

Scanning Microscopic Light Scattering of Inhomogeneous Polyacrylamide Gel

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By scanning microscopic light scattering the inhomogeneity of the network structure in both as-prepared and swollen gels were studied. The samples of chemically cross-linked gels were prepared varying the prepared concentration ϕ_0 in the same ratio of cross-linker to monomer, in order to ϕ_0 -dependence of the inhomogeneity. It was found that the inhomogeneity has a couple of regions controlled by ϕ_0 . In low ϕ (semi-dilute) region, both the amplitudes of static and dynamic fluctuations increase by large-swelling. In high ϕ_0 (semi-concentrated) region, the increment of static fluctuation by swelling is larger than that of dynamic fluctuation. In intermediate ϕ_0 region, the increment of the static inhomogeneity by swelling is minimum. The dynamic fluctuation is dominated by the volume fraction at measurement; nevertheless if the swelling-induced growth of the static inhomogeneity is strong, the polydispersity of dynamic fluctuation increases and the average of the relaxation time shifts to high value.

Key words: light scattering, gels, inhomogeneity, swelling, fluctuation

1. INTRODUCTION

Chemically cross-linked gels inevitably contain the static inhomogeneity due to the concentration fluctuation in the pre-gel solution in preparation [1, 2], due to the formation process of clusters [3] and so on. In the present study the static and dynamic fluctuation in polyacrylamide (PAA) gels has been investigated in both as-prepared and equilibrium swollen states by scanning microscopic light scattering (SMLS). To make the variously inhomogeneous gels, the sample gels are prepared varying the concentration in preparation ϕ_0 in the same ratio of cross-linker to monomer. From our previous study[4], it was found that the swelling ratio of the PAA gels as a function of ϕ_0 has a couple of regions independently of the ratio of cross-linker to monomer. The network structures in two regions have different characters of fractals and entanglements respectively. These characters are related to the inhomogeneity of gels. Thus the detail investigation of the inhomogeneity yields a good understanding of the properties of the gel network.

The light scattering study of inhomogeneous gels is in general difficult. If the characteristic wave length of inhomogeneity is larger than scattering volume, the property determined at a measuring position does not corresponds to an intrinsic property, but is a local property. Thus in the case of the study of inhomogeneous gels, measurement has to be performed at a lot of position and a time- and space-averaged property, i.e. an ensemble-averaged property, has to be determined. By virtue of SMLS, the scattering volume can be focused within several micrometers and both local and ensemble-averaged properties with inhomogeneity can be determined, ranging over some millimeters.

The previous light scattering studies of gels

always treated as-prepared gels and hardly treated swollen gels. Since the volume of the swollen gels is varied by measuring condition, the sample fixing and the optical adjustment of the swollen gels are difficult. Moreover the scattering intensity of the swollen gel is in general weak and is hard to be observed. In the present study, the equilibrium swelling ratio of samples were previously determined and the sample gels for SMLS were prepared to swell the appropriate dimensions in measurement. By SMLS the appropriate scattering volume is selected and is focused to gain the scattering intensity and improve accuracy of measurement.

2. EXPERIMENTAL

Sample PAA gels were prepared by radical copolymerization of acrylamide (AA) monomer and N,N'-methylenebisacrylamide (BIS) cross-linker (Wako Chemicals Co.) in aqueous solution. The pre-gel solutions were prepared varying the prepared concentration ϕ_0 systematically with the same ratio of the cross-linker to the monomer (BIS/AA=0.246mol%). In order to avoid the hydrolysis, all the operations of the reactions were carried out in 6.0°C. The pre-gel solutions were filtered with a micron-filter of 0.22mm pore size to remove the dust particles and bubbled with nitrogen to purge oxygen. To initiate redox polymerization, initiator ammonium persulfate and accelerator N,N,N',N'-tetramethylethylenediamine (Wako Chemicals Co.) were add to the pre-gel solutions to give the net concentrations of 0.4mg/ml and 4ml/ml respectively. As soon as the addition, the solutions were transferred into both the sample glass tubes of 4.5mm inner diameter for as-prepared sample gels, and the glass molds of 1-3mm inner diameter for swollen sample gels. After 24 hours the later gels in the molds were pushed out from

the molds and soaked in a large amount of water in 2 weeks at room temperature to wait for the swelling equilibrium. Then the swollen gels were transferred into the sample glass tubes for swollen sample gels.

The equilibrium swelling-ratio of the swollen sample gel was determined by cathetometer (accuracy 0.01mm). Before measurements the sample gels were kept at 30.0°C in 24 hours to wait for the swelling equilibrium. The diameters of the gels L were measured. The apparent swelling ratio α was determined by $\alpha = (L/L_0)^3$, where L_0 is the inner diameter of the gel mold. The actual swelling ratio Q was determined by $Q = 1/\phi = \alpha/\phi_0$, where ϕ is the volume fraction of swollen gels in equilibrium, and ϕ_0 is that of as-prepared gels in preparation.

In the present study, we newly constructed a SMLS apparatus to measure both the local scattering intensity and the auto-correlation function of that. The detail explanation of this apparatus will be presented elsewhere [5]. The temperature stability of the light-scattering cell was better than 0.01°C. In the present work all measurements were made at the same temperature of 30.00°C. The scattering measurements were performed at the same scattering angle of 95°.

3. RESULTS AND DISCUSSION

The swelling behavior of the sample gels is shown in Fig.1. It is found that α as a function of ϕ_0 has a couple of regions. In low ϕ_0 region α decreases sharply as ϕ_0 increases, while in high ϕ region α increases gradually as ϕ_0 increase. There is the crossover concentration between the two regions. The Q also has the two kinds of ϕ_0 -dependences and the change of the dependences occurs at the crossover concentration. In our previous study [4], it has been found that this nature was universally observed independently of the ratio of cross-linker to monomer. It suggests that in the each region the different gels with the different nature of network structure is formed. In the following, we study the properties of the different kinds of inhomogeneity due to the different networks.

The position-dependence of the time-averaged scattering intensity $\langle I \rangle_T$ is shown in Fig.2. As the gel swells, $\langle I \rangle_T$ increases and the dispersion of $\langle I \rangle_T$ also grows. In some cases of swollen gels the ratio of maximum to minimum of $\langle I \rangle_T$ was more than 10. It means that $\langle I \rangle_T$ does strongly depends on the position in the sample. Therefore measurement has to be made at a lot of the different positions and the ensemble-averaged properties have to be determined.

For each sample both in as-prepared and swollen states, the ensemble-averaged scattering intensity $\langle I \rangle_E$ was determined by the average of

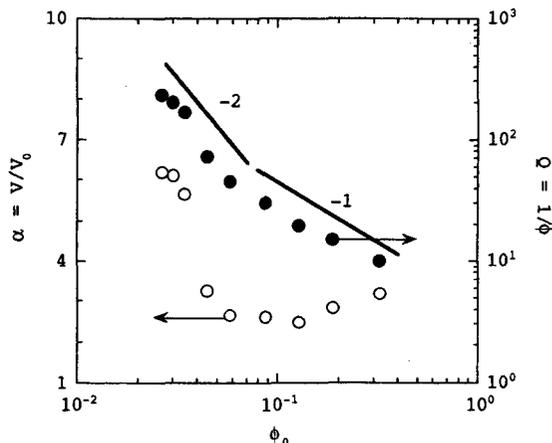


Fig.1: The apparent and actual swelling ratios, α and Q , as functions of the prepared volume fraction ϕ_0 . Solid lines indicate a couple of the power-law behavior of Q .

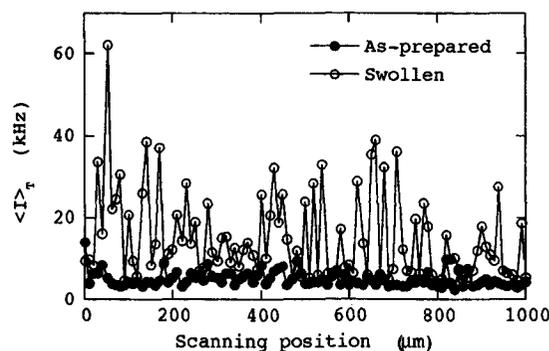


Fig.2: An example of the position dependence of the time-averaged scattering intensity $\langle I \rangle_T$ of as-prepared and swollen gels. This is of the sample prepared in $\phi_0 = 0.045$.

a hundred and more of $\langle I \rangle_T$ measured at different positions in the sample. Figure 3 shows the ϕ_0 -dependence of $\langle I \rangle_E$. The $\langle I \rangle_E$ in as-prepared state decreases as ϕ_0 increases. By swelling $\langle I \rangle_E$ grows. The swelling induced intensity-growth has been observed by small angle neutron scattering [1]. In the present study, the intensity-growth is definitely observed by SMLS. Such a phenomenon has been explained that gels contain the inherent inhomogeneity due to the fluctuation of the concentration in preparation and the inhomogeneity grows as the gels swell.

It is found that there is the difference in the ϕ_0 -dependence of $\langle I \rangle_E$ of swollen gels between low ϕ_0 region and high ϕ_0 region. In low ϕ_0 region $\langle I \rangle_E$ decreases as ϕ_0 increases. On the contrary in high ϕ_0 region $\langle I \rangle_E$ increases as ϕ_0 increases. There is the minimum of $\langle I \rangle_E$ between these regions. It means that the gel prepared at the intermediate ϕ_0 has small $\langle I \rangle_E$ in equilibrium swollen state.

For each sample, a hundred and more of the time-averaged auto-correlation function of scattering intensity $g_T^{(2)}(t)$ were determined at different positions and the time-averaged auto-correlation functions of scattering electric field

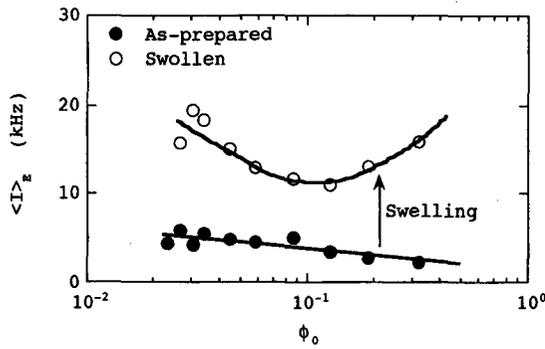


Fig.3: The ensemble-averaged scattering intensity $\langle I \rangle_E$, as a function of the prepared volume fraction ϕ_0 of as-prepared and swollen gels. Solid curves are the guide to the eye.

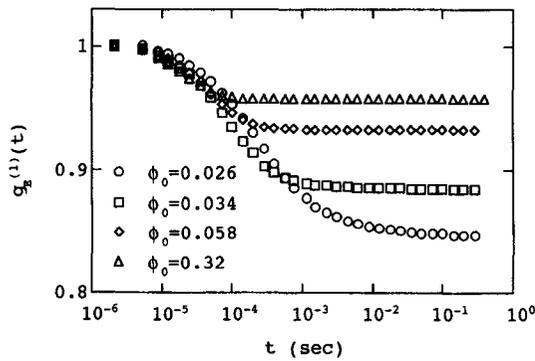


Fig.4: The examples of the ensemble-averaged correlation functions of swollen gels.

$g_T^{(1)}(t)$ were calculated by

$$g_T^{(1)}(t) = \sqrt{1 + g_T^{(2)}(t) - g_T^{(2)}(0)} \quad (1)$$

Then from the set of $g_T^{(1)}(t)$, an ensemble-averaged auto-correlation function $g_E^{(1)}(t)$ was calculated by [5]

$$g_E^{(1)}(t) = \left\langle \langle I \rangle_T g_T^{(1)} \right\rangle_S / \langle \langle I \rangle_T \rangle_S \quad (2)$$

where $\langle \dots \rangle_S$ means the space-average. The examples of obtained $g_E^{(1)}(t)$ of swollen gels are shown in Fig.4. It is found that as ϕ_0 decreases the profile of $g_E^{(1)}(t)$ broadens due to the polydispersity of relaxation time. The extrapolating value of $g_E^{(1)}(t)$ in $t \rightarrow \infty$, i.e. baseline $g_E^{(1)}(\infty)$ decreases as ϕ_0 decreases. It means the increment of the dynamic component of $g_E^{(1)}(t)$.

In the use of $g_E^{(1)}(\infty)$, the component due to dynamic fluctuation $\langle I_F \rangle_E$ and that due to static fluctuation $\langle I_C \rangle_E$ can be determined by

$$\langle I_F \rangle_E = (1 - g_E^{(1)}(\infty)) \langle I \rangle_E \quad (3)$$

$$\langle I_C \rangle_E = g_E^{(1)}(\infty) \langle I \rangle_E \quad (4)$$

where it should be noted that $\langle I \rangle_E = \langle I_F \rangle_E + \langle I_C \rangle_E$. The $\langle I_F \rangle_E$ and $\langle I_C \rangle_E$ of the as-prepared

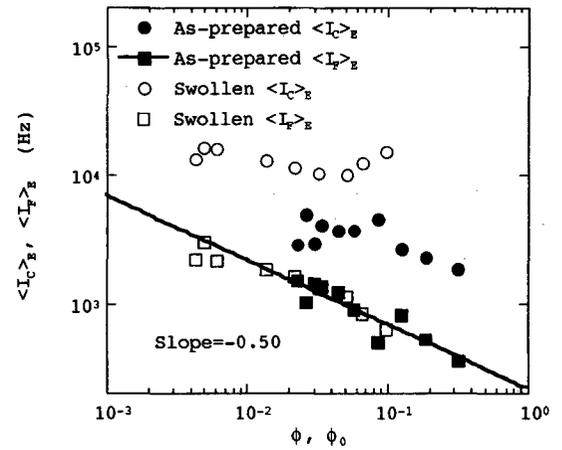


Fig.5: The static and dynamic components of the ensemble-averaged intensity, $\langle I_C \rangle_E$ and $\langle I_F \rangle_E$, as functions of the volume fraction of as-prepared and swollen gels. Solid line indicates the power-law formula.

gels as a function of ϕ_0 , and those of the swollen gels as a function of ϕ were calculated (Fig.5). It is found that both $\langle I_F \rangle_E$ of the as-prepared and the swollen gels behave as the same decreasing power-law function of ϕ_0 . It means that $\langle I_F \rangle_E$ depends on the concentration of network at measurement and does not depend on that at preparation. The exponent of the power-law function is found to be -0.50 . Here we try to estimate it.

On the basis of harmonically-bound chain motion theory [5], the correlation function of gels is written by

$$g_H^{(1)}(\mathbf{q}, t) = \exp \left[-\mathbf{q}^2 \xi^2 \left\{ 1 - \exp \left(\frac{D}{\xi^2} t \right) \right\} \right] \quad (5)$$

where \mathbf{q} is the scattering vector, ξ is the effective size of the mesh that puts the blob under constraint, and D is the diffusion coefficient of the blob [6]. The mesh size ξ is scaled with the polymerization index N as $\xi \sim N^\nu$ where $\nu = 1/2$ in Θ solvent and $\nu = 3/5$ in good solvent. On the analogy of the crossover concentration, $\phi \sim N^{1-3\nu}$ and then $\xi \sim \phi^{\nu/(1-3\nu)}$. If $\langle I \rangle_E \sim \phi$ and the case of $\mathbf{q}^2 \xi^2 < 1$ is considered, $\langle I_F \rangle_E$ is estimated as

$$\langle I_F \rangle_E \propto (1 - g_H^{(1)}(\infty)) \langle I \rangle_E \sim \phi^{\frac{1-\nu}{1-3\nu}} \quad (6)$$

Since in good solvent $\nu = 3/5$, we obtain $\langle I_F \rangle_E \sim \phi^{-1/2}$. This corresponds with the results.

On the other hand it is found that $\langle I_C \rangle_E$ of the as-prepared gels behaves like a decreasing power-law function of ϕ_0 . The slope of this is different from that of $\langle I_F \rangle_E$. Moreover the $\langle I_C \rangle_E$ of the swollen gel has the different dependence from the others. While in low ϕ , $\langle I_C \rangle_E$ decreases as ϕ increases like the others, in high ϕ , on the contrary $\langle I_C \rangle_E$ increases as ϕ

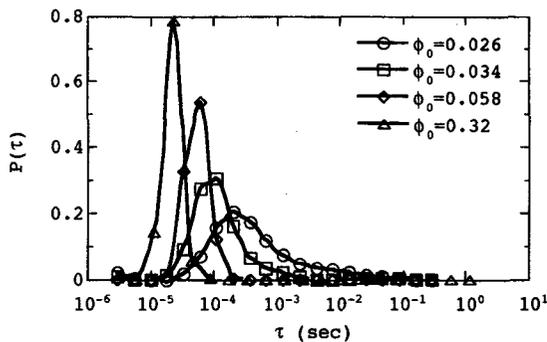


Fig.6: The examples of the relaxation-time distribution of swollen gels, obtained by the inversed Laplace transform.

increases. Thus ϕ -dependence of $\langle I_C \rangle_E$ of the swollen gels is different between in low ϕ and in high ϕ . It seems that such a behavior is due to a couple of regions observed in the swelling behavior $\alpha(\phi_0)$ shown in Fig.1.

In the comparison of Fig.5 with Figs.1 and 3 it is mentioned that the mechanisms of the swelling induced $\langle I \rangle_E$ -increment are different between in low ϕ_0 region and in high ϕ_0 region. In low ϕ_0 region as the gel swells well, both $\langle I_F \rangle_E$ and $\langle I_C \rangle_E$ increases and then $\langle I \rangle_E$ increases. On the other hand in high ϕ_0 region as the gel swells little, the increasing ratio of $\langle I_C \rangle_E$ is higher than that of $\langle I_F \rangle_E$, and then $\langle I \rangle_E$ increases.

In order to study the relaxation time τ of $g_E^{(1)}(t)$, we use the inversed Laplace transform (ILT) method for analysis. The ILT method is useful since it does not need any assumptions for the profile of $g_E^{(1)}(t)$. The examples of the relaxation-time distribution calculated by the ILT method $P(\tau)$ are shown in Fig. 6. These were obtained from $g_E^{(1)}(t)$ of swollen gels that are shown in Fig. 4. It is found that the distribution of $P(\tau)$ becomes broad as ϕ_0 decreases.

From $P(\tau)$ the ensemble-averaged relaxation time τ and the deviation of τ were determined (Fig.7). It is found that the τ of the as-prepared gels is scaled with ϕ_0 . Its slope is -0.59 . The τ is estimated from the diffusion coefficient D as $\tau = 1/q^2 D \sim \xi \sim \phi^\nu / (1-3\nu)$. In the case of good solvent $\nu = 3/5$, $\tau \sim \phi^{-3/4}$. It is somewhat different to the result.

On the other hand, τ increases as gels swell. It means that D decreases as the size of mesh increases; this is consistent with the blob model. The ϕ_0 -dependence of τ of the swollen gels is seen to be similar to the ϕ_0 -dependence of α shown in Fig.1. Thus τ of the swollen gels is replotted as a function of ϕ . Then it is found that $\tau(\phi)$ of the swollen gels is scaled by the same power-law function of $\tau(\phi_0)$ of the as-prepared gels. Its behavior corresponds to $\langle I_F \rangle_E$ shown in Fig.5. It means that the dynamic fluctuation is controlled by the volume fraction at measure-

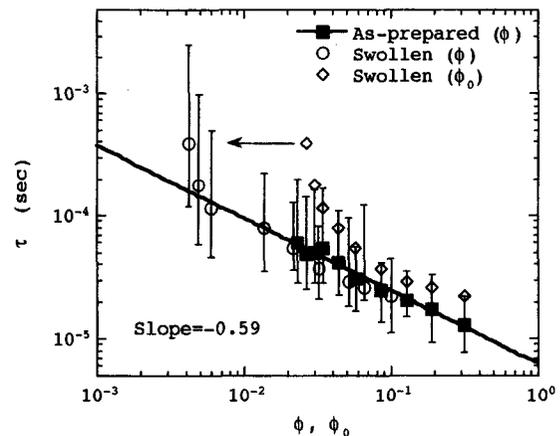


Fig.7: The relaxation time τ as functions of the preparing volume fraction in ϕ_0 of as-prepared and swollen gels. Error bars indicate the deviations of τ . Solid line indicates the power-law formula.

ment.

The deviation of τ is shown in Fig.7 by error bars. The deviation increases as the gel swells. The increasing ratio of the deviations of the swollen gel to the as-prepared gel is larger in low ϕ_0 and in high ϕ_0 than in intermediate ϕ_0 . It is similar to the ϕ_0 -dependence of α (Fig.1) and that of $\langle I_C \rangle_E$ (Fig.5) of the swollen gels. In particular in the case of low ϕ_0 , the deviation of τ is seen to be so large, and $\tau(\phi)$ of the swollen gels separates from the power-law behavior. It suggests that the deviation has relation with the inhomogeneity of gels; In the swollen gels the inhomogeneity effects the dynamic fluctuation and then the deviation of τ increases. If the inhomogeneity is especially so strong, the average of τ is affected and shifted.

4. CONCLUSION

By scanning microscopic light scattering the inhomogeneity of both the as-prepared and swollen gels was investigated. It has been found that the behavior of the inhomogeneity has a couple of regions controlled by the prepared concentration, that is consistent with the swelling behavior. It was also found that the strong static-inhomogeneity effects the dynamic fluctuation.

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