

Anomalous cross-link density dependence of scattering from charged gels

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A light scattering experiment has been carried out to investigate the effect of the spatial inhomogeneity of a weakly charged gel as a function of cross-link density. It has been observed that an anomalous cross-link density dependence of the scattering light intensity occurs when the temperature is varied. While in the good solvent (soluble) regime the gel becomes more inhomogeneous with increasing cross-link density, in the poor solvent (insoluble) regime the inhomogeneity decreases with the degree of cross linking. The latter effect is the signature of microphase separation in charged gels in poor solvent, recently analyzed by Rabin and Panyukov. [S1063-651X(97)50807-5]

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A gel is a three-dimensional “network” comprising long chain molecules lightly cross-linked each other and a large amount of solvent [1,2]. The network implies that the structure of gel is topologically frozen. Because of the network structure, a gel is a self-sustainable matter with a finite shear modulus [3]. The topological constraint leads to the presence of nontrivial spatial inhomogeneity of the cross-link density on length scales typically of the order of a few hundred angstroms. This inhomogeneity gives rise to excess scattering from gels, the origin of which has been debated for more than two decades [4–7]. One way to estimate the spatial inhomogeneity is to measure scattering intensity $I(q)$, where q is the scattering vector. The long-wavelength limit of $I(q)$, i.e., $I(q \rightarrow 0)$, is related to the longitudinal modulus M as [2]

$$M = \frac{(\Delta b)^2 k_B T}{I(q \rightarrow 0)} \phi^2, \quad (1)$$

where Δb is the contrast factor [e.g., for the case of neutron scattering the difference in the scattering lengths of the solute (network) and the solvent], $k_B T$ is the thermal energy, ϕ is the volume fraction of the solute. For polymer gels, M can be expressed as $M = K + 4\mu/3$ [3], where K and μ are the osmotic bulk and shear moduli, respectively. Since μ is positive, it can be shown that the longitudinal modulus of gels is always larger than that of polymer solutions [8], resulting in $I(0)_{\text{gel}} < I(0)_{\text{soln}}$. However, experimentally it is observed that $I(q)_{\text{gel}}$ is larger than $I(q)_{\text{soln}}$ irrespective of q [2,7,9]. In order to account for this contradiction, a number of theories or models have been proposed, such as those by Panyukov and Rabin [10], Horkay and co-workers [11], Bastide *et al.* [6], and Onuki [12]. The consensus is that inhomogeneity of gels is created by the random introduction of cross links. For gels studied in the reaction bath in good solvent this inhomogeneity is masked by the excluded volume repulsion, which tends to swell the strongly cross-linked regions and homogenize the density of the gel. The inhomogeneity can be revealed by swelling or stretching the network, or by reducing the quality of solvent, all of which lead to separation

into polymer-rich regions and polymer-poor regions, with high and low cross-link density, respectively. It has been generally accepted that the spatial inhomogeneity in gels increases with increasing cross-link densities [7,9,13].

We report here that the gel inhomogeneity can decrease with increasing cross-link densities by choosing the conditions of gel preparation and measurement. We employ here the ensemble-averaged scattering intensity $\langle I \rangle_E$ as a measure of the gel inhomogeneity. Since gels have nonergodic nature, the scattering intensity at a given angle varies with position and is different from the time-averaged scattering intensity [14]. The usefulness of $\langle I \rangle_E$ to characterize the gel inhomogeneity was demonstrated by Rouf *et al.* [15] in the discussion of butterfly-like scattering patterns observed in deformed gels by small-angle neutron scattering. In this paper, we demonstrate that an anomalous cross-link density dependence of the scattering intensity, i.e., an opposite cross-link density dependence of $\langle I \rangle_E$, takes place for weakly charged gels and we discuss its physical meaning in comparison with the Rabin-Panyukov theory for the structure factor of weakly charged gels [16].

A series of poly(*N*-isopropylacrylamide-co-acrylic acid) (NIPA:AAc) gels were prepared by redox polymerization. 3.397 g of NIPA, 0.104 g of AAc, and 20 mg of ammonium persulfate were dissolved in 45 ml of deionized water. Then the solution was divided to 9 vessels in equal portions and the prescribed amounts of *N,N'*-methylenebisacrylamide (BIS) were added to each vessel, followed by filtration, degassing, and cooling in a refrigerator for about 15 min before polymerization and cross-linking reaction were initiated. The reaction was triggered by adding 24 μl of *N,N,N',N'*-tetramethylethylenediamine (accelerator) in 10-mm-diameter test tubes at 20 °C. The concentrations of BIS, C_{BIS} (cross linker), were chosen to be 0, 2, 4, 6, 8, 12, 16, 20, and 24 mM. A stoichiometric reaction was assumed. Thus, a series of weakly charged gels of NIPA:AAc (=668 mM:32 mM) having a series of cross-link densities were prepared. These reactor-batch samples were used for light scattering experiments without further treatment.

Light scattering experiments were carried out on a laboratory-made optics, which has a 10 mW He-Ne laser, a thermostatted silicon oil bath, and a photon correlator, DLS-7, Otsuka Electric., Co. Scattering intensities at arbi-

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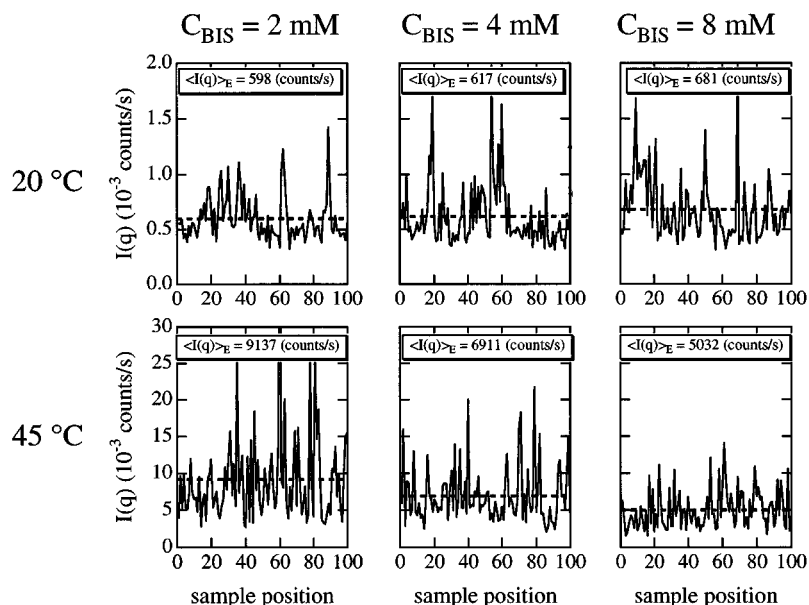


FIG. 1. Speckle patterns of gels with different cross-linker concentrations, C_{BIS} 's at (a) 20 °C (upper) and at (b) 45 °C (lower). The horizontal dashed line indicates the ensemble average of the scattering intensity $\langle I \rangle_E$.

trary positions in a gel were observed at the scattering angle of 60°, i.e., at the magnitude of the scattering vector $q = 9.93 \times 10^{-4} \text{ \AA}^{-1}$. Then, the ensemble-averaged scattering intensity $\langle I \rangle_E$ was obtained by averaging the scattering intensity observed at 100 different positions. The irradiated volume is estimated to be less than 400^3 \mu m^3 . The temperature of samples was regulated within an error of 0.1 °C. Whenever the temperature was changed, one day was allowed for gel equilibration. Although 24 h might be not enough for the gel to reach equilibrium, we adopted this procedure because $\langle I(q) \rangle_E$'s obtained after 24 and 48 h were found to be nearly identical.

The upper part of Fig. 1 shows speckle patterns of NIPA:Aac gels at 20 °C for (a) $C_{\text{BIS}}=2 \text{ mM}$, (b) $C_{\text{BIS}}=4 \text{ mM}$, and (c) $C_{\text{BIS}}=8 \text{ mM}$. The scattering intensity at each position p at time t consists of static and dynamic fluctuations, which is symbolically given by

$$I(p, t) = I_C(p) + I_F(t), \quad (2)$$

where $I_C(p)$ and $I_F(t)$ are the intensity components of the static inhomogeneity and dynamic fluctuations. The dashed line indicates the ensemble average $\langle I \rangle_E$, which is obtained by

$$\langle I \rangle_E \equiv \langle I(p, t) \rangle_E = \langle I_C(p) \rangle_E + \langle I_F(t) \rangle_T, \quad (3)$$

where $\langle \rangle_T$ indicates the time average; note that $\langle I_F(t) \rangle_E = \langle I_F(t) \rangle_T$ because of the ergodic nature of the time-fluctuating component. The upper part of Fig. 1 shows that $\langle I \rangle_E$ increases with cross-link densities. However, as shown in the lower part of Fig. 1, the average of intensity speckle patterns of the same series of gels decrease with C_{BIS} when observed at 45 °C. This phenomenon is quite unusual since it has been believed that spatial inhomogeneities increase with increasing cross-link densities. Note that $\langle I \rangle_E$ of NIPA:Aac gels increases with temperature because NIPA gels have a hydrophobic nature [17]. NIPA homopolymer gels shrink at about 33 °C (close to the so-called Θ temperature), and the

NIPA:Aac gel undergoes a discrete shrinking transition at around 50 °C [17]. Thus, both I_C and I_F increases with temperature.

Figure 2 shows the plots of $\langle I \rangle_E$ at various temperatures as a function of the degree of polymerization between cross-links N . Note that N is inversely proportional to the cross-link density. The value of N was estimated by stoichiometry. The upturn at low N means that the gel inhomogeneity becomes larger due to an increase of hydrophobic moiety around the cross links. As a matter of fact, gels became opaque for $N < 20$. Below 40 °C, $\langle I \rangle_E$ is a decreasing function of N . This is what is expected. However, above 40 °C, there appears a region where $\langle I \rangle_E$ increases with N . Note that in this region an opposite N dependence of $\langle I \rangle_E$ appears at temperatures above Θ .

Although most of the theories dealing with the structure factor of gels do not predict such an anomaly, i.e., the opposite dependence of the scattering intensity on cross-link densities, the theory recently proposed by Rabin and Panyukov [16] (RP) seems to be able to account for the anomaly. The

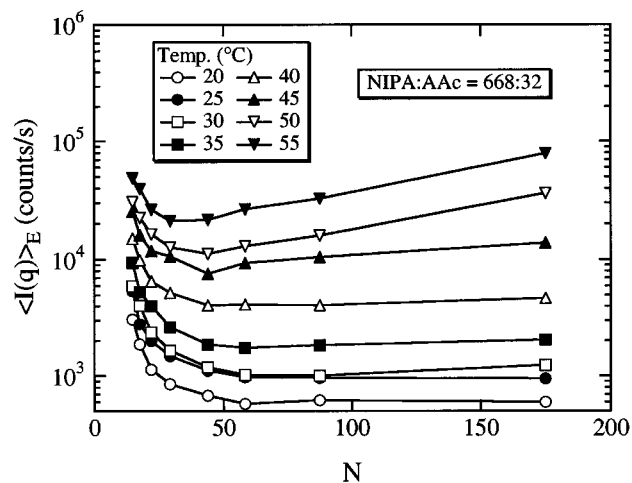


FIG. 2. Dependence of $\langle I \rangle_E$ on the degree of polymerization between cross-link N for gels at various temperatures.

RP theory deals with instantaneously cross-linked networks of Gaussian phantom chains with excluded volume. In this theory, the structure factor $S(q)$ consists of the correlator of thermal fluctuations, G_q , and the part of static density inhomogeneities, C_q . It is given by

$$S(q) = G_q + C_q, \quad (4)$$

$$G_q = \frac{a^{-3} \phi N g_q}{1 + w_q g_q}, \quad (5)$$

$$C_q = \frac{a^{-3} \phi N}{(1 + w_q g_q)^2 (1 + Q^2)^2} \times \left[6 + \frac{9}{w_s - 1 + (1/2) Q^2 (\phi_0 / \phi)^{2/3} \phi_0^{-1/4}} \right], \quad (6)$$

where a and N denote the segment length and the average degree of polymerization between cross links, respectively. ϕ_0 and ϕ are the volume fractions of polymer networks at preparation and at measurement, respectively, and Q is the dimensionless wave vector defined by $Q \equiv a N^{1/2} q$, where q is the scattering vector. The function g_q is given as follows:

$$g_q = \frac{1}{Q^2/2(4 + Q^2)^{-1} + 1} + \frac{2(\phi/\phi_0)^{2/3} \phi_0^{1/4}}{(1 + Q^2)^2}. \quad (7)$$

The parameters w_q and w_s are dimensionless interaction parameters in the final state (which is assumed to be in the Θ or poor solvent) and in the state of preparation (in a good solvent), respectively, and are expressed by

$$w_q = (1 - 2\chi + \phi) \phi N + \frac{1_B f^2 \phi N^2}{Q^2 + 1_B f \phi N}, \quad (8)$$

$$w_s = \phi_0^{5/4} N + \frac{1_B f_0^2 \phi_0^{5/4} N^2}{Q^2 (\phi_0 / \phi)^{2/3} + 1_B f_0 \phi_0^{5/4} N}, \quad (9)$$

where χ and 1_B are the Flory's interaction and a dimensionless Bjerrum length, respectively. f_0 and f denote the degree of ionization at preparation and at measurement, respectively. Since the details of the behavior of Eqs. (4)–(8) are described elsewhere [16,18] we focus here on the possible anomaly in $S(q)$ with respect with N .

Figure 3 shows the calculated structure factor $S(q)$, Eq. (4), for various values of N with $\phi = \phi_0 = 0.07$, $f = f_0 = 0.0457$, and (a) $\chi = 0.70$ or (b) $\chi = 0.83$. The values of f_0 and ϕ_0 are chosen in order to match the experimental condition and the choice $\phi = \phi_0$ and $f = f_0$ indicates that the gels studied are so-called reactor batch gels. The choice of parameters in Fig. 3(a) corresponds to the effective good solvent case, where electrostatic effects (Coulomb repulsion and counterion entropy) overcome the intermonomer attraction due to hydrophobic interactions. In the case, the scattering is dominated by static inhomogeneities produced by the random process of cross linking and the maximum occurs at $q = 0$ (the electrostatic contribution is suppressed at higher q , giving rise to the secondary peaks). When the quality of solvent is reduced, one arrives at the effective poor solvent regime and microphase separation takes place at a finite value of q . In this region, the opposite N dependence appears

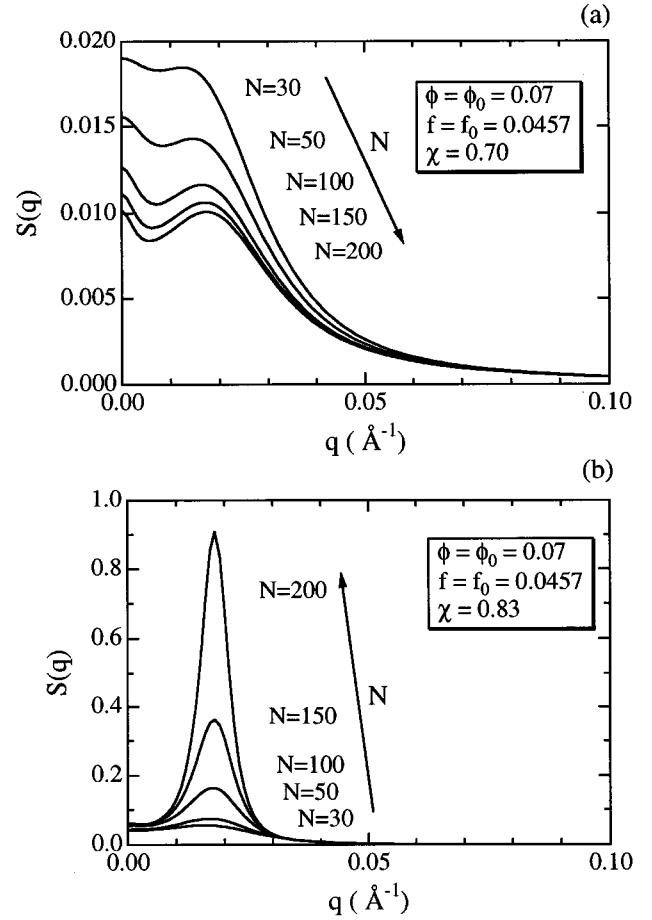


FIG. 3. Theoretical static structure factor $S(q)$ for gels having different N 's. Note that the N dependence of $S(q)$ changes by a slight modification of χ , i.e., from (a) 0.70 to (b) 0.83.

[Fig. 3(b)]. It can be seen that the opposite N dependence of $S(q)$ occurs in a wide range of q including $q = 0$.

Figure 4 shows the variation of $S(q)$ at $q = 0.001 \text{ \AA}^{-1}$ as a function of N for various values of χ . The q value is chosen to be close enough to that of speckle observation ($q = 9.93 \times 10^{-4} \text{ \AA}^{-1}$). Though the scales of $S(q)$ and

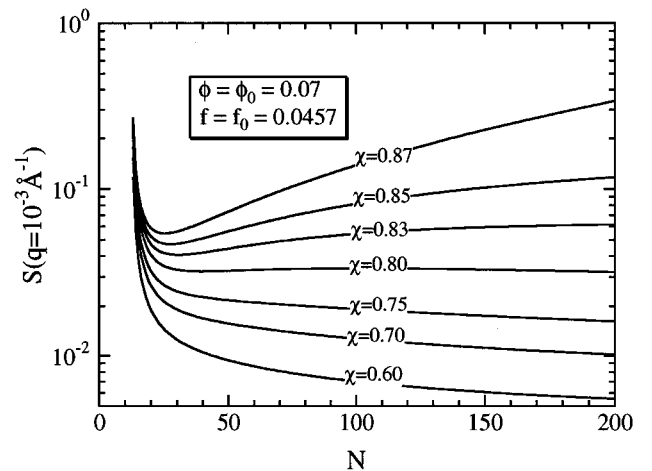


FIG. 4. The variation of $S(q)$ at $q = 0.001 \text{ \AA}^{-1}$ with various χ 's.

$\langle I \rangle_E$ are different, the N dependence of $\langle I \rangle_E$ is successfully reproduced by choosing appropriate values of χ . The critical χ ($=\chi_c$) where the anomaly occurs is determined to be $\chi_c \cong 0.80$ in this case.

Now we discuss the physical meaning of the anomalous N dependence of $\langle I \rangle_E$ observed in the weakly charged gels. It can be considered that, in charged gels, there are three competitive effects, namely, (i) the repulsion due to the excluded volume effect and/or the electrostatic interaction among ionized groups on the polymer chains, (ii) the hydrophobic attraction among hydrophobic groups on the chains, and (iii) the attraction between the charged chains and their counterions and the counterion entropy. The latter factors tend to suppress macrophase separation in charged gels in good solvents, which would lead to localization of counterions in only a part of the total volume of the gel, and result in microphase separation [16,18]. The N dependence of $S(q)$ is determined by a competition of these interactions. The difference of the N dependence of $S(q)$ will be explained as follows: the increase of the number of cross-link points in the gel leads to a formation of two kinds of regions with higher and lower cross-link densities. At the value of χ ($<\chi_c$), the repulsive interaction is more dominant than the attractive one. Since an initial gel was prepared at $\chi < \chi_c$, the polymer chains themselves intend to remain in an expanded state. The polymer chain conformation in the gel may be disturbed only by the nonuniform distribution of cross-link points. We can easily guess that the more cross-link points are introduced, the more inhomogeneous the gel becomes. Such a phenomenon is normally observed in uncharged gels by small-angle x-ray scattering [9] and by dynamic light scattering [13]. On the other hand, when one brings the gel prepared at $\chi < \chi_c$ to the region with $\chi > \chi_c$, the repulsive interaction due to the ionized groups and the attractive interaction due to the hydrophobic groups must coexist in the gel. In a polyelectrolyte solution in a poor solvent, this would result in microphase separation and the appearance of a long-wavelength density variation on a characteristic length scale determined by the interplay between

hydrophobic and electrostatic effects [19]. In a gel, the appearance of such inhomogeneities is affected by the presence of cross links, which suppress density variations on a length scale larger than the average size of the network chain and therefore one expects that the gel should become more homogeneous with decreasing N .

We would like to emphasize that the gels studied here are prepared from monomers. Therefore, the cross-link inhomogeneity can be created during polymerization and cross linking. This preparation is different from the gels discussed by Bastide and Leibler [6], i.e., instantaneously cross-linked networks. This is why the NIPA:AAc gels have an inherent spatial inhomogeneity even in a reactor-batch state. However, the interesting finding here is that the degree of spatial inhomogeneities can be either enhanced or suppressed when viewed as a function of N depending on temperatures. The following should be noted here. The difference in the gel preparation methods between the experiment (NIPA:AAc gels) and the RP theory (instantaneous cross linking of polymer solutions) is not essential in discussing the anomaly, since the inherent inhomogeneity simply behaves as an offset. The anomalous N dependence of $S(q)$ at finite q (seen in Fig. 3) is exclusively observed in a weakly charged gel in a poor solvent. A further justification of the presence of this anomaly will be made in the forthcoming paper [18].

In conclusion, the spatial inhomogeneity of gels was studied with the light scattering technique. As a measure of the spatial inhomogeneity, the ensemble-averaged intensity was studied as a function of the cross-link density and temperature. The existence of the region where the spatial inhomogeneity decreases with increasing cross-link densities was found, as predicted by the RP theory for weakly charged gels.

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