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Small-Angle Neutron-Scattering Study on Preparation Temperature Dependence of Thermosensitive Gels

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ABSTRACT: The microscopic structure of temperature-sensitive polymer gels consisting of poly(*N*-isopropylacrylamide) (PNIPA) has been investigated in terms of small-angle neutron scattering. The spatial inhomogeneities, characteristic of polymer gels, in the PNIPA gels were evaluated as a function of the gel preparation temperature, T_{prep}, as well as the cross-link concentration, C_{X}. It was found that the spatial inhomogeneities increase with increasing T_{prep} or C_{X}. The effects of T_{prep} and C_{X} on the gel structure were successfully separated by a quantitative analysis of the structure factor with the Panyukov−Rabin theory. The effective degree of polymerization between cross-links, N, exhibited the opposite dependence with respect to T_{prep} and C_{X}. N was found to decrease with increasing C_{X}, while it increased with increasing T_{prep}. The temperature dependence of the Flory interaction parameter and the presence of the cross-link saturation threshold are also addressed with a discussion of the physical implication of these parameters.

Introduction

A polymer gel, a network consisting of long polymer chains immersed in a solvent, possesses a very complicated structure and dynamics compared to the corresponding polymer solution due to restriction of the chain motion by cross-links.[1,2] The cross-links connecting polymer chains can be either permanent or temporal. Gels of the former type are often called chemical gels and the latter physical gels. Each chain between neighboring cross-links is at least topologically “frozen” at the junction point as far as the lifetime of cross-links is long enough compared to the diffusion of the polymer segment.[3] A covalently cross-linked gel is a typical example of polymer gels and is usually synthesized by conventional radical polymerization starting from the constituent monomer and cross-linking agents. Gels can be alternatively made by introducing cross-links to a polymer solution, which can be done by chemical reaction of the side functional groups or by irradiation of γ-ray or electron beam. In most cases, these methods allow one to obtain a homogeneous and elastic polymer network. However, it should be recognized that the structure is considerably different from sample to sample, depending on the way of sample preparation.

It is well-known that polymeric gels have unique structural inhomogeneities in the microscopic point of view. Because of Brownian motion, the concentration of a pre-cross-linked polymer (or monomer) solution randomly fluctuates in space. However, an introduction of cross-links to the polymer solution instantaneously quenches the concentration fluctuations to some extent. This results in the emergence of nonvanishing spatial inhomogeneities, which are characterized by a strong forward scattering in small-angle neutron (SANS) and X-ray scattering (SAXS) and by strong sample position dependence of light-scattering intensity called speckle patterns.[4−8] Owing to both experimental and theoretical efforts in the past decade, it becomes clear that gels have inhomogeneous and hierarchical structures ranging from several tens to hundreds of nanometers in addition to thermal concentration fluctuations. The former increases with cross-linking density,[9,10] whereas the latter remains rather constant as long as the observation condition is the same.[11,12]

We have been studying the structure and dynamics of poly(*N*-isopropylacrylamide)(PNIPA) gels as a model system of the thermosensitive gels. PNIPA linear polymers exhibited a sharp conformation transition in water around its lower critical solution temperature (LCST $\approx$ 32 °C) by releasing structured water molecules around the polymer chains.[13−15] PNIPA gels cross-linked by methylenebis(acrylamide) (BIS) also exhibited a volume phase transition at the slightly higher temperature of 34 °C.[16,17] According to our previous work on a series of PNIPA gels prepared at different preparation temperatures, T_{prep}, the dynamic component of the light-scattering intensity is rather independent of T_{prep}, whereas the frozen component of the light-scattering intensity drastically increased with T_{prep} above 23 °C.[12] Since both T_{prep} and the cross-linker concentration, C_{X}, affect the inhomogeneities in gels, it is of importance to elucidate separately the roles of preparation temperature and cross-linker for a better understanding of the structure of polymer gels.

In this paper, we investigate the correlation between cross-linking formation and preparation condition for chemically cross-linked gels in a wide range of momentum transfers in order to establish a method of quantitative analysis of inhomogeneities as well as thermal fluctuations for polymeric gels. We will demonstrate how the gel preparation condition affects the resultant network structure, We also address the physical sig-

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Table 1. Sample Concentrations

C_{NIPA}	C_{BIS}	C_{X}	T_{prep} (°C)			
(mA)	(mM)	($2C_{\mathrm{BIS}}/(2C_{\mathrm{BIS}} + C_{\mathrm{NIPA}})$)	10	20	25	27
690	0	0	-	-	-	-
690	4.3	1.2	-	-	-	-
690	8.6	2.4	-	-	-	-
690	12.9	3.6		-	-	-
690	15.4	4.3	-	-	-	-
690	17.9	4.9		-	-	-
690	20.2	5.5		-	-	-
690	22.4	6.1	-	-	-	-
690	25.0	6.8			-	
690	28.0	7.5		-	-	
690	30.0	8.0	-			
690	32.0	8.5		-		
690	35.0	9.2	-	-		
690	40.0	10.4	-			
690	45.0	11.5	-			
690	50.0	12.7	-			
690	54.0	13.5	-			
690	58.0	14.4	-			

[a] Hyphens in this table indicate the preparation temperatures employed in this study.

nificance of the concept of the cross-linking saturation threshold (CST), which defines the maximal achievable density of cross-links in a gel.[18,19]

Experimental Section

Poly(*N*-isopropylacrylamide) (PNIPA) hydrogels having different cross-linker concentrations were prepared by copolymerizing NIPA monomer and *N*,*N′*-methylenebis(acrylamide) (BIS; the cross-linking monomer) in deuterated water at given preparation temperatures. The preparation temperatures employed in this study are indicated by a hyphen in Table 1, where C_{BIS}, C_{NIPA}, and C_{X} denote molar concentrations of BIS and NIPA and the cross-linking density is defined by

$$C_{\mathrm{x}} = \frac{2C_{\mathrm{BIS}}}{2C_{\mathrm{BIS}} + C_{\mathrm{NIPA}}} \tag{1}$$

respectively. The samples for the SANS experiments were prepared in quartz cells and used without further treatment, such as drying and immersion. Note that a gel containing hydrophobic groups often leads to association during drying process and the resultant dried gel does not recover its original conformation even by immersion in the same solvent.[20]

The SANS experiments were carried out on the research reactor, SANS, at Institute of Solid State Physics, The University of Tokyo, located at Japan Atomic Energy Laboratory, Tokai, Japan. A flux of cold neutrons with a wavelength of 7.0 Å was irradiated to the sample, and the scattering intensity profile was collected with an area detector of 128 × 128 pixels (0.5 mm/pixel). The sample-to-detector distance was set to be 4 m, which covered the accessible q range, which was 0.01−0.078 $Å^{-1}$. Here, q is the scattering vector. The sample was placed in a brass chamber with quartz windows and the chamber was thermoregulated within an error of ±0.1 °C at the sample position with a NESLAB 110 water-circulating bath. The sample thickness was 4 mm. The scattering intensities were circularly averaged by taking account of the detector inhomogeneities, corrected for cell scattering, fast neutrons, transmission, and incoherent scattering, and then calibrated to the absolute intensities with a polyethylene standard sample (Lupolen).

Theoretical Background

Because of formidable complexity of microscopic structure of gels, such as the chain length and its distribution between neighboring cross-links and topological problem, a complete solution describing the network structure for inhomogeneous system has not been proposed yet. Another complexity of gels lies in the spatially frozen inhomogeneities of gels, i.e., non-canceled-out concentration fluctuations, as introduced in the Introduction. Despite these difficulties, several phenomenological functions have been proposed in the literature.[21−25] In any case, it is essential to acquire the following parameters to describe a gel: the interaction parameter between the polymer segment and the solvent, the correlation length, the inter-cross-linking distance, and so on. Panyukov and Rabin proposed a statistical theory for describing the structure factor of gels. Since the Panyukov−Rabin (PR) theory[18,26] succeeded in deriving a theoretical expression of the frozen concentration fluctuations in addition to thermal concentration fluctuations, we employ the PR theory in order to elucidate the effects of cross-links and preparation temperature on the microscopic structure of gels.

According to the PR theory, the scattering intensity, $I(q)$, can be decomposed to two fluctuating components of the structure factor, $S(q)$, i.e., the dynamic correlator, $G(q)$, and the static correlator, $C(q)$. The former represents the thermal fluctuations of the reference polymer solution, while the latter is related to the built-in inhomogeneities introduced by cross-linking. Hence, the total scattering intensity is written by

$$I(q) = KS(q) = K[G(q) + C(q)] \tag{2}$$

where q and K are the scattering vector and the proportional constant, respectively.

The thermal correlator, $G(q)$ can be written by

$$G(q) = \frac{\phi N g(q)}{1 + wg(q)} \quad \text{(for gels)} \tag{3}$$

or

$$G(q) = \frac{\phi N}{\frac{Q^2}{2} + w} \quad \text{(for solutions)} \tag{4}$$

where

$$g(q) = \frac{1}{Q^2/2 + (4Q^2)^{-1} + 1} + \frac{2}{(1 + Q^2)^2(\phi_0/\phi)^{2/3}} \tag{5}$$

is the thermal correlator in the absence of the excluded volume effect and

$$w = (1 - 2\chi + \phi)\phi N \tag{6}$$

is the excluded volume parameter. ϕ and ϕ_0 are the volume fraction of the gel at sample preparation and at observation, respectively. N is the average degree of polymerization between cross-links. Q is the reduced scattering vector normalized by the monomer fluctuating radius. The static correlator, which corresponds to the contribution from the frozen structure of gels, is given by

$$C(q) = \frac{\phi N}{[1 + wg(q)]^2(1 + Q^2)^2} \left[6 + \frac{9}{w_0 - 1 + (^1/_2)Q^2\left(\frac{\phi_0}{\phi}\right)^{2/3}}\right] \tag{7}$$

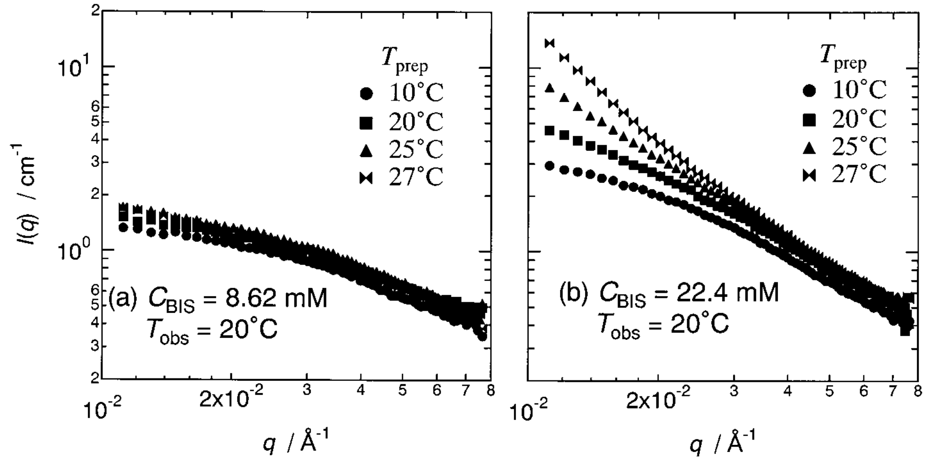

Figure 1. Double logarithmic plots of the neutron scattering intensity, $I(q)$, vs the scattering vector, q, for gels prepared at different temperatures, T_{prep}, and with (a) $C_{\text{BIS}} = 8.62$ and (b) 22.4 mM.

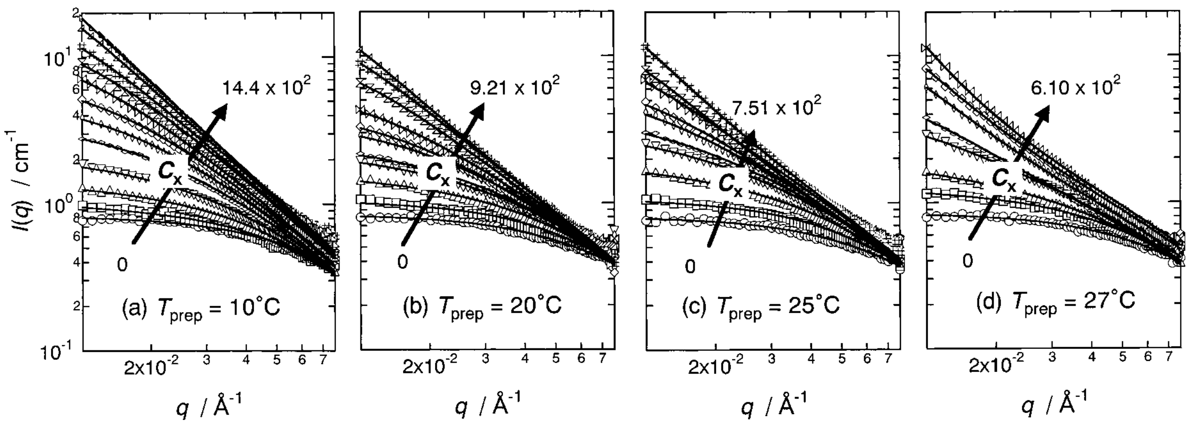

Figure 2. $I(q)$s for NIPA gels prepared at (a) $T_{\text{prep}} = 10$, (b) 20, (c) 25, and (d) 27 °C and with various cross-linker concentrations, C_Xs.

where w_0 is the excluded volume parameter at sample preparation,

$$w_0 = (1-2\chi_0 + \phi_0)\phi_0 N \tag{8}$$

The scattering intensity diverges at $q = 0$, when w_0 approaches unity, which is a signature of cross-linking saturation threshold (CST). The CST can be considered as a point where the number of cross-links introduced to the gel becomes equal to the number of binary contact of monomers. Because of this physical limitation, any additional cross-linking is no longer formed above the CST, resulting in the scattering function becoming independent of cross-linker concentration.[19]

Results and Discussion

1. T_{prep} and C_{BIS} Dependence of the Scattering Intensity. Figure 1 shows the double logarithmic plots of the neutron scattering intensity, $I(q)$, vs the scattering vector, q, for gels prepared at different temperatures, T_{prep}, with (a) $C_{\text{BIS}} = 8.62$ and (b) 22.4 mM. The observation temperature was fixed to be 20 °C. It is clear from the figures that $I(q)$s for gels with $C_{\text{BIS}} = 8.62$ mM are much lower than those with $C_{\text{BIS}} = 22.4$ mM and are independent of T_{prep}. It should be noted here that the light-scattering (LS) intensity is strongly dependent on T_{prep} even for the case of $C_{\text{BIS}} = 8.62$ mM. It is due to the difference of the length scale covered in the experiments, i.e., several tens of nanometers for SANS and hundreds of nanometers for LS. On the other hand, for $I(q)$s for gels with $C_{\text{BIS}} = 22.4$ mM, a noticeable T_{prep} dependence is observed as indicated in Figure 1b, and the scattering intensity increased with increasing T_{prep}, particularly at the lower scattering vector region. This increase is due to the enhancement of structural inhomogeneities in the gels. In our previous work,[19] we demonstrated the importance of the cross-linking saturation threshold (CST). It is considered that additional cross-links are no longer formed above the CST. For example, the scattering function for a NIPA gel with $T_{\text{prep}} = 25$ °C approached CST around $C_{\text{BIS}} = 22.4$ mM. The threshold is predicted by the PR theory, of which characteristic feature is a power-law-like behavior in the small angle scattering experiment. Above this cross-linker concentration, the observed scattering function diverges at small q, and the resultant gel becomes opaque. For example, an up-turn of the scattering intensity function at lower q was found for the gel prepared at 27 °C, where the condition exceeded the CST. The gel is slightly opaque, so the light-scattering intensity is hard to measure because of multiple scattering. Even in the case of such a high cross-linker concentration, the gel prepared at 10 °C seems to be rather homogeneous, suggesting that higher amounts of cross-links can be introduced without noticeable increase in inhomogeneities.

Figure 2 exhibited the $I(q)$s prepared at (a) 10, (b) 20, (c) 25, and (d) 27 °C, as a function of the cross-linker

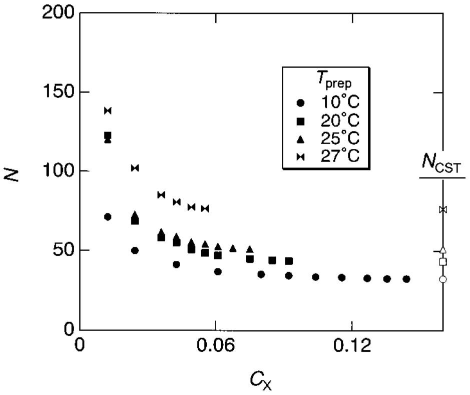

Figure 3. Degree of polymerization between cross-links, N, as a function of C_X evaluated by the PR analysis. N is a decreasing function of C_X irrespective of T_{prep}.

concentration, C_X. As shown in the figure, the scattering function for the PNIPA solutions (the lowest curves with the symbols of open circles) exhibited an Ornstein–Zernike (OZ) type behavior. On the other hand, a power-law-like function was observed for the highest cross-linker concentrations. Such a systematic variation in $I(q)$s from an OZ to a power-law-type functions seems to be universal irrespective of the preparation temperature. However, the maximum cross-linker concentration to reach the CST condition, $C_{X,CST}$ is dependent on T_{prep}. $C_{X,CST}$ is a decreasing function of T_{prep} from $C_{X,CST} = 14\%$ for $T_{prep} = 10$ °C to $C_{X,CST} = 6.1\%$ for $T_{prep} = 27$ °C. This point will be discussed later.

The cross-linker concentrations employed in this work are much larger than those in the literature. However, the scattering-length density of BIS is very close to that of NIPA. Hence, it is not necessary to treat BIS as a third component as far as SANS is concerned. Hence, we will treat the system as a two-component system in the analysis of the structure factor.

The solid lines indicated in the figures are the results of curve fitting with the PR theory. First, we determined Flory's χ parameter for the PNIPA solutions using eqs 4 and 6 where simple approximations, i.e., elimination of (i) the elastic free energy term and (ii) the short-wave contribution to the structure factor, are applied. Needless to say, eq 4 is equivalent to a Lorentz function for semidilute polymer solutions. Second, Flory's parameter at sample preparation, χ_0, for a gel having the highest cross-linking density was determined using eqs 2–8, while the value of χ evaluated above was fixed. Thus, we obtained the information about Flory's parameter at both observation and sample preparation conditions, i.e., χ and χ_0. Finally, the values of N were evaluated by curve fitting for all the gels by fixing both χ and χ_0. As can be seen from the figures, the PR theory well reproduces the experimental results.

2. Variation of the Structural Parameters of Gels with T_{prep} and C_{BIS}. Figure 3 shows the degree of polymerization between cross-links, N, as a function of C_X evaluated by the PR analysis. N is a decreasing function with C_X irrespective of T_{prep}. According to eq 7, $C(q = 0)$ diverges when $w_0 = 1$. Therefore, N_{CST}, i.e., the lowest degree of polymerization between cross-links, can be calculated by

$$N_{CST} = \frac{1}{(1 - 2\chi_0 + \phi_0)\phi_0} \tag{9}$$

As shown in the figure, N smoothly falls and approaches the calculated N_{CST} for all the T_{prep}. On the other hand, N increased with increasing T_{prep} at constant C_X. This phenomenon can be explained as follows. In the case of PNIPA hydrogels, the excluded volume effect becomes weaker with increasing T_{prep} because PNIPA aqueous solutions have a lower critical solution temperature. Hence, cross-linking formation is expected to be much easier and a CST is attained easier for higher T_{prep}. In another word, a less number of cross-linking points will be formed, resulting in a larger value of N. In this case, the gels prepared at higher temperatures have a comparatively loose network structure. It accounts well for the T_{prep} dependence of equilibrium swelling behavior as reported before.

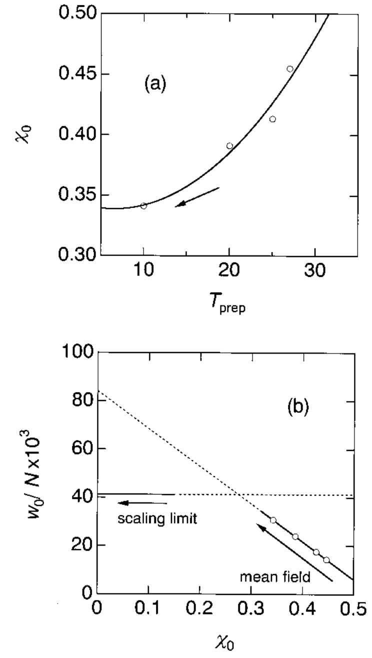

Figure 4. (a) T_{prep} dependence of Flory's interaction parameter at sample preparation, χ_0. (b) χ_0 dependence of the excluded volume parameter normalized by N, w_0/N. w_0/N is a decreasing function of χ_0 in the context of the mean field assumption, whereas that of the scaling approach is independent of χ_0 as indicated by eq 11. It can be found from the figure that the mean field approach is valid in this study since the evaluated χ_0s are well above the crossover.

Figure 4a shows the plots of χ_0 vs T_{prep}. The Flory's interaction parameter at sample preparation, χ_0, increased with T_{prep} and reached 0.5 around 32 °C, which is consistent with the cloud point of the PNIPA solutions.[27] On the other hand, χ_0 approaches about 0.34 for lower preparation temperatures. It is noteworthy here that unlike the van der Waals interacting system, where the Flory interaction parameter varies linearly with temperature, χ_0 is a strong function of temperature particularly near the LCST. This is one of the most prominent features of hydrophobically interacting systems like PNIPA aqueous solutions.

As we reported before, one should apply the scaling limit approach instead of the mean field approach when a gel is placed in a good solvent, where the strong interaction dominates the conformation of PNIPA chains. As shown in Figure 4b, the excluded volume parameter normalized by N

$$\frac{w_0}{N} = (1 - 2\chi_0 + \phi_0)\phi_0 \quad \text{(mean field)} \tag{10}$$

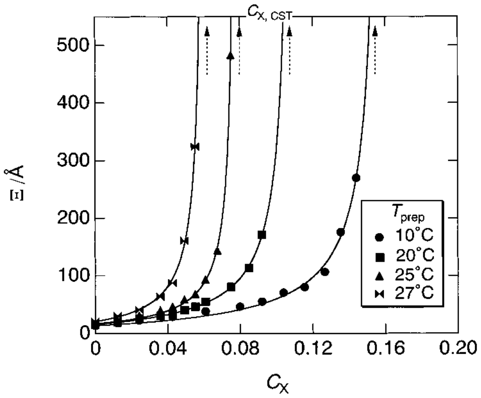

Figure 5. Inhomogeneity correlation length Ξ as a function of C_X with T_{prep}'s. For all preparation temperatures, Ξ drastically increased with C_X and diverges at each critical cross-linking density, $C_{X,CST}$.

is expected to crossover from a χ_0-dependent function to a χ_0-independent function with the following form

$$\frac{w_0}{N} = \phi_0^{5/4} \quad \text{(scaling limit)} \tag{11}$$

where the open circles denote the values of w_0/N calculated with T_{prep}'s. Both functions seem to merge around $\chi_0 = 0.28$ in this condition, and w_0/N becomes independent of χ_0 below this value.

Another interesting parameter of gels, which can be drawn from the curve-fitting analysis, is the inhomogeneity correlation length, Ξ, which corresponds to the screening length of the static correlator. Ξ is calculated with the following equation

$$\Xi = \frac{a}{\sqrt{12[(1 - 2\chi_0 + \phi_0)\phi_0 - 1/N]}} \tag{12}$$

where a is the segment length of PNIPA. In Figure 5, Ξ is plotted with C_X. For all preparation temperatures, Ξ drastically increased with T_{prep} and diverges at each critical cross-linking density. It is found from the figure that the higher the preparation temperature, the lower the $C_{X,CST}$. The solid lines indicate the results of curve fitting with the following empirical form

$$\Xi = \left(\frac{A}{C_{X,CST} - C_X}\right)^{\gamma} + B \tag{13}$$

where A and B are constants and γ is the critical exponent. A, $C_{X,CST}$, and γ are adjustable parameters, while B is calculated with $N \to \infty$. As shown in the figure, eq 13 with $\gamma = 1$ seems to work well for a series of gels. The physical meaning of Ξ is a characteristic size of clustered consisting of cross-linked network of which concept is the same as the model proposed by Bastide and Leibler.[28] If this model applies, C_X can be re-read as a parameter proportional to the bond probability in a percolating systems and γ is the critical exponent related to the correlation length of the clusters.[29] Here, γ is expected to be $^1/_2$ for the mean-field model and 0.88 for the three-dimensional percolation. The observed value of 1 seems to support the point that the critical saturation obeys the latter model.

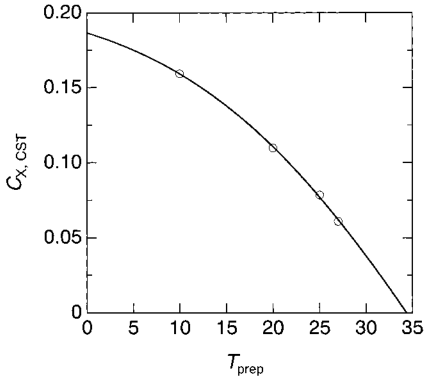

Figure 6. T_{prep} dependence of $C_{X,CST}$, i.e., the effective number of cross-links. The $C_{X,CST}$ is smoothly connected with a single curve and approach zero around the LCST.

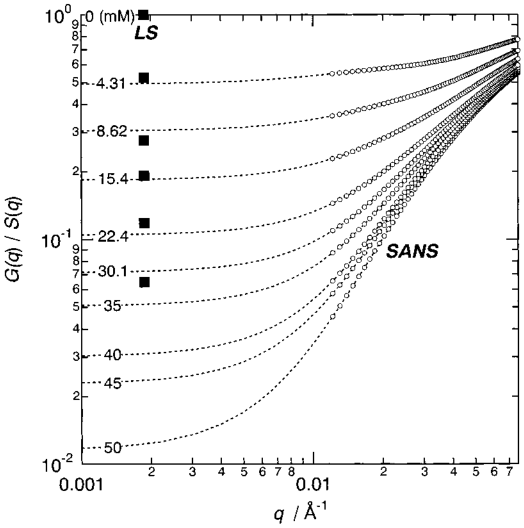

Figure 7. Ratio of $G(q)/S(q)$ for NIPA gels prepared at T_{prep} = 10 °C as a function of q, where $G(q)$ and $S(q)$ denote the fluctuating components of the ensemble average of the scattering intensity, respectively. The open circles denote the data obtained by the SANS experiment. On the other hand, the filled squares denote those obtained by light scattering (LS).

Figure 6 shows the T_{prep} dependence of $C_{X,CST}$, i.e., the effective number of cross-links. The solid line is drawn for the eye. When the preparation temperature is raised, polymer chains before the gelation threshold would have a more compact conformation. Hence, it can be concluded that cross-linking formation is much easier in a gel prepared at high temperatures than in a strongly interacted system, i.e., polymer chains prepared at lower temperatures, resulting in lowering $C_{X,CST}$. Interestingly, the $C_{X,CST}$ approaches zero around the LCST (≈34 °C). This means that the number of binary contact introduced by cross-linking necessary for a macroscopic phase separation decreases with increasing T_{prep} and no additional binary contact by cross-linking is allowed above the LCST.

3. Scattering Vector q Dependence of the Degree of Inhomogeneities. Finally, let us discuss the degree of inhomogeneity as a function of the scattering vector. In Figure 7 is plotted the ratio of $G(q)/S(q)$ for NIPA gels prepared at T_{prep} = 10 °C as a function of q, where $G(q)$ and $S(q)$ denote the fluctuating components of the ensemble average of the scattering intensity, respectively. The open circles denote the data obtained by the SANS experiment. On the other hand, the filled squares denote those obtained by a series of light-scattering (LS) experiments with a He−Ne laser at a scattering angle of 90°. As shown in the figure, the PR theory predicts that the ratio of fluctuating component in the scattering intensity decreases with lowering q. In other words, the inhomogeneities become larger with increasing length scale; from nanometer orders (SANS) to micrometer order (LS). Note that there is no frozen component present for the PNIPA solution ($C_X = 0$ mM) and the inhomogeneities increase with C_X. It is rather surprising, the $G(q)/S(q)$ observed by LS well fits to the theoretically predicted lines for all C_Xs. However the following fact should be noted. Since the theory does not exclude the prediction of the structure factor in the LS region, the agreement is quite reasonable, at least qualitatively. As a matter of fact, in one of the previous papers, we employed the PR theory to predict the charge effect on the inhomogeneities in the LS regime.[30,31] It should be noted here that the inhomogeneities are not so significant in the local scale covered by SANS (for $q > 0.05$ Å$^{-1} \approx 1/20$ Å). This q dependence seems to be quite reasonable because the SANS is sensitive to the length scale-up to a few tens of angstroms and the inhomogeneities ranging from nanometers to micrometers become indistinguishable with the eye of neutron and can be more clearly observed by LS.

Conclusions

The microscopic structures of polymer gels have been investigated for a series of PNIPA having various cross-link concentrations, C_X, as a function of gel preparation temperature, T_{prep}. The quantitative analysis of SANS intensity functions was carried out by curve fitting with the theoretical structure factor proposed by Panyukov and Rabin. The curve fitting allowed us to extract the structure parameters describing the inhomogeneities of gels, such as the average degree of polymerization between cross-links, N, Flory's interaction parameters between PNIPA and water both at gel preparation, χ_0, and at observation, χ, and the inhomogeneity correlation length, Ξ. The conclusions drawn are as follows: (1) The T_{prep} dependence of inhomogeneities becomes explicit for gels prepared at high cross-linker concentrations. (2) There exists the cross-link saturation threshold, $C_{X,CST}$, above which the structure factor becomes insignificant with respect to C_X. The CST is characterized by a power-law behavior of the structure factor. Ξ diverges at the CST. (3) The divergence of Ξ is analogous to the percolation threshold of a three-dimensional percolation model with the observed critical exponent of $\gamma = 1$. (4) The higher the T_{prep}, the lower the $C_{X,CST}$. (5) N is a decreasing function of C_X, but an increasing function of T_{prep}. The former is easily understood from the stoichiometry, i.e., the inverse proportionality of N and C_X (for an ideal case), while the latter indicates the increasing efficiency of cross-linking with increasing T_{prep}. (6) χ_0 is a strong function of T_{prep} and steeply increases by approaching the LCST. This is deduced to be one of the reasons of sharp temperature dependence of the phase behavior of PNIPA. (7) The q dependence of the ratio of dynamic component in the scattering intensity to the total intensity, $G(q)/S(q)$, is nicely connected between the SANS and LS regimes, which covers the nanometer to micrometer length scales. It is found that $G(q)/S(q)$ is q dependent and the degree of inhomogeneity (the inverse of the ratio) is less dominant in the SANS region rather than in the LS region.

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