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Effect of Degree of Cross-Linking on Spatial Inhomogeneity in Charged Gels. 2. Small-Angle Neutron Scattering Study

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ABSTRACT: The structural inhomogeneities in a weakly charged gel consisting of (*N*-isopropylacrylamide-*co*-acrylic acid) (NIPA−AAc) have been investigated by small-angle neutron scattering (SANS) as a function of cross-linking density (CD) and temperature. The CD and temperature dependence of the scattered intensity profiles, $I(q)$, indicated the presence of an anomalous CD dependence of the scattering intensity, where q is the magnitude of the scattering vector. At temperatures below 42 °C, $I(q)$ was a monotonically decreasing function of q and increased with CD at $q \leq 0.08$ Å^{-1}. However, above 45 °C, $I(q)$ started to have a distinct peak around $q = 0.02$ Å^{-1} and the CD dependence of $I(q)$ became classifiable into two regimes depending on temperature; one where $I(q)$ increases with CD, and the other where $I(q)$ decreases with CD. Since a similar phenomenon, called “inversion”, has already been observed by light scattering, it is concluded here that the inversion is a universal phenomenon observed in a wide range of the q space from 10^{-4} to 10^{-2} Å^{-1}. The physical meaning of this inversion is discussed on the basis of the Rabin−Panyukov theory proposed for weakly charged gels.

Introduction

One of the characteristic features of gel making is a fixation of topological structure by introduction of cross-links into a polymeric system. Therefore, it is no exaggeration to say that the degree of cross-linking is one of the most important parameters that determine the properties of the gel. Although the difference between a gel and the corresponding polymer solution with the same concentration has been discussed in many papers,[1−9] the cross-linking density (CD) dependence of a gel has been paid limited attention to our knowledge. The effects of cross-linking have been studied so far experimentally[8−16] and theoretically.[17−19] As one of the results, it has been believed that the microstructure in the polymer gels becomes more inhomogeneous as the CD increases. For example, Mallam et al. showed that the scattered intensity, $I(q)$, increased with CD in a wide range of the scattering vector, q, i.e., in both the light-scattering (LS) and small-angle X-ray-scattering (SAXS) regimes.[8] Schosseler et al.[10] observed by small-angle neutron scattering (SANS) that, in a poly(acrylic acid) (PAAc) gel system, an introduction of *N*,*N*′-methylenebis(acrylamide) (BIS; cross-linker) resulted in an increase in $I(q)$’s, particularly at small q regions. According to their interpretation, the different reactivity ratios of the two comonomers, i.e., AAc and BIS, lead to formation of structural inhomogeneities with an inhomogeneous distribution of cross-linkers. Cohen et al.[10] found by SAXS that, in polyacrylamide gels, an excess scattering at the small q region appears as the cross-linker concentration increases. Furthermore, Shibayama et al.[13] found by LS that the ensemble average of the scattered intensity increased with CD for *N*-isopropylacrylamide gels. All of these examples indicate that the spatial inhomogeneities in gels increase with CD.

Recently, we found that the spatial inhomogeneities decrease with increasing CD in weakly charged polymer gels, i.e., poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPA/AAc) gels in water, if the experimental condition is carefully chosen.[15,16] In the case of polymer gels, the light-scattered intensity is sample-position-dependent even if the gel is homogeneously prepared.[20−22] This is due to the presence of frozen inhomogeneities. It is necessary, therefore, to take the ensemble average in order to study the structure of the gel. We observed that the ensemble average of scattered intensity, $\langle I(q)\rangle_E$, has an anomalous CD dependence.[15,16] There is a region where $\langle I(q)\rangle_E$ decreased with CD in the parameter space. This phenomenon, an inversion of the CD dependence of the structural inhomogeneities, was explained as a competition between two effects of cross-linking: (1) introduction of the inhomogeneities in the gel due to the existence of the coarse and dense parts of CD and (2) suppression of the inhomogenizing move by topological freezing. We also found that the inversion can be reproduced by theoretical calculation of the structure factor, $S(q)$, on the basis of the Rabin−Panyukov theory,[19] proposed for weakly charged polymer gels in a poor solvent. The theory indicates that inhomogeneities in a gel increase or decrease with increasing CD, depending on the conditions, such as temperatures, degrees of ionization, and network volume fractions at experiment and at preparation, respectively. Here, we discuss the CD dependence of $I(q)$ obtained by SANS and compare it with the theoretical prediction of $S(q)$.

There are two aims in this paper. First, we will demonstrate that the inversion of the CD dependence of $I(q)$ takes place not only in the LS regime but also in the SANS regime. Second, we will evaluate the structural parameters of gels by conducting a fitting of the

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observed $I(q)$'s with calculated $S(q)$'s based on the Rabin–Panyukov theory.[19] The physical meaning of fitting parameters, i.e., Flory interaction parameter, degree of polymerization between cross-linking points, and degree of ionization, is discussed in detail.

Theoretical Background

As reported in the previous paper,[15,16] it was possible to reproduce an inversion of CD dependence of the ensemble average of the light-scattered intensity, $\langle I\rangle_E$, by using the recent theory of Rabin and Panyukov (RP).[19] Since this experimental study is closely related to the theoretical prediction, it is worthy to review the RP theory: The structure factor, $S(q)$, consists of two contributions from thermal fluctuations, $G(q)$, and static density inhomogeneities, $C(q)$,

$$S(q) = G(q) + C(q) \tag{1}$$

$$G(q) = \frac{\phi N g(q)}{1 + w(q)\, g(q)} \tag{2}$$

$$C(q) = \frac{\phi N}{[1 + w(q)\, g(q)]^2 (1 + Q^2)^2} \times \left[6 + \frac{9}{w_0(q) - 1 + (1/2)Q^2(\phi_0/\phi)^{2/3}{\phi_0}^{-1/4}}\right] \tag{3}$$

where a and N are the segment length (8.12 Å for NIPA[23,24]) and the average degree of polymerization between cross-linking points, respectively. ϕ_0 and ϕ are the volume fractions of polymer networks at preparation (the initial state) and at experiment (the final state), respectively. Q ($=aN^{1/2}q$) is the dimensionless wave vector. The function $g(q)$ is given by

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

The functions $w(q)$ and $w_0(q)$ denote the effective second virial coefficients in the final and initial states, respectively, and are given by

$$w(q) = (1 - 2\chi + \phi)\phi N + \frac{l_B f^2 \phi N^2}{Q^2 + l_B(f + 2\hat{c}_s)\phi N} \tag{5}$$

$$w_0(q) = {\phi_0}^{5/4} N + \frac{l_B {f_0}^2 {\phi_0}^{5/4} N^2}{Q^2(\phi_0/\phi)^{2/3} + l_B f_0 {\phi_0}^{5/4} N} \tag{6}$$

where f, f_0, and $\hat{c}_s$ represent the degree of ionization in the final and initial states, and the reduced salt concentration (i.e., the ratio of the concentration of salt to the monomer concentration inside the gel), respectively. χ is the Flory interaction parameter at the state of experiment. l_B is the dimensionless Bjerrum length given by $l_B = 4\pi L_B/a$. The Bjerrum length, L_B, is often fixed to be 7 Å, which is the value for aqueous solutions at 25 °C. However, we used here the following equation in order to take into account the temperature dependence.[24,25]

$$L_B = \frac{e^2}{4\pi\epsilon k_B T} \tag{7}$$

where e, ϵ, k_B, and T denote the elementary electric charge, the dielectric constant of the solvent, the Boltzmann constant, and the temperature at experiment, respectively.

Experimental Section

Samples. Two kinds of mixtures of *N*-isopropylacrylamide (NIPA) and acrylic acid (AAc) monomers with NIPA/AAc = 668 mM/32 mM and 636 mM/64 mM were dissolved in 40 mL of D_2O including 20 mg of ammonium persulfate (polymerization initiator), respectively. Each solution was divided into eight vessels with equal amounts, and then the given amounts of *N*,*N*′-methylenebis(acrylamide) (BIS; cross-linker) were added to each solution. Then, the solutions were filtered with a 0.2 μm micropore filter. Gelation was initiated in a test tube thermostated at 20 °C by adding 24 μL of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED; accelerator). The final concentrations of BIS, C_{BIS}, with respect to the total monomer concentration, were 0 (cross-linking density, CD = 0 mol %), 2 (0.28), 4 (0.57), 6 (0.85), 8 (1.1), 12 (1.7), 16 (2.2), and 24 (3.3) mM. The obtained transparent gels were sifted by a 500 μm sieve to small pieces in order to obtain quick thermal equilibration upon a change of temperature. The smashed gels were sealed in a brass cell with a pair of quartz windows and a rubber O-ring. Thus, sealed gels were used for SANS experiments without further treatment. Note that no part of the gel sample touches the brass cell because of the O-ring spacer. The sample thickness was 2 mm.

SANS. Small-angle neutron-scattering (SANS) experiments were carried out on the 8 m SANS facility (NG1) at the National Institute of Standards and Technology. The neutron beam with a wavelength of 9 Å irradiated gel samples in the brass cell whose temperature was varied from 30 to 54 °C by a 3 deg step. At least 30 min was allowed before each measurement in order to approach thermal equilibrium. The scattered neutrons were counted with a two-dimensional detector and circularly averaged by taking account of the detector inhomogeneities. The averaged data were corrected for cell scattering, fast neutrons, transmission, and then scaled to the absolute intensity.

Results and Discussion

1. Theoretical Prediction of $S(q)$. It is very important to survey the parameter dependence of $S(q)$ because it has many parameters, such as the degree of ionization, f and f_0, the volume fractions of the network, ϕ and ϕ_0, and temperature T (or the Flory interaction parameter, χ). Particularly, f (and f_0) plays an important role for the microphase separation in the weakly charged gel.[19,24,25] Parts a–c of Figure 1 show the calculated $S(q)$'s for various values of (a) f's, (b) ϕ's, and (c) χ's, respectively. Note that f_0 and ϕ_0 are fixed to be the same as f and ϕ, respectively, because reactor-batch gels are studied. Here, needless to say, $S(q)$ is in proportion to the scattered intensity function, $I(q)$. It is clear from these figures that all $S(q)$'s with different sets of parameters have a single peak at q_{peak} and $S(q)$ is strongly dependent on all of these parameters, i.e., f, ϕ, and χ. $S(q)$ increases with decreasing f, with increasing ϕ, and with increasing χ. However, q_{peak} is dependent only on f but not on ϕ or χ. In Figure 1a, the f dependence of $S(q)$ is ascribed to the fact that a larger ionization leads to stabilization of concentration fluctuations by stronger osmotic pressure generated mainly by the counterions. This is why $S(q_{peak})$ decreases and q_{peak} moves to a high q region with increasing f. Compared to the f dependence, the interpretation of the ϕ dependence is rather simple. Due to an increase of scattering contrast by increasing concentration, $S(q)$ increases with

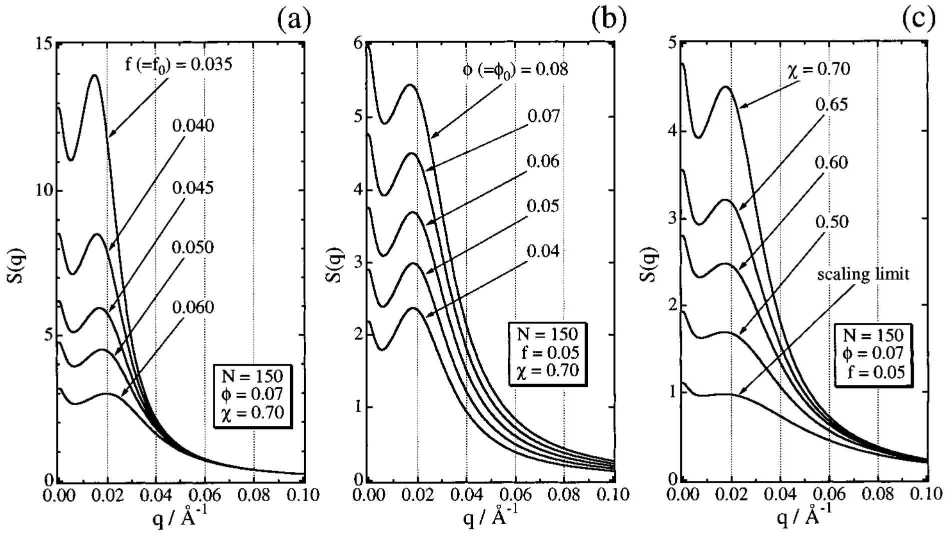

Figure 1. Calculated structure factor, $S(q)$, with the RP theory: (a) f dependence; (b) ϕ dependence; (c) χ dependence. The "scaling limit" in (c) indicates that $S(q)$ is calculated not with eq 5 but with eq 8.

ϕ, as shown in Figure 1b. Note that $q_{\rm peak}$ does not shift noticeably with ϕ. Figure 1c shows that χ is responsible for the shape of $S(q)$ by maintaining the position of $q_{\rm peak}$. The higher χ, the larger the concentration fluctuations, resulting in an increase of $S(q)$. It should be noted here that in the case of a good solvent regime, i.e., $\chi < 0.5$, $S(q)$ has to be calculated with the following equation

$$w(q) = \phi^{5/4}N + \frac{l_{\rm B}f^2\phi^{5/4}N^2}{Q^2 + l_{\rm B}(f + 2\hat{c}_{\rm s})\phi^{5/4}N} \quad \text{(scaling limit)} \tag{8}$$

instead of eq 5, which is given by assuming the scaling limit for a good solvent system. Surprisingly, $S(q)$ has a scattering maximum even in the good solvent regime, as shown in Figure 1c. This is one of the unique features of the RP theory. However, as will be discussed later, this is one of the disagreements between the theoretical prediction and experimental observation since no scattering maximum is observed in the scattered intensity, $I(q)$, for gels in a good solvent. Anyway, by summarizing the parameter dependence of $S(q)$, it is concluded that f is the most important parameter to determine $q_{\rm peak}$.

2. Inversion in the CD Dependence of *I*(*q*). Figure 2 shows scattering functions at various temperatures for NIPA/AAc (668 mM/32 mM) gel with $C_{\rm BIS}$ = 8 mM (CD = 1.1 mol %). The $I(q)$ increases dramatically with increasing temperature from 33 to 51 °C, particularly above 39 °C. The scattering maximum around q = 0.02 Å^{-1} appears at temperatures higher than 42 °C. It has already been discussed that this peak results from a microphase separation due to competition between hydrophobic (shrinking) and electrostatic (or Donnan potential) (swelling) interactions.[24-26] It should be noted here that the peak position of $I(q)$, i.e., $q_{\rm peak}$, in this work is noticeably larger than those in ref 25. This is due to the difference of the sample preparation, i.e., reactor-batch gels (this work) and rinsed gels (ref 25). Since the effect of the residue in the reactor batch is discussed in ref 25, we do not repeat it here.

Figure 3 shows $C_{\rm BIS}$ dependence of $I(q)$'s at various temperatures for the gels of NIPA/AAc (636 mM/64 mM). In these figures, the solid lines indicate the theoretical curves calculated with the RP theory. It should be noted that all of the gels are in swollen state at these temperatures.[27] Therefore, the appearance of the peak or the change of $I(q)$ does not come from a disturbance from gel shrinking. Let us focus on the CD dependence of $I(q)$, and then we will discuss the fitting parameters in the next section. Roughly speaking, $I(q)$'s at 39 °C are in the systematic order with respect to $C_{\rm BIS}$ except for $C_{\rm BIS} \leq 4$ mM; i.e., the higher $C_{\rm BIS}$, the larger $I(q)$. On the other hand, at T = 48°C, $I(q)$ decreases with increasing $C_{\rm BIS}$ for $0 < q \leq 0.03$ Å^{-1}. A similar phenomenon is observed more clearly in NIPA/AAc (668 mM/32 mM) as shown in Figure 4. Though $I(q)$ of the gel with $C_{\rm BIS}$ = 24 mM is the highest at 39 °C, that with $C_{\rm BIS}$ = 2 mM becomes highest for $T \geq 42$ °C. At these temperatures, $I(q)$ decreases with CD. Though the order of $I(q)$'s at $C_{\rm BIS}$ = 0 and 2 mM does not obey this rule, it might be within an experimental error.

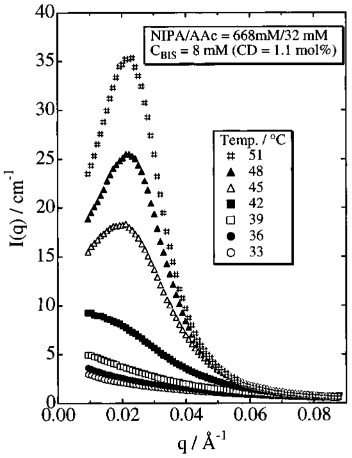

Figure 2. Temperature dependence of the scattering intensity, $I(q)$, for NIPA/AAc (668 mM/32 mM) with $C_{\rm BIS}$ = 8 mM.

Figure 5 shows the $C_{\rm BIS}$ dependence of $I(q)$ at q = 0.02 Å^{-1} for (a) NIPA/AAc = 636 mM/64 mM and (b) NIPA/AAc = 668 mM/32 mM. In the case of (a), I(q = 0.02 Å^{-1}) at low temperatures (i.e., 39, 42, and 45 °C) increases with $C_{\rm BIS}$. However, $I(q = 0.02$ Å$^{-1})$ decreases with $C_{\rm BIS}$ when T is raised to 48 °C and above it. For T = 54 °C, $I(q = 0.02$ Å$^{-1})$ increases again with $C_{\rm BIS}$. This

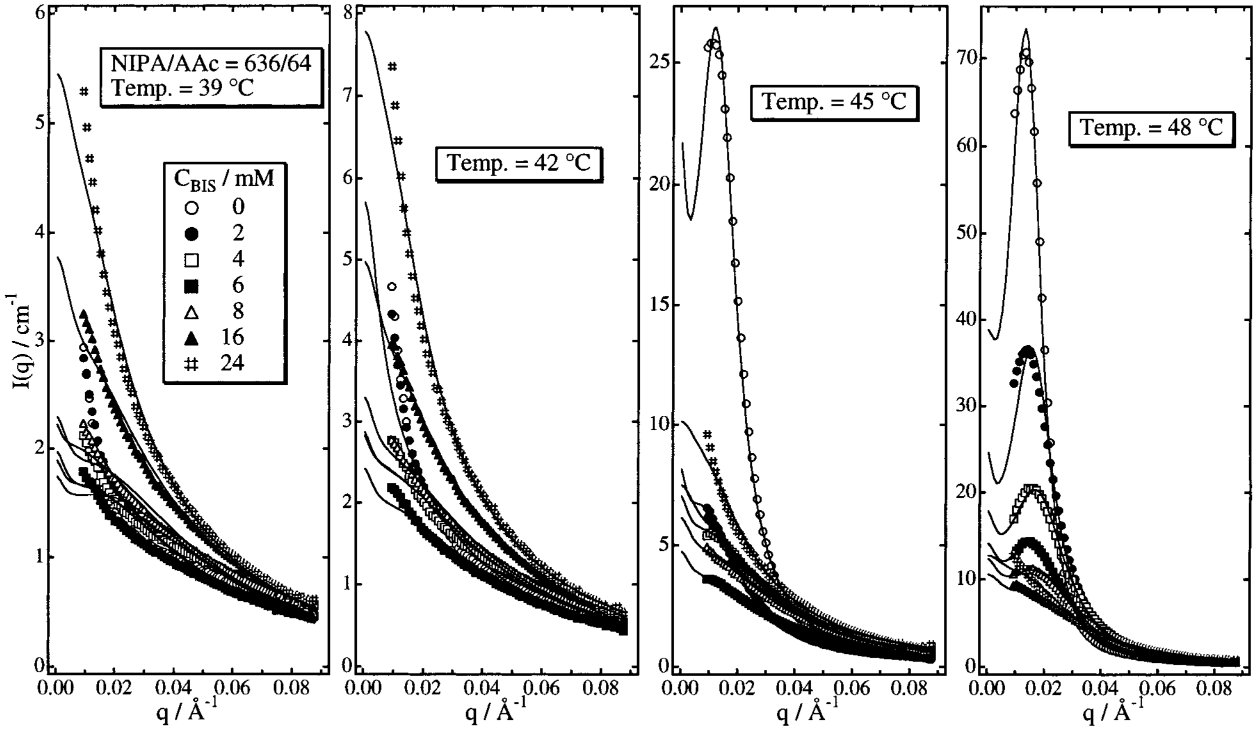

Figure 3. C_{BIS} dependence of $I(q)$ at various temperatures for NIPA/AAc (636 mM/64 mM) gels. The solid lines indicate the RP theoretical fitting results.

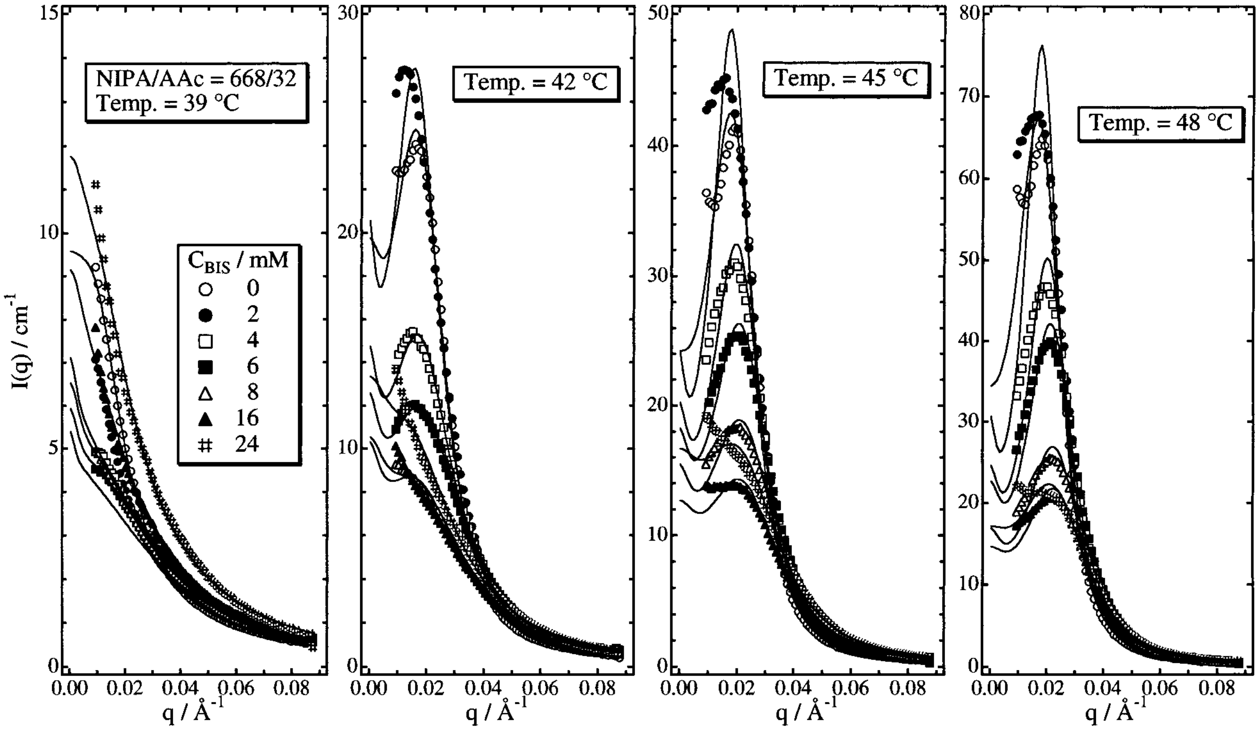

Figure 4. C_{BIS} dependence of $I(q)$ at various temperatures for NIPA/AAc (668 mM/32 mM) gels. The solid lines indicate the RP theoretical fitting results.

phenomenon is also in good agreement with the results obtained by LS experiment (see Figure 6 of ref 16). The theory also predicts an upturn of $I(q)$ with C_{BIS} at higher temperatures. Therefore, Figure 5a clearly shows the presence of an inversion of the C_{BIS} dependence of $I(q)$ although the examination of the inversion is limited to one particular value of q. In Figure 5b the inversion is more clearly seen and the characteristic temperature at which the inversion occurs lies between 39 and 42 °C. Therefore, the inversion is observed in both gels having different degrees of ionization.

In our previous paper, we observed that the inversion is very sensitive to the degree of ionization, f, the network volume fraction, ϕ, and temperature. The temperature at which an inversion takes place was in good agreement at least qualitatively with the theoreti-

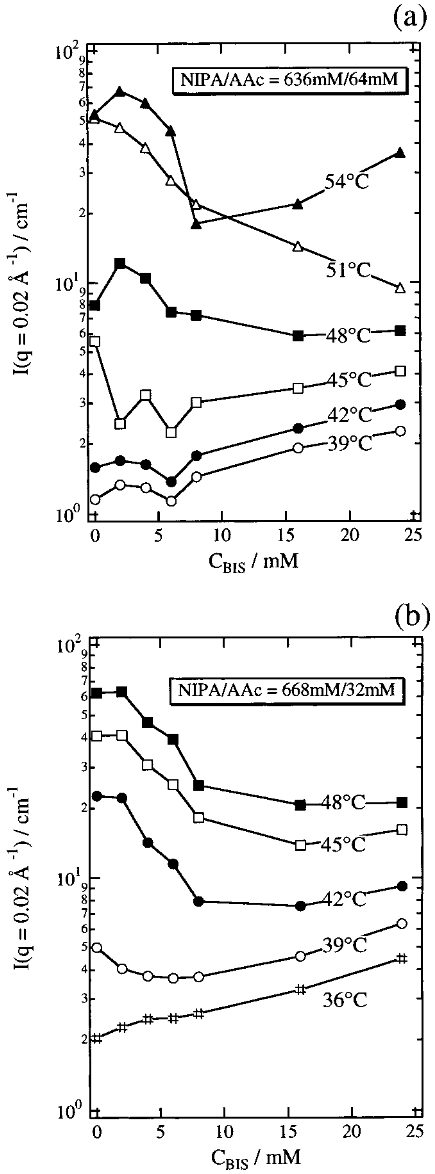

Figure 5. C_{BIS} dependence of I(q = 0.02 Å^{-1}) at various temperatures for (a) NIPA/AAc (636 mM/64 mM) and (b) NIPA/AAc (668 mM/32 mM). Lines are drawn for the eye.

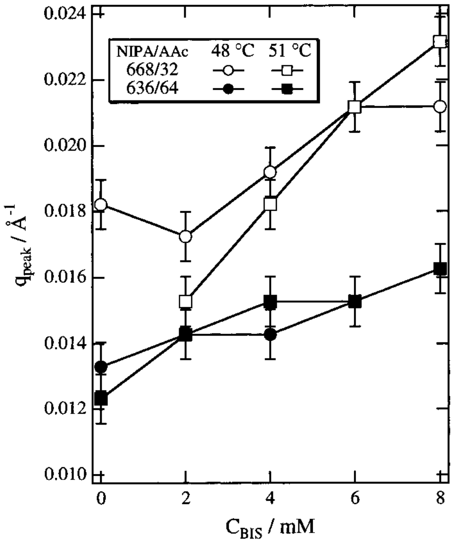

Figure 6. Cross-linker concentration, C_{BIS}, dependence of the peak position of $I(q)$.

cal prediction of the interaction parameter at inversion, χ_c,[16]

$$\chi_c = \frac{1}{2}\left(\phi + 1 + \frac{f}{\phi}\right) \tag{9}$$

Figure 6 shows the C_{BIS} dependence of the peak position at 48 and 51 °C. The peak position, q_{peak}, increases with C_{BIS}. This means that the characteristic size of concentration fluctuations, D $(=2\pi/q_{\mathrm{peak}})$, decreases with increasing CD. This tendency may be reasonable since cross-links suppress the spatial inhomogeneities owing to the charges on the network chain. On the other hand, q_{peak} does not seem to depend on temperature in this temperature range for both gels although $I(q_{\mathrm{peak}})$ changes significantly. This is in good accordance with the theoretical prediction (see Figure 1c). Regarding f dependence, it is found that a strong composition dependence of q_{peak} is observed; i.e., the higher the ionization (636/64), the smaller q_{peak}. This result is contrary to our previous result[25] and theoretical prediction (Figure 1a). This unexpected result will be discussed in the following part.

3. Fitting of SANS Intensity Functions. As shown in Figures 3 and 4, the SANS curve fitting with the RP theory is more or less satisfactory. The fitting was carried out by three-floating-parameter fitting with eq 1. The three parameters were (1) the intensity-scaling constant, (2) the degree of ionization on the network, f $(=f_0)$, and (3) the Flory interaction parameter, χ. For the fitting process, the average degree of polymerization between cross-linking points, N, was fixed to be a stoichiometrical value, i.e., $C_{\mathrm{NIPA}}/C_{\mathrm{BIS}}$, where C_{NIPA} is the concentration of NIPA monomers in the reaction batch. In the case of C_{BIS} = 0 mM, however, we conducted a four-parameter-fitting by floating N since the stoichiometrical value becomes undeterminant. It should be noted here that the quality of fitting became better by taking account of the temperature dependence of the Bjerrum length (eq 7).

Parts a and b of Figure 7 show C_{BIS} dependence of the fitted χ parameters for NIPA/AAc (636 mM/64 mM) and NIPA/AAc (668 mM/32 mM), respectively. It seems to be common that the fitted χ parameter increases with temperature. However, the C_{BIS} dependence of χ is quite interesting. In Figure 7a, the fitted χ values are independent of C_{BIS} at low temperatures (i.e., 39 and 42 °C). Though the χ value is expected to be slightly lower than 0.5 at these temperatures, the fitted values are much lower. This result must be ascribed to an employment of eq 5 for the curve fitting. As shown in Figure 1c, $S(q)$ has a scattering maximum even for $\chi < 0.5$ (the scaling regime). On the other hand, such a scattering maximum is never observed in SANS intensity functions for weakly charged gels in the good solvent regime. Therefore, in the curve-fitting process, the theory requires an unrealistically small value of χ in order to fit the experimental curve. As a matter of fact, the RP theory does not provide any specific value of χ for $\chi < 0.5$ (see eq 8). Therefore, these numbers are due to an artifact of curve fitting by using eq 5. Contrary to this, an interesting behavior of χ appears at temperatures higher than 45 °C. The value of χ decreases with increasing C_{BIS} at 45 and 48°C. On the other hand, at $T > 51$ °C, χ becomes almost constant or slightly increases with C_{BIS} in a wide range of C_{BIS}. By

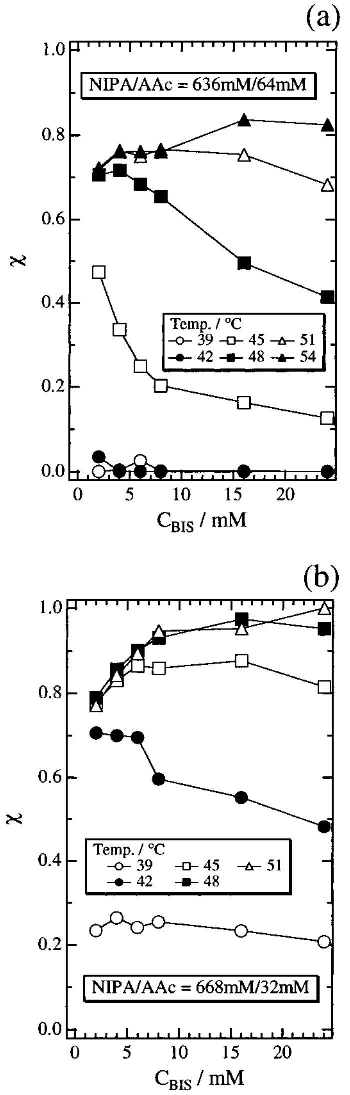

Figure 7. C_{BIS} dependence of χ parameter: (a) NIPA/AAc (636 mM/64 mM) gels; (b) NIPA/AAc (668 mM/32 mM) gels. Lines are drawn for the eye.

comparison of Figure 3 with Figure 7a, the following fact can be drawn: The temperature (45 °C) at which the inversion of the C_{BIS} dependence of $I(q)$ in Figure 3 starts to occur corresponds to that where the negative dependence of χ on C_{BIS} appears in Figure 7a. Though the estimation of values of χ by the curve fitting with the RP theory is still an open question, the change of the C_{BIS} dependence of χ with temperature seems to correlate with that of $I(q)$. Figure 7b shows almost the same story as (a). However, it should be noted that, in the case of NIPA/AAc (668 mM/32 mM), the inversion of CD dependence takes place at a lower temperature (42 °C) because the degree of ionization is lower than that of NIPA/AAc = 636 mM/64 mM.

Parts a and b of Figure 8 show the C_{BIS} dependence of the fitted values of f ($=f_0$). The dashed lines in the figures denote the f value in the case of perfect dissociation of AAc comonomers. This figure discloses three interesting features, although we expected an invariance of f with respect to temperature and C_{BIS}: (1) The fitted f increases with temperature at the same C_{BIS}. (2) The fitted f increases with C_{BIS} for a given temperature. (3) The fitted f is underestimated in the case of NIPA/AAc (636 mM/64 mM) and overestimated for NIPA/AAc (668 mM/32 mM). Since f affects the position of q_{peak} most sensitively, as already demonstrated in Figure 1a, the variation of fitted f with respect to C_{BIS} as well as temperature is due to the shift of q_{peak} in the observed $I(q)$'s. However, the variation of the fitted f with C_{BIS} and temperature is more complicated than expected. A plausible answer has not been given so far.

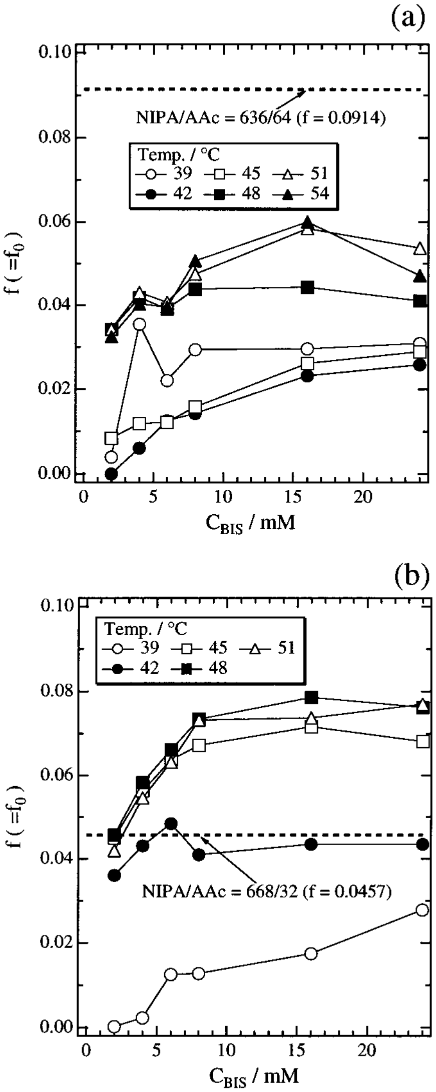

Figure 8. C_{BIS} dependence of the degree of ionization, f: (a) NIPA/AAc (636 mM/64 mM) gels; (b) NIPA/AAc (668 mM/32 mM) gels. The dashed lines in the figures denote the f value in the case of perfect dissociation of AAc comonomers. Lines are drawn for the eye.

4. Possible Explanation of the Unexpected *f* Dependence of *I*(*q*). Figure 1 predicts that q_{peak} moves to a larger value of q with increasing f. In reality, however, such behavior was not observed by the experiment, as shown in Figure 6. This difference possibly comes from the existence of the residue, such as the copolymerization initiator or accelerator, in the case of this experiment. In the previous paper,[22] we studied the pH and salt concentration dependence of the microstructure of NIPA/AAc gels and found that q_{peak} decreases with increasing pH. It is deduced that AAc monomers are fully ionized for pH > 7 and a microphase separation is less favorable. Because of strong osmotic pressure, the concentration fluctuations are suppressed. On the other hand, in the case where f is quite low for pH < 5, a microphase separation is easy to establish. That is, q_{peak} for pH < 5 is smaller than that for pH >

7. Now, in the reactor batch, both the accelerator (TEMED; base) and initiator (ammonium persulfate; acid) are still present as residue in addition to the acidity of AAc itself. Therefore, it can be deduced that the pH of the gel with NIPA/AAc (668 mM/32 mM) is even higher than that with NIPA/AAc = 636 mM/64 mM and both have a significant salt concentration. This is probably why q_{peak} of the latter is empirically lower than that of the former as compared with the theoretical prediction.

It might be ideal to conduct this type of experiment with fully rinsed gels. However, it is impossible to remove these residues and even a tiny amount of residue affects considerably the phase behavior and $I(q)$ in the case of charged gels. In addition, the previous LS studies were conducted on unrinsed gels. Therefore, it was necessary to use unrinsed gels in order to compare the LS and SANS results. This is why we employed the reactor-batch gels (i.e., unrinsed gels) in this study.

By comparison of the theoretical prediction with the experimental results, the following facts are disclosed: First, an inversion of $S(q)$ in the C_{BIS} dependence is observed by SANS as well as by light scattering. At low temperatures, $S(q)$ increases with C_{BIS} but decreases with C_{BIS} at high temperatures. The low-temperature behavior is explained by an introduction of frozen inhomogeneities via cross-link formation. On the other hand, the high-temperature behavior is interpreted as suppression of microphase separation via a pinning effect of the cross-links. Second, curve fitting of $I(q)$ with the theory is satisfactory at high temperatures as compared to that at low temperatures. The Rabin−Panyukov theory is derived by assuming a Gaussian network with excluded volume. However, in the good solvent regime, the Coulombic interaction is so strong that it breaks down the assumption of a mean field type calculation. This is why the theory works better in the poor solvent regime. Thus, the parameters evaluated by the curve fitting may be meaningful exclusively for those obtained in the poor solvent regime.

In this paper, we demonstrated that the presence of the inversion can be detected by SANS. Combination of this finding with those reported previously, it is now clear that the inversion can be detected in a wide range of the q space. In fact, we have recently obtained the interesting result about f dependence of the scattering intensity by light scattering.

Conclusion

The cross-linking density (CD) dependence of the spatial inhomogeneities for a weakly charged polymer gel has been investigated by means of small-angle neutron scattering (SANS). The SANS intensity, $I(q)$, showed the inversion of CD dependence. $I(q)$ increases with CD at low temperature (in a good solvent) and decreases with CD at high temperatures (in a poor solvent). This behavior is due to the competition between two effects of cross-linking; the introduction of inhomogeneities and suppression of the inhomogenizing move of polymer chains. SANS profiles were successfully fitted with the equation proposed by Rabin and Panyukov by floating the fitted parameters, f and χ. However, it is also clarified that a further justification and/or refinement of theoretical treatment may be necessary so as to obtain a better agreement between the theoretical prediction of $S(q)$ and the observed $I(q)$.

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