Diffusion of Poly(ethylene oxide) Chains in Gelling and Nongelling Aqueous Mixtures of Ethyl(hydroxyethyl)cellulose and a Surfactant by Pulsed Field Gradient NMR

Harald Walderhaug, Anna-Lena Kjøniksen, and Bo Nyström*

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

Received: April 25, 1997; In Final Form: August 20, 1997[⊗]

Tracer diffusion of poly(ethylene oxide) (PEO) in solutions and gels of ethyl(hydroxyethyl)cellulose (EHEC) in the presence of different amounts of the anionic surfactant sodium dodecyl sulfate (SDS) has been studied with the aid of pulsed field gradient NMR. The decay of the spin−echo function exhibits a single-exponential profile. The results suggest that the diffusion of the PEO chains decreases as the matrix concentration increases, while the thermoreversible gelation process does not seem to affect the tracer diffusion rate significantly. The observed obstruction effects registered by the probe molecules depend on the concentration of the matrix polymer (EHEC) and surfactant concentration, but not on the molecular weight of the probe polymer. In the absence of EHEC, the interaction between PEO and SDS gives rise to a gradual expansion of the coil dimensions as the level of surfactant addition increases. The profile of the spin−echo attenuation, obtained from self-diffusion of the matrix polymer, exhibits a more complex behavior than that of the tracer, with initially a stretched exponential ("fast" diffusion) followed by a single exponential ("slow" diffusion) decay.

Introduction

Diffusion of probe molecules of different sizes in polymer solutions and gels is important in a variety of contexts including biological transport, separations, and polymer dynamics. Tracer diffusion of homopolymer chains in a polymer network, e.g., a polymer gel or a semidilute solution, depends upon structure and mobility of the environment as well as on the chain length of probe polymer and specific interactions between the cosolute and the matrix polymer. The probe diffusion in polymer solutions and gels has been investigated by dynamic light scattering[1−7] and, more recently, pulsed gradient spin−echo (PGSE) NMR spectroscopy.[8−18] The results have been analyzed on the basis of various theoretical models.[19−30] The PGSE technique enjoys certain advantages over others in that it is capable of measuring diffusion coefficients over a wide range from fast diffusion (above 10^{-6} m^2 s^{-1}) to very slow diffusion (10^{-14} m^2 s^{-1}), and the technique can provide individual self-diffusion coefficients from mixtures of diffusing molecules,[31] without the need for any artificial labeling.

NMR tracer diffusion results[15,16] of octaethylene glycol dodecyl ether (C$_{12}$E$_8$) and of low molecular weight poly(ethylene oxide) (PEO) in solutions of ethyl(hydroxyethyl)cellulose (EHEC) at different temperatures have recently been reported. The results revealed a reduction of the mobility of the probe molecules with increasing concentration of the matrix polymer (EHEC).

In the present work, the tracer diffusion of PEO chains with molecular weights of 120 000 and 288 000 has been measured with the aid of the PGSE technique at different temperatures in gelling and nongelling aqueous systems of ethyl(hydroxyethyl)-cellulose (EHEC) in the presence of various amounts of the anionic surfactant sodium dodecyl sulfate (SDS). It is well established[32−35] that aqueous solutions of this EHEC sample in the presence of a moderate concentration of an ionic surfactant exhibit a thermoreversible sol−gel transition in the semidilute regime (ca. 1 wt %), where the polymer molecules overlap each other. Upon heating, these systems undergo a transformation from a moderate viscous solution to a clear and stiff gel.

However, it should be noted that at higher concentrations of SDS no gel is formed at elevated temperature (see Table 1).

Recently, EHEC self-diffusion of gelling EHEC−SDS systems was studied[36] by means of the PGSE technique. A complex picture emerged, where the decay of the spin−echo attenuation was initially described by a stretched exponential ("fast" diffusion) followed by a single exponential ("slow" diffusion). The present investigation will show that the diffusion behavior of the PEO chains in EHEC−SDS systems is simple under certain conditions, with practically a single-exponential profile of the spin−echo attenuation.

The aim of this study is to gain insight into the interaction between the probe polymer and the matrix polymer in solution and during gelation and to explore how the level of surfactant addition affects the mobility of the probe molecules. This work may also provide useful information about changes of the network structure during the process of gelation.

Experimental Section

Materials and Solution Preparation. The EHEC sample, designated Bermocoll DVT 89017, was manufactured by Akzo Nobel Surface Chemistry AB, Stenungsund, Sweden, and utilized in all experiments reported here. The degree of substitution of ethyl groups DS$_{ethyl}$ = 1.9/anhydroglucose unit, and molar substitution of ethylene oxide groups MS$_{EO}$ = 1.3/anhydroglucose unit. The number average molecular weight of this polydisperse sample ($M_w/M_n \approx 2$) is approximately 80 000. All these data have been given by the manufacturer. The surfactant SDS was obtained from Fluka and was used as received.

Dilute EHEC solutions were dialyzed against pure water for several days to remove salt (impurity from the manufacturing) and were thereafter freeze-dried. As dialyzing membrane, regenerated cellulose with a molecular weight cutoff of 8000 (Spectrum Medical Industries) was used. After freeze-drying, the polymer was redissolved in aqueous media with desired SDS concentrations. Two sharp fractions of PEO with molar masses of M = 120 000 (M_w/M_n = 1.02, batch no. 20835-7) and M = 288 000 (M_w/M_n = 1.06, batch no. 20838-7) were used as tracer and obtained from Macherey-Nagel, Germany. These data were

Diffusion of Poly(ethylene oxide) Chains

J. Phys. Chem. B, Vol. 101, No. 44, 1997 **8893**

TABLE 1: Gel Temperatures of Gel-Forming Systems and Indication of Systems Which Are Not Gelling in the Considered Temperature Range[a]

concentration		gel temperatures at the SDS concentrations given		
EHEC wt %	PEO wt %	4 m*m*	8 m*m*	20 m*m*
0.5	0.5	no gel	no gel	no gel
1	0.5	35 (37) °C	no gel	no gel
2	0.5	35 (34) °C	no gel (39 °C)	no gel

[a] Values in the parentheses indicate the gel temperatures in the absence of the tracer polymer.

all given by the manufacturer. The samples were prepared by weighing the components, and the solutions were homogenized by stirring at room temperature for several days in order to reach equilibrium and to allow any time-dependent effect to settle.[37] Tracer diffusion measurements were carried out on EHEC–SDS systems in the presence of fixed amounts of PEO of 0.5 and 0.25 wt % for the molecular weights of PEO of 120 000 and 288 000, respectively. These PEO concentrations are located in the dilute regime.

NMR Experiments. The EHEC self-diffusion and the PEO tracer diffusion coefficients were determined with the PGSE technique, which has been described in detail previously.[38] All measurements were carried out in 5 mm NMR tubes on a Bruker DMX-200 spectrometer. The EHEC self-diffusion coefficients were determined by using the stimulated pulse sequence.[39,40] The longitudinal eddy current delay sequence (the so-called "preemphasis adjustment") was employed in all experiments. The attenuation of the spin–echo amplitude after Fourier transformation was sampled as a function of the magnitude g of the applied gradient pulse (0.5 ≤ g ≤ 8 T/m).

The gradient delivery system is completely electronically controlled. The field gradients for the experimental setup with the actual probehead interfaced have been calibrated by the manufacturer. This calibration was checked by routine using a sample of dry glycerol at 25 °C. At various observation times Δ, and with the other parameters inside the interval used in this study, these experiments gave a diffusion coefficient that agreed with the literature value[41] of 1.7×10^{-12} m^2 s^{-1}. The measurements were performed by varying the magnitude of the applied magnetic field gradient g and by keeping the width of the gradient pulses δ (typically 3 ms) and Δ constant during an experiment. All measurements were performed in the narrow pulse width approximation, i.e., with $\delta \ll \Delta$. To reveal possible anomalous diffusion behavior,[42,43] several experimental series were carried out at different values of Δ. However, no deviation from ordinary Ficks behavior was detected in the tracer diffusion measurements under the present experimental conditions. The experiments were performed in the temperature range 25–40 °C. The sample was allowed to equilibrate for about 1 h at each temperature of measurement. By using a variable temperature control unit, the temperature constancy was better than ±0.5 °C. The temperature settings were calibrated by using an ethylene glycol sample giving easily measurable shift differences between the two proton NMR signals that depend strongly on temperature.

The result of Stejskal and Tanner's analysis[44] of the PGSE experiment is the standard equation for the spin–echo amplitude A

$$A(2\tau,g) = A_0 \exp(-2\tau/T_2) \exp[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)] \quad (1)$$

where τ is the time between the π and $\pi/2$ radio frequency pulses, T_2 is the transverse relaxation time, and γ is the gyromagnetic ratio of the nucleus under consideration (the ^{1}H

nucleus here). This equation is often used in a normalized form to remove the effects of transverse relaxation

$$\Psi \equiv A(g)/A(0) = \exp[-Dk^2 t_{\text{eff}}] \quad (2)$$

where $A(g)$ and $A(0)$ are the echo amplitudes with and without the field gradient pulses, respectively, $k \equiv \gamma g \delta$ and the effective diffusion time $t_{\text{eff}} \equiv \Delta - \delta/3$.

To account for possible polydispersity effects of the polymer sample, we have analyzed the spin–echo attenuation data by using the method of cumulants[45,46] and the stretched exponential function.[47] In terms of the second-order cumulant expansion, the attenuation Ψ of the echo signal can be expressed as[13]

$$\ln \Psi = -\langle D \rangle X + {}^1\!/_2 (\mu_2 X^2) \quad (3)$$

with $X = \gamma^2 g^2 \delta^2 t_{\text{eff}}$, where $\langle D \rangle$ is an average diffusion coefficient, μ_2 is the second moment of polydispersity of $\langle D \rangle$, i.e., $\mu_2 = \langle (D - \langle D \rangle)^2 \rangle$. In the present tracer diffusion measurements, the polydispersity index $\mu_2/\langle D \rangle^2$ was small (≤ 0.07). The spin–echo attenuation data can also be described by a stretched exponential of the following form[47]

$$\Psi = \exp[-(XD_{\text{se}})^\beta] \quad (4)$$

where β ($0 < \beta \leq 1$) is a measure of the width of the distribution of self-diffusion coefficients and the quantity D_{se} is some effective self-diffusion coefficient. A mean diffusion coefficient can be calculated from the relation[47] $1/D_{\text{mean}} = (1/\beta)\Gamma(1/\beta)(1/D_{\text{se}})$, where Γ denotes the gamma function. In the fitting procedure of spin–echo attenuation data, the variables D_{se} and β are treated as adjustable parameters. A value of $\beta \approx 0.95$ is typical for the present NMR data. The value of β, as well as the value of the polydispersity index $\mu_2/\langle D \rangle^2$, suggests that the profile of the spin–echo attenuation of the probe molecules is practically a single exponential. These two methods yield identical values of the tracer diffusion coefficient. As will be discussed below, the spin–echo attenuation functions obtained from the self-diffusion measurements of the matrix polymer (EHEC) show a more complex behavior.

Results and Discussion

Figure 1a shows a typical spin–echo attenuation plot at different observation times for the diffusion of PEO ($M = 120$ 000) chains in the EHEC(1 wt %)/SDS (4 mM) system at 37 °C (a gel has been formed at this temperature; see Table 1). The nearly single-exponential profile of the decay functions is always observed, both in the gel and the sol phase, for the present tracer diffusion experiments. The condensation of the experimental points onto a straight line in Figure 1b, suggesting a time-independent Fickian diffusion behavior of the PEO chains.

As a comparison, an echo attenuation plot for the matrix polymer EHEC in the aqueous system PEO–EHEC (1 wt %)/SDS (8 mM) at 25 °C is depicted in the inset of Figure 1b at two different observation times. It is evident that the spin–echo functions for EHEC exhibit a more complex behavior than that of the tracer (PEO) polymer. The solid curves have been fitted with the following equation:[36]

$$\Psi_{\text{EHEC}} = A \exp[-(XD_{\text{fe,app}})^\beta] + (1 - A)\exp(-XD_{\text{se,app}})$$

where $0 \leq A \leq 1$ describes the contribution of the "fast" decay of the attenuation. The first and the second term of this equation denote the ("fast") stretched exponential and the single-exponential ("slow") diffusion mode, respectively. In this study
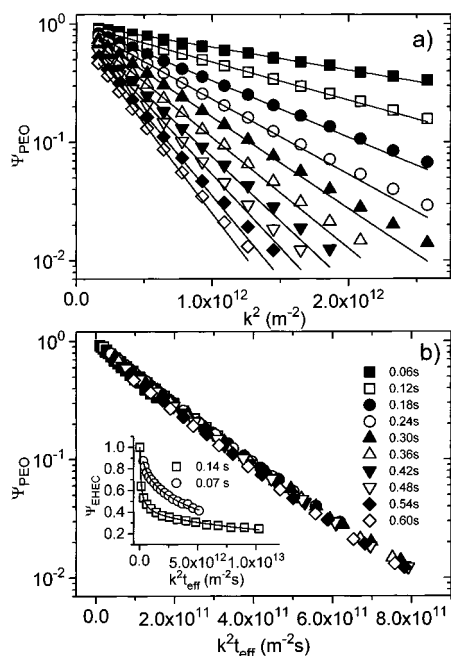
Figure 1. Proton spin−echo attenuation functions plotted in the forms (a) Ψ_{PEO} versus k^2 and (b) Ψ_{PEO} versus $k^2 t_{eff}$ for PEO ($M_{PEO} = 120\,000$, 0.5 wt %) in the EHEC (1 wt %)/SDS (4 mm) system at 37 °C and at the observation times indicated. The inset plot shows the proton spin−echo attenuation function for EHEC in the PEO ($M_{PEO} = 120\,000$, 0.5 wt %)/SDS (8 mm) system at 25 °C and at the observation times indicated.

the value of the "fast" apparent mean self-diffusion coefficient $D_{fe,app}$ is in the range 10^{-10}–10^{-11} m^2 s^{-1} and the "slow" apparent self-diffusion coefficient $D_{se,app}$ is about 10^{-14} m^2 s^{-1}. The above equation has been used previously[36] in the analysis of EHEC self-diffusion data in gelling and nongelling aqueous systems of EHEC in the presence of SDS. It was argued that the "fast" component may be associated with cooperative diffusion,[48] while the "slow" mode reflects self-diffusion of the individual chains. For ordinary Fickian diffusion, a plot of Ψ_{EHEC} versus $k^2 t_{eff}$ should condense the data points onto a single curve, but time-dependent self-diffusion coefficients are clearly revealed in the inset plot of Figure 1b. It is likely that some of the complex features, e.g., the nonexponential profile of the spin−echo attenuation, observed for the matrix polymer may be associated with polydispersity effects. The anomalous diffusion behavior of EHEC at different temperatures in gelling and nongelling aqueous systems of EHEC in the presence of SDS has been reported and discussed in a recent study.[36] Therefore, most of the attention in the present work will be focused on tracer diffusion, which under the present experimental conditions appears to be more simple. In passing, we may note that anomalous diffusion behavior has been reported[43,47,49−55] for other complex systems, and may indicate disordered or fractal-like[42,52,56] systems, where correlated motions and long memory effects[39,57] give rise to a non-Markovian stochastic process and anomalous[43] diffusion.

Before we discuss the tracer diffusion results in more detail, the interaction between PEO and SDS in the absence of EHEC will first be elucidated. The interaction between SDS and PEO is well established through various experimental methods.[58−67] The properties of solutions containing both a polymer and a surfactant have been explained by assuming the formation of a polymer−surfactant complex or micelle-like clusters,[60,61,68,69] resulting from the binding of the surfactant ions onto the polymer chain. In the presence of an ionic surfactant (as in the
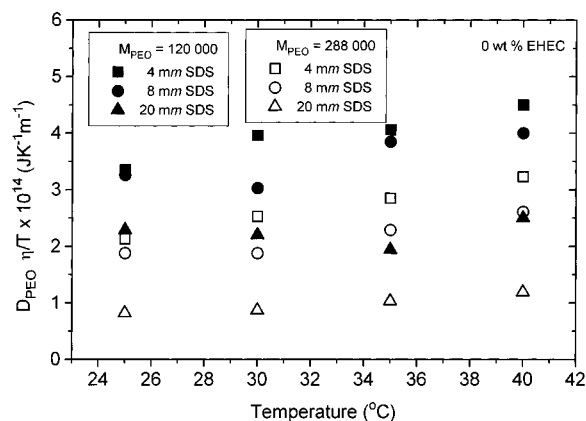

Figure 2. Temperature dependence of the reduced tracer diffusion coefficient ($M_{PEO} = 120\,000$, 0.5 wt % and $M_{PEO} = 288\,000$, 0.25 wt %) in the absence of EHEC and at the surfactant concentrations indicated.

present case), the bound ionic surfactant endows an apparent polyelectrolyte character to the initially nonionic PEO.

The onset of aggregation of surfactant in the presence of polymer is characterized by a critical aggregation concentration cac,[61] which has the properties of a critical micelle concentration (cmc). Above cac, the association continues up to the saturation concentration c_2, where free micelles start to form. Hence, beyond c_2, all the added SDS forms regular SDS micelles. For PEO−SDS systems, at the PEO concentrations considered in this study, the values[61] of cac and c_2 are about 4 mM and 25 mM, respectively. We may note that the critical aggregation concentration of SDS is much lower than the cmc (8 mM) for SDS. The SDS concentrations employed in this work are in the region where polymer−surfactant clusters are formed. In this context we should note that it has been shown from calorimetric measurements[67] that the interaction of PEO with SDS resembles that of the EHEC−SDS system.

The temperature dependence of the reduced self-diffusion coefficient $D_{PEO}\eta/T$ (corrected for trivial temperature and viscosity effects of the solvent) of PEO (in the dilute concentration regime) in the presence of different amounts of SDS is shown in Figure 2 for two molecular weights of PEO. The general trend, for both molecular weights, is that the reduced self-diffusion coefficient decreases with increasing surfactant concentration. This can probably be attributed to a coil expansion, resulting from electrostatic repulsions between the charged SDS aggregates along the polymer chain. This picture is consistent with a recent study,[66] where it was argued from viscosity measurements that a PEO coil saturated with SDS is swollen compared to a free coil in a good solvent. However, the polymer is not fully stretched as is observed with certain strong polyelectrolytes. As expected, the bahavior is similar for the two PEO fractions, but the values of the reduced self-diffusion coefficient for the low molecular weight sample are higher than the corresponding ones for the high molecular weight sample. This suggests that an increase in molecular weight of PEO only scale-up the overall dimensions of the polymer−surfactant clusters.

A temperature dependence of the reduced self-diffusion coefficient can be traced in Figure 2, and this trend indicates a weak temperature induced contraction of the polymer coils. This effect can probably be explained by the increased hydrophobicity of PEO at elevated temperatures. As a consequence the polymer coils will shrink and be less flexible, avoiding water contact.

Since both PEO and EHEC show interaction with SDS, it is relevant to compare their ability to interact with SDS. To judge which of the polymers exhibits the strongest interaction with
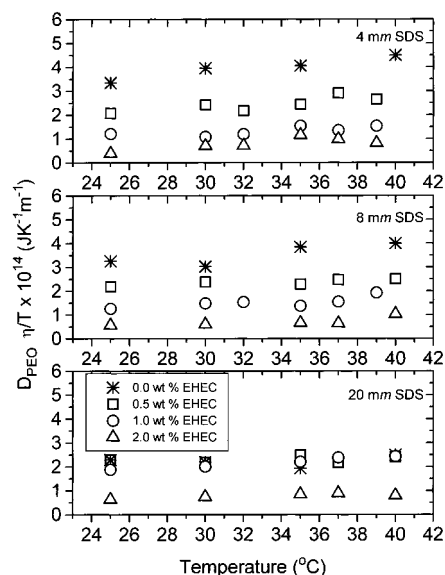
Diffusion of Poly(ethylene oxide) Chains

J. Phys. Chem. B, Vol. 101, No. 44, 1997 **8895**

Figure 3. Temperature dependence of the reduced tracer diffusion coefficient (M_{PEO} = 120 000, 0.5 wt %) at the surfactant and polymer concentrations indicated.
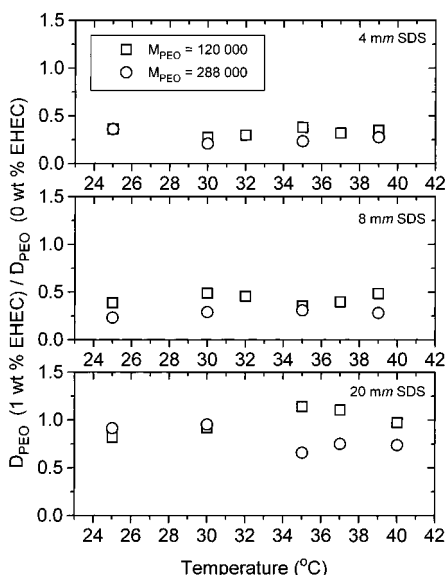

Figure 4. Temperature dependence of the normalized tracer diffusion coefficient in the presence of 1 wt % EHEC and at the surfactant concentrations and tracer molecular weights indicated.

SDS, we may consider their respective cac values. In the case of EHEC, the anionic surfactant SDS can interact both with the ethyl end groups and the EO groups, and this polymer is more hydrophobic with a significantly lower cac value (1.5 mM[70]) than that (4 mM[61]) of PEO. This indicates that, in systems with both EHEC (higher concentration) and PEO, most of the SDS will be bound to EHEC.

Before we discuss the results in Figures 3 and 4, it may be instructive to give a brief outline of the model of Cabane et al.[71] for the description of temperature induced gelation in EHEC−ionic surfactant systems. In the absence of surfactant, a temperature rise induces a macroscopic phase separation of the semidilute EHEC solution into a polymer-rich phase and an excess aqueous phase. Upon addition of an ionic surfactant, e.g., SDS, to the solution of EHEC, adsorption of the surfactant to the polymer chains occurs and the phase separation behavior of the EHEC polymer is modified, because the surfactant causes fragmentation of large domains of the polymer-rich phase into microscopic "lumps"[71] which are stabilized by the bound ionic

surfactant on the surfaces of these "lumps". Each "lump" is formed by the loose association of polymer segments belonging to different polymer molecules, and the adsorption of ionic surfactant gives rise to a polyelectrolyte character of the "lump". Small angle neutron scattering experiments[71] on EHEC−ionic surfactant systems have shown that the "lump" sizes increase at elevated temperature and decrease with increasing surfactant concentration. In a recent surfactant NMR self-diffusion study[36] on EHEC−SDS systems, it was found that the amount of surfactant bound to the polymer is roughly independent of temperature, even when the gel transition region is approached. These results indicate that at a constant surfactant concentration, a temperature increase favors the growth of the "lumps". The concentration of EHEC should also affect the size and the growth of the "lumps". If the concentration of EHEC increases at a given level of surfactant addition, a temperature raise is expected to favor the formation of "lumps". In gelling systems, the permanent connectivity of the gel network is provided by the growing "lumps" and the swelling properties are generated by the electrostatic repulsions of the ionic surfactant.

Figure 3 shows the temperature dependence of the reduced tracer diffusion coefficient of PEO (M = 120 000) at different matrix (EHEC) and SDS concentrations for gelling and non-gelling PEO−EHEC−SDS systems. We have found no significant differences in gel-forming properties between these systems and those depicted in Table 1. In the presence of 8 mm SDS, no temperature-induced gel is formed at the highest matrix concentrations, but only high-viscous solutions are obtained. At surfactant concentrations of 4 and 8 mm, a similar simple obstruction effect is observed, i.e., the reduced tracer diffusion coefficient decreases as the matrix concentration increases. However, in the presence of 20 mm SDS a more complex situation emerges. In this case, an "effective" obstruction effect is only detected for the highest matrix concentration, while for the other EHEC concentrations the values of the reduced tracer diffusion coefficient are practically the same over the considered temperature range.

These findings may be rationalized in the following way. At the highest level of surfactant addition (20 mm), the conjecture is that the "lumps" break down (the connectivity of the system is lost) and the network is disrupted.[71] This picture is consistent with recent rheological results[72] on the EHEC−SDS system. Upon breakdown of the network structure one should expect reduced restrictions on the mobility of the probe molecules. Furthermore, we should note that, for the matrix concentration of 1 wt % in the presence of 20 mm SDS, the values of the reduced tracer diffusion coefficient are significantly higher than the corresponding ones at 4 and 8 mm SDS. The observed additional obstruction effect of the reduced tracer diffusion coefficient for the highest matrix concentration in the presence of 20 mm SDS suggests that this surfactant concentration is not sufficiently high to break down the "lumps"/network at this EHEC concentration. This is supported by the high viscosity of this solution.

Let us now focus our attention on the temperature dependence of the reduced tracer diffusion coefficient (see Figure 3). Except for the weak temperature dependence observed in the absence of EHEC, the reduced tracer diffusion coefficient is practically independent of temperature for both thermally gelling and nongelling systems in the studied temperature range. It is noteworthy that no slowing down of the diffusivity of the tracer polymer is detected during the sol−gel transition. This finding suggests that the available space for tracer diffusion is not considerably reduced during the gelation process and that the probe chains are not captured in the matrix network. As stated

earlier in this work, the self-diffusion coefficients of the EHEC chains under the prevailing conditions seem to be in the order of 10^{-14} m^2 s^{-1}. If the probe chains to any significant degree had been captured in the matrix network, at least some trace of a diffusivity in this range should be visible in the echo attenuation data for the PEO chains. Furthermore, it is not unlikely that we had observed a nonexponential decay of the spin−echo function, reminiscent of that depicted in the inset plot of Figure 1b for the matrix polymer.

Figure 4 shows the effects of probe molecular weight and temperature on the tracer diffusion behavior in systems of 1 wt % matrix concentration and with different levels of SDS addition. The values of the normalized tracer diffusion coefficient D_{PEO}(1 wt % EHEC)/D_{PEO}(0 wt % EHEC) for the two molecular weights of PEO are practically the same, independent of temperature and surfactant concentration. However, we may note that the values of the normalized tracer diffusion coefficient are higher in the presence of 20 m*m* SDS than those at the lower surfactant concentrations. At the highest surfactant concentration, the polymer network is disrupted and we expect that the mobility of the probe chains is less obstructed than at the lower levels of surfactant addition. The results in Figure 4 are another indication of that the polymer network is "open" and that not even the rather long tracer chains are trapped in the network during the gelation process. In this context we may note that an enhanced hindrance to tracer diffusion is usually observed[16,17,73−75] when the molecular weight of the probe molecules increases.

From the present study a rather "idyllic" picture of tracer diffusion in polymer solutions and gels emerges. However, it should be stressed that in general a more complex situation prevails. Dynamic light-scattering measurements[34] on gelling and nongelling EHEC−SDS systems have revealed that the dynamic features in solutions and gels of EHEC are intricate. Furthermore, recent NMR tracer diffusion measurements[76] of PEO in EHEC−SDS systems have shown that anomalous diffusion behavior may come into play at higher matrix concentrations than considered here. It was also found that, for a high molecular weight ($M \approx 1 \times 10^6$) of PEO, anomalous tracer diffusion was observed already at a matrix concentration of 1 wt %. These findings suggest that both the matrix concentration and the molecular weight of the tracer are important factors for the appearance of the anomalous diffusion behavior.

Summary and Conclusions

In this study, tracer diffusion measurements of PEO (two molecular weights) in gelling and nongelling aqueous systems of EHEC in the presence of various amounts of SDS were carried out at different temperatures. The main results can be summarized in the following way: (1) The spin−echo attenuation functions, characterizing tracer diffusion of PEO in EHEC−SDS systems, can under the considered conditions be described by approximately a single exponential. The attenuation functions of the matrix polymer (EHEC) are more complex with a nonexponential behavior, and the diffusion coefficients are time dependent. (2) The diffusion of PEO in SDS solutions, without matrix polymer, suggest an expansion of the coils with increasing surfactant concentration. This phenomenon is attributed to electrostatic repulsions between the charged SDS aggregates along the polymer chain. (3) In EHEC−SDS systems at moderate surfactant concentrations, an enhanced obstruction effect of the tracer diffusion is observed with increasing matrix concentration. However, at a high surfactant concentration (20 m*m*), an enhanced obstruction effect is only

observed for the highest matrix concentration (2 wt %). The less pronounced obstruction effect observed for the lower matrix concentrations can be attributed to the disruption of the polymer network structure at this high level of surfactant addition. (4) We have not observed any effect of the molecular weight of the probe molecules on the normalized tracer diffusion coefficient. (5) Under the experimental conditions considered here, the hindrance to tracer diffusion is unchanged during the thermoreversible gelation process of the EHEC−SDS systems at a given matrix concentration. This indicates that the available space to diffusion is not significantly changed during the sol−gel transition, and the PEO chains are not captured by the matrix polymer network.

References and Notes

(1) Martin, J. E. *Macromolecules* **1984**, *17*, 1279.
(2) Ullmann, G. S.; Ullmann, K.; Lindner, R. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 692.
(3) Numasawa, N.; Hamada, T.; Nose, T. *J. Polym. Sci. Polym. Phys. Educ.* **1986**, *24*, 19.
(4) Lodge, T. P.; Markland, P. *Polymer* **1987**, *28*, 1377.
(5) Chu, B.; Wu, D. *Macromolecules* **1987**, *20*, 1606.
(6) Borsali, R.; Duval, M., Benmouna, M. *Macromolecules* **1989**, *22*, 816.
(7) Brown, W.; Zhou, P. *Macromolecules* **1991**, *24*, 1820.
(8) von Meerwall, E. D. *Adv. Polym. Sci.* **1983**, *54*, 1.
(9) Blum, F. D. *Spectroscopy* **1986**, *1*, 32.
(10) Garrido, L.; Mark, J. E.; Ackerman, J. L.; Kinsey, R. A. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2367.
(11) Gibbs, S. J.; Johnson, C. J., Jr. *Macromolecules* **1991**, *24*, 6110.
(12) Daivis, P. J.; Pinder, D. N.; Callaghan, P. T. *Macromolecules* **1992**, *25*, 170.
(13) Nose, T. *Ann. Rep. NMR Spectrosc.* **1993**, *27*, 217.
(14) Baba, J.; Kubo, T.; Takano, A.; Nose, T. *Polymer* **1994**, *35*, 145.
(15) Zhang, K.; Jonströmer, M.; Lindman, B. *J. Phys. Chem.* **1994**, *98*, 2459.
(16) Zhang, K.; Lindman, B.; Jonströmer, M. In *Cellulose and Cellulose Derivatives: Physico-Chemical Aspects and Industrial Applications*; Kennedy, J. F., Phillips, G. O., Williams, P. A., Eds.; Woodhead Publishing, Ltd.: Cambridge, U.K., 1995; pp 307−314.
(17) Tokita, M.; Miyoshi, T.; Takegoshi, K.; Hikichi, K. *Phys. Rev. E* **1996**, *53*, 1823.
(18) Matsukawa, S.; Ando, I. *Macromolecules* **1996**, *29*, 7136.
(19) Ogston, A. D.; Preston, B. N.; Wells, J. D. *Proc. R. Soc. London, Ser. A* **1973**, *333*, 297.
(20) Langevin, D.; Rondelez, F. *Polymer* **1978**, *19*, 875.
(21) Altenberger, A. R.; Tirrell, M. *J. Chem. Phys.* **1984**, *80*, 2208.
(22) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(23) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558.
(24) Hess, W. *Macromolecules* **1987**, *20*, 2587.
(25) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, A. Z. *Macromolecules* **1987**, *20*, 1107.
(26) Nyström, B.; Roots, J. *Macromolecules* **1991**, *24*, 184.
(27) Akcasu, A. Z.; Nägele, G.; Klein, R. *Macromolecules* **1991**, *24*, 4408.
(28) Johansson, L.; Elvingson, C.; Löfroth, J.-E. *Macromolecules* **1991**, *24*, 6024.
(29) Weber, H.; Paul, W. *Phys. Rev. E* **1996**, *54*, 3999.
(30) Ngai, K. L.; Phillies, G. D. J. *J. Chem. Phys.* **1996**, *105*, 8385.
(31) Söderman, O.; Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1994**, *26*, 445.
(32) Carlsson, A. Ph.D. Dissertation, Lund University, 1989.
(33) Nyström, B.; Roots, J.; Carlsson, A.; Lindman, B. *Polymer* **1992**, *33*, 2875.
(34) Nyström, B.; Lindman, B. *Macromolecules* **1995**, *28*, 967.
(35) Nyström, B.; Walderhaug, H.; Hansen, F. K.; Lindman, B. *Langmuir* **1995**, *11*, 750.
(36) Walderhaug, H.; Nyström, B.; Hansen, F. K.; Lindman, B. *J. Phys. Chem.* **1995**, *99*, 4672.
(37) Nilsson, S.; Holmberg, C.; Sundelöf, L.-O. *Colloid Polym. Sci.* **1994**, *272*, 338.
(38) Stilbs, P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1987**, *19*, 1.
(39) Kärger, J.; Pfeifer, H.; Heink, W. *Adv. Magn. Reson.* **1988**, *12*, 1.
(40) Burstein, D. *Concepts Magn. Reson.* **1996**, *8*, 269.
(41) Hrovat, M. I.; Wade, C. G. *J. Magn. Reson.* **1981**, *44*, 62.
(42) Blinc, R.; Lahajnar, G.; Zidansek, A. *Croat. Chem. Acta* **1992**, *65*, 439.
(43) Stepisnik, J. *Physica B* **1993**, *183*, 343.
(44) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(45) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.

(46) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1983**, *16*, 968.

(47) Nyström, B.; Walderhaug, H.; Hansen, F. K. *J. Phys. Chem.* **1993**, *97*, 7743.

(48) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085.

(49) Peterlin, A. *Makromol. Chem.* **1983**, *184*, 2377.

(50) Zupancic, I.; Lahajnar, G.; Blinc, R.; Reneker, D. H.; Vanderhart, D. L. *J. Polym. Sci. Polym. Phys. Ed.* **1985**, *23*, 387.

(51) Fleischer, G.; Geschke, D.; Kärger, J.; Heink, W. *J. Magn. Reson.* **1985**, *65*, 429.

(52) Callaghan, P. T. *Principles of Nuclear Magnetic Resonance Microscopy*; Oxford University Press: New York, 1991.

(53) Kärger, J.; Fleischer, G. *Trends Anal. Chem.* **1994**, *13*, 145.

(54) Price, W. S. *Ann. Rep. NMR Spectrosc.* **1996**, *32*, 51.

(55) Appel, M.; Fleischer, G.; Kärger, J.; Fujara, F., Siegel, S. *Europhys. Lett.* **1996**, *34*, 483.

(56) Cohen-Addad, J. P. *Prog. Nucl. Reson. Spectrosc.* **1993**, *25*, 1.

(57) Vlad, M. O. J. *Mod. Phys. B* **1993**, *7*, 2539.

(58) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36.

(59) Shirahama, K. *Colloid Polym. Sci.* **1974**, *252*, 978.

(60) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639.

(61) Cabane, B.; Duplessix, R. *J. Phys. (Paris)* **1982**, *43*, 1529.

(62) Francois, J.; Dayantis, J.; Sabbadin, J. *Eur. Polym. J.* **1985**, *21*, 165.

(63) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.

(64) van Stam, J.; Almgren, M.; Lindblad, C. *Prog. Colloid Interface Sci.* **1991**, *84*, 13.

(65) Brown, W.; Fundin, J.; da Graca Miguel, M. *Macromolecules* **1992**, *25*, 7192.

(66) Chari, K.; Antalek, B.; Lin, M. Y.; Sinha, S. K. *J. Chem. Phys.* **1994**, *100*, 5294. Also see: Antalek, B.; Chari, K. *Mod. Phys. Lett. B* **1995**, *9*, 1555.

(67) Wang, G.; Olofsson, G. *J. Phys. Chem.* **1995**, *99*, 5588.

(68) Shirahama, K.; Tsujii, K.; Takagi, T. *J. Biochem.* **1974**, *75*, 309.

(69) Nagarajan, R.; Kalpakci, B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1982**, *23*, 41.

(70) Kamenka, N.; Burgaud, I.; Zana, R.; Lindman, B. *J. Phys. Chem.* **1994**, *98*, 6785.

(71) Cabane, B.; Lindell, K.; Engström, S.; Lindman, B. *Macromolecules* **1996**, *29*, 3188.

(72) Nyström, B.; Kjøniksen, A.-L.; Lindman, B. *Langmuir* **1996**, *12*, 3233.

(73) Wheeler, L. M.; Lodge, T. P. *Macromolecules* **1989**, *22*, 3399.

(74) Phillies, G. D. J. *J. Phys. Chem.* **1989**, *93*, 5029.

(75) Furukawa, R.; Arauz-Lara, J. L.; Ware, B. R. *Macromolecules* **1991**, *24*, 599.

(76) Walderhaug, H.; Nyström, B., submitted for publication.