Structural Characterization of Inhomogeneous Poly(methyl methacrylate) Gels by Time-Dependent Diffusion NMR Spectroscopy

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ABSTRACT: A series of inhomogeneities were introduced to poly(methyl methacrylate) (PMMA) gels by carrying out the polymerization of PMMA network in the presence of various amounts of polystyrenes (PS) ($M_w = 400\,000$). The pulsed-field-gradient stimulated-echo ^{1}H NMR measurements were performed for the PMMA gel samples with variable diffusion time Δ, which enabled us to investigate the PMMA gel network structure on the basis of the diffusional behavior of the large probe molecule (PS) and a small probe molecule (unreacted monomer) in PMMA gels. The diffusion behavior of the large PS probe molecule proved to significantly dependent on the amount of PS that had been added in the gelation batch. The analysis of PGSE ^{1}H NMR measurements strongly suggested that the PS diffusion consists of two diffusion components, while it changes to a single mode with increasing the PS concentration. These results were ascribed to the course of the phase separation resulting from development of "open" network structure that was induced by the PS probe molecule in the gelation batch.

Introduction

A better understanding of the network structure of polymer gels is required for the development of fundamental research work on polymer gel as well as its practical application. The spatial inhomogeneity that inherently exists in chemically cross-linked polymer gels has so far been detected by light scattering as speckles;[1,2] the relationship between the speckles and spatial inhomogeneity has been analyzed.[3−9] The gel structure is also available through investigations on the diffusional behavior of probe molecules in the gel network.[10−27] However, some problems associated with the inhomogeneity in the gel network size remain due to intermolecular interactions between the network and the probe molecules.

In our previous work,[26] poly(methyl methacrylate) (PMMA) gels were prepared with radical polymerization by cross-linking methyl methacrylate monomer with ethylene glycol dimethacrylate as cross-linking monomer in toluene containing polystyrenes (PSs) with M_w from 4000 to 400 000. The diffusion coefficients of the PSs as probe molecules in the PMMA gels were measured by the pulsed-field-gradient (PFG) ^{1}H NMR method with the diffusion time Δ varied. On the basis of the probe diffusion data, it has been confirmed that the PMMA gel thus prepared has an inhomogeneous network structure, consisting of an "open region" where PMMA chains are considerably dilute and a "dense" one where the diffusion of the probe PS chains is significantly restricted. Further, we observed[27] diffusional behaviors of different probe PS samples (M_w: 4000−400 000) and chloroform as solvent in the same PMMA gel matrix with the diffusion-time-dependent ^{1}H PFG NMR. The diffusion of the solvent and the smallest PS with $M_w = 4000$ proved to be of a single mode, but the other PS molecules showed a multimode diffusional behavior. The restricted diffusion was observed only for the largest probe PS with $M_w = 400\,000$. On the basis of these diffusion behaviors of the probe molecules, we have successfully characterized the gel network structure in terms of the mesh size and the dimension of the two regions: open and dense.

In our previous works mentioned above,[26,27] all PMMA gel samples prepared were transparent, which suggested that any substantial macrophase separation did not occur in the gels. However, it may be expected that pronounced inhomogeneity of the PMMA gels such as macrophase separation between PMMA and PS should also be detected by the relevant NMR technique. Thus, in the present study, we aim to prepare poly(methyl methacrylate) (PMMA) gels that have different levels of phase separation (inhomogeneities for the network size) by performing the PMMA gelation in the presence of a polystyrene (PS with $M_w = 400\,000$) with various PS concentrations from 6 to 50 mg/mL. Since the network inhomogeneity is expected to develop with increasing the PS concentration, network structures including micro- to macrophase separation will be introduced to the gel. Inhomogeneities thus introduced into the PMMA gels are characterized through estimation of the diffusion coefficients of probe molecules in the PMMA gels by the pulsed-field-gradient stimulated-echo ^{1}H NMR method to envisage the phase separation process occurring during the pertinent gel network formation from the viewpoint of the probe polymer diffusional processes.

Experimental Section

Materials. Deuterated toluene used as solvent was purchased from Aldrich Chemical Co. Methyl methacrylate (MMA) as monomer and 2,2′-azobis(isobutylonitrile) (AIBN) used as a polymerization initiator were purchased from Kanto Chemical Co., Inc. Ethylene glycol dimethacrylate (EGDM) used as cross-linking monomer was purchased from Aldrich Chemical Co., Inc. The polymerization inhibitor contained in MMA and EGDM was removed off by shaking with 10% NaOH aqueous solution and with water in sequence. The obtained MMA and EGDM were dried with sodium sulfate and then were distilled in vacuum. Linear atactic polystyrene (PS) with $M_w = 400\,000$ was purchased from Polysciences, Inc., and Aldrich Chemical Co.

The radical copolymerization of MMA and EGDM in addition to PS initiated by AIBN was performed in deuterated toluene solution at 75 °C for 1 day, and then the gelation was made.[11,28] PS was added as a diffusional probe polymer during the gelation process. MMA (1.4 mol/L), EGDM (47.7 mmol/L), and AIBN (4.6 mmol/L) were dissolved in deuterated toluene, and this stock solution was divided and transferred into an NMR sample tube of 5 mm diameter. Four different pregel solution samples (transparent) were prepared using this stock solution with various PS concentrations $C_{PS} = 6$, 10, 20, or 50 mg/mL in deuterated toluene [PMMA gel samples 1−4, respectively]. All the pregel solution samples in

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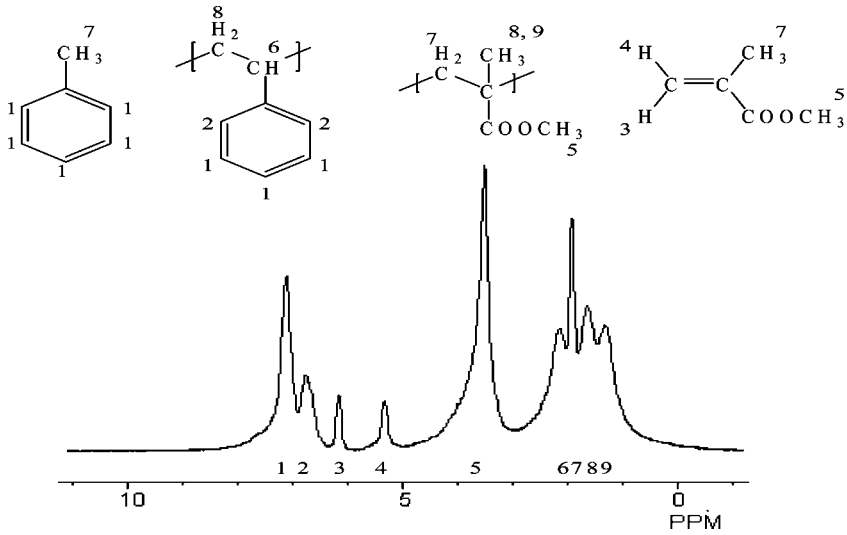

Figure 1. ^{1}H NMR spectrum of PMMA gel (sample 4) containing PS with $M_w = 400\,000$ and deuterated toluene. The solvent contains a very small amount of toluene as impurity.

NMR sample tubes were deoxygenated by bubbling nitrogen gas for 10 min, and then gelation was carried out at 75 °C for 1 day. Four rodlike PMMA gel samples containing PS were obtained. PMMA gel samples 1 and 2 were transparent, while samples 3 and 4 appeared slightly opaque, showing a sign of phase separation. The swelling degree of the polymer gel (Q) is defined as the mass ratio of swollen polymer gel ($M_{swollen}$) to dried one (M_{dry})

$$Q = M_{swolllen}/M_{dry} \quad (1)$$

Q values of all the PMMA gels used in this work were about 6. The concentration of cross-linked is 0.034 units per MMA monomer unit. From the obtained diffusion coefficient $D_0 = 2.0 \times 10^{-11}$ m^2/s of 400 000 M_w PS in toluene dilute solution (6 mg/mL), the hydrodynamic radius was obtained to be 19.5 nm by using the Stokes−Einstein equation. The approximate averaged pore size is 2.7 nm, which is roughly estimated by using the fraction of EGDM cross-linking.

Measurements. The diffusion coefficient (D) measurements on probe PSs in PMMA gels were carried out at room temperature by a Bruker DSX-300 NMR spectrometer operating at 300.11 MHz for ^{1}H with pulsed-field-gradient generator (the maximum field-gradient strength: 11.6 T/m) by using a pulsed-field-gradient stimulated-echo pulse sequence ($\pi/2$ pulse$-\tau_1-\pi/2-\tau_2-\pi/2$ pulse).[29,30] The spectral width and the number of data points are 2 kHz and 2048, respectively. The D values were determined by using the relationship between echo signal intensities and field-gradient parameters:

$$\ln\left[\frac{A(g)}{A(0)}\right] = -\gamma^2 g^2 D_i \delta^2\left(\Delta - \frac{\delta}{3}\right) \quad (2)$$

where $A(g)$ and $A(0)$ are echo signal intensities at $t = 2\tau$ with and without the field gradient pulse being the strength g, respectively. τ is the pulse interval, γ the gyromagnetic ratio of the proton, g the field gradient strength, δ the duration of the gradient pulses, and Δ the gradient pulse interval which is the so-called "diffusion time". If the probe diffusion consists of multicomponents, the total echo attenuation is given by a superposition of contributions from the individual components. In the case of two-component systems the signal intensity is expressed as

$$\frac{A(g)}{A(0)} = f_1 \exp\left[-\gamma^2 g^2 D_1 \delta^2\left(\Delta - \frac{\delta}{3}\right)\right] + f_2 \exp\left[-\gamma^2 g^2 D_2 \delta^2\left(\Delta - \frac{\delta}{3}\right)\right] \quad (3)$$

where D_i is the diffusion coefficients of the ith component, f_i the fractional proton number of the ith component, and $f_1 + f_2 = 1$. The fractions for the first and second diffusion components can be determined from the intercept of the least-squares-fitted straight line at larger g values. In the present study, eq 3 was used for multicomponent cases when the analysis satisfyingly reproduce the experimental results. The Δ, δ, and g values employed in these experiments are 40−1000 ms, 0.04−4.0 ms, and 0−10 T/m, respectively.

Results and Discussion

^{1}H NMR Spectrum of PMMA Gel Sample and the Assignment. A typical ^{1}H NMR spectrum of a PMMA gel (sample 4) at room temperature is shown in Figure 1. The spectral assignments are straightforwardly made by using reference data of PS, PMMA, and toluene that is contained in commercial deuterated toluene as an isotope impurity.[31−34] All of the peaks are numbered from downfield to upfield. Peak 1 overlaps with two peaks coming from the *m*- and *p*-phenyl protons of PS and phenyl protons of toluene. Peak 2 comes from the *o*-phenyl protons of PS. Peaks 3 and 4 are assigned to the methylene protons of unreacted MMA, suggesting that MMA of about one-third of the feed remains in each sample. Peak 5, the largest one, is assigned to the methoxy protons of PMMA and unreacted MMA. Area of peak 5 is larger than an area of 3 compared with peak 3. The asymmetric line shape of peak 5 is caused by bad shims. Peaks 6−9 are assigned to the main chain protons of PS and PMMA and methyl protons of unreacted MMA. The diffusion coefficients of the PS and the MMA were estimated as shown below by use of peak 2 and peak 4, respectively.

Diffusion Behaviors of PS in PMMA Gels. The PGSE ^{1}H NMR measurements have been made for PMMA gel samples 1−4 containing PS with $M_w = 400\,000$ with the diffusion time $\Delta = 60$ ms at room temperature in order to investigate the diffusion behavior of PS in PMMA gels and the PMMA gel network structure. Figure 2 shows the plots of $\ln[A(g)/A(0)]$ against $\gamma^2 g^2 \delta^2(\Delta - \delta/3)$ for the phenyl peak for PS with $\Delta = 60$ ms in PMMA gel samples 1−4, respectively.

First of all, we note that the diffusion behavior of PS is significantly dependent on the PS concentration. The change from the nonlinear plots to the linear ones for samples 1−4 means that the diffusion mode of the PS varied from a two-component mode to a single-component one with an increase in the PS concentration.

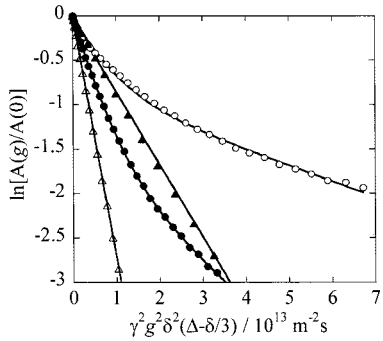

Figure 2. Diffusional stimulated echo attenuations of PSs in PMMA gels [(○) sample 1, (●) sample 2, (Δ) sample 3, and (▲) sample 4] with deuterated toluene as solvent by varying field gradient strength g with the diffusion time $\Delta = 60$ ms at room temperature.

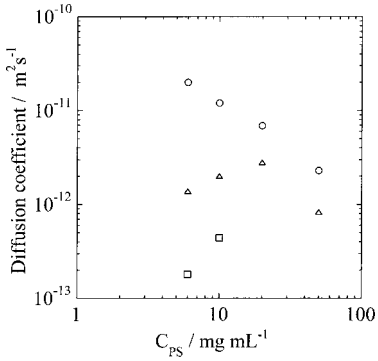

Figure 3. Diffusion coefficients (D_0) of PSs in deuterated toluene solution (○), the diffusion coefficients of fast diffusion component (D_{fast}) of PSs in PMMA gel samples (Δ), and the diffusion coefficients of slow diffusion component (D_{slow}) of PSs in PMMA gel samples (□) as a function of the PS concentration (C_{PS}).

The nonlinear plots of samples 1 and 2 may be analyzed as two diffusion components. The diffusion coefficients of the fast and slow diffusion components (as indicated by D_{fast} and D_{slow}, respectively) and the corresponding fractions (f_{fast} and f_{slow}, respectively) that were determined by eq 3 are plotted in Figure 3. On the other hand, the single diffusion coefficients of PS (D) for samples 3 and 4 are determined from the slope of the respective straight lines by eq 2. Thus, the obtained D and f values thus obtained are listed in Table 1. The diffusion coefficients are plotted as a function of C_{PS} in Figure 3, where the open circles are D_0 values, i.e., diffusion coefficients of the PS ($M_w = 400\,000$) in pure deuterated toluene solution at the same concentration as used in the gel samples.

In order to extract some information on the network structure from the diffusion coefficient data, we plotted D/D_0, instead of D, against C_{PS} (Figure 4). It is noted here that the D/D_0 values significantly increase with C_{PS}. This dependency of the D/D_0 on PS concentration suggests that the "open" structure introduced by the coexistence of PS in the PMMA gel-forming process gradually predominates with an increase in the PS concentration, probably reflecting the phase separation process of the PMMA/PS system.

It has been well-known that PS is incompatible with PMMA under certain conditions, and the resultant phase separation depends on polymer molecular-weight and concentration.[35,36] Thus, in the present system, it is expected that micro- and/or macrophase separation occurs during the gelation process, and there locally exists the "open network structure" where PMMA chains are considerably dilute. Actually, the appearance of samples 3 and 4 was slightly milky and turbid, a sign of phase separation. With increasing C_{PS}, phase separation in the gel

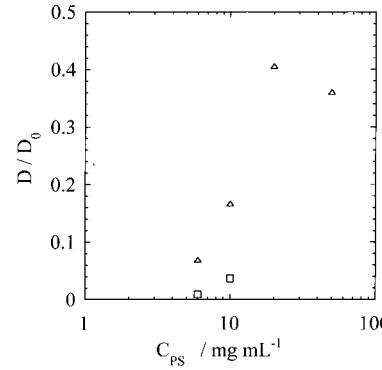

Figure 4. Diffusion coefficients of fast diffusion component (Δ) and slow diffusion component (□) normalized by diffusion coefficients (D/D_0) of PSs in deuterated toluene solution as a function of the PS concentration (C_{PS}).

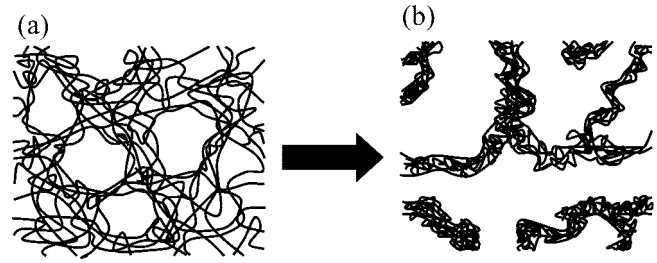

Figure 5. Schematic diagram for the supposed network structures of PMMA gel samples 1, 2 (a) and 3, 4 (b): (a) lower C_{PS} and (b) higher C_{PS}, where the phase separation was developed.

Table 1. Diffusion Coefficients of PSs in PMMA Gels Obtained by the PGSE ^{1}H NMR Method

	diffusion coefficient (m^2 s^{-1})		fraction of diffusion component	
sample	D_{fast}	D_{slow}	f_{fast}	f_{slow}
1	1.4×10^{-12}	1.8×10^{-13}	0.55	0.45
2	2.0×10^{-12}	4.4×10^{-13}	0.77	0.23
3	2.7×10^{-12}		1.00	0.00
4	0.8×10^{-12}		1.00	0.00

sample proceeded so that the "open" network structure predominated in the PMMA gel samples, and this process manifested with an increase in the D/D_0 values.

In order to illustrate this situation, network structures of PMMA gel samples 1, 2 and 3, 4 are schematically shown in parts a and b of Figure 5, respectively. From the viewpoint of diffusion process of PS, three kinds of network regions may be envisaged: one is the "open" region and exists commonly in Figure 5a,b. In this region, the diffusion of PS must be close to free one in solvent. In the second and the third regions in (a) and (b), respectively, however, PMMA network chains are entangled to different extents; in the second region (equivalent to the "dense region" in our previous studies),[27] diffusion of PS is substantially interfered with by the PMMA network. On the other hand, in the third region PS chains are not able to enter into the region due to the dense PMMA network structure. Thus, the present experimental result suggests that at the later stage of the phase separation PS molecules were excluded from such a concentrated PMMA network region because of the inherent incompatibility of the two polymers.

On the basis of the above supposed network structures, one may understand why the diffusion behavior of PS changed from a double-component mode to a single one with an increase in C_{PS}. This shows that in the first region PMMA chains are considerably dilute, and then PS molecules diffuse freely in some degree. Here, the fast diffusion component in samples 1, 2 and the single component in samples 3, 4 are both assigned

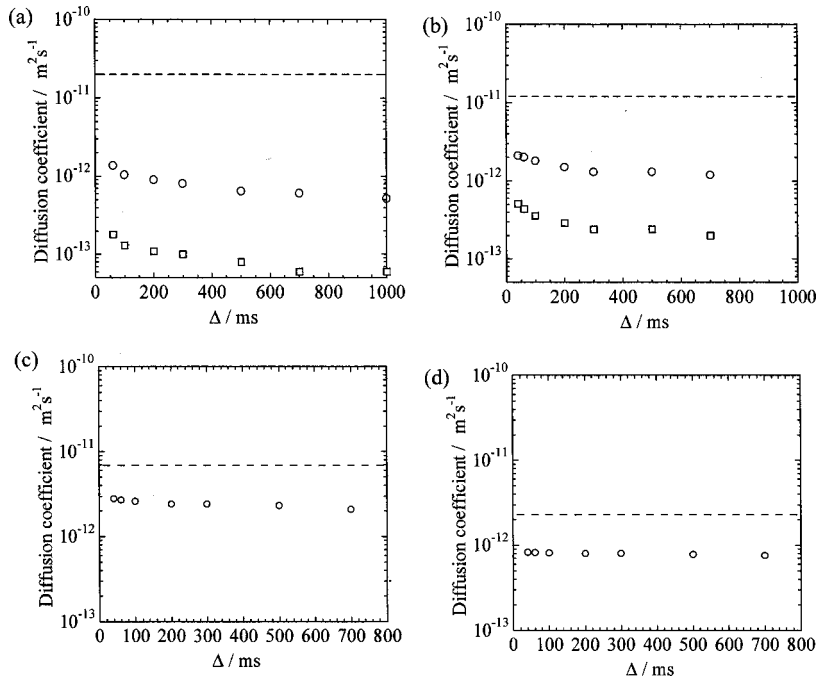

Figure 6. Δ dependence of diffusion coefficients of probe PSs (M_w = 400 000), where the broken line is the D of PS in deuterated toluene solution, the D of fast diffusion component of PS: in PMMA gel (○) and the D of slow component of PS (□) in PMMA gel [(a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4].

as the PS molecules in the first region. In the second region PS molecules are strongly confined or trapped. The PS molecules in the second region correspond to the slow diffusion component in samples 1 and 2. With further increase in C_{PS}, the second region changes to the third region, to which no PS molecules are accessible. Samples 3 and 4 showed only single-component diffusion. Although the third region is not directly detected by the diffusion experiments of the probe PS (M_w = 400 000), it should be quite reasonable to suppose it on the basis of the alteration of the diffusion mode with C_{PS}.

The same thing can be inferred from the component fraction data. The f_{slow} values of samples 1 and 2 are 0.45 and 0.23, respectively. The significant decrease in the slow component with increasing C_{PS} seems to be consistent with the supposed trend that the second region diminishes with the phase separation.

Dependence of Diffusion Coefficient of PS on the Diffusion Time Δ In order to elucidate the PS diffusion behavior in PMMA gel, the PGSE ^{1}H NMR measurements have been made with varying the diffusion time Δ. For samples 1 and 2, the diffusion coefficients for the fast and slow diffusion components (as indicated by D_{fast} and D_{slow}, respectively) and the corresponding fractions (f_{fast} and f_{slow}, respectively) were determined by using eq 3, and D_{fast} and D_{slow} are plotted in Figure 6a,b. The single diffusion coefficients of PS (D) for samples 3 and 4 were determined from the slope of the respective straight lines by eq 2. The diffusion coefficients are plotted in Figure 6c,d.

For samples 1 and 2, the respective fractions f_{fast} and f_{slow} are almost constant irrespective of different diffusion time Δ values. This means that PS chains corresponding to the fast and the slow diffusion components do not exchange within Δ. In other words, PS molecules are confined in the open region and the dense region, respectively, at least within Δ.

It is known that particles confined to any closed space undergo the so-called restricted diffusion.[37] When the size of the closed space is comparable to diffusion distance of particles during Δ, the diffusion of some particles is not "free" but "restricted". Thus, the measured diffusion coefficient becomes apparent and decreases as a function of Δ. In the system for samples 1 and 2, D significantly decreases with increasing Δ value (Figure 6a,b), which is typical for the restricted diffusion. PS chains in PMMA gel samples 1 and 2 are confined within the open region and the dense region within Δ. These experimental results seem to be consistent with the constant f values as well as with the scheme shown in Figure 5a. On the other hand, for samples 3 and 4, the diffusion is of single mode, and the Δ dependence of D values is much less significant compared with those for samples 1 and 2. This suggests that the diffusion of PS in the former samples is not a typical restricted diffusion. The "open" structure in gel samples is so much developed that PS molecules may enjoy almost a free diffusion. These experimental results seem to be just corresponding to the scheme as shown in Figure 5b.

Diffusion Behavior of Unreacted MMA in the PMMA Gels. Finally, we note the diffusion behavior of small molecules, i.e., unreacted MMA in PMMA gel matrix. Utilizing the vinyl peak of the unreacted MMA, PGSE ^{1}H NMR measurements on the small molecule diffusion were performed for PMMA gel samples 1−4 with varying Δ. The experimental data lie on a straight line in the Δ range from 60 to 500 ms, and the slope of the plots is independent of the diffusion time Δ. This clearly shows that the diffusion of the small molecule is a single mode and not restricted. The diffusion coefficient of MMA (D) as obtained from the slope of the straight line is also independent of the polymer concentration; for samples 1−4, D (10^{-9} m^2 s^{-1}) = 1.4, 1.5, 1.5, and 1.4, respectively. The constancy of the diffusion coefficient of the small probe means that the overall density of PMMA matrix in all the samples is also constant irrespective the difference in the phase transition level, since diffusion coefficients of probe molecules in gel matrix should depend on the matrix density.[15,17] On the other hand, with this small probe, inhomogeneities of PMMA gel samples were not detected from the diffusion behavior. These experimental results suggest that different levels of inhomogeneities of gel samples

can be detected by employing probe molecules having different sizes.

Conclusion

In our previous studies,[26,27] we reported that network structures of polymer gels, especially the microscopic inhomogeneity, may be detected through the diffusion behavior of probe molecules of different sizes which can be obtained by using the time-dependent diffusion NMR spectroscopy. In the present study, we have found that the same NMR procedure is available also to examine changes in the network inhomogeneity as resulted by macroscopic phase separation. The PS probe (M_w = 400 000), which is much larger than the mesh size, distinctly changed the diffusion behavior from the dual mode to the single one reflecting the course of the phase separation, while the small probe (MMA) was unable to detect the inhomogeneity change. Thus, our studies in series so far demonstrated that the time-dependent NMR method using probe molecules with different sizes is effective for structural analysis of gel network. In order to establish this procedure, however, diffusion behaviors of medium-size PS probes comparable to the gel mesh are also to be analyzed. In a subsequent paper, we report unique diffusion behaviors of the medium-size probes and establish the interrelation between the probe diffusion behaviors and the gel network structure.

Supporting Information Available: Diffusional stimulated echo attenuations of PSs and MMA and Δ dependence of f_{fast} and f_{slow}. This material is available free of charge via the Internet at http://pubs.acs.org.

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