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Diffusion of probe polystyrenes with different molecular weights in poly(methyl methacrylate) gels and inhomogeneity of the network structure as studied by time-dependent diffusion NMR spectroscopy

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Abstract

Poly(methyl methacrylate) (PMMA) gels have been prepared with radical polymerization by cross-linking methyl methacrylate monomer using 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 in the PMMA gels swollen in deuterated chloroform have been measured by pulsed field-gradient (PFG) ^{1}H NMR method with the diffusing time Δ varied. From the experimental results, it is found that the network structure of PMMA gels prepared in the presence of PSs with $M_w = 4000$ and 400,000 are relatively homogeneous and inhomogeneous, respectively, within the Δ range from 40 to 500 ms.

Keywords: Polymer gel; Diffusion; Field gradient NMR

1. Introduction

Polymer gels are generally inhomogeneous for the network size, and properties of polymer gels naturally depend on their spatial inhomogeneity. The existence of spatial inhomogeneity has been detected by light scattering as speckles [1,2]. As for chemically-crosslinked polymer gels, the relationship between speckles and spatial inhomogeneity has been elucidated [3–8].

On the other hand, network size and its distribution of polymer gels have also been studied through the diffusional behavior of probe molecules in the gel phase [9–13], since the diffusion of probe molecules is greatly affected by intermolecular interactions of probe molecules with polymer network. Most recently, Yamane et al. have elucidated inhomogeneity of network size for a polystyrene gel [14] and poly(acrylic acid) gels [15] through the diffusional behavior of probe low molecular weight molecules such as amino acids in the relevant gel by using time-dependent diffusion NMR, and have demonstrated that it is an excellent means for obtaining information about inhomogeneity of network size for the polymer gels. It is known that pulsed-field-gradient (PFG) NMR method [16–20] is a powerful technique for studying diffusion in polymer systems [14,15,21–33]; PFG ^{1}H NMR method enables us to estimate the diffusion coefficients of key probe molecules in a polymer network by varying the interval time between two field-gradient pulses (Δ) in the pulsed-field-gradient spin-echo (PFGSE) or pulsed-field-gradient stimulated-echo (PFGStE) pulse sequence corresponding to the diffusing time of probe molecules [11,14,15,34].

From such a background, in this work we aim to prepare poly(methyl methacrylate) (PMMA) gels that have different levels of inhomogeneities for the network size, and try to characterize the inhomogeneity through observation of the diffusion coefficients of probe molecules in the polymer gels by PFGStE ^{1}H NMR method. The series of inhomogeneities are to be introduced to the gel by preparing the PMMA network in the presence of polystyrenes (PSs) with a wide range of M_w (4000, 19,000, 29,000, 50,000, 170,000, 400,000), because PMMA is incompatible with PS. Thus, the respective incorporated PSs are conveniently employed as the probe molecules to investigate the intentionally formed inhomogeneous network.

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2. Experimental

2.1. Materials

Deuterated chloroform used as the immersing solvent was purchased from Merck Co. Methyl methacrylate (MMA) as monomer, 2,2′-azobisisobutylonitrile (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 (PSs) with a range of M_w from 4000 to 400,000 were purchased from Polysciences, Inc. and Aldrich Chemical Co.

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 absence of PS[PMAA gel sample 1], and in the presence of PS with M_w = 4000, 19,000, 29,000, 50,000, 170,000 or 400,000 [PMMA gel sample 2–7, respectively] at 75 °C for 1 day [10,35]. In these experiments, the PS concentrations were set at 20, 10, or 6 mg/mL, for sample 2, samples 3–6, and sample 7, respectively, so as to be retained under the overlap concentration of the PSs in the solution [36]. The seven solution samples were deoxygenated by bubbling nitrogen gas for 10 min, and then gelation was carried out by incubating the sealed solution samples. Rod-like PMMA gels containing PS 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})

$$Q = \frac{M_{swollen}}{M_{dry}} \tag{1}$$

The Q values of all PMMA gels used in this work were about 12.

2.2. 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-τ_1-$\pi/2$-τ_2-$\pi/2$ pulse) [16,17]. The spectral width and the number of data points are 6 kHz and 2048, respectively. The D values were determined by using the relationship between echo signal intensities and field-gradient parameters:

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

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, and Δ the gradient pulse interval which is the so-called 'diffusing time'. The echo signal intensity was measured as a function of g. A plot of $\ln[A(g)/A(0)]$ against $\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$, that is, 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 two components, at least in the measurement timescale, the total echo attenuation is given by a superposition of contributions from the individual components.

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

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. The Δ, δ and g values employed in these experiments are 40–500 ms, 0.04–2.0 ms, 0–11.0 T/m, respectively.

3. Results and discussion

3.1. PFGStE ^1H NMR spectra and their assignments

Typical PFGStE ^1H NMR spectra of PMMA gel sample 2 containing probe PS with $M_w = 4000$ and $CDCl_3$ at room temperature are shown as a function of the field-gradient strength (g) in Fig. 1. The spectral assignments are straightforwardly made by using reference data of PS, PMMA and $CHCl_3$ that is contained in commercial $CDCl_3$ as an isotope impurity. All of the peaks are numbered from downfield to upfield. Peak 1 overlaps with two peaks coming from the o-phenyl protons of PS and $CHCl_3$. Peak 2 comes from the m- and p-phenyl protons of PS. Peak 3, the most intense one, is assigned to the methoxy protons of PMMA. Peaks 4–7 are assigned to the main chain protons of PS and PMMA as indicated in Fig. 1. From these spectra, it is seen that the intensities of peaks for PS and $CHCl_3$ decayed with an increase in the field-gradient strength. This means that PS and $CHCl_3$ are diffusing in the PMMA network. On the other hand, the intensities of peaks for PMMA network chains do not decay. This is natural because the PMMA network chains are only undergoing fast random fluctuations and its displacement is extremely small. From the plots of $\ln[A(g)/A(0)]$ against

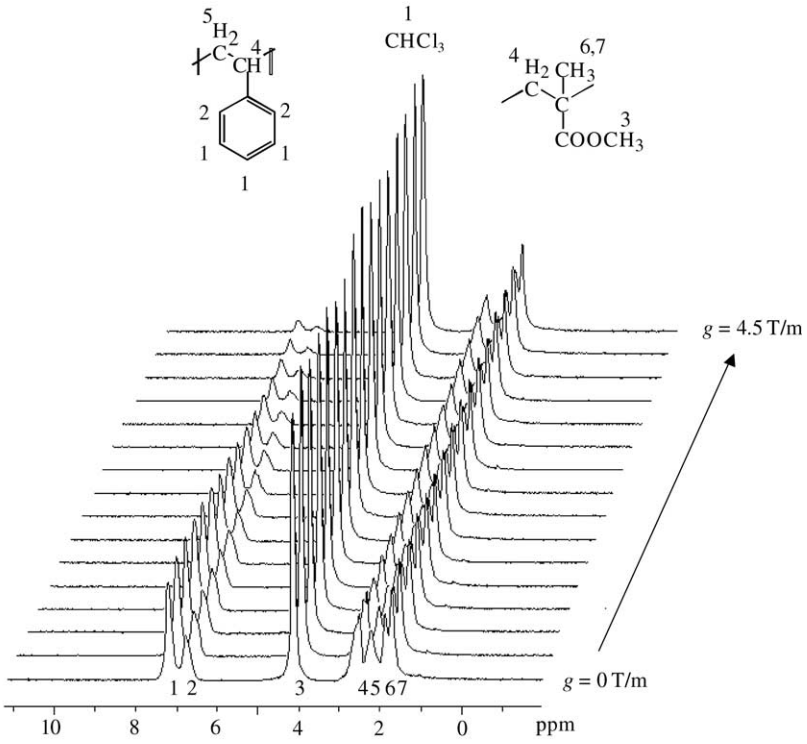

Fig. 1. PFGStE ^{1}H NMR spectra of PMMA gel[PMMA gel sample 2] containing PS with $M_w = 4000$ and $CDCl_3$ by varying field gradient pulse strength (g). The solvent contains a very small amount of $CHCl_3$ as impurity.

$\gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ for the PS phenyl peak at 6.6 ppm, the diffusion coefficient can be determined as described below.

3.2. Diffusional behavior of PSs in the PMMA gels

We carried out PFGStE ^{1}H NMR experiments for PMMA gel samples at the diffusing time of $\Delta = 40$ ms and observed diffusional behavior of PSs in the PMMA gels. Fig. 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 PSs in PMMA gels[PMMA gel samples 1–7] and PS in $CDCl_3$ solution. In Fig. 2(a) and (b), the data for PSs in PMMA gel samples 2 and 3 reasonably lie on a straight line in the Stejskal-Tanner plot. It can be said that the network of the PMMA gels is homogeneous in the Δ timescale. However, in Fig. 2(c)–(g), the data for PSs in PMMA gel samples 4–7 (open triangle data) appreciably deviate from a straight line. As shown later, these data were successfully analyzed in terms of Eq. (3). Namely, the diffusion of the PSs within these gel samples consists of two components, fast and slow ones. This strongly suggests that PMMA samples 2–7 contain, at least, two kinds of network structures, e.g. open and dense ones.

To confirm that the two-component-decay is originated from such an inhomogeneity introduced by PS that was present during the gel-forming process, we also examined the diffusional behaviors of PSs in PMMA sample 1. A PMMA sample 1, which was prepared without PS, was placed in deuterated chloroform solution of PSs with $M_w = 4000$ and 29,000, respectively, for two weeks to allow the PSs to penetrate into the PMMA gel. In Fig. 2(a) and (c), the open square data are for the PS echo decay in the PMMA gel prepared in the absence of PS. As seen from Fig. 2(a) and (c), the open square data lie reasonably on a straight line in the Stejskal–Tanner plot. Therefore, it can be said that the network of the PMMA gel prepared without PS is homogeneous in the Δ timescale. Consequently, it is apparent that the addition of PS with $M_w =$ 29,000 leads to inhomogeneity for the relevant PMMA gel.

Actually, it is well known that blends of PS and PMMA are miscible at low molecular weight, but become immiscible at high molecular weight [37–40]. Kuhn et al. [37,38] reported that PMMA and PS in benzene solution would become incompatible with increasing both or either of the molecular weights, while no appreciable phase separation was observed at least for a combination of PS with $M_w = 2.07 \times 10^4$ and PMMA with $M_w = 1.6 \times 10^6$. The latter finding seems to be consistent with the present result for the PMMA gel sample 3. Callaghan et al. [39] reported that when M_w of PS and PMMA were 2950 and 2400, respectively, the binary blends were completely miscible, while phase separation occurred when either or both M_w of PS and PMMA were increased, and the phase boundaries were predicted to be caused by the UCST-type behavior. In the present study, since PMMA gels were prepared in the presence of PS, it is expected that micro or macro phase separation occur in the gelation process; consequently, inhomogeneities are introduced to the gel. The effect of PS's M_w on the formation of network in the PMMA gel will be explained as follows. Since M_w of PMMA gradually becomes increased with the progress of polymerization in the gelation process, the lager the M_w of PS, the earlier the phase separation starts and the more inhomogeneous structure will be introduced to the gel, and vice versa.

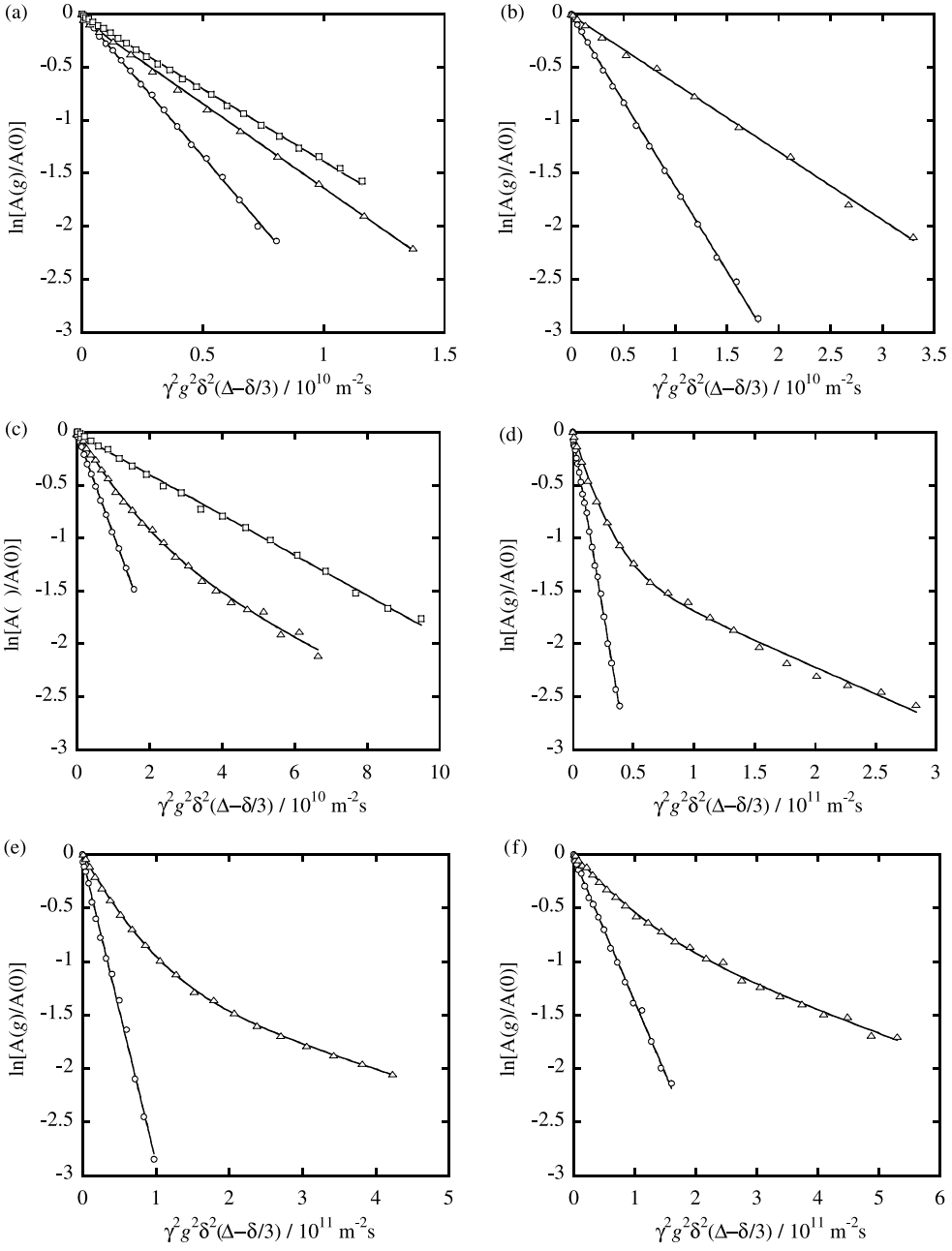

Fig. 2. Diffusional stimulated echo attenuations of PSs with different M_ws in PMMA gels[PMMA gel samples 1–7] with $CDCl_3$ as solvent, respectively, and PS in $CDCl_3$ solution by varying field gradient strength g. (○) PS in $CDCl_3$ solution; (□) in PMMA gel prepared without PS[PMMA gel sample 1]; (△) in PMMA gels prepared with PS[PMMA gel samples 2–7]; M_ws of PSs are (a) 4000, (b) 19,000, (c) 29,000, (d) 50,000, (e) 170,000 and (f) 400,000.

3.3. Dependence of diffusion coefficient on the diffusing time Δ

The PFGStE ^{1}H NMR measurements have been made for PMMA gel samples 1 and 7 containing PS with $M_w = 4000$ and 400,000, respectively, at room temperature with varying the diffusing time Δ, in order to investigate the diffusional behavior of PS in PMMA gels and the PMMA gel network structure. Fig. 3 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 $M_w = 4000$ in PMMA gel sample 2 by varying Δ. It is shown that the experimental data lie on a straight line in the Δ range from 40 to 500 ms, and the slope of the plots is independent of the diffusing time Δ. This shows that PS with $M_w = 4000$ in PMMA gel sample 2 has a single diffusion component during the diffusing time Δ in the range from 40 to 500 ms. It can be said that the network-size of PMMA gel sample 2 is homogeneous in the Δ timescale. The diffusion coefficient of PS (D) is determined from the slope of a straight line by using Eq. (2) as 1.6×10^{-10} m^2/s. Thus, the D/D_0 value, where D_0 is the diffusion coefficient of PS in $CDCl_3$ solution at the same polymer concentration as PMMA gel sample 2, is a constant, 0.6, in the Δ range from 40 to 500 ms. Therefore, it can be said that the translational diffusion of PS in the PMMA gels is significantly restrained due to intermolecular interactions

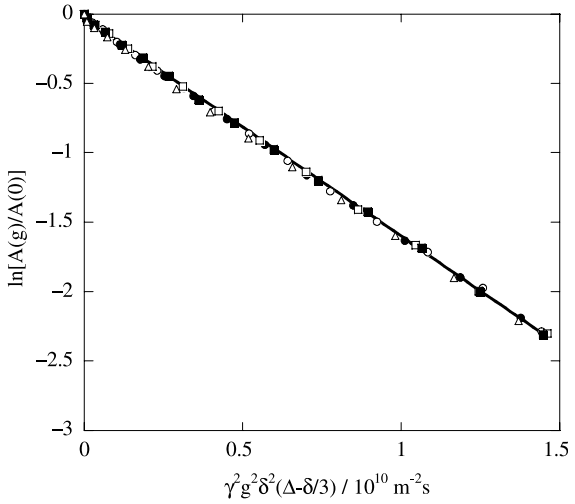

Fig. 3. Diffusional stimulated echo attenuation of PS (M_w = 4000) in PMMA gel sample 2 with $CDCl_3$ as solvent by varying field gradient strength g at room temperature, where Δ = 40 ms (○), Δ = 60 ms (●), Δ = 100 ms (□), Δ = 300 ms (■) and Δ = 500 ms (△).

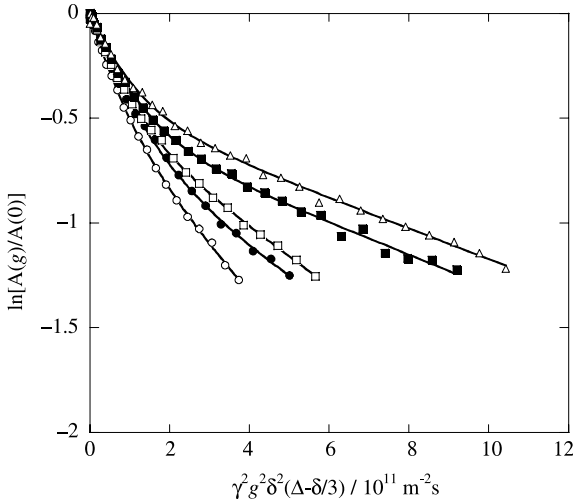

Fig. 4. Diffusional stimulated echo attenuation of PS (M_w = 400,000) in PMMA gel sample 7 with $CDCl_3$ as solvent by varying field gradient strength g at room temperature, where Δ = 40 ms (○), Δ = 60 ms (●), Δ = 100 ms (□), Δ = 300 ms (■) and Δ = 500 ms (△).

between PS and the PMMA network, and/or the simple obstruction by PS.

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.

$$\langle z^2 \rangle = 2Dt \tag{4}$$

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.

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

Consequently, by substituting the D values determined at Δ = 40, 60, 100, 300 and 500 ms into Eq. (5), the corresponding diffusion distances d can be obtained to be 3.6, 4.7, 5.7, 9.8 and 12.6 μm, respectively. The d values in these experiments are much larger than the network size (4 nm) at equilibrium swelling that is approximately estimated by using the fraction of EGDM cross-linking. Therefore, as seen from the obtained d values, it can be said that PS chains are going through some network cells within the diffusing time Δ.

Fig. 4 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 (M_w = 400,000) in PMMA gel sample 7 with $CDCl_3$ as solvent. It is shown that the experimental data do not lie on a straight line at Δ = 40, 60, 100, 300 and 500 ms. These data proved to be successfully analyzed in terms of Eq. (3). Namely, this means that PS with M_w = 400,000 in the PMMA gel has two diffusion components such as the fast diffusion component and the slow diffusion component in the Δ range from 40 to 500 ms. 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) that were determined by using Eq. (3) are listed in Table 1. As seen from Table 1, the D_{fast}/D_0 only slightly changes from 0.92 to 0.85 while the D_{slow}/D_0 significantly decreases from 0.17 to 0.06, with increasing the Δ value. On the other hand, the fractions, f_{fast} and f_{slow}, are independent of Δ. By substituting the D values determined at Δ = 40, 60, 100, 300 and 500 ms into Eq. (5), the diffusion distances for the fast diffusion component (d_{fast}) are obtained to be 1.0, 1.2, 1.5, 2.6 and 3.3 μm, respectively, and the diffusion distances for the slow diffusion component (d_{slow}) to be 0.4, 0.4, 0.5, 0.7 and 0.9 μm, respectively.

On the basis of these experimental results, we may obtain information on the network structure of the PMMA gel. First we note that D_{fast}/D_0 is close to unity and significantly larger than that for the PS with M_w = 4000 in spite of the much larger radius of gyration for the former than the latter. This means that the diffusion of PS with M_w = 400,000 is subject to relatively weaker restriction via intermolecular interactions with the PMMA gel network. On the other hand, the much lower D_{slow}/D_0 values indicate that the PMMA gel sample 7 contains highly dense network structures as probed by the PS with M_w = 400,000.

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' almost

Table 1
Determined diffusion coefficients of probe PS with M_w = 400,000 in PMMA gel sample 7 as a function of diffusing time by PFGStE ^{1}H NMR method

Diffusing time Δ (ms)		Diffusion coefficient (m^2 s^{-1})	D/D_0	Fraction of diffusion component
40	D_{fast}	1.2×10^{-11}	0.92	0.34
	D_{slow}	2.2×10^{-12}	0.17	0.66
60	D_{fast}	1.2×10^{-11}	0.92	0.34
	D_{slow}	1.7×10^{-12}	0.13	0.66
100	D_{fast}	1.2×10^{-11}	0.92	0.36
	D_{slow}	1.4×10^{-12}	0.11	0.64
300	D_{fast}	1.1×10^{-11}	0.85	0.35
	D_{slow}	0.9×10^{-12}	0.07	0.65
500	D_{fast}	1.1×10^{-11}	0.85	0.35
	D_{slow}	0.7×10^{-12}	0.06	0.65

the same structure during the diffusion time. On the other hand, the former may be realized if the pertinent PS molecules are confined, or trapped, within the dense network structure, the size of which is comparable to the estimated diffusion distance ($\sim 10^{-6}$ m), during the diffusion time Δ; namely, the estimated diffusion coefficients must be only apparent because the diffusion distance is limited up to the local size of the dense structure.

Further, from the experimental finding that the f_{fast} and f_{slow} are almost constant irrespective of different diffusing time Δ, it can be said that PS chains in the open and large-size and the dense and small-size network structures, which are corresponding to the fast diffusion component and the slow diffusion component, do not exchange within the Δ range from 40 to 500 ms. This means that PS for the fast diffusion component is also confined in the open structures within the diffusing time.

It can be concluded that the network structure of PMMA gels prepared in toluene solutions of PSs with $M_w = 4000$ and 400,000 are homogeneous and inhomogeneous, respectively, within the Δ range from 40 to 500 ms as elucidated by ^{1}H PFG-NMR.

References

[1] Pusey PN, van Megen W. Physica A 1989;157:705.
[2] Ikkai F, Shibayama M. Phys Rev E 1997;56:R51.
[3] Shibayama M. Macromol Chem Phys 1998;199:1.
[4] Shibayama M, Tsujimoto M, Ikkai F. Macromolecules 2000;33:7868.
[5] Mallam S, Horkay F, Hecht AM, Geissler E. Macromolecules 1989;22:3356.
[6] Schosseler F, Skouri R, Munch JP, Candau SJ. J Phys II 1994;4:1221.
[7] Cohen Y, Ramon O, Kopelman IJ, Mizrahi S. J Polym Sci, Polym Phys Ed 1992;30:1055.
[8] Okay O. Prog Polym Sci 2000;25:711.
[9] Doi M, Edward SF. The theory of polymer dynamics. Oxford: Clarendon Press; 1986.
[10] Bancil R, Pajević S. Koňák Č. Macromolecules 1990;23:3380.
[11] Callaghan PT, Coy A. Phys Rev Lett 1992;68:3176.
[12] Nydén M, Olle S, Gunnar K. Macromolecules 1999;32:127.
[13] Won J, Lodge TP. J Polym Sci, Part B: Polym Phys 1993;31:1897.
[14] Yamane Y, Matsui M, Kimura H, Kuroki S, Ando I. Macromolecules 2003;36:5655.
[15] Yamane Y, Ando I, Buchholz FL, Reinhardt AR, Schlick S. Macromolecules 2004;37:9841.
[16] Hahn EL. Phys Rev 1950;80:580.
[17] Stejskal OE, Tanner EJ. J Chem Phys 1965;42:288.
[18] Price SW. Annu Rep NMR Spectrosc 1996;32:51.
[19] Callaghan PT. Principles of nuclear magnetic resonance microscopy. Oxford: Clarendon Press; 1991.
[20] Kimmich R. NMR: tomography, diffusiometry, relaxometry. Berlin: Springer; 1997.
[21] Matuskawa S, Ando I. Macromolecules 1996;29:7136.
[22] Gao Z, Schlick S, Matsukawa S, Ando I, Rossi G. Macromolecules 1999;31:8124.
[23] Kanesaka S, Kimura H, Kuroki S, Ando I, Fujishige S. Macromolecules 2004;37:453.
[24] von Meerwall ED, Ferguson RDJ. J Chem Phys 1981;74:6956.
[25] Snurr RQ, Kärger JJ. J Phys Chem B 1997;101:6469.
[26] Callaghan PT, Jolley KW, Lelievre RB, King KJ. Colloid Interface Sci 1983;92:332.
[27] Callaghan PT, Sonderman O. J Phys Chem 1983;87:1737–44.
[28] Fisher E, Kimmich R, Beginn U, Möller M, Fatkullin N. Phys Rev E 1999;59:4079.
[29] Nagashima K, Strashko V, Macdonald PM, Jenkins RD, Bassett DR. Macromolecules 2000;33:9329.
[30] Winnik MA, Bystryak SM, Chassenieux C, Strashko V, Macdonald PM, Siddiqui J. Langmuir 2000;16:4495.
[31] Ghi PY, Hill DJ, Whittaker AK. Biomacromolecules 2002;3:554.
[32] Lin G, Zhang J, Cao H, Jones AA. J Phys Chem B 2003;107:6179.
[33] Wentrup-Byrne E, Hill DJ, Whittaker AK. Biomacromolecules 2004;5:1194.
[34] Ohtuka A, Watanabe T. Carbohydr Polym 1996;30:135.
[35] Pekcan Ő, Yilmaz YJ. Appl Polym Sci 1997;63:1777.
[36] Miyaki Y, Eninaga Y, Fujita H. Macromolecules 1978;11:1180.
[37] Krause S. J Macromol Sci, Rev Macromol Chem 1972;7:251.
[38] Kuhn R, Cantow HJ, Burchard W. Angew Makromol Chem 1968;2:157.
[39] Callaghan TA, Paul DR. Macromolecules 1993;26:2439.
[40] Russell TP. Macromolecules 1990;23:890.