Self-Diffusion Coefficients of Hydrophobic Ethoxylated Urethane Associating Polymers Using Pulsed-Gradient Spin-Echo Nuclear Magnetic Resonance

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ABSTRACT: The self-diffusion coefficients of hydrophobic ethoxylated urethane associating polymers of different molecular weights, but constant length of the hydrophobic end cap, were measured in aqueous solution using a pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) technique. With increasing concentration, all polymers registered a decrease in their mean diffusion coefficient accompanied by an increase in the dispersion of the diffusion coefficient about the mean. Both effects correlated with the pronounced concentration-dependent viscosity increase characteristic of such polymers. The presence of hydrophobic end caps decreased the diffusion coefficient by more than an order of magnitude relative to control polymers of identical size but lacking hydrophobic modifications. The results are consistent with the predictions of the transient micelle network model of network formation by such polymers and yield an estimate of the size (20 nm radius) and aggregation number (1 micelle contains 20 hydrophobic chains) for the associated clusters.

Introduction

The HEUR (hydrophobic ethoxylated urethane) associating polymers are rheology modifiers exhibiting a combination of Newtonian behavior at low shear rates with shear thinning at only relatively high shear rates.[1] They consist of a poly(ethylene glycol) (PEG) backbone, chain-extended by diisocyanates and end-capped by long-chain alkanols. There are currently two different views regarding the origin of their rheological behavior. One opinion deems that in aqueous solution these polymers associate into a three-dimensional network of small micelles, as illustrated schematically in Figure 1.[2] In such as "closed" association model the well-defined micelles are formed by the aggregation of hydrophobic groups at the ends of looped chains, with the only dangling ends being due to chains missing a hydrophobic substituent at one end. With increasing polymer concentration a network forms consisting of micelles linked to one another by bridging chains. The major rheological properties of HEUR associating polymers can be modeled by assuming that, with increasing polymer concentration, the proportion of bridging chains to looping chains gradually increases, resulting in network formation.[3] The network remains essentially transient due to the finite rate of disengagement of the chain ends from the micelles. In contrast, the "open" association model proposes that aggregates are formed by successive accretion of unimers into loosely-defined hydrophobic sites.[4,5] This model is based on light scattering studies which indicate that the apparent weight-average molecular weight of the polymer in aqueous solution increased with increasing polymer concentration.

The closed association model (also dubbed the "microgel"[2] or "transient micellar network"[3] models) and the open association model[4,5] yield distinctly different expectations regarding molecular behavior as a function of polymer concentration, in particular with respect to polymer diffusion. Pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) spectroscopy is a convenient method for measuring self-diffusion coefficients and has been applied to study diffusion in a broad spectrum of physical situations,[6,7] including hydrophobically end-capped poly(oxyethylene) associating polymers of the general HEUR-type.[8,9] The latter

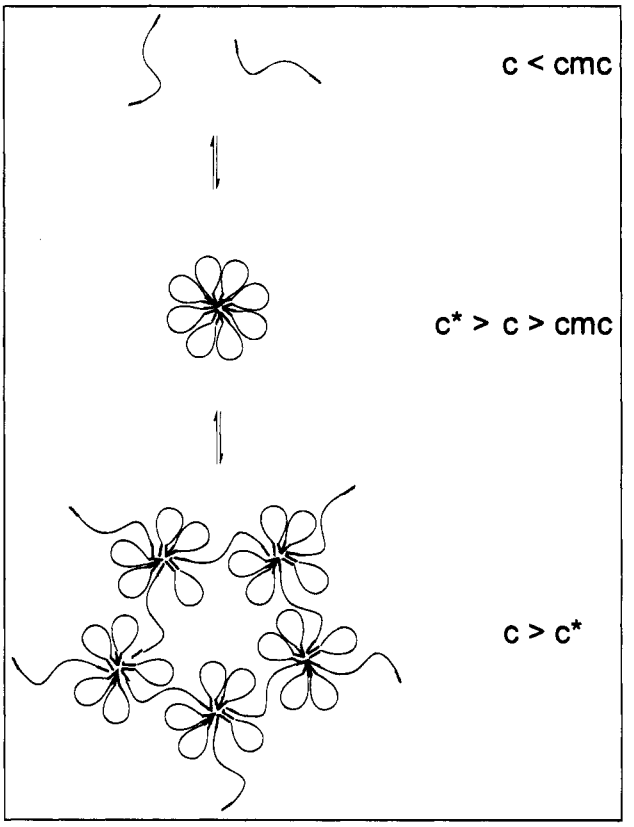

Figure 1. Schematic of the "transient micellar network" model for the associating polymer structure in water. At concentrations above the critical micelle concentration (cmc) hydrophobic association sites form from looped chains. At higher concentration a number of bridging chains arise which link the micelles into a network. Eventually the number of bridging chains exceeds the number of looping chains, the network spans the entire solution, and the system gels.

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Table 1

polym designation	mol wt (M_n)	end group	polym designation	mol wt (M_n)	end group
6RDJY-107	26 800	$C_{16}H_{33}$	46RCHX23-1	16 600	H
46RCHX22-2	34 200	$C_{16}H_{33}$	46RCHX23-2	34 000	H
3RDJY-14	48 000	$C_{16}H_{33}$	46RCHX23-4	67 000	H

authors investigated the effects of varying the length of the hydrophobic end cap and demonstrated that the self-diffusion coefficients of their associating polymers were best described in terms of a distribution which broadens continuously with increasing concentration. Simultaneously, the mean self-diffusion coefficient underwent a dramatic decrease at a concentration where rheology data indicate that the solution viscosity rises abruptly.

We reported here on the self-diffusion coefficients of HEUR associating polymers having different molecular weights but constant chain length of the hydrophobic end cap, as obtained using PGSE NMR. These particular associating polymers have been extensively characterized in other laboratories, both with regard to their rheological behavior[10] and the molecular properties of such systems.[2] For comparison we have performed parallel studies on control polymers of identical backbone structure but lacking the hydrophobic end caps.

Our general conclusion is that the length of the polymer backbone is less important to the ultimate behavior of such polymers than the length of the hydrophobic end cap. At low polymer concentrations the diffusing species displays a hydrodynamic radius of 20 nm, consistent with a micellar aggregate containing 10 polymer chains. With increasing concentration the apparent size of the diffusing species increases and the rate of polymer diffusion decreases to the point that, at higher concentrations, the observed diffusion is no longer purely Fickian. The results are generally consistent with the microgel and transient micellar network models.[2,3]

Experimental Section

The HEUR associating polymers and the control polymers lacking hydrophobic end caps were obtained from Dr. Richard D. Jenkins, Union Carbide Chemicals and Plastics Co., Inc., UCAR Emulsion Systems, Cary, NC. Their number-average molecular weights (M_n) are listed in Table 1. The chemical characterization of these associating polymers using ^{1}H NMR has been reported.[11] Traces of residual solvent or unreacted long-chain alcohol were removed by recrystallizing the associating polymers from ethyl acetate at room temperature and lyophilizing from benzene. To prepare samples for PGSE NMR measurements, in each case a stock solution consisting of 1 wt % polymer in 99.9% deuterium oxide was prepared by hydrating the dried polymer over a period of 24–48 h with the appropriate volume of deuterium oxide. Care was taken to avoid exposing the solutions to light. Solutions of lower polymer concentration were prepared by serial dilution of the stock solution directly into an NMR tube. The NMR tubes were then sealed and stored in the dark at 4 °C until use.

PGSE NMR measurements were performed using an MRI (magnetic resonance imaging) probe with actively shielded gradient coils (Doty Scientific, Columbia, SC) installed in a Chemagnetics CMX 300 NMR spectrometer operating at 300 MHz for protons. A standard Stejskal–Tanner PGSE sequence [$(90°_x)$–τ–$(180°_y)$–τ], with gradient pulses during τ,[12] was employed. Particulars regarding the 90° pulse length (23 μs), interpulse delay (250 ms), recycle delay (30 s), spectral width (10 kHz), data size (4K), line broadening (10 Hz), and number of acquisitions (16–2048 scans) are those noted in the parentheses. The PGSE experiments were performed at 23 °C, and the gradient pulse was applied to the z-direction only. It was necessary to use several levels of gradient strength between ca. 20 and 200 G/cm, depending on the polymer concentration. The lower ranges of gradient strengths were calibrated by using the diffusion coefficient of 2 vol % H_2O in D_2O ($D = 1.9 \times 10^{-9}$ m^2/s)[13] (see eq 1 in the following section). In the case of higher gradients, a sample of 50 wt % poly(ethylene glycol) (PEG) in HDO, which could be measured with both low and high gradient strengths, was used as the calibration standard.[14] The precision of the measured self-diffusion coefficients was good at low gradient strength, the error being estimated at less than 5%. At higher gradient strengths the error was larger due to the consequent exaggeration of small imbalances in the two gradient pulses but in all cases was less than 15%. Gradient pulse imbalances can both shift the position of the echo maximum and distort its phase (see, for example, ref 15). To overcome this problem, we have implemented a widely-used method,[16–18] in which the duration of the second gradient pulse is altered to compensate for any such imbalance. When proper compensation is applied, the echo position and phase are correct, and Fourier transformation of the echo beginning at its maximum yields the corresponding spectrum free of intensity and phase distortion.

Results

The PGSE NMR pulse sequence consists of a pair of magnetic field gradient pulses (duration δ and amplitude G), the first being applied between the two radio-frequency (rf) pulses of the usual spin-echo NMR sequence and the second between the last rf pulse and the appearance of the spin-echo signal. For isotropic diffusion characterized by a single diffusion coefficient, in a homogeneous magnetic field where the residual gradient G_0 is negligible, the intensity, $I_{2\tau}$, of the NMR signal at time 2τ following the start of the PGSE pulse sequence is related to the diffusion coefficient D according to eq 1 where G is the pulsed-gradient strength, δ

$$I_{2\tau}/I_0 = \exp[-(\gamma G\delta)^2(\Delta - \delta/3)D] \quad (1)$$

the duration of the gradient, Δ the interval between the gradients, τ the rf pulse interval, and γ the magnetogyric ratio.[12] The effect of T_2 (spin–spin relaxation time) is constant when τ is kept constant and is contained within the term I_0. The diffusion coefficient can be derived from the slope of a plot of the logarithm of the signal intensity as a function of $\delta^2(\Delta - \delta/3)$ once the gradient strength G is known. The latter is obtained by calibration with a sample of known diffusion coefficient, as described in the Experimental Section.

Figure 2 shows a series of ^{1}H NMR spectra of the M_n 48 000 C16 HEUR associating polymer (3RDJY-14) at 0.5 wt % in deuterium oxide, for various durations of the field gradient pulse. The left-most spectrum was obtained with a very short gradient pulse and shows two resonances, one arising from the residual protons in deuterium oxide (HDO) and the other from the ethylenic protons of the PEG chains of the HEUR associating polymer. Other expected resonances, such as those of the diisocyanate chain extenders or the methylenes of the hexadecanol hydrophobic end caps, do not appear, either because of their small numbers relative to the PEG protons or because of their shorter spin–spin (T_2) relaxation times relative to the PEG protons. Note that all the expected resonances, including the methylenes of the hexadecanol end caps, are readily apparent in the ^{1}H NMR spectra of C16 HEUR associating polymers dissolved in chloroform.[11] If the associated state which forms in aqueous solution involves hindered molecular motion, such as would be expected within a micellar cluster, then T_2 shortens and

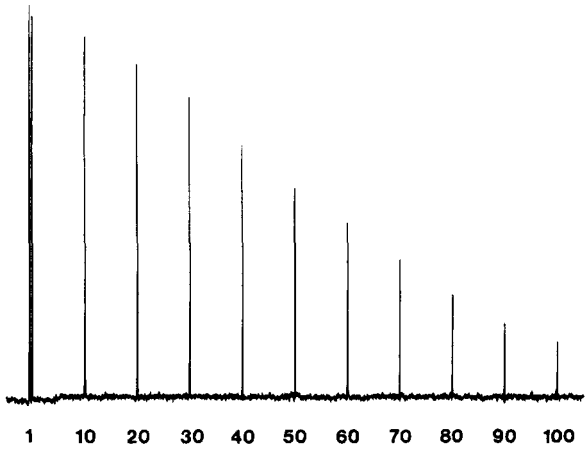

Figure 2. Proton NMR spectra of the M_n 48 000 C16 HEUR associating polymer at 0.5 wt % in deuterium oxide at room temperature, showing the attenuation of the proton signals with increasing duration of the gradient pulse δ, indicated in milliseconds. In this instance the gradient pulse amplitude was 58.0 G/cm, while the value of $\Delta = \tau = 250$ ms.

the NMR linewidth increases. Thus, for the τ value used in these measurements (250 ms), the resonance signal of the hydrophobic end caps is expected to be largely suppressed. With increasing gradient pulse duration, the HDO resonance intensity quickly decreases to zero, which is anticipated given the rapid diffusion of water and the rather high gradient strengths used in this particular experiment. For longer gradient pulse durations, only the PEG methylene resonance signal remains and its intensity decays exponentially with increasing duration of the gradient pulse.

Figure 3A illustrates typical plots of the logarithm of the signal intensity of the PEG-backbone protons as a function of the gradient pulse duration for two concentrations of the M_n 34 200 C16 HEUR associating polymer (46RCHX22-2), 0.1 and 1.0 wt % in deuterium oxide. At 0.1 wt % the decrease in the intensity is apparently monoexponential, indicating a single effective rate of diffusion for all polymer molecules in the sample (but see below for further discussion of this point). However, at 1.0 wt % the intensity decrease shown in Figure 3A is quite evidently multiexponential. Some likely origins of such a nonlinear decay include restricted diffusion and polydispersity. Similar multiexponential decays are observed at high concentrations for all the HEUR associating polymers with hydrophobic end caps. In contrast, the decay of the signal intensity for the control polymers lacking hydrophobic end caps is at all concentrations apparently monoexponential.

One method for analyzing such a multiexponential decay is to use a "stretched exponential" of the form shown in eq 2.[9] The parameter β is a measure of the

$$I_{2\tau}/I_0 = \exp\{-[(\gamma G\delta)^2(\Delta - \delta/3)D_e]^\beta\} \qquad (2)$$

width of the distribution of the diffusion coefficients about the mean value, where $0 \le \beta \le 1$, such that when $\beta = 1$, the diffusion coefficient is monodisperse. The parameter D_e is an effective self-diffusion coefficient, which is related to the mean diffusion coefficient, D_m, via the gamma function, Γ, according to eq 3 where X

$$1/D_m = \int_0^\infty \exp[-(XD_e)^\beta]\, dX = (1/\beta)(1/D_e)\Gamma(1/\beta) \qquad (3)$$

$= (\gamma G\delta)^2(\Delta - \delta/3)$. Ideally, β and D_e are obtained from a two-parameter nonlinear least-squares fit of eq 2 to the diffusion data. However, values for β and D_e can also be estimated by plotting $\ln[\ln(I_0/I_{2\tau})]$ versus $\ln(X)$, which should be linear with a slope equal to β and an intercept equal to $\beta \ln(D_e)$. Figure 3B shows the results of such an analysis for polymer concentrations identical to those in Figure 3A. The values of β equal 0.987 and 0.573 for 0.1 and 1.0 wt % solutions, respectively, of the M_n 34 000 C16 HEUR associating polymer, while the corresponding values of D_e are 8.05×10^{-12} and 9.57×10^{-14} m^2 s^{-1}. Therefore, using eq 3, the mean diffusion coefficients, D_m, for these two cases equal 8.00×10^{-12} and 5.98×10^{-14} m^2 s^{-1}, respectively.

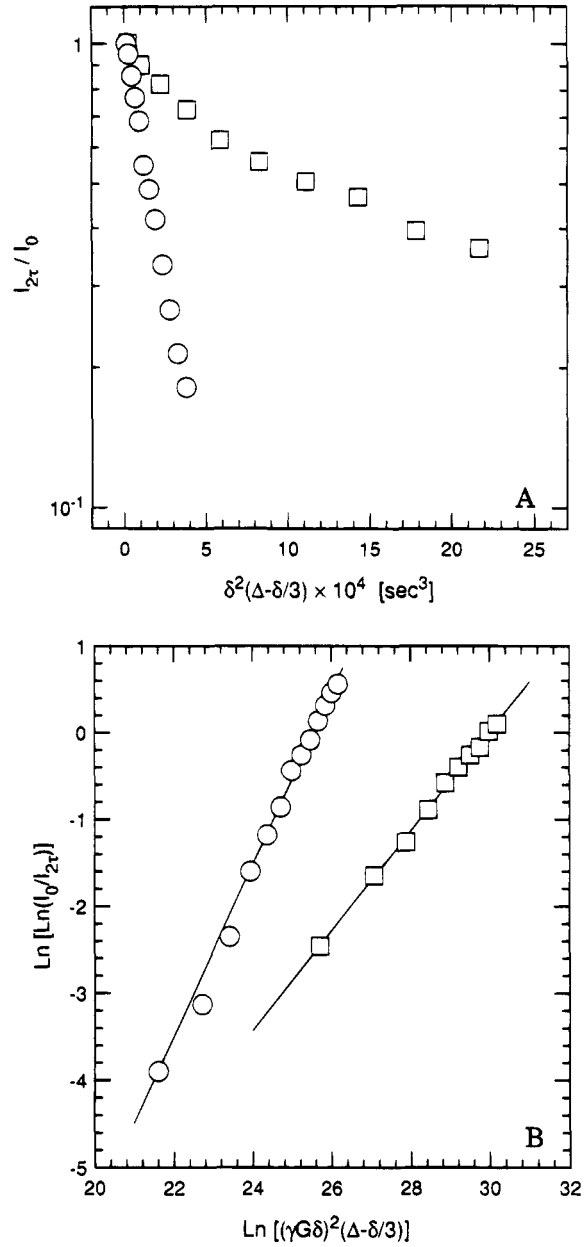

Figure 3. (A) Logarithm of the proton NMR signal intensity ($\ln I$) versus $\delta^2(\Delta - \delta/3)$ for the case of the M_n 34 200 C16 HEUR associating polymer at 0.1 wt % in deuterium oxide, gradient amplitude 58 G/cm, $\Delta = 250$ ms (circles), and at 1.0 wt % in deuterium oxide, gradient amplitude 181 G/cm, $\Delta = 250$ ms (squares). (B) Determination of the width of the distribution of diffusion coefficients (β) and the effective diffusion coefficient (D_e) using a linearized version of eq 2. β corresponds to the slope, while the intercept corresponds to $\beta \ln D_e$. The data points are those in A, while the solid lines are fits using eq 2 with the slopes and intercepts noted in the text.

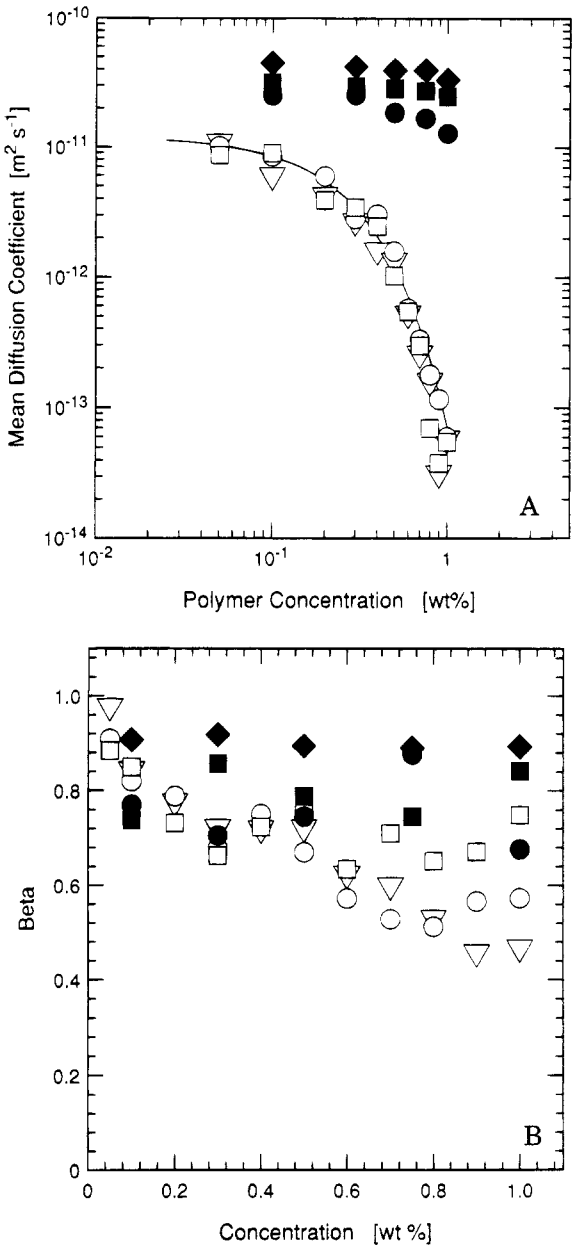

Figure 4. (A) Mean diffusion coefficients as a function of concentration for both the control and the C16 HEUR associating polymers. Open squares, M_n 26 800 C16 HEUR associating polymer. Open circles, M_n 34 200 C16 HEUR associating polymer. Open triangles, M_n 48 000 C16 HEUR associating polymer. Closed diamonds, M_n 16 600 control polymer. Closed squares, M_n 34 000 control polymer. Closed circles, M_n 67 000 control polymer. The solid line is the fit to the universal scaling law of eq 9 using the parameters in Table 2 for the case of the M_n 34 200 C16 HEUR associating polymer. (B) Distributions of diffusion coefficients about mean values as a function of concentration for the control and the associating polymers. Symbol designations are identical to those in A.

Figure 4A compares the mean diffusion coefficients of the various C16 HEUR associating polymers and their corresponding controls across a range of concentrations. The control polymers exhibit a progressive decrease in their mean diffusion coefficient with increasing concentration, the higher molecular weight species diffusing at a slower rate. In fact, they behave in accordance with standard dilute hydrodynamic theory in which D_0, the observed polymer diffusion coefficient extrapolated to zero concentration, scales according to M^a.[19] For the control polymers we find a equal to -0.50 ± 0.05, which is in reasonable agreement with one's expectations for a good solvent,[15] given that only three molecular weights were tested. The HEUR associating polymers, in contrast, all display profoundly slower diffusion at comparable concentrations, exhibit a much reduced dependence of the diffusion coefficient on molecular weight, and show evidence that two different concentration regimes exist. The breakpoint between the two regimes occurs at a concentration corresponding to that at which there is a rapid increase in the viscosity of solutions of such polymers. Overall, this behavior is essentially identical to that reported by Persson et al.[8] and Walderhaug et al.[9] for their HEUR-type associating polymers.

Figure 4B compares the values of β for the various C16 HEUR associating polymers and their controls over the same range of concentrations. In general, with increasing polymer concentration the dispersion of the diffusion coefficients about the mean value increases. However, any differences between C16 HEUR associating polymers of different molecular weights are small relative to the concentration dependence of the quantity β for any one molecular weight. For the control polymers, in contrast, the polymer molecular weight appears to be the important factor determining β, while concentration has little impact, at least in the range of concentrations investigated here. It is noteworthy that the dispersion of the diffusion coefficients for the HEUR associating polymers is narrower than that of the control polymers at the lowest concentrations but wider at the highest concentrations.

Discussion

PGSE NMR diffusion coefficient measurements on associating polymers provide several types of information regarding the topology of their various associated states. For purposes of discussion, and because of the different nature of the information available, it is convenient to divide the concentration dependence of the diffusion coefficients into two regimes. The dividing line between the two is determined according to eq 4 where

$$2Dt \gg \langle r^2 \rangle \tag{4}$$

D is the self-diffusion coefficient, $t = \Delta - \delta/3$ is the diffusion time for the PGSE NMR experiment, and $\langle r^2 \rangle$ is the square of the dimension of the object which is diffusing.[6] When $2Dt$ is substantially larger than the molecular dimensions, the experiment measures true center-of-mass diffusion. For a single species diffusing in a homogeneous medium the signal attenuation in the PGSE NMR experiment will be monoexponential. However, multiexponential attenuations can occur if the diffusing species is polydisperse in molecular weight[20] or experiences restricted diffusion due to inhomogeneity in the surrounding medium.[21] Before considering the origin of the multiexponential signal attenuations observed with HEUR associating polymers at higher concentrations, we will first discuss the diffusion results for the concentration region in which the intensity decays are virtually monoexponential.

Toward Infinite Dilution. In this concentration region, where the signal attenuations are monoexponential, one is observing purely center-of-mass diffusion of a species having a narrow size distribution, and the diffusion coefficients so obtained are readily interpreted in terms of the size of the diffusing species. For the HEUR associating polymers the size of the diffusing

Table 2

polymer mol wt	end group	D_0[a] ($\times 10^{-11}$ m^2 s^{-1})	R_h[b] (nm)	α[c]	γ[c]
26 800	$C_{16}H_{33}$	1.4	17.5	0.647	1.052
34 200	$C_{16}H_3$	1.2	20.4	0.351	1.164
48 000	$C_{16}H_{33}$	1.1	22.7	0.491	1.025
16 600	H	4.7	5.2		
34 000	H	3.1	7.9		
67 000	H	2.3	10.5		

[a] From extrapolating the mean diffusion coefficient to zero concentration. [b] From eq 5 assuming the solution viscosity equals that of pure water. [c] From eq 9.

species reflects the aggregation number of the micelle. From the Stokes–Einstein equation, the hydrodynamic radius of the diffusing species, R_h, depends on the self-diffusion coefficient D, the Boltzmann constant k, the absolute temperature T, and the solution viscosity η, according to eq 5. Extrapolating the concentration

$$R_h = kT/6\pi\eta D \tag{5}$$

dependence of the diffusion coefficient toward infinite dilution, one obtains the limiting diffusion coefficient, listed in Table 2 for each of the polymers investigated here. Substituting into eq 5, and assuming that the solution viscosity should approach that of water, yields the limiting hydrodynamic radius R_h, again listed in Table 2 for each species. The values for the control polymers agree well with literature values for comparable polymers. For instance, Devanand and Selser[22] reported that the molecular weight dependence of the hydrodynamic radius of PEG in aqueous solution obeyed the relationship shown in eq 6.

$$R_h\,(\text{nm}) = 0.0145 M_w^{0.571\pm0.009} \tag{6}$$

Using M_n = 34 000 and M_w/M_n = 1.7,[2] eq 6 predicts a hydrodynamic radius equal to 7.6 nm, in good agreement with the value of 7.9 nm obtained from PGSE NMR.

For the M_n 34 200 C16 HEUR associating polymer, eq 5 yields a hydrodynamic radius of 20.4 nm, a value which is in excellent accord with the results of dynamic light scattering experiments on the identical compound,[2] as well as PGSE NMR measurements on closely related polymers.[8,9] The larger size of the diffusing species found for all of the HEUR associating polymers relative to their controls indicates that these polymers assume an aggregated state even at very low concentrations. In fact, the onset of aggregation occurs at concentrations well below the lowest concentration measured in the present study.[1]

From the size of the aggregated species one can extract the aggregation number for the micelle, representing the number of hydrophobic end groups which associate to form a micelle. For the case of a hard sphere the mass of the aggregated species, M, is related to its radius, r, through the intrinsic viscosity $[\eta]$ via eq 7.

$$[\eta]M = (10\pi/3)N_A r^3 \tag{7}$$

The intrinsic viscosity of the M_n 34 200 C16 HEUR associating polymer in aqueous solution has been measured to be 1.1 dL/g.[2] Applying eq 7 yields M equal to approximately 460 000. With M_n = 34 200 and M_w/M_n = 1.7,[2] one calculates a cluster size of between 8 and 13 polymer chains, depending on whether one chooses

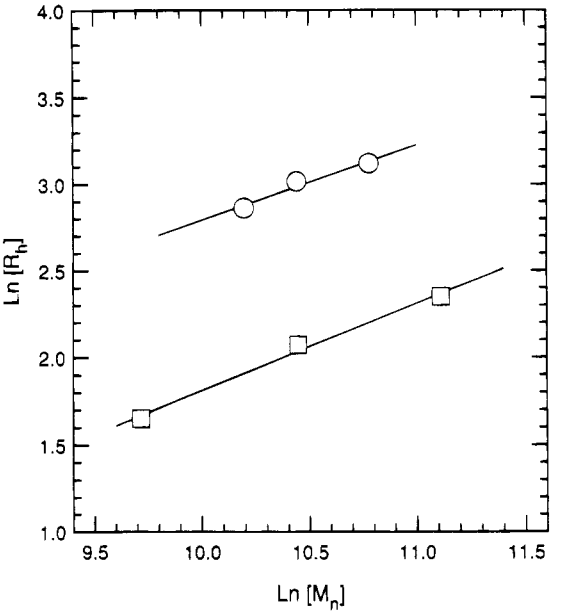

Figure 5. Scaling law describing the dependence of the size of the diffusing species on the molecular weight of the constituent polymers for the C16 HEUR associating polymers (circles) and the control polymers (squares). The solid lines represent fits to the data using eq 8 and the parameters described in the text.

to employ M_n or M_w in the calculation. So the aggregation number falls between 16 and 26 hydrophobic chain ends per micelle.

Aggregation numbers lower than these by approximately a factor of 2 have been estimated for similar polymers using PGSE NMR results.[8,9] However, these researchers assumed that the hydrodynamic radius of both the associated and unassociated species scale according to $M^{0.53}$. While this assumption is reasonable for the control polymers, it is not obvious that the same scaling constant should pertain in the case of a strongly chain-end associated polymer. Let us assume, instead, that in the low concentration regime the size of the micelles, rather than the size of the associating polymers within a micelle, follows a scaling law similar to that expected for free polymers in dilute solution, i.e.,

$$R = K(nM)^a \tag{8}$$

where M is the molecular weight of a single polymer chain and n is the number of chains contributing to a cluster. If K and n are independent of molecular weight, a graph of $\ln(R_h)$ versus $\ln(M)$ will be linear with slope a and an intercept equal to $\ln(Kn^a)$.

Figure 5 compares the results of such an analysis for the controls versus the C16 HEUR associating polymers. The linearity is reasonable for both cases, with a equal to 0.50 ($\pm$0.05) and 0.44 ($\pm$0.04) for the control and the HEUR polymers, respectively. The exponent a for the control polymers is exactly that anticipated from the molecular weight dependence of D discussed previously. On the other hand, the scaling exponent for the C16 HEUR associating polymers is smaller than expected even if water were a Θ solvent for PEG. Others have reached similar conclusions regarding the molecular weight scaling constant for HEUR associating polymers. Specifically, Ou-Yang and Gao in their study of the binding of C12 and C16 HEUR associating polymers to polystyrene latex spheres observed that the thickness of the adsorbed layer at saturation scaled according to

a equal to 0.46.[23] Although both the latter study and the present report investigated just a limited range of molecular weights, so that only qualitative conclusions are warranted, these are, nevertheless, compelling. First, any calculation of the aggregation number based on the assumption that a equals 0.53 for both the free unimer and the unimer in the associated state will tend to yield an underestimate relative to a calculation based on the observed values of a. This explains the differences in the aggregation numbers reported previously[8,9] versus the present report. Second, the lower value of a found for the HEUR associating polymers relative to the controls indicates a reduction in chain configurational freedom, consistent with the type of conformational constraints expected within an associated state. Third, substituting eq 8 into eq 7 leads to the prediction that the intrinsic viscosity of the HEUR associating polymers scales according to $M^{1/3}$, which can be verified experimentally. The inference is that due to associations the size of the diffusing species for the HEUR associating polymers grows with increasing molecular weight at a rate which is slower than one expects for a random-flight model of chain configurations. Fourth, the apparent success of eq 8 in describing the dependence of the size of the micelles on the molecular weight of the component polymer chains suggests that the cluster size n is relatively constant over the range of molecular weights available. This too is a prediction which can be verified experimentally via further viscosity and PGSE NMR measurements.

The question of the aggregation number in micelles of associating polymers is central to understanding the nature of the association process. Operationally, it is important to distinguish between the cluster size and the aggregation number. As we use it, the cluster size refers to the number of polymer chains associating with a micelle in the concentration regime wherein there are virtually no bridging chains. The aggregation number always refers to the number of hydrophobic groups associated with a hydrophobic site. Two different views have emerged regarding the aggregation number for associating polymers. Small aggregation numbers (less than 10 hydrophobes per association site) have been inferred from fitting viscoelastic response data to classical rubber elasticity models,[10] from PGSE NMR diffusion measurements[9] as mentioned previously, and from Monte Carlo simulations of the transient associations of chains with sticky ends.[24] They are also inherent to the open association model in the low concentration regime.[4,5] Alternatively, larger aggregation numbers (10 or more polymer chains per micelle) have been deduced from dynamic light scattering studies[2] and from modeling of rheological behavior using a transient network theory.[3] Hence, the present PGSE NMR diffusion coefficient measurements favor the transient network theory where at low concentrations the HEUR associating polymers aggregate into micelles consisting of approximately 10 polymer chains.

The Dilute Regime. Operationally, one defines the dilute regime as corresponding to concentrations less than the apparent c^*, normally considered to correspond to the point at which neighboring polymer chains begin to overlap. From diffusion coefficient measurements c^* is readily determined using the inflection point in a plot of $1/D$ versus concentration.[6] For the M_n 34 200 C16 HEUR associating polymer such an analysis yields c^* equal to 0.5 wt %. In fact, using this method similar values of c^* are obtained regardless of the molecular weight of the particular HEUR associating polymer. This runs contrary to one's expectations regarding the molecular weight dependence of c^* for nonassociating polymers. Walderhaug et al.[9] measured values of c^* in this same fashion for several HEUR-type associating polymers of molecular weight 15 000 with different hydrophobic end cap chain lengths. These authors reported a distinct decrease in c^* with increasing chain length of the hydrophobic end cap. Thus, the "overlap" concentration c^* for the associating polymers is virtually independent of molecular weight and entirely dependent on the length of the end cap.

A simple calculation shows that the classical definition of c^* as an overlap concentration is inappropriate for associating polymers. Starting from a micellar cluster composed of 10 polymer chains of molecular weight 34 000 and having a radius of 20 nm, one can estimate that such spheres would fill space at a concentration of 1.7 wt %, which is far above the observed value of 0.5 wt %. In fact, at this calculated concentration of c^* the diffusion is so slow that it is beyond our ability to measure using PGSE NMR with our current instrumental configuration. A more appropriate definition of c^* for associating polymers might be the concentration at which network ramification occurs. In any case, we will employ c^* in an operational sense to indicate a behavioral transition. Note that, for the control polymers, all concentrations tested here fall below c^*.

In the concentration regime $c < c^*$ the mean diffusion coefficient of the associating polymers decreases with increasing concentration while simultaneously the width of the distribution of diffusion coefficients about the mean value increases, i.e., the signal attenuations become increasingly multiexponential. Before attempting to interpret these findings in molecular terms it is essential to understand the origin of the multiexponential signal decays. The two most likely possibilities are restricted diffusion and size polydispersity. Restricted diffusion implies that free diffusion is interrupted by an impermeable or semipermeable barrier on a distance scale which is intermediate between the molecular scale $\langle r^2 \rangle$ and the mean-square displacement defined by the experimental diffusion time, i.e., $Dt = \langle \Delta x^2 \rangle$. A proof of the presence of restricted diffusion is that the observed diffusion coefficient depends on the diffusion time t in the PGSE NMR experiment.[21] Although we have not exhaustively examined all polymers at all concentrations, our preliminary findings indicate little dependence of the diffusion coefficient on the value of Δ for concentrations below the apparent c^*. Polydispersity of molecular weight, on the other hand, is not expected to yield diffusion coefficients which depend on the value of Δ provided the inequality in eq 4 is satisfied for all species involved and provided that the T_2 depends only minimally on molecular weight.[20] Consequently, we ascribe the observed multiexponential signal attenuations at concentrations below c^* to polydispersity of diffusant size. It follows that the value of β in eq 2 reflects in some fashion this polydispersity. It is important to recognize, however, that the parameter β contains no information regarding the shape of the size distribution curve, and its use can even obscure details. For instance, it is very difficult to decide whether a continuous or a discrete size distribution is most appropriate without prior knowledge of the physical state of the system. Methods for dealing with these issues have been reported recently.[25]

Given that we consider that β reflects size polydispersity in the concentration region $c < c^*$, several interesting features become evident. With regard to the control polymers, the value of β is virtually independent of concentration and highly dependent on molecular weight. Since no associations or entanglements are expected, no change in polydispersity with concentration would be anticipated. The polydispersity of the various control polymers is unknown, but given that both the control and HEUR associating polymers are produced via a step–step polymerization, one expects their polydispersities to be similar (i.e., for the M_n 34 200 C16 HEUR $M_w/M_n = 1.7$[2]). Carothers–Flory statistical theory indicates that M_w/M_n should increase with increasing overall molecular weight for a step–step polymerization process.[19] Hence, polydispersity would seem to explain all aspects of the concentration dependence of the parameter β for the control polymers.

In contrast, for the HEUR associating polymers the parameter β decreases dramatically with increasing concentration and is largely independent of molecular weight. It seems important that the aggregates formed by the HEUR associating polymers at low concentrations possess a narrower distribution of diffusion coefficients than that of the corresponding control polymers. This is despite the additional complication of chemical heterogeneity, since ^{1}H NMR reveals that approximately 20% of the M_n 34 200 C16 HEUR associating polymers have only a single, rather than a double, end cap.[11] If one assumes that the tendency to associate is dictated by the hydrophobic end cap rather than the length of the water-soluble backbone, then the molecular weight distribution within any one cluster should mirror that of the polymer population as a whole. Random aggregation statistics then predict a narrowing of the size distribution of the aggregated state relative to the nonaggregated state.

Several groups have reported viscosity data for the HEUR associating polymers,[10] including the dilute concentration regime for the M_n 34 200 C16 HEUR associating polymer.[2] Employing the viscosity data of Yekta et al.[2] and the mean diffusion coefficients reported here, the hydrodynamic radius calculated from the Stokes–Einstein relationship for the M_n 34 200 C16 HEUR associating polymer increases from a value of 20.4 nm at infinite dilution to a maximum of 42.7 nm at 0.3 wt % polymer concentration. At concentrations near c^*, for the conditions used in our PGSE NMR measurements, the hydrodynamic radius appears to decrease. We suspect that this latter effect is more apparent than real and is related to the choice of the diffusion time parameter in our PGSE NMR measurements, as will be discussed below.

The combination of increasing size and increasing polydispersity with increasing concentration suggests the presence of "supra-aggregates" consisting of two or more micellar clusters joined together by bridging chains. An alternate explanation is that the size increases via accretion of polymer chains into existing clusters, which leads to the prediction that the aggregation number likewise increases with increasing concentration while the size dispersion should not change markedly. This is at odds with the behavior observed here via PGSE NMR and with the data of Yekta et al.,[2] which suggests that the aggregation number is constant in this concentration range. An increase in the apparent size of the diffusing unit with the concentration of associating polymer has been observed previously, for example, using light scattering,[2] and is consistent with the "microgel" model proposed by Winnik and coworkers[2] and the transient micellar network model of Annable et al.[3]

Semidilute Regime. The dividing line between the dilute and the semidilute concentration regimes, c^*, is characterized in our hands by a sharp decrease in the diffusion coefficients of the associating polymers and a further increase in the dispersion of the diffusion coefficients about their mean values. It is not coincidental that these effects occur at the same concentration at which the viscosity of such solutions undergoes a dramatic increase. In several cases we probed the gradient strength or diffusion time dependence of the signal attenuation and observed considerable effect of the choice of these parameters on the effective diffusion coefficient, even at concentrations just above the apparent c^*. This suggests the possibility that one is dealing with restricted diffusion and may explain the apparent decrease of the hydrodynamic radius of the diffusing unit as the polymer concentrations near c^*. Clearly, an extensive study of the gradient strength and diffusion time dependence of the signal attenuations for concentrations greater than c^* will be necessary before a molecular interpretation is warranted.

Despite these limitations some insights can be extracted from the diffusion data in this region. For example, it has been asserted that a universal scaling law describes the concentration and molecular weight dependence of transport properties in polymer solution.[26] For polymer self-diffusion coefficients this hydrodynamic scaling law takes the form

$$D(c) = D_0 \exp(-\alpha c^{\gamma}) \tag{9}$$

where D_0 is the self-diffusion coefficient in the limit of infinite dilution and α and γ are scaling parameters. The solid line in Figure 4A is calculated using eq 9 and the parameters shown in Table 2 for the M_n 34 200 C16 HEUR associating polymer. The fit is quite good, as it is for all the different molecular weight HEUR associating polymers, the details for which are likewise given in Table 2. The values of both α and γ are remarkably similar to those reported by Walderhaug et al.[9] for their C16 HEUR-type associating polymer of molecular weight 15 000 and are not systematically dependent on the polymer molecular weight.

The latter authors likewise showed that the mode-coupling model of Ngai et al.[27] could be applied to provide a measure of the strength of the interaction between the polymer chains and their environment. Equation 10 is the scaling expression for diffusion in the semidilute region ($c/c^* > 1$) where c^* is the operational "overlap" concentration. The exponent y is con-

$$D/D^* = (c/c^*)^y \tag{10}$$

centration dependent and by combining eqs 9 and 10 equals

$$y = \frac{\ln[D_0 \exp(-\alpha c^{\gamma})/D^*]}{\ln[c/c^*]} \tag{11}$$

where D^* is the mean diffusion coefficient at c^*, and other parameters have been defined previously. An explicit expression for the coupling parameter n is then derived to be

$$n = -(2 - 3a + 3ay - y)/(3a - 3ay + y) \tag{12}$$

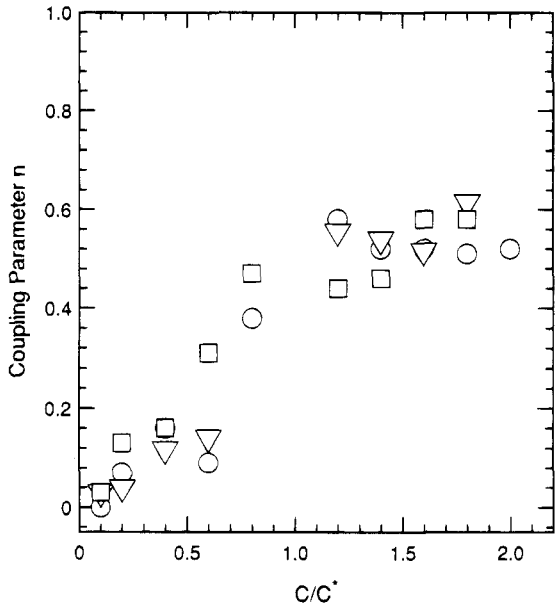

Figure 6. Coupling parameter n as a function of reduced concentration c/c^* for the various C16 HEUR associating polymers. Open squares, M_n 26 800 C16 HEUR associating polymer. Open circles, M_n 34 200 C16 HEUR associating polymer. Open triangles, M_n 48 000 C16 HEUR associating polymer.

where a is the scaling parameter relating molecular weight and the radius of gyration in eq 8 and $0 < n < 1$. Figure 6 shows how the coupling parameter n varies with concentration for the three C16 HEUR associating polymers studied here. It can be seen that there is a steady increase in n with increasing concentration for the region $c < c^*$. This is interpreted as indicating that chain motions are influenced in a steadily increasing fashion by coupling to the surroundings, i.e., the increase in the number of bridging polymers links micelles to one another. At $c = c^*$ there is a transition to a decreased dependence of n upon concentration. Physically, this must be viewed as a consequence of the ramification of the polymer network with increasing concentration. Caution must be exercised in interpreting the observed behavior of n in the region $c > c^*$ because we recognize that we have not fully explored the diffusion time dependence of the effective diffusion coefficients in this concentration regime.

Concluding Remarks

These PGSE NMR diffusion studies of C16 HEUR associating polymers indicate that the length of the polymer backbone is secondary to the length of the hydrophobic end cap as an effector of associating behavior. It is found that the PGSE NMR data are characterized by a distribution of diffusion coefficients, which are most readily analyzed using a stretched exponential. At low concentrations the associating polymers aggregate to form micelles comprised of approximately 10 polymer chains. The dependence of the diffusion coefficients on polymer concentration and the dispersion of the diffusion coefficients about the mean values support the transient micellar network model of association as propounded independently by Yekta et al.[2] and Annable et al.[3]

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