Rheology and Aggregation Behavior of Hydrophobically Modified Urethane Ethoxylate in Ethylene Glycol−Water Mixtures

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Received October 9, 2002; Revised Manuscript Received May 26, 2003

ABSTRACT: The association behaviors of hydrophobically modified urethane ethoxylate polymer (HEUR) in ethylene glycol−water mixtures were studied by laser light scattering and rheological techniques. The ratio, R_g/R_h decreases from 1.5 to 1.1 when ethylene glycol (EG) concentration increases from 0 to 20 wt %. It then increases to ∼1.3 at EG of 30 wt % and decreases to 0.8 at EG of 70 wt %. When the molar ratio of ethylene glycol to water exceeds 1, HEUR precipitates from the solvent mixture. Addition of ethylene glycol to water produces a poor and less polar solvent mixture for HEUR, which decreases the aggregation number of the micellar core. It also lowers the solvation of HEUR chains, giving rise to a more compact chain conformation. The contribution of these two factors is responsible for the transformation of a flower to a starlike micelle. Shear-thickening behavior was observed for HEUR in water and in ethylene glycol−water mixtures, but the magnitude of the shear-thickening is reduced for solvent mixtures with higher ethylene glycol contents. The viscosities, relaxation times, and the number of mechanically active junctions decrease with increasing temperatures and ethylene glycol concentrations.

Introduction

The association behaviors of amphiphilic polymers have attracted much interest in the past decades due to its wide industrial application and theoretical importance.[1] These polymers contain both hydrophobic and hydrophilic groups. In aqueous media, aggregates or micelles are formed through hydrophobic interaction, which is dictated by the chemical composition and structure of the polymeric system.

Hydrophobically modified urethane ethoxylate (HEUR) is one type of associative polymers widely used as viscosity modifiers in paint formulations, paper coatings, cosmetics, building products, electroplating, lubrication, and textiles industries.[2] HEUR contains a hydrophilic backbone consisting of urethane linked poly(ethylene oxide) (PEO) with both ends capped with the hydrophobically modified alkyl chains. Significant literature and reviews on the association behaviors of HEUR in aqueous media have been reported.[1,3−14] In dilute solution, flowerlike micelles are formed at concentration greater than the critical micelle concentration (cmc) for HEUR polymer with MW > 20 000 Da and hydrophobic groups larger than $C_{12}H_{25}$ alkyl chain. Using fluorescence quenching, static and dynamic laser light scattering techniques, flowerlike micellar aggregates of HEUR with $C_{16}H_{33}$ hydrophobes were found to contain ∼10−11 polymer chains. In semidilute solution, individual HEUR micelles are connected through bridging chains to form a temporary network structure that imparts large viscosity increase to the polymer solution.[15] Under moderate strain or stress deformation, some looping chains are converted to bridging chains, resulting in shear thickening as observed by the viscosity increase in the viscosity profile.[5]

Ethylene glycol (EG) is an environmental friendly nonaqueous polar solvent, which is widely used in many applications such as in personal home care and biomedical products. It has many characteristics similar to water and the hydroxyl groups can form a hydrogen bond with water. In addition, it also possesses a high cohesive energy and high dielectric constant.[16] Addition of EG into water decreases the polarity of the mixed solvent. Such solvent mixtures will have a significant impact on the micellization or aggregation behavior of amphiphilic molecules. Until recently, some studies on the behavior of ionic surfactants in EG−water mixtures have been reported, but relatively few studies have been performed on nonionic surfactants in EG−water mixtures.[17−22] It was reported that the cmc shifts to a higher value when EG was added into nonionic surfactant solutions, while the aggregation number and the size of the micelles decreased. The micellization of nonionic surfactant in the EG−water mixtures is controlled by the structure breaking ability of EG and the interaction of the cosolvent with the surfactant headgroups. Alexandridis et al. reported several studies on the behavior of Pluronic PEO−PPO−PEO block copolymers in mixtures of water and glycols.[23−26] The micelle radii and dimension of hydrophobic core, micelle aggregation numbers and polymer volume fractions in the micelle core and corona decreased with increasing cosolvent−water ratio in mixed solvents containing ethanol. However, addition of glycerol led to a higher aggregation number and higher volume fraction in the micelle corona. On the basis of the glycol relative polarity, a hypothesis on the phase behavior was proposed. When the solvent mixtures were changed from a polar to a nonpolar character, the microstructure of the phases transformed from cubic to hexagonal structure, followed by a bicontinuous and eventually lamellar structure.

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10.1021/ma025728+ CCC: $25.00
Published on Web 07/09/2003

Table 1. Summary of (a) Physical Properties of EG−Water Mixtures, (b) Molecular Properties of Dilute HEUR22 in EG−Water Mixtures, and (c) Macroscopic Rheological Properties of HEUR22 in EG−Water Mixtures

	EG content (wt %)								
properties	0	5	10	20	30	40	50	60	70
(a) Physical Properties of the Mixed Solvents									
η(solvents) (mPa s)	0.89	1.13	1.24	1.56	2.10	2.35	3.18	4.10	5.71
n_D^{25}	1.333	1.337	1.342	1.352	1.362	1.372	1.382	1.392	1.418
(b) Molecular Properties of Dilute HEUR22 in Mixed Solvents									
dn/dC (mL/g)	0.149	0.140	0.140	0.141	0.111	0.105	0.068	0.070	0.068
M_w ($\times 10^{-6}$ g/mol)	1.41	1.68	1.23	1.20	0.81	1.46	2.37[a]	1.60[a]	1.36[a]
A_2 (10^{-5} mL mol/g^2)	1.99	3.19	3.54	4.79	−5.78	6.58	6.61	6.04	−4.76
R_g (nm)	53	52	53	56	55	85	107	116	109
D_0 (10^{-12} m^2/s)	7.11	5.21	3.94	2.69	2.51	1.29	0.741	0.515	0.285
k_D (10^{-12} m^2 L/g s)	−7.79	−2.37	−1.37	−0.591	−0.783	−0.256	−0.119	−0.0108	−0.0154
R_h (nm)	35	38	45	52	41	72	93	103	134
R_g/R_h	1.51	1.37	1.18	1.08	1.34	1.18	1.15	1.13	0.81
cmc (mg/mL)	0.20	0.20	0.30	0.40	0.50	0.50	0.50	0.48	0.45
(c) Macroscopic Rheological Properties of Semidilute HEUR 22 in Mixed Solvents									
η_o (Pa s)	29.99	39.19	35.24	19.56	7.50	2.11	0.76	0.35	0.09
E_a (kJ/mol)	71.6	76.1	77.9	82.7	82.1	81.6	70.4	62.8	41.3
λ (s)	0.229	0.214	0.181	0.108	0.053	0.018	0.019	0.020	0.021
G_N^o (Pa)	131	183	195	180	141	95	40	18	5
ν_{eff} (mol/m^3)	0.056	0.078	0.083	0.077	0.060	0.040	0.017	0.008	0.002

[a] Only apparent MW, as unimers co-exit with aggregates.

For amphiphilic HEUR polymer, water is a good solvent for PEO due to the hydrogen bonding but a poor solvent for the end-capped alkyl chains. At concentration exceeding the cmc, flowerlike micelles are formed in aqueous solution. Since the PEO segment of the HEUR chain has a chemical composition similar to that of EG, addition of EG into water produces a less polar solvent environment, which alters the micellization or the aggregation behavior of HEUR chains. Although the micellar structure of HEUR in aqueous solution is well documented, no studies on the aggregation behavior of HEUR in EG−water mixtures have been reported. In this paper, the microscopic and macroscopic properties of HEUR in EG−water mixtures were studied using light scattering and rheological techniques, respectively. The former provides microscopic information on the conformation of HEUR chains and the aggregated structure, which can then be used to explain the observed macroscopic viscoelastic properties of HEUR solution in mixed solvent systems.

Experimental Section

Materials. The HEUR designated as HEUR22 was synthesized by Dow Chemicals (former Union Carbide) by condensation polymerization. It has a urethane-coupled poly(ethylene oxide) backbone and both ends are capped with hydrophobic $C_{16}H_{33}$ alkyl chain. The GPC results revealed that it has a M_n of 50 000 Da and M_w/M_n of 1.56. The ethylene glycol (EG) was purchased from Merck and the deionized water was from the Millipore Alpha-Q water purification system. The mixed solvents were first prepared according to the weight percentage of EG in water, and the 2 wt % HEUR22 solutions were prepared by dissolving HEUR in premixed solvent mixtures. The solutions were stirred and equilibrated for 24 h before rheological measurements were performed. Solutions for light scattering measurements were diluted from the 2 wt % stock solutions and kept in the dark for at least 24 h prior to the measurements. It was found that HEUR22 is not soluble in water-EG mixtures when the EG concentration exceeds 80 wt %.

Rheology. A Carri-Med CSL 500 rheometer, fitted with a 40 mm cone of 2° cone angle was used to measure the rheological properties of HEUR22 solutions. For the viscosity of EG−water solvent mixtures, a Contraves LS40 rheometer equipped with a cup of 11 mm and a bob of 8 mm was used. The temperature was controlled within ±0.1 °C using a Julabo water bath. The refractive indexes were measured using an Atago-3T Abbe refractometer. Both the refractive indexes and viscosities of EG−water solvent mixtures increase with EG concentration as shown in Table 1.

Laser Light Scattering. Static and dynamic light scattering were carried out using a Brookhaven laser light-scattering system. The equipment consists of a power adjustable 488 nm argon ion laser and a BI9000AT digital correlator. For static light scattering, the measurement angles were varied from 30 to 120° at intervals of 15°, and a Zimm plot was used to analyze the static light scattering data. The refractive index increment dn/dC was measured with a Brookhaven BI-DNDC differential refractometer. For dynamic light scattering, the inverse Laplace transformation routine (REPES) supplied with the Gendist software package was used to analyze the time correlation function (TCF), and the probability of reject was set at 0.5.

Results and Discussion

Dilute Solution. Static light scattering (SLS) provides information on time-averaged properties of the system. eq 1 depicts the basic relationship for analyzing the static light scattering data,[27]

$$\frac{K(C - \mathrm{cmc})}{R_\theta} = \frac{1}{M_w}\left(1 + \frac{q^2 R_g^2}{3}\right) + 2A_2(C - \mathrm{cmc}) \quad (1)$$

where K ($= 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}C)^2/N_A\lambda^4$) is an optical constant with N_A, n, and λ being the Avogadro's number, the solvent refractive index, and the wavelength of the incident light in vacuum, respectively. C is the polymer concentration in g/mL and R_θ is the excess Rayleigh ratio at scattering angle θ . The scattering vector **q** is defined as the wave vector difference between the incident and scattering beams with the value of $q = 4\pi n \sin(\theta/2)/\lambda$. The refractive index increments, (dn/dC) measured using a differential refractometer are summarized in Table 1. It is evident that the refractive indices, n, increase but the refractive index increment (dn/dC) exhibits a sharp decrease at EG content of 20−30 wt % where its magnitude decreases from 0.140 to 0.111 mL/g). Figure 1 shows a typical Zimm plot of HEUR22 in a solvent mixture containing 10 wt % EG. From the Zimm plot, the weight-averaged molecular weight (M_w),

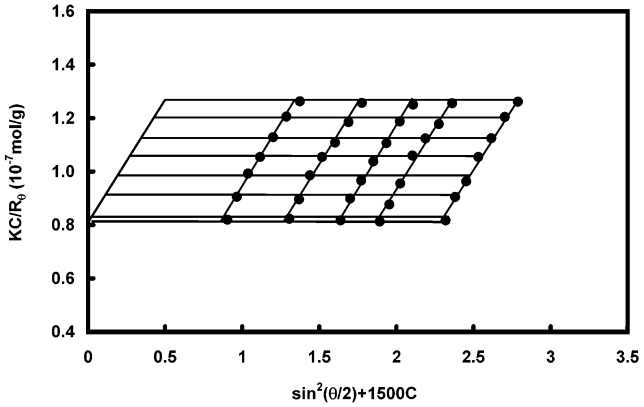

Figure 1. Typical Zimm plot for HEUR22 in 10 wt % EG−water mixtures.

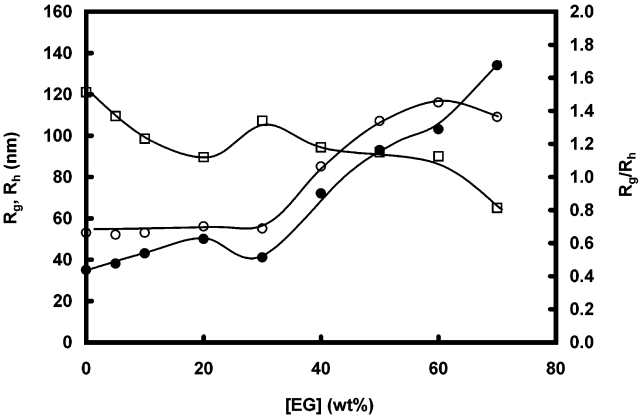

Figure 2. EG concentration dependence of R_g (○), R_h (●), and R_g/R_h (□) for 0.1 wt % HEUR22 in EG−water mixtures at 298 K.

the *z*-averaged radius of gyration (R_g), and the second virial coefficient were determined. The numerical values are summarized in Table 1, and the dependence of R_g on the EG content of the mixed solvent is shown in Figure 2. It is evident that R_g possesses a constant value of ∼53 ± 2 nm until a EG concentration of 30 wt % and it then increases to ∼112 ± 4 nm at 70 wt % EG.

Dynamic light scattering (DLS) measures the instantaneous fluctuations of the scattered light produced by Brownian dynamics of polymer molecules.[28,29] For dilute polymer solutions, the hydrodynamic radius, R_h could be determined from DLS measurements. The angular dependence of decay times for different concentrations of HEUR22 in EG−water solvent mixtures was examined. The inverse Laplace transform (ILT) of REPES was used to analyze the time correlation function to yield the decay time distribution functions. At EG concentration lower than 40 wt %, only one peak was observed in the decay time distribution functions for scattering angles ranging from 45 to 120°, where the decay time decreases with increasing scattering angles. However, when EG concentration exceeds 40 wt %, two decay modes were observed. Figure 3 shows that the decay time distribution functions of 0.1 wt % HEUR22 in different proportions of EG−water mixtures. The decay times shift to larger values with increasing amounts of EG. However, increasing the proportion of EG also results in a corresponding increase in the viscosity of the solvent mixtures as shown in Table 1.

The linear relationship of the decay rates (i.e., the inverse of the decay times), and q^2 indicates that all the

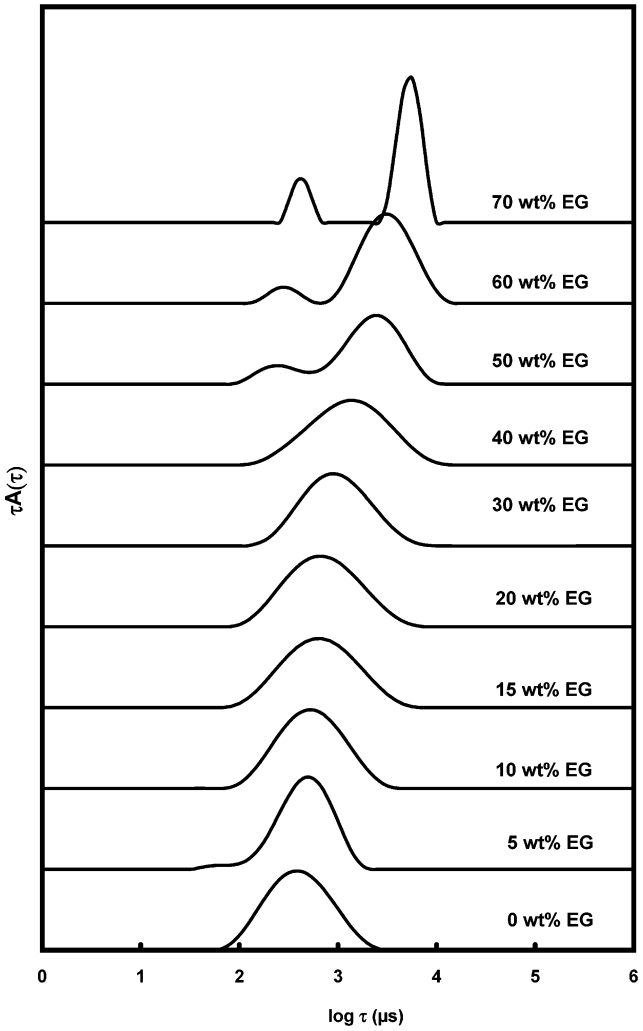

Figure 3. Decay time distribution functions measured at a scattering angle of 90° for 0.1 wt % HEUR22 in the EG−water mixtures at 298 K.

decay modes are attributed to the translational diffusion, and the slope corresponds to the diffusion coefficients. The polymer concentration dependence of the diffusion coefficients was examined and found to decrease linearly with polymer concentrations (Figure 4). On the basis of the relationship

$$D = D_0(1 + k_D C + ...) \tag{2}$$

the diffusion coefficient at infinite dilution D_0 and diffusion second virial coefficient k_D were determined. The values of D_0 and k_D are listed in Table 1. It is interesting that k_D becomes less negative as the percentage of EG is increased, which corresponds to the reduction in the interactions between solvent and polymer.

From the Stokes−Einstein equation (eq 3)

$$R_h = \frac{k_B T}{6\pi\eta D_0} \tag{3}$$

the hydrodynamic radius, R_h was determined. In the equation, k_B is the Boltzmann constant, T the absolute temperature, and η the solvent viscosity. The calculated R_h values are summarized in Table 1 and plotted against EG concentrations as shown in Figure 2. Initially, R_h increases gradually to ∼50 nm at 20 wt %

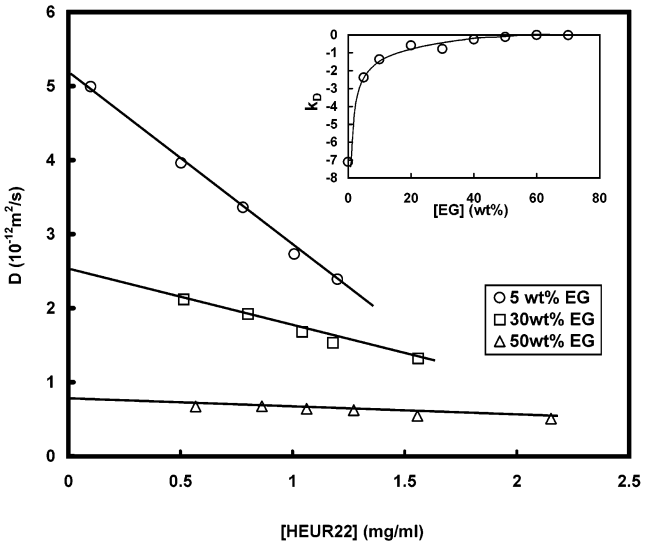

Figure 4. Concentration dependence of the diffusion coefficients for HEUR22 in EG−water mixtures. The insert reveals the relationship between k_D and EG concentrations.

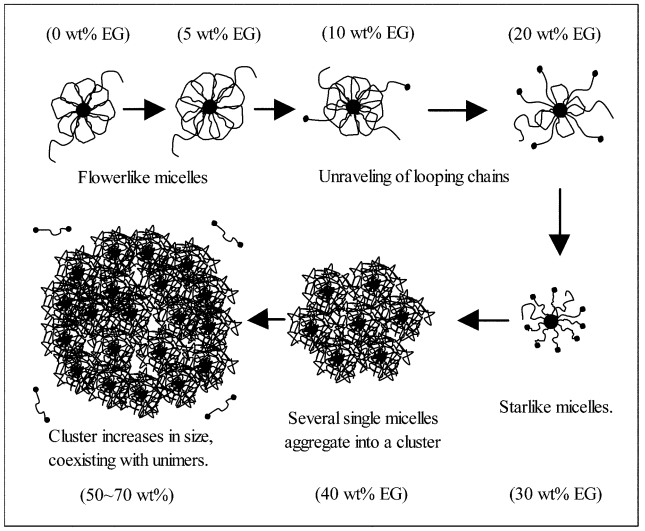

Figure 5. Proposed microstructure of dilute HEUR22 in varying amounts of EG−water mixtures.

EG and then decreases to 41 nm at 30 wt % EG, and it increases sharply to ∼110 nm at 70 wt % EG.

The ratio, R_g/R_h can be used to examine the polymer chain conformation and its compactness,[28,30] where R_g/R_h values at various EG contents are summarized in Table 1. The ratio, R_g/R_h decreases from 1.5 to 1.1 when EG concentration increases from 0 to 20 wt %. It then increases to ∼1.3 at EG of 30 wt % and finally decreases to 0.8 at EG of 70 wt %. At high EG content, the solvent mixtures become poorer and the HEUR chains become more compact as reflected by R_g/R_h of 0.8.

Combining the SLS and DLS data, the effect of EG on the conformation of the aggregate could be evaluated. Dilute HEUR polymers with M_n of 50 000 Da containing $C_{16}H_{33}$ end groups assemble via the closed association mechanism to form flowerlike micelles. The micelle consists of a hydrophobic $C_{16}H_{33}$ core and a corona of ∼8 looping PEO chains and 1−2 linear PEO chains (Figure 5 for 0 wt % EG).[31,32] Addition of small amounts of EG (5 wt %) disrupts the hydrogen bonds between water and PEO segments. This reduces the hydrophilicity of PEO segments, making the HEUR chains more hydrophobic, which marginally increases the aggregation number of the micellar core (from ∼18 to 21 hydrophobes) as calculated from the molecular weight (see Table 1). When the EG concentration is increased to 30 wt %, the molecular weight of the flower micelles decreases, indicating that the number of polymer chains in the micelles has decreased slightly. No unimer was observed; hence, the reduction in the aggregation number gives rise to a larger number of micelles of slightly smaller size. The presence of larger proportion of EG leads to the dehydration of the PEO chain segments, which yields a more compact chain conformation. The combination of these two effects (decreasing number of HEUR chains and a more compact PEO chain conformation) should result in a gradual decrease in R_g and R_h values.[16] However, our experimental results indicate a different trend, where R_g remains essentially unchanged while R_h increases slightly from 35 to 52 nm when EG content is increased from 0 to 20 wt %. We conjecture that the increase in the R_h is attributed to the gradual unraveling of looping PEO chains to produce a mixture of looping and dangling PEO chains, whose hydrophobes are now exposed to a less polar solvent mixture. The presence of increasing number of dangling chains produces the trend observed for R_h and R_g as shown in Figure 2. As more dangling chains are produced, the flowerlike micelles are then transformed into starlike micelles as shown in Figure 5 (EG ∼ 30 wt %). The constant R_g and small reduction in the R_h when EG content is increased from 20 to 30 wt % is indicative of the shrinkage of PEO chains due to the poorer polymer/solvent interaction and the increasing proportion of "unassociated hydrophobes". This behavior is confirmed by the negative second virial coefficient (A_2) at 30 wt % EG content.

The cmc values (Table 1) for the HEUR micelles in different EG/water mixtures were determined based on the polymer concentration dependence of the scattering intensity. It is evident that the cmc values increase from 0.2 to 0.5 mg/mL as the EG content is increased from 0 to 30 wt %, which is identical to that observed for nonionic surfactant in less polar solvents.[16] When larger aggregates are produced at EG of 40 wt % and beyond, the cmc becomes independent of the solvent mixture. Further increase in EG content makes the solvent quality poorer, which induces several micelles to agglomerate (slow decay mode), producing complexes that minimize the contact surface area between the micelles and solvent mixture. Both R_g and R_h of the slow mode increase and the A_2 values become positive again. At the same time, HEUR unimers with an averaged hydrodynamic radius of 10 nm were detected by laser light scattering (the fast decay mode), and the peak area increases with the EG concentrations. At EG content exceeding 50 wt %, larger proportion of unimers are present; hence, the molecular weights are the apparent weight-averaged molecular weights of HEUR unimers and the agglomerate, which give rise to a lower M_w. The increase in the MW from 0.81×10^5 to 2.37×10^6 as EG content increases from 30 to 50 wt % corresponds to the progressive increase in the number of chains in the aggregate. At EG concentration of 70 wt %, the poorer solvent quality gives rise to a negative A_2, and R_g/R_h exhibits a value of 0.8, which is close to the value of a hard sphere. However, at EG concentration exceeding 78 wt % EG, the HEUR polymer becomes insoluble.

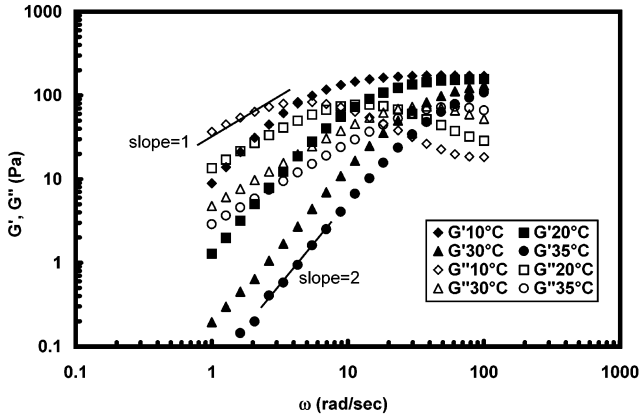

Figure 6. Angular frequency dependence of storage modulus G' and loss modulus G'' for 2 wt % HEUR22 in 5 wt % EG−water mixtures at different temperatures.

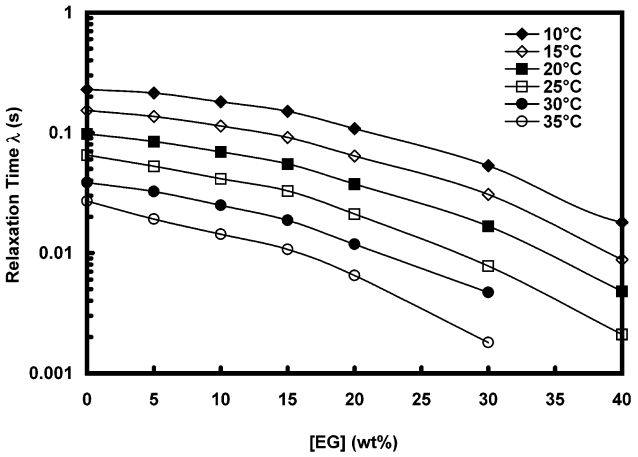

Figure 7. Relationship of the Maxwell relaxation times, λ, and EG concentrations for 2 wt % HEUR22 in EG−water mixtures at different temperatures.

Water and EG act as hydrogen donors by forming hydrogen bonds. However, all three constituents, i.e., water, EG, and PEO, are possible hydrogen acceptors. Although EG and PEO have similar structure, EG has a greater capacity to form hydrogen bonds. Thus, the presence of EG decreases the amounts of hydrogen bonds between water and ether groups of PEO chains, which reduces the solubility of PEO chains in water/EG mixtures. In addition, EG also decreases the polarity of the solvent mixtures, which lowers the hydrophobicity of the $C_{16}H_{33}$ alkyl chains. The decrease in the aggregation number of the micelle has been observed for nonionic surfactants.[16,17,22] On the basis of the molecular information determined from static and dynamic light scattering measurements, we proposed a likely microstructure and the accompanying association mechanism of HEUR in different proportion of water/EG content as shown schematically in Figure 5.

Semidilute Solution. From the hypothesis presented above on the effects of EG content on the microstructure of HEUR micellar aggregates, we will examine the viscoelastic properties of semidilute HEUR solutions in EG−water mixtures.

Figure 6 shows the angular frequency dependence of the moduli of 2 wt % HEUR22 in 5 wt % EG−water mixtures at different temperatures. It is clear that G' and G'' can be adequately described by the single mode Maxwell model. Both G' and G'' values decrease with increasing temperatures. The crossover angular frequency, ω_o is related to the inverse of network relaxation time, λ. From the figure, the crossover frequency ω_o increases or the relaxation time, λ decreases with increasing temperatures. The relaxation times could also be determined from the second-order region described by eq 4,

$$\lambda = \lim_{\omega \to 0}\left(\frac{G'}{\omega^2 \eta'}\right) \tag{4}$$

where G' is the storage modulus, ω the angular frequency and η' the dynamic viscosity with a value of (G''/ω). The relaxation times determined from the inverse of the crossover frequency and eq 4 are identical. The network relaxation time represents the time taken by the polymer network to reach an equilibrium state after deformation. Annable et al. identified the Maxwell relaxation time with the exit rate of the hydrophobe from the micellar junction.[4] The higher the exit rate, the lower the relaxation time. At high temperature, the increased thermal motion of HEUR polymer chains causes the exit rate of the hydrophobe to increase. Annable et al. and Tam et al. have observed that the relaxation times decreased as the temperature increased for the HEUR polymer in aqueous system.[4,5]

The relaxation time λ was plotted against EG concentration at various temperatures as shown in Figure 7. The relaxation time decreases with increasing EG concentrations. The addition of EG into HEUR polymer solution resulted in the decrease in the solvent polarity, which lowers the hydrophobicity of the alkyl chains in the mixed solvents. This enhances the exit rate, which leads to a reduction in the network relaxation time.

The plateau modulus, G_N^o for the HEUR polymer system is approximately related to G' at high angular frequency. G_N^o increases with applied stress, and reaches a maximum at the viscosity maxima of the shear-thickening region. At higher levels of applied stress, the plateau modulus cannot be accurately determined, because the viscoelastic data deviate from the simple Maxwell-type fluid. However, the magnitude of the plateau modulus could be estimated from the following equation:

$$G_N^{\,0} = \frac{\eta_0}{\lambda} \tag{5}$$

where η_o is zero shear viscosity and λ is relaxation time. The number of mechanically active junction, ν_{eff} can be evaluated from G_N^o values based on eq 6,

$$G_N^{\,0} = \nu_{\text{eff}} RT \tag{6}$$

where R is the gas constant, and T is the absolute temperature in kelvin. The determination of ν_{eff} provides important information on the number of bridging chains connecting the HEUR micelles. The mechanical properties of the polymer solution strongly depend on the value of ν_{eff}. It is observed that G_N^o or ν_{eff} decrease with increasing temperatures. When the temperature increases, bridge to loop transition is enhanced due to the shifts in the HLB values. This is consistent with the reduction in the number of bridging chains (ν_{eff}).

Figure 8 shows that dependence of the plateau modulus, G_N^o and the mechanically active junction number, ν_{eff}, on the EG content. G_N^o and ν_{eff} increase

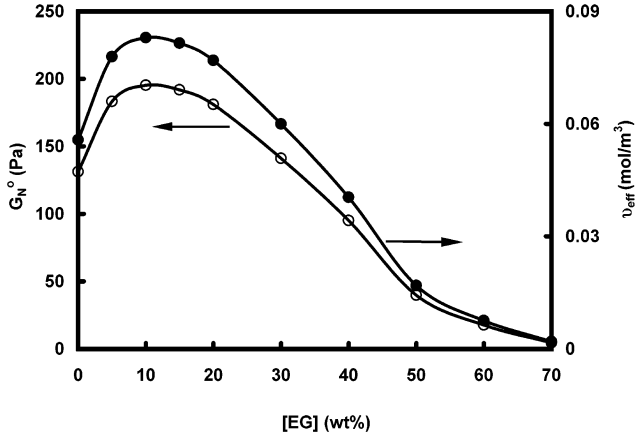

Figure 8. EG concentration dependence of both G_N^o and υ_{eff} for 2 wt % HEUR22.

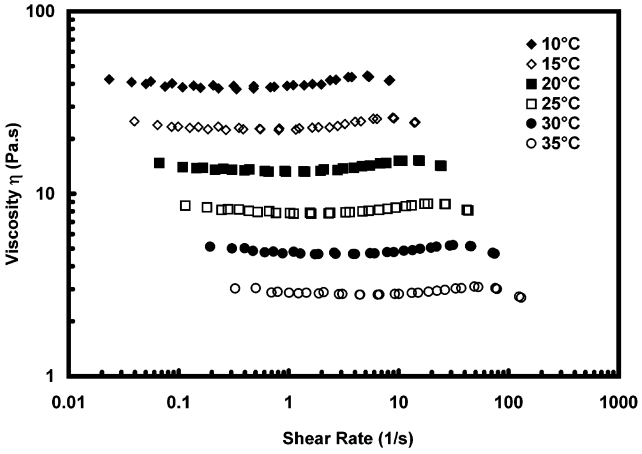

Figure 9. Shear rate dependence of shear viscosity for 2 wt % HEUR22 in the 5 wt % EG−water mixture at different temperatures.

initially and reach a maximum of 200 Pa and 0.083 mol/m^3, respectively, at 10 wt % EG. As the EG content is increased to 70 wt %, they then decrease to ~5 Pa and 0.002 mol/m^3 respectively. The numerical data are summarized in Table 1. At low content of EG (0−5 wt %), the aggregation number increases slightly as indicated from SLS measurements. In semidilute solution, such small increase can be derived from the free unassociated micelles without affecting the number of mechanically active junctions. However, at higher EG content (5−15 wt %), the decrease in the aggregation number will result in the transformation of looping to bridging chains. The loop-to-bridge transformation produces a larger number of mechanically active junctions for EG content up to 10−15 wt %. Further increase of EG content makes the solvent mixtures less polar, which dehydrates the PEO segments and results in the shrinkage of PEO chains. When the EG content exceeds 30 wt %, the hydrophobicity of micellar core would have decreased to a level where the hydrophobes in the micellar core could be readily detached from the core by Brownian motions resulting in the overall reduction in the mechanically active junctions, which progressively becomes smaller as evident from Figure 8.

The shear rate dependence of the viscosity of 2 wt % HEUR22 in 5 wt % EG−water mixture at different temperatures is shown in Figure 9. The solution behaves as a Newtonian fluid at low shear rates, and becomes

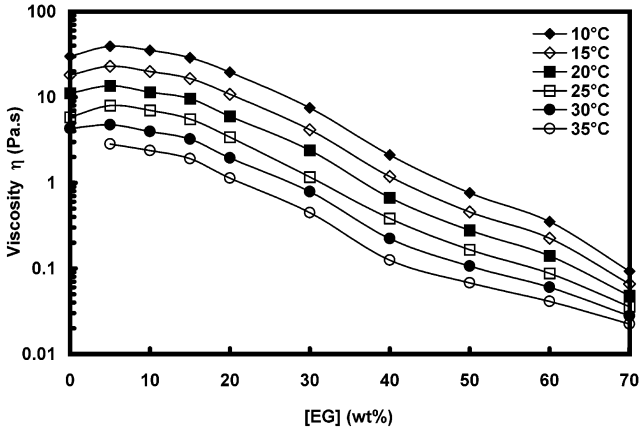

Figure 10. Relationship of the low shear viscosity and the content of the EG for 2 wt % HEUR22 in EG−water mixtures at different temperatures.

shear thickening at moderate shear rates, and then shear-thins at relatively high shear rates. The viscosities decrease with increasing temperatures according to the Arrhenius relationship. Shear-thickening behavior is more evident at low temperatures and it becomes less apparent at higher temperatures. For HEUR in low to moderate amounts of EG, the viscosity profile exhibits similar trends as pure HEUR−water system. Tam et al. commented that the shear thickening is the result of a shear-induced increase in the density of mechanically active chains.[5,8] The reduction in the magnitude of shear thickening corresponds to a reduction in the elasticity. At higher temperature, the proportion of bridging chains decreases due to bridge-to-loop transition, which lowers the magnitude of shear thickening.

The dependence of low shear viscosity on EG concentration for 2 wt % HEUR22 in EG−water mixtures at various temperatures is shown in Figure 10. The viscosity increases slightly with addition of up to 5 wt % EG, but it then decreases with further increase in EG concentration. The viscosity is slightly more temperature sensitive at 5 wt % than at 70 wt % EG, signifying the different magnitude in the activation energy, E_a. The viscosity values and other molecular information are summarized in Table 1.

The viscosity is related to the relaxation time, λ and the number of mechanically active junction, ν_{eff} as described by eq 7:

$$\eta = g\lambda\upsilon_{eff} \tag{7}$$

As shown in Table 1, the maximum λ and ν_{eff} are at 0 and 10 wt % EG, respectively. The increasing and decreasing trend for the viscosity described previously are dictated by the above equation due to the combinatory contribution from the relaxation time and the number of mechanically active junctions.

The shear-thickening behavior of HEUR22 in EG−water mixtures is clearly evident; the extent of shear-thickening decreases with EG content. The maximum viscosity is observed at a strain of 1 and the magnitude of shear thickening for pure aqueous system is more significant (peak viscosity ~ 120% of η_0) than that in 70 wt % EG (peak viscosity ~ η_0). The shear-thickening is the result of shear-induced increase in the density of mechanically active chains. The flower to star transition and the decrease in the mechanically active junctions with increasing EG concentrations give rise to the reduction in shear thickening.

By conducting the viscosity measurement of a viscoelastic solution at different temperatures, the activation energies, E_a could be evaluated based on the Arrhenius expression,

$$\eta_0 = A \exp\left(\frac{E_a}{RT}\right) \tag{8}$$

where η_0 is low shear viscosity, A is a pre-exponent factor, R is the gas constant, T is the absolute temperature and E_a is the activation energy. The activation energies E_a of HEUR in different EG concentrations as determined from the Arrhenius equation are summarized in Table 1. It is evident that E_a increases with EG concentrations and reaches a maximum of 83 kJ/mol at ~30 wt % EG and decreases subsequently. The activation energy can be used to quantify the strength of the polymer network, where E_a represents the total energy attributed to the lifetime of the hydrophobic junction and junction densities in the network. With increasing EG concentration, ν_{eff} increases to a maximum at 12−15 wt % EG and then decreases and reaches a similar level as in pure water at ~35 wt % EG, where it then decreases rapidly to a negligible value at 70 wt % EG. On the other hand, E_i (activation energy of each chain exiting the micellar core) should increase slightly to 5 wt % EG and then decrease marginally to EG of ~30 wt %, and beyond this, it should then decrease rapidly, which produces the trend in the activation energy shown in Table 1.

The viscoelastic properties of semidilute HEUR solutions in the EG−water mixtures are supported by the molecular information derived from laser light scattering measurements.It shows succinctly that the macroscopic properties, such as bulk viscosity and modulus derived from molecular behavior of polymer chains and micelles, can be explained from microscopic measurements such as those determined from dynamic and static light scattering techniques.

Conclusions

The association behaviors of HEUR polymer in EG−water mixtures were examined by laser light scattering the rheological techniques. At low content of EG (<5 wt %), a small increase in the aggregation number is observed due to the disruption of hydrogen bonds between water and PEO, which produces a slightly more hydrophobic polymer chain. With increasing EG content, the solvent becomes less polar, which decreases the aggregation number as well as the conformation of the polymer backbone. One end of the looping chain in HEUR flower micelles is released, which transforms the flowerlike micelle into a starlike micelle. Such microstructural change is confirmed by microscopic (laser light scattering) and macroscopic (rheological) results. With further increase in EG concentrations, the solvent mixture becomes a poor solvent (as indicated by the negative second virial coefficient) for HEUR and several HEUR micelles associate and precipitate from the solvent mixture, when the content of EG exceeds 78 wt %.

Acknowledgment. We would like to acknowledge the financial support provided by Ministry of Education and the Singapore-MIT Alliance.

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MA025728+