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Adsorption of Hydrophobically End-Capped Poly(ethylene oxide) on Poly(tetrafluoroethylene) Latex Particles: Light Scattering Study

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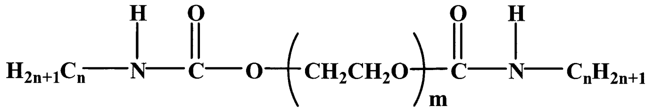
ABSTRACT: The adsorption of an associating polymer, hydrophobically end-capped poly(ethylene oxide) urethane resin (HEUR), on PTFE latex was investigated in aqueous solution by static and dynamic light scattering. A PTFE latex (stabilizer free)/HEUR/water system (probe−polymer interaction system) was compared with a PTFE latex (with stabilizer)/PEO/water system (probe−polymer noninteraction system). Static light scattering studies show that there was no size difference in the PTFE latex (with stabilizer)/PEO/water solution by increasing the PEO concentration, but there was an increase of particle size in the PTFE latex/HEUR/water solution by increase the HEUR concentration. The stabilizer prevents interaction between PTFE and PEO in the PTFE latex (with stabilizer)/PEO/water system, but HEURs are attached on the PTFE particles in the PTFE latex/HEUR/water system. In polarized and depolarized dynamic light scattering studies, a ν parameter in "stretched exponential" form of translational diffusion was a sensitive index for showing particle and polymer interaction in the solution, but the parameter of rotational diffusion was not sensitive. The plot of the quotient D_R/D_T vs polymer concentration shows two transitions in the PTFE latex/HEUR/water system. In the PTFE latex (with stabilizer)/PEO/water system, however, the value of D_R/D_T was constant by increasing PEO concentration. On the basis of these experimental data, we suggest three step adsorption mechanisms: molecular adsorption on PTFE particle at low HEUR concentration, C_{HEUR} < 8 mg/mL; growing of micellar structure at the intermediate concentration, 8 mg/mL < C_{HEUR} < 15.6 mg/mL; and micellar adsorption after saturation on the PTFE surface at high concentration, C_{HEUR} > 15.6 mg/mL.

Introduction

The stability of particles in solution has been of interest in colloid science. Dispersion forces, which are caused by differences in the dielectric constants between particles and solvent molecules, attract large particles and generate large aggregates.[1] In colloid science, surfactants and a polymer are used in order to prevent particle aggregation. It is well-known that polymers or surfactants in colloid suspensions are adsorbed onto the surface of colloidal particles. The absorbed molecules form impenetrable layers on the surface of particles, so the layers prevent attraction between particles. To verify the interaction between particles and stabilizers, dynamics on the stability of colloids and adsorption of additives have been investigated through various techniques. Many researchers have reported that an important parameter is the hydrodynamic thickness of the layer, which determines its effectiveness in steric stabilization. Measuring hydrodynamic thickness of the layer or the adsorption isotherm has been used in order to reveal the adsorption mechanism of stabilizers onto particles.[2−8]

Hydrophobically end-capped poly(ethylene oxide) urethane resin (HEUR) is known as the representative water-soluble associating polymer, which is widely used as rheology control agents for paints, inks, and cosmetics. Figure 1 shows the structure of HEUR.



$$H_{2n+1}C_n-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-O-\left(CH_2CH_2O\right)_m-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-C_nH_{2n+1}$$

Figure 1. Molecular structure of hydrophobically end-capped poly(ethylene oxide) urethane resin (n = 18, m = 90).

HEUR consists of a long poly(ethylene oxide) (PEO) main chain and two short hydrocarbon end chains, which are connected to both ends of PEO by urethane bonds. Over the past decade, fundamental studies of HEUR in water have been extensively conducted using a variety of techniques because of HEUR's potential in a nonionic surfactant, stabilizer, and suspending agent.[9−12] It has been known that the water-insoluble hydrocarbon side chains of HEUR associate to form micelle-like clusters at a concentration, critical micelle concentration (cmc). These micelle-like clusters are spherical-shaped. They are composed of two phases: a hydrophobic core in the dispersed phase and hydrophilic loop in the continuum phase in contact with water. When the concentration exceeds the cmc, micelles are bridged to each other, and the viscosity of solution abruptly increases. At higher concentrations, networks of micelles grow progressively throughout the entire solution.[13−16]

The adsorption of HEUR onto colloidal particles has been investigated using fluorescence, light scattering, and viscosity measurements.[17−21] According to recent reports,[22] the two hydrophobic end groups of HEUR adsorb onto the surface of polystyrene latex particles. At low surface coverage, HEURs form a pancake-like structure on the surface of latex. At high surface coverage, the "pancake" configuration changes to the "brush" form. However, the associating property of HEUR was not considered in these studies because the interpretation of the DLS data of multiple layering or bridging can be ambiguous. It is also difficult to identify a clear trend for the viscosity and mobility of the particle in the polymer solution. Under shear flow, the HEUR solutions both with and without particles show a New-

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tonian behavior at low shear rates, followed by a shear thinning region.[21]

Our interest in here is how the associating property of HEUR affects the adsorption mechanism onto colloidal particles. Though translational diffusion of particles can give information on the adsorption of HEUR, it is not enough to completely define the adsorption mechanism of HEUR. We utilized depolarized dynamic light scattering as well as polarized dynamic light scattering in order to define the adsorption mechanism of HEUR onto colloidal particles using rotational and translational dynamics of particles. In many studies, polystyrene latex particles or titanium dioxide particles have been used as probe particles. These particles are geometrically and optically isotropic particles that do not exhibit depolarized scattering light.[23] Our choice is poly(tetrafluoroethylene) (PTFE) latex particles, which are optically anisotropic and slightly elongated particles that exhibit strong depolarized scattering because of their semicrystalline internal structure. The dynamic properties of PTFE latex particles in various solutions have been studied by many researchers.[24−27] It is known that polarized and depolarized scattering signals of PTFE latex particles are much stronger than for most other polymers. Thus, PTFE latex particles have been used as probes in order to gain new insights into the polymer/solvent system.[28]

This paper shows the translational and rotational diffusion of PTFE absorbed HEUR, which is measured by depolarized and polarized dynamic light scattering.[29] To confirm the adsorption of HEUR onto PTFE latex particles, the PTFE/HEUR/water system is compared with a PTFE (with stabilizer)/poly(ethylene oxide)/water system, in which PTFE latexes do not interact with polymers. The distinction of two different systems, probe−polymer interaction system and noninteraction system, is available by size information and an analysis using stretched exponential form. Finally, we will explain a change of rotational dynamics in accordance with the adsorption of HEURs onto particles.

Experimental Section

Materials. HEUR ($C_{18}EO_{90}C_{18}$) was synthesized by reaction of poly(ethylene oxide) which is end-capped with hydroxyl group (PEO, Fluka, $M_w = 4000$, PDI = 1.1) and octadecyl isocyanate (Aldrich). The degree of substitution was about 0.95, which was determined by NMR analysis. A detailed synthesis method for HEUR has been reported elsewhere.[10,30] PTFE latex (ALGOFLON, D60V, Lot No. BR-6, produced by Ausimont) was kindly provided by Prof. P. S. Russo of Louisiana State University, Baton Rouge, LA.. The provided PTFE latex was already stabilized by nonionic surfactant, ∼3%, denoted (with stabilizer) in this paper. Nonionic surfactant in solution was removed by dialysis to make a polymer−particle interacting system.

Sample Preparation. PTFE latex/HEUR/water and PTFE latex (with stabilizer)/PEO/water dust-free solutions were prepared. After HEUR was dissolved in methanol, the solution was directly put into precleaned light scattering cell (13 mm × 100 mm test tube) using a 0.45 μm membrane filter. The filtered solution was dried in a vacuum oven. Dialyzed stock solution was added to the dried light scattering cell, and HEUR was dissolved in stock solution by sonication. PTFE latex (with stabilizer)/PEO/water solution was prepared using undialyzed stock solution. After PEO ($M_w = 4000$, the same molecular weight used in the synthesis of HEUR) was dissolved in deionized water, the solution was filtered into precleaned light scattering cell using a 0.2 μm membrane filter. Undialyzed stock solution was added to the PEO aqueous solution. The HEUR and PEO concentrations were varied from 0 to 21.5 mg/mL and from 0 to 16.9 mg/mL, respectively. The final PTFE latex concentration of all solutions was 68.4 μg/mL.

Light Scattering Measurements. A Spectra-Physics argon ion laser producing vertically polarized light of $\lambda_0 = 488$ nm was used. The detector optics employed optical fibers coupled to an ALV/SO-SIPD/DUAL detection unit that employed an EMI PM-28B power supply and ALV/PM-PD preamplifier/discriminator. The correlator was an ALV-5000/E/WIN multiple tau correlator with 288 exponentially spaced channels. The sampling time of the correlator ranged from 10^{-6} to 100 s. The cylindrical scattering cell was located in a bath of index matching solvent (decaline) that was maintained at room temperature. The scattered light was passed through 400 and 200 μm pinholes. Two focal lens and two Glan-Thomson polarizers were used. Two sets of a focal lens and a polarizer were placed in front of the laser and pinhole, respectively.[26] Each correlation function was gathered at six different angles from $\theta = 30°$ to 105°. For the SLS experiments, intensities were measured from $\theta = 30°$ to 90°.

Result and Discussion

Light scattering measurements were performed for characterization of HEUR/water, PEO and PTFE latex/water ternary solutions, PTFE latex/HEUR/water ternary solutions, and PTFE latex (with stabilizer)/PEO/water quaternary solutions. For static light scattering studies, a Guinier plot was used in order to measure the size of scattering species. The radius of gyration, R_g, of scatterers could be obtained from the Guinier equation, $\ln I(q) = \ln I(0) - q^2 R_g^2/3$,[31] where $I(q)$ is the angular dependent scattered intensity and q is the magnitude of scattering vector ($q = 4\pi n \sin(\theta/2)/\lambda_0$, where n is the refractive index of solvent, θ is the scattering angle, and λ_0 is the wavelength of the incident beam in vacuo). The polarization sense was Vv polarized.

Dynamic light scattering studies were carried out in Vv (polarized) and Hv (depolarized) geometries. Capital letters, V (vertical polarization) and H (horizontal polarization), represent the polarization sense of the detected light. Lower case letters mean the polarization sense of incident light. The intensity correlation function, $g^{(2)}(\tau)$, obtained by running dynamic light scattering instruments, and $g^{(2)}(\tau)$ is related to the electric field correlation function, $g^{(1)}(\tau)$, by the following equation, $g^{(2)}(\tau) = B(1 + f\,|g^{(1)}(\tau)|^2)$. Here, τ is the lagtime, B is the baseline, and f is an instrumental parameter determined by deviation from an ideal correlation. The relaxation time distributions were obtained by analyzing $g^{(1)}(\tau)$ by inverse Laplace transformation. The inverse Laplace transformation analysis was conducted by CONTIN algorithm, which was programmed by ALV-5000/E/WIN multiple tau correlator with 288 exponentially spaced channels. To obtain diffusion coefficients, $g^{(1)}(\tau)$ was fitted to the relationship between $g^{(1)}(\tau)$ and decay rate (Γ), $g^{(1)}(\tau) = \exp(-\Gamma\tau)$. In Vv geometry, $g^{(1)}{}_{Vv}(\tau)$ is an exponential with a decay rate, Γ_{Vv}, which is related to the translational diffusion coefficient (D_T) through the following equation, $\Gamma_{Vv} = D_T q^2$. For optically anisotropic particles, $g^{(1)}{}_{Hv}(\tau)$ in Hv geometry is an exponential with a decay rate, Γ_{Hv}, which is related to the translational diffusion coefficient and the rotational diffusion coefficient (D_R) through the following the equation, $\Gamma_{Hv} = D_T q^2 + 6D_R$. D_T is related to the hydrodynamic radius, R_H, of the scatterer through the Stokes−Einstein equation, $D_T = k_b T/6\pi\eta R_H$, where k_b is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity.

Characterization of HEUR/Water or PTFE/Water. We investigated micellization and association prop-

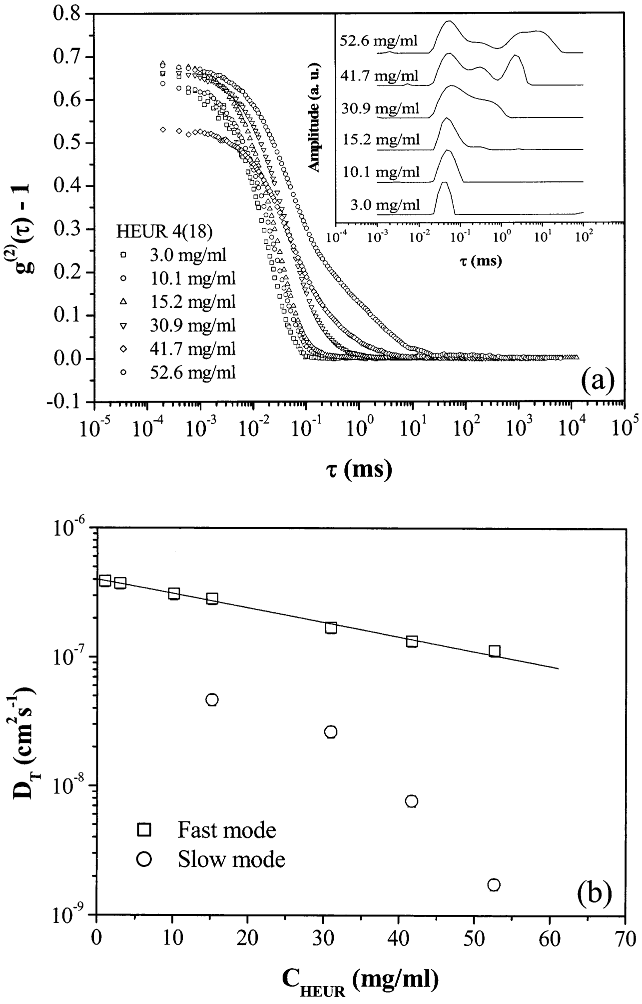

Figure 2. (a) Correlation functions of HEUR/water system with various concentrations. Inset is the relaxation time (τ) distributions of HEUR aqueous solutions at a scattering angle of 90° in Vv geometry. From bottom to top, HEUR concentrations on inset are 3.0, 10.1, 15.2, 30.9, 41.7, and 52.6 mg/mL. (b) Fast and slow modes of translational diffusion coefficients depending on HEUR concentrations. Solid line is the fitting data of the fast mode by the stretched exponential form.

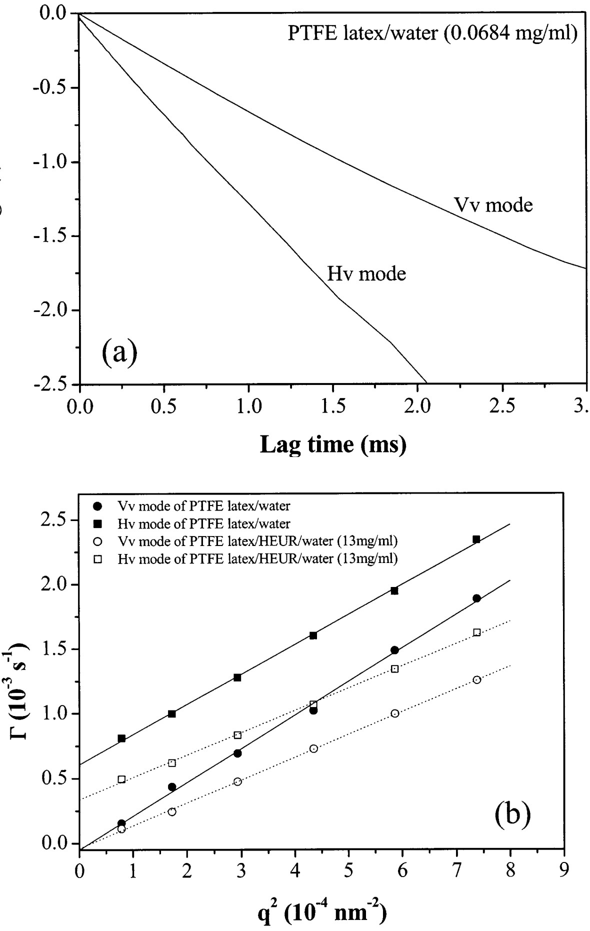

Figure 3. (a) Semilog plot of typical Vv and Hv correlation function of PTFE latex at a scattering angle of 90°. (b) Γ vs q^2 plot of PTFE latex/water solutions (filled symbol and solid line) and PTFE latex/HEUR/water solutions (open symbol and dot line) by Hv and Vv measurement.

erties of HEUR in water. In cmc, HEUR unimers associate to form micelle-like clusters. The cmc was measured by the probe fluorescence technique, which is a method to use the polarity sensitive property of pyrene molecules.[13] The cmc was 0.4 mg/mL for the HEUR used in this experiment. Above the cmc, the association property of HEUR was measured by the DLS. Figure 2 shows the concentration dependence of the correlation functions at 90° of scattering angle of HEUR/water solution. The inset is the fitting data by the CONTIN algorithm.

As shown in Figure 2a, only one mode that decay time is about 0.03 ms exists at a concentration of 3 mg/mL. This mode can be deduced to having a hydrodynamic radius of 6.7 nm using the Stokes−Einstein equation. From 10.1 to 15.2 mg/mL, slow mode arises gradually. It is a process that micelles are bridged by HEUR unimers. Above 15.2 mg/mL, the shift of the slow mode peak occurs. At 52.6 mg/mL, the decay time of the slow mode is about 5−25 ms. At all concentrations, the fast mode is sustained as a major mode. These results indicate that the secondary association of HEUR is mainly occurred by bridging between aggregates. Translational diffusion coefficients data of fast mode are fitted with stretched exponential form, $D = D_0 \exp(-\alpha c^{\nu})$, where α and ν are arbitrary parameters and D_0 is a diffusion coefficients in the limit of zero concentration. In HEUR/water solution, it is known that diffusion of micelle-like clusters follows the stretched exponential.[32] In our system, α, ν, and D_0 are 0.025, 1.021, and 4.0×10^{-7} cm^2 s^{-1}. Hydrodynamic radius of fast mode in the limit of zero concentration is 6.1 nm (Figure 2b). Both slow and fast modes are diffusive, so we can assume that the fast mode is the micellar diffusion and the slow mode is due to large aggregates by the transient network of HEUR micelles.

The diffusion coefficient of PEO in water deduced from DLS was 1.56×10^{-6} cm^2 s^{-1} at a concentration of 176.5 mg/mL PEO. The hydrodynamic radius of PEO deduced from the diffusion coefficient was in agreement with an empirical relationship, R_H (nm) = $0.0145 M_w$ (g/mol)$^{0.571}$.[33] This relationship has been applied to PEO chains whose molecular weight is larger than 30 000 g/mol, we could find that the relationship could be applicable to PEO chains of small molecular weight, M_w = 4000 g/mol. We confirmed that the diffusion coefficient of PEO did not change with increasing concentration. Each PEO molecule exists separately, and PEO molecules do not form any aggregates in water.

Figure 3a shows typical correlation functions in the Hv and Vv geometries of a 68.4 μg/mL of PTFE latex/water solution. The correlation functions in the Hv and

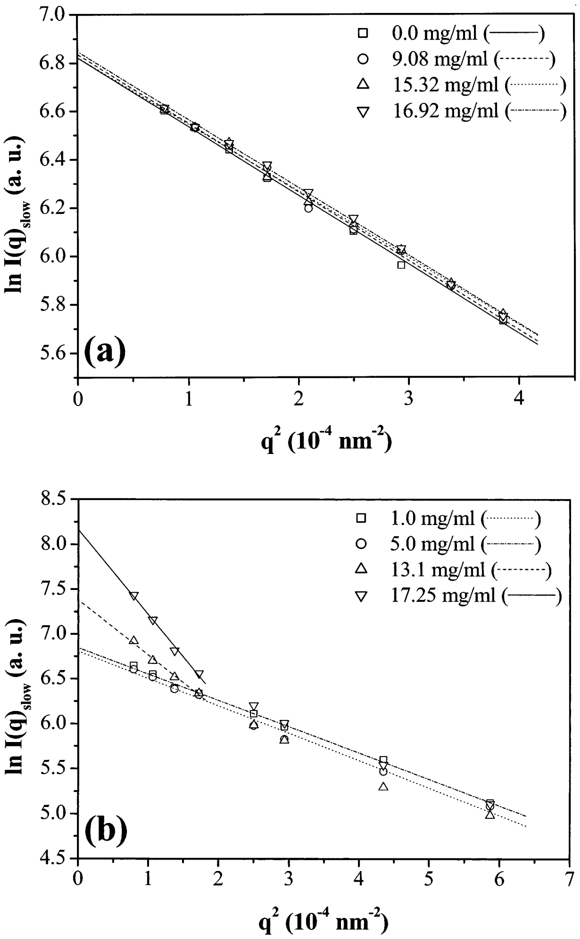

Figure 4. (a) Guinier plots of PTFE latex (with stabilizer)/PEO/water solutions. (b) Guinier plots of PTFE latex/HEUR/water solutions. All Guinier plots were plotted for the slow modes.

Vv geometries are single-exponential decays. Figure 3b shows a Γ vs q^2 plot of PTFE latex/water solutions by Hv and Vv measurement (filled symbols and solid lines). From this angular dependence relation, Γ vs q^2 of Vv data, a hydrodynamic radius of 95.0 nm was obtained by the equations $\Gamma_{Vv} = D_T q^2$, $\Gamma_{Hv} = D_T q^2 + 6D_R$, and $D_T = k_b T/6\pi\eta R_H$. The radius of gyration of PTFE latex from Guinier plot was 90.6 nm. Adding HEUR, the diffusion coefficient of the PTFE latex was decreased by lowering the slope of the plot (open symbols and dotted lines). These effects will be discussed in next section.

Static Light Scattering. Static light scattering studies were performed on PTFE latex/HEUR/water ternary solutions and PTFE latex (with stabilizer)/PEO/water quaternary solutions.

Figure 4a shows the Guinier plots of PTFE latex (with stabilizer)/PEO/water quaternary solutions at various concentrations. In Figure 4a, the slope of the Guinier plot almost does not change with increasing concentration of PEO. Because the scattering intensity of PEO is much weaker than PTFE latex, we can assume that the slope of Guinier plot is due to PTFE latex particles. The size of PTFE latex which depends on the slope of the ln $I(q)$ vs q^2 plot does not change with increasing concentration of PEO, where the stabilizer molecules prevent the interaction between PTFE latex and PEO. However, the PTFE in HEUR solution has totally different behavior. Figure 4b shows the Guinier plots deduced from the slow mode of PTFE latex/HEUR/water ternary solution at various concentrations. The fast mode and slow mode are showed in an inset of Figure 7. The amplitudes of the slow mode, $A_s(q)$, and the fast mode, $A_f(q)$, are the relative contribution to the scattering intensity of the system. Scattering intensity of the slow mode is given by $I_s(q) = (A_s(q)/A_s(q) + A_f(q))I_{total}(q)$. As shown in Figure 4b, the initial slope of the Guinier plot at high HEUR concentrations is steeper than at low HEUR concentrations. Higher HEUR concentrations leads to a steeper slope in the Guinier plot. The size of the scattering species abruptly increases at the concentration of 19 mg/mL of HEUR, from 90.5 to 156.5 nm. Uncertainties were estimated at 4%. Figure 5 shows how the PEO and the HEUR changes the radius of gyration of PTFE latex with increasing concentration, which deduced from the Guinier plot. The size of PTFE latex, 90.5 nm, does not change appreciably with PEO concentration from 0 to 16.9 mg/mL, where the stabilizer molecules prevent the interaction between PTFE latex and PEO. The estimated uncertainty is 2%. However, the size of PTFE latex in HEUR solution increases with increasing HEUR concentration. Changes in the sizes of the PTFE particles are observed in the higher concentration over the cmc of HEUR. The size difference does not cause aggregation of the PTFE particles, since the range of the size is less than the aggregates of PTFE latex. This indicates that added HEUR interacts with PTFE latex and increases the size of the scattering species, possibly PTFE latex with absorbed HEUR, which is getting larger with increasing HEUR concentration. In $C_{HEUR} < 14$ mg/mL, the radius of gyration of PTFE particles increases gradually, but in $C_{HEUR} > 14$ mg/mL, the radius of gyration of particles dramatically increases. Because hydrodynamic diameter of HEUR micelle is about 12 nm, we could conclude that the gradual size increasing in $C_{HEUR} < 14$ mg/mL is not due to micellar adsorption. The dramatic size increasing in $C_{HEUR} > 14$ mg/mL could be the micellar adsorption. Supplements for these static data are provided by dynamic experiments in next section.

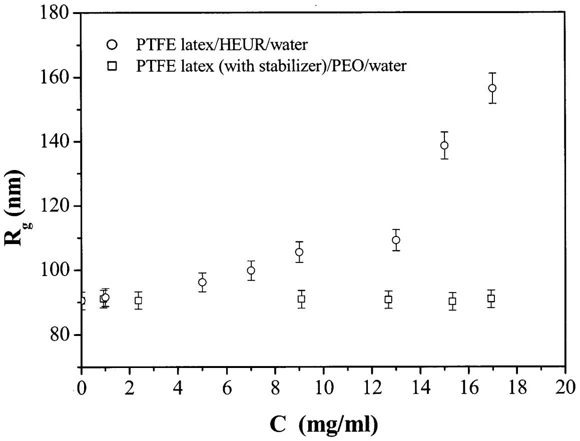

Figure 5. Radius of gyration for the PTFE particle in HEUR and PEO solution deduced from the slow mode of the Guinier plot.

Dynamics of PTFE Latex (with Stabilizer)/PEO/Water Solution. To characterize the diffusion of PTFE latex in a polymer solution, the concentration dependence of the diffusion coefficients was fitted with the stretched exponential form, $D = D_0 \exp(-\alpha c^{\nu})$, which describes diffusion of probe as the polymer matrix concentration increases.[34-39] In the stretched exponential form, D is the diffusion coefficient of the probe

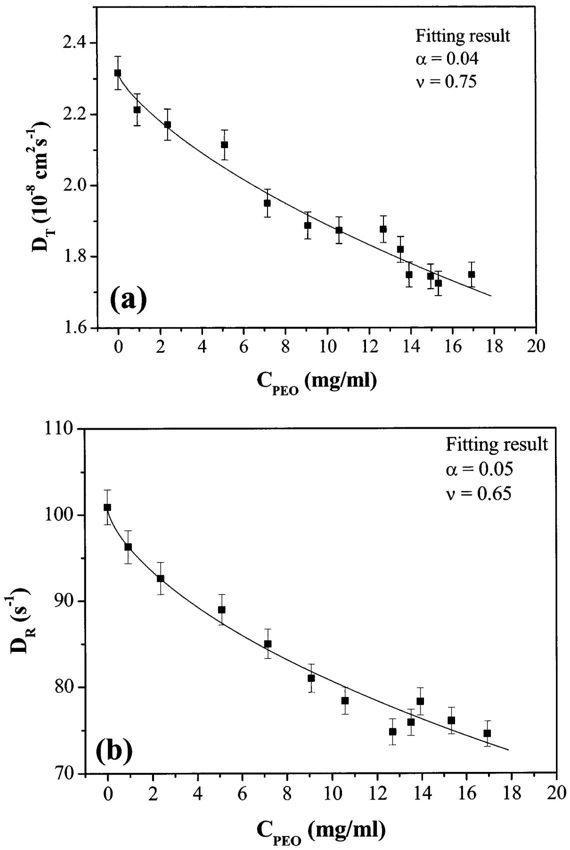

Figure 6. (a) Concentration dependence of translational diffusion coefficient and (b) rotational diffusion coefficient as a function of concentration of PEO in PTFE latex (with stabilizer)/PEO/water quaternary solutions. The solid lines represent fitting results with stretched exponential form.

particle in polymer solution, D_0 is the diffusion coefficient of the probe particles in solvent, c is the concentration of polymer, α and ν are scaling parameters.

Figure 6a shows the concentration dependence of D_T of PTFE latex in PTFE latex (with stabilizer)/PEO/water quaternary solutions. The solid line in Figure 6a shows a fit to the stretched exponential form using means of nonlinear least-squares fitting method; the corresponding α and ν values are 0.04 and 0.75, respectively. Many studies suggest that the c^ν dependence with $0.5 \leq \nu \leq 1.0$ is more appropriate in suspensions of more flexible or shorter length chains. Phillies et al. reported the diffusion properties of polystyrene latex spheres in poly(ethylene oxide)/water solutions.[38] In the presence of stabilizer (Triton X-100), α and ν ranges of polystyrene latex spheres with various sizes/PEO ($M_w = 7500$)/water were $0.035 \leq \alpha \leq 0.052$ and $0.75 \leq \nu \leq 0.83$, respectively. Our system is similar to their system except for PTFE latex and molecular weight of PEO. Because the interaction between PTFE latex and PEO is prevented by the stabilizer, the hindrance or obstruction effect of PEO causes a reduction in the translational diffusivity of PTFE latex. The obstruction effect has been explained by the common form $D_T = k_bT/f$ (where f is the drag coefficient of the scatterers in the ternary system), which indicates that the polymer hinders the probe motions.[38] The concentration dependence of the rotational diffusion coefficients is shown in Figure 6b. This was also fitted with the stretched exponential form; the corresponding α and ν values are 0.05 and 0.65, respectively. The rotational diffusion of probe in PEO solution has not been reported so far, but it fits well with the stretched exponential form.

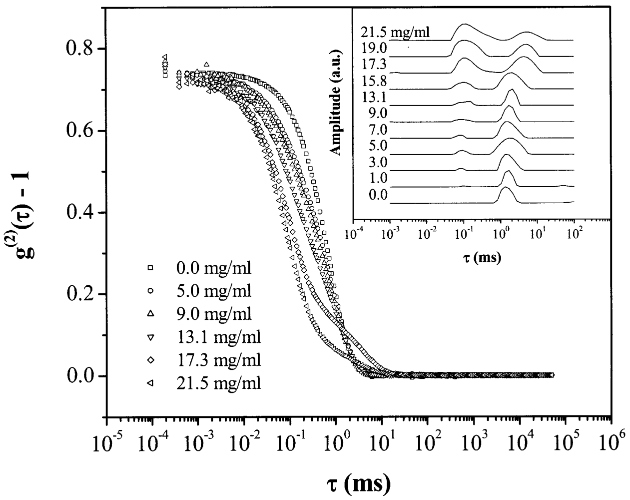

Figure 7. Correlation functions of HEUR/water system with various concentrations. Inset is the relaxation time (τ) distributions of PTFE latex/HEUR/water solutions at a scattering angle of 60°. From bottom to top, HEUR concentrations on inset are 0.0, 1.0, 3.0, 5.0, 7.0, 9.0, 13.1, 15.8, 17.3, 19.0, and 21.5 mg/mL.

Dynamics of PTFE Latex/HEUR/Water Solution. The situation of PTFE latex/HEUR/water solution is different from the PTFE latex (with stabilizer)/PEO/water solution. In this system, the adsorption of HEUR to PTFE latex was expected and the obstruction effect was not observed. Figure 7 shows the intensity correlation functions and the relaxation time distribution functions at various HEUR concentrations at a scattering angle at 60° in Vv geometry.

Two modes are examined, fast mode and slow mode, which are caused by the translational diffusion of HEUR micelles or aggregates and PTFE latex. The slow mode gradually moves to a slower relaxation time range with increasing HEUR concentration. At a HEUR concentration of 17.3 mg/mL, the slow mode has large shift in a slower direction. The amplitude of the fast mode grows with increasing HEUR concentration. Above 15.8 mg/mL HEUR, peaks of fast mode become broader and shift to a slower relaxation time range. This indicates bridging by HEUR unimers between HEUR micelles.

Figure 8 shows the HEUR concentration dependence of the translational diffusion coefficients of scatterers in Vv geometry. It seems to be ambiguous to fit with the stretched exponential form. At low HEUR concentration, however, the stretched exponential form could be fitted to the experimental data very well. The solid line of Figure 8 shows a fit with the stretched exponential form; α and ν values were 0.05 and 0.40, respectively. Brown and Rymden suggested that the value of ν in stretched exponential form is highly sensitive to the interactions between the polystyrene latex and polymer.[39] They studied the bridging interactions in polystyrene/(hydroxyalkyl)cellulose/water solutions and found that the diffusion of polystyrene yielded a ν value of approximately 0.3. As mentioned above, when interactions do not exist, a ν value is larger than 0.5. A larger ν value means a significant depression in the translational diffusion coefficients. This fact indicates that interaction in ternary solution yields a steeper depression than the case of an obstruction effect. The ν value, 0.4, of PTFE latex/HEUR/water solutions is much

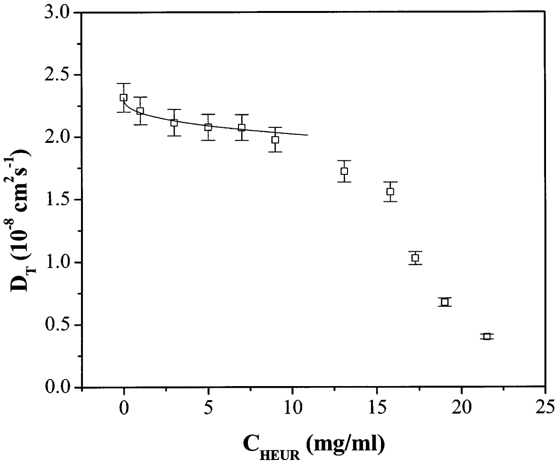

Figure 8. Translational diffusion coefficient as a function of concentration of HEUR in PTFE latex/HEUR/water solutions. The solid lines represent fitting results with stretched exponential form.

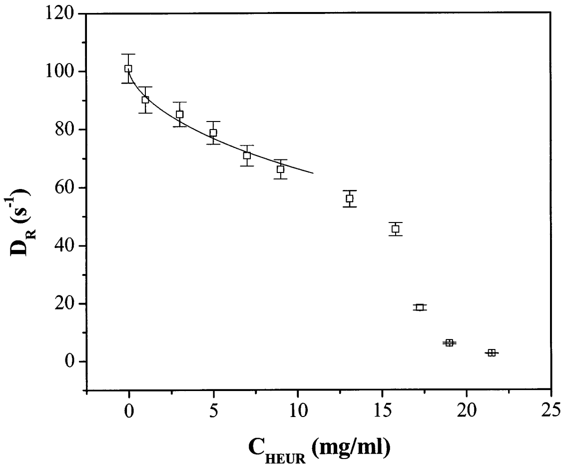

Figure 9. Rotational diffusion coefficient as a function of concentration of HEUR in PTFE latex/HEUR/water solutions. The solid lines represent fitting results with stretched exponential form.

smaller than the ν value of PTFE latex (with stabilizer)/PEO/water solutions, 0.75. Therefore, the steeper depression of diffusion coefficient is due to an interaction between HEUR and PTFE latex; it is not due to an obstruction effect of HEUR.

Figure 9 shows the HEUR concentration dependence of the rotational diffusion coefficients of scatterers in Hv geometry. For a fit at the low concentration region with the stretched exponential form, α and ν values were 0.05 and 0.40, respectively. Fitting parameter α and ν values were 0.10 and 0.62, respectively. The ν value does not largely differ from a ν value of PTFE latex (with stabilizer)/PEO/water solutions, 0.65. A ν value from the rotational diffusion coefficients cannot provide evidence for adsorption or the obstruction mechanism. Above a concentration of 7 mg/mL HEUR, the stretched exponential form could not be applied appropriately, so we tried to come up with another interpretation.

Primary and Secondary Adsorption of HEUR. Cush et al. conducted a rotational and translational diffusion study of rodlike particles, TMV, in dextran aqueous solutions.[40] They found out that the quotient D_R/D_T of TMV decreased suddenly above a definite concentration of dextran aqueous solution. It was thought that the quotient D_R/D_T of TMV canceled due to macroscopic viscosity. The sudden decrease was interpreted as the onset of topological constraints to rotational motion of the TMV. We applied this idea to our two systems, PTFE latex (with stabilizer)/PEO/water quaternary solutions and PTFE latex/HEUR/water ternary solutions. The ln(D_R/D_T) data of two systems are plotted in Figure 10.

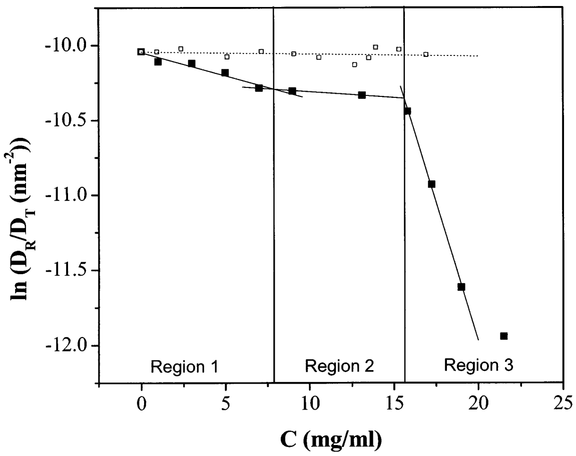

Figure 10. Semilog plot of the quotient D_R/D_T in PTFE latex/HEUR/water (closed square, solid line) and PTFE latex (with stabilizer)/PEO/water (open square, dotted line) as a function of concentration of HEUR and PEO. The solid lines and the dotted line represent results of linear least-squares fitting.

The D_R/D_T of PTFE PTFE latex (with stabilizer)/PEO/water quaternary solution (open square, dotted line) does not change as the concentration of PEO was increased. The dotted line in Figure 10 shows a fit with the linear least-squares fitting. The value of the slope is approximately zero. As mentioned in previous sections, there are no interactions between polymer and PTFE latex and between polymer and polymer in this system. Consequently, the absence interaction in the system results in no change in D_R/D_T. In the case of the PTFE latex/HEUR/water ternary solutions, however, a trend of D_R/D_T significantly differs from it of the PTFE latex (with stabilizer)/PEO/water system. D_R/D_T decreases gradually below approximately 8.0 mg/mL HEUR. In the concentration range of 8.0−15.6 mg/mL, D_R/D_T is nearly paralleled with the case of PTFE latex (with stabilizer)/PEO/water quaternary solutions. D_R/D_T decreases dramatically above 15.6 mg/mL HEUR. This decrease in D_R/D_T indicates that the depression rate of the rotational diffusion coefficients is faster than the depression rate of the translational diffusion coefficients. In other words, a degree of constraint in rotational diffusion is greater than the degree of constraint in translational diffusion. A possible explanation for the decrease of D_R/D_T when there is no interaction between the probe and polymer is that the overlapping of polymer matrix physically traps the probe.[40] Another possible explanation is that interactions between probe and polymer discourage the probe from its rotational diffusion. The solid lines in Figure 10 are fitting result with the linear least-squares fitting. The concentration range can be divided into three regions; two transition points, 8.0 and 15.6 mg/mL, were obtained. The values of three slopes were -3.10×10^{-2}, -7.94×10^{-3}, and -3.67×10^{-1}. The slope in this graph represents the magnitude of constrain to rotational diffusion of the particles. In the previous sections, we verified strong interactions between PTFE latex and HEUR with the

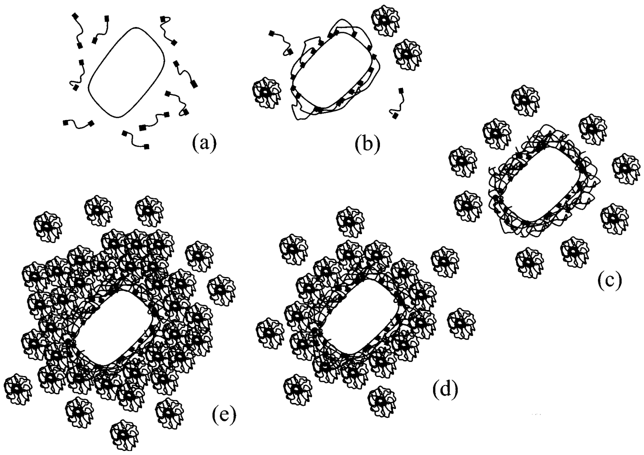

Figure 11. Schematic representation for primary and secondary adsorption mechanism of HEUR to PTFE latex as HEUR concentration raises.

stretched exponential form at low HEUR concentrations. In the Guinier plot, size increasing of scatterers was examined all over the concentration range. In region 1, some HEUR unimers are absorbed onto the surface of PTFE latex. While HEUR absorbed PTFE latex particles diffuse in HEUR solution, unabsorbed HEUR unimers strongly interact with them. In region 2, aggregation of HEUR unimers forms HEUR micelles. The quotient D_R/D_T is nearly maintained on a parallel level with it of PTFE latex (with stabilizer)/PEO/water solution. This indicates the interactions between HEUR absorbed PTFE latex and HEUR or HEUR micelles are weak, since the reduction of translational and rotational diffusion is mainly due to the obstruction by HEUR micelles. In region 3, the degree of D_R/D_T dropping is much larger than for regions 1 and 2. In the previous Guinier plot, the sizes of the scatterers significantly increase. Therefore, a dramatic falling of D_R/D_T is caused by the adsorption of HEUR micelles. To reflect these results, a difference between values of the slopes of region 1 and 3 might be caused by a factor concerned with size of interacting species, HEUR unimers or HEUR micelles, with PTFE latex.

Figure 11 shows the schematic representation of an adsorption property of HEUR to PTFE latex. In low HEUR concentration, $C_{\mathrm{HEUR}} < 8$ mg/mL, the primary adsorption of HEUR unimers occurs, where the obstruction is caused by the HEUR in solution (Figure 11a,b). In 8 mg/mL $< C_{\mathrm{HEUR}} <$ 15.6 mg/mL, HEUR micelles are formed by associating of HEUR unimers. HEUR micelles prevent translational and rotational diffusion of the particles, and the adsorption of HEUR is a minor effect in this region (Figure 11c). When C_{HEUR} exceeds 15.6 mg/mL, HEUR micelles are associated with HEUR absorbed PTFE latex by HEUR unimers and micelles (Figure 11d,e). This adsorption is the secondary micellar adsorption.

Conclusion

The adsorption process of HEUR onto optically anisotropic colloidal probes, PTFE latex, was revealed by a comparative study of a probe−polymer interaction system and probe−polymer noninteraction system. Static light scattering experiments of PTFE latex/HEUR/water (probe−polymer interaction system) showed the increase of size of probe particles by increasing concentration of HEUR. Depolarized light scattering technique which may be a valuable supplement to static and dynamic light scattering was conducted to verify the interaction between the particles and polymers. The quotient D_R/D_T plot was examined in the probe−polymer interaction system. In the probe−polymer noninteraction system, a decrease in D_R/D_T was not observed, but in the probe−polymer interaction system, a dramatic change of D_R/D_T was observed. Two drops of D_R/D_T occurred when $C_{\mathrm{HEUR}} < 8.0$ mg/mL and $C_{\mathrm{HEUR}} > 15.6$ mg/mL. This indicates that two adsorption processes occur separately; the primary adsorption is the adsorption HEUR onto PTFE latex, and the secondary adsorption is the adsorption of HEUR micelle onto PTFE latex cooperatively. When the particles are in between these regions, PTFE particles are saturated by the HEUR micelles. The depolarized light scattering experiment becomes a strong tool for studying the interaction between the optically anisotropic particles and the associating polymers.

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