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Light Scattering of Dilute Hydrophobically Modified Alkali-Soluble Emulsion Solutions: Effects of Hydrophobicity and Spacer Length of Macromonomer

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ABSTRACT: A novel comb water-soluble associative polymer (hydrophobically modified alkali-soluble emulsion (HASE)), comprising of a random copolymer of methacrylic acid (MAA), ethyl acrylate (EA), and 1 mol % of hydrophobically modified macromonomers, was studied using laser light scattering and rheological techniques. The hydrophobic substituents are separated from the backbone by a poly(ethylene glycol) (PEG or PEO) spacer chain. The hydrophobicity of the hydrophobic substituents and the length of PEO spacers control the microstructure of the aggregates or clusters. In dilute solution regime, the relaxation times of both unimers and aggregates are almost independent of hydrophobic groups and PEO spacer length. The aggregates are formed via the closed-association mechanism, and the balance of electrostatic and hydrophobic interactions controls their microstructures. However, by varying the hydrophobicity and the length of the PEO spacer chains, the internal conformation of the aggregates changes. Results from static and dynamic light scattering are consistent with the trends observed from rheological measurements.

Introduction

Associative polymers are macromolecules with attractive groups that are either attached at the ends or randomly grafted along the backbones. They are an important class of materials suitable for coating applications due to their thickening properties.[1−3] The research activity in this field has gained momentum, as many issues are yet to be resolved.[4−12] Water-soluble associative thickeners (AT's) are one type of associative polymers which are good candidates for thickening agents in environmentally friendly coating applications.[13] At present, three common types of associative thickeners, i.e., hydrophobically modified ethylene oxide urethane (HEUR), hydrophobically modified hydroxyethylcellulose (HMHEC), and hydrophobically modified alkali-soluble emulsions (HASE), are available for use to the paint industry. However, most of the research activities on associative thickeners are devoted to the HEUR and HMHEC system, as they are relatively simpler than the HASE system.[14] Hence, the understanding on the dynamics and microstructure of HASE polymer in solutions is less well developed than that of HEUR and HMHEC.

HASE polymers are comblike polymers, whose backbone possesses moderately high molecular weight of up to 200 000−250 000. The backbone is a random copolymer of methacrylic acid (MAA) and ethyl acrylate (EA). Small amounts of hydrophobically moieties are grafted onto the backbones through short poly(ethylene oxide) hydrophilic segments via ethoxylate linkages. The grafted chains are referred to as macromonomers in this study. The chemical structure of HASE polymer is shown in Figure 1. When HASE dissolves in water at low pH value, the polymers are in the form of latex particles. When base is added, the methacrylic acids on the polymer backbone are neutralized, and the polymer becomes soluble. However, this polymer is more complex when compared to telechelic HEUR system due to the charged backbones and the comblike structure. For telechelic HEUR system, the hydrophobes are located at both ends of the water-soluble backbones. In the past few years, several studies on the rheological behavior

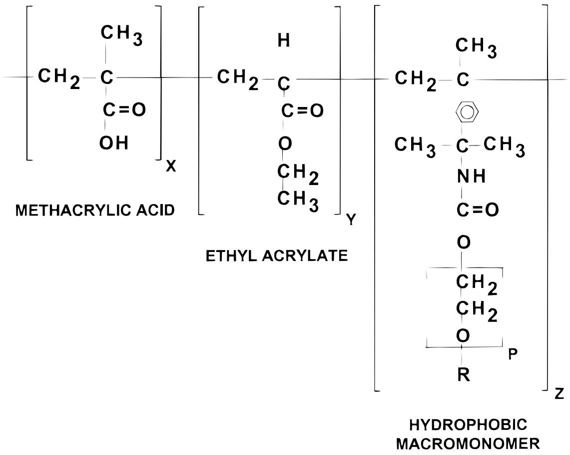

Figure 1. Chemical structure of model HASE polymers.

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Table 1. Characteristics of Macromonomers Used in the Synthesis of Model HASE Polymers

polymer designation	hydrophobe	actual EO	surfactant M_n by hydroxyl[a]	surfactant GPC M_n/M_w[b]	AM calcd M_n[c]	AM GPC M_n/M_w[b]	PDI of AM[d]	weight composition MAA/EA/AM[e]
HASE Polymer with Varying Hydrophobicity								
HASE-EO35C01	C_1H_3	36.8	1654.1	1760/1855	1885	2281/2475	1.09	38.73/45.95/15.32
HASE-EO35C04	C_4H_9	34.4	1587.8	1789/1886	1789	2287/2467	1.08	38.95/46.20/14.85
HASE-EO35C08	C_8H_{17}	31.6	1520.3	1788/1880	1722	1979/2100	1.06	39.17/46.46/14.37
HASE-EO35C12	$C_{12}H_{25}$	34.6	1902.5	2017/2137	2104	2551/2771	1.09	38.56/45.74/15.70
HASE-EO35C16	$C_{16}H_{33}$	33.9	1736.7	2033/2135	1938	2259/2362	1.05	38.47/45.64/15.89
HASE-EO35C20	$C_{20}H_{41}$	31.8	1700.2	2320/2454	1902	2474/2618	1.06	38.59/45.78/15.64
HASE Polymer with Varying Spacer Chain Length								
HASE-EO00C20	$C_{20}H_{41}$	0	298.6	506/507	500	632/633	1.00	43.61/51.74/4.65
HASE-EO05C20	$C_{20}H_{41}$	4.2	483.1	700/740	684	836/870	1.04	42.88/50.87/6.25
HASE-EO10C20	$C_{20}H_{41}$	10.5	761.7	1082/1172	963	1255/1344	1.06	41.81/49.61/8.58
HASE-EO20C20	$C_{20}H_{41}$	19.9	1175.3	1376/1450	1377	1563/1642	1.05	40.33/47.84/11.83
HASE-EO25C20	$C_{20}H_{41}$	23.9	1352.4	1704/1828	1554	1916/2053	1.07	39.72/47.12/13.15
HASE-EO35C20	$C_{20}H_{41}$	31.8	1700.2	2320/2454	1902	2474/2618	1.06	38.59/45.78/15.64
HASE-EO40C20	$C_{20}H_{41}$	41.6	2129.7	3179/3410	2331	3342/3582	1.07	37.27/44.21/18.52

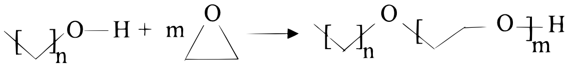
[a] Absolute number-average MW measured by the hydrolysis number technique. The technique is a titration that assumes a monodisperse sample where each molecule contains only one hydroxyl group. [b] GPC molecular weight relative to polystyrene standards in THF at 35 °C using a Waters 150C. [c] Number-average molecular weight of macromonomer calculated by adding the hydroxyl number-average MW to 210.3, the molecular weight of meta-TMI. [d] Polydispersity index of macromonomer determined by the ratio M_w/M_n. [e] Monomer composition in weight percent required to give a molar composition of 49.06%/50.01%/0.90% of MAA/EA/AM. (Note: AM refers to associative macromonomer.)

of HASE polymer solutions at high polymer concentrations had been reported.[14−25] To gain a better understanding on the supramolecular assembly of the polymer chains and their microstructure, laser light scattering studies on dilute HASE solutions were performed.[26,27] It was found that salt concentrations and pHs significantly alter the microstructure and the solution properties. Because the backbones of HASE contain MAA, increasing pH will enhance the neutralization of MAA groups, which causes the apparent size and configuration of the aggregates to increase due to electrostatic repulsive forces. After full neutralization of MAAs, the apparent hydrodynamic sizes become independent of pH. However, with increasing salt concentrations in fully neutralized solution, the backbone becomes more flexible due to the shielding of the electrostatic repulsion by the salt ions and the apparent hydrodynamic sizes decrease with the increasing salt concentrations. For very dilute model HASE at pH of 9 in 0.1 M NaCl aqueous solutions, HASE polymers associate to form aggregates through the closed association mechanism. A polymer aggregate contains about five polymer chains with more than one-association junction points. This complicates the determination of aggregation number by fluorescence techniques.[24]

For dilute HASE polymer at pH of 9 in high salt solutions, associations are predominantly driven by the hydrophobic interactions between the macromonomers. Hence, the characteristics of the macromonomers play an important role in controlling the solution properties and the association mechanism. The size of the hydrophobes and the length of PEO spacers were systematically varied. The closed association mechanisms and the scaling relations were utilized to interpret the light scattering results. Viscosity measurements were carried out, and the data were compared with the diffusion coefficients obtained from light scattering.

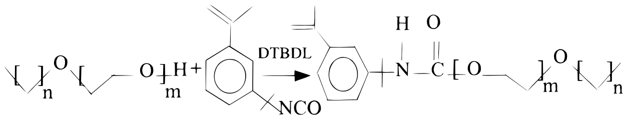
Experiments

Materials. The polymers examined in this study are identical to that employed in our previous publications.[26,27] A brief description on the synthesis of the macromonomer will be given here. Surfactant precursors for the macromonomers were prepared by reacting ethylene oxide with an alcohol according to



The alcohols were used as received without further purification and ethoxylated in a pressure autoclave at 140 °C and 70 psi using 0.25% potassium hydroxide (based on total reaction mass) as catalyst. Ethylene oxide was added in small aliquots to keep the reaction temperature and pressure constant. After complete addition of the ethylene oxide, the reaction mixture was held at temperature and pressure to ensure complete conversion of ethylene oxide. The liquid product was poured from the reactor hot and had only a slight trace of amber color. The product solidified on cooling to room temperature. Its molecular weight was measured by end group analysis (hydroxyl number). The titration of the hydroxyl end groups provides a measure of the absolute number-average molecular weight of the surfactant (see Table 1). The molecular weight distributions of the samples (i.e., polydispersity) were measured by gel permeation chromatography (GPC) using tetrahydrofuran (THF) solvent. The molecular weights are relative to poly(styrene) standards, so they were used to assess the breadth of the distribution and for relative comparisons (see Table 1). The number-average molecular weight obtained by hydroxyl number was used in subsequent calculations.

Macromonomers were prepared by reacting the surfactant precursors with a stoichiometric amount of meta-TMI (isopropenyl benzyl isocyanate), based on the hydroxyl number-average weight of the surfactant, according to



The surfactant was melted and heated to 85 °C under nitrogen sparged to prevent decomposition of the surfactant. Once melted, 0.1% dibutyltin dilaurate (DBTDL) catalyst (based on total reaction mass) was added to the reaction mixture and allowed to mix thoroughly. Then, the meta-TMI was added, and after the initial exotherm (typically 7 °C), the reaction mixture was held at 85 °C for another 4 h to ensure complete conversion of the isocyanate. The product was packaged in a jar while hot and solidified on cooling to room temperature. The molecular weight and molecular weight distributions of the macromonomers were measured by gel permeation chromatography; the GPC results are shown in Table 1 and parts a and b of Figure 2 for macromonomers with varying hydrophobicity and spacer chain length, respectively. The molecular weight distributions are reasonably narrow, and the reaction

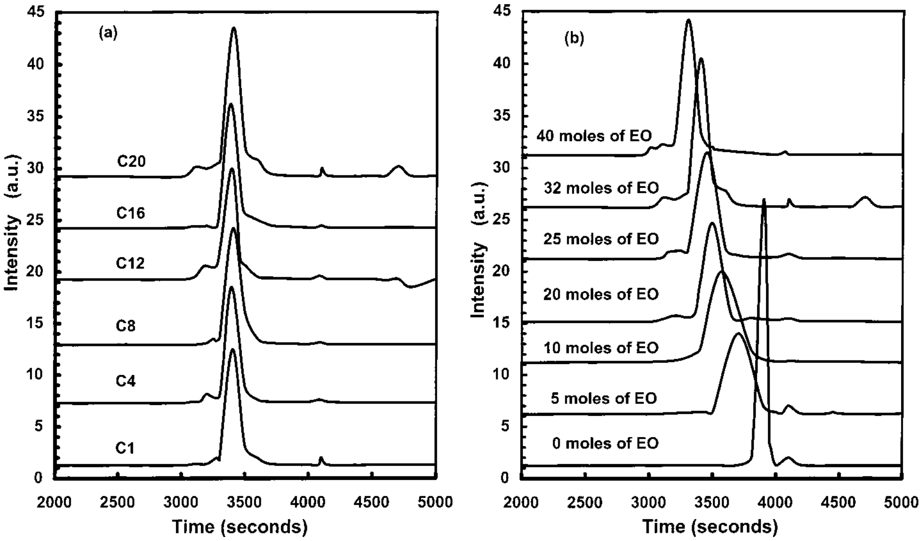


Figure 2. GPC of macromonomers with (a) C1 to C20 hydrophobes with ~35 mol of PEO and (b) C20 hydrophobes with different spacer chain length (moles of EO).

proceeds to completion as the molecular weights are very close to within approximately 10% of the expected values. (Note that the molecular weight of the macromonomer used to calculate the fractions of ethyl acrylate, methacrylic acid, and macromonomer used in the subsequent emulsion polymerization was calculated by adding the molecular weight of the meta-TMI, i.e., 201.25, to the hydroxyl number-average molecular weight of the surfactant precursor.)

The details of the synthesis procedures of HASE polymers using the emulsion polymerization technique were described elsewhere.[15,18] The HASE polymers used in the study on the effect of hydrophobes are designated as HASE-EO35C1 to HASE-EO35C20, where R (the hydrophobes) are linear alkyl chains comprised of CH_3 to $C_{20}H_{41}$, p (the number of repeat EO unit) is about 35, and the molar ratios MAA:EA:macromonomer are 49:50:1. The model HASE polymers used for studying the effects of PEO spacers are designated as HASE-EO00C20 to HASE-EO40C20, where p varies from 0 to 40, respectively, $R = C_{20}H_{41}$, and the molar ratios MAA:EA: macromonomer were also maintained at ratios of 49:50:1. Table 1 depicts the details of these model polymers. Details on the sample dialysis and solution preparation were the same as described in our previous studies.[27,28]

For all the samples, AMP (2-amino-2-methylpropanol) was used to adjust pH to ~ 9 and NaCl was used to adjust the ionic strength. The salt concentrations for all the measurement samples were kept at 0.1 M NaCl. Water used was purified through a Millipore water purified system (Alpha-Q, Millipore Co.) and a 0.45 μm filter. All the samples were kept at room temperature for 24 h to equilibrate the samples prior to testing. The measurement temperature was kept at 298 ± 0.1 K using a PolyScience (model 9105, Polyscience. Inc.) water bath. To calculate the apparent M_w, the refractive index increments of polymers (dn/dC) were measured using a differential refractometer. The values are 0.239, 0.242, 0.265, 0.246, 0.248, and 0.276 mL/mg respectively for HASE-EO35C1 to HASE-EO35C20 and 0.238 mL/mg for HASE-EO40C20. The errors in the dn/dC were estimated to be about 5%.

Equipment. A Brookhaven BIS200 laser scattering system equipped with a 522-channel Brookhaven BI9000 digital multiple τ correlator was used to perform the static and dynamic light scattering experiments. The light source is a power adjustable vertically polarized 350 mW argon ion laser with a wavelength of 488 nm. The inverse Laplace transform of REPES[29] supplied with the GENDIST software package was used to analyze the time correlation function (TCF), and the probability of reject was set to 0.5.

Viscosity measurements were carried out using the Contraves LS40 controlled rate rheometer. The rheometer was fitted with the MS41S/1S concentric cylinder measuring system consisting of a cup with diameter of 12 mm and a bob with the diameter of 11 mm and the height of 8 mm.

Results and Discussion

HASE polymer solutions at high pH values (~9) exhibit a unique and interesting behavior when compared to conventional polymer solutions due to the strong hydrophobic associations. The association gives rise to the viscosity enhancement. An important issue to address is how the macromonomer structure controls the polymer conformation in dilute solutions, which then dictates the rheology of the concentrated solutions. After neutralization, the polymer backbones possess the characteristics of polyelectrolytes. From previous studies on polyelectrolyte solutions, it is found that addition of excessive amount of salt can effectively shield the electrostatic interaction.[30] The details of salt effect on the dilute HASE solutions were described in our earlier publications.[26,31] To study the effect of the modified hydrophobic groups and effect of the PEO spacers, 0.1 M NaCl was used to shield the electrostatic repulsion. The intrinsic viscosities were carried out in our laboratory, and it was found that the intrinsic viscosity for the very dilute HASE-EO35 and HASE-C20 series are almost the same i.e., $[\eta] \sim 2$ dL/g. Hence, the overlap concentration, $C^* = 1/[\eta]$, is ~ 0.5 wt %.[32]

Dilute HASE Solutions with Different Hydrophobes. When the polymer concentrations are lower than the overlap concentration, C^*, the polymer solution is considered to be in the dilute solution regime. The properties of dilute HASE-EO35C16 solutions and the concentration dependence were described elsewhere.[27] In that paper, the closed association mechanism was proposed, where clusters consisting of 5−6 polymer chains are formed in dilute solution regime. The closed association mechanism approaches one that is more open when the polymer concentration increases to the overlap concentration. We are therefore interested in examining the effects of macromonomer structure on the nature of the association of dilute HASE polymer solutions.

The HASE-EO35 polymers described in Table 1 consist of a series of model polymers whose chemical composition are kept constant but the sizes of the hydrophobic groups are varied from C_1 to C_{20} hydrocar-

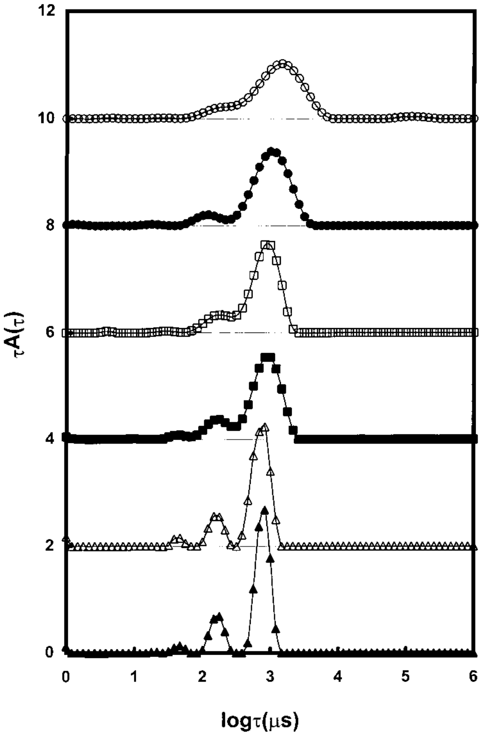


Figure 3. Relaxation time distribution functions of 0.1 wt % HASE-EO35 series with different hydrophobes: C1 (▲), C4 (△), C8 (■), C12 (□), C16 (●), C20 (○) alkyl chain, in 0.1 M NaCl aqueous solutions, at pH 9 and 298 K; measurement angle of 75°.

bon alkyl chains. For the ordinary surfactant, the size of the hydrophobe alters the micellar properties, such as the aggregation number and the micellar size.[33] Water-soluble associative polymers, which are macromolecules with hydrophobic and hydrophilic groups, possess properties similar to surfactants. Thus, the size of hydrophobic group should affect the solution properties, similar to surfactants. Since HASE possesses a charged polymer backbone, the electrostatic repulsion and the backbone rigidity will have a controlling effect on the micellization behavior of the hydrophobic macromonomer.

The dynamics of polymer chains can be successfully examined using the dynamic light scattering technique.[34,35] As described in previous studies, two main distribution peaks in the relaxation time distribution function were observed.[27] The fast peak is due to the translational diffusion of the unimers, and the slow peak is due to the translational diffusion of aggregates formed by 5−6 polymer chains. A small fastest peak was also observed in the distribution function, and the origin of this peak is still unclear. However, there is the possibility that this small fastest peak is attributed to the internal mode.

Figure 3 shows the relaxation time distribution of 0.1 wt % HASE-EO35 series in 0.1 M NaCl aqueous solutions at pH of 9 and 298 K. It is clear that the relaxation times for the fast mode remain constant when the carbon number of the macromonomer is varied from C_1 to C_{20}. However, the relaxation times of slow mode do not change much over the carbon number of C_1 to C_{16}, but it shifts to longer relaxation time for the C_{20} alkyl chain. This trend was further confirmed by analyzing the data over five different angles and plotted as Γ vs q^2. The slope of the straight line yields the diffusion coefficient that does not change with carbon number from C_1 to C_{16}. This implies that the size of hydrophobe does not significantly influence the relaxation times of both the fast and the slow modes (except for HASE-EO35C20 where some minor difference is evident); hence, the microstructures of each model polymer are considered to be identical. On the basis of this, the closed association mechanism is appropriate for describing the association mechanism of HASE with macromonomer that possesses varying hydrophobic modification.

In addition, from Figure 3, it is obvious that, with increasing carbon number, the amplitude (or height) ratio of fast and the slow modes, A_f/A_s, decreases. This implies that the intensities contributed by the slow mode become more significant as the alkyl chain of the macromonomer increases. In the dilute HASE solutions, the unimers and the aggregates are in dynamic equilibrium. When the hydrophobicity of the modified hydrophobes is increased, the stronger hydrophobic interactions cause the unimers to associate to form oligomers or aggregates, thereby lowering the number of unimers and broadening the size distribution as shown in Figure 3. This equilibrium shifts in favor of the creation of more aggregates, which give rises to the lower A_f/A_s ratio.

In dilute solution, both the fast and the slow modes are caused by the translational diffusion of the unimers and the aggregates, respectively. From the expression

$$D = \frac{\Gamma}{q^2} \tag{1}$$

the translational diffusion coefficients can be determined, where D is the translational diffusion coefficient and Γ is the decay rate, which is the inverse of the relaxation time, τ. q is the scattering vector ($q = (4\pi n \sin(\theta/2))/\lambda$, where θ is the scattering angle, n is the refractive index of the solution, and λ is the wavelength of the incident light). If the Stokes−Einstein equation is used, the apparent hydrodynamic radius, R_h, can also be obtained:

$$R_h = \frac{kT}{6\pi\eta D} \tag{2}$$

where k is the Boltzman constant and η is the solvent viscosity. The results of diffusion coefficients and the apparent hydrodynamic radius are summarized in Table 2.

Static light scattering (SLS)[36] is used to determine the molecular weight of the HASE-EO35 series polymers. The details of the SLS experiments and data analysis using the Zimm plot are described elsewhere.[27] The weight-averaged molecular weights determined directly from the Zimm plot are given in Table 2. It is evident that the weight-averaged molar masses of the HASE-EO35 series are similar except for the HASE-EO35C20 system.

In the dynamic light scattering of dilute conventional polymer solutions, many studies have focused on the scaling relation between the diffusion coefficient and molecular weight or the hydrodynamic radius and the molecular weight.[37−44] This scaling relation is described by

$$R_h = kM^{\alpha} \tag{3}$$

where k and α are constants for the same or similar polymers and M is the molar mass. Although the scaling

Table 2. Summary of Results of Viscosity, Static, and Dynamic Light Scattering of Dilute HASE-EO35 Series Solutions (0.1 wt %) in 0.1 M NaCl Aqueous Solutions at pH 9 and 298 K

HASE polymers	M_w ($\times 10^5$) from SLS	D_f (10^{11} m^2/s)	D_s (10^{12} m^2/s)	η ($\times 10^3$) (Pa s)	R_h(f) (nm)	R_h(s) (nm)	R_g (nm)	$\rho = R_g/R_h$
HASE-EO35C01	9.90	1.69	2.84	1.06	15	86	144	1.67
HASE-EO35C04	9.71	1.70	3.08	1.12	14	80	128	1.60
HASE-EO35C08	9.84	1.67	3.05	1.09	15	80	132	1.65
HASE-EO35C12	9.29	1.59	2.64	1.17	15	86	137	1.59
HASE-EO35C16	9.63	1.56	2.74	1.09	16	90	145	1.61
HASE-EO35C20	19.90	1.41	2.40	1.21	17	102	182	1.78

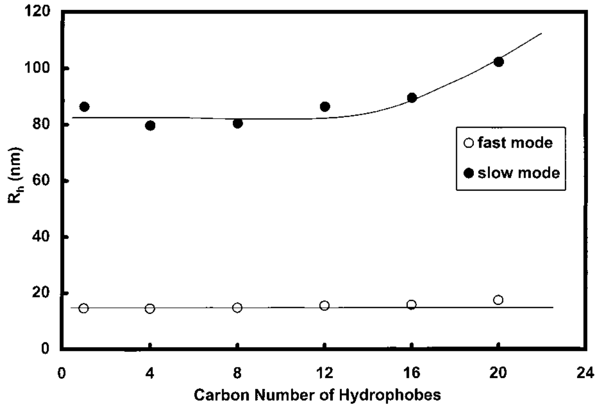


Figure 4. Relationship of apparent hydrodynamic radius and carbon numbers of the hydrophobes in 0.1 M NaCl aqueous solutions, at pH 9 and 298 K.

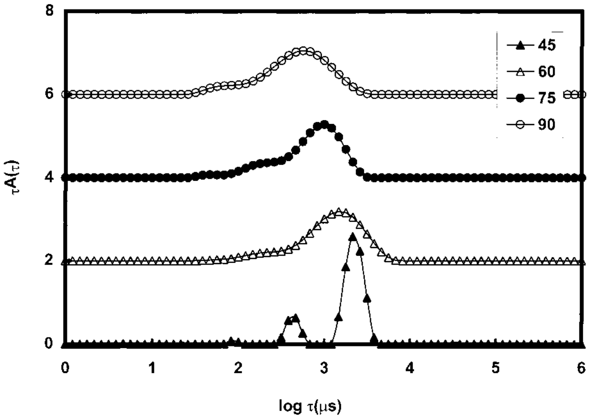


Figure 5. Relaxation time distribution functions of 0.1 wt % HASE-EO00C20 in 0.1 M NaCl aqueous solution, at different measurement angles, pH 9, and 298 K.

relation for HASE has not been established, it is believed that similar scaling relationship exists based on recent studies on unmodified HASE polymers (MAA/EA copolymers) carried out in our group.[45] The observation that the relaxation times of unimers do not change with the size of the hydrophobes agrees with the scaling relation since the molecular weights of the HASE-EO35 series polymer backbones are similar. This result is further demonstrated by the independence of the apparent hydrodynamic radius of unimers on the carbon number of the hydrophobes as shown in Figure 4. Small deviations observed in the hydrodynamic radius of unimers are consistent with the small variations in the molecular weight of each of the model HASE-EO35 series polymers.

The dependence of apparent hydrodynamic radius of aggregates on the carbon number of the hydrophobe is also described in Figure 4. The hydrodynamic radii of aggregates are identical for C_1 to C_{16} alkyl chains, but it increases slightly for the C_{20} alkyl chain. On the basis of the molecular weights (M_w) given in Table 2, the M_w of HASE aggregates (C_1 to C_{16}) is identical ($\sim$ 930 000 to 990 000) while the M_w of HASE-EO35C20 increases by approximately 2 times ($\sim 2 \times 10^6$). The above results are easily understood using the scaling relation as described for the unimers.

Considering the closed association mechanism and microstructure of dilute HASE solutions as described in our previous study,[27] the trend described in Figure 4 can be interpreted as follows. For an ordinary surfactant, the hydrophobicity of the macromonomer alters the aggregation number and hence the micellar size of the aggregate. The micellar size increases (corresponding to the increase in the aggregation number) with increasing carbon number of the hydrophobes. However, the main difference between the combed HASE system and ordinary surfactant is that the surfactant-like macromonomers are grafted onto a stiff polyelectrolyte backbone; hence, they cannot associate freely to form hydrophobic domains. Because of this, a HASE polymer aggregate contain more than one hydrophobic cores (or junctions), in contrast to telechelic HEUR polymer, where the aggregate contains a single hydrophobic core. Thus, the aggregation number of each junction point is far from being at its optimum. With increasing hydrophobicity of the macromonomer, the aggregation number of each hydrophobic junction increases, resulting in a decrease in the number of junction points inside the aggregates. However, such reorganization has a minimal impact on the hydrodynamic volume or size of the aggregate as depicted in Figure 4. However, when the hydrophobicity is sufficiently high (as in the case of HASE-EO35C20 polymer), the equilibrium between the electrostatic repulsion and the hydrophobic attraction will shift, where the hydrophobic interactions dominate. Under such condition, more unimers can associate together to form larger aggregates with higher molar mass and hydrodynamic radius.

Viscosity measurements were also carried out and used to compare with the data obtained from light scattering. Since the polymer concentrations are very low and the network structures have not been formed, all solutions exhibit Newtonian behavior; i.e., the shear viscosity is independent of the shear deformation. The results of low shear viscosity are summarized in Table 2. In dilute solution regime, the hydrophobes do not significantly affect the solution viscosity, which agrees with the light scattering data.

Dilute HASE Solutions with Different PEO Spacers. All the HASE polymers discussed previously contain fairly similar PEO spacers but varying hydrophobicity. In this section, another series of model HASE polymers with a C_{20} hydrophobe but different PEO spacers will be examined. The details of this series are described in Table 1. Figure 5 shows the relaxation time distribution function of a 0.1 wt % HASE-EO00C20 measured at different detection angles. Similar behavior

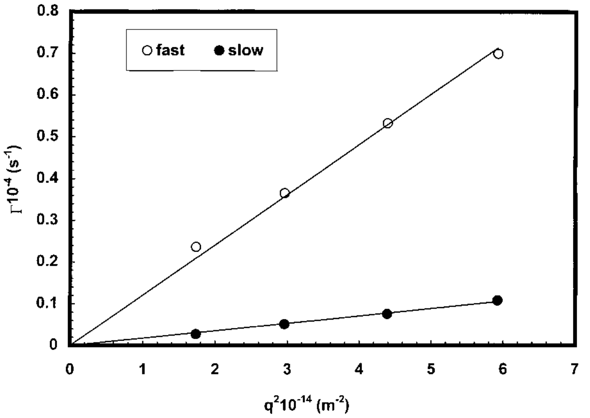


Figure 6. Relationship of relaxation rates Γ and q^2 for 0.1 wt % HASE-EO00C20 in 0.1 M NaCl aqueous solution at pH 9 and 298 K.

is observed for the other polymers with identical hydrophobes but different PEO spacer.

From the figure, two main relaxation peaks in the relaxation time distribution function are observed. The two main peaks shift to the left and merge when the measurement angles are increased. The details of the interpretation for the shifting and merging of peaks have been previously described.[27,31] The q^2 dependence of Γ as shown in Figure 6 confirms that the two main peaks are caused by the translational diffusion. Similar to the HASE polymers with different hydrophobes with identical PEO spacer, the two main peaks are due to the translational diffusion of the unimers (fast mode) and the translation diffusion of the aggregates (slow mode). At the detection angle of 45°, a very small fastest peak in the short relaxation time, characterizing the internal motions of the polymer coil, may exist since qR_g is close to unity under the prevailing measuring condition.[34] On the basis of the theories of internal mode, as the measurement angle is increased ($qR_g > 2$), this mode merges with the fast mode, giving only two peaks at larger angles. This is consistent with the previous discussions on the significance of qR_g.

Figure 7 shows the distribution functions obtained for 0.01 wt % HASE polymer with different PEO spacer chains. From the plot, it is evident that by increasing the length of the PEO spacer, the location of the two main peaks does not change significantly, except for HASE-EO40C20. The small fluctuations are probably due to systematic variation of the polymer attributed to the synthetic process. Since the molecular weights of unimers are approximately identical for the polymers with varying length of PEO spacers, the apparent hydrodynamic radius of unimers in the dilute solution regime should remain constant.

Increasing the length of hydrophilic PEO spacer will result in a decrease in the hydrophobicity of the macromonomer, and thus the aggregation number will decrease.[33] Since the hydrophobic macromonomers are distributed along the polymer backbone, the stiffness of the backbone and the accessibility of the hydrophobes (controlled by the PEO spacer) dictate the nature of association. Earlier studies by our group indicated that the aggregation number of each junction increases when the PEO spacer length increases.[46] This implies that polymers with longer PEO spacers should contain fewer hydrophobic junctions since the hydrophobes can more readily associate to form junctions with higher aggregation number. On the other hand, a shorter PEO spacer will yield more junctions with smaller aggregation number. Since the backbone typifies that of a polyelectrolyte chain, the persistent chain length is higher than uncharged backbone due to electrostatic repulsion from charges along the backbone. Even though the hydrophobicity of the macromonomer with short PEO spacer is higher than that with a long PEO spacer (since PEO is hydrophilic in nature), the association is predominantly controlled by the accessibility of the hydrophobes to interact with one another. Short PEO spacer promotes the formation of many junctions, each with fewer number of hydrophobes. On the other hand, longer PEO spacers produces fewer junctions, but each with larger aggregation number.

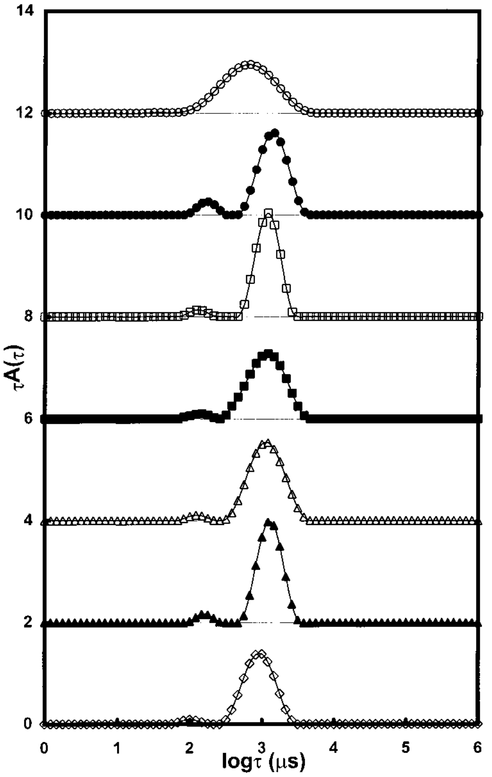


Figure 7. Relaxation time distribution functions of 0.01 wt % HASE-C20 polymer series with different PEO spacers: 0 (◇), 5 (▲), 10 (△), 15 (■), 25 (□), 35 (●), 40 mol (○), in 0.1 M NaCl aqueous solutions, at pH 9 and 298 K.

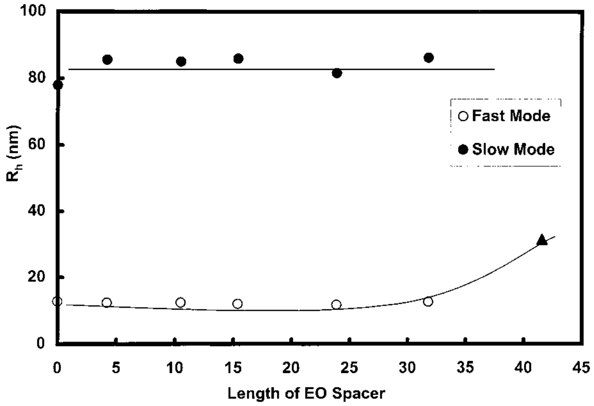


Figure 8. Relationship of apparent hydrodynamic radius and length of PEO spacers for 0.01 wt % HASE in 0.1 M NaCl aqueous solutions, at pH 9 and 298 K (▲ is the R_h of HASE-EO40C20).

Figure 8 depicts the relationship of apparent hydrodynamic radius and the PEO spacer for the dilute HASE

Table 3. Summary of Results of Viscosity, Static, and Dynamic Light Scattering of Dilute HASE-C20 Series Solutions (0.01 wt %) in 0.1 M NaCl Aqueous Solutions at pH 9 and 298 K

HASE polymers	D_f (10^{11} m^2/s)	D_s (10^{12} m^2/s)	η ($\times 10^3$) (Pa s)	R_h(f) (nm)	R_h(s) (nm)
HASE-EO00C20	1.92	3.15	1.13	13	78
HASE-EO05C20	1.98	2.87	1.15	12	86
HASE-EO10C20	1.97	2.89	1.02	12	85
HASE-EO15C20	2.03	2.86	1.04	12	86
HASE-EO25C20	2.08	3.01	1.07	12	82
HASE-EO35C20	1.94	2.85	1.21	13	86
HASE-EO40C20		7.80	0.99		31

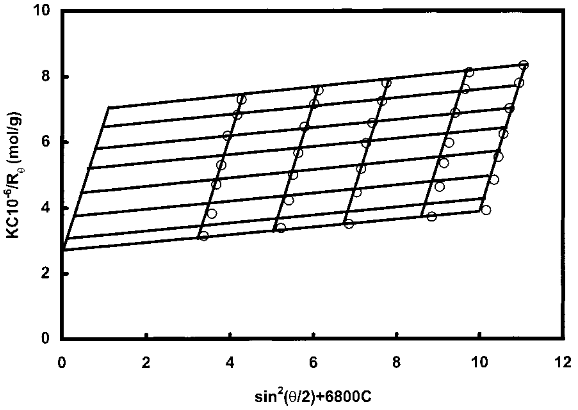


Figure 9. Static light scattering (Zimm plot) of dilute HASE-EO40C20 in 0.1 M NaCl aqueous solutions at pH 9 and 298 K. Angles range from 30° to 135°; concentrations range from 0.05 to 0.15 wt %.

polymers in 0.1 M NaCl, at pH of 9 and 298 K. It is evident that the apparent hydrodynamic radii are independent of the PEO spacer, except for 40 mol of PEO. Since the polymer hydrophobes associate to produce more than one junction points within the aggregate, increasing the PEO spacer from 0 to 32 mol does not alter the size of the aggregate. It however alters the number of junction points and aggregation number of each junction without altering the nature or size of the unimers or aggregates as summarized in Table 3.

However, for a PEO spacer of 40 mol, a significantly different result is obtained. Only one peak in the distribution function is evident, and the relaxation time of that peak lies between the fast and slow relaxation modes of polymers with PEO spacer of 0−32 mol. This is clearly evident from Figure 7 where the fast mode is not distinguishable. A possible reason is that the fast and slow peaks have merged to form a single broader peak, which is not distinguishable by the GENDIST software, and that the structure is not similar to the other polymers. To confirm this, we conducted static light scattering experiments (Zimm plot shown in Figure 9) on the HASE-EO40C20 polymer and observed that both the weight-averaged molecular weight and radius of gyration are lower than the other model polymers. The molecular weight is only 370 000 Da, and the radius of gyration, R_g, is 62 nm. This suggests that the microstructure of the polymer with 41.6 mol of PEO is different from the rest of the model polymers. In fact, it is likely that only smaller aggregates with a broader size distribution are present, and the smaller size is either due to a more compact structure or due to fewer polymer chains.

On the basis of theoretical calculation using the average bond length of the respective atoms, it is found that the PEO spacer of 41.6 mol exceeds the critical distance where two hydrophobes along the same backbone can associate to form a intramolecular associative junction. The microstructure of dilute HASE-EO40C20 takes the form of an aggregate with probably one or two junction points containing larger number of hydrophobes. This will give rise to a smaller aggregate, which are more compact. Rheological investigations indicate that the dilute solution viscosity of the polymers is independent of the PEO spacer length. The numerical values are summarized in Table 3. The trends seem to correlate with the results from dynamic light scattering experiments.

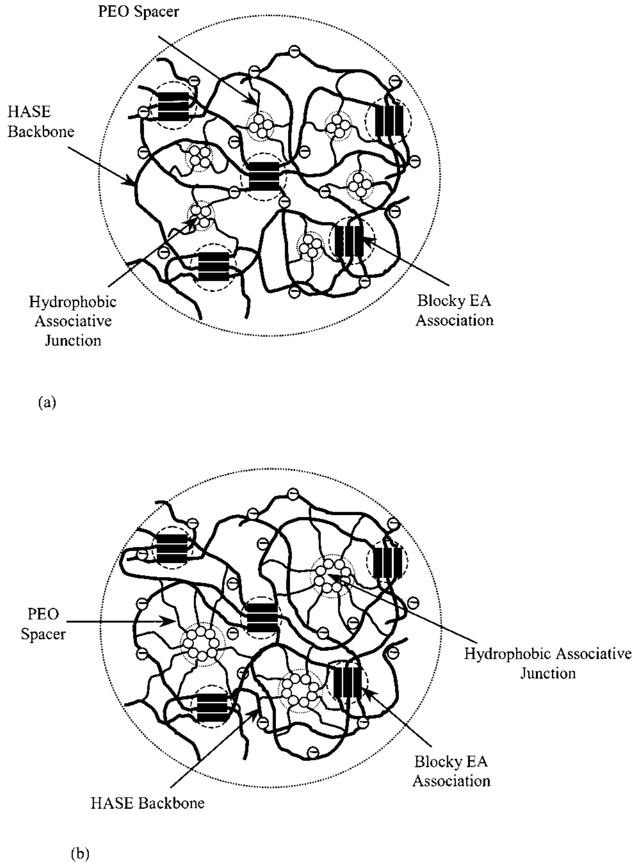


Figure 10. Microstructure of a HASE aggregate for (a) small hydrophobes or short PEO spacer length and (b) large hydrophobes or long PEO spacer length.

Winnik and co-workers showed that the model HASE polymers possess two hydrophobic domains in aqueous solution.[47] Using fluorescence quenching technique on a model HASE polymer with C20 hydrophobe, they observed that the long decay time corresponds to micelle-like structures formed by the $C_{20}H_{41}$ substituents of the polymer. An aggregate contains ca. 5 polymer chains with two micellar cores, giving rise to a mean aggregation number of 55. In addition, they speculate that the short lifetime hydrophobic domains are made up of ethyl acrylate-rich sequences along the polymer backbone. Their results corroborated the findings from our recent studies, which indicated that the EA segments are sufficiently blocky to form hydrophobic associations with other EA blocks or the hydrophobic macromonomers.[26] On the basis of our current understanding of the molecular characteristics of these HASE model polymers in aqueous solutions, a refined microstructure of the aggregate based on the earlier microstructure is suggested.[27] A pictorial representation of a model HASE aggregate in dilute solution is shown in Figure 10. It is evident that there are two types of association junctions in a HASE aggregate. One comes from the blocky EA segments of the backbone and the other from the macromonomer. For the association junctions derived from the macromonomer, the aggregation numbers per junction increases with the hydrophobicity of the macromonomer and the length of PEO spacer chain. However, the number of junctions within the aggregate decreases with the increasing the hydrophobicity of the macromonomer and the length of PEO spacer chain.

Conclusions

Dilute HASE polymers with different hydrophobes and PEO spacers associate through intermolecular and intramolecular interactions to produce aggregates containing about five polymer chains. An equilibrium between the unimers and the aggregates prevails, arising from the balance of hydrophobic attraction and electrostatic repulsive forces. Increasing the hydrophobes leads to the increase of the hydrophobic attraction. If the hydrophobic attraction does not exceed the electrostatic repulsion, the number of polymer chains per aggregate remains constant. However, the number of junctions per aggregates and the aggregation number in each junction vary depending on the characteristic of the macromonomer. Increasing the size of hydrophobe results in the reduction of the number of junctions, but each junction contains a larger number of hydrophobes. However, if the hydrophobic interaction is strong enough to balance the electrostatic repulsion, larger aggregates will be formed. Increasing the length of PEO spacer gives rise to the increase in the accessibility of the hydrophobes to form hydrophobic domains. Hence, increasing the length of PEO also results in the reduction in the number of junctions containing a larger number of hydrophobes. When the length of the PEO spacer exceeds a critical length, the hydrophobes form more intramolecular junctions (e.g., for HASE-EO40C20), and smaller aggregates are produced.

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