Study of Self-Diffusion of Molecules in a Polymer Gel by Pulsed-Gradient Spin-Echo ^{1}H NMR. 2. Intermolecular Hydrogen-Bond Interaction between the Probe Polymer and Network Polymer in *N*,*N*-Dimethylacrylamide−Acrylic Acid Copolymer Gel Systems

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ABSTRACT: Dynamics and structure of swollen *N*,*N*-dimethylacrylamide (DMAA)−acrylic acid (AA) copolymer gels, poly(*N*,*N*-dimethylacrylamide) (PDMAA) gels, and poly(acrylic acid) (PAA) gels have been studied as a function of the degree of swelling (Q) under a state of equilibrium with deuterated water (D_2O) as a solvent and poly(ethylene glycol) (PEG) as a probe polymer by NMR methods. The self-diffusion coefficient (D) and ^{1}H spin−spin relaxation time (T_2) of PEG in the gel have been determined by the pulsed-gradient spin-echo ^{1}H NMR method and Carr−Purcell/Meiboom−Gill ^{1}H NMR method, respectively. From these experimental results, it was found that the D and ^{1}H T_2 values of PEG in the PAA gel are much smaller than those in PDMAA gel. This shows that the "loose" complex between the PEG and PAA network in the gel is formed by intermolecular hydrogen-bond interactions. From the experimental results on (DMAA−AA) copolymer gels with varying mole fractions of AA (f_{AA}), it was found that the D and ^{1}H T_2 values in the gels with $f_{AA} \geq 0.9$, which have long consecutive AA sequences in the network, become much smaller than those in the gels with $f_{AA} < 0.5$. This shows that the complexation is greatly influenced by the length of the consecutive AA sequences.

Introduction

The molecular motion of a probe polymer in a gel is greatly affected by intermolecular interactions with the network polymer. Therefore, the elucidation of the dynamical behavior of the probe polymer helps us to understand deeply the intermolecular interactions in the gel system.

In some cases the network polymer may exist as a spatial obstruction in gel systems that consist of probe polymer, network polymer without any functional groups interacting strongly with probe polymer, and solvent being good solvent for both the probe polymer and the network polymer. In this system, the dynamical behavior of the gel system can be understood by taking into account only the hydrodynamic interaction. We have already reported the results obtained by pulsed-gradient spin-echo (PGSE) ^{1}H NMR experiments that the diffusion coefficient (D) of poly(ethylene glycol) (PEG) as probe polymer in a poly(*N*,*N*-dimethylacrylamide) (PDMAA) gel system is reasonably explained by the hydrodynamic interaction with the network polymer as $D/D^0 = \exp(-\kappa R)$, where D^0 is the diffusion coefficient for an isolated probe polymer, κ^{-1} is the dynamical screening length, and R is the hydrodynamic radius of the probe polymer,[2] and so in this system the hydrodynamic interaction is predominant as intermolecular interactions between the probe polymer and network polymer.

On the other hand, the molecular dynamics of the probe polymer is strongly affected in polymer gel systems with various kinds of intermolecular interactions between the probe polymer and network polymer, such as hydrogen-bonding interaction, hydrophobic interaction, Coulomb interaction, etc. For example, by addition of an aqueous PEG solution into the aqueous poly(acrylic acid) (PAA) solution, the complex between PEG and PAA is formed by the formation of hydrogen bonds between the oxygen atoms of PEG and the carboxyl groups of PAA,[3−5] and also in the poly(methacrylic acid) (PMAA) hydrogel the complex between PEG and PMAA is formed by the same interaction.[2] The justification for the formation of such complexes has been carried out by macroscopic methods such as viscosity measurement for solutions and mass measurement for gels. Nevertheless, in order to clarify more clearly such intermolecular interactions between the probe polymer and network polymer in the gel systems, systematic studies by the microscopic method such as NMR spectroscopy are needed.

In this work, we aim to clarify the effect of intermolecular hydrogen-bond interactions between PEG (probe polymer) and the network polymer in *N*,*N*-dimethylacrylamide (DMAA)−acrylic acid (AA) copolymer gel systems on the dynamic behavior by measuring the diffusion coefficient and ^{1}H spin−spin relaxation time (T_2) by the PGSE ^{1}H NMR method and by Carr−Purcell/Meiboom−Gill ^{1}H NMR method, respectively, and, on the basis of the results, to elucidate the formation of the loose complex.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMAA) monomer kindly supplied by Kojin Chemical Co. Ltd., *N*,*N*′-methylenebis(acrylamide) (MBAA) used as the cross-linking monomer, and $K_2S_2O_8$ used as the polymerization initiator were used after purification, as described in a previous paper.[1] Acrylic acid (Tokyo Kasei Kogyo Co. Ltd.) was distilled at 318 K under a pressure of 1733 Pa. Poly(ethylene glycol) (M_w = 4250 and M_w/M_n = 1.03, where M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively) used as the probe polymer was purchased from Polyscience, Inc. Isotope-labeled (99.8%) deuterated water (D_2O) used as the solvent (purchased from Aldrich Chemical Co., Inc.)

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contained a very small amount of HDO and was used as the ^{1}H NMR signal for the diffusion coefficient measurement in gels.

(DMAA−AA) copolymer gels were prepared by radical copolymerization of DMAA (0.2−1.6 mol/L), AA (1.8−0.4 mol/L), and MBAA (0.2−12.4 mmol/L) initiated with $K_2S_2O_8$ (0.02 mol/L) in D_2O at 313 K. The mole fraction of AA (f_{AA}) was varied from 0.2 to 0.9. Similarly, PDMAA gels were prepared by polymerization of DMAA (2.0 mol/L) and MBAA (0.2−12.4 mmol/L), and PAA gels, by polymerization of AA (2.0 mol/L) and MBAA (0.2−12.4 mmol/L). The obtained gels were soaked in D_2O for 3 days to remove the remaining monomer, initiator, and linear polymers formed as a byproduct and in D_2O solutions of 0.5−0.05 wt % PEG for 3 days to reach an equilibrium of swelling. The D_2O solution of PEG was repeatedly changed.

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})

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

Measurements. The self-diffusion coefficient (D) measurements on HDO and PEG in (DMAA−AA) copolymer gels were carried out by means of a JEOL GSX-270 NMR spectrometer operating at 270.1 MHz for ^{1}H with a homemade pulse gradient generator at 303 K. Spectral width, data points, and field gradient strength G were 4.0 kHz, 4096, and 5.9 T m^{-1}, respectively.

The D values were determined by using the relationship between echo signal intensity and pulse field gradient parameters:

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

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. τ is the pulse interval, γ is the gyromagnetic ratio of the proton, and Δ is the gradient pulse interval. The echo signal intensity was measured as a function of δ. The τ, Δ, and δ values employed in these experiments were 30, 30, and 0.001−2.0 ms, respectively.

The ^{1}H spin−spin relaxation time (^{1}H T_2) was measured by the Carr−Purcell/Meiboom−Gill method[7] operating at 270.1 MHz for ^{1}H at 303 K.

Results and Discussion

PGSE ^{1}H NMR Spectra and Their Assignment. Typical spin-echo ^{1}H NMR spectra of a (DMAA−AA) copolymer (f_{AA} = 0.5) gel at Q = 67 containing PEG and HDO are shown as a function of field gradient pulse length (δ) in Figure 1.

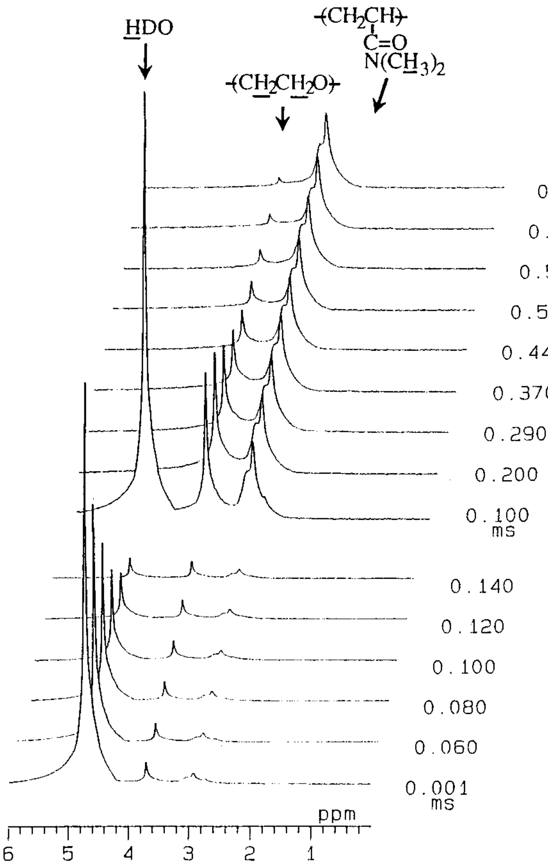


Figure 1. Spin-echo ^{1}H NMR spectra of a (DMAA−AA) copolymer gel (Q = 67, DMAA/AA = 50 mol/50 mol) containing PEG with M_w = 4,250 as the probe polymer and HDO as the solvent by varying the field gradient pulse duration (δ).

Peaks at 4.73, 3.72, and 2.93 ppm can be assigned to HDO, methylene protons of PEG, and methyl protons of the DMAA unit, respectively, by using reference data on the PEG solution and PDMAA gel without PEG. Peaks assigned to methylene and methine protons of the DMAA unit and AA unit appear strongly in the NMR experiment with a single pulse and decay during echo time (2τ) because these protons are restrained in molecular motion and have short T_2. The plots of ln[$A(\delta)/A(0)$] against $\gamma^2G^2\delta^2(\Delta-\delta/3)$ for peaks at 4.73 and 3.72 ppm show that the experimental data lie on a straight line. This means that the individual diffusant of HDO and PEG in the gel has a single-component diffusion during the observation time. Every measurement for diffusion coefficient in this work shows a single-component diffusion.

Diffusion Coefficient of HDO in DMAA−AA Copolymer Gels. The diffusion coefficients of HDO (D_{HDO}) contained in PDMAA gels, PAA gels, and (DMAA−AA) copolymer gels with PEG were determined by the PGSE ^{1}H NMR method at 303 K with varying Q and f_{AA}. The D_{HDO} values obtained were plotted against Q as shown in Figure 2.

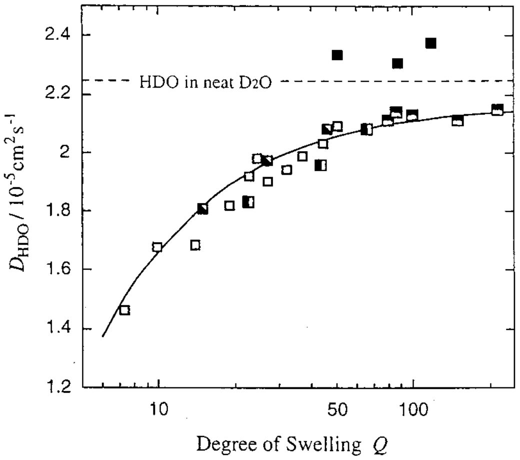


Figure 2. Dependence of the diffusion coefficient of the water molecule (D_{HDO}) on the degree of swelling (Q) in (DMAA−AA) copolymer gels containing PEG with M_w of 4250 at 303 K. The mole fraction of AA in gels, f_{AA}, is (□) 0 mol %, (◩) 20 mol %, (◧) 50 mol %, (⬒) 90 mol %, and (■) 100 mol %.

As seen from this figure, D_{HDO} increases as Q is increased. The molecular motion of HDO is not affected by a change of f_{AA} in the region of f_{AA} < 0.9. This means that the translational motion of the HDO molecule increases as the size of the network becomes large. The dynamical behavior of a solvent in a gel can be analyzed by the modified free volume theory.[8−11] As reported

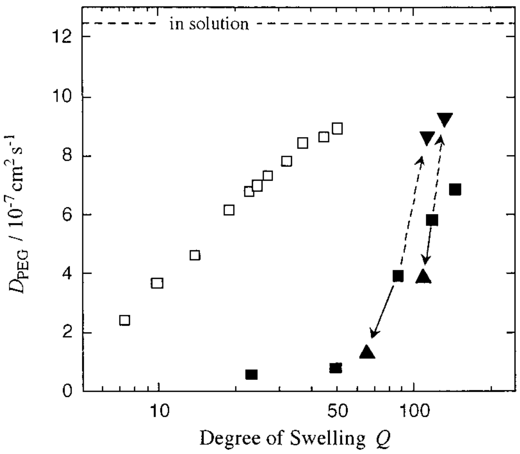


Figure 3. Dependence of the diffusion coefficient of PEG with M_w of 4250 (D_{PEG}) in PDMAA gels (□), PAA gels (■), PAA gels soaked in 0.15 mM HCl (▲), and PAA gels soaked in 30 mM trimethylamine (▼) on the degree of swelling (Q) at 303 K. The diffusion coefficient of PEG with M_w of 4250 in 1 wt % aqueous solution at 303 K is indicated by the dashed line.

previously, D_{HDO} in a PDMAA gel can be expressed by the following equation.[1]

$$D_{HDO} = D^0_{HDO} \exp[Q^{-1}/(Q^{-1}f_{solv} - f_{solv}{}^2/\beta)] \qquad (3)$$

where D^0_{HDO}, f_{solv}, and β are the self-diffusion coefficient and the fractional free volume of deuterated water in infinite swollen gel ($Q \to \infty$) and the proportionality constant for the fractional free volume to the volume fraction of solvent, respectively. From a least-squares fitting to the experimental data for PDMAA gels using eq 3, we can determine D^0_{HDO}, f_{solv}, and β to be 2.16×10^{-5} cm^2 s^{-1}, 0.178, and 0.079, respectively. The solid curve shown in Figure 2, which is calculated by using eq 3 and parameters obtained for PDMAA gels, agrees well with the experimental data obtained for (DMAA−AA) copolymer gels with an f_{AA} value less than 0.9. This indicates that the diffusion of HDO is independent of the concentration of carboxylic acid group in this region. D_{HDO}'s in PAA gels are larger than those in (DMAA−AA) copolymer gels. This may be because the concentration of H$^+$ ions dissociated from carboxylic acid groups in PAA gels, which diffuse faster than HDO, is higher than that in the (DMAA−AA) copolymer gel.

Diffusion Coefficient of PEG in DMAA−AA Copolymer Gels. In order to investigate the translational motion of PEG contained in PDMAA gels and PAA gels as the probe polymer, the diffusion coefficient of PEG (D_{PEG}) was determined by the PGSE ^{1}H NMR method at 303 K by varying Q of the gel. The obtained D_{PEG} values were plotted against Q as shown in Figure 3.

The D_{PEG} value in the PDMAA gel is smaller than that in aqueous 1 wt % PEG solution (dashed line) and increases as Q is increased. From the plot of ln(−ln(D/D^0) against ln Q, it was shown that this behavior is followed by $D/D^0 = \exp(-Q^uR)$, as reported previously.[1] Therefore, it can be said that the translational motion of PEG in the PDMAA gel is restrained by hydrodynamic interaction with the polymer network. This means that the polymer network is working as only a spatial obstruction for the displacement of PEG.[12] The D_{PEG} value in PAA gels is much smaller than that in the PDMAA gel. This suggests that the loose complex of the PEG and PAA network is formed by intermolecular hydrogen-bond interactions between the oxygen atoms of PEG and the carboxyl groups of PAA.[5] By

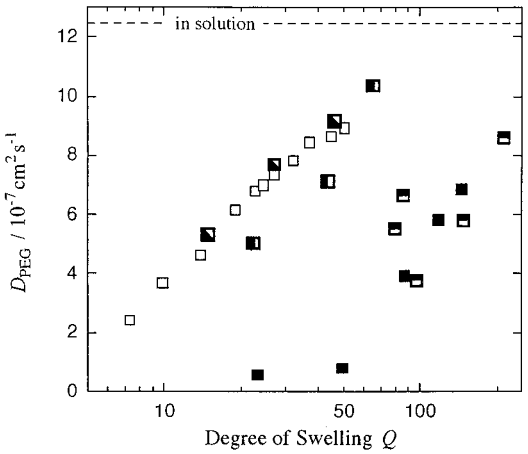
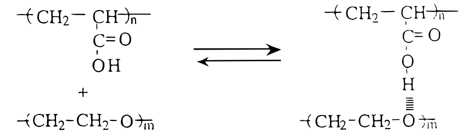


Figure 4. Dependence of the diffusion coefficient of PEG with M_w of 4250 (D_{PEG}) in (DMAA−AA) copolymer gels on the degree of swelling (Q) at 303 K. The diffusion coefficient of PEG with M_w of 4250 in 1 wt % aqueous solution at 303 K is indicated by the dashed line. The mole fraction of AA in gels, f_{AA}, is (□) 0 mol %, (◩) 20 mol %, (◧) 50 mol %, (⬒) 90 mol %, and (■) 100 mol %.

Scheme 1



addition of a small amount of HCl into the solution for the gel to be 0.15 mM in concentration, the gel shrinks and D_{PEG} is decreased, as shown by arrows in Figure 4. The complexation arises from the intermolecular hydrogen-bond interaction between oxygen atoms of PEG and the carboxylic groups of AA units in the undissociated state, as shown above.

Therefore, it can be said that the addition of HCl leads to an increase in the amount of undissociated carboxylic groups on going from the left side to the right side in the Scheme 1 and so enhances the formation of the complex and induces the shrinkage of the gel. This leads to slow diffusion of PEG. On the other hand, by addition of trimethylamine (20 mM), the gel swells and D_{PEG} is increased, as shown by arrows with dashed lines in Figure 3. It can be said that the addition of amine decreases the amount of undissociated carboxylic group and so inhibits the formation of the complex. This leads to fast diffusion of PEG and the swelling of the gel.

For the detailed understanding of the complexation of the PEG and gel network, D_{PEG} in (DMAA−AA) copolymer gels was measured and the obtained D_{PEG} values were plotted against Q, as shown in Figure 4.

It can be said that D_{PEG} has almost a constant value in the range of $f_{AA} < 0.5$ and is drastically decreased in the range of $f_{AA} \geq 0.9$, even though Figure 4 shows some scatter, which is probably caused by the inhomogeneity of the gels in polymer concentration. From these results, it is suggested that when f_{AA} is small, that is, the AA unit is isolated in DMAA sequences, the molecular motion of PEG is not strongly restrained by weak intermolecular interaction with AA units, but when f_{AA} is large, that is, consecutive AA units are distributed in the network, intermolecular interactions between PEG and consecutive AA segments are enhanced and so the molecular motion of PEG is strongly restrained.[13]

^{1}H T_2 of PEG in DMAA−AA Copolymer Gels. The T_2 value reflects the molecular motion.[14,15] In the

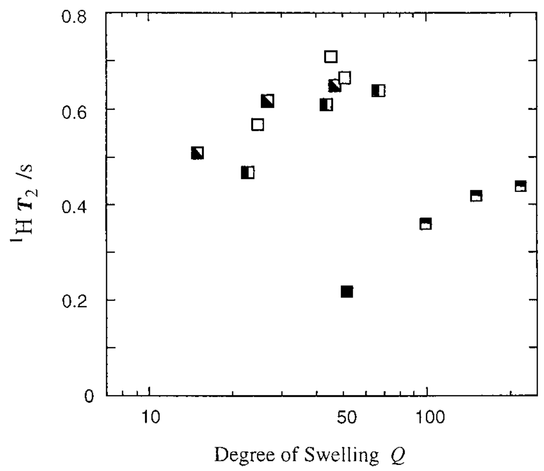


Figure 5. Dependence of ^{1}H T_2 of PEG with M_w of 4250 in (DMAA−AA) copolymer gels on the degree of swelling (Q) at 303 K. The mole fraction of AA in gels, f_{AA}, is (□) 0 mol %, (◩) 20 mol %, (◧) 50 mol %, (⬒) 90 mol %, and (■) 100 mol %.

molecular motion of PEG in D_2O solution, the segmental motion is a dominant factor compared with the translational motion and rotational motion of a whole molecule. In order to investigate the segmental motion of PEG contain in PDMAA gels, PAA gels, and (DMAA−AA) copolymer gels, the ^{1}H T_2 of PEG was measured by the CPMG method at 303 K by varying Q and f_{AA} of the gel. Figure 5 shows the plot of the obtained ^{1}H T_2 values against Q.

The ^{1}H T_2 values of PEG in (DMAA−AA) copolymer gels with $f_{AA} < 0.5$ decrease as Q is decreased. This means that the correlation time for the segmental motion of the PEG molecule increases with a decrease in the size of the network. It is thought that the segmental motion of PEG is restrained by hydrodynamic interaction with the polymer network in these gels, as the molecular motion of PEG is not strongly restrained by the intermolecular hydorgen-bond interaction with AA units in the gels with $f_{AA} < 0.5$, as indicated by the experimental data on D_{PEG}.

The ^{1}H T_2 value of PEG in (DMAA−AA) copolymer gels with $f_{AA} \geq 0.9$ is much smaller than that with $f_{AA} < 0.5$, and this behavior is similar to that of D_{PEG}. Therefore, it can be said that the loose complex between PEG and AA units in the network polymer, which needs any specified consecutive units of AA, restrains the segmental motion of PEG as well as the translational motion of PEG. The considerations for the decrease of D_{PEG} that the hydrogen-bond interaction between a part of the segment in PEG and the polymer network strong enough to restrain the translational motion of the PEG molecule is formed and that the dominant parts of segments in PEG, which do not form hydrogen bonds, may undergo fast segmental motion may not be accepted. Instead, it can be considered that the complex is stabilized through hydrogen-bondings between the whole PEG chain and consecutive AA units in the network polymer. This is consistent with the result of the diffusion coefficient measurement that D_{PEG} does not decrease in (DMAA−AA) copolymer gels with $f_{AA} <$ 0.5.

It can be concluded as follows. The D and ^{1}H T_2 values for PEG (probe polymer) in swollen (DMAA−AA) copolymer gels with various mole fractions of AA units were determined by using the PGSE method and Carr−Purcell/Meiboom−Gill method. From these experimental results, it was found that the D and ^{1}H T_2 values for PEG in (DMAA−AA) copolymer gels with $f_{AA} \geq 0.9$ are much smaller than those in (DMAA−AA) copolymer gels with $f_{AA} < 0.5$ because of the loose complexation of PEG and consecutive AA units in the network. Further, it has been demonstrated that the ^{1}H NMR methods are useful means for elucidating the intermolecular interaction through the observation of molecular dynamics.

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