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Volume phase transition of *N*-isopropylacrylamide gels crosslinked by a crosslinker with six hands

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Crosslinkers play an essential role in determining the physical properties of gels. We synthesized a new type of crosslinker with three vinyl groups [trisacrylaminomethan (TRI), which joins six polymer chains per single molecule]. We found that *N*-isopropylacrylamide (NIPA) gels crosslinked with the new crosslinker gel at a much lower fraction of crosslinker than the gel crosslinked with popular *N*,*N*′-methylenebisacrylamide (BIS). We also found that the NIPA gels with TRI crosslinker displayed larger discrete volume changes at the volume phase transition. We discuss the effects of the average length of NIPA chains between two crosslinkers on the volume phase transition as well as the effects of inhomogeneity in gels caused by a low fraction of crosslinker.

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I. INTRODUCTION

Polymer gels are composed of linear polymers, gel solvent, and crosslinkers; a crosslinker is what makes a polymer gel what is called gel. Gels with a higher fraction of crosslinker have a higher elastic modulus than those with a lower fraction of crosslinker. Here the fraction of crosslinker is defined as $\frac{[\text{crosslinker}]}{[\text{monomer}]+[\text{crosslinker}]}$, where $[A]$ indicates the molar fraction of component A. The gels with lower fractions of crosslinker are generally softer and swollen more than those with higher fractions of crosslinker in good solvents. With lowering the fraction of crosslinker further, gels become too soft to keep molded shapes, and finally, the products become the solution of branched polymers. The average distance between two adjacent crosslinking points is expected to be larger for the gels with a smaller fraction of crosslinker, which enables the gels to swell more in good solvents, as mentioned above.

The number of the functional groups of the crosslinker affects the topological structure of the gel and, as a result, determines the physical properties of the gel. Flory's simple theory of gelation predicts that a crosslinker with a larger number of functional groups enables the gel formation at a smaller fraction of crosslinker [1]. Thus, the crosslinkers with a larger number of functional groups enable us to make a gel that swells larger in good solvents with a smaller fraction of crosslinker.

One of the most extreme materials with a multifunctional crosslinker is a hydrogel crosslinked with small crystals of Laponite reported by Haraguchi *et al.* [2]. The unit cell of the Laponite is described as $\mathrm{Na}^{+0.7}[(\mathrm{Si}_8\mathrm{Mg}_{5.5}\mathrm{Li}_{0.3})\mathrm{O}_{20}(\mathrm{OH})_4]^{-0.7}$. Single Laponite crystal consists of about 2000 unit cells on average, and it has discotic form with a diameter of about 30 nm and thickness of about 1.0 nm (Rockwood Ltd.). When the Laponite crystals are used as crosslinker, each crystal crosslinks a few thousand chains due to the electric charge on the surface of the crystal. The *N*-isopropylacrylamide (NIPA)-Laponite gels change the volume drastically by the temperature change, and these gels are tough against an external force. However, the discrete volume phase transition of NIPA-Laponite gel has not been observed even at the very small fraction of crosslinker.

One of the most studied systems of gels that exhibit discrete volume change is the NIPA hydrogel with *N*,*N*′-methylenebisacrylamide (BIS) as crosslinker (BIS gel). The BIS gel swells at low temperatures (below around 10 °C) and deswells at high temperatures (above about 33 °C) due to the hydrophobic interaction between the isopropyl groups of the side chain of the NIPA molecules. BIS gels with a low fraction of crosslinker undergo discontinuous volume change at the specified temperature in water. This phenomenon was first discovered by Tanaka *et al.* and was called the volume phase transition of gels [3,4]. BIS, which has two vinyl groups and joins four polymer chains per molecule, has been commonly used as the crosslinker in the various studies on volume phase transition. Concerning the critical behavior of gels, BIS gels are the most studied gels. Li *et al.* [5] and Arai *et al.* [6] obtained the critical exponents of the BIS gel.

Atta reported that the copolymer gel of acrylic acid and NIPA with melaminetriacrylamide as crosslinker and reported that this gel showed a faster response and larger volume change than the gel synthesized with BIS as the crosslinker. This crosslinker has three vinyl groups so it can join six polymer chains per single molecule [7].

In this paper we present a new type of gel crosslinked by a crosslinker with three vinyl groups, trisacrylaminomethan (TRI) [8], which joins six polymer chains per molecule. We have studied the volume phase transition of a gel crosslinked with BIS or TRI at fixed polymer concentration by varying the fraction of crosslinker. We preindicate that the reason for the difference of the volume phase transition we found is dependent on the number of NIPA chains connected by a single crosslinker.

II. MATERIALS AND METHOD

We obtained NIPA and other chemicals except the crosslinker from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) and purified NIPA molecules by recrystallization from cyclohexane. The crosslinker, BIS, was obtained from Sigma-Aldrich (St. Louis, MO, U.S.A.) and was used without further purification. Another crosslinker TRI was synthesized as described in the following section.

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A. Synthesis and purification of triacrylaminomethan crosslinker

We synthesized TRI according to the method of Yoshisue *et al.* [8]. Several drops of concentrated sulfuric acid were added to a stirred solution of acrylamide (24.1 g) and hydroquinone (0.1 g) in toluene (150 mL), and then the solution was heated to 80 °C. Ethylorthoformate (17 g) was added slowly to the heated solution during the period of 1 hour, and the reaction mixture was refluxed for 0.5 hour. After cooling, the precipitated product was filtered off by suction, and the second crop was obtained from evaporation of the filtrate. The product was purified by ethanol. The structure of the product was confirmed by nuclear magnetic resonance (NMR) spectroscopy.

B. Important parameters of gels

Two important parameters C_{tot} and F_{BIS} or F_{TRI} of gel are defined as follows: C_{tot} (total concentration of polymer component of gel at the polymerization) is defined as [monomer] + [crosslinker], F_{BIS} and F_{TRI} (fraction of crosslinker) are defined as $\frac{[\text{crosslinker}]}{[\text{monomer}]+[\text{crosslinker}]}$. The total concentration (C_{tot}) is the fraction of the gel network (polymer + crosslinker) to the solvent at the moment of synthesis, and the fraction of crosslinker shows the ratio of the crosslinker to the linear component of the gel network. We synthesized gels with various fractions of crosslinker while the total concentration C_{tot} was fixed at 0.027.

C. Synthesis of NIPA gels

NIPA and crosslinker (BIS or TRI) were dissolved in ultrapure water. The mixture of pregel solution was cooled by ice water and was de-oxygen-gassed using nitrogen gas. The initiator, ammonium persulfate (AP), solution, and the promoter, *N,N,N′,N′*-tetramethylethylenediamine (TEMED), were added to the pregel solution. In this study, the molar ratio of these chemicals to the NIPA monomer was fixed for all the gels as [NIPA monomer]:[AP]:[TEMED] = 100 : 0.426 : 0.735. There was a short latent period before the beginning of the polymerization. In this period, the pregel solution was infused into a test tube that contained many microcapillaries with an inner diameter of 0.64 mm. The pregel solution was kept at 5 °C in the refrigerator for one day till the completion of the polymerization reaction. After gels were taken out from the microcapillaries, gels were washed in a large amount of ultrapure water for a few days in the refrigerator to remove residual chemicals. Washed gels were cut into small pieces (length ≈1 cm) and used for the measurement.

D. Measurement of swelling parameters

The sample gel was immersed in ultrapure water in a microcapillary with an inner diameter of 1.9 mm. Both sides of the microcapillary were permanently sealed by epoxy resin and were put into the temperature controlled glass case with insulator. We took care so that the water in the microcapillary did not touch the resin seal. The temperature inside of the glass case was controlled by water flow from a temperature controlled water circulator. The accuracy of the temperature of the bath was 0.01 °C, and the room temperature was controlled at 22 °C ± 1 °C. We measured the temperature inside the microcapillary for each acquisition using a calibrated thermistor. The sample was equilibrated at each temperature for at least 24 hours before the measurement. While the gel was in the coexistence state, it had to be kept at the same temperature. As we could not change the temperature of the bath until the gel at the transition reached equilibrium, all the rest of the gels were kept at the same temperature for a long time, which made the sampling interval rather irregular. The sample diameter d was measured at each temperature using a video microscope and a software (“ruler” version 0.02). The swelling ratio $(\frac{d}{d_0})^3$ was calculated using observed d for each gel, where d_0 is the diameter of cylindrical gel at the polymerization. We monitored the change of the swelling ratio of gels, by increasing the temperature slowly and steadily.

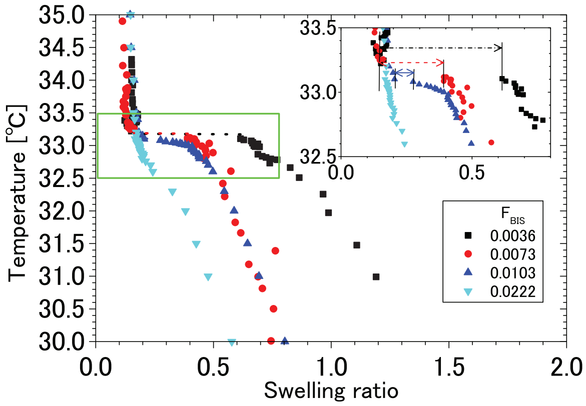

FIG. 1. (Color online) Temperature dependencies of the swelling ratio $\frac{V}{V_0} = (\frac{d}{d_0})^3$ of the BIS gel. The fractions of crosslinker BIS are given in the legend. The total concentration of polymer at the synthesis was 0.027 for all the gels. The closeup at the vicinity of discrete transition is given in the inset. The width of discrete phase transition increased with decreasing fraction of crosslinker as presented with arrowed lines in the inset.

III. RESULTS AND DISCUSSION

A. Temperature dependencies of swelling ratio and the volume phase transition of BIS gel

The fractions of crosslinker F_{BIS}, of the BIS gels studied here are 0.0036, 0.0073, 0.0103, and 0.0222. The samples with a lower fraction of crosslinker than 0.0036 did not maintain their shape, i.e., those were in the sol phase. The temperature dependencies of the swelling ratios of the BIS gel are shown in Fig. 1. All the gels with a fraction of crosslinker less than 0.0222 exhibited volume phase transition (discontinuous volume change) around 33.0–33.5 °C. The lower the fraction of crosslinker, the larger discontinuous volume change was observed.

B. Temperature dependencies of swelling ratio and the volume phase transition of TRI gel

Figure 2 shows the temperature dependence of swelling ratio $\frac{V}{V_0} = (\frac{d}{d_0})^3$ of the TRI gels. The gels crosslinked with TRI gelled at far less fractions of crosslinker than those with BIS. The fractions of crosslinker F_{TRI} of the studied TRI gels

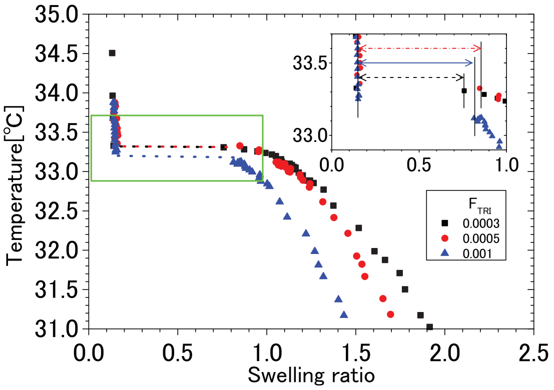

FIG. 2. (Color online) Temperature dependencies of the swelling ratio $\frac{V}{V_0} = (\frac{d}{d_0})^3$ of TRI gel. The fractions of crosslinker TRI are given in the legend. The total concentration of polymer at the synthesis was 0.027 for all the gels. The closeup at the vicinity of the discrete transition is given in the inset. The widths of the transitions are presented with arrowed lines. In this system, the gel with a rather larger fraction of crosslinker of 0.0005 exhibited the largest discrete volume change although the gel with the lowest fraction of crosslinker usually exhibits the the largest discrete volume change.

were 0.0003, 0.0005, and 0.0010. The swelling ratios against temperature of the TRI gel are shown in Fig. 2. Because the solubility of TRI is rather small (0.035[g/100g-H_2O] at room temperature), the maximum fraction of crosslinker studied here was 0.0010. All the TRI gels studied here exhibited volume phase transitions. The TRI gel showed larger discrete volume change than the BIS gel as seen in Fig. 2. All the gels in the shrunken state displayed approximately the same swelling ratios, not depending on the kind of crosslinker. However, gels displayed a different swelling ratio at the swollen state or phase transition point. It is very important to mention that the largest discrete volume change was observed not in the gel with the smallest fraction of crosslinker 0.0003, but in the gel with 0.0005.

C. Relation between swelling ratio and fraction of crosslinker at low temperatures

Although the actual distances between crosslinking points are not uniform, just to discuss the effect of different crosslinkers using a single parameter, we introduce the average distance between crosslinking points L as follows. Assuming the homogeneous distribution of crosslinkers, L is defined as $L = (\frac{V_S}{N_{Cr}})^{\frac{1}{3}}$, where V_S and N_{Cr} correspond to the volume of the solvent and number of crosslinkers at the time of synthesis, respectively. For large value of L (lower fractions of crosslinker), L may not represent the real structure of the gel. For example, the sample with too low fraction of crosslinker ends up with the branched polymer solution without gelation, while L can still be defined.

The new crosslinker TRI makes it possible to form a gel network at a lower fraction of crosslinker than BIS because TRI has two more hands than BIS. As a result, L can be larger for TRI gels, and larger L makes the TRI gel swell more in a good solvent at low temperature than BIS gels.

Using this parameter L, we discuss the effects of crosslinkers on the swelling ratio. In Fig. 3, we plot the swelling ratio at 25.0 °C as a function of L. This result indicates that the swelling ratio of NIPA gels crosslinked BIS or TRI is a smooth, monotonically increasing function of L, and it is very clear that the gels with larger L exhibited the larger swelling ratio at low temperature where water is a good solvent for NIPA.

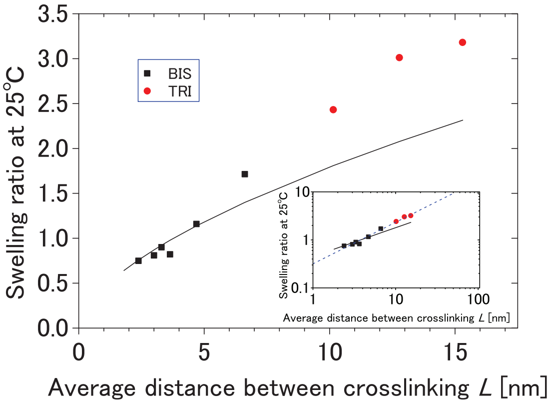

FIG. 3. (Color online) Evolution of the swelling ratio $\frac{V}{V_0}$ at 25.0 °C as a function of the average distance between crosslinking points L. The swelling ratio is proportional to $L^{\frac{3}{5}}$ in the area of $L \leqslant$ 5.0 nm as shown as the solid curve, which is explained by assuming $\frac{V}{V_0} \propto (\frac{R_g}{R_0})^3 \propto L^{\frac{3}{5}}$. Inset shows the double logarithmic plot of the same data. The broken line represents a power-law slope of 0.86 obtained by fitting all observed points, while the solid line shows the slope of $\frac{3}{5} = 0.60$.

This result can be explained by a simple scaling argument as follows: When a gel is polymerized, the conformation of polymer chain between crosslinkers can be assumed to be Gaussian; $M_w \propto L^2$. Thus, when polymerized gels reach a swollen state in good solvents, the swelling ratio should be scaled as $\frac{R_g}{R_0} \propto L^{\frac{1}{5}}$, where R_0 and R_g is the chain's reach at the polymerization and in the good solvent, respectively. This simple argument provides that the gel with large L swells more than that with smaller L in good solvents, as seen in Fig. 3. The solid curve in Fig. 3 represents $aL^{\frac{3}{5}}$, where a is a proportionality constant. In the area of $L \leqslant 5.0$ nm, the swelling ratios fit the line drawn under the assumption; $\frac{V}{V_0} \propto (\frac{R_g}{R_0})^3 \propto L^{\frac{3}{5}}$. We also tried to fit all observed points in the double logarithmic plot by a straight line as seen in the inset of Fig. 3. The slope of the solid line that fits well for $L \leqslant$ 5.0[nm] is $\frac{3}{5} = 0.60$, and that of the broken line is found to be 0.86 ± 0.04. In the short L region, the swelling ratios are proportional to $L^{\frac{3}{5}}$. However, in the long region, the swelling ratios deviate from the curve. We considered that the swelling ratios are not proportional to $L^{\frac{3}{5}}$ in the long L area because gels with long L have an inhomogeneous structure.

D. Swelling ratio of gels at high temperatures

As seen in Figs. 1 and 2, all the gels showed approximately the same swelling ratio in the shrunken state above 34.0 °C. These results indicate that the swelling ratio of the system of the deswollen side is determined by the concentration C_{tot} of the gel. So we can postulate that L has some correlation with the width of the transition between swollen and deswollen states.

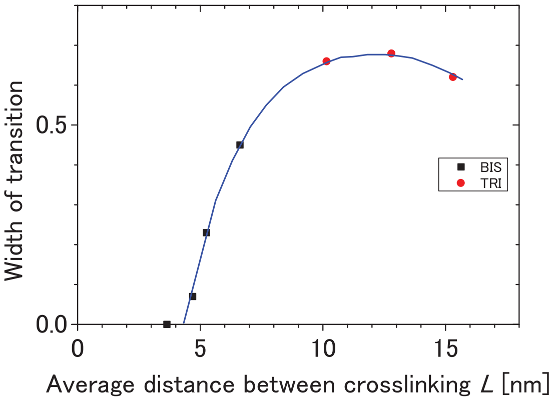

FIG. 4. (Color online) Evolution of the width of transition as a function of average distance between crosslinking. The solid curve is shown to facilitate visualization. Average distance between crosslinking L seems to be proportional to the width of transition in the short L region, while that saturates in the long L region.

E. Relation between L and width of first order transition: Inhomogeneity of the gel network

The swelling ratio was a smooth and monotonic function of L as seen in Fig. 3, and the volume of the gels at the deswollen side was independent of L for all the gels observed here. However, the width of the first order transition between the swollen and deswollen sides of the gel was not a monotonic function of L. The relation between L and the width of discontinuous volume change is shown in Fig. 4. Here the width of the transition is defined by $V_s - V_d$, where V_s and V_d are the volumes of the gel at the both ends of the transition. In the area of $L \leqslant 4.5$ nm, the width of the transition is zero because the volume changes were continuous. For smaller values of L (from 4.5 to 6.5 nm), the width of the transition seems to increase linearly with L. However, the width of the transition seems to be saturated at the region about from 10 to 13 nm.

To understand these results, we must point out that the volume phase transition of the NIPA gel system is always found close to the sol-gel boundary, where the gel is soft compared to those with higher concentrations of crosslinker. From the view point of percolation theory, the gel that is close to the sol-gel boundary has a large correlation length ξ, which is related to the largest loop of the polymer chain in the gel and related to the inhomogeneity of the gel as well. When ξ is large, the gel is believed to be very inhomogeneous.

When the gel is close to the gelation threshold, the structure of the gel is represented by a length scale ξ, which diverges at the gelation threshold. The divergence of ξ is related to the well known fact that the inhomogeneity in the gel at the gelation boundary also diverges.

The network structures of the BIS gels and TRI gels were analyzed using scanning microscopic light scattering (SMILS), developed by Furukawa *et al.* [9]. The relaxation time, reflecting the size of the internal structure, was calculated from the ensemble-averaged correlation function by inverse Laplace transform. To overcome the nonergodic problem, we calculated the ensemble-averaged properties using time-averaged properties obtained at more than ten positions of sample gels. As seen in Fig. 5, the correlation functions of BIS

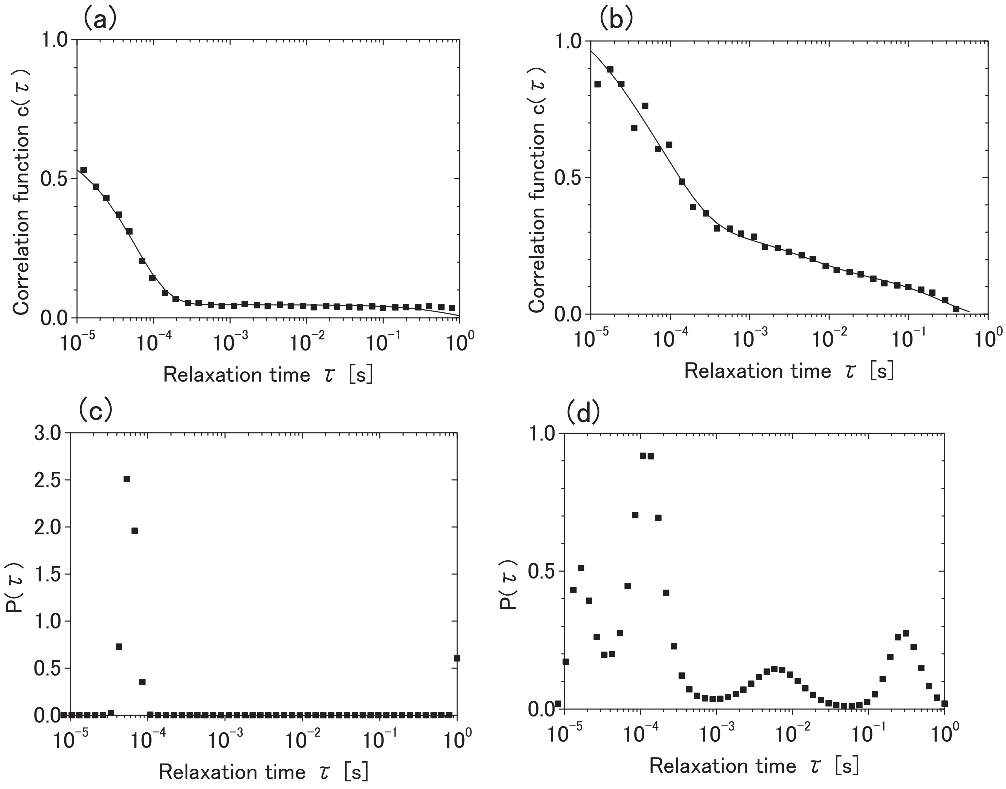

FIG. 5. Ensemble averaged intensity correlation functions and their characteristic time distribution function for BIS gel of (a,c) $F_{\mathrm{BIS}} = 0.0036$ and (b,d) TRI gel of $F_{\mathrm{TRI}} = 0.0003$.

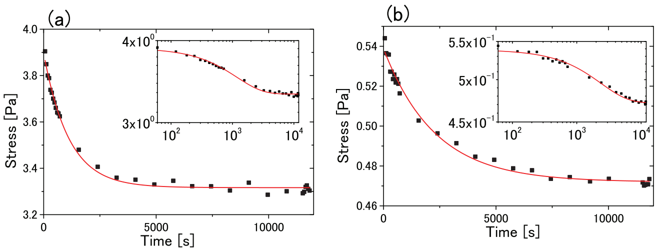

FIG. 6. (Color online) Stress relaxation of (a) BIS gel ($F_{\mathrm{BIS}} = 0.012$) and (b) TRI gel ($F_{\mathrm{TRI}} = 0.0010$) acquired at 30.0 °C. Insets represent log-log plots. The solid curves are the best-fit results to exponential function. The amplitudes of the stress of BIS gel and TRI gel are different because they depend on the strength of the gel, which is usually proportional to the densities of effective crosslinkers and effective chain in the gel.

gels relaxed quickly to the final value; however, the correlation functions of TRI gels decreased very slowly and displayed the significant multi-exponential nature of the correlation function. In the characteristic time distribution function, the BIS gel has a single peak in Fig. 5. On the other hand, the TRI gel has some peaks in a slower time region. We consider that the peaks in the faster time region are caused by gel modes and that the peaks in the slower time region are related to something to make inhomogeneities. Thus we have to postulate that TRI gels have larger inhomogeneity compared to the usual BIS gels.

The stress relaxation of gels can be measured by measuring the tensile force imposed on the gel and diameter. The tension due to stretching is equal to the tensile force divided by the cross-sectional area of the sample. In Figs. 6(a) and 6(b), the relaxation process of tension of the BIS gel and TRI gel rods against the about 10% of the total length uniaxial stretching are plotted as a function of time after the application of the stretching, and the time course of the relaxation process are fitted to the exponential function. Using these fitting results, the relaxation times are calculated to be 1.1×10^3 s and 2.3×10^3 s, respectively. These long relaxation processes of the stress are related to the dissolution of entanglement. The relaxation time of the BIS gel is in good agreement with Hirotsu's results [10]. However, the TRI gel has two times longer relaxation time than the BIS gel. Thus, we conclude that the TRI gel has many entanglements or inhomogeneity that makes the relaxation time longer than BIS gels.

We believe that the discrete volume phase transition is suppressed by such inhomogeneity of the gel for the large ξ limit. As seen in Fig. 4, the width of the transition reaches a plateau at $L \approx 12$ nm and seems to go down with L. We consider that this plateau appeared because of the increase of inhomogeneity in the gel. Such a plateau also appeared on another type of gel in Fig. 7. The width of the transition of the gel crosslinked with a hybrid of BIS and TRI was measured. We also synthesized gels with two types of crosslinkers with various fractions of crosslinker while the total concentration C_{tot} was fixed at 0.027, and the ratio of BIS and TRI was fixed at 1 mol : 1 mol. The fraction of crosslinker is defined as $\frac{[\mathrm{BIS}]+[\mathrm{TRI}]}{[\mathrm{monomer}]+[\mathrm{BIS}]+[\mathrm{TRI}]}$, and L is defined as $L = (\frac{V_{\mathrm{S}}}{N_{\mathrm{B}}+N_{\mathrm{T}}})^{\frac{1}{3}}$, where N_B and N_T correspond to the number of BIS and TRI, respectively. As seen in Fig. 7, the plateau appears at $L \approx 10$ nm, and the width of the transition seems to go down with L beyond $L \approx 10$ nm [11].

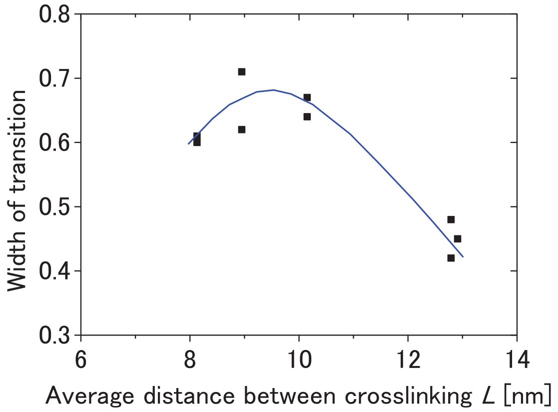

FIG. 7. (Color online) Evolution of the width of the transition of the gel crosslinked with a hybrid of BIS and TRI as a function of average distance between crosslinking.

It was previously reported that the increase of the inhomogeneity suppressed the volume phase transition of gels. Suzuki *et al.* investigated the effects of guest molecules on the volume phase transition properties of gels. They used submicron gel balls with different composition from the bulk gel as inhomogeneity and discussed the macroscopic swelling behavior of the NIPA gels qualitatively in relation to the introduced inhomogeneity [12]. They demonstrated that the volume phase transition is quite robust against the introduction of inhomogeneity to the system, but they also showed that the introduction of too much inhomogeneity suppressed the discrete transition and converted the transition to the continuous one.

F. Lowest fraction of crosslinker of gelation

It is very important to stress here that the new crosslinker TRI makes it possible to synthesize the NIPA gel at about ten times smaller fraction of crosslinker than BIS, while the difference expected by the simple Flory's theory argument is only $6/4 = 1.5$. The observed approximately ten times difference cannot be explained by the number of the functional group of the crosslinker. The most simple assumption that explains such a difference is the cluster formation of crosslinker TRI, which makes the apparent functionality of the crosslinking much higher than separated crosslinkers. We assume that such a cluster formation is caused by the high probability of the reaction with another crosslinkers (TRIs) related to the larger number of functional groups as well as the low solubility of TRI in water. Thus, we have to postulate that the cluster formation of TRI crosslinker plays an essential role in causing the gelation at extremely low fraction of crosslinker. Thus the TRI crosslinker plays as multifunctionality crosslinker in water. Our preliminary results of the TRI gel formation in dimethyl sulfoxide (DMSO), which is a good solvent for TRI and NIPA, confirmed that the TRI gel cannot be formed at such a low fraction of crosslinker as 0.0010. Because the cluster formation is not formed in a good solvent, the TRI crosslinker plays truly three functionalities.

IV. SUMMARY

We synthesized a new type of NIPA gel using TRI as crosslinker. The TRI gel exhibited the first order transition as well as the well-known BIS gel. We discussed the width of the volume phase transition, distance of crosslinking, and inhomogeneity. The averaged distance between crosslinking points L was defined, and we postulate that L has some correlation to the width of the transition. To complete the investigation of the effect of crosslinker functionality on the collapse transition of NIPA gels, we have to include an analysis of any change in transition dynamics. So we are measuring stress relaxation of TRI gels in more detail.

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