Study of Self-Diffusion of Molecules in Polymer Gel by Pulsed-Gradient Spin-Echo ^{1}H NMR. 3. Stearyl Itaconamide/*N*,*N*-Dimethylacrylamide Copolymer Gels

Shingo Matsukawa[†] **and Isao Ando***

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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ABSTRACT: Intermolecular hydrophobic interactions between poly(ethylene glycol) oleyl ether (PEG-Ole) as probe polymer and network polymer in stearyl itaconamide (SIA)/*N*,*N*-dimethylacrylamide (DMAA) copolymer gel swollen with water, in which the micelle of SIA is immobilized by copolymerization, have been studied through the diffusion coefficient (D) determined by the pulsed-gradient spin-echo ^{1}H NMR method with the field gradient strength of 22.3 T m^{-1} and ^{1}H spin−lattice relaxation time (T_1) and ^{1}H spin−spin relaxation time (T_2) by the ^{1}H pulse NMR method. From these experimental results, it was found that in the diffusion process PEG-Ole in SIA/DMAA copolymer gel takes the mobile and immobile states, and ^{1}H T_2 of PEG-Ole in SIA/DMAA copolymer gel is shorter than that of PEG. This shows that the comicellization of PEG-Ole and SIA is induced by hydrophobic interaction between the oleyl group in PEG-Ole and the stearyl group in SIA. Furthermore, to elucidate kinetics of the incorporation of PEG-Ole into the micelle and the release of PEG-Ole from the micelle, the mean residence lifetimes of the aggregated and unaggregated states have been determined on the basis of the experimental results obtained as a function of the intervals of gradient pulses.

Introduction

The diffusional behavior of molecules in gel systems gives us information about intermolecular interaction in the systems and their structure. In gel systems without specific interactions between probe molecule and network polymer, the network exists as a spatial obstruction, and then the diffusion of probe molecule is governed by hydrodynamic interaction between probe molecule and network polymer through the movement of solvent.[1−4] Under the existence of interactions between probe molecule and polymer network such as hydrogen-bonding, hydrophobic, or Coulomb interactions, the diffusion of probe molecule is strongly affected by the interactions.[5] The diffusional behavior of molecules in gel is also affected by morphological structure. In the diffusion process with barriers for movement of probe molecules, the intrabarrier diffusion coefficient, barrier spacing, and barrier permeability can be determined by measuring the restricted diffusion of solvent varying the observation time in diffusion measurement.[6−8] From the diffusion process of probe polymer, the structure can be elucidated for the gel which has the impenetrable regions produced by retrogradation,[3] distribution of pore sizes,[4] or diffusion channel formed by crystallization of network polymer.[9]

We have previously reported the diffusional behavior of poly(ethylene glycol) (PEG) as probe polymer in poly(*N*,*N*-dimethylacrylamide) (PDMAA) gels[10] and in *N*,*N*-dimethylacrylamide (DMAA)/acrylic acid (AA) copolymer gels[11] by using the pulsed-gradient spin-echo (PGSE) ^{1}H NMR method. It was found that the diffusional process of PEG in PDMAA gel follows $D/D_0 = \exp(-\kappa R)$, where D is the diffusion coefficient of PEG in the gel, D_0 the diffusion coefficient of an isolated PEG, κ^{-1} the dynamical screening length, and R the hydrodynamic radius of probe polymer, and that κ^{-1} is proportional to $Q^{0.71}$ where Q is the degree of swelling, and so the diffusion of PEG is predominantly restrained by hydrodynamic interaction between probe polymer (PEG) and network polymer (PDMAA). Further, it was found that the molecular motion of PEG in the DMAA/AA copolymer gel copolymerized with more than 90 mol % of AA is strongly restrained by the formation of complex stabilized by hydrogen bonds between oxygen atoms of PEG and carboxyl groups of PAA segments. From these results, it was demonstrated that the PGSE ^{1}H NMR method is a very useful means for elucidating intermolecular interaction between probe polymer and network polymer.[12]

In the PGSE ^{1}H NMR method, the observation time is clearly defined as the time interval between two field gradient pulses in which molecules are allowed to diffuse. Therefore, the analysis for the result of diffusion measurements varying the time interval makes it possible to elucidate the spatial and morphological structure of inhomogeneous gels and to determine the exchange time between the states of diffusant interacted and uninteracted with the polymer network.

From such a background, in this work, we aim to elucidate intermolecular hydrophobic interactions between PEG oleyl ether (PEG-Ole) as probe polymer and network polymer in the stearyl itaconamide (SIA)/DMAA copolymer gel swollen with water, in which the micelle of SIA is immobilized by copolymerization, through the diffusion coefficient determined by the PGSE ^{1}H NMR method, and ^{1}H spin−lattice relaxation time (T_1) and spin−spin relaxation time (T_2) determined by the ^{1}H pulse NMR method. Furthermore, on the basis of the diffusion coefficient experiments varying the observation time, we attempt to estimate the mean residence lifetime for PEG-Ole aggregated and unag-

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[†] Present address: Department of Food Science and Technology, Tokyo University of Fisheries, Konan, Minato-ku, Tokyo, Japan.

* Corresponding author.

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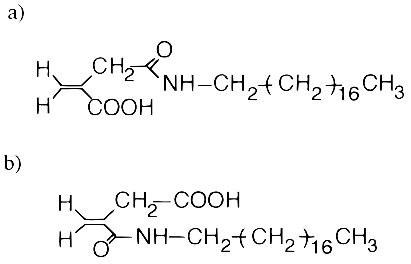
Scheme 1



gregated with the micelle immobilized in the polymer network.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide monomer was kindly supplied by Kojin Chemical Co. Ltd. *N*,*N*-Methylenebis(acrylamide) (MBAA) as cross-linking monomer and $K_2S_2O_8$ as polymerization initiator were used after purification as described in the previous paper.[10] Poly(ethylene glycol) (PEG; weight-average molecular weight $M_w = 1500$) and PEG-oleyl ether (PEG-Ole) ($M_w = 1200$, and $D_n = 20$, where D_n is the average number of repeating units of PEG) used as probe polymers were purchased from Polyscience, Inc., and Tokyo Chemical Industry Co. Ltd., respectively. The 99.8% isotope-labeled deuterated water (D_2O) used as solvent was purchased from Aldrich Chemical Co., Inc., in which a very small amount of HDO is contained and is used as ^1H NMR signal for the diffusion coefficient measurement in gels.

Stearyl itaconamide was obtained as follows. Stearylamine (10.78 g, 0.04 mol) was dissolved into 200 mL of tetrahydrofuran and stirred in a water bath at 288 K, and itaconic acid (5.31 g, 0.041 mol) was added to the solution. After 7 min, the mixture became turbid with precipitate and was stirred at room temperature for 12 h. The precipitate was separated from the solution by filtration to obtain stearyl itaconamide, and the yield was 51% (8.15 g). High purity of the product was recognized by ^1H and ^{13}C NMR spectra, but it was not determined that stearyl itaconamide form obtained is (a) or (b) in Scheme 1.

The cloud points of aqueous solutions of stearyl itaconamide (0.02 mol/L) neutralized by *tert*-butyl amine (tert-BA) with 1.4 and 1.8 mol equiv were 328 and 317 K, respectively.

SIA/DMAA copolymer gels were prepared as follows. SIA (0.15 mol/L) neutralized with *tert*-BA (0.3 mol/L), DMAA (1.5 mol/L), and MBAA (0.15–2.4 mmol/L) was dissolved by H_2O at 320 K and was radical copolymerized by $K_2S_2O_8$ (0.015 mol/L) at 323 K. The obtained gels were soaked in acetone and then in aqueous solution of *tert*-BA at 323 K for 1 day, respectively, to remove the remaining monomer, initiator, and linear polymers formed as a byproduct. Further, the gels were soaked in D_2O for 3 days to replace the solvent in the gel by D_2O. D_2O was repeatedly changed. The gels were stored in D_2O solution of 0.5 wt % PEG-Ole and in 0.5 wt % PEG for the preparation of the gel containing the probe polymer of PEG-Ole and PEG, respectively, for more than 3 days in order to reach an equilibrium of the permeation of probe polymer and the swelling of gel. Similarly, PDMAA gels were prepared by radical polymerization of DMAA (2.0 mol/L) and MBAA (0.8–6.4 mmol/L) as described in the previous paper[10,11] and stored in D_2O solution of 0.5 wt % PEG-Ole.

The degree of swelling of the polymer gel (Q) is defined as the ratio of the mass of equilibrium swollen polymer gel at 313 K (M_{swollen}) to the mass of freeze-dried polymer (M_{dry}):

$$Q = M_{\mathrm{swollen}}/M_{\mathrm{dry}} \tag{1}$$

Measurements. The self-diffusion coefficient (D) measurements on HDO and probe polymers in SIA/DMAA copolymer gels were carried out by means of a JEOL GSX-270 NMR spectrometer operating at 270.1 MHz for ^1H with a homemade pulse-gradient generator at 303 K. The probe used is specially designed to suppress the eddy current induced by the application of high-strength field gradient pulse. Spectral width, data points, and field gradient strength G were 4.0 kHz, 4096, and 22.3 T m^{-1}, respectively. The echo signal intensity was measured as a function of the gradient pulse length δ. The pulse interval τ, the gradient pulse interval Δ, and δ values employed in these experiments were 30–240 ms, 30–240 ms, and 0.001–0.738 ms, respectively.

^1H T_1 and ^1H T_2 were measured by using the inversion recovery method[13] and the Carr–Purcell/Meiboom–Gill method,[14] respectively, operating at 270.1 MHz for ^1H at 303 K.

PGSE ^{1}H NMR Spectral Analysis. In the PGSE ^1H NMR experiments, echo signal intensity decays depending upon the displacement of proton. For the proton in the molecule undergoing the random movement with a single-component diffusion, which follows Gaussian distribution, the echo signal attenuation is given by[15]

$$A(\delta)/A(0) = \exp(-\gamma^2 G^2 \delta^2 D T_{\mathrm{d}}) \tag{2}$$

where $A(\delta)$ and $A(0)$ are echo signal intensities at $t = 2\tau$ with and without the magnetic field gradient pulse being the length δ, respectively. γ is the gyromagnetic ratio of proton and T_d the diffusion time. For the random movement, the mean-square displacement in the z direction $\langle z^2 \rangle$ after T_d is given by

$$\langle z^2 \rangle = 2DT_{\mathrm{d}} \tag{3}$$

Therefore, substitution of eq 3 into eq 2 gives

$$A(\delta)/A(0) = \exp(-\gamma^2 G^2 \delta^2 \langle z^2 \rangle/2) \tag{4}$$

It is found that $(\gamma G \delta)^{-1}$ should be the same order with $\langle z^2 \rangle^{1/2}$ to discriminate the echo signal attenuation by the displacement of proton.

In the PGSE experiment with the gradient pulse interval Δ, taking into account the displacement during the time δ, the echo signal attenuation is given by

$$A(\delta)/A(0) = \exp[-\gamma^2 G^2 \delta^2 D(\Delta - \delta/3)] \tag{5}$$

For a mixture of the two components such as the mobile and immobile components with different diffusion coefficients, the total echo signal attenuation is given by the sum of the contributions of the individual components. When the difference in T_2 between the individual components is very small, the echo signal attenuation for a mixture of the two components with different diffusion coefficient is expressed by

$$A(\delta)/A(0) = p_1 \exp[-\gamma^2 G^2 \delta^2 D_1(\Delta - \delta/3)] + p_2 \exp[-\gamma^2 G^2 \delta^2 D_2(\Delta - \delta/3)] \tag{6}$$

where D_i is the diffusion coefficient of the ith component, p_i is the fractional proton number of the ith component, and $p_1 + p_2 = 1$.

When the diffusant translates into some regions, of which each has a different diffusion coefficient, the observed echo signal attenuation of the diffusant depends on the residence lifetime in each of the regions. For example, in any system with two regions in which the diffusant has the same chemical shift, the time derivative of the echo signal attenuation of the diffusant in the ith region, Ψ_i, can be described as follows.

$$\mathrm{d}\Psi_1/\mathrm{d}t = -R_1\Psi_1 - \Psi_1/\tau_1 + \Psi_2/\tau_2 \tag{7a}$$

$$\mathrm{d}\Psi_2/\mathrm{d}t = -R_2\Psi_2 + \Psi_1/\tau_1 - \Psi_2/\tau_2 \tag{7b}$$

where $R_i = \gamma^2 G^2 \delta^2 D_i + 1/T_{2,i}$ and τ_i is the mean-residence lifetime in the ith region. When the difference in T_2 between the individual regions is negligibly small, the solution for eqs 7a and 7b is given by Zimmerman and Brittin.[16]

If the displacement by the fluctuational motion of network segment follows a Gaussian distribution, the $\langle z^2 \rangle^{1/2}$ can be

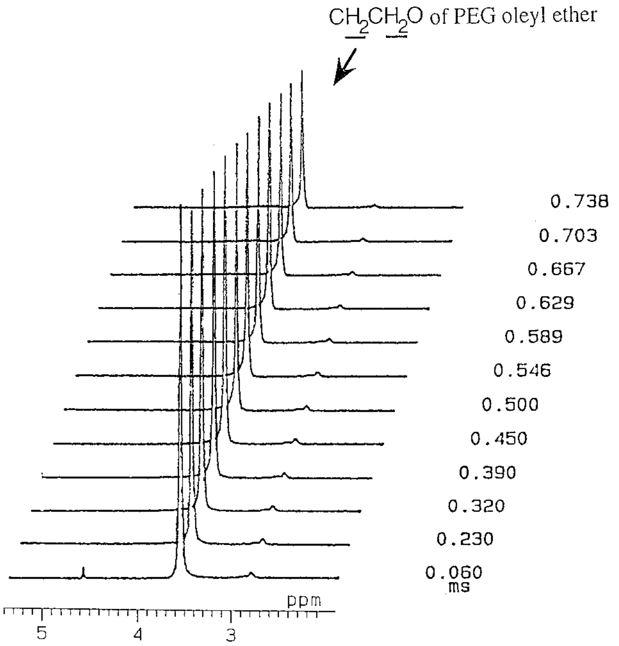


Figure 1. Spin-echo ^{1}H NMR spectra of SIA/DMAA copolymer gel with the degree of swelling $Q = 78$ containing PEG-Ole with $M_w = 1200$ as probe polymer and HDO as solvent by varying field-gradient pulse length (δ) from 0.060 to 0.738 ms.

assumed to be comparable to κ^{-1}. In the diffusion process of PEG ($M_w = 20\,000$) in PDMAA gel, it was shown that the relationship between κ^{-1} and Q is given by $\kappa^{-1} \sim Q^{0.71}$, and the κ^{-1} value for the gel with $Q = 25$, in which $D/D_0 = \exp(-1)$, is equal to the hydrodynamic radius of PEG of 4.2 nm.[10,17] Thus, we have

$$\kappa^{-1} = 4.2(Q/25)^{0.71}\ (\mathrm{nm}) \qquad (8)$$

Results and Discussion

PGSE ^{1}H NMR Spectra and Its Assignment. Typical spin-echo ^{1}H NMR spectra of a SIA/DMAA copolymer gel with $Q = 78$ containing PEG-Ole and HDO are shown as a function of field-gradient pulse length (δ) in Figure 1.

The spectrum has sharp peaks completely separated from each other under the application of strong field gradient. Peaks at 4.73, 3.72, and 2.93 ppm can be assigned to HDO, methylene protons of ethylene group in PEG-Ole, and methyl protons of DMAA, respectively, by using reference data on PEG solution and PDMAA gel. Small peaks at 2.05, 1.39, 1.35, and 0.90 ppm in the expanded spectrum were assigned to protons at the allylic position of the oleyl group in PEG-Ole, methyl protons of *tert*-BA, aliphatic protons in the stearyl group and in the oleyl group, and methyl protons in the stearyl group and in the oleyl group, respectively. From the intensity decay of peaks at 4.73 and 3.72 ppm, the D values for HDO and PEG-Ole were determined. The decay of peak at 2.93 ppm was used for the estimation of the decay owing to the instrumental effect.

Diffusion Coefficient of HDO in SIA/DMAA Copolymer and PDMAA Gels. The diffusion coefficients of HDO (D_{HDO}) contained in SIA/DMAA copolymer gel with PEG-Ole ((SIA/DMAA)/PEG-Ole system) and PDMAA gel with PEG-Ole (PDMAA/PEG-Ole system), and in SIA/DMAA copolymer gels with PEG ((SIA/DMAA)/PEG system) were determined by the PGSE ^{1}H NMR method with Δ of 30 ms at 303 K varying δ from 0.001 to 0.050 ms and were plotted against Q as shown in Figure 2.

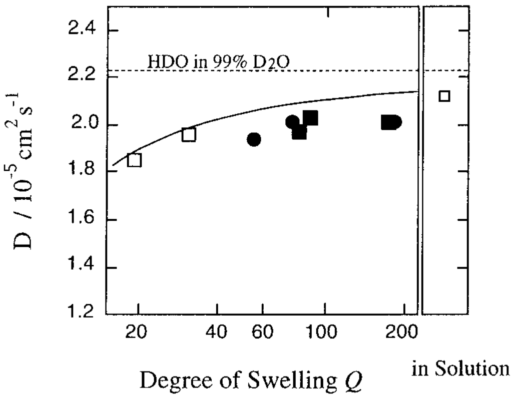


Figure 2. Dependence of the diffusion coefficient of water molecule (D_{HDO}) on the degree of swelling Q in a PDMAA gel containing PEG-Ole (□), in a SIA/DMAA copolymer gel containing PEG (●), in a SIA/DMAA copolymer gel containing PEG-Ole (■), and in solution containing PEG-Ole (□) at 303 K.

We have previously reported that the D_{HDO} values in a PDMAA gel can be expressed by the following equation based on the modified free volume theory [10,11]

$$D_{\mathrm{HDO}} = D_{\mathrm{HDO},0} \exp[Q^{-1}/(Q^{-1} f_{\mathrm{solv},0} - f_{\mathrm{solv},0}{}^2/\beta)] \qquad (9)$$

where $D_{\mathrm{HDO},0}$ and $f_{\mathrm{solv},0}$ are D_{HDO} and the fractional free volume of deuterated water (f_{solv}) in infinite swollen gel ($Q\ \infty$), respectively. β is the proportionality constant of f_{solv} to the volume fraction of solvent. The solid curve shown in Figure 2 was obtained by using eq 9 and parameters obtained from D_{HDO} values in PDMAA gels. D_{HDO} values in the (SIA/DMAA)/PEG system and in the (SIA/DMAA)/PEG-Ole system are below the solid curve. This result may be due to the structure of SIA/DMAA copolymer gels, in which the micelle of the stearyl groups acts as a spatial obstruction and HDO molecules diffuse by a roundabout way, and the apparent value of D_{HDO} is reduced.[8,19] This effect of the gel structure on the apparent diffusion coefficient is clarified on the basis of diffusion coefficients for probe polymers varying the interval of field gradient pulses (the observation time for diffusion). The D_{HDO} values in the PDMAA/PEG-Ole system and in PEG-Ole solution are also slightly below the solid curve. This is due to the existence of the micelle of PEG-Ole which becomes a spatial obstruction for the diffusion of HDO molecules.

Diffusional Behavior Measurements for Probe Polymers in SIA/DMAA Copolymer Gels. The PGSE ^{1}H NMR spectra were measured with Δ of 30 ms varying δ from 0.060 to 0.108 ms for the (SIA/DMAA)/PEG system and the PDMAA/PEG-Ole system. The plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2 G^2 \delta^2(\Delta - \delta/3)$ for the peak at 3.72 ppm were obtained as shown in Figure 3.

It is seen that the experimental data lie on a straight line. This means that in the (SIA/DMAA)/PEG system and in the PDMAA/PEG-Ole system the diffusion process of probe polymer is a single component during the observation time.

For the analysis of the diffusion coefficient of PEG-Ole in SIA/DMAA copolymer gels from the echo signal attenuation, the measurement with Δ of 30 ms required large δ up to 0.738 ms, which is corresponds to $(\gamma G\delta)^{-1}$ of 227 nm. Then, the echo signal intensity at 2.93 ppm for the methyl protons of the DMAA units reduces as

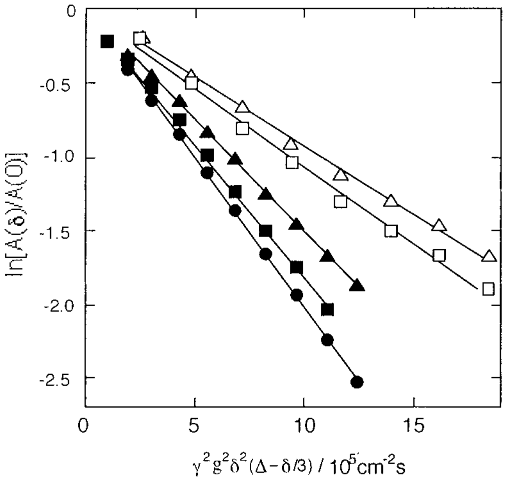


Figure 3. Diffusional spin-echo attenuation of PEG-Ole in PDMAA gels with the degree of swelling $Q = 19$ (■) and $Q = 30$ (●) and that of PEG in SIA/DMAA copolymer gels with $Q = 53$ (▲), $Q = 74$ (□), and $Q = 177$ (△).

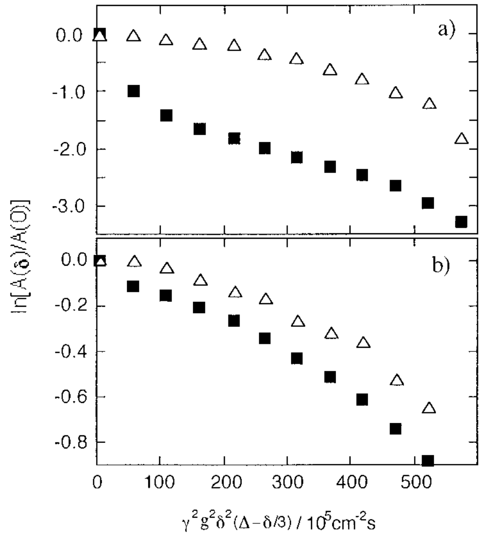


Figure 4. Spin-echo attenuation for PEG-Ole (△) and CH_3 of DMAA unit (■) in SIA/DMAA copolymer gels with the degree of swelling $Q = 169$ (a) and $Q = 78$ (b).

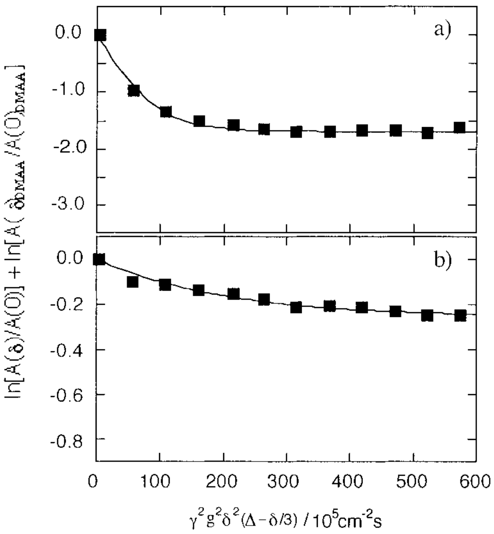


Figure 5. Diffusional spin-echo attenuation for PEG-Ole in SIA/DMAA copolymer gel with the degree of swelling $Q = 169$ (a) and $Q = 78$ (b) corrected by using eq 11. The solid curves are calculated by using eq 12.

shown in Figure 4, though the network does not move by translational diffusion.

The fluctuational displacements of the network for the SIA/DMAA copolymer gels with $Q = 78$ and 169 can be estimated to be 9.3 and 16.0 nm, respectively, by using eq 8 and the assumption of $\langle z^2\rangle^{1/2} \sim \kappa^{-1}$. These displacements are too small as compared with the value of $(\gamma G\delta)^{-1}$ which induces the reduction of the echo signal intensity. And also, there exists no sol component of the polymer network because the signal for the network does not decay in long Δ. Therefore, it is considered that the reduction of the echo signal comes from the instrumental effect such as the residual field gradient, as descried by von Meerwall and Kamat.[18] If such an effect is taken into account, the echo signal attenuation can be expressed in the form

$$A(\delta)/A(0) = \exp(T_{\mathrm{dis}} + T_{\mathrm{inst}}) \qquad (10)$$

where T_{dis} is the term contributed to the decay by the displacement and T_{inst} is that by the instrumental effect. The attenuation for the signal at 2.93 ppm $A(\delta)_{\mathrm{DMAA}}/A(0)_{\mathrm{DMAA}}$ gives the evaluation of T_{inst} for signals in the same spectra. Therefore, the T_{dis} value for PEG-Ole in the gel is given by subtracting T_{inst} from the attenuation for the PEG-Ole in the following way:

$$T_{\mathrm{dis}} = \ln[A(\delta)/A(0)] - T_{\mathrm{inst}} = \ln[A(\delta)/A(0)] + \ln[A(\delta)_{\mathrm{DMAA}}/A(0)_{\mathrm{DMAA}}] \qquad (11)$$

The T_{dis} values were plotted against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ as shown in Figure 5. It is shown that the plots deviate from a straight line.

This means that PEG-Ole in the SIA/DMAA copolymer gel has predominantly two components with different diffusion coefficients during the observation time. To explain such a diffusion process, we consider that a part of PEG-Ole diffuses with D_2 among micelles in the gel and another aggregates with micelles immobilized in polymer network and so does not almost diffuse. Thus, as $D_1 = 0$ in eq 6, we have the following expression on the assumption that the difference in T_2 between these components is negligible.

$$T_{\mathrm{dis}} = (1 - p_2) + p_2 \exp[-\gamma^2G^2\delta^2D_2(\Delta - \delta/3)] \qquad (12)$$

The solid curves shown in Figure 5 were obtained from the least-squares fittings to the experimental data using eq 12. From these results, D_2 values are given to be 5.42×10^{-8} and 2.23×10^{-7} cm² s⁻¹ for the gels with $Q = 78$ and 169, respectively, and also p_2 is given as to be 0.82 and 0.23, respectively. Since in the low-Q region the plots for PEG-Ole in the gels with $Q = 14$ and 21 show very slow decay, each of them may be analyzed as a single-component way instead of the two-component way using eq 5 to be 0.9×10^{-8} and 0.3×10^{-8} cm² s⁻¹, respectively.

To clarify the effect of hydrophobic interactions between probe polymers and polymer networks on the diffusional behavior of probe polymers, the D values obtained for PEG (D_{PEG}) and PEG-Ole ($D_{\mathrm{PEG-Ole}}$) in the systems of (SIA/DMAA)/PEG, PDMAA/PEG-Ole, and (SIA/DMAA)/PEG-Ole are plotted against Q as shown in Figure 6a.

On the basis of D values in solution (Figure 6b), the solid line and dashed line were obtained for PEG with

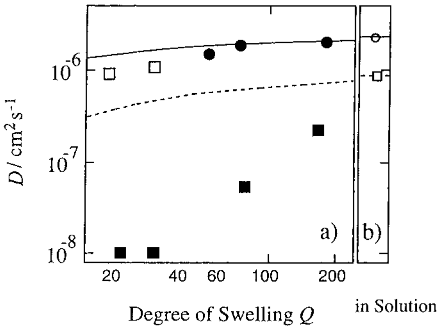


Figure 6. (a) Plots of the diffusion coefficient (D) for PEG-Ole with M_w of 1200 in PDMAA gel (□), for PEG with M_w of 1500 in SIA/DMAA copolymer gel (●), and for PEG-Ole with M_w of 1200 in SIA/DMAA copolymer gel (■) against the degree of swelling Q at 303 K. The solid line and dashed line are calculated by using eq 13 for PEG with $M_w = 1500$ and for micelle of PEG-Ole with $D = 5.45 \times 10^{-7}$ cm^2 s^{-1} in solution, respectively. (b) Plots of the diffusion coefficient (D) for PEG with M_w of 1500 in 0.5% solution (○) and for PEG-Ole with M_w of 1200 (●) in 0.1% solution at 303 K.

$M_w = 1200$ and for the micelle of PEG-Ole, respectively, by using the following equation,[10,11] which was obtained for D_{PEG} in PDMAA gel,

$$D = D_{soln}/(D_{HDO,neat}/D_{HDO}) \exp(-R/Q^{0.71}) \quad (13)$$

where D_{soln} and $D_{HDO,neat}$ are D of probe polymer in dilute solution and D_{HDO} in neat D_2O, respectively. R is the hydrodynamic radius of PEG and the micelle of PEG-Ole in solutions, and $R = kT/6\pi\eta_s D_{soln}$, where η_s is the viscosity of solvent. The D_{PEG} value in the SIA/DMAA copolymer gel is almost the same as that calculated for PEG in PDMAA gel on the basis of the D value in 0.5% solution (solid line). Therefore, it can be said that there is no strong specific interaction between PEG and the network in the (SIA/DMAA)/PEG system except for hydrodynamic interaction. The slight deviation of experimental data from the solid line may come from the micelle structure of the SIA/DMAA copolymer gel, which makes PEG diffuse by a roundabout way, in a similar manner as described for D_{HDO}. The $D_{PEG-Ole}$ value in PDMAA gel is larger than that calculated for the micelle of PEG-Ole in PDMAA gel on the basis of D value in 0.1% solution (dashed line). Therefore, it is considered that PEG-Ole molecule exists as a smaller micelle in PDMAA gel than that in 0.1% solution. The $D_{PEG-Ole}$ value in the (SIA/DMAA)/PEG-Ole system, which is obtained for the component diffusing among micelles of SIA, is much smaller than $D_{PEG-Ole}$ in the PDMAA/PEG-Ole system. From this result, it is suggested that hydrophobic interactions between the oleyl group of PEG-Ole and the stearyl group of SIA restrain the diffusion of PEG-Ole molecule during the diffusion of PEG-Ole among SIA micelles, besides the formation of co-micelle of PEG-Ole and SIA.

^{1}H T_1 and T_2 of Probe Polymers in SIA/DMAA Copolymer Gels. ^{1}H T_1 and T_2 reflect any molecular motion that can induce fluctuating local magnetic fields.[13,14] For probe polymers of PEG and PEG-Ole in D_2O, the contribution of segmental motion to ^{1}H T_1 and T_2 is the dominant factor rather than that of the translational motion of a whole molecule. Therefore, by using ^{1}H T_1 and T_2 data, it is possible to investigate intermolecular interaction between probe polymer and network with a deep knowledge for molecular motion, in addition to the results of the diffusion coefficient experiments.[11]

^{1}H T_1 and T_2 for the PEG part of PEG-Ole and PEG in the systems of (SIA/DMAA)/PEG, PDMAA/PEG-Ole, and (SIA/DMAA)/PEG-Ole are measured by the inversion recovery method and the CPMG method at 303 K by varying Q as shown in Figure 7, a-1 and a-2, respectively.

^{1}H T_1 and T_2 for PEG in the SIA/DMAA copolymer gel are almost the same as those in 0.5% solution. This means that the network in the (SIA/DMAA)/PEG system does not restrain the segmental motion of PEG. Therefore, it is considered that PEG does not have strong specific interaction with the polymer network. The ^{1}H T_1 and T_2 for PEG-Ole ($T_{1,PEG-Ole}$ and $T_{2,PEG-Ole}$, respectively) in PDMAA gel are larger than those in 0.5% solution. Therefore, the correlation time for the segmental motion of PEG-Ole in PDMAA gel is shorter than that in 0.5% solution. This shows that PEG-Ole molecule exists as a smaller micelle in PDMAA gel than that in 0.5% solution. These results for systems of (SIA/DMAA)/PEG and PDMAA/PEG-Ole agree with the results obtained by D measurements.

The $T_{1,PEG-Ole}$ value in the SIA/DMAA copolymer gel is slightly smaller than that in 0.5% solution, and the $T_{2,PEG-Ole}$ in the SIA/DMAA copolymer gel is much smaller than that in 0.5% solution. ^{1}H T_1 becomes the minimum in molecular motion with the correlation time (τ_c) of the same order with $1/\omega \sim 4$ ns, where ω is the resonance frequency, and on the other hand, ^{1}H T_2 is decreased by a decrease in molecular motion with relatively long correlation time. Therefore, this result means that the segmental motion of the PEG group in PEG-Ole with long τ_c is obviously restrained and that with short τ_c is fairly remained in the (SIA/DMAA)/PEG-Ole system. From the results of $D_{PEG-Ole}$ and relaxation times, $T_{1,PEG-Ole}$ and $T_{2,PEG-Ole}$, it is found that the PEG-Ole molecule decreases in the translational motion and in the fluctuational motion of the PEG part with long τ_c due to the immobility of the oleyl groups which interacts strongly with the micelle of the stearyl group in the network, but the segmental motion of the PEG part with short τ_c remains to some degree.

In the ^{1}H T_1 and T_2 experiments, PEG-Ole in the SIA/DMAA copolymer gel has a single component for the relaxation process despite the existence of two components with different diffusion coefficients. This means that the PEG-Ole molecule is undergoing fast exchange between the aggregated and unaggregated states with the micelle, and so an averaged value is observed. The rate of exchange between the two states will be estimated in the next section.

Measurements Varying Observation Time. By varying the gradient pulse interval Δ in PGSE ^{1}H NMR measurements, one can see molecular movement in different observation times. The diffusion coefficient measurements varying the observation time for probe polymer in the SIA/DMAA copolymer gel give us detailed information about the structure of the gel and the residence lifetime of probe polymer in aggregated and unaggregated states with the micelle immobilized in the network.

Figure 8 shows the echo signal attenuation obtained by PGSE ^{1}H NMR measurements with Δ of 30, 120, and 240 ms for PEG in the SIA/DMAA copolymer gel with $Q = 177$.

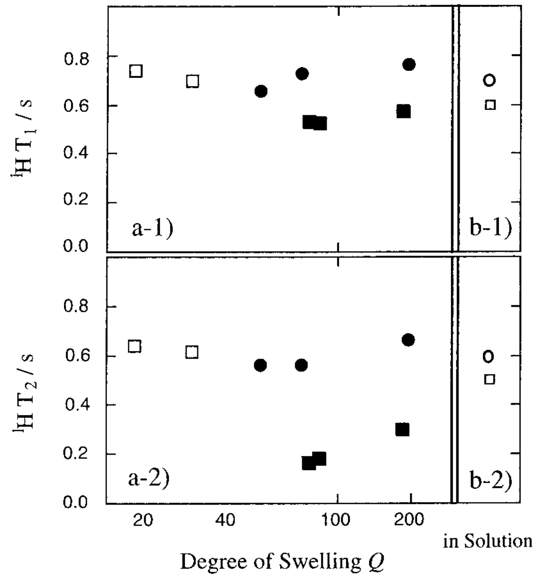


Figure 7. (a) Plots of ^{1}H T_1 (a-1) and ^{1}H T_2 (a-2) for PEG-Ole with M_w of 1200 in PDMAA gel (□), for PEG with M_w of 1500 in SIA/DMAA copolymer gel (●), and for PEG-Ole with M_w of 1200 in SIA/DMAA copolymer gel (■) against the degree of swelling Q at 303 K. (b) Plots of ^{1}H T_1 (b-1) and ^{1}H T_2 (b-2) for PEG with M_w of 1500 in 0.5% solution (○) and for PEG-Ole with M_w of 1200 (●) in 0.1% solution at 303 K.

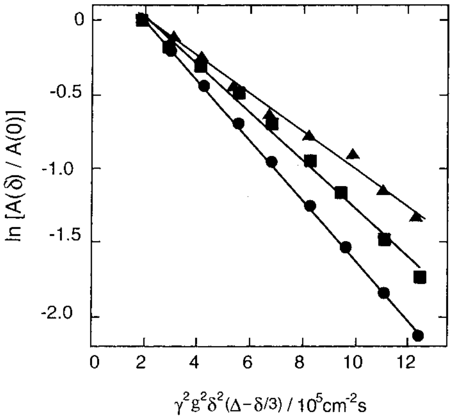


Figure 8. Diffusional spin-echo attenuation for PEG with M_w of 1500 in SIA/DMAA copolymer gel with $Q = 177$ measured with the pulsed-gradient interval $\Delta = 30$ ms (■), 120 ms (●), and 240 ms (▲).

Since the obtained data lie on individual straight lines, it can be said that PEG in the (SIA/DMAA)/PEG system has a single-component diffusion during the observation time. However, the slope of the straight line decreases as Δ increases, and the apparent diffusion coefficients for PEG are determined from the measurements with Δ of 30, 120, and 240 ms to be 2.02×10^{-6}, 1.63×10^{-6}, and 1.26×10^{-6} cm^2 s^{-1}, respectively. From these results, it is thought that PEG diffuses among the micelles in the SIA/DMAA copolymer gel with a single component and takes a roundabout way to avoid the impermeable region made up of the micelle.

To elucidate the kinetics of the incorporation into the micelle and the release from the micelle for PEG-Ole in the SIA/DMAA copolymer gel with $Q = 169$, PGSE ^{1}H NMR spectra were measured with Δ of 30, 60, and 120 ms. The T_{dis} values obtained by using eq 11 were plotted against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ in Figure 9.

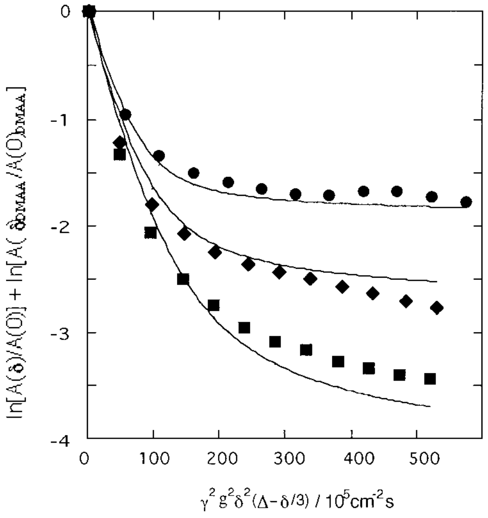


Figure 9. Diffusional spin-echo attenuation for PEG-Ole with M_w of 1200 in SIA/DMAA copolymer gel with $Q = 169$ measured with the pulsed-gradient interval $\Delta = 30$ ms (▲), 60 ms (■), and 120 ms (●) and corrected by using eq 11.

As seen from this figure, the plots depend on Δ. This means that PEG-Ole changes the diffusional state in a comparable time to the observation time as being aggregated and unaggregated with the micelle immobilized in the polymer network. We can calculate Ψ_1 and Ψ_2 numerically by using eqs 7a and 7b with the PGSE ^{1}H NMR experiments: before the first field gradient pulse, between the first and second field gradient pulses, and after the second field gradient pulse under the condition with the field gradient pulse δ. Here, it is thought that the average value of $T_{2,\mathrm{PEG-Ole}}$ in the aggregated state $T_{2,agg}$ and $T_{2,\mathrm{PEG-Ole}}$ in the unaggregated state $T_{2,un}$ is identical with $T_{2,\mathrm{PEG-Ole}}$ in the SIA/DMAA copolymer gel as obtained by the CPMG method (0.30 s) and that $T_{2,un}$ is identical with $T_{2,\mathrm{PEG-Ole}}$ in the PDMAA gel (0.67 s)

$$p_{agg}/T_{2,agg} + p_{un}/T_{2,un} = p_{agg}/T_{2,agg} + p_{un}/0.67 = 1/0.30 \quad (14)$$

where $p_{agg} = \tau_{agg}/(\tau_{agg} + \tau_{un})$ and $p_{un} = \tau_{un}/(\tau_{agg} + \tau_{un})$. τ_{un} and τ_{agg} are the mean residence lifetimes in the unaggregated state and in the aggregated state, respectively. By the computer simulation, $D_{\mathrm{PEG-Ole}}$ in the unaggregated state, $T_{2,agg}$, τ_{un}, and τ_{agg} are obtained to be 3.2×10^{-7} cm^2 s^{-1}, 120 ms, 53 ms, and 119 ms, respectively, and solid curves obtained using these values are shown in Figure 9.

Conclusions

D, ^{1}H T_1, and ^{1}H T_2 values for PEG-Ole in SIA/DMAA copolymer gels were successfully determined by using the the PGSE method, the inversion recovery method, and the CPMG method, respectively. It was found that the D and ^{1}H T_2 values for probe polymer in the (SIA/DMAA)/PEG-Ole system are much smaller than those in systems of PDMAA/PEG-Ole and (SIA/DMAA)/PEG due to the comicellization of PEG-Ole and SIA induced by hydrophobic interaction between the oleyl group in PEG-Ole and the stearyl group in SIA. In the PGSE experiments with large G and δ values, the signal decay owing to the instrumental effect was evaluated by using the decay of signal for the polymer network and used for the correction of the signal decay of probe polymer to obtain the decay owing to the displacement of probe polymer. From the PGSE experiments with various gradient pulse intervals, the mean residence lifetimes of PEG-Ole in the aggregated and unaggregated states with the micelle immobilized in the network were determined. Further, it has been demonstrated that PGSE ^{1}H NMR experiments with large G as a function of the gradient pulse interval are a useful method to elucidate intermolecular interaction between polymers through the observation of molecular dynamics and kinetics in the formation of aggregates.

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