A Study of Self-Diffusion of Molecules in Polymer Gel by Pulsed-Gradient Spin−Echo ^{1}H NMR

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Received March 20, 1996; Revised Manuscript Received June 11, 1996[⊗]

ABSTRACT: Pulsed-gradient spin−echo (PGSE) ^{1}H NMR experiments were carried out on swollen poly(*N*,*N*-dimethylacrylamide) (PDMAA) gels with various degrees of swelling (Q) under a state of equilibrium with deuterated water (D_2O) as solvent and poly(ethylene glycol) (PEG) as a probe polymer, of which the molecular weight ranged from 4250 to 20000. Self-diffusion coefficients of PEG and HDO in D_2O solvent (containing a small amount of HDO) in the gels were determined. From these results, the diffusion coefficient for HDO in the gel (D_{HDO}) was found to increase with an increase in Q and asymptotically approach the diffusion coefficient for HDO in neat D_2O. This behavior was reasonably explained by the modified free volume theory. Further, it was found that the diffusion coefficient for PEG (D_{PEG}) in the gel is followed by $D_{\mathrm{PEG}}/D^0_{\mathrm{PEG}} = \exp(-\kappa R)$, where D^0_{PEG} is the diffusion coefficient for an isolated PEG, κ^{-1} the dynamical screening length, and R the hydrodynamic radius of PEG, and that κ^{-1} is proportional to $c^{-0.71}$, where c is the polymer concentration.

Introduction

A better understanding of the diffusional behavior of low-molecular-weight and high-molecular-weight molecules in a polymer gel is needed for the development of fundamental research work on polymer gels as well as practical work. The diffusion of probe polymers in gel systems has been studied for substantial elucidation of polymer dynamics. Network polymer chains in the gel are more immobile than polymer chains in semidilute solution at the same polymer concentration because of the existence of chemically cross-linking points. Therefore, the diffusion of a probe polymer chain in gels has been successfully studied by the dynamic light scattering (DLS) method[1−3] and forced Rayleigh scattering (FRS)[4,5] to elucidate the existence of a reptation regime where the diffusion of the matrix chains must be negligibly slow relative to a probe polymer.[6−10] However, it is difficult to apply these methods to various polymer gel systems because solvents have to be isorefractive with the polymer network for DLS measurement and the photochromic probe polymer has to be prepared for FRS measurement.

Recently, it has been demonstrated that NMR gives very useful information about the structure and dynamics of polymer gel systems as reviewed by the present authors.[11] The spin−lattice relaxation time (T_1) and spin−spin relaxation time (T_2) give information about the microscopic molecular motion of solvent[12−16] and probe polymer in polymer network.[17] Also, ^{1}H NMR imaging can provide spatial information about the diffusion process of molecules in gels.[18−20] Additionally, the pulsed-gradient spin−echo (PGSE) ^{1}H NMR method has become a powerful technique for studying self-diffusion in polymer systems.[21,22] Using this method, there have been some studies carried out to investigate the diffusional behavior of polymer in network polymers[23,24] or solvent in gels.[13,25] In spite of the importance of understanding the dynamical behavior of probe polymer in gel systems, especially in hydrogel systems, there has been little systematic study on the dynamical behavior through the determination of the self-diffusion coefficient.

In this work, we have attempted to elucidate the dynamics of water and poly(ethylene glycol) (PEG) in poly(*N*,*N*-dimethylacrylamide) (PDMAA) gel swollen with water as functions of weight-average molecular weight (M_w) of PEG and degree of swelling (Q) of PDMAA gel under a state of equilibrium by means of the PGSE ^{1}H NMR method.

Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMAA) monomer, kindly supplied by Kojin Chemical Co. Ltd., was distilled at 341 K under a pressure of 1463 Pa. *N*,*N′*-Methylenebis(acrylamide) (MBAA) used as the cross-linking monomer was recrystallized from ethanol solution twice. $K_2S_2O_8$ used as the polymerization initiator was recrystallized from aqueous solution. Poly(ethylene glycol) (PEG) (M_w = 4250, 10 890, and 20 000; $M_w/M_n < 1.19$, where M_w and M_n are weight-average molecular weight and number-average molecular weight, respectively) used as probe polymers were purchased from Polysciences, Inc. Deuterated water (D_2O; 99.8% isotope labeled) used as solvent was purchased from Aldrich Chemical Co., Inc., in which a very small amount of HDO is contained.

Poly(*N*,*N*-dimethylacrylamide) (PDMAA) gels were prepared by radical copolymerization of DMAA (2.0 mol/L) and MBAA (0.2−51.2 mmol/L) initiated with $K_2S_2O_8$ (0.02 mol/L) in D_2O at 313 K with 1% PEG. PDMAA gels obtained were soaked in D_2O solution of 1% PEG for 3 days to remove the remaining monomer, initiator, and linear polymers formed as a byproduct and to reach an equilibrium of swelling. The D_2O solution of 1% PEG was repeatedly changed.

The degree of swelling 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})

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

In Figure 1a the Q values of PDMAA gels are plotted against the mole fraction of cross-linking agent (MBAA) for DMAA (f_c). As seen from this figure, swollen PDMAA gel samples are in the range Q = 7.5−50, where a decrease in Q indicates an increase in cross-linking. At a state of equilibrium swelling, the relation between the density of cross-linking point (N_c) and Q is given by[26]

$$N_c \approx Q^{-5/3} \tag{2}$$

Therefore, N_c can be estimated using eq 2. The efficiency of

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[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

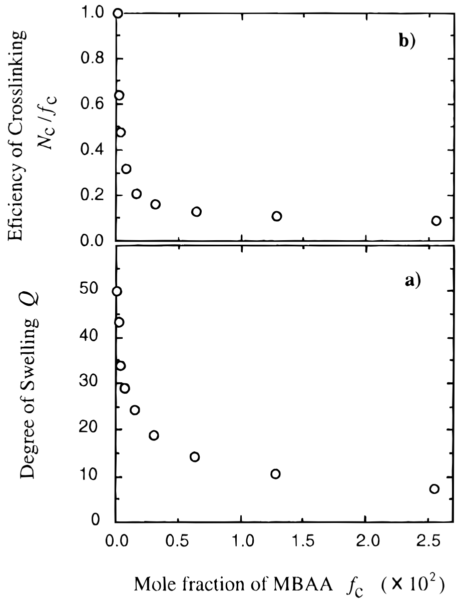

Figure 1. (a) Dependence of the degree of swelling (Q) of PDMAA gel on f_c at 303 K, where f_c is mole fraction of *N*,*N*-methylenebis(acrylamide) (MBAA) used as cross-linking reagent. (b) Plot of N_c/f_c against f_c, where it is assumed that $N_c/f_c = 1.0$ at $f_c = 0.01$. N_c was estimated from the experimental Q value using eq 2.

cross-linking (N_c/f_c), that is the ratio of the amount of MBAA contributed to cross-linking to that of MBAA added, is plotted against f_c as shown in Figure 1b, where it is reasonably assumed that when $f_c = 0.01$, $N_c/f_c = 1.0$. It is found that the efficiency of cross-linking decreases with an increase in f_c because when the degree of cross-linking is highly advanced, further reaction for both of the two vinyl groups of MBAA is strongly hindered.

Measurements. The self-diffusion coefficient measurements on HDO and PEG in a PDMAA gel were carried out by means of a JEOL GSX-270NMR spectrometer operating at 270.1 MHz for ^{1}H with a home-made pulse gradient generator at 303 K. Spectral width, data points, and field gradient strength were 4.0 kHz, 4096, and 5.9 T m^{-1}, respectively. The relationship between echo signal intensity and pulse field gradient parameters is given by

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

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 the gyromagnetic ratio of the proton, G the field gradient strength, D the self-diffusion coefficient, and Δ the gradient pulse interval. The echo signal intensity was measured as a function of δ. Plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2 G^2 \delta^2 (\Delta - \delta/3)$ give a straight line with a slope of $-D$. Therefore, the D value can be determined from its slope. The τ, Δ, and δ values employed in these experiments were 30, 30, and 0.06–2.0 ms, respectively.

Dynamical Analysis of Solvent and Probe Polymer in a Polymer Gel

The dynamical behavior of solvent in a gel can be analyzed by the modified free volume theory proposed by Fujita.[27] The self-diffusion coefficient D is related to the friction coefficient ζ by the equation $D = kT/\zeta$, where k is the Boltzmann constant and T the absolute temperature. The dependence of ζ on solvent concentration is expressed as an exponential function of the fractional free volume f. Then, the ratio of ζ at any polymer concentration to ζ at a reference concentration (ζ_r) is given by

$$\zeta/\zeta_r = \exp[B(1/f - 1/f_r)] \qquad (4)$$

where f_r is f at a reference concentration and B is the minimum hole-size parameter required for the displacement of solvent, which is independent of the polymer concentration and is assumed to be 1. If f is linearly proportional to the increase of volume fraction of solvent at a constant temperature, f can be expressed in the form[27−29]

$$f = f_r + \beta(v - v_r) \qquad (5)$$

where v is the volume fraction of solvent, v_r the volume fraction of solvent at a reference concentration, and β the proportionality constant. An assumption of eq 5 in the free volume theory was originally introduced to the polymer–solvent mixtures in the sufficiently low solvent concentration region.[29] However, the free volume theory is used to elucidate the dependence of diffusion of solvent in polymer solution[30−32] and gel[33] on solvent concentration in the large solvent concentration region. Thus, by substituting eq 5 into eq 4 we have

$$\zeta/\zeta_r = \exp[-(v - v_r)/f_r(f_r/\beta + v - v_r)] \qquad (6)$$

From this equation, we have the following expression with the assumption that solvent in infinite swollen gel is chosen as a reference, that is $v_r = 1$.

$$D_{\mathrm{HDO}} = D^0_{\mathrm{HDO}} \exp[(1 - v)/\{(1 - v)f_{\mathrm{solv}} - f_{\mathrm{solv}}{}^2/\beta\}] \qquad (7)$$

where D^0_{HDO} and f_{solv} are the self-diffusion coefficient and the fractional free volume of deutrated water in infinite swollen gel, respectively. As the volume fraction of polymer may be approximated to be the same as the weight fraction of polymer, $1 - v \approx Q^{-1}$. Thus, we have

$$D_{\mathrm{HDO}} = D^0_{\mathrm{HDO}} \exp[Q^{-1}/(Q^{-1}f_{\mathrm{solv}} - f_{\mathrm{solv}}{}^2/\beta)] \qquad (8)$$

The dynamical behavior of probe polymer in a gel can be analyzed by the ratio of the screening length of polymer network to the dimensional size of PEG. It is shown that the diffusion of a particle (D) in semidilute polymer solution[34−36] and in a polymer gel[37] is followed by the following relation

$$D/D^0 = \exp(-\kappa R) \qquad (9)$$

where D^0 is the the diffusion coefficient of an isolated particle, R the radius of a particle, and κ^{-1} the dynamical screening length of polymer chain. When $D/D^0 = e^{-1}$, κ^{-1} is equivalent to R. This relation has also been employed for elucidating the self-diffusional behavior of random-coil polymers in solution[7] and gel,[2] in which κ^{-1}s are large enough for probe polymers to have the same motion as a hard sphere rather than the reptational motion. In these cases, the interchain hydrodynamic interactions more significantly contribute to the diffusion process compared with the topological constraints. For this, the hydrodynamic radius of a probe polymer can be replaced by R. When the topological constraints cannot be neglected, compared with the interchain hydrodynamic interactions, D_s becomes larger than the value expected from eq 9. When the diffusion coefficient of an isolated PEG (D^0_{PEG}) is determined from the diffusion coefficient of PEG in aqueous dilute solution($D^{\mathrm{soln}}_{\mathrm{PEG}}$), it is necessary to take into account the

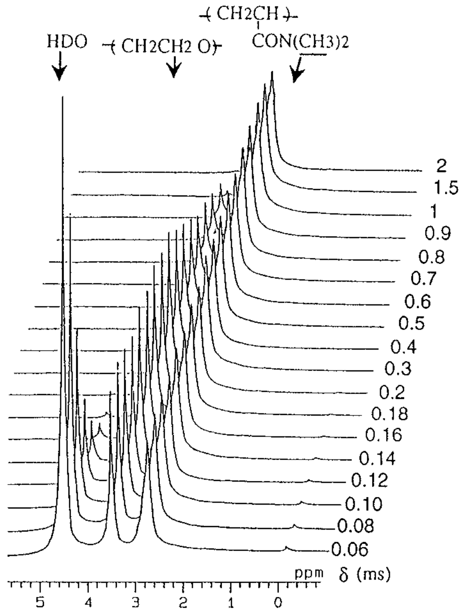

Figure 2. Spin–echo ^{1}H NMR spectra of PDMAA gel with $Q = 46.3$ containing PEG with $M_w = 20\ 000$ as probe polymer and HDO as solvent by varying field gradient pulse duration (δ).

change of local friction of polymer, which is estimated by the change for the diffusion coefficient of solvent.[38] Then, D^0_{PEG} is given by

$$D^0_{PEG} = D^{soln}_{PEG}/(D^{neat}_{HDO}/D_{HDO}) \qquad (10)$$

where D^{neat}_{HDO} is the diffusion coefficient of HDO in D_2O. In this work, the diffusional behavior of water and PEG in a PDMAA gel has been analyzed by the above-mentioned eqs 8 and 9.

Results and Discussion

PGSE ^{1}H NMR Spectra and Their Assignment. Typical spin–echo ^{1}H NMR spectra of a PDMAA gel ($Q = 46.3$) containing PEG ($M_w = 20\ 000$) and HDO are shown as a function of magnetic field gradient pulse length (δ) in Figure 2.

Peaks at 4.73, 3.72, and 2.93 ppm can be assigned to HDO, methylene protons of PEG, and methyl protons of PDMAA, respectively, by comparison with reference data on PEG solution and PDMAA gel without PEG. The intensity decay for peaks at 4.73 and 3.72 ppm is influenced by the velocity of diffusion of corresponding molecules. The peak at 2.93 ppm does not decay. The PDMAA network is undergoing random fluctuating motion, where the displacement is too small to induce the decay of the peak. This is due to insufficient strength of the gradient field to measure such a motion in the shorter observation time (the time interval between the two gradient pulses) compared with the time scale of molecular motion, which comes from the limitation of the present instrument. For peaks at 4.73 and 3.72 ppm, plots of $\ln[A(\delta)/A(0)]$ against $\gamma^2G^2\delta^2(\Delta - \delta/3)$ are shown in Figure 3. It is seen that the experimental data lie on a straight line. This means that the individual diffusants of HDO and PEG in the gel have a single component diffusion during the observation time. From the slopes of the obtained straight lines, the D values of HDO and PEG were determined with the standard error of $(2.02 \pm 0.03) \times 10^{-5}$ and $(1.96 \pm 0.05) \times 10^{-7}$ cm^2 s^{-1}, respectively.

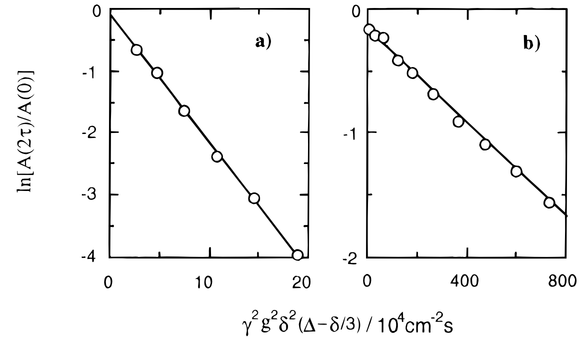

Figure 3. Diffusional spin–echo attenuation of HDO (a) and PEG (b) with $M_w = 20\ 000$ in a PDMAA gel with $Q = 46.3$ by varying field gradient pulse duration (δ). From the slope of the solid straight line, D_{HDO} and D_{PEG} were obtained to be 2.02×10^{-5} and 1.96×10^{-7}, respectively, using eq 3.

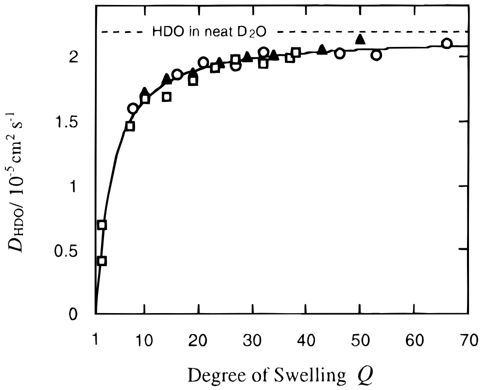

Figure 4. Dependence of the diffusion coefficient of water molecule (D_{HDO}) on the degree of swelling (Q) in a PDMAA gel containing PEG with M_w = 4250 (□), 10 890 (▲), and 20 000 (○) at 303 K.

Diffusion Coefficient of HDO in a PDMAA Gel. The diffusion coefficients of HDO (D_{HDO}) contained in a PDMAA gel were determined by the PGSE ^{1}H NMR method at 303 K varying Q and M_w of PEG contained in the gel. The D_{HDO} values obtained were plotted against Q as shown in Figure 4. As seen from this figure, D_{HDO} increases as Q is increased, and is almost independent of M_w of PEG contained in the gel. The change of D_{HDO} in the small-Q region is much larger than that in the large-Q region. The D_{HDO} value in the large-Q region asymptotically approaches that for HDO in neat D_2O (2.22×10^{-5} cm^2 s^{-1}). Therefore, it can be said that the intermolecular interaction between water and polymer network, of which the strength depends on the size of a network, restrains translational motion of the water. There is almost no effect on the molecular motion of HDO by the change of M_w of PEG, indicating that the diffusion of HDO is independent of M_w of PEG.

We can understand more clearly the dynamical behavior of water in the gel system using eq 8 obtained from the modified free volume theory.[27] The solid curve obtained from a least-squares fitting to the experimental data using eq 8 is shown in Figure 4. The theoretical curve agrees well with the experimental data. From this result, the diffusion coefficient for HDO in infinite swollen gel ($Q \rightarrow \infty$) is obtained to be $D^0_{HDO} = 2.16 \times 10^{-5}$ cm^2 s^{-1}, which is lower than HDO in neat D_2O (2.22×10^{-5} cm^2 s^{-1}). This means that the diffusion coefficient for HDO in neat D_2O is different from the Q-extrapolated value to the infinite Q given by the modified free volume theory for the Q dependence of the diffusion coefficient.[30] The diffusion coefficient for an

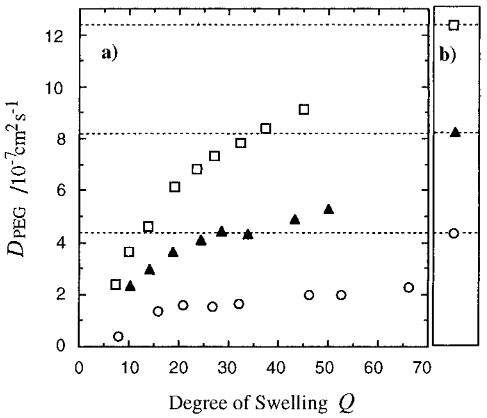

Figure 5. (a) Dependence of the diffusion coefficient of PEG (D_{PEG}) in PDMAA gel on the degree of swelling (Q) at 303 K. (b) The diffusion coefficients of PEG in 1 wt % aqueous solution at 303 K. M_{w}s of PEGs used are 4250 (□), 10 890 (▲), and 20 000 (○).

isolated HDO molecule in bulk PDMAA ($Q \rightarrow 1$) obtained from Figure 4 was 2.5×10^{-7} cm^2 s^{-1}.[33,39] It is seen that the translational motion of an isolated water in bulk polymer is more strongly restrained compared to that in the gel. Further, it can be said that the rapid decrease of D_{HDO} in the small-Q region can be explained by the decrease in free volume.

Diffusion Coefficient of PEG in a PDMAA Gel. In order to investigate the translational motion of PEG contained in PDMAA gel as a probe polymer, the diffusion coefficient of PEG (D_{PEG}) was determined by the PGSE ^{1}H NMR method at 303 K varying Q and M_{w} of PEG contained in the gel. The D_{PEG} values obtained were plotted against Q in Figure 5a. It was found that D_{PEG} increases as Q is increased and also depends on M_{w} of PEG. The D_{PEG} value in the gel is smaller than that at 1 wt % aqueous PEG solution ($D_{\mathrm{PEG}}^{\mathrm{soln}}$) at 303 K as shown in Figure 5b. Therefore, it can be said that the translational motion of PEG in the gel is more restrained by large intermolecular interaction with polymer network as compared with PEG in aqueous solution and that PEG with higher M_{w} is more strongly restrained.

Next, we are concerned with the relationship between the degree of restraint in molecular motion of PEG in the gel and the ratio of the screening length of polymer network to the size of PEG. The dynamical behavior of PEG in the gel can be analyzed by using eq 9.

The relationship between the dynamical screening length (κ^{-1}) and the concentration of network polymer (c) or the degree of swelling (Q) is expressed by

$$\kappa^{-1} \sim c^{\mathrm{u}} = Q^{-\mathrm{u}} \tag{11}$$

where u may be a constant in the range from -0.5 to -1.0 but depends largely on the polymer species.[35] Substitution of eqs 10 and 11 into eq 9 gives

$$D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}/D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}} = \exp(-Q^{\mathrm{u}}R) \tag{12}$$

It is convenient to rewrite it in the form

$$\ln\left(-\ln \frac{D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}}{D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}}}\right) = u \ln Q + \ln R \tag{13}$$

The log−log plot of the $\ln(-\ln(D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}/D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}}))$ value against the degree of swelling (Q) using the experimental data (Figure 5) is shown in Figure 6. The three straight lines for PEG with different M_{w} have almost the same slope but different intercepts. As R in aqueous PEG solution is assumed to be same as that in gel, we have

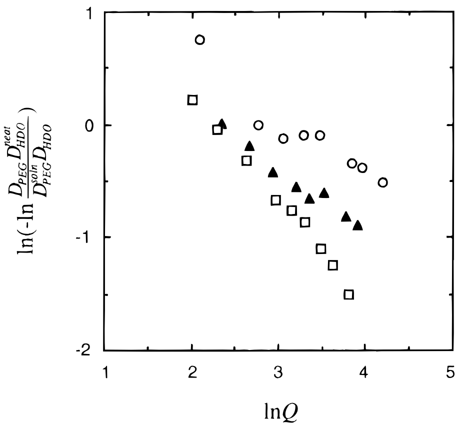

Figure 6. Plot of $\ln(-\ln(D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}/D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}}))$ against ln Q at 303 K. M_{w}s of PEGs used are 4250 (□), 10 890 (▲), and 20 000 (○).

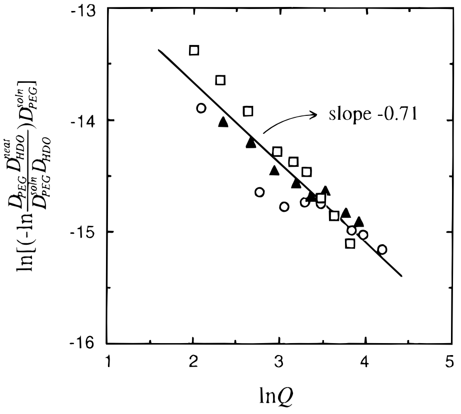

Figure 7. Plot of $\ln[(-\ln(D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}/D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}}))D_{\mathrm{PEG}}^{\mathrm{soln}}]$ against ln Q at 303 K. M_{w}s of PEGs used are 4250 (□), 10 890 (▲), and 20 000 (○).

$$R = kT/6\pi\eta_{\mathrm{s}}D_{\mathrm{PEG}}^{\mathrm{soln}} \tag{14}$$

where η_{s} is the viscosity of solvent in solution. Substitution of eq 14 into eq 13 gives

$$\ln\left[\left(-\ln \frac{D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}}{D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}}}\right)D_{\mathrm{PEG}}^{\mathrm{soln}}\right] = u \ln Q + \ln(kT/6\pi\eta_{\mathrm{s}}) \tag{15}$$

In Figure 7, the $\ln[(-\ln(D_{\mathrm{PEG}}D_{\mathrm{HDO}}^{\mathrm{neat}}/D_{\mathrm{PEG}}^{\mathrm{soln}}D_{\mathrm{HDO}}))D_{\mathrm{PEG}}^{\mathrm{soln}}]$ value calculated using the experimental data is plotted against ln Q. A straight line with a slope of -0.71 is obtained and so $u = -0.71$. Therefore, we have $\kappa^{-1} \sim Q^{0.71} = c^{-0.71}$. Depending on the nature of network and solvent, there are a variety of theoretical calculations for the concentration dependence of the dynamical screening length.[35] de Gennes[40] proposed theoretically that for flexible polymer chains in a gel with good solvent the relationship $\kappa^{-1} \sim c^{-0.75}$ is obtained. Our experimental results were close to this prediction.

Conclusion

The diffusion coefficients for both PEG (probe polymer) and HDO (solvent) in swollen PDMAA gels with various degrees of swelling Q under a state of equilibrium were reasonably determined by the PGSE ^{1}H NMR method. From these experimental results, it is found that the D_{HDO} values are well explained by free volume theory in a wide region of Q, the D_{PEG} values are followed by $D/D^0_{\mathrm{PEG}} = \exp(-\kappa R)$, and the dynamical screening length κ^{-1} is proportional to $c^{-0.71}$, which is close to the value proposed theoretically by de Gennes. Further, it has been demonstrated that the PGSE NMR method provides a useful methodology to elucidate the diffusional behavior of molecules in gels.

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