SANS AND DLS STUDIES ON STRUCTURE AND DYNAMICS OF RADIATION CROSS-LINKED POLY(N-ISOPROPYLACRYLAMIDE) GELS: COMPARISON WITH CHEMICALLY CROSS-LINKED GELS.

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The comparison of gel structure and dynamics was made between two types of poly(N-isopropyl-acrylamide) (NIPA) gels cross-linked by methylenebisacrylamide(BIS) and by γ-ray radiation. The cross-linking density dependence for the BIS gels and the γ-ray gels was examined by SANS and a significant difference in the gel structure was observed. The experimental results were well reproduced by the Panyukov-Rabin(PR) theory and the values of the degree of polymerization between cross-links, N, were quantitatively obtained. Cross-linking density dependence of cooperative diffusion coefficient obtained by dynamic light scattering was also examined in order to compare the dynamics for both gels.
Key words: γ-ray radiation, DLS, SANS, hydrogel, N-isopropylacrylamide

1. INTRODUCTION

It is well known that polymer gels have structural inhomogeneities due to restriction of local chain mobility. The inhomogeneities have been extensively studied in terms of light and neutron scattering experiments by taking into account the fact that gels have two types of concentration fluctuations, i.e., thermal fluctuations and frozen inhomogeneities.[1,2] In our previous work, we evaluated a degree of inhomogeneities for chemically cross-linked gels (BIS gel) as a function of cross-linking density by dynamic light scattering (DLS).[3] Spatial distribution of cross-links, however, depends on the reactivity ratio of chemical constituents and may affect the frozen inhomogeneities. In order to elucidate the nature of structural inhomogeneities, we made a comparison between chemically cross-linked gels and γ-ray irradiated gels (hereafter we simply call γ-ray gels), whose cross-linking points are expected to be randomly distributed in the space.

Apart from structural investigation of polymer gels, a study on stimuli response of temperature sensitive gels is an interesting subject from the engineering point of view. The rate of gel shrinking can be accelerated by designing special gels, such as, (i) a gel which has a strong shrinking tendency introduced by dangling chains,[4-6] (ii) microporous gels prepared by γ-ray irradiation,[7] or (iii) a gel having a pathway for water molecules by incorporating hydrophilic chains.[8] Recently, Kokufuta and co-workers also reported that Poly(N-isopropylacrylamide) gels cross-linked by γ-ray radiation exhibit a rapid shrinking when the temperature was raised above the volume phase transition temperature[9]. Although studies on rapid shrinking of gels became popular for application to stimuli responsible polymer gels, the shrinking mechanism has not been fully elucidated yet. This is another motivation to study the microscopic structure of the γ-ray cross-linked gels.

2. EXPERIMENTAL

Two types of poly(N-isopropylacrylamide)(PNIPA) gels were prepared by redox polymerization and by γ-ray irradiation for comparison of the network structures. The BIS gels having different cross-linking densities were synthesized at 25 °C, in the presence of N,N,N',N'-tetramethylethylenediamine (TEMED; accelerator), N,N'-methylenebis(acrylamide) (BIS; cross-linker), and ammonium persulfate (initiator). Molar concentration of BIS varies from 0 to 22.4 mM while that of NIPA was kept to be 690mM. The details of sample preparation for BIS gels are described elsewhere.[3] For the preparation of γ-ray gels, PNIPA was prepared in benzene with

azobisisobutyronitrile (AIBN) as initiator at 60°C in advance to γ-ray irradiation. The molecular weight of PNIPA was evaluated to be $M_w=1.25 \times 10^6$ by size exclusion chromatography. γ-ray irradiation was carried out by using a ^{60}Co source at 0°C in an ice chamber to suppress possible chain association reaction of PNIPA by heat. The γ-ray gels having different cross-linking densities were obtained with different irradiation times at constant dose rate of about 1Mrad/h. Here, it is expected that the cross-linking density simply increases with the irradiation time.

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 Laboratories, Tokai, Japan. A flux of cold neutrons of 7.0 Å was irradiated to the sample, and the scattered intensity profile was collected with an area detector of 128 x 128 pixels. The sample-to-detector distance was set to be 4 m, which covered the accessible q range being 0.01 to 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 thickness was about 3 mm. Scattered intensities were circularly averaged by taking account of 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).

Dynamic Light Scattering (DLS) measurements were carried out with a DLS/SLS-5000 compact goniometer, ALV, Langen, coupled with an ALV photon correlator. A 22-mW helium-neon laser (the wavelength in vacuum; λ = 632.8 nm) was used as the incident beam. All the measurements were carried out at 20 °C at the scattering angle of 90°. The acquisition time for each run was 30 s.

3. THEORY

The PR theory assumes an instantaneously cross-linked single Gaussian chain. Here, the excluded volume effect is taken into account.[10] According to the theory, the scattered intensity consists of two contributions, i.e., thermal fluctuations, $G(q)$ and frozen inhomogeneities, $C(q)$,

$$S(q) = G(q) + C(q) \qquad (1)$$

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

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

where ϕ is the volume fraction of a gel and Q is the

reduced wave vector defined by

$$Q = \frac{a}{\sqrt{6}} N^{1/2} q \qquad (4)$$

with a, N, q being the segment length, the degree of polymerization between cross-links and the wave vector, respectively. w and w_0 are the excluded volume parameters at observation and at sample preparation, respectively. Mean field approach gives the following expression for w and w_0,

$$w(q) = (1 - 2\chi + \phi)\phi N \qquad (5)$$

$$w_0(q) = (1 - 2\chi_0 + \phi_0)\phi_0 N \qquad (6)$$

where χ is the Flory's interaction parameter. $g(q)$ is the thermal correlation function without excluded volume effect,

$$g(q) = \frac{1}{Q^2/2 + (4Q^2)^{-1} + 1} + \frac{2}{(1 + Q^2)^2 (\phi_0/\phi)^{2/3}} \qquad (7)$$

Evaluation of cooperative diffusion coefficient was conducted by the following way. The intensity-intensity time correlation function, $g^{(2)}(\tau)$ is obtained by DLS measurements and, in many cases, $g^{(2)}(\tau)$ can be fitted with a single-exponential function with an apparent cooperative diffusion coefficient, D_A.[11] However, the scattered intensity depends strongly on the sample position due to the non-ergodicity of gels.[1,12] According to the previous works,[3,12] the following relation is obtained,

$$\frac{\langle I \rangle_T}{D_A} = \frac{2}{D} \langle I \rangle_T - \frac{\langle I_F \rangle_T}{D} \qquad (8)$$

where D is the cooperative diffusion coefficient of the gel, $\langle I \rangle_T$ is the time-average scattered intensity, and $\langle I_F \rangle_T$ is the dynamic component of $\langle I(q) \rangle_T$. By plotting $\langle I \rangle_T / D_A$ as a function of $\langle I \rangle_T$, both $\langle I_F \rangle_T$ and D can be evaluated from the intercept and the slope, respectively.

4. RESULTS AND DISCUSSION

Figure 1 shows double logarithmic plots of scattered intensity, $I(q)$, having different cross-linking densities for a series of (a) BIS gels and (b) γ-ray gels, where C_x denotes the molar ratio of the cross-linkers to the total monomer concentration for the chemical gels as defined in the experimental section. In figure 1b, only the radiation doses are shown as an index of cross-linking density for the γ-ray gels. For the BIS gel, $I(q)$ increased and became a power law function with increasing the cross-linking density. On the other hand, any significant cross-linking density dependence or a power-law behavior was not observed for the γ-ray gels, although $I(q)$ slightly increased with increasing cross-linking density. In order to analyze our SANS data further, we applied the PR theory. The solid lines inserted in the

figure indicate theoretical curves obtained by fitting with eq (1) - (7). As shown in the figure, the curve fitting was satisfactorily carried out for all the samples except for the case of the highest radiation dose, which was slightly opaque due to excess radiation dose (3.00 Mrad). The theory seems to work well as far as the molecular weight of pre-polymer chains is long enough (e.g. $M_w > 10^5$). It was also found that the PR theory succeeded to reproduce the increasing of the static contribution with
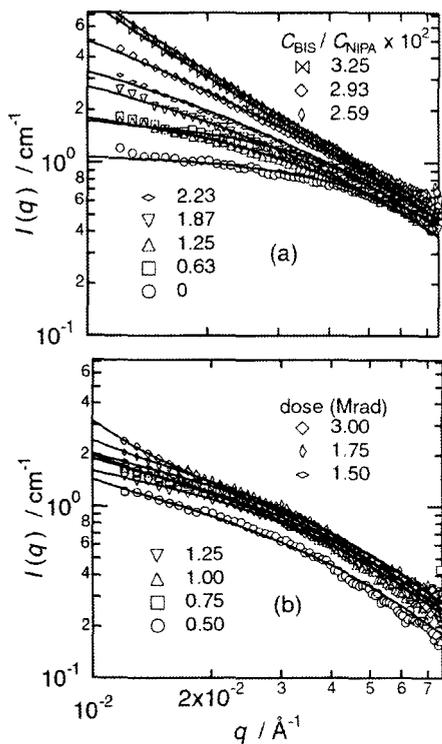

Figure 1. Double logarithmic plots of $I(q)$ having different cross-linking densities for (a) the BIS gels and (b) the γ-ray gels.

increasing the cross-linking density for the BIS gels although the results were not shown here.

The evaluated values of N by the analysis systematically increased by decreasing C_{BIS} from 97 to 153 for the BIS gels whereas the value of N for the γ-ray gels was around 91 irrespective of the cross-linking densities except for that of the highest cross-linking density. (Figure 2)

Let us address this problem. There are three possibilities to explain this phenomenon. First one is the effect of chain entanglement. If the chain entanglement plays an essential role in a concentrated network structure, the apparent N may not change even if actual cross-linking density is varied. This point was also discussed by Urayama and coworkers for poly(dimethylsiloxane) gels near their swelling equilibrium based on the results by small angle X-ray scattering.[13] However, our gels are not at an equilibrium

swollen state, where entanglement effects are less significant as discussed by Shibayama et al.[14] In addition, if the chain entanglement plays an important role, an extraordinary rapid response upon temperature stimulation, observed in the γ-ray gels, cannot be achieved. Therefore, the hypothesis does not explain the experimental results about rapid response. Second possibility is that the scattering function may depend on
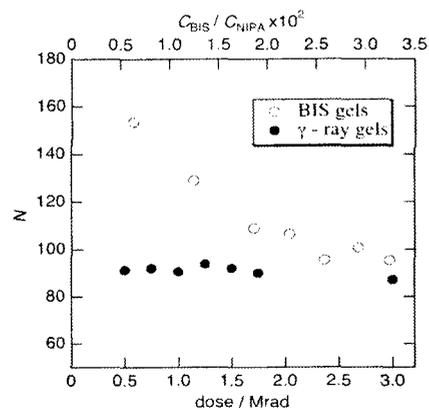

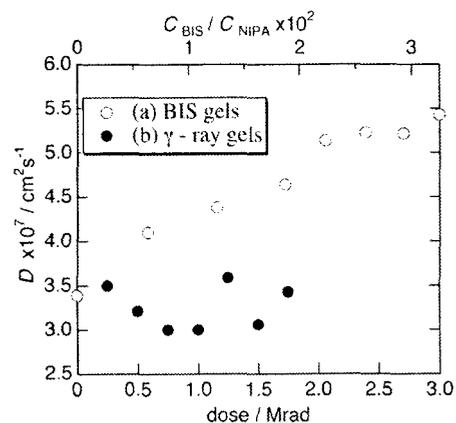Figure 2 Cross-linking density dependence of N for (a) the BIS gels and (b) the γ-ray gels.

Figure 3 Cross-linking density dependence of D for (a) the BIS gels and (b) the γ-ray gels.

radiation dose for a lower q region, e.g., the light scattering regime even if a noticeable change is not detected in SANS regime. However, we observed that the cross-linking density dependence for the cooperative diffusion coefficient, D, obtained by dynamic light scattering exhibited quite similar behavior to the present results. That is, D increased with C_x for the chemical gels, while it remained constant irrespective of the irradiation dose for the γ-ray gels. Therefore, at present, we believe the third second possibility, which is the competition of the chain scission and the cross-linking as discuss in the literature[15-17] This accounts well for the invariance of N with respect to dose.

Related to these phenomena, we conjecture that such a chain scission is one of the most plausible reasons for PNIPA γ-ray gels exhibiting a rapid shrinking upon temperature jump.[9] As discuss in the literature, introduction of mobile end-free chains into a network fastens volume response of gels 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[4] 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.[18] In the case of our γ-ray gels, it is deduced from the above results that dangling chains are formed during γ-ray radiation as competing reactions of the cross-linking formation and the chain scission, resulting in fast response for the temperature stimulation.

The cross-linking density dependence for the BIS gels and the γ-ray gels has been examined by SANS and DLS. N obtained by SANS and D by DLS systematically changed with cross-linking density for the BIS gels, while those for γ-ray gels were rather constant irrespective of the radiation dose. The analysis with the PR theory suggested that the competition of chain scission and cross-linking occurs during γ-ray irradiation with conserving N more ore less, resulting in generation of the many dangling chains in the polymer network.

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