NMR Diffusion and Relaxation Time Studies of HEUR Associating Polymer Binding to Polystyrene Latex

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ABSTRACT: Binding of a HEUR (hydrophobic ethoxylated urethane) associating polymer (AP) (MW 51 000, C16 hydrophobic end caps) to polystyrene latex (diameter 168 nm) was investigated by a combination of NMR diffusion, relaxation time, and adsorption measurements. Adsorption of the HEUR AP to the latex particles could be quantified by ^{1}H NMR using a depletion method and could be described by a Langmuir isotherm. The latex-bound HEUR AP exhibited a spin−lattice relaxation time (T_1) identical to that measured in bulk solution. The spin−spin relaxation time (T_2) of the adsorbed HEUR AP was, however, much shorter than that measured in bulk solution, an effect attributed to the slow rotational tumbling of the large latex particles. Diffusion of the free HEUR AP remaining in solution upon addition of latex was enhanced due to depletion of the polymer concentration in the bulk solution and the consequent breakup of the associated network. Diffusion of the latex-bound HEUR AP reflected the diffusion of the latex particles themselves.

Introduction

Hydrophobic ethoxylated urethane (HEUR) associating polymers (APs) are widely used as rheology modifiers in paints and coatings formulations, and their use is spreading into other applications, such as enhanced oil recovery and aviation antifreeze formulations.[1−3] They consist of a poly(ethylene oxide) (PEO) backbone, chain-extended by diisocyanates and end-capped by long-chain alkanols. The growing importance of HEUR APs as controllers of rheological behavior has prompted interest in describing their mechanisms and modes of interaction, both with one another and with other formulation components such as latex and surfactant.

A variety of techniques indicate that in aqueous solution, at low concentrations, HEUR APs, and other such telechelic hydrophobically modified polymers, self-associate into discrete clusters of defined size. The architecture of the resulting “rosette” consists of a core of hydrophobes surrounded by a corona of water-soluble polymer backbones looping back into the core. With increasing concentration, bridging chains begin to appear, linking “rosettes” into a progressively growing network which eventually spans the entire solution. This “microgel” model, proposed by Yekta *et al.*,[4] and independently by Annable,[5] explains the major rheological properties of HEUR APs alone in aqueous solution.

Interactions between HEUR APs and latex have likewise received attention. From fluorescence,[6] light scattering,[7] adsorption equilibria,[8,9] and viscosity measurements,[10] a picture has emerged in which the hydrophobic groups of the HEUR APs stick onto the hydrophobic latex surface, resulting in an adsorption process readily described by a Langmuir isotherm. At low surface coverage, the HEUR APs adopt a “pancake” profile, which alters to a “brush” configuration at high surface coverage.[7]

Despite these impressive gains in understanding the behavior of HEUR APs, only a few idealized systems have been investigated in any depth. A plethora of questions remain regarding the impact of chemical variations, whether of the APs themselves or on the latex surface. In addition, the role of surfactant and the interactions occurring in AP/latex/surfactant/water systems require clarification.

NMR diffusion studies are particularly suited to probing such complex systems because the details of their macromolecular architecture, and any changes therein, often have profound consequences for molecular diffusion.[11,12] Moreover, the diffusion of individual components within a complex mixture can usually be measured independently, and simultaneously, in a nonperturbing fashion. The pulsed gradient spin−echo (PGSE) NMR technique has been applied to investigate diffusion of HEUR APs[13] and closely related polymers[14] in aqueous solution. The diffusion results support the “microgel” model, provide a measurement of the size of the “rosettes”, and yield an estimate of their aggregation number. Although PGSE NMR studies of associating polymers in the presence of surfactant have begun to appear,[15] to date no PGSE NMR studies on HEUR AP−latex interactions have been reported.

In this report we describe NMR diffusion and relaxation time measurements of the binding of a HEUR AP to polystyrene latex. We demonstrate that binding to the latex depletes the bulk HEUR AP concentration and, thereby, *enhances* diffusion of the remaining free HEUR AP. In contrast, the diffusion coefficient of the latex-bound HEUR AP is characteristic of the diffusion of the latex particles themselves.

Experimental Section

Sample Preparation. HEUR AP having 51 000 molecular weight and hexadecyl end caps was obtained from Dr. Richard D. Jenkins, Union Carbide Chemicals, Cary, NC. Traces of residual solvent or unreacted long-chain alcohol were removed by recrystallizing the polymer from ethyl acetate at room temperature and lyophilizing from benzene. Polystyrene latex (168 nm diameter) suspended in aqueous solution was obtained from Dr. Michael Devon, Dow Chemical Co., Midland, MI. Any surfactant in the latex was removed by an ion exchange treatment. The purified latex was diluted to 8.1 wt % solids using double-distilled (dd) H_2O and stored in the dark at room temperature.

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To prepare samples for NMR diffusion and relaxation time measurements, a stock solution of 2 wt % HEUR AP in dd H_2O was prepared by hydrating the dried polymer over a period of 48 h. Aliquots of these stock solutions were mixed with the requisite volume of the latex stock solution and diluted with dd H_2O to obtain the final concentration. After 48 h equilibration, an aliquot of each ternary mixture was centrifuged to obtain a supernatant and a pellet fraction. To test for desorption, the latex-containing pellet was resuspended to its original volume with dd H_2O, and the centrifugation/resuspension cycle was repeated.

PGSE NMR Diffusion Coefficient Measurements. PGSE NMR measurements were made using a 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 was employed, $[(90°_x)-\tau-(180°_y)-\tau-\text{acquistion}]$, with gradient pulses during τ.[16] Particulars regarding the 90° pulse length (21 μs), the interpulse delay (250 ms), the recycle delay (10 s), the spectral width (10 kHz), the data size (8K), the line broadening (10 Hz), and the number of acquisitions (8−1288 scans) are those noted in the parentheses unless stated otherwise. In this study, the PGSE experiments were performed at 23 °C and the gradient pulse was applied to the z-direction only. It was necessary to use two levels of gradient strength, 70 and 130 G/cm, depending on the polymer diffusion coefficient. The lower range of gradient strength was calibrated by using the diffusion coefficient of 2 vol % H_2O in D_2O ($D = 1.902 \times 10^{-9}$ m^2/s).[17] In the case of higher gradients, a sample of 10 wt % PEO in HDO, which could be measured with both low and high gradient strengths, was used as the calibration standard. At low gradient strength, the error in the measured self-diffusion coefficients is estimated at approximately 5%, except for polymer concentrations less than 0.05 wt %, where the error is about 10%. At higher gradient strengths, gradient pulse imbalances can shift the position of the echo maximum and distort its phase.[18] To overcome this problem, we have implemented a widely used method, described in detail elsewhere,[19] 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.

NMR T_1 and T_2 Relaxation Time Measurements. Spin−lattice relaxation times (T_1) were measured using the standard inversion−recovery pulse sequence, $[(180°_x)-\tau-(90°_x)-\text{acquisition}]$. T_1 values were obtained by fitting the intensities to the equation

$$\ln\left[\frac{(I_\infty - I_\tau)}{2I_\infty}\right] = -\frac{\tau}{T_1} \tag{1}$$

where I_∞ is the intensity when the delay time τ approaches infinity. Spin−spin relaxation times (T_2) were measured using a spin−echo pulse sequence, $[(90°_x)-\tau-(180°_y)-\tau-\text{acquisition}]$. T_2 values were obtained by fitting the intensities to the equation

$$\ln\left[\frac{I_\tau}{I_0}\right] = \frac{-2\tau}{T_2} \tag{2}$$

for different values of the pulse interval τ where I_0 is the intensity for $\tau = 0$.

NMR Assay of HEUR AP Binding to Latex. The amount of HEUR AP adsorbed onto latex particles was obtained by the depletion method, in which the HEUR AP concentration in the supernatant fraction following centrifugation was quantified using a single-pulse ^{1}H NMR excitation technique. For this purpose, a series of aqueous solutions of HEUR AP of known concentration were employed as calibration standards, using the height of the water resonance as an internal standard.

Results and Discussion

PGSE NMR Self-Diffusion Coefficient Measurements. The PGSE NMR pulse sequence consists of a pair of magnetic field gradient pulses interleaved with the two radio-frequency (rf) pulses of the usual spin−echo NMR sequence. For isotropic diffusion 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 application of the PGSE pulse sequence is related to the diffusion coefficient D and the pulse program parameters according to eq 3,

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

where G is the pulsed gradient strength, δ the duration of the gradient, Δ the interval between the gradients, τ the rf pulse interval, and γ the magnetogyric ratio.[16] 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 can be obtained by calibration with a sample of known diffusion coefficient, as described in the Experimental Section.

It is not unusual to observe a nonlinear dependence of $\ln(I_{2\tau}/I_0)$ on $\delta^2(\Delta - \delta/3)$, due to restricted diffusion,[20,21] size polydispersity,[22,23] or other reasons. In such instances, it is sometimes useful to employ a "stretched exponential" to extract a mean diffusion coefficient, as indicated in eq 4.[14]

$$I_{2\tau} = I_0 \exp(-[(\gamma G \delta)^2(\Delta - \delta/3)D_e]^\beta) \tag{4}$$

The parameter β is a measure of the width of the distribution of diffusion coefficients, and $0 \le \beta \le 1$, so that for a monodisperse diffusion coefficient $\beta = 1$ and eq 4 reverts to eq 3. 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 5,

$$\frac{1}{D_m} = \int_0^\infty \exp[-(XD_e)^\beta]\,dX = (1/\beta)(1/D_e)\Gamma(1/\beta) \tag{5}$$

where $X = (\gamma G \delta)^2(\Delta - \delta/3)$.

Figure 1 shows a series of ^{1}H NMR spectra of a mixture of 0.6 wt % HEUR AP plus 4 wt % polystyrene latex in water for various durations of the field gradient pulse. The leftmost spectrum was obtained with a very short gradient pulse, so that diffusional effects will be minimal. This spectrum shows two resonances, one arising from the protons in water and the other from the ethylene protons of the PEO chains of the HEUR AP. Other protons of the HEUR AP do not appear due to either their short spin−spin relaxation times (T_2) or their lower abundance. Proton signals from the polystyrene latex particles are not observed whatsoever, presumably due to the very short spin−spin relaxation time (T_2) anticipated for such large solid particles with minimal internal molecular mobility.

With increasing gradient pulse duration, the NMR signal intensity from both the water and the HEUR AP decreases exponentially as a function of the self-diffusion coefficient. The small water molecules diffuse very quickly, and their proton signal disappears almost immediately as the gradient pulse duration is increased. The large HEUR APs diffuse slowly, and their proton

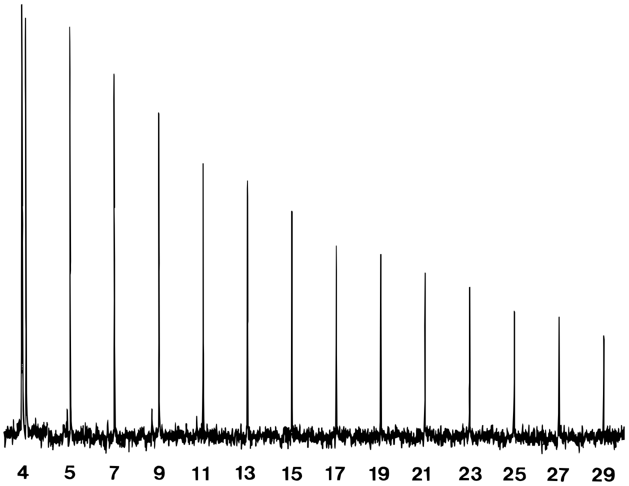

Figure 1. A series of PGSE proton NMR spectra of a mixture of the 51 000 molecular weight HEUR AP (0.6 wt %) plus polystyrene latex (4.0 wt %) in water at room temperature for different values of the gradient pulse duration, δ, indicated in milliseconds. In this case, the gradient strength was 72 G cm^{-1} while $\Delta = \tau = 250$ ms.

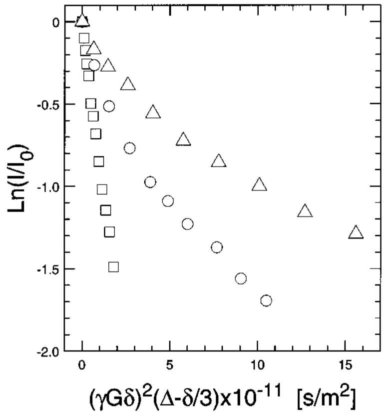

Figure 2. Typical intensity decays of the HEUR AP proton signal in the PGSE NMR experiment as a function of the universal parameter $(\gamma G\delta)^2(\Delta - \delta/3)$ for the following mixtures: squares, 0.1 wt % HEUR AP; triangles, 0.6 wt % HEUR AP; circles, 1.0 wt % HEUR AP plus 4 wt % polystyrene latex. The self-diffusion coefficient is extracted from such data according to eq 4 as described in the text.

signal endures, progressively decreasing in intensity with longer gradient pulses.

Figure 2 shows the manner in which the signal intensity of the ethylene protons of the PEO backbone of the HEUR AP decreases as a function of the gradient pulse duration for three representative situations: 0.1 wt % HEUR AP in water, 0.6 wt % HEUR AP in water, and 1 wt % HEUR AP plus 4 wt % polystyrene latex in water.

For the case of 0.1 wt % HEUR AP, the NMR signal intensity decreases rapidly, in an approximately linear fashion, with increasing gradient pulse duration. This indicates relatively rapid diffusion with a narrow distribution of diffusion coefficients. Other types of studies in analogous systems indicate that in this concentration range the solution viscosity is not far removed from that of water and one is observing the diffusion of the discrete “rosettes” of the “microgel” model, which have not yet begun to bridge and form a network.[4,8]

When the concentration of the HEUR AP is increased to 0.6 wt %, the NMR signal intensity decreases much more slowly with increasing gradient pulse duration, and the decay is decidedly nonlinear. At these concentrations, it is known that the viscosity of HEUR AP–water mixtures undergoes a profound increase.[4,8] The origin of the viscosity increase is the formation of a network of hydrophobic clusters linked by bridging polymers. The observed diffusing units are larger than the discrete “rosettes” and are of diverse size. Consequently, diffusion is slow, and there is a distribution of diffusion coefficients manifest as a nonlinear decay in plots of the type shown in Figure 2. If the HEUR AP concentration is increased to 1.0 wt %, diffusion slows even further, to the extent that, on the scale of Figure 2, there appears to be little decrease in signal intensity (data not shown).

For the case of 1.0 wt % HEUR AP plus 4 wt % polystyrene latex, the decay of the NMR signal intensity with increasing gradient pulse duration indicates that the observed diffusion is much more rapid than that of the 0.6 wt % HEUR AP case, despite the overall greater polymer concentration. The nonlinearity of the signal decay is evident. At first glance, this result is in accordance with one’s expectation that binding of the HEUR AP to the latex surface should deplete the polymer concentration in the bulk solution, thereby reversing network formation, reducing viscosity and enhancing diffusion. However, several critical questions need to be addressed before any such conclusion can be justified or quantitative information extracted. In particular, it is essential to know the degree to which the HEUR AP bound to the latex particle’s surface, versus the HEUR AP remaining in the bulk solution, contributes to the observed NMR signal. This will be a function of the relative size of the two populations, their diffusion characteristics, their NMR relaxation behavior in the two environments, and the rate of exchange between the two populations.

Self-Diffusion of HEUR AP in the Absence of Latex. An essential reference point for understanding the effects of latex on HEUR AP diffusion is the diffusion of the HEUR AP alone in water. Parts A and B of Figure 3 show the mean self-diffusion coefficients and β values, respectively, of the HEUR APs in water as a function of concentration in the absence of latex. In general, the diffusion coefficients decrease with increasing HEUR AP concentration. At a concentration of 0.6 wt %, there is an abrupt decrease in the diffusion coefficients, corresponding to the concentration at which the viscosity begins to rapidly increase. This behavior is essentially identical to that of other HEUR APs of various molecular weights, but having the same length of hydrophobic modifiers, reported previously.[13] The concentration dependence of the diffusion coefficient is readily described by a universal scaling equation,[24]

$$D(c) = D_0 \exp(-\alpha c^{\gamma}) \qquad (6)$$

where $D_0 = 1.08 \times 10^{-11}$ m^2 s^{-1} is the self-diffusion coefficient in the limit of infinite dilution and $\alpha = 4.53$ and $\gamma = 1.12$ are scaling parameters. These are determined from a least-squares fit of eq 6 to the diffusion data, and the result is the solid curve shown in Figure 3A.

The dispersion of the self-diffusion coefficients about their mean value likewise undergoes a rather abrupt transition in the region of 0.6 wt % HEUR AP as shown in Figure 3B, from an almost monodisperse diffusion coefficient at low concentrations ($\beta \approx 1$) to a rather broad dispersion of diffusion coefficients about the mean value at higher concentrations ($\beta \approx 0.6$). Again, this is the

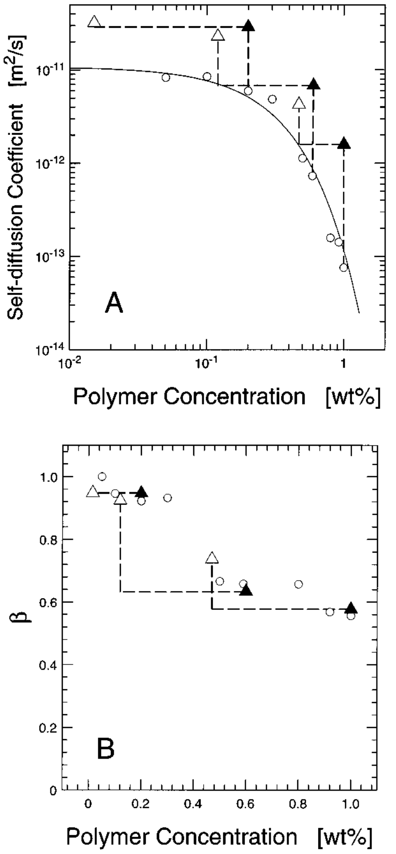

Figure 3. (A) Mean self-diffusion coefficient of HEUR AP as a function of concentration and the effects of polystyrene latex addition. Open circles are for HEUR AP alone in water. The solid line corresponds to the universal scaling law eq 6 with the parameters listed in the text. The effect of adding 4 wt % latex is indicated by the dashed line directed to the closed triangle at the relevant weight percent HEUR AP. The self-diffusion coefficient of the HEUR AP in the corresponding supernatant fraction obtained by centrifugation is indicated by the open triangle. The dashed lines are intended to indicate the change in the free HEUR AP concentration before and after addition of latex. (B) Dispersion of the self-diffusion coefficients about their mean values versus the HEUR AP concentration and the effects of the addition of latex. The value of β was obtained by a nonlinear least squares fit of eq 4 to the signal intensities such as shown in Figure 1.

behavior exhibited by all HEUR APs having C16 hydrophobic modifiers, regardless of molecular weight.[13]

Another useful reference point is the diffusion behavior of a control polymer of identical backbone structure and molecular weight, but lacking hydrophobic end-cap modifiers. Although a control polymer of the precise molecular weight is not available, the self-diffusion coefficients of a series of such control polymers, identical in every respect but their size and spanning a range of molecular weights, has been described.[13] Their self-diffusion coefficients obey a simple power law with respect to molecular weight:

$$D_0 = 1.15 \times 10^{10}\left[\frac{kT}{\pi\eta}\right]M_{\mathrm{w}}^{-0.57\pm0.01} \qquad (7)$$

where D_0 is the diffusion coefficient in the limit of infinite dilution, k is the Boltzmann constant, T is the absolute temperature, η is the viscosity, and M_{w} is the molecular weight. The expected concentration dependence of the self-diffusion coefficient of any such control polymer can be obtained by interpolation from others in the series. Typically for such control polymers, the diffusion coefficients are rather monodisperse ($\beta \approx 0.8$) and remain so over a wide concentration range.

Table 1. Adsorption of HEUR AP to Polystyrene Latex

HEUR AP concn[a] (wt %) initial	final	HEUR AP adsorbed per latex particle	surface area per adsorbed HEUR AP[b] (nm²)
0.2	0.05	1100	80
0.6	0.12	3300	27
1.0	0.47	3700	24

[a] Concentration was determined using ^{1}H NMR, as described in the Experimental Section, for the initial HEUR AP solution and the supernatant obtained by centrifugation following addition of 4 wt % latex and equilibration for 48 h. [b] Based on the surface area of a latex particle 168 nm in diameter.

NMR Assay of HEUR AP Adsorption onto Polystyrene Latex. Levels of HEUR AP binding to polystyrene latex were assayed by a depletion method, described in the Experimental Section, using the ^{1}H NMR spectrum of the supernatant retrieved following centrifugation of fully equilibrated HEUR AP + latex + water mixtures. In the three particular mixtures chosen, the latex content was kept constant at 4 wt %, while the total HEUR AP concentration was either 0.2, 0.6, or 1.0 wt %. Note that these initial HEUR AP concentrations fall in the low-viscosity region, the high-viscosity region, and at the breakpoint between the two. As detailed in Table 1, adsorption onto 4 wt % polystyrene latex reduces the HEUR AP concentration in the bulk solution to 0.05, 0.12, and 0.47 wt %, respectively. This corresponds to the binding of 1100, 3300, and 3700 HEUR AP per latex particle, respectively. Alternately, one may calculate that each such HEUR AP occupies a surface area equal to 80, 27, and 24 nm^2, respectively.

Adsorption of HEUR AP to polystyrene latex is reversible. The mixtures were subjected to a cycle of centrifugation, followed by resuspension with serum replacement and further centrifugation. The latex-rich pellet was easily resuspended by mild vortexing, presumably because the adsorbed HEUR AP confers steric stability to the particle suspension. When the supernatant fraction from different centrifugation–resuspension cycles was monitored via ^{1}H NMR, HEUR AP was readily detected, and repeated cycling led to further HEUR AP desorption.

The adsorption data in Table 1, although minimal for the purpose, fit a Langmuir adsorption isotherm with an equilibrium association constant of 31 (wt %)$^{-1}$ and a saturation binding level of 7.7×10^{-8} mol m^{-2} (or 22 nm^2 surface area per HEUR AP). This indicates that adsorption has approached saturation for the two samples at higher HEUR AP concentrations. The value of the adsorption equilibrium constant translates into a Gibbs' free energy change of -35 kJ mol^{-1}. Richey *et al.*[9] reported that adsorption of a pyrene-end-capped poly(ethylene oxide) (PAT) of molecular weight 60 000 onto polystyrene latex particles followed a Langmuir isotherm, with an equilibrium association constant of 5 (wt %)$^{-1}$ and an area per PAT molecule of 13 nm^2 at saturation. Their equilibrium constant converts to a Gibbs' free energy change of -25 kJ mol^{-1}. The agreement between the two results is acceptable when it is considered that aromatics generally exhibit a smaller free energy change than alkanes of equal carbon numbers when moving from a hydrophilic to a hydrophobic environment.[25]

Ou-Yang *et al.*[7] reported that HEUR associating polymers adsorbed on polystyrene latex particles undergo a transition from a flat "pancake" profile to a

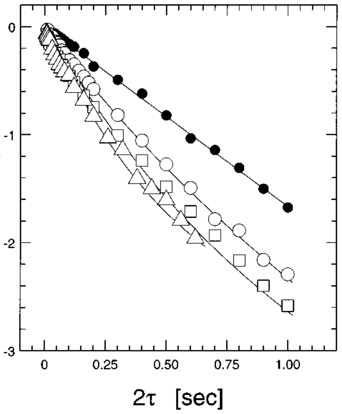

Figure 4. Determination of the spin–spin relaxation time from the spin–echo signal intensity of the HEUR AP as a function of the echo delay time 2τ: closed circles, supernatant from the 1 wt % HEUR AP + 4 wt % latex mixture; open circles, intact 1 wt % HEUR AP + 4 wt % mixture; squares, intact 0.6 wt % HEUR AP + 4 wt % latex mixture; triangles, intact 0.2 wt % HEUR AP + 4 wt % latex mixture. The solid lines are simulations based on a model assuming two populations in slow exchange with one another, as described in the text and using the parameters listed in Table 2.

protruding “brush” configuration when the surface area per HEUR AP falls below 26 nm^2. Thus, for the two HEUR AP + latex + water mixtures at higher polymer concentrations, the adsorbed HEUR AP likely assumes a “brush” configuration. In contrast, the adsorbed HEUR AP at the lowest polymer concentration investigated here probably takes on the “pancake” profile.

NMR T_1 and T_2 Relaxation Times of Free and Latex-Bound HEUR AP. Relaxation time measurements were performed on the various HEUR AP + latex + water mixtures before centrifugation (i.e., on the intact mixture) and on the supernatant retrieved after centrifugation (i.e., with the latex removed). We note that the supernatant fraction from the centrifugation step was optically clear and apparently free of latex particles.

For the determination of T_1, the HEUR AP resonance intensity in each of the three different HEUR AP + latex + water mixtures and their supernatant fractions following centrifugation exhibit a single straight line in a plot of $\ln(I_\infty - I_0)/2I_\infty$ versus τ (data not shown). Moreover, the values of T_1 measured in the three different HEUR AP + latex + water mixtures are each similar to one another ($T_1 \approx 0.5-0.6$ s) and to the values of T_1 measured in the corresponding supernatants. Thus, on the basis of T_1 measurements, it is not possible to differentiate whether the bound and free HEUR AP are in fast or slow exchange on the NMR time scale. We note that T_1 is expected to be most sensitive to changes in the spectral density of fast motions, such as internal polymer segmental translations and rotations. It would seem that, for HEUR APs, these fast motions are not altered upon binding to latex to a degree sufficient to alter the measured T_1 in mixtures of free and bound HEUR AP.

In contrast, the results of the T_2 determinations were very different for the three different HEUR AP + latex + water mixtures and for the supernatants versus the intact mixtures. Some representative situations are shown in Figure 4. For all the supernatant fractions, the HEUR AP resonance intensity decreased with increasing spin–echo delay time τ in a manner indicating a single T_2 value, and the particular value of T_2 was always longer than measured in the intact mixture (details of T_2 results are listed in Table 2). However, in the intact mixtures the HEUR AP signal decay was always curvilinear, indicating the presence of (at least) two populations, having different T_2 relaxation times, and in slow exchange with one another.

Table 2. Spin–Spin Relaxation Times and Diffusion Coefficients for HEUR AP in the Presence of Polystyrene Latex

sample compn[a]	fractional population	T_2[b] (ms)	D_c[c] (m^2 s^{-1})	β
1% HEUR AP + 4% latex				
bound	0.53	240	4.50×10^{-13}	0.90
free	0.47	600	5.15×10^{-12}	0.71
supernatant		600	4.10×10^{-12}	0.71
0.6% HEUR AP + 4% latex				
bound	0.74	220	2.25×10^{-12}	0.90
free	0.26	710	2.38×10^{-11}	0.92
supernatant		700	2.30×10^{-11}	0.92
0.2% HEUR AP + 4% latex				
bound	0.80	170	3.0×10^{-12}	0.90
free	0.20	850	4.0×10^{-11}	0.88
supernatant		850	3.2×10^{-11}	0.88

[a] Bound and free refer to the two populations assumed to coexist in the intact mixture. [b] See text for explanation of simulation.

The T_2 decays of the intact mixtures shown in Figure 4 may be simulated by assuming the existence of two HEUR AP populations, corresponding to HEUR AP free in solution versus bound to the polystyrene latex, in slow exchange with one another on the NMR time scale. The fractional populations in the two states should correspond to the experimentally determined values listed in Table 1, while it is reasonable to assume that the T_2 of the free HEUR AP is approximately that measured for the supernatant fraction. The only variable becomes the T_2 of the latex-bound HEUR AP. The simulated T_2 decays for the HEUR APs in the three different HEUR AP + latex + water intact mixtures are shown as the solid lines in Figure 5, with the corresponding values of T_2 and fractional populations of the bound and free states as indicated in Table 2. The simulations satisfactorily reproduce the experimental behavior.

The values of T_2 for the latex-bound HEUR AP required to reproduce the experimental T_2 decays are all much shorter than the values of T_2 for the free HEUR AP. Elementary NMR relaxation theory indicates that the T_2 relaxation time is sensitive to changes in the spectral density of both slow and fast motional correlation times. It is plausible to suppose that the correlation time for overall rotational tumbling for latex-bound HEUR AP should relate to the size of the latex particle, and so should increase relative to HEUR AP free in solution. For instance, the rotational tumbling correlation time, calculated using the Stokes-Einstein equation for the case that the viscosity equals that of pure water, increases from 58 μs for a HEUR AP “rosette” of 40 nm diameter to 4.3 ms for a HEUR AP bound to a latex particle of 168 nm diameter. We note, however, that overall rotational tumbling is just one of many possible contributions to the effective motional correlation time for a macromolecule with a high degree of internal flexibility, such as a HEUR AP.

Self-Diffusion of HEUR AP in the Supernatant Fraction. Given the fact that the HEUR AP population in the intact HEUR AP + latex + water mixtures consists of at least two populations (free and bound), before analyzing their PGSE NMR results, it is useful to examine the diffusion behavior of the HEUR AP in the supernatant fraction obtained following centrifugation. These diffusion coefficients are shown in Figure

3A as the open triangles at the corresponding free HEUR AP concentrations, the latter determined as described in the Experimental Section.

In every case, the addition of latex increases the diffusion of the free HEUR AP to the extent that its diffusion coefficient lies above the value anticipated for the corresponding HEUR AP concentration in the absence of latex. For the case of 0.6% and 0.2% initial HEUR AP concentrations, the diffusion coefficient measured in the supernatant fraction is characteristic of control polymers lacking hydrophobic modifications, as calculated using eq 7. Moreover, the dispersion of the diffusion coefficients of the HEUR APs in the supernatant fractions about their mean value, as indicated by the size of the exponent β shown in Figure 3B (open triangles), is characteristic of a narrow distribution of diffusion coefficients. Thus, it would appear that the polystyrene latex does more than merely bind HEUR AP and deplete its concentration in the bulk. In addition, latex actively inhibits network or "microgel" formation by the remaining free HEUR AP.

One explanation for this unexpected effect of latex is to be found in the fact that the HEUR AP with which we are dealing is not chemically homogeneous, having on average 1.7 hydrophobes per molecule.[26] One may calculate, therefore, that the HEUR AP preparation is a mixture of doubly modified (76%), singly modified (18%), and nonmodified (6%) species. If one assumes further that those polymers with two hydrophobic modifications per chain bind with the highest affinity to the latex surface, it is readily seen that the polymer remaining free in solution will be characterized by a lower average number of hydrophobes per molecule. Eventually, the free polymer will become incapable of self-association, so network or "microgel" formation is precluded. In support of this conjecture is the observation that even at low HEUR AP concentrations, when the available latex surface is far from saturated with polymer molecules, HEUR AP binding is not quantitative and some 20% remains free in solution.

Self-Diffusion of HEUR AP in the Intact Latex Mixture. Armed with the adsorption and relaxation time data described above, we are in a position to interpret the results of PGSE NMR measurements of HEUR AP diffusion in the presence of polystyrene latex. Of pre-eminent importance is the fact that two populations coexist, HEUR AP bound and free, that these two populations are in slow exchange with one another, and that they have different T_2 relaxation times.

In all cases, the addition of 4% latex causes the mean diffusion coefficient of the HEUR APs to increase substantially, as indicated in Figure 3A by the vertical dashed lines to the closed triangles at the appropriate concentrations. The dispersion about the mean HEUR AP diffusion coefficients, as indicated by the values of β in Figure 3B, remain relatively constant upon latex addition. Since the HEUR AP exists as a mixture of bound and free polymers in slow exchange, the mean diffusion coefficient is a weighted average of the diffusion coefficients of these two populations. The intensity decay resulting from application of the PGSE NMR pulse sequence may, therefore, be considered to consist of a linear combination of two signals, one from each population,[27] according to eq 8,

$$I_{2\tau}/I_0 = f_A \exp[-2\tau/T_{2,A} - [(\gamma G\delta)^2(\Delta - \delta/3)D_{e,A}]^{\beta_A}] + f_B \exp[-2\tau/T_{2,B} - [(\gamma G\delta)^2(\Delta - \delta/3)D_{e,B}]^{\beta_B}] \quad (8)$$

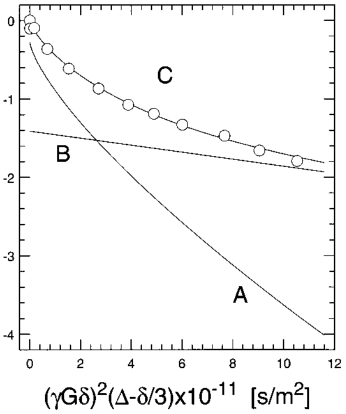

Figure 5. Simulation of the PGSE NMR intensity decay for the intact 1 wt % HEUR AP + 4 wt % latex mixture assuming two populations in slow exchange with one another. Line A corresponds to the behavior of the free HEUR AP while line B corresponds to the behavior of the latex-bound HEUR AP. The behavior is predicted using eq (8) with fitting parameters listed in Table 2, as described in the text. Line C is a linear combination of A and B, over which the actual experimental data have been plotted.

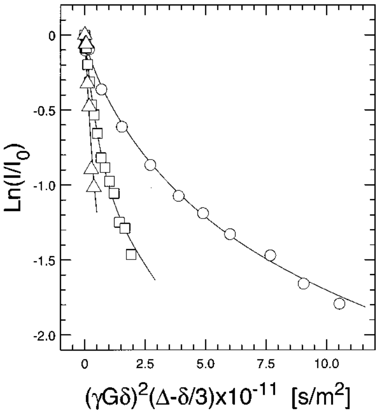

Figure 6. Simulation of the PGSE NMR intensity decays for 1 (circles), 0.6 (squares), and 0.2 wt % (triangles) HEUR AP plus 4 wt % latex. See Figure 5 and Table 2.

where the subscripts A and B refer to free and bound HEUR AP, respectively, and f_i, $T_{2,i}$, $D_{e,i}$, and β_i are the fractional occupancy, the T_2 relaxation time, the effective diffusion coefficient, and the dispersion of the diffusion coefficient of the indicated population. The fractions of free and bound HEUR AP have been established earlier, while their T_2 relaxation times have been estimated as described above. For $D_{e,A}$ and β_A we use the corresponding values measured in the supernatant fractions. The value of β_B is set to 0.9, to reflect the rather small size polydispersity of the polystyrene latex. The remaining variable is $D_{e,B}$, the diffusion coefficient of the HEUR AP bound to the latex particles.

A typical simulation of the PGSE NMR intensity decay of the intact HEUR AP + latex + water mixtures is shown in Figure 5 for the case of 1 wt % HEUR AP. The solid lines A and B represent the intensity decays in the PGSE NMR experiment as a function of the gradient pulse duration for the two populations, free and bound, given the parameters listed in Table 2. Solid line C is the linear combination of A and B and, quite evidently, is a satisfactory fit to the experimental data.

The simulations for all three different initial HEUR AP concentrations to which 4% latex was added are compared in Figure 6. The values of $D_{e,B}$, the diffusion coefficient of latex-bound HEUR AP, extracted by fitting to the two-site model are listed in Table 2. Since the viscosity of the HEUR AP + latex + water mixtures has not been measured, the Stokes–Einstein equation cannot be applied to estimate an apparent size of the diffusing unit. However, the fitted values of the diffusion coefficients of the bound HEUR AP are near to or less than the diffusion coefficient which one calculates from the Stokes–Einstein equation for a sphere having a diameter corresponding to the size of the latex particle employed here and immersed in a solution with viscosity equal to that of pure water at room temperature. Moreover, the latex-bound HEUR AP always exhibits a diffusion coefficient at least one order of magnitude lower than the corresponding free HEUR AP. We conclude that the apparent diffusion coefficient for the latex-bound HEUR AP reflects the diffusion of the latex particle itself.

Given the number of variables in eq 8, it is not too surprising that one is able to simulate the PGSE NMR intensity decays. The simulations shown are not unique in the quality of the fit to the experimental data. However, we reiterate that two of the variables, f_i and $T_{2,i}$, were independently determined and were not allowed to vary during the simulation of the PGSE NMR data. Two other variables, $D_{e,A}$ and β_A, were estimated from the behavior of the supernatant fraction and were not allowed to vary during the simulations. One may argue that the supernatant fraction differs from the interstitial bulk solution in the intact HEUR AP + latex + water mixture because of obstruction effects present in the latter but not the former. Various obstruction models have been proposed.[28-30] Typically, for the weight fraction of latex employed here, obstruction effects are expected to decrease the diffusion coefficient in bulk interstitial solution in the intact mixture by less than a factor of 2 relative to the value measured in the supernatant fraction. This is not a large enough effect to fundamentally alter the conclusions suggested by the simulations above.

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