T_{tr}, defined as an average of temperatures for the onset and completion of the discontinuous change, increases with increasing load. The degree of the discontinuity increases with increasing load for the curves, but the discontinuity for the curve without loading is rather small compared with that for the other curves. No hysteresis is observed for the curves except for the highest load; namely, T_{tr} is identical both on heating and cooling. On the other hand, the curve at four weights shows hysteresis. For the curve at the highest load, the transition temperature and degree of the discontinuity, both of which were defined as an average on heating and cooling, show the highest values. The estimated discontinuity range in d/d_{30} is almost identical for the curves under loading, while that for the curve without weight is very narrow and is shifted to the upper side. In this study, the measurements were performed at an interval of 0.1 °C, meaning that the change in diameter may be classified as a discontinuous transition even if the actual change is continuous, when the change is very steep. The upward shift and the narrowing of the discontinuity range for the unloaded curve suggests the possibility that the T dependence curve of
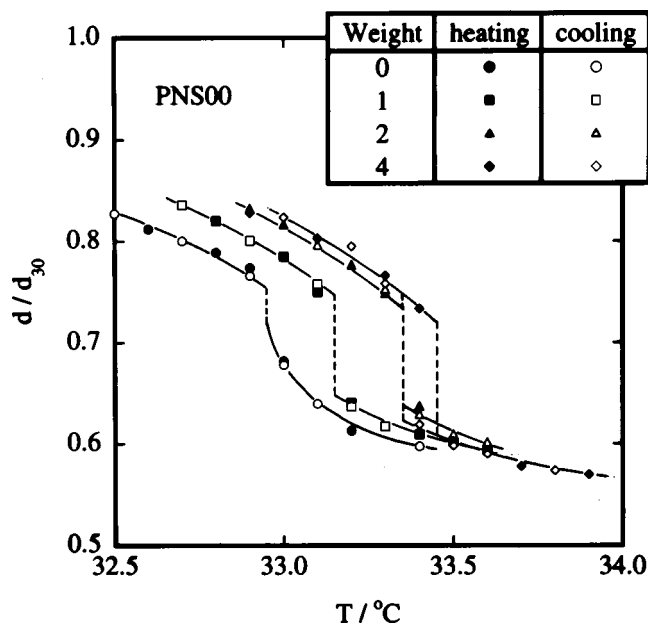
FIG. 2. Temperature T dependence curves of the reduced diameter d/d_{30} for PNS00. Here, d stands for the diameter and d_{30} is that at 30.0 °C. The curves were drawn as a guide to the eye.

FIG. 3. Temperature T dependence curves of the reduced diameter d/d_{30} for PNS10. Here, d stands for the diameter and d_{30} is that at 30.0 °C. The lines were drawn as a guide to the eye.

d is continuous for the unloaded curve. Even in this case, there exist two possibilities: one corresponds to the second order transition and the other is the steep change with a finite slope. Although we cannot distinguish one from the other definitely only from the experimental results shown here, the curve without loading must be closer to the curve showing the second order transition. Then, we regard here the change in the unloaded curve as the second order transition and also T_{tr} for the curve as the critical temperature T_c. This means that PNS00 has the critical composition (polymer concentration); namely, the gel shows the volume phase transition of the second order in the stress-free state.

Figure 3 shows a similar plot for PNS10. A discontinuity is also observed on all curves, and only the curve at the highest load shows the hysteresis behavior, as is the case of PNS00. The degree of the discontinuity in diameter is relatively large for all curves, suggesting that for PNS10 the discontinuous change actually occurs in every circumstance investigated in this study. The transition temperature and the degree of discontinuity increase with increasing load.

The transition temperature T_{tr} is plotted against the stress at 30.0 °C (σ_{30}) in Fig. 4. As can be seen from the figure, T_{tr} increases linearly with increasing load except in the case of the highest load for both types of specimens, and saturation of T_{tr} is observed for the curves at high stresses. Comparing T_{tr} at the same stress level, PNS10 shows higher T_{tr} than that of PNS00. The similar behavior has also been reported by Suzuki *et al.*[8] As shown in Fig. 1, the linear region observed in stress–strain behavior, which we may call the mechanical linear region, extended up to the highest load for both gels. Thus, the linear region on the T_{tr} vs σ_{30} plot, which we call the thermodynamical linear region, becomes narrow compared with the mechanical linear region. The two curves in Fig. 4 are parallel, suggesting that the effects of mechanical stress on T_{tr} are almost identical for both types
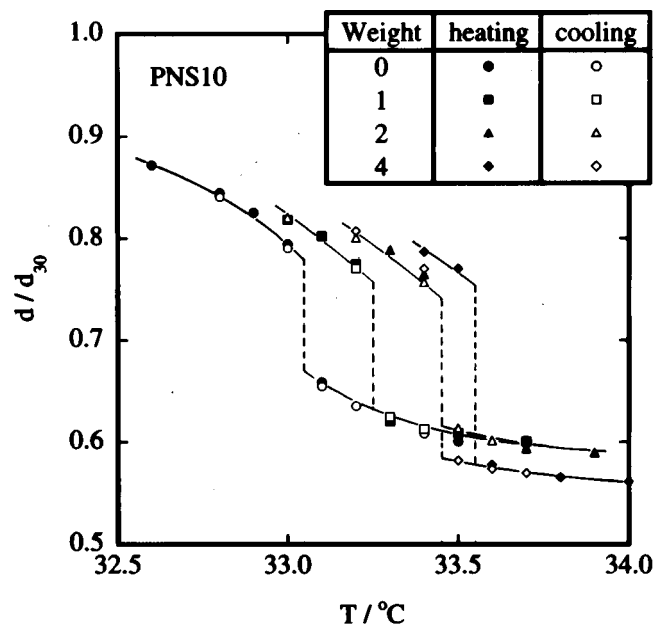
of gels. The region above the curve corresponds to the collapsed state while the region below the curve to the swollen state, meaning that the curve is a phase boundary between these two phases. As can be seen from the curve for PNS00, it is also understood that the boundary starts from the critical point. The tension (or stress) dependence curves of T_{tr}, as the curves in this figure, have been obtained for various PNIPA based polymer gels,[6–8] but so far it has not been noticed that the dependence curve actually corresponds to the phase boundary for the gel specimen. The existence of
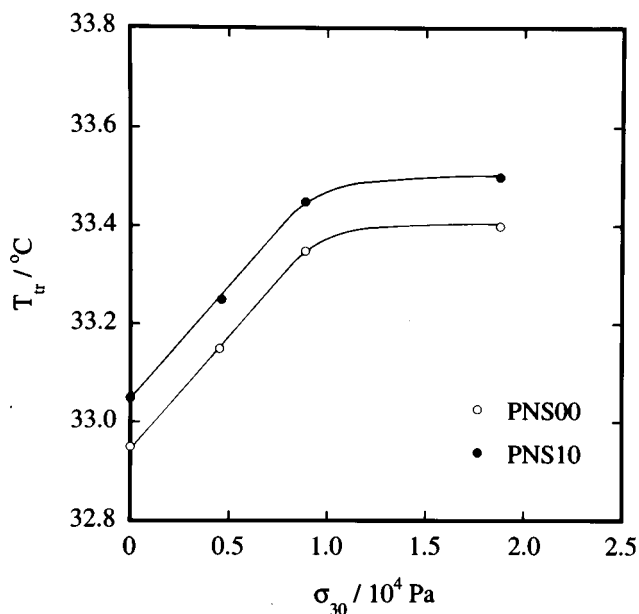

FIG. 4. A plot of transition temperature T_{tr} against applied stress at 30.0 °C σ_{30} for PNS00 and PNS10. The curves were drawn as a guide to the eye.
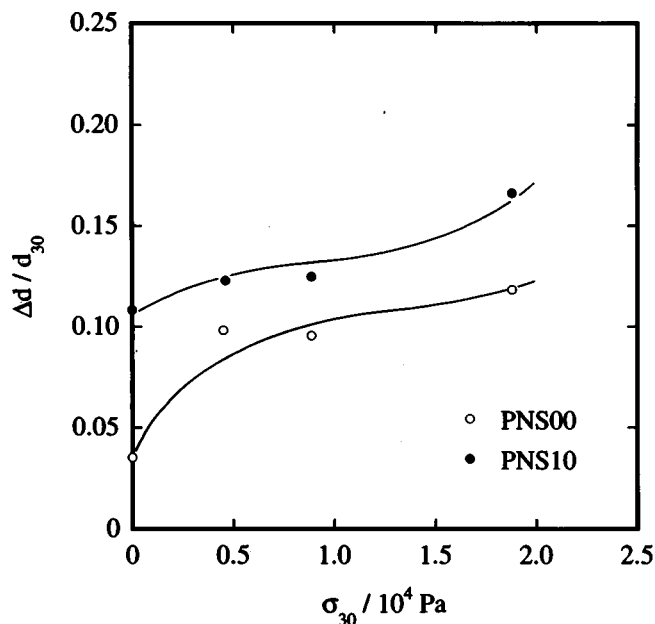
FIG. 5. A plot of degree of discontinuity measured in the reduced diameter $\Delta d/d_{30}$ against applied stress at 30.0 °C σ_{30} for PNS00 and PNS10. Here, Δd is the change in diameter at the transition temperature and d_{30} is the diameter at 30.0 °C. The curves were drawn as a guide to the eye.

FIG. 6. A plot of the reduced volume against temperature T for PNS00. Here, V is the volume, V_c being the volume at the critical point. The numerals stand for the number of weight. The curves were drawn as a guide to the eye. The region inside the dashed curve corresponds to the unstable region.

the phase boundary enables us to apply the conventional thermodynamical relations valid for systems undergoing the first order phase transition to the polymer gels if the stress is converted appropriately into pressure. For example, using the Clapeyron equation we can estimate the change in thermodynamical quantities, such as entropy and enthalpy at the volume phase transition. Figure 5 shows a plot of the degree of discontinuity in diameter estimated at T_{tr} against σ_{30} for PNS00 and PNS10. As a measure of the discontinuity, the discontinuous jump in d (Δd) normalized by d_{30} is used. As stated previously, we regarded PNS00 without loading as a specimen showing the second order transition. In this sense, the corresponding data point in this figure must be zero, but here the nonzero value, obtained directly from Fig. 2, is plotted. For both gels, $\Delta d/d_{30}$ appears to fall on a convex curve at small stresses, and the data point at highest stress deviates upward from the curve. The curve for PNS10 is located upward compared with the curve for PNS00.

Figure 6 shows how the volume V of PNS00 changes with T. In the figure, a reduced variable defined by $(V/V_c)-1$ is used, where V_c is the value of V at the critical point and was estimated from the curve without metal weight, which we regarded as undergoing the second order transition. The transition curve without loading is drawn to show a continuous transition. This figure excludes the data at highest weights, which showed the nonlinearity in the T_{tr} vs σ_{30} plot. It is clear that the curves under loading have a larger volume than those without loading over the entire range of T examined and V for the curves increases with increasing load. The transition temperature T_{tr} also moves to the higher temperature side and the degree of discontinuity becomes large, as the applied load increases. In the stress-free state, T_{tr} for a PNIPA gel prepared at the monomer concentration of 10 wt. % and the same NIPA/BIS ratio as PNS00 became
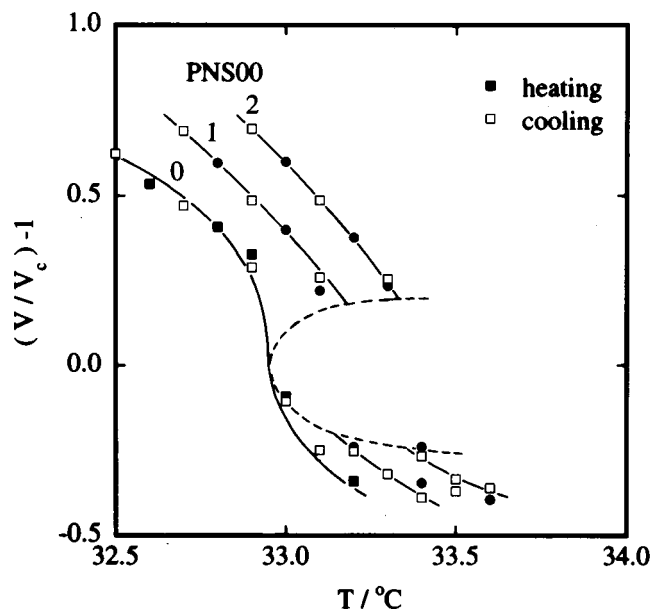
1.2 °C higher than that of PNS00. The degree of discontinuity was also larger for the 10 wt. % specimen. These indicate that the effects of tension on the transition behavior can be explained chiefly by the increased volume (or decreased polymer concentration) due to the application of mechanical stress.

B. Landau model for volume phase transition under tension

Tanaka *et al.* have proposed a theory[2] to explain the basic feature of the volume phase transition of polymer gels using the Flory-type free energy, but the theory is applicable only to the ionic gels with higher ion contents. Even using the Flory-type free energy, a quantitative description for the volume phase transition of the PNIPA based polymer gels swollen by water cannot be made at present. This is because the transition is accompanied by the dehydration of the solvent molecules; namely, the dehydration of the hydrophobic solvation. For these systems a phenomenological model must be useful for the detailed analysis of the volume phase transition. The Landau-type phenomenological theory[12,13] appears very attractive to explain the volume phase transition of electrically neutral polymer gels because the theory gives an essence of the physics of volume phase transition in a simple form, although the theory has been recognized to bear several defects and the applicability is also limited to the semiquantitative level. In addition, the Landau model has an advantage that the effects of an external field, such as mechanical stress on the transition behavior, can be easily taken into account as a perturbation term. Here, a simple model within a frame of the Landau theory is shown on the basis of the experimental results obtained in this study.

Polymer gels in solvent change their volume by the application of the mechanical stress.[3,9–11] From the thermodynamical point of view, this originates from the fact that the system is semiopen, namely the solvent molecules can move freely through the interface between gel and solvent phases. The reswelling by the application of mechanical stress is considered to occur because the system is unstabilized by the applied stress at a constant volume and then the system moves to a new equilibrium state under deformation by changing the volume. This volume change occurs isotropically even if the applied mechanical stress (or deformation) is anisotropic,[11] indicating that the reswelling process may be accounted for simply by the difference in a swelling pressure between deformed and nondeformed states, and the polymer network is expanded to balance with the solvent pressure. Since the average pressure generated by the application of the mechanical stress is given by $-\text{Tr}\,\boldsymbol{\sigma}/3$ using a stress tensor $\boldsymbol{\sigma}$, we can define a swelling pressure ΔP acting outwards inside the gel by

$$\Delta P = \frac{\text{Tr}\,\boldsymbol{\sigma}}{3}. \tag{3}$$

This quantity determines the degree of volume change between the loaded and unloaded states. Usually, the reference frame to describe the deformation is chosen to be the nondeformed state of the gels. It should be noted that ΔP in Eq. (3) is different in meaning from the swelling pressure (or the osmotic pressure) used in a usual sense, because ΔP has not vanished, even in the equilibrium state. The value of ΔP is positive when the gels swell by the application of the mechanical stress.

The experimental results obtained in this study showed for the PNIPA and NIPA-SA copolymer gels that the second order transition as well as the first order transition can occur depending on the magnitude of stress. The PNIPA gel (PNS00) without loading especially had the critical composition. As stated previously, the stress dependence curve of T_{tr} could be interpreted as a phase boundary between the swollen and collapsed states in the pressure–temperature plane, and the curve for PNS00 started from the critical point. These features are expressed by the Landau model for the second order phase transition under an extended field. We write the terms of interest in the expression of the free energy density g as

$$g = A\left[\frac{B}{2}(\beta - \beta_c)\varphi^2 + \frac{C}{4}\varphi^4 - h\varphi\right], \tag{4}$$

$$h = \Delta P + k(\beta - \beta_c), \tag{5}$$

where A, B, and C are positive constants, and $\beta = 1/T$. The quantity β_c is the value of β at the critical point, namely, $\beta_c = 1/T_c$. The parameter β was introduced to convert the negative T dependence of V for the PNIPA and NIPA-SA copolymer gels into a conventional form. The order parameter φ is defined using the polymer concentration in the gel c and that at the critical point c_c as $\varphi = c - c_c$. The last term in the right-hand side of Eq. (4) is added as a perturbation to take into account basically the effects of volume change by the application of mechanical stress. This functional form

was introduced from the analogy to the van der Waals fluids.[12] The equation $h = 0$ determines the phase boundary of the gels near the critical point and the constant k in Eq. (5) corresponds to the slope of the boundary (for example, the curve in Fig. 4). The model characterized by Eqs. (4) and (5) has a wide applicability to the volume phase transition under tension; namely, the second order transition is realized when no external field exerts on the system ($h \equiv 0$), while the transition is smeared when h keeps a constant sign over the whole range of β. If h changes its sign at a certain value of β in the region of $\beta < \beta_c$, the first order transition occurs there and the transition point is identified by $\beta = \beta_c - (\Delta P/k)$. When the first order transition takes place, $(T_{tr} - T_c)$ scales with ΔP as

$$(T_{tr} - T_c) \sim \Delta P. \tag{6}$$

The coexistence curve has the form of

$$(T_{tr} - T_c) \sim \varphi^2. \tag{7}$$

When the deformation is a uniaxial elongation, Eq. (6) leads the linear relation $(T_{tr} - T_c) \sim \sigma$. It is clear that this relation holds well for PNS00 at low stresses since T_{tr} for the unloaded curve was regarded as T_c (Fig. 4). The thermodynamical linear region in the plot of T_{tr} vs σ_{30} was narrower than the mechanical linear region in the plot of ϵ_{30} vs σ_{30}. The narrowness of the thermodynamical linear region might be because this linear region corresponds to the critical region.

The introduction of ionic groups to the network chains increased the volume of the gel. This may be considered because a solvent pressure p changed by the introduction of ionic groups. When a new type of swelling pressure $\Delta\Pi$ defined by

$$\Delta\Pi = p - p_0 \tag{8}$$

is introduced, $\Delta\Pi$ determines the volume change by the introduction of ionic groups to the network chain in the nondeformed state. In the above equation, p_0 stands for p in a neutral gel with the same number of crosslinks (PNS00 in this study). By replacing ΔP in Eqs. (5) and (6) by $(\Delta P + \Delta\Pi)$, the above model may be applied to the analysis of the effects of the applied stress as well as the introduction of ionic groups on the transition behavior as long as the composition of the gel is rather close to the critical composition. In the unloaded state the volume phase transition of PNS10 was discontinuous, while that for PNS00 was continuous. In addition, T_{tr} for PNS10 was higher than that for PNS00. These may be explained by an existence of a positive $\Delta\Pi$ for PNS10. The linear relation between T_{tr} and σ_{30} was also observed for PNS10. The fact that the linear relation between T_{tr} and σ_{30} was also observed for PNS10 suggests that the V–T curve showing the second order transition is obtained by applying relatively small compressional stress because the force must reduce ΔP.

IV. CONCLUSION

The effects of the mechanical stress on the volume phase transition of PNIPA and NIPA-SA copolymer gels were investigated in the relatively low stress region. The unloaded

PNIPA gel showed the behavior close to the second order phase transition. The character of the first order transition became clear in the loaded states, and the transition temperature increased with increasing applied stress. Similar behavior was observed for the NIPA-SA copolymer gel, but the copolymer gel showed the first order transition in the whole stress range investigated. The change in the transition behavior by the application of the mechanical stress originated chiefly from the volume change in the gels by the applied mechanical stress. The thermodynamical linear region, where the transition temperature varies linearly with applied stress, was narrower than the mechanical linear region determined by the stress–strain relation of the gels. It was found that the curve of the transition temperature against applied stress corresponds to the phase boundary between the swollen and collapsed phases for the gels. On the basis of the experimental results, we proposed a phenomenological model describing the volume phase transition of the polymer gels in the frame of the Landau-type free energy expression.

ACKNOWLEDGMENTS

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