polymer

Small angle neutron scattering studies on structural inhomogeneities in polymer gels: irradiation cross-linked gels vs chemically cross-linked gels

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Abstract

A comparison of network structure in a solvent was made for two types of poly(N-isopropylacrylamide) gels cross-linked by chemical reaction with N,N'-methylenebisacrylamide (BIS) (chemical gels) and by γ-ray irradiation (γ-ray gels). The cross-linking density dependence for these gels was examined by small angle neutron scattering (SANS). The SANS results indicated an increase of frozen inhomogeneities with an introduction of cross-links for both chemical and γ-ray gels. However, it was found that the effect of cross-linking is much stronger in the chemical gels than in the γ-ray gels. The differences in the structure were successfully interpreted by a statistical-mechanical theory of gels proposed by Panyukov–Rabin (Phys. Rep. 269 (1996) 1). The degree of polymerization between cross-links, N, was a decreasing function of cross-linking content for both types of gels, while that for the γ-ray gels was a weak function of irradiation dose. Quantitative analyses on BIS concentration and γ-ray dose dependence led to an experimental evidence of the existence of cross-linking saturation threshold. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

A polymer gel is a three-dimensional network consisting of long chain molecules cross-linked to each other. It possesses both solid- and liquid-like properties [1–3]. It can be regarded as solid because of the presence of a finite elastic modulus and ability of shape retention. On the other hand, it exhibits similar phenomena to those of a semi-dilute polymer solution, such as cooperative diffusion. Gels may be indistinguishable with the corresponding polymer solutions on the scale at several nanometers. However, if we zoom out the view to the distance comparable to the inter-cross-link distance, we should observe the effects of cross-links playing an important role in the physical properties. It is easy to envisage that polymer chains are

instantaneously frozen at the gel point, leading to an emergence of non-cancelled-out concentration fluctuations, i.e. an appearance of inhomogeneous structures.

One of the interesting properties of polymer gels is that a gel can be a gigantic single molecule because of its network structure. It embodies monomer–solvent interaction as a volume change in a macroscopic scale. A typical example is a volume phase transition of poly(N-isopropylacrylamide) (PNIPA) gel in water [4–6]. A PNIPA gel is normally made by cross-linking with N,N'-methylene bisacrylamide (BIS). It undergoes a discrete swelling or shrinking transition by a change of temperature. In general, however, since a volume change of a gel is governed by diffusion of solvent molecule passing through the gel network, it normally takes hours to days for a centimeter-size gel to reach a swelling equilibrium. This is a major drawback for application to stimuli responsive polymer gels, such as sensor, actuators, and drug-delivery systems [1,7]. Kokufuta et al. recently

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reported that PNIPA gels cross-linked by γ-ray irradiation at 0 °C exhibit a rapid shrinking when the temperature was raised above the volume phase transition temperature [8]. According to our recent experiments, it was found that the deswelling kinetics of the γ-ray gels strongly depended both on gel preparation condition and cross-linking density [9]. For example, the γ-ray gels prepared at 20 °C exhibited the rapid shrinking below 3 Mrad. Although the relationship between the shrinking mechanism and microscopic structure of gels has not been fully elucidated yet, it is obvious that the difference in shrinking kinetics is related to the frozen inhomogeneous structures of gels originated by introduction of cross-links.

A pioneering work on the frozen inhomogeneities in gels was carried out by Candau et al. [10], who argued two significant contributions in scattered intensity, that is, contributions from thermal fluctuations and from built-in structural inhomogeneities introduced by cross-links. Later, the non-ergodic medium theory for glasses and gels proposed by Pusey and van Megen [11] has triggered an advancement of investigations on gel structures [12–19] by combining light scattering (LS) and small-angle neutron scattering (SANS) or small-angle X-ray scattering. Onuki [20] developed a theory to account for scattering functions of deformed gels by incorporating frozen inhomogeneities. Recently, Panyukov and Rabin proposed a more comprehensive theory (PR theory) [21,22] for polymer gels using a replica field theory. The theory assumed an instantaneous cross-linked network consisting of a single Gaussian chain with excluded volume effects by deeply taking into account the condition both at sample preparation and observation. The theory was then extended by Rabin and Panyukov [23] to describe weakly charged polymer gels. The validity of the theory was examined by Shibayama et al. for gels with various degrees of ionization [24] and for deformed gels [25]. In the case of the weakly charged gels, a scattering maximum was observed in the structure factor when the solvent became poor to the polymer. Although the emergence of such a scattering peak was successfully reproduced by the Rabin–Panyukov theory [23] any good accordance between experiment and the theory has not been achieved yet for neutral gels. In this paper, we revisit the original PR theory and apply a mean field approach to investigate the structure of neutral gels having different cross-linking histories.

Cross-links are expected to be introduced randomly in space for γ-ray cross-linked gels (hereafter we call γ-ray gels), whereas the distribution of cross-linking points for the chemically cross-linked gels (chemical gels) are more inhomogeneous due to difference in the reactivity ratios of monomers and cross-linkers [26,27] and the reaction itself is diffusion limited. Therefore, we conjectured that the γ-ray gels were more homogeneous from microscopic point of view than chemical gels prepared by conventional radical polymerization starting from monomers and cross-linkers.

In this study, we discuss the difference in the structure between the chemical gels and γ-ray gels by deeply taking into account the effect of structural inhomogeneities introduced in the networks.

2. Experimental section

PNIPA gels were employed as a model system to study the structure of gels because they are chemically stable at a temperature much lower than the volume phase transition temperature (≈ 33 °C) [28]. Two types of PNIPA gels were prepared in deuterated water by redox polymerization and by γ-ray irradiation for comparison of the network structures. The chemical gels having different cross-linking densities were synthesized at 20 °C, in the presence of N,N,N',N'-tetramethylethylenediamine (accelerator), BIS (cross-linker), and ammonium persulfate (APS; initiator). Molar concentration of BIS, C_{BIS}, was varied from 0 to 35 mM while that of NIPA, C_{NIPA} was kept to be 690 mM. NIPA monomer, supplied by Kohjin Chemical Co., was purified by recrystallization prior to use. Reagent grade BIS and APS were purchased from Wakenyaku Co. Ltd and were used without further purification. The details of sample preparation are described elsewhere [29].

PNIPA solutions without cross-linker were prepared by above method in advance to the γ-ray irradiation. Irradiation of γ-ray was carried out by using a ^{60}Co source, where the sample was regulated with a thermostat bath at 20 °C. The γ-ray gels having different cross-linking densities were obtained with different irradiation times, 0.5–16 h, at constant dose rate of about 1 Mrad/h. All the samples were transparent. The γ-ray gels with higher irradiation dose (i.e. 16 Mrad) exhibited volume shrinking after irradiation.

SANS experiments were carried out on the research reactor, SANS-U, at Institute for Solid State Physics, The University of Tokyo, located at Japan Atomic Energy Research Institute, Tokai, Japan. A flux of cold neutrons with a wavelength of 7.0 Å was irradiated to the sample, and the scattered intensity profile was collected with an area detector of 128×128 pixels. The sample-to-detector distance was set to be 4 m, which covered the accessible q range being $0.01–0.078$ Å^{-1}, where q is the scattering vector. The sample was placed in a brass chamber with quartz windows and the chamber was thermo-regulated within an error of ± 0.1 °C at the sample position with a NESLAB 110 water circulating bath. The sample thicknesses were in the range of 2.28 and 4.0 mm, depending on the samples. Scattered intensities were circularly averaged by taking into account the detector inhomogeneities, corrected for cell scattering, fast neutrons, transmission, and incoherent scattering, and then scaled to the absolute intensities with a polyethylene standard sample (Lupolen).

3. Theoretical background

3.1. Panyukov–Rabin theory

Here, we briefly summarize the Panyukov–Rabin (PR) theory [21,22]. The scattering function of a gel consists of a sum of two contributions, i.e. dynamic correlator, $G(q)$, and static correlator, $C(q)$. The former represents thermal concentration fluctuations of the corresponding polymer solution, while the latter is related to built-in inhomogeneities introduced by cross-links. Hence, the scattering function is written by

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

where q is the scattering vector. Experimentally, observed scattered intensity can be given by

$$I(q) = KS(q) \tag{2}$$

where K is the contrast factor and is defined by

$$K = \frac{N_A}{v_B}\left[b_A\left(\frac{v_B}{v_A}\right) - b_B \right]^2 \tag{3}$$

where N_A, b_i, and v_i are the Avogadro's number, the scattering length, and the molar volume of the component, i, respectively.

The PR theory assumes an instantaneously cross-linked single Gaussian chain. Here, the excluded volume effect is taken into account. The thermal correlator, $G(q)$ can be written by

$$G(q) = \frac{\phi N g(q)}{1 + wg(q)} \tag{4}$$

where $g(q)$, w, ϕ, and N are the thermal correlator in the absence of the excluded volume effect, the excluded volume parameter, the volume fraction of a gel and the degree of polymerization between cross-links, respectively. Here, we note that the factor of a^3, the segment volume, has been multiplied to the original equations of PR theory expressing $G(q)$ in order to define the dimensionless scattering function as described before [24]. w can be expressed as follows if one employs a mean field model

$$w = (1 - 2\chi + \phi)\phi N \qquad \text{(the mean field)} \tag{5}$$

where χ is the Flory's interaction parameter.

The most important feature of gels that differs from the corresponding polymer solutions may be a memory effect of the initial condition. Once a gel is formed, its structure is more or less fixed depending on the initial condition, resulting in an emergence of the frozen structure. Certainly, a new balance between mixing and elastic free energies is attained at the moment of cross-linking, but it varies according to the condition at observation. Thus, one should also take into account the parameters at the initial condition for the study of gels [30]. Hereafter, we express the parameters for the condition of sample preparation with subscript zero. Then, $g(q)$ is expressed by

$$g(q) = \frac{1}{Q^2/2 + (4Q^2)^{-1} + 1} + \frac{2}{(1 + Q^2)^2(\phi_0/\phi)^{2/3}} \tag{6}$$

where ϕ_0 and Q are the volume fraction at sample preparation and the reduced scattering vector, respectively. Q is defined by

$$Q = \left(\frac{1}{6}Na^2\right)^{1/2} q \tag{7}$$

where a is the segment length.

The static correlator, which corresponds to the contribution from the frozen structure of gels, is given by

$$C(q) = \frac{1}{[1 + wg(q)]^2(1 + Q^2)^2}\left[6\phi N + \frac{9S_0(\lambda q)}{\lambda^3} \right] \tag{8}$$

where λ and $S_0(q)$ are the linear swelling ratio, and the structure factor at gel preparation, respectively, which are given by

$$\lambda = \left(\frac{\phi_0}{\phi}\right)^{1/3} \qquad \text{(the mean field)} \tag{9}$$

and

$$S_0(q) = \frac{\phi_0 N}{w_0 - 1 + \dfrac{Na^2q^2}{12}} \tag{10}$$

where w_0 is the excluded volume parameter at sample preparation. Note that Eq. (9) gives the linear swelling ratio in the context of the mean field theory. When the strong concentration fluctuations are corrected by re-normalizing the fluctuation distance, the swelling ratio, Eq. (9) is modified to

$$\lambda = \left(\frac{\phi_0}{\phi}\right)^{1/3}\phi_0^{-1/8} \qquad \text{(the scaling limit)} \tag{11}$$

Note that such a scaling correction can be applied only for the limit of a good solvent condition.

The scattering function 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 introduced cross-links becomes equal to the number of binary contact of monomers in the corresponding polymer solution. Similar to Eq. (5), in the mean field approach, w_0 can be expressed by

$$w_0 = (1 - 2\chi_0 + \phi_0)\phi_0 N \qquad \text{(the mean field)} \tag{12}$$

On the other hand,

$$w_0 = \phi_0^{5/4} N \qquad \text{(the scaling limit)} \tag{13}$$

when the scaling approach is employed. As indicated in Eq. (10), the total structure factor, $S_0(q)$, has a well-known Lorentzian form. Thus we newly introduced an inhomogeneity-correlation length, Ξ, which can be expressed by

the following equation,

$$\Xi = \sqrt{\frac{Na^2}{12(w_0 - 1)}} \tag{14}$$

This inhomogeneity-correlation length is a characteristic length scale of inhomogeneous structure created by cross-linking. $S_0(q)$ also contains both thermal and frozen contributions, and is hardly decomposed into individual contributions. Note that Ξ mainly reflects the contribution from $C_0(q)$ around gelation threshold [31]. In other words, the inhomogeneities become largest for a gel around gelation threshold. A direct observation of Ξ is impossible because the information of Ξ is buried in $S_0(q)$. Hence, we alternatively evaluate Ξ by curve fitting of experimental $S(q)$s.

As mentioned earlier, $G(q)$ corresponds to the scattering contribution from thermal fluctuations. Therefore, an analysis of $G(q)$ can be carried out with the scattering function for PNIPA solutions since it does not contain $C(q)$. However, strictly speaking, $G(q)$ expressed by Eq. (4) is not an appropriate form to represent the scattering function for PNIPA solutions since $g(q)$ in Eq. (6) still contains an elastic contribution represented by the term represented $(4Q^2)^{-1}$ as originally introduced by de Gennes [32], and discussed by Shibayama et al. [33]. Such a contribution does not exist in the scattering function for a polymer solution. In addition, the second term of the right-hand side of Eq. (6) represents the memory effect of the sample preparation, which does not exist in the scattering function of a polymer solution. In this case, the leading term of Eq. (6), i.e. the first term of the right-hand side of Eq. (6), is essential. By taking into account of these facts, we propose a scattering function for polymer solutions by assuming, $g(q) = (Q^2/2)^{-1}$, i.e.

$$G(q) = \frac{\phi N}{w + (Q^2/2)} \tag{15}$$

$$G(q) = \frac{1}{1 - 2\chi + \phi + \dfrac{a^2 q^2}{12\phi}} \tag{16}$$

$$G(q) = \frac{G(0)}{1 + \xi^2 q^2} \tag{17}$$

It is needless to mention that Eq. (17) is a well-known Lorentzian function. Here,

$$\xi = \frac{a}{\sqrt{12\phi(1 - 2\chi + \phi)}} \tag{18}$$

is the thermal correlation length. In the case of semi-dilute polymer solutions, ξ is often evaluated with Eq. (17) for small-q range. However, it should be noted that the above approximation holds for $Q > 2$. This criterion comes from the fact that both Eqs. (6) and (15) are decreasing functions of Q for $Q > 2$ and eventually merge at larger Q, while Eq. (6) approaches zero at $Q = 0$ due to the effect of non-local term. Another important fact worth-mentioned is

that ξ is not a function of N as is the case of polymer solutions.

4. Results and discussion
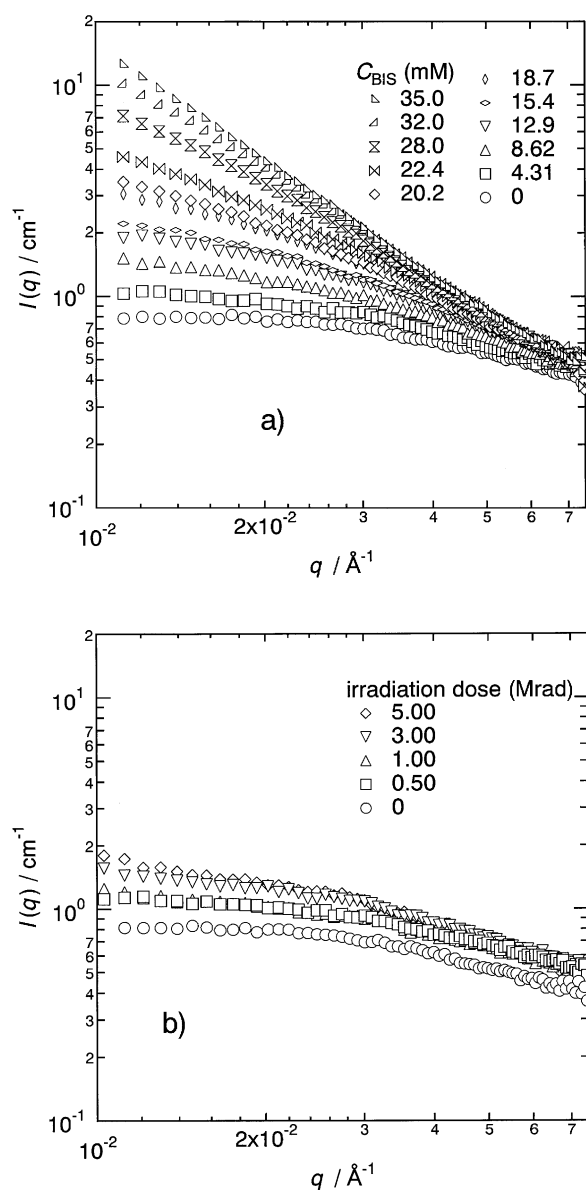
4.1. Structure parameters of PNIPA solutions

Fig. 1 shows double logarithmic plots of the scattered intensity functions, $I(q)$, observed at 20 °C for a series of (a) the chemical gels, and (b) the γ-ray gels having different cross-linking densities, where C_{BIS} denotes the cross-linker

Fig. 1. Double logarithmic plots of the scattered intensity functions, $I(q)$, observed at 20 °C for a series of (a) the chemical gels, and (b) the γ-ray gels having different cross-linking densities. C_{BIS} denotes the molar concentration of the cross-linkers in the system for the chemical gels. The irradiation doses are shown as an index of cross-linking density for the γ-ray gels.

concentration for the chemical gels. In Fig. 1(b), only the irradiation doses are shown as an index of cross-linking density. Here, it is expected that the cross-linking density simply increases with irradiation time. Fig. 1(a) shows that $I(q)$ for the chemical gels increases and becomes a power law function with increasing the cross-linking density (i.e. the case of $C_{BIS} = 35.0$ mM). Similar results were reported earlier by other workers [17–19,34,35] and analyzed with phenomenological scattering functions, such as a combination of Gaussian and Lorentzian functions [17,18].

On the other hand, surprisingly, no significant cross-linking density dependence or a power-law behavior is present for the γ-ray gels as shown in Fig. 1(b), although $I(q)$ slightly increases with increasing with irradiation dose. The comparison of the structures factors for the chemical gels and γ-ray gels strongly indicates that the microscopic structures of these two types of gels are quite different and the difference is increasing with increasing cross-linking density. In order to understand the physical origin of the difference in the structure of the chemical and γ-ray gels, we carried out a more quantitative analysis of $I(q)$ by using the PR theory.

In Fig. 2, $I(q)$s for the PNIPA solution obtained with different sample-to-detector distances, i.e. 4 and 1 m, are shown after superposition. The solid line indicates the fitting result with Eq. (17). Here, we note again that $G(q)$s for a series of gels are not equivalent with that for the corresponding polymer solution and are slightly different due to the contribution from the elastic response. As a results, we obtained $\chi = 0.364$ and $\xi = 14.2$ Å for the PNIPA solution according to Eqs. (16) and (18), respectively, where known values for the other parameters, i.e. $\phi = 0.078$ and $a = 8.12$ Å [33,36], were employed. The contrast factor K was also floated in this analysis as a vertical shift factor for the scattered intensity to the
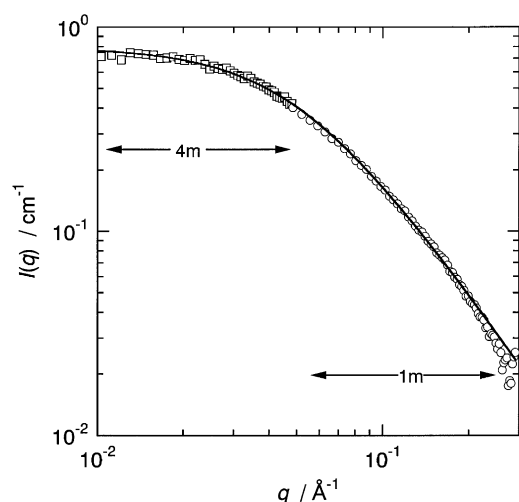
theoretical scattering function. The obtained value of K was in the range of 0.24–0.32, which is in accord with the calculated value within experimental error. As can be seen in the figure, Eq. (15) seems to work well in the wide range of the wave vector ($0.01 \leq q \leq 0.2$ Å^{-1}). We should note, however, that the deviation of the experimental data from the Lorentz function becomes significant due to the effect of chain cross-section in the range beyond our accessible q range.

Next, we evaluate the Flory's interaction parameter for both chemical gels and γ-ray gels at sample preparation, χ_0 by the mean filed approach. In order to evaluate χ_0 accurately, we needed to employ data of $I(q)$, which has a significant positive deviation at low q region, i.e. large contribution from $C(q)$. For this reason, the scattering profile having highest cross-linking density, $C_{BIS} = 35$ mM, was chosen. An example of intensity decomposition with the PR theory is shown in Fig. 3(a), where the dotted and dashed lines denote $G(q)$ and $C(q)$ represented in Eqs. (4) and (8), respectively. By employing the known values, $\phi = \phi_0 = 0.078$, $a = 8.12$ Å and $\chi = 0.364$ as fixed parameters, we obtained $\chi_0 = 0.388$, $N = 42.9$, $K = 0.181$. The value of K is slightly different from that of the corresponding polymer solution, which is within the experimental error. Next, the series of scattering data having the intermediate cross-link densities were analyzed using Eqs. (4) and (8) by the same procedure applied for $C_{BIS} = 35$ mM. Note that the theoretical curves for the cases of $C_{BIS} = 0$ mM and 0 Mrad were obtained with Eq. (17) as discussed in the previous paragraph in conjunction with Fig. 2. The adjustable parameters are only N and K, while the obtained parameters χ and χ_0 are employed as fixed parameters. The results of curve fitting are very successful as shown in Fig. 3(a). Though the physical meaning of the fitted parameter N will be discussed later, it should be noted that N controls the ratio of $G(q)$ and $C(q)$ on the total scattering function, $S(q)$. Namely, if N increases (i.e. the cross-linking density decreases), $C(q)$ is suppressed. On the other hand, $C(q)$ becomes dominant with decreasing N.

Subsequently, a similar analysis was conducted for the γ-ray gels. The known values, $\chi = 0.364$, $\chi_0 = 0.388$ are fixed in this analysis since both the observed and gel temperature are same with the chemical and γ-ray gels. The results of the curve fit for the γ-ray gels were displayed in Fig. 3(b). As shown in the figure, the curve fitting was satisfactorily carried out for all the samples.

4.2. Comparison of the degrees of polymerization between chemical and γ-ray gels

Fig. 4 shows the values of N evaluated by the PR analysis as a function of cross-linking density for the chemical gels (open circles) and the γ-ray gels (filled circles). As expected, N decreased with the degree of cross-linking and approached an asymptotic value for both the chemical

Fig. 2. $I(q)$s for the PNIPA solution obtained with different sample to detector distances, i.e. 4 and 1 m. The accessible q range was 0.01–0.20 Å^{-1}. The solid line indicates the result fitted with Eq. (17).
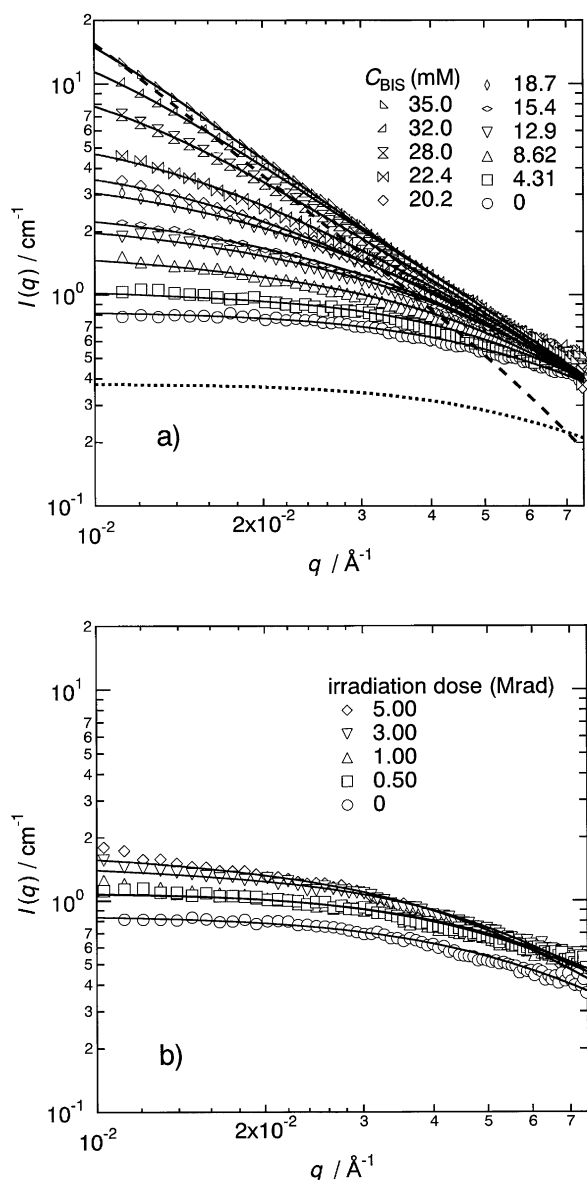
Fig. 3. Double logarithmic plots of the scattered intensity functions, $I(q)$, observed at 20 °C for a series of (a) the chemical gels, and (b) the γ-ray gels having different cross-linking densities. The solid lines indicate the fitting results with the PR theory for (a) the chemical gels, and (b) the γ-ray gels. The example of the intensity decomposition with the theory is also shown, where the dotted and dashed lines denote $G(q)$ and $C(q)$ represented in Eqs. (4) and (8), respectively.

and γ-ray gels. The limit is called the CST and will be discussed latter. Although the results for higher doses were not shown here for the γ-ray gels, a volume shrinking of gels was observed for 16 Mrad, which is located far below CST. Thus, it can be concluded that the efficiency of the cross-linking formation for the γ-ray gels is much higher than that for the chemical gels and a less number of cross-links is required to form γ-ray gels. This is due to the fact that the molecular weight of the pre-gel PNIPA molecules is quite large, resulting in an effective cross-linking by γ-ray irradiation.
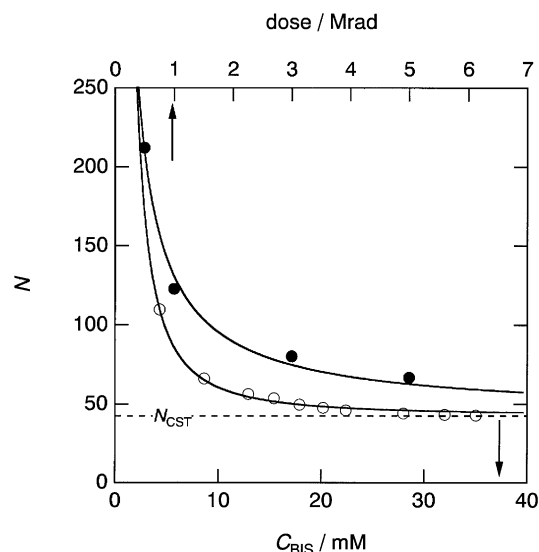

Fig. 4. The experimental results for N evaluated by the PR analysis as a function of cross-linking density for the chemical gels (○) and the γ-ray gels (●).

4.3. Critical cross-linking density and inhomogeneity correlation length

Now, we discuss the critical cross-linking density. Cross-links are formed between monomer units whose chains are actually contacting during the process of gelation. Therefore, the number of cross-linking points does not exceed that of the binary contact points in the corresponding semi-dilute solution. This fact leads to the following statement. There should be a limiting value of cross-linking density or degree of polymerization between cross-links. This limiting value is called the CST as described in the original paper of the PR theory [21]. The location of CST is determined by the balance of the numbers of such contacts and cross-links and is defined where the reduced excluded volume parameter is unity at $q = 0$ (Eq. (10)). By substituting $w_0 = 1$ into Eqs. (12) and (13), we obtained the limiting value for CST for the case of mean field approach,

$$N_{CST} = \frac{1}{(1 - 2\chi_0 + \phi_0)\phi_0} \tag{19}$$

and for the scaling limit approach,

$$N_{CST} = \phi_0^{-5/4} \tag{20}$$

N_{CST} was estimated to be 42.6 by substituting $\chi_0 = 0.388$ and $\phi_0 = 0.078$ into Eq. (19).

Fig. 5 shows the C_{BIS} and irradiation dose dependence of the inhomogeneity-correlation length at sample preparation, Ξ, for both types of gels calculated with Eq. (14). Ξ for the chemical gels is a strong function of C_{BIS}, while that for γ-ray gels is rather constant irrespective of the irradiation dose. The CST can be calculated as follows. First, we calculate the zero-cross-linking limit for Ξ. Note that Ξ
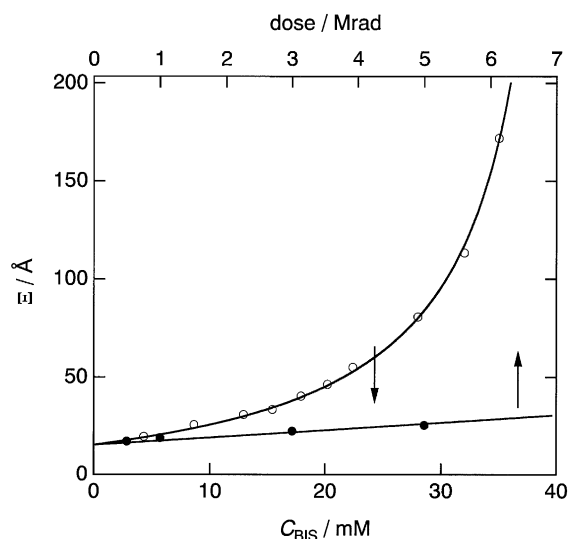
Fig. 5. C_{BIS} and irradiation dose dependence of the inhomogeneity-correlation length at sample preparation, Ξ, for the chemical gels (○) and the γ-ray gels (●) calculated with Eq. (14).

seems to approach an asymptotic non-zero value for the chemical gels as shown in the figure. Then, by substituting $N \to \infty$ into Eq. (14), we obtain,

$$\Xi_{N \to \infty} = \frac{a}{\sqrt{12(1 - 2\chi_0 + \phi_0)\phi_0}} \tag{21}$$

for the mean field approach and,

$$\Xi_{N \to \infty} = \frac{a}{\sqrt{12}} \phi_0^{-5/8} \tag{22}$$

for the scaling limit approach. Using Eq. (21), we calculated the asymptotic value $\Xi_{N \to \infty} = 15.3$ Å for both gels, which is almost the same with the thermal correlation length for uncross-linked system, $\xi(= 14.2$ Å$)$ described above. According to the postulation of divergence for Ξ around CST, we proposed an empirical form for Ξ so as to interpolate both limits, i.e. $N \to 0$ and $N \to \infty$, which is given by,

$$\Xi = \left(\frac{A}{C_{BIS, CST} - C_{BIS}} \right)^\gamma + B \tag{23}$$

with

$$B = \left[\Xi_{N \to \infty} - \left(\frac{A}{C_{BIS, CST}} \right)^\gamma \right] \tag{24}$$

where $C_{BIS, CST}$ is the critical cross-linking density, A and B are constants, γ is a critical exponent. By performing curve fitting with Eqs. (23) and (24), $C_{BIS, CST} = 42.6$ mM and $\gamma = 1.00$ were evaluated. As a consequence, we succeeded in an evaluation of the critical cross-linking density. The critical exponent, γ seems to be close to unity, suggesting that Ξ is a reciprocal function of $(C_{BIS, CST} - C_{BIS})$. Similarly, the location of CST for the γ-ray gels was roughly estimated to 263 Mrad, which were much larger
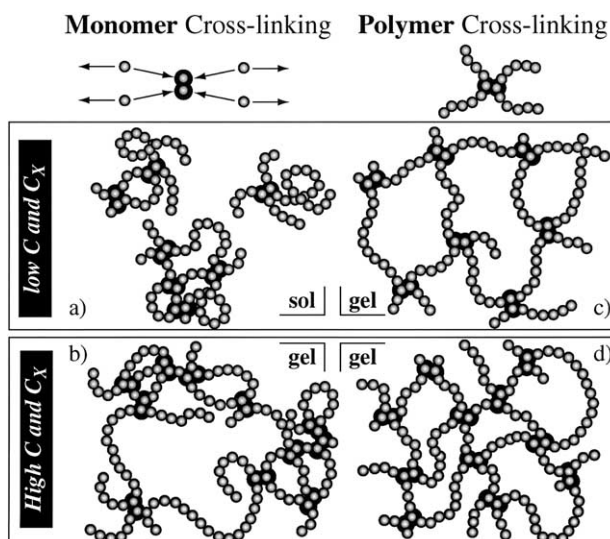

Fig. 6. Schematic representation of PNIPA gels cross-linked by (a), (b) chemical reaction with cross-linker and by (c), (d) irradiation of γ-ray. The efficiency of network formation is drawn in (a) and (c), i.e. the chemical gels do not form a gel but remain in sol sate at low monomer concentrations, C and/or low cross-linking densities, C_x, while the γ-ray gels may form a gel even at the same condition.

than the highest irradiation dose of 16 Mrad, where a noticeable volume shrinking appeared.

4.4. Remarks on the rapid shrinking of γ-ray gels

As discuss in the literature, an introduction of mobile end-free chains into a network fastens the response of volume change upon temperature stimulation. For example, Okano and co-authors reported that PNIPA gels containing free mobile graft chains exhibited a rapid response for the volume shrinking [37] of gels. Hirotsu and co-authors also found PNIPA gels in the presence of hydrophilic linear polymer chains exhibited a similar characteristic feature. Shibayama and Nagai reported that chemically cross-linked PNIPA gels also exhibit rapid shrinking due to the existence of free dangling chain as far as the initial monomer concentration at sample preparation is low enough [9].

It is deduced from the above results that a less number of cross-links is required to form the γ-ray gels than the chemical gels. As can be seen in Fig. 4, the N values for the γ-ray gels are larger than that for the chemical gels. Similar results are obtained by dynamic LS and dilatometry experiments, which will be reported in the forthcoming paper. For the chemical gels, microgel-like 'clusters' are considered to be formed during gelation process due to (1) the mismatch of the reactivity ratios of the cross-linker to the constituent monomers and (2) intra-molecular cyclic reaction in the cross-linking clusters as shown in Fig. 6(a) and (b). This phenomenon seems to be inherent in radical polymerization as far as the polymerization is starting from monomers without any controls [26,27,38]. As the results,

they have 'junction point inhomogeneities' in addition to the effect of frozen concentration fluctuations called 'structural inhomogeneities'. On the contrary, as shown in Fig. 6(c) and (d), the γ-ray gels cross-linked from prepolymers are more homogeneous than the chemical gels since cross-links are introduced randomly in space by γ-ray irradiation as described in Section 1. Note that structural inhomogeneities still exist in the γ-ray gels. Thus, cross-liking formation and subsequent gelation for the γ-ray gels are easier than the chemical gels, since the latter have a higher penalty on infinite network formation. This difference is drawn in Fig. 6(a) and (c), i.e. the chemical gels do not form a gel but remain in sol sate at low monomer concentrations, C, and/or low cross-linking densities, C_x, while the γ-ray gels may form a gel even at the same condition. As the results, gels having lower cross-linking density would lead to quick response for the thermal stimulation.

5. Conclusions

Structural analyses for two types of PNIPA gels, i.e. chemical gels and γ-ray gels, have been investigated by SANS. In addition to scattering described by a Lorentz-type function corresponding to PNIPA solutions, an excess scattering was observed for the chemical gels at low q region, which became dominant with increasing cross-linking density. As reported in literature [18], this excess scattering was explained as appearance of built-in inhomogeneities introduced by cross-links. On the other hand, the scattering functions for the γ-ray gels were found to be unchanged irrespective of irradiation dose. In order to elucidate these phenomena, a quantitative SANS analysis was carried out by the PR theory. The observed scattering intensity functions were successfully reproduced with the PR theory, from which the degree of polymerization between cross-links, N, and the inhomogeneity correlation length, Ξ, were evaluated as a function of degree of cross-linking.

The following facts are disclosed in this work. (1) The γ-ray gels have very different microscopic structures compared with those of the chemically cross-linked gels. The inhomogeneities increase with increasing cross-linker concentration for the case of chemical gels, while less irradiation dose dependence was observed for the inhomogeneities in the γ-ray gels. (2) The weak irradiation-dose dependence of the γ-ray gels is deduced to be due to random cross-linking and absence of the micro-gel cluster formation during gelation process. (3) This lower cross-linking density may lead to a rapid shrinking capability of γ-ray gels reported in the literature because of generation of long inter-cross-linking chains and many dangling chains in the polymer network. (4) There exists a limiting value of N below which the value of N does not decrease with increasing cross-linking density, C_{BIS}, for $C_{BIS} > C_{BIS, CST}$.

This is the first experimental evidence of the presence of the CST.

Acknowledgments

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