Diffusional Behaviors of Polystyrenes with Different Molecular Weights in the Same PMMA Gel Network Elucidated by Time-Dependent Diffusion NMR Spectroscopy

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ABSTRACT: Diffusional behaviors of probe polystyrenes (PSs) with M_w = 4K, 19K, 29K, and 400K and chloroform as solvent were observed in the same PMMA gel matrix with the diffusing time varied (4−500 ms) by diffusing-time-dependent ^{1}H NMR in order to elucidate how the same gel network structure is differently detected by the probes with different sizes. The diffusion of the solvent and the smallest PS with M_w = 4K proved to be of a single mode, which is safely ascribed to the sufficiently small size of the probes compared with the network mesh (∼1.5 nm). The other PS molecules that should be larger than or comparable to the mesh size showed a multimode diffusional behavior, which was analyzed as a dual mode diffusion composed of a fast component and a slow one. Thus, those larger PS molecules were capable to "probe" the inhomogeneity for the mesh size distribution of the network. On the other hand, the so-called restricted diffusion or diffusing-time dependence for the diffusion coefficient D was observed only for the largest probe PS with M_w = 400K, and the fast diffusion component and the slow diffusion component with the diffusing time were recognized. This means that the PS chains were entrapped within a dense or an open structure during the measurement time, respectively. On the basis of these diffusion behaviors of probe molecules, the mesh and region sizes were estimated; for the open network structure the region size was scaled to be on the order of micrometers at least, while the mesh size of the dense region was to be larger than 1.5 nm and must be considerably smaller than 30 nm.

Introduction

Polymer gels have been employed as matrixes in solid-phase peptide synthesis, some catalysts, column chromatography, ion-exchange resins, and so on. Functionalities displayed by the above systems are closely associated with diffusional behaviors of molecules and structure of polymer gel systems which must be a function of network size and the distribution. Especially, the diffusion process of small molecules must be closely correlated with the matrix structure and the dynamics as reported by many papers.[1−3]

Recently, the diffusion of small molecules as a probe in polymer gel has been studied by means of the pulsed field-gradient (PFG) NMR method to find an interesting phenomenon that the probe diffusion is varied from single-component to multicomponent mode, depending on the structure of gel matrix, size of probe molecules, and the diffusing time of probe molecules.[4−7] In a previous work,[7] we prepared poly(methyl methacrylate) (PMMA) gels in the presence of polystyrene (PS) of different molecular weights in order to introduce a mesh size inhomogeneity into the cross-linked structure by utilizing the incompatibility of PMMA and PS. As expected, the network structure of the resultant gel samples prepared in the presence of larger PSs proved to be inhomogeneous, since the probe PS diffusion was successfully analyzed by a dual mode diffusion consisting of a fast mode and a slow one. The fast and the slow mode diffusions, in turn, must reflect that the PS molecules are moving through an "open" and a "dense" network structure, respectively. We have found that the inhomogeneity in the PMMA gel network thus detected was enhanced with increasing the probe PS size. This tendency, however, must be complex, since two separate effects may be involved there, namely, the presence of a larger PS would induce a more distinct inhomogeneity to the surrounding PMMA network during the cross-linking reaction and/or the diffusion of a larger PS may also be affected even by a larger mesh. In order to distinguish these two PS size effects for probing the gel inhomogeneity through PS diffusion, the following two kinds of measurements would be appropriate: (1) diffusion of one PS probe in differently prepared PMMA gels and (2) diffusion of different PS probes in one PMMA gel. Here, we are interested in how a same gel network is "seen" by PS probes of different sizes, rather than how they induce different network structures. Thus, in the present study we perform the second diffusion measurement to clarify the effect of the probe PS size on the diffusion through an inhomogeneous PMMA network. Further, in order to extend the "sight" of the probes than in the previous work,[7] the diffusing time(Δ) was widely varied in the range 40−500 ms. With this "time-dependent diffusion NMR", one may estimate the size of the open and the dense regions, respectively.

Experimental Section

Materials. Deuterated chloroform ($CDCl_3$) used as solvent was purchased from Merck Co. Methyl methacrylate (MMA) as monomer, 2,2′-azobis(isobutyronitrile) (AIBN) used as a polymerization initiator, and toluene 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 polystyrenes with a range of M_w from 4K to 400K were purchased from Polysciences, Inc. and Aldrich Chemical Co. The PSs have very narrow distribution of molecular weight (M_w/M_n = 1.04−1.09).

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In bulk $CDCl_3$ solution without gel matrix, all PSs have single diffusion component.

PMMA gels were prepared by free-radical copolymerization of MMA (1.4 mol/L) and EGDM (47.7 mmol/L) initiated by AIBN (4.6 mmol /L) in dehydrated toluene in the presence of PS (6 mg/mL) with M_w = 400K at 75 °C for 1 day.[2,3] The solution samples were deoxygenated by bubbling nitrogen gas for 10 min, and then gelation was carried out by incubating the sealed solution sample. Rodlike PMMA gel containing PS with M_w of 400K thus prepared were dried in vacuum for 6 h to remove off the remaining monomer and toluene. Dried PMMA gels were immersed in $CDCl_3$ for 24 h again to reach at equilibrium swelling. The swelling degree of the polymer gel (Q) is defined as the ratio of the mass of swollen polymer gel ($M_{swollen}$) to the mass of dried polymer (M_{dry}):

$$Q = M_{swolllen}/M_{dry} \tag{1}$$

The Q value of the PMMA gel used in this work was about 12.

The PMMA gel was employed as a common gel matrix for different PS probes with M_w of 4K, 19K, 29K, and 400K, which are indicated by PS(4K), PS(19K), PS(29K), and PS(400K), respectively. Preparation of gel samples containing one of the probe PSs was performed as follows. Before evacuating a gel sample that had contained PS(400K), the diffusion coefficient of PS(400K) was measured as a function of diffusing time Δ, as described below. Then, the PS molecules were all extracted by immersing the gel sample into pure $CDCl_3$, which was refreshed several times over ca. 2 months until the gel showed no PS signals on NMR spectrum. Next, the evacuated gel sample was immersed into a 1 wt % PS-(4K) solution in order to let the PS be absorbed in the gel. After the NMR measurement on the gel sample thus prepared, another evacuation−immersion (absorption)−NMR measurement cycle was repeated for the other PSs. The evacuation and absorption processes were accomplished in more than a few days. Although we attempted to immerse PS(50K) into the gel, 2 weeks immersion was proved to be in vain. Thus, measurements for larger PS probes except for PS(400K) could not be performed. Finally, the PMMA gel sample was immersed into pure $CHCl_3$ in order to measure the diffusion coefficient of the solvent $CHCl_3$.

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 ^1H with pulsed field-gradient generator (the maximum field-gradient strength: 11.6 T/m) by using a pulsed-field-gradient stimulated-echo (PFGStE) pulse sequence ($\pi/2$ pulse$-\tau_1-\pi/2-\tau_2-\pi/2$ pulse).[8−13] The spectral width and the number of data points are 2 kHz and 2048, respectively. The Δ, δ, and g values employed in these experiments are 40−500 ms, 0.04−2.0 ms, 0−10.0 T/m, respectively.

The D values were determined by using the relationship between echo signal intensities and field-gradient parameters

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

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 "diffusing time". The echo signal intensity was measured as a function of g. The plot of $\ln[A(g)/A(0)]$ against $\gamma^2g^2\delta^2(\Delta - \delta/3)$, that is, the Stejskal−Tanner plot, gives a straight line with a slope of $-D$ if the probe diffusion consists of a single component. Then, the D value can be determined from its slope.

If the probe diffusion consists of multicomponents, at least in the measurement time scale, the total echo attenuation is given by a superposition of contributions from the individual components.

$$\frac{A(g)}{A(0)} = \sum f_i \exp\left[-\gamma^2 g^2 D_i \delta^2\left(\Delta - \frac{\delta}{3}\right)\right] \tag{3}$$

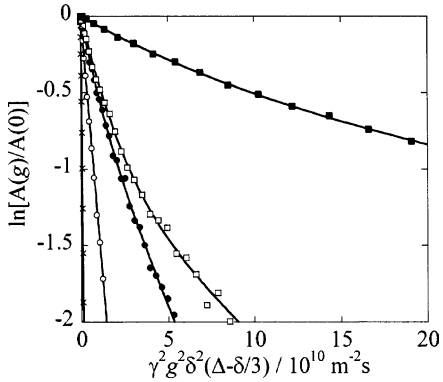

Figure 1. Diffusional stimulated echo attenuations of $CHCl_3$ (×) and PSs [PS(4K) (○), PS(19K) (●), PS(29K) (□), and PS(400K) (■)] in the PMMA gel with deuterated chloroform as solvent by varying field gradient strength g at room temperature with the diffusing time Δ = 40 ms.

where D_i is the diffusion coefficients of the ith component and f_i the fractional proton number of the ith component.

To determine D_i and f_i by solving eq 3, the diffusion process consisting of two components of the fast diffusion component and the slow diffusion component consists of components is assumed by

$$\frac{A(g)}{A(0)} = f_1 \exp\left[-\gamma^2 g^2 D_1 \delta^2\left(\Delta - \frac{\delta}{3}\right)\right] + f_2 \exp\left[-\gamma^2 g^2 D_2 \delta^2\left(\Delta - \frac{\delta}{3}\right)\right] \tag{4}$$

where $f_1 + f_2 = 1$. 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.

Further, we used the SPLMOD approach proposed by Johnson Jr.[13] to determine D_i and f_i by solving eq 3 in order to recognize reasonability of the above-mentioned conventional method used here. The SPLMOD approach is a method of doing inverse Laplace transform[14] of eq 3 method to determine D_i and f_i. In this approach the initial guesses are not required, and then the diffusion coefficient(s) and the fraction(s) of polymer gel system with the one, two, and three diffusion components are automatically determined. The obtained D_i and f_i values were compared with those the conventional method. It will be shown below that the two approaches give almost the same results within experimental errors.

Results and Discussion

Diffusional Behavior of PSs in the PMMA Gel. Figure 1 shows the experimental results according to eq 2 at Δ = 40 ms. The linear lines for the solvent and PS(4K) correspond to a single-mode diffusion, while the curved plots of the other systems (PS(19K), PS(29K), and PS(400K)) mean that the diffusion was of multimode. Here, we analyzed the multimode diffusion as a two-component (dual-mode) diffusion.

The diffusion coefficients (D, D_{fast}, and D_{slow}) and the fractions were estimated respectively by eq 2 or 3. Obtained D and f values are listed in Table 1 together with diffusion coefficients in the bulk solution (D_0). The molecular weight dependence of the D values of PS probes is shown in Figure 2. The observed decreasing tendency of the D values with M_w, being accompanied by transition from single-mode to dual-mode diffusion, demonstrates that the probe diffusion is affected or obstructed by gel matrix to different extents depending on the probe size, as discussed in the previous work.

Namely, the mobility of PS molecules may reflect the difference in the surrounding network density when the probe size is larger than a critical size, which must be comparable to the network mesh of the dense region. This can be seen from the markedly large difference in the fast and slow diffusion

Table 1. Diffusion Coefficients of Probe Molecules in the PMMA Gel Estimated by the PFGStE ^{1}H NMR Method

	$CHCl_3$	PS (M_w = 4K)	PS (M_w = 19K)	PS (M_w = 29K)	PS (M_w = 400K)
D_0 (m^2/s)	2.4×10^{-9}	$2.7 \times 10^{-10} \pm 0.2 \times 10^{-11}$ ($R_h \sim 1.5$ nm)	$1.6 \times 10^{-10} \pm 0.1 \times 10^{-11}$ ($R_h \sim 2.5$ nm)	$9.4 \times 10^{-11} \pm 0.6 \times 10^{-12}$ ($R_h \sim 4.3$ nm)	$1.3 \times 10^{-11} \pm 0.1 \times 10^{-12}$ ($R_h \sim 31$ nm)
D (m^2/s) in PMMA gel synthesized in the presence of PS(400K)	$1.9 \times 10^{-9} \pm 0.3 \times 10^{-11}$	$1.4 \times 10^{-10} \pm 0.2 \times 10^{-11}$	D_{fast} $1.2 \times 10^{-10} \pm 0.3 \times 10^{-11}$ ($f_{fast} = 0.35 \pm 0.04$) D_{slow} $2.9 \times 10^{-11} \pm 0.1 \times 10^{-11}$ ($f_{slow} = 0.65 \pm 0.04$)	D_{fast} $8.0 \times 10^{-11} \pm 0.2 \times 10^{-11}$ ($f_{fast} = 0.56 \pm 0.03$) D_{slow} $1.3 \times 10^{-11} \pm 0.6 \times 10^{-12}$ ($f_{slow} = 0.44 \pm 0.03$)	D_{fast} $1.3 \times 10^{-11} \pm 0.4 \times 10^{-12}$ ($f_{fast} = 0.34 \pm 0.04$) D_{slow} $2.1 \times 10^{-12} \pm 0.2 \times 10^{-12}$ ($f_{slow} = 0.66 \pm 0.04$)
D^a (m^2/s) in PMMA gel synthesized in the presence of the probe PS		$1.6 \times 10^{-10} \pm 0.1 \times 10^{-11}$	$6.4 \times 10^{-11} \pm 0.8 \times 10^{-12}$	D_{fast} $9.5 \times 10^{-11} \pm 0.2 \times 10^{-11}$ ($f_{fast} = 0.51 \pm 0.06$) D_{slow} $2.0 \times 10^{-11} \pm 0.2 \times 10^{-11}$ ($f_{slow} = 0.49 \pm 0.06$)	D_{fast} $1.3 \times 10^{-11} \pm 0.4 \times 10^{-12}$ ($f_{fast} = 0.34 \pm 0.04$) D_{slow} $2.1 \times 10^{-12} \pm 0.2 \times 10^{-12}$ ($f_{slow} = 0.66 \pm 0.04$)

[a] Values obtained in our previous work (ref 7).

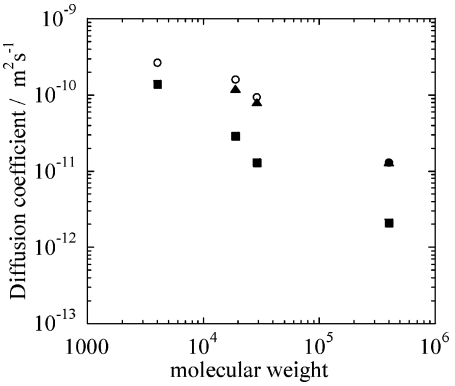

Figure 2. M_w dependence of diffusion coefficients of probe PSs: (○) in deuterated chloroform solution, (▲) fast diffusion component of PS in PMMA gel, (■) slow diffusion component in PMMA gel.

coefficients in Table 1, which were ascribed to those in the open and the dense region, respectively.

According to our previous work,[7] the network size inhomogeneity of PMMA gel was enhanced with increasing the PS M_w; in other words, the most homogeneous network was obtained by PS-free cross-linking. In the case of PMMA gel that was prepared in the presence of PS(400K) (sample 7 in the previous work), microphase separation was to be induced at the initial stage of the polymerization cross-linking reaction of MMA by the presence of such a large PS chains incompatible with PMMA, which seemed to result in the more inhomogeneous network. Thus, it should be interesting to compare the present D values with those obtained in the respective original gel matrix, namely, gels prepared in the presence of the respective probe PSs. Table 1 also contains the data that were estimated with the same analysis. It can be seen that the present D values for PS(4K) and PS(29K) are somewhat lower than those for the original gels. This seems to indicate that the network prepared in the presence of PS(400K) is more inhomogeneous, namely, the dense region is more developed and/or the dense mesh is finer, compared with those prepared in the presence of PS probes of lower molecular weights.

Further, it should be noted here that D_{fast}/D_0 values increase with M_w of PSs. This curious result means, at least apparently, that obstruction by the PMMA network of the open region becomes less significant for larger PS probes. However, this may be a reflection of averaging the "sight" of the probe molecules. Namely, a smaller probe PS can also "see" (or experience) the region of far site. Then, a small probe in an open region may also see a denser region, thus resulting in smaller D_{fast} values and vice versa. The smaller probe molecules may diffuse without appreciable obstruction in the polymer matrix, even in the dense region, because of their small size. Thus, the mesh size of the dense region must be larger than the hydrodynamic radius of PS(4K), $R_h \sim 1.5$ nm (Table 1). The largest probe PS (400K) differently "sees" the open and the dense region. The much smaller D_{slow} than D_{fast} may be partly ascribed to the large size of the probe PS(400K). This means that the mesh size of the dense region must be significantly smaller of the R_h, 31 nm (Table 1). These points will be discussed in more detail in the next section.

Dependence of Diffusion Coefficient on the Diffusing Time Δ. We have carried out the PFGStE NMR measurements of solvent ($CHCl_3$) and PS (M_w = 4K, 19K, 29K, and 400K) in the same PMMA gel matrix with the diffusing time varied (4−500 ms). For the results of the $CHCl_3$ with the diffusing time Δ varied from 4 to 300 ms, all the data obtained with different Δ values are on a straight line. This means that the diffusion coefficient of the solvent and its diffusion behavior do not change within the diffusing time.

Figure 3 shows the corresponding results for the PS probes obtained with Δ vales from 40 to 500 ms. All the PS probes except for PS(400K) showed a comparable tendency with the solvent. Although the experimental data in the cases of PS(19K) and PS(29K) were slightly scattered, they are not systematic and may be expressed with a single curve, as shown in the figure. Namely, the multimode diffusion of the three PS probes may be approximated with the same pair of diffusion coefficients, being independent of the diffusing time employed. On the other hand, the result of PS(400K) was distinctly different from the others above; the experimental data for different Δ vales are on different curves. In the Figure 3d, slopes of the plots of PS(400K) decrease with an increase in the diffusing time in the range 40−500 ms. Namely, the restricted diffusion was observed only for PS(400K). These results suggested that the diffusion mechanism of PS(400K) differ from that of the other PSs.

Before going ahead, here, we will discuss the D values obtained by the conventional method with assumption of the two diffusion components judging from the Stejskal−Tanner plot and the SPLMOD method by Johnson Jr.[13] as summarized for PS(400K) in Table 2. It is recognized that the determined D and f results were in good agreement with each other. This means that two approaches for the present polymer gel systems are reasonable to determine the D and f values.

We can see from Table 2 that D_{fast} and D_{slow} decrease with an increase in Δ, and the former decrement is much smaller than the latter. The decreasing tendency of the diffusion coefficient with diffusing time suggests that the so-called

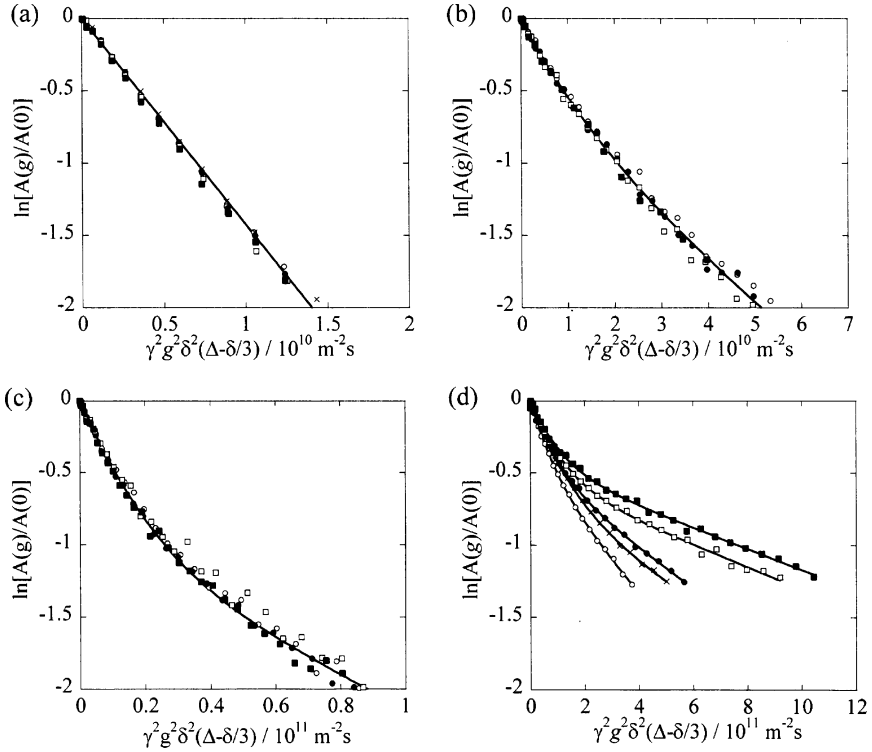

Figure 3. Diffusional stimulated echo attenuations of PSs in the PMMA gel [(a) PS(4K), (b) PS(19K), (c) PS(29K), and (d) PS(400K)] with deuterated chloroform as solvent by varying field gradient strength g at room temperature. The diffusing time was varied as $\Delta = 40$ ms (○), $\Delta = 60$ ms (×), $\Delta = 100$ ms (●), $\Delta = 300$ ms (□), and $\Delta = 500$ ms (■).

Table 2. Diffusion Coefficients of Probe PS with $M_w = 400\,000$ in the PMMA Gel as a Function of Diffusing Time by the PFGStE ^{1}H NMR Method

diffusing time Δ (ms)		diffusion coefficient ($m^2\,s^{-1}$)	fraction of diffusion component	diffusion distance (μm)
		by SPLMOD		
40	D_{fast}	1.4×10^{-11} ($\pm 0.1 \times 10^{-11}$)	0.35 (±0.03)	1.1
	D_{slow}	2.3×10^{-12} ($\pm 0.2 \times 10^{-12}$)	0.66 (±0.03)	0.4
60	D_{fast}	0.9×10^{-11} ($\pm 0.1 \times 10^{-11}$)	0.46 (±0.05)	1.0
	D_{slow}	1.7×10^{-12} ($\pm 0.2 \times 10^{-12}$)	0.54 (±0.05)	0.5
100	D_{fast}	1.2×10^{-11} ($\pm 0.6 \times 10^{-12}$)	0.37 (±0.01)	1.5
	D_{slow}	1.4×10^{-12} ($\pm 0.5 \times 10^{-13}$)	0.64 (±0.01)	0.5
300	D_{fast}	1.0×10^{-11} ($\pm 0.5 \times 10^{-12}$)	0.41 (±0.01)	2.4
	D_{slow}	0.8×10^{-12} ($\pm 0.4 \times 10^{-13}$)	0.59 (±0.01)	0.7
500	D_{fast}	1.0×10^{-11} ($\pm 0.9 \times 10^{-12}$)	0.35 (±0.02)	3.2
	D_{slow}	0.7×10^{-12} ($\pm 0.4 \times 10^{-13}$)	0.64 (±0.02)	0.8
		by conventional method (assumed two components)		
40	D_{fast}	1.3×10^{-11} ($\pm 0.4 \times 10^{-12}$)	0.34 (±0.04)	1.0
	D_{slow}	2.1×10^{-12} ($\pm 0.2 \times 10^{-12}$)	0.66 (±0.04)	0.4
60	D_{fast}	1.2×10^{-11} ($\pm 0.5 \times 10^{-12}$)	0.47 (±0.02)	1.2
	D_{slow}	1.6×10^{-12} ($\pm 0.8 \times 10^{-13}$)	0.63 (±0.02)	0.4
100	D_{fast}	1.2×10^{-11} ($\pm 0.1 \times 10^{-12}$)	0.37 (±0.02)	1.5
	D_{slow}	1.4×10^{-12} ($\pm 0.6 \times 10^{-13}$)	0.63 (±0.02)	0.5
300	D_{fast}	1.2×10^{-11} ($\pm 0.3 \times 10^{-12}$)	0.37 (±0.01)	2.7
	D_{slow}	0.84×10^{-12} ($\pm 0.3 \times 10^{-13}$)	0.63 (±0.01)	0.7
500	D_{fast}	1.1×10^{-11} ($\pm 0.4 \times 10^{-12}$)	0.35 (±0.01)	3.3
	D_{slow}	0.7×10^{-12} ($\pm 0.2 \times 10^{-13}$)	0.65 (±0.01)	0.8

"restricted diffusion" occurs in this system. In other words, the PS chains are confined in the open or the dense region during the diffusion, and any appreciable transverse across the two regions does not occur. Namely, if the coming-in and going-out of the probe between the two regions freely occurred, the observed diffusion parameters must be independent of the diffusing time, which was actually observed for the smaller PS probes. The time-dependent decrease in the D values thus observed for PS(400K) may be safely ascribed to the significantly larger molecular size (31 nm) compared with the approximate mesh size (3.4 nm) of the network at equilibrium swelling that is roughly estimated by using the fraction of EGDM cross-linking, as shown in Table 1. For this approximately network mesh size estimation, the effect from chain entanglements was disregarded.

The above discussion may be quantitatively reconsidered in terms of diffusion distance, which would give us an estimate of dimension of the dense and the open regions. The diffusion coefficient D can be related with the mean-square displacement $\langle z^2 \rangle$ in the z direction from the starting point after the diffusion time Δ by the following equation

$$\langle z^2 \rangle = 2Dt \tag{5}$$

where t is equal to Δ. The $\langle z^2 \rangle$ value gives us information on the diffusion distance d that reflects the experimental results as expressed by the following equation:

$$d = \sqrt{\langle z^2 \rangle} = \sqrt{2Dt} \tag{6}$$

Consequently, by substituting the D values of PS(400K) determined at $\Delta = 40$, 60, 100, 300, and 500 ms into eq 6, the diffusion distances are obtained to be shown as Table 2. The d values in these experiments are much larger than the averaged mesh size (3.4 nm) at equilibrium swelling. Therefore, as seen from the obtained d values, it can be said that PS chains are going through many network mesh cells within the diffusing time Δ.

As above-mentioned, the D_{slow} values significantly decrease with an increase in Δ, whereas the D_{fast} values only slightly decreases. The latter means that the "open" network structure is so large (probably order of 10^{-5} m) that PS chains "see" a matrix with almost the same mesh size during the diffusion time or actually confined within the open region. On the other hand, the former corresponds to a situation that the pertinent PS molecules are confined, or trapped, within the dense network structure. Because the estimated diffusion coefficients are only apparent, namely, the nominal diffusion distance is limited up to the local size of the dense region within which the probe was entrapped, then the size of the confinement must be comparable to the estimated diffusion distance ($\sim 10^{-6}$ m), during the diffusion time Δ.

Further, the f_{fast} and f_{slow} are almost constant irrespective of different diffusing time Δ. This experimental fact means that PS chains in the open and larger size region and the dense and smaller size one do not exchange within the Δ range from 40 to 500 ms. This is also consistent with the supposed confinement of the PS probe within the open and the dense regions during the diffusing time.

The relation between the determined D values and the diffusing time Δ is summarized for the respective probe molecules as follows. In the case of the smallest probe molecules, $CHCl_3$ and PS(4K), which must be smaller than the network mesh size of the dense region, the probe diffusion at $\Delta \approx 0$ is, in principle, divided into two classes: one is fast diffusion in the open region, and the other is slow diffusion in the dense region. There, each of the probe diffusions does not recognize the network mesh but feels the polymer chain only as an obstacle. For $\Delta > 0$, $CHCl_3$ and PS(4K), which are smaller than the network mesh size, can move through the gel network rather freely. This enables a prompt averaging of the initial two components diffusion into the single-component one within the shortest diffusing time of the present PFG-NMR experiment (4 or 40 ms).

In the case of medium-size probes, PS(19K) and PS(29K), which are moderately larger than the network mesh. Consequently, probe diffusion in the dense region recognizes each network mesh and has a broad distribution of diffusion coefficients corresponding to the distribution of gel network. Averaging of the two components diffusion (fast diffusion in the open region and slow diffusion that has a broad distribution of diffusion coefficients in dense region) into the single component needs a considerably long time in comparison with experimental diffusing time of the PFG-NMR experiments. For that reason, its diffusion behavior apparently does not change within diffusing time.

The largest probe PS (400K), which must be much larger than the mesh size of the dense region, also keeps the two-component diffusion. In this case, however, the diffusion components are confined in the dense and the open regions. They do not exchange within the diffusing time scale. This confinement is, of course, to be ascribed to the mesh fineness, much smaller than the probe PS size. Thus, no significant changes in D values, which must be caused by such exchange, were observed within several hundreds of milliseconds.

Theoretically, the diffusional behaviors of probe molecules in gels have been interpreted by polymer dynamics model theories: Rouse dynamics, medium region dynamics (for example, entropic trapping model), and reptation dynamics.[15] In this stage, we could not really refer our experimental results to polymer dynamics model theories. Then, more detailed studies referring to polymer dynamics model theories in similar gel systems will be done in the future.

In conclusion, we have presented a systematic way to estimate mesh sizes and region sizes, each of which has a population in heterogeneous gel matrix, by utilizing a set of probe molecules of different sizes together with the time-dependent diffusion NMR spectroscopy. This methodology may be generally developed to examine and establish the gel structure and the diffusion behaviors of small molecules for many complex systems including biological ones.

References and Notes

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