PHYSICAL REVIEW E VOLUME 54, NUMBER 2 AUGUST 1996

Surface tension of the polymer network of a gel

Takato Nakamura, Mineo Hattori, Hideya Kawasaki,* Keiichi Miyamoto, Masayuki Tokita,† and Takashi Komai
Department of Chemistry for Materials, Faculty of Engineering, Mie University, Tsu 514, Japan

(Received 25 August 1995)

The surface tension of poly(*N*-isopropylacrylamide) gel is measured as a function of temperature. It is found that the surface tension of the gel suddenly decreases as the gel undergoes the discontinuous volume phase transition. The surface tensions of the polymer network of the gel are evaluated on the basis of a simple theory. The results yield that the surface tension of the poly(*N*-isopropylacrylamide) gel is mainly determined by the area occupied by the polymer chain on the surface of the gel in most of the temperature regions. In addition, it is also found that the surface tension of the polymer network of the gel shows a singular behavior in the immediate vicinity of the volume phase transition temperature of the gel. [S1063-651X(96)08608-4]

PACS number(s): 82.70.Gg, 47.20.Dr

INTRODUCTION

Gels are a typical two-component system that consist of the cross-linked polymer network and the solvent. It has been established that the gels show a volume phase transition in response to changes of external conditions such as temperature, solvent composition, and *p*H [1]. Many physical properties of the gels show singular behaviors in the vicinity of the volume phase transition point of the gel [2–4]. Such singularities of the physical properties of the gel are attributed to the density fluctuations of the polymer network and the divergence of the correlation length of the gel.

It is one of the main focus of recent condensed matter physics to gain the information of the singular behavior of the physical quantities in the transition region [5]. Although the theoretical context of the critical phenomena is well understood in rather simple systems, little is known about complex systems such as polymer gels. The detailed aspects of the volume phase transition of the gels are, therefore, still a matter for discussion. The volume phase transition of the gel has been studied using smaller gel pieces in recent studies; the typical size of the sample gel was the order of 100 μm [6,7]. The surface properties of the gels are increasingly effective in the volume phase transition of the small gels since the relative area of the surface becomes larger as the size of the gel becomes smaller [8]. An accurate estimate of the surface free energy is required for a detailed discussion of the volume phase transition of the small gels. Besides this, it may also be possible to discuss surface structures of the gels by detailed analysis of the surface properties of gels having different chemical and network structures. However, not much attention is paid to the surface properties of gels so far [9].

In this paper, we would like to report the detailed studies on the surface tensions of the poly(*N*-isopropylacrylamide) gel (NIPA gel). The surface tension of the poly(acrylamide) gel (AAm gel) is also measured in this study as a reference. The NIPA gel is known to show a discontinuous volume phase transition in water when the temperature is raised [10,11]. The hydrophobic interactions between side chains are the main driving force of the volume phase transition of the NIPA gel. Exact measurements of the surface tensions of these gels are yet to be done and the relationship between the surface tension of the NIPA gel and the volume phase transition are not yet known.

EXPERIMENT

Materials

The monomer, NIPA (Eastman Kodak Co.), was purified by recrystallization from toluene and *n*-hexane. The AAm monomer (electrophoresis grade) was purchased from BioRad laboratories and used without further purification. The cross-linking agent, *N*,*N′*-methylene-bis-acrylamide obtained from BioRad laboratories, was used without further purification. The photopolymerization initiator, 2-(3-trimethyl-amino-2-hydroxypropoxy)-3,4-dimethyl-9H-thioxanthone-9-one-*m* chloride (KAYACURE QTX, Nihon Kayaku Co., Ltd), was used without further purification. The conventional radical polymerization was made using ammonium persulfate (initiator; BioRad laboratories) and *N*,*N*,*N′*,*N′*-tetramethyl ethylene diamine (accelerator; BioRad laboratories). The probe material for the measurements of contact angles, *n*-decane (special grade, >99%), was purchased from Wako pure chemicals Industries Inc., and used without further purification. All glassware used in this study were made of Pyrex. The ion-exchanged and doubly distilled water was used as the solvent for the measurement of contact angles.

Preparation of gels

In this study two polymerization techniques were used; one is the conventional radical polymerization and the other is photopolymerization.

The AAm gel was obtained by the conventional radical polymerization of AAm and the cross-linker. The AAm monomer and the cross-linker were dissolved into water at concentrations of 693 and 7 mM, respectively. Then 60 μl of accelerator was added to the 25 ml of the above solution. The pre-gel solution thus obtained was degassed for 20 min

---

*Present address: Department of Chemistry, Faculty of Science, Kyushu University, 812, Fukuoka, Japan.

†Author to whom correspondence should be addressed.

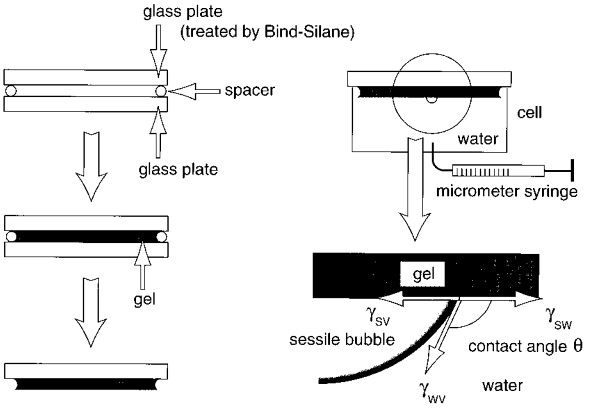

FIG. 1. Schematic representation of the preparation of the sample gel and the measurement of contact angles. The sample gel is polymerized between the gap of the gel mold that consists of two glass plates and spacers. The surface of the one glass plate is treated by the Bind-Silane. The gel is, therefeore, bound to the glass plate chemically. The sample gel is then immersed into water in the temperature controlled cell of the goniometer. The sessile bubble of the air (saturated vapor of water) or n-decane is attached on the surface of the gel from the lower side. Then the contact angle between the sessile bubble and the gel is measured at equilibrium. The contact angles of both edges of the sessile bubble are measured. The subscripts, S, V, and W in this figure indicate the gel, the air (vapor of water), and water, respectively. The contact angle θ is determined by the balance between three interfacial tensions γ_{SV}, γ_{SW}, and γ_{WV}. The definition of the contact angle is also shown.

at a temperature of 5 °C. The initiator, 250 μl of the 0.1-g/ml-aqueous solution of ammonium persulfate, was added to the pre-gel solution. The solution was stirred gently and then poured into the gap of the gel mold. The gelation was completed within 30 min.

The photopolymerization technique was applied to prepare the NIPA gel since this method is useful even under the lower reaction temperatures. Here, we briefly describe the outline procedure of the photopolymerization technique. The details of the photopolymerization method and the characterization of the resultant gels will be reported elsewhere [12]. The NIPA monomer and the cross-linker were dissolved in distilled water at concentrations of 693 and 7 mM, respectively. The molar fraction of the cross-linker was thus fixed at a concentration of 1 (mole percent) mol % in both gels of AAm and NIPA. The photo initiator (0.2 mol % of total monomer) was dissolved into the pre-gel solution and degassed for 20 minutes at 5 °C. The gelation was then made under a nitrogen atmosphere at 10 °C by irradiating the uv light at a wavelength of 365 nm. The onset of the gelation was observed within 30 min under these experimental conditions. The solution was kept under the same conditions for 6 h to ensure the complete reaction.

The gel mold used in this study, which is schematically shown in Fig. 1, was designed to prepare a flat and thin slab of gel. The gel mold consists of two Pyrex glass plates. These glass plates were fixed by spacers of thickness 1.2 mm. The surface of one of the two glass plates was treated by Bind-Silane (Pharmacia LKB Biotechnology) by which the surface of the glass plate becomes active in forming covalent bonds between the polymer network of the gel. The sample gel was, therefore, tightly fixed on the surface of the glass plate. The glass plate, which is not treated with the Bind-Silane, was carefully removed from the gel under water after the gel was prepared. The sample gel was soaked in a large amount of water several times in order to equilibrate and wash away the residual chemicals. Then the gel was set in the cell of the contact angle measurement apparatus.

Contact angle measurement

The surface tension of the gel was evaluated by the sessile bubble method [13]. A goniometer (type A-2010 A, Erma Inc.), equipped with a temperature controlled cell, was used in this study. After the sample gel was immersed in water in the cell of the goniometer, a bubble of air or a drop of n-decane was attached to the surface of the gel that was exposed to water as schematically illustrated in Fig. 1. The volumes of sessile bubbles were controlled; the diameter of the sessile bubble was maintained 1 mm with a micrometer syringe. Then the contact angle between the gel and the sessile bubble was measured as a function of temperature. The temperature was changed between 5 to 50 °C with an accuracy better than 0.1 °C. All the apparatus was set on an optical table to avoid external mechanical disturbances. The measurements were made at an equilibrium state of the gel.

THEORETICAL BACKGROUND

In this section, we consider the theoretical background of recent advances in the analysis of the surface tensions of materials. When a sample of solid, for instance a hydrogel, and a sessile bubble of air, which is saturated with water vapor, are kept contact under water (solvent) as schematically shown in Fig. 1, the surface tension of each phase is in equilibrium. Then the contact angle θ_V is defined [13]. The balance between three surface tensions yields the following Young's equation:

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SW}} + \gamma_{\mathrm{WV}} \cos(\theta_V). \tag{1}$$

Here, γ_{IJ} denotes the surface tension between two phases I and J. The subscripts S, V, and W represent the solid phase, the vapor phase of water, and the liquid phase of water, respectively. When the bubble of air is replaced by other sessile bubbles, such as a liquid, which is immiscible with the solid and the solvent, a similar equation also holds in this system. The contact angle of this system θ_L is, however, generally different from the above system because the surface tension of the liquid is different from that of air:

$$\gamma_{\mathrm{SL}} = \gamma_{\mathrm{SW}} + \gamma_{\mathrm{WL}} \cos(\theta_L). \tag{2}$$

The subscript L denotes the phase of the liquid that is immiscible with water and solid.

Consider now the surface tension of a simple material γ_I. It has been shown that the surface tension of a material can be divided into two components: the nonpolar component that arises from the dispersive Lifshitz–van der Waals interaction (LW component: γ_I^{LW}, and the polar component due to the interactions between the electron donor and the electron acceptor [14–17]. The latter component is frequently called an acid-base component AB component: γ_I^{AB}).

$$\gamma_I = \gamma_I^{\mathrm{LW}} + \gamma_I^{\mathrm{AB}}. \tag{3}$$

Many studies have been made so far to evaluate the surface tensions of the materials theoretically. In spite of the extensive studies, a definite theoretical framework has yet to be established. It is, however, suggested experimentally that the harmonic mean approximation of the surface tension components gives better results for the polymer, water, and organic liquid systems [18,19]. Since the gel consists of the polymer network and water, we apply the harmonic mean approximation to obtain the surface tension components. If the harmonic mean approximation is assumed, the following relationship is obtained:

$$\gamma_{IJ} = \gamma_{IV} + \gamma_{JV} - 4\left(\frac{\gamma_{IV}^{\mathrm{LW}}\gamma_{JV}^{\mathrm{LW}}}{\gamma_{IV}^{\mathrm{LW}} + \gamma_{JV}^{\mathrm{LW}}}\right) - 4\left(\frac{\gamma_{IV}^{\mathrm{AB}}\gamma_{JV}^{\mathrm{AB}}}{\gamma_{IV}^{\mathrm{AB}} + \gamma_{JV}^{\mathrm{AB}}}\right). \tag{4}$$

Here, subscripts *I*, *J*, and *V* refer to phases *I*, *J*, and *V*, respectively.

The above equation can be rewritten as follows for the present case of two sessile bubbles of the vapor and the liquid and the gel in water.

$$\gamma_{SW} = \gamma_{SV} + \gamma_{WV} - 4\left(\frac{\gamma_{\mathrm{SV}}^{\mathrm{LW}}\gamma_{\mathrm{WV}}^{\mathrm{LW}}}{\gamma_{\mathrm{SV}}^{\mathrm{LW}} + \gamma_{\mathrm{WV}}^{\mathrm{LW}}}\right) - 4\left(\frac{\gamma_{\mathrm{SV}}^{\mathrm{AB}}\gamma_{\mathrm{WV}}^{\mathrm{AB}}}{\gamma_{\mathrm{SV}}^{\mathrm{AB}} + \gamma_{\mathrm{WV}}^{\mathrm{AB}}}\right). \tag{5}$$

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 4\left(\frac{\gamma_{\mathrm{SV}}^{\mathrm{LW}}\gamma_{\mathrm{LV}}^{\mathrm{LW}}}{\gamma_{\mathrm{SV}}^{\mathrm{LW}} + \gamma_{\mathrm{LV}}^{\mathrm{LW}}}\right) - 4\left(\frac{\gamma_{\mathrm{SV}}^{\mathrm{AB}}\gamma_{\mathrm{LV}}^{\mathrm{AB}}}{\gamma_{\mathrm{SV}}^{\mathrm{AB}} + \gamma_{\mathrm{LV}}^{\mathrm{AB}}}\right). \tag{6}$$

The subscript *S* in these equations denotes the gel in the present case. The combination of the above two equations and Young's equations yields the following equations:

$$\gamma_{\mathrm{SV}}^{\mathrm{LW}}\left(\frac{\gamma_{\mathrm{WV}}^{\mathrm{LW}}}{\gamma_{\mathrm{SV}}^{\mathrm{LW}} + \gamma_{\mathrm{WV}}^{\mathrm{LW}}} - \frac{\gamma_{\mathrm{LV}}^{\mathrm{LW}}}{\gamma_{\mathrm{SV}}^{\mathrm{LW}} + \gamma_{\mathrm{LV}}^{\mathrm{LW}}}\right) + \gamma_{SV}^{AB}\left(\frac{\gamma_{\mathrm{WV}}^{\mathrm{AB}}}{\gamma_{\mathrm{SV}}^{\mathrm{AB}} + \gamma_{\mathrm{WV}}^{\mathrm{AB}}} - \frac{\gamma_{\mathrm{LV}}^{\mathrm{AB}}}{\gamma_{\mathrm{SV}}^{\mathrm{AB}} + \gamma_{\mathrm{LV}}^{\mathrm{AB}}}\right)$$

$$= \frac{\gamma_{\mathrm{LW}}\cos(\theta_L) + \gamma_{\mathrm{WV}} - \gamma_{\mathrm{LV}}}{4}. \tag{7}$$

$$\gamma_{\mathrm{SV}}^{\mathrm{LW}}\frac{\gamma_{\mathrm{WV}}^{\mathrm{LW}}}{\gamma_{\mathrm{SV}}^{\mathrm{LW}} + \gamma_{\mathrm{WV}}^{\mathrm{LW}}} + \gamma_{\mathrm{SV}}^{\mathrm{AB}}\frac{\gamma_{\mathrm{WV}}^{\mathrm{AB}}}{\gamma_{\mathrm{SV}}^{\mathrm{AB}} + \gamma_{\mathrm{WV}}^{\mathrm{AB}}} = \frac{\gamma_{\mathrm{WV}}[1 + \cos(\theta_V)]}{4}. \tag{8}$$

These equations indicate that the components of the surface tension of a gel are $\gamma_{\mathrm{SV}}^{\mathrm{LW}}$ and $\gamma_{\mathrm{SV}}^{\mathrm{AB}}$, and hence the total surface tension of the gel γ_{SV}, can be determined independently by solving these equations [19]. It is, however, postulated from the theory that at least two different sessile bubbles of known surface tensions are necessary to evaluate the absolute value of the surface tension of the gel. It is further required that temperature dependence of surface tensions of sessile bubbles should be known to gain the information on the temperature dependence of surface tension of the gel. Out of many candidates, air (vapor of water) and *n*-decane were chosen for the sessile bubbles of the present study because the values of surface tensions and their temperature dependence have been already reported [20]. The measurements are, therefore, done in the ternary systems of gel-water-air and gel-water-*n*-decane in the present study.

Since the sessile bubbles are immiscible with the polymer network of the gel and water, the bubbles contact only the surface of the gel. On the other hand, the volume phase transition of the gel is mainly governed by the interactions that arise within the gel. The presence of the sessile bubbles, therefore, does not affect the volume phase transition of the NIPA gel. In addition, the volumes of sessile bubbles are controlled to become about 1 mm. The surface of the gel is much larger than the area that contacts the bubble. The effects of the bubble, even if they exist, are negligible.

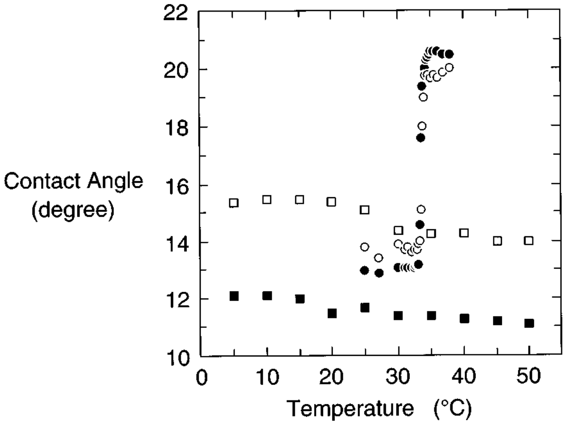

FIG. 2. The temperature dependence of the contact angles of AAm gel, □, ■, and NIPA gel, ○, ●. The open symbols represent the contact angles measured in the system of gel-air-water. The closed symbols are the contact angles measured in the system of gel-*n*-decane-water. All the data shown in this figure are obtained in the heating process.

RESULTS

The temperature dependence of the contact angles of AAm gel and NIPA gel systems is shown in Fig. 2. The contact angles measured upon increasing temperature are

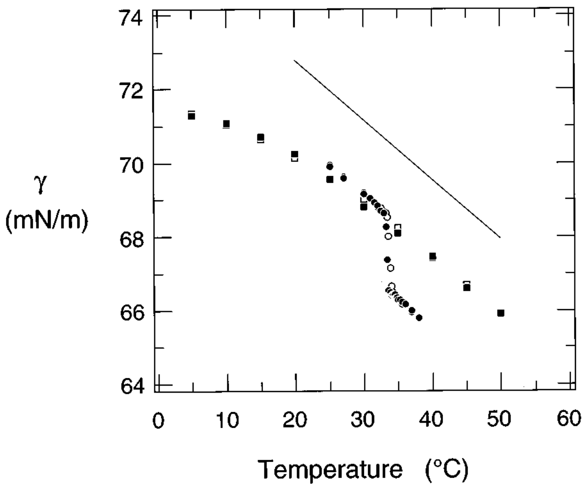

FIG. 3. The temperature dependence of the total surface tensions of AAm gel, □, ■, and NIPA gel, ○, ●. The open symbols represent the surface tensions obtained upon increasing temperature. The closed symbols correspond to the surface tensions that are obtained in the process of lowering temperature. The straight line expresses the extrapolated temperature dependence of the surface tension of water. The values of the surface tension of water are cited from Ref. [17].

shown in this figure for the sake of simplicity because almost all the data points taken in the process of raising temperature and that taken in the process of decreasing temperature are overlapped with each other. It is clear from this figure that the contact angles between the AAm gel and air and/or n-decane gradually decrease with increasing temperature. On the other hand, the contact angles between the NIPA gel and these sessile bubbles suddenly increase at a temperature of about 33 °C.

The total surface tensions of AAm and NIPA gels are calculated from the contact angles, the surface tensions of air, and that of n-decane as described in the preceding section. The results are plotted in Fig. 3 as a function of temperature. It is found from this figure that the surface tension of the AAm gel decreases monotonically with increasing temperature. In contrast, the surface tension of the NIPA gel decreases abruptly at about 33 °C. It is also found that the temperature dependence of the surface tension of the NIPA gel is entirely reversible. The temperature dependence of the AB component and the LW component of the surface tension is also shown in Fig. 4 with the swelling curve of the NIPA gel. It is found that the AB component of the surface tension suddenly decreases at the volume phase transition temperature of the NIPA gel while the LW component, though it seems to show a small cusp at the phase transition temperature, decreases monotonically with the temperature.

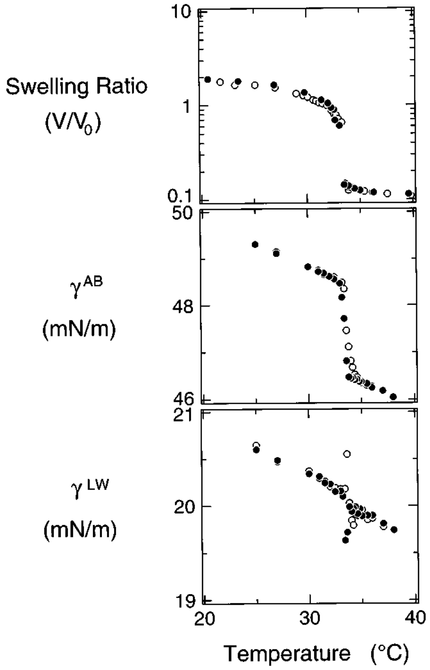

FIG. 4. The temperature dependence of the swelling ratio, the AB component of the surface tension, and the LW component of the surface tension of NIPA gel. The open symbols represent the results obtained in the process of raising temperature. The closed symbols are the results obtained by lowering temperature.

DISCUSSION

The surface properties of simple liquids and simple solids have been studied in detail from both theoretical and experimental points of view [21]. It has been well established that the slope of the tangential line of the temperature dependence of surface tension $d\gamma/dT$ as well as the absolute value of the surface tension γ is a relevant measure of the surface properties of the one-component system. The temperature dependence of the surface tension is studied in many simple systems so far. It is confirmed by these studies that the surface tension of the one-component system is a decreasing function of the temperature. Although the gel is a typical two-component system that consists of the polymer network and the solvent, the surface tensions of both gels decrease with temperature as is shown in Fig. 3. It is found from Fig. 3 that the absolute value of the surface tensions of these gels are close to that of water [20,21]. Besides, the slope of the tangential line of the temperature dependence of surface tension of these gels at about 20 °C is found to be about -0.11 mN/m K. This value is also close to the reported value of water -0.138 mN/m K [21]. These results strongly suggest that the surface properties of these gels are mainly governed by the fluid component of the gel rather than the polymer network of the gel itself. Most of the area of the surface of these hydrogels is, therefore, occupied by the solvent. These results are in good agreement with the structural features of gels since a fraction of the polymer network of these gels is much less than that of the solvent. In this dilute system, however, the surface tension of the NIPA gel shows an abrupt decrease at the volume phase transition temperature. The decrease of the surface tension corresponds to the sudden decrease of the AB component of the surface tension. It has been already suggested that the hydrophobic interactions within the system contribute only to the AB component of the surface tension [22,23]. The reversible decrease of both surface tensions, γ and γ^{AB}, of the NIPA gel are, therefore, the characteristic of the NIPA gel in which the hydrophobic interaction is the main driving force of the phase transition.

In order to analyze the experimental results quantitatively, we first discuss the effects of the surface concentration of the polymer chain on the surface tension of the gel. Since the polymer network of the NIPA gel is chemically cross-linked, the total mass of the polymer network in the gel is constant in the entire temperature region. The volume change of the NIPA gel, therefore, occurs only by exchange of water with the surrounding environment. The bulk concentration of the polymer network in the gel is a function of the swelling ratio and hence the temperature. The surface concentration of the polymer chain is, thus, also a function of the temperature. The effects of swelling of the gel on the surface concentration of the polymer chain, therefore, should be taken into account. We assume that the surface tension of the NIPA gel can be written as follows because the gel is a dilute system of the polymer network and the solvent:

$$\gamma_{\mathrm{gel}}=(1-\phi_{\mathrm{surface}})\gamma_{\mathrm{water}}+\phi_{\mathrm{surface}}\gamma_{\mathrm{network}}. \tag{9}$$

Here, γ_{gel}, γ_{water}, and $\gamma_{\mathrm{network}}$, are the surface tensions of the NIPA gel, water, and the polymer network of the NIPA gel, respectively. The surface concentration of the polymer network is denoted as ϕ_{surface}. The above equation is rewritten as follows to evaluate the surface tension of the polymer network of the NIPA gel:

$$\gamma_{\text{network}}=\gamma_{\text{water}}-\frac{\gamma_{\text{water}}-\gamma_{\text{gel}}}{\phi_{\text{surface}}}. \tag{10}$$

Here, the surface concentration of the polymer network is a function of the swelling ratio of the gel.

The swelling behaviors of the gel strongly depend on the restraint applied to the sample gel, that is, the way the sample gels are fixed [24]. It is, therefore, indispensable to take into account the preparation procedure in order to calculate the surface concentration of the polymer network from the bulk concentration of the polymer network. The sample gel used in this study is a thin slab of which one surface is chemically fixed to the glass plate. The swelling of the gel is uniaxial, namely, only the thickness of the gel varies as a result of the swelling. Assuming a uniform density distribution of the polymer network in the equilibrium state, ϕ_{surface} can be written as follows:

$$\phi_{\text{surface}}=\phi_0 \Big/ \left(\frac{l}{l_0}\right), \tag{11}$$

where ϕ_0, l, and l_0 are the fraction of the polymer network at the reference state, the thickness of the gel, and in the reference state, respectively. The ratio of the thickness of the gel l/l_0 is written as follows using the swelling ratio of the NIPA gel, V/V_0 and/or ϕ_0/ϕ:

$$\frac{l}{l_0}=\left(\frac{V}{V_0}\right)^{1/3}=\left(\frac{\phi_0}{\phi}\right)^{1/3}. \tag{12}$$

The combination of Eqs. (10–12) yields the following equation for the polymer network of the NIPA gel:

$$\gamma_{\text{network}}=\gamma_{\text{water}}-\frac{\gamma_{\text{water}}-\gamma_{\text{gel}}}{\phi_0^{2/3}\phi^{1/3}}. \tag{13}$$

Substitution of Eq. 3 into Eq. 13 also yields a similar relationship for the components of the surface tension:

$$\gamma^{\text{AB}}_{\text{network}}=\gamma^{\text{AB}}_{\text{water}}-\frac{\gamma^{\text{AB}}_{\text{water}}-\gamma^{\text{AB}}_{\text{gel}}}{\phi_0^{2/3}\phi^{1/3}},$$

$$\gamma^{\text{LW}}_{\text{network}}=\gamma^{\text{LW}}_{\text{water}}-\frac{\gamma^{\text{LW}}_{\text{water}}-\gamma^{\text{LW}}_{\text{gel}}}{\phi_0^{2/3}\phi^{1/3}}. \tag{14}$$

Thus all the surface tensions of the polymer network of the NIPA gel, γ_{network}, $\gamma^{\text{AB}}_{\text{network}}$, and $\gamma^{\text{LW}}_{\text{network}}$, can be calculated from the surface tensions and the swelling ratio of the NIPA gel. These surface tensions of the polymer network are calculated and the results are plotted in Fig. 5 as a function of temperature.

It is found from these figures that the surface tension of the polymer network of the NIPA gel is almost constant in either lower and higher temperature regions, but abruptly increases in the narrow temperature region, which coincides with the volume phase transition temperature of the NIPA gel. Although the polymer network is much denser at higher temperature region, γ_{network} is almost the same as that of lower temperatures. These results indicate that the surface tension of the polymer network of the gel for the unit area of occupied polymer chain is almost constant in the temperature region studied here. The reversible decrease of surface tension of the NIPA gel, which shown in Fig. 3, is, therefore, mainly caused by the variation of the surface concentration of the polymer network of the gel due to the volume phase transition.

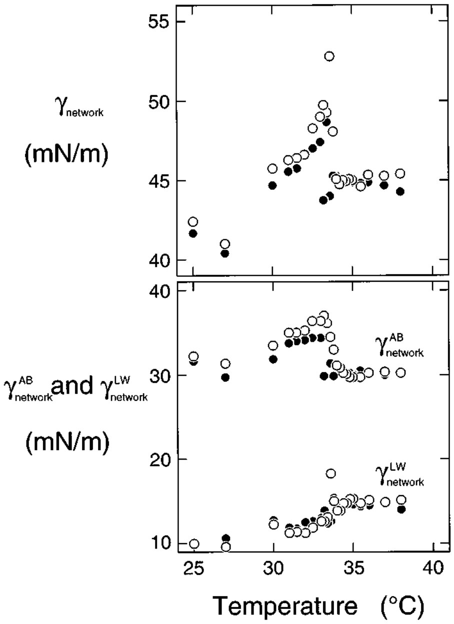

FIG. 5. The temperature dependence of the surface tensions of the polymer network of the NIPA gel. The open and closed symbols are the results obtained in the processes of increasing and decreasing temperature.

It is also clear from these figures that both surface tensions of the polymer network and the AB component of the surface tension show the cusp at the volume phase transition temperature of the gel. On the other hand, the LW component is a monotonic function of the temperature in the entire region. These results again indicate that the singularity of the surface tension of the polymer network of the NIPA gel is caused by the hydrophobic interactions. The cusp of the γ_{network} at the volume phase transition temperature corresponds to the singularity of the second term in Eq. 13, $\gamma_{\text{water}}-\gamma_{\text{gel}}/\phi_0^{2/3}\phi^{1/3}$, since γ_{water} is not singular in the entire temperature region studied here. It is also obvious from Fig. 3 that the numerator of the second term increases at the volume phase transition temperature. The singularity of the γ_{network} at the phase transition temperature is, therefore, caused by the abrupt increase of the surface concentration of the polymer chain. Such an anomaly of the surface concentration of the polymer chain presumably indicates the effects of density fluctuations on the polymer network of the gel due to the phase transition.

It has been well established that the density of the polymer network fluctuates in time and space in the vicinity of the volume phase transition temperature of the NIPA gel [2,25,26]. The swelling curve of the NIPA gel goes into the unstable region under present experimental conditions. Therefore, two mechanisms can be attributed to the density fluctuations in the gel. One is the static density fluctuations due to the micro phase separation of the gel that diverge at the coexistence line. The other is the dynamic fluctuations that diverge at the spinodal line. In either case, the density fluctuations of the polymer network may create a nonuniform distribution of the polymer chain on the surface of the gel. The inhomogeneity created by those density fluctuations cannot be estimated correctly in the framework of the present analysis because the surface tension of the polymer network is evaluated on the basis of Eq. (9) whereas, the surface tension of the NIPA gel is assumed to be expressed by the linear combination of the surface tensions of the polymer network and water. The results indicate, therefore, that the simple approximation presented in this paper is valid only in the regions far from the transition point. In this regard, the measurements of the surface tension of the critical gel are of interest since the information of the divergence of the dynamic fluctuations can be derived [27,28]. Such studies will promote a better understanding of the singular behavior of the surface tension of the NIPA gel and are now in progress.

In this paper, we demonstrate the surface properties of the NIPA gel. The surface tensions of the polymer network of the NIPA gel show singular behaviors at the volume phase transition point. These results strongly suggest that the density fluctuations of the polymer network influence the surface properties of the gel. It is expected that the density fluctuations of the polymer network also varies with the surface structure of the gel. The surface structure of the gel that undergoes the volume phase transition becomes rough according to the inhomogeneous density distribution of the polymer network. The effects of the surface structure should also be taken into account in the detailed analysis of the singular behavior of the surface tension. Recent direct observation of the surface structure of the NIPA gel in the transition region will be of importance to clarify the singular behavior of the surface tension of the NIPA gel [29]. The combined studies on the surface structure and the surface properties of the gel will open a new insight into the volume phase transition of the gels.

CONCLUSION

It is found that the surface tension of poly(*N*-isopropylacrylamide) gel abruptly decreases at the volume phase transition temperature of the gel. A simple analysis, in which both the concentration of the polymer on the surface of the gel and the geometry of the swelling are taken into account, yields that the surface tension of the poly(*N*-isopropylacrylamide) gel is mainly governed by the concentration of the polymer chain on the surface of the gel. Furthermore, it is found that the surface tension of the polymer network of the gel shows a cusp in the immediate vicinity of the volume phase transition temperature.

ACKNOWLEDGMENTS

The authors want to thank Professor A. Suzuki of Yokohama National University for his fruitful discussions. One of the authors (M.T.) acknowledges the financial support from the New Energy and Industrial Technology Development Organization (NEDO), Japan and from Shinsei-Shigen Kyokai.

---

[1] T. Tanaka, M. Annaka, F. Ilmain, K. Ishii, E. Kokufuta, A. Suzuki, and M. Tokita, NATO ASI series, **H64**, 683 (1992).
[2] T. Tanaka, S. Ishiwata, and C. Ishimoto, Phys. Rev. Lett. **38**, 771 (1977).
[3] T. Tanaka, Phys. Rev. A **17**, 763 (1978).
[4] M. Tokita and T. Tanaka, Science **253**, 1121 (1991).
[5] H. E. Stanley, *Introduction to Phase Transition and Critical Phenomena* (Oxford University Press, New York, 1971).
[6] A. Suzuki and T. Tanaka, Nature (London) **346**, 345 (1990).
[7] H. Kawasaki, T. Nakamura, K. Miyamoto, M. Tokita, and T. Komai, J. Chem. Phys. **103**, 6241 (1995).
[8] The ratio, f, of the surface area and the volume of a spherical gel of the radius r is expressed as follows: $f=4\pi r^2/\frac{4}{3}\pi r^3 \propto r^{-1}$. The contribution of surface, therefore, becomes dominant as the radius of the gel becomes smaller, i.e., $r\rightarrow 0$. See, for instance, S. Hirotsu, Macromolecules **25**, 4445 (1992), for the experimental studies on the swelling of the gels.
[9] J. Zhang, R. Pelton, and Y. Deng, Langmuir **11**, 2301 (1995).
[10] Y. Hirokawa and T. Tanaka, J. Chem. Phys. **81**, 6379 (1984).
[11] S. Hirotsu, Y. Hirokawa, and T. Tanaka, J. Chem. Phys. **87**, 1392 (1987).
[12] T. Nakamura, H. Kawasaki, K. Miyamoto, M. Tokita, and T. Komai (unpublished).
[13] See, J. D. Andrade, S. M. Ma, R. N. King, and D. E. Gregonis, J. Colloid Interface Sci., **72**, 488 (1979), for the definition of the contact angle of ternary system of gel–water–sessile bubble.
[14] C. J. van Oss, R. J. Good, and M. K. Chaudury, Langmuir **4**, 884 (1988).
[15] C. J. van Oss, L. Ju, M. K. Chaudury, and R. J. Good, J. Colloid Interface Sci. **128**, 313 (1989).
[16] C. J. van Oss, M. K. Chaudury, and R. J. Good, J. Chem. Rev. **88**, 927 (1988).
[17] R. J. Good and van C. J. van Oss, in *Modern Approaches to Wettability*, edited by M. E. Schrader and R. Leab (Plenum, New York, 1992).
[18] S. Wu, J. Adhesion **5**, 39 (1973).
[19] F. Garbassi, M. Morra, and E. Occhiello, *Polymer Surfaces* (Wiley, Chichester, 1994).
[20] M. L. Kerkeb, F. Gonzalez-Caballero, and E. Chibowski, J. Colloid Interface Sci. **159**, 439 (1993).
[21] A. W. Adamson, *Physical Chemistry of Surfaces*, 5th ed. (Wiley, New York, 1990), and references cited therein.
[22] C. J. van Oss, *Polymer Surfaces and Interfaces*, edited by W. J. Feast, H. S. Munro, and R. W. Richards (Wiley, Chichester, 1993).
[23] C. J. van Oss and R. J. Good, J. Dispersion Technol. **9**, 355 (1988).
[24] A. Suzuki and S. Kojima, J. Chem. Phys. **101**, 10003 (1994).
[25] T. Tanaka, Phys. Rev. A **17**, 763 (1978).
[26] E. S. Matsuo, M. Orkisz, S.-T. Sun, Y. Li, and T. Tanaka, Macromolecules **27**, 6791 (1994).
[27] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Clarendon, Oxford, 1938).
[28] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
[29] A. Suzuki, M. Yamazaki, and Y. Kobiki, J. Chem. Phys. **104**, 1751 (1996).