

Hydrophobically Modified Associative Polymer Solutions: Rheology and Microstructure in the Presence of Nonionic Surfactants

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We report on the rheology and morphology of a hydrophobically modified alkali-swellaable emulsion (HASE) polymer solubilized in alkaline media containing nonionic surfactants. The HASE polymer consists of complex alkylaryl hydrophobes composed of oligomeric nonylphenol condensates attached to a poly(ethyl acrylate-*co*-methacrylic acid) backbone. The complex linear viscoelastic response of the polymer in alkaline solution suggests an unentangled network with an appreciable fraction of microgel. The concentration and hydrophile–lipophile balance (HLB) of nonionic surfactants profoundly affect the solution rheology. A surfactant of high HLB inhibits the dynamic network connectivity of the HASE polymer, as demonstrated by reductions of both the steady-shear viscosity and the dynamic storage modulus. The shear-induced structuring previously reported for this polymer is also progressively diminished as the surfactant concentration is increased. In contrast, the addition of a low-HLB surfactant promotes system structuring, as evidenced by (i) increases in the shear viscosity and the high-frequency plateau modulus and (ii) retention of the ability to undergo shear-induced structuring. We also employ cryofracture-replication transmission electron microscopy for the first time with regard to HASE associative polymers to examine the morphological characteristics of selected systems. The morphology of the HASE polymer in both latex and solubilized form appears more complex than previously anticipated, and a reasonable interpretation of these new data is provided.

Introduction

Hydrophobically modified alkali-swellaable emulsion (HASE) polymers are complex terpolymers derived from the copolymerization of ethyl acrylate, methacrylic acid, and an ethoxylated macromer of a nonionic surfactant.¹ Thus, HASE polymers are structurally similar to “poly-soaps,” macromolecules bearing many grafted amphiphilic segments.² Although HASE polymers are commercially important as rheology modifiers in aqueous paints and coatings, they are complex in terms of their microstructural and compositional heterogeneity.^{3–5} As a consequence, an understanding of the dynamics and morphology of HASE polymer networks is less well developed than that of associating polymers possessing simpler architectures, e.g., telechelic polymers composed of poly(ethylene glycol) with terminal hydrophobes.^{6–11} This difference reflects the more complex architecture of HASE systems and their controlled synthesis by emulsion polymerization in a complex multiphase environment.^{12–15} In particular, the precise assignment of essential parameters, such as the mean number of hydrophobes residing in a junction domain (i.e., the aggregation number), constitutes a formidable challenge.¹⁶ Recent experimental studies of HASE polymers have addressed several relevant issues: the effects of

hydrophobe size and side-chain length on solution rheology,^{17–19} flow behavior in parallel superposed steady/dynamic shear,^{20,21} physicochemical changes during solubilization,²² interactions with surfactants,^{23–25} and effects of added electrolytes on rheological behavior in the dilute regime.²⁶ In the present study, we explore the rheological and morphological characteristics of HASE polymers in solutions containing nonionic surfactants.

Because most water-soluble polymeric rheology modifiers are employed in formulations containing surfactants or other amphiphilic species, polymer–amphiphile interactions are of considerable technological and theoretical interest.^{27,28} Polymer–surfactant interactions are manifested macroscopically in the solution rheology and can involve conformational transitions due to surfactant adsorption, microphase separation because of complexation, or network modification through the formation of mixed micelles.²⁹ Mixed-micelle formation is of particular relevance regarding HASE polymers, as the network junctions involve dynamic association of hydrophobic groups. In the case of nonionic amphiphiles exhibiting low water solubility, the microstructure of a formulation can be intrinsically complex and can be further modified by the inclusion of a polymeric species.³⁰ Several studies have examined the impact of surfactant phase behavior on both the rheology of polymer–amphiphile systems and the development of systems capable of thermoreversible gelation. For example, Panmai et al.³¹ have examined the rheological behavior of hydrophobically modified hydroxyethylcellulose and poly(acrylamide) in the presence of a range of surfactants. Under conditions favoring spherical surfactant micelles, interchain hydrophobic interactions

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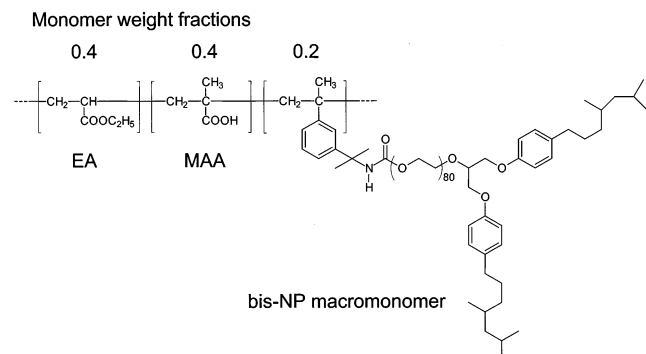


Figure 1. Idealized chemical structure of the HASE polymer examined in the present study. The hydrophobes consist of a mixture of oligomeric condensates of nonylphenol, with the major component being the bis-nonylphenyl moiety.

are effectively screened at high surfactant concentrations. The viscosity, however, remains unchanged under conditions favoring worm- or rodlike micelles.

Kaczmarek et al.³² have explored the interaction of several associating polymers in the presence of both sodium dodecylsulfate (SDS) and an octylphenol ethoxylate. The nonionic surfactant promotes structuring of the system in the presence of hydrophobically modified ethoxylate urethane (HEUR) polymers with large terminal hydrophobes. While Deguchi et al.³³ have examined the gelation of cholesterol-modified pullulan in the presence of SDS, Løye et al.^{30,34} have investigated the thermoreversible gelation of hydrophobically modified poly(acrylic acid)s in the presence of linear alcohol ethoxylates. Interactions of a HASE polymer with nonionic surfactants is also the subject of the present study, in which alkylphenol ethoxylates of different hydrophile–lipophile balance (HLB) and vastly different degrees of aqueous solubility are employed. In similar fashion, Candau and co-workers³⁵ have recently studied the interaction of hydrophobically modified poly(acrylamide)s with surfactants and report that the amphiphile-induced change in low shear viscosity is attributable to modified dynamics of the transient network. This modification, in turn, reflects the formation of mixed junction domains that incorporate the surfactant and polymer-bound hydrophobes. In this work, we seek to elucidate the effect of surfactant phase behavior on the mechanism by which a hydrophobically modified polymer of relatively complex molecular architecture interacts with surfactant molecules. The data reported here are discussed in light of recent theoretical considerations of associating polymer systems, and suitable comparisons with other classes of water-borne polymers exhibiting transient associations are provided.

Experimental Section

A. Materials. The hydrophobes of the HASE polymer examined here (depicted in Figure 1) consisted of oligomeric condensates of nonylphenol, with the major hydrophobic component being the bis-nonylphenyl moiety. The mean degree of ethoxylation in the macromer was ~ 80 , and the weight fractions of ethyl acrylate, methacrylic acid, and macromer employed in the polymer synthesis were 0.4, 0.4, and 0.2, respectively. Full details of the emulsion polymerization used to synthesize this polymer were previously detailed.¹⁹ The HASE latex was prepared at ~ 30 wt % solids under “starved feed” conditions. Recent analysis of HASE polymers

prepared in this manner by high-field (400 MHz) ^1H NMR spectroscopy revealed³⁶ that the fractions of monomeric residues in the polymer were comparable to the individual monomer fractions in the monomer feed mixture. Fractionation of HASE polymers in a separate study,³ however, indicated the existence of considerable compositional heterogeneity, as evidenced by an unequal distribution of macromer throughout the chain population.

Molecular weight determination of HASE polymers was performed by conventional GPC analysis. Nonaqueous GPC of HASE polymers in polar solvents such as dimethylformamide was riddled with problems arising from nonsteric exclusion of the polymer from the pores of the stationary phase, whereas aqueous GPC was adversely affected by supramolecular chain aggregation.³⁶ To overcome these complications, the ester/urethane linkages of the HASE polymer were subjected to alkaline hydrolysis, which yields a copolymer of sodium acrylate/methacrylate that is amenable to characterization by aqueous GPC. Prior analysis³⁷ of HASE polymers prepared in similar fashion to the one investigated in the present study suggested that \bar{M}_w is about 250 000. Because the polymer formula shown in Figure 1 corresponds to a macromer mole fraction of ~ 0.0055 , the mean number of hydrophobes (“stickers”) per chain was estimated to be ~ 15 . Dilute solution viscometry revealed that the intrinsic viscosity, $[\eta]$, of the HASE polymer was ~ 4.8 dL g $^{-1}$ at 25 °C in 0.05 M NaCl at pH 9. The HASE polymer latex was purified by dialysis (using a Spectropore 7 cellulose membrane with a cutoff at $M = 50$ 000) to remove serum electrolyte and excess anionic stabilizer. The nonionic surfactants employed here were supplied by Union Carbide (now Dow): Tergitol NP6, a nonylphenol ethoxylate with a mean degree of ethoxylation of ~ 6 [NP6], and Tergitol NP10, a nonylphenol ethoxylate with a mean degree of ethoxylation of 10 [NP10]. Both surfactants were used without further purification.

B. Formulations. The polymer latex was dissolved in aqueous 2-amino-2-methyl-1-propanol (AMP) at a concentration of 0.006 mol of amine/g of polymer, yielding a pH of ~ 9 . Samples were prepared at a constant ionic strength (0.05 M NaCl) by combining the requisite amounts of purified latex; distilled/deionized water; 0.5 M NaCl; 1.0 M AMP; and, where appropriate, nonionic surfactant. The rheology of the HASE polymer in the absence of surfactant was investigated at polymer concentrations between 0.4 and 1.2 g dL $^{-1}$. The polymer concentration in solutions consisting of NP6 and NP10 was held constant at 0.6 and 1.0 g dL $^{-1}$, respectively. The concentration of NP6 was varied from 0.05 to 1.5 g dL $^{-1}$, and the concentration of NP10 ranged from 0.1 to 1.1 g dL $^{-1}$. All samples were centrifuged (2500 rpm for 5 min) to remove entrained air and subsequently allowed to sit for several days prior to rheological analysis.

C. Rheology. Rheological tests were performed in steady and dynamic shear using a Rheometrics Scientific DSR controlled-stress rheometer equipped with appropriate cone-and-plate and concentric cylinder geometries. Steady-shear data at low strain rates ($\dot{\gamma} < 10^{-2}$ s $^{-1}$) were derived from sequential creep experiments, thus ensuring that the duration of each test was sufficient to attain a steady strain rate. High-frequency (ω) dynamic data, expressed in terms of the dynamic storage and loss moduli (G' and G'' , respectively), were

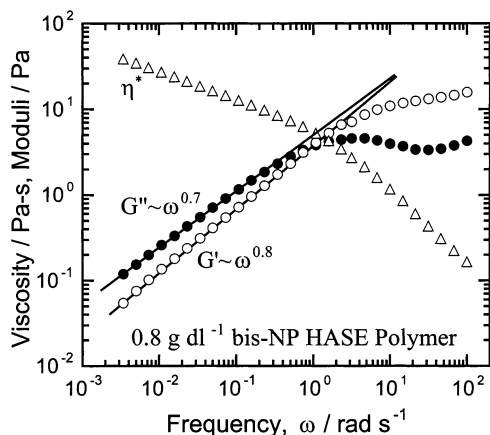


Figure 2. Frequency dependence of the small deformation material functions for a 0.8 g dL⁻¹ solution of the HASE polymer solubilized in the presence of AMP in 0.05 M NaCl.

obtained using a conical-cylinder geometry on a Rheometrics Scientific RMS800 controlled-strain rheometer. All experiments were conducted at 25 ± 0.1 °C. The steady-shear response of the polymer/surfactant systems was sensitive to shear history, thereby necessitating the use of preshear to obtain reproducible data. Application of a shear stress sufficient to generate a strain rate of ~ 5 s⁻¹ effectively eliminated shear history effects. Preshearing was performed for 180 s, followed by a rest period of 120 s, prior to the start of each steady-shear experiment. Solvent evaporation was prevented by coating the exposed edges of a test solution with a thin layer of low-viscosity poly(dimethylsiloxane) fluid (Dow Corning DC200, 10 cS).

D. Microscopy. Cryofracture-replication transmission electron microscopy (TEM), also known as freeze-fracture TEM (although care is exercised to avoid cooling-induced crystallization³⁸), was performed to visualize the microstructure of the HASE/surfactant solutions prepared here. A small drop of solution was gently placed in the well of a brass sample holder so that the meniscus extended beyond the top of the well. The assembly was rapidly plunged into liquid ethane cooled by liquid nitrogen to induce sample vitrification, and then transferred under liquid nitrogen to a previously cooled brass base, which was subsequently inserted into the specimen chamber of a JEOL JFD-9000C cryofracture-replication unit maintained at -170 °C and ca. 10^{-6} Torr. Once thermal equilibration was achieved, the specimen was fractured with a microtome blade, and the fresh fracture surface was first lightly etched, shadowed with Pt/C at an angle of 45° and then stabilized with C deposited at 90° off the horizontal. Resultant replicas were cleaned in successive water baths and imaged on a Zeiss EM902 electron spectroscopic microscope operated at 80 kV in zero-loss mode ($\Delta E = 0$ eV). Negatives were digitized at 600 dpi for presentation purposes.

Results and Discussion

A. Linear Viscoelastic Response of the HASE Polymer. The linear viscoelastic response of the HASE polymer solutions in the absence of added surfactant is typified by the data provided in Figure 2, where the frequency spectra of the complex viscosity (η^*) and dynamic moduli (G' and G'') are displayed. These data are reminiscent of a reversible network wherein inter-

chain interactions are transient, in which case the system does not behave as a physical gel. That is, a transition occurs from an elastic-dominated response ($G' > G''$) at high frequencies ($\omega > 1$ rad s⁻¹) to a viscous-dominated response at lower frequencies. Examples of systems exhibiting similar viscoelastic behavior include solutions of a hydrophobically modified galactomannan ether,³⁹ galactomannan/borate,⁴⁰ and poly(vinyl alcohol)/borate.⁴¹ The dynamics of such a transient network can be described in terms of a terminal relaxation time, τ_{network} , that is governed by both the kinetics of hydrophobic disengagement and the mean number of hydrophobes on a chain for comb (graft) copolymers.⁴² Various procedures have been established to ascertain τ_{network} from the frequency dependence of the dynamic moduli.^{43,44} In the present case, τ_{network} can be conveniently estimated from the reciprocal of ω associated with the maximum in the loss modulus, G'' , that occurs at the onset of the elastic plateau region.²⁰ The connectivity of the network can be expressed as a plateau or pseudoequilibrium modulus, G_N , given by the value of G' at ω corresponding to τ_{network} . Alternatively, G_N can be calculated by integrating across the maximum in G'' as follows:⁴⁵

$$G_N = \frac{2}{\pi} \int G'' d \ln \omega \quad (1)$$

The upper limit of this integration must be set to exclude the onset of the transition zone for concentrated polymer systems such as melts. Although the G_N values calculated from the above approaches differ slightly, they exhibit similar dependence on polymer concentration.²⁰

At experimentally accessible time scales shorter than τ_{network} , interchain connectivity is maintained as a consequence of hydrophobe association in micellar domains. In certain types of hydrophobically associating polymers, connectivity arises exclusively from interchain association of the hydrophobes.^{7,46} In other systems, however, chain entanglements also contribute to the network structure.⁴³ Recent theoretical treatments of associating polymers consider both scenarios.^{42,47,48} In the case of unentangled chains, the linear dynamics can be considered Rouse-like, modified by the presence of associative groups or stickers.^{42,47} In analogous fashion, the dynamics of entangled networks of associating polymers can be described by a similar modification of reptation theory.⁴⁸ The critical question of whether chain entanglements are significant in solutions of HASE polymers is considered in more detail below.

At time scales much longer than τ_{network} , the dynamic moduli are seen in Figure 2 to decrease according to a power-law relation. An interesting feature of these data is that a fully terminal response is not achieved even at the lowest experimentally accessible frequencies. Specifically, the exponents describing the frequency dependence of the moduli are much less than the values of 1 expected for $G''(\omega)$ and 2 expected for $G'(\omega)$. Note also that $\eta^*(\omega)$ does not attain a limiting value at low ω , in marked contrast to the behavior of hydrophobically associating polymers for which complete stress relaxation occurs at comparable time scales. An example of such a polymer is hydrophobically modified poly(acrylamide) prepared by micellar polymerization.⁴³ The apparent weak power-law dependence of $G'(\omega)$ and $G''(\omega)$ in Figure 2 persists for almost 3 decades in frequency and strongly suggests the superposition of a

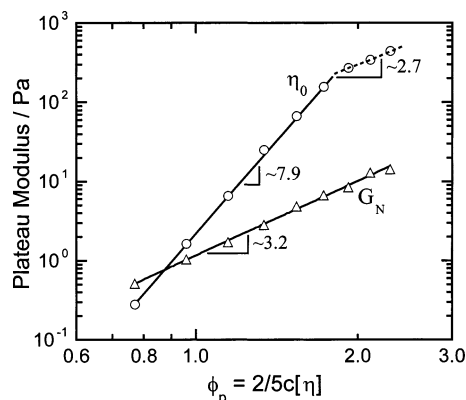


Figure 3. Scaling of the zero-shear viscosity and plateau modulus as functions of polymer concentration.

slow mode of stress relaxation in addition to that arising from the reversible network.

It is interesting to note at this juncture that a similar superposition of a single Maxwell mode over a power-law spectrum of relaxation times has been previously reported⁴⁹ for solutions of a telechelic associative polymer containing latex particles. In this case, power-law behavior dominates at long time scales and has been attributed to colloidal processes linked to diffusion of the latex particles. In a prior rheological study of HASE polymers, we have also noted¹⁹ a weak power-law dependence of $G'(\omega)$ and $G''(\omega)$, which we attributed to a microstructure composed of close-packed swollen microgel particles whose compressibility dictates the magnitude of the elastic modulus. A reasonable explanation of these unexpected observations clearly requires an improved understanding of the microstructure in systems containing carboxy-functional latex particles swollen in the presence of alkali.

The scaling behavior of the zero-shear viscosity, η_0 , and plateau modulus, G_N , as functions of the effective polymer volume fraction is presented in Figure 3. Examining the polymer concentration on a volumetric basis is useful in that it permits assessment of the extent of coil overlap and provides insight into whether chain entanglements are likely to impact viscosification. Rubinstein and Semenov⁴² have recently provided a thorough theoretical treatment of the linear rheology of comb-type associating polymers. In an earlier work, Leibler et al.⁴⁸ have considered the case of entangled networks in which the chains contain numerous associating groups. Both treatments assume that the stickers on the chains associate pairwise to simplify the description of the network structure in terms of the fraction of stickers that are free (unassociated) or involved in either intra- or intermolecular association. In contrast to these models, the polymer considered in the present study most likely forms micellar junctions in a fashion analogous to nonionic surfactants.¹⁶

With this difference notwithstanding, it is nonetheless useful to compare the predictions of these recent theories with the experimental results reported here. In particular, the formalism proposed by Rubinstein and Semenov⁴² predicts several distinct concentration regimes (for both unentangled and entangled systems) that reflect changes in network topology due to an increase in the concentration of associating polymer.⁵⁰ At very low polymer concentrations, single chains remain molecularly dispersed in solution. At higher concentrations, these chains aggregate into clusters that

are relatively long-lived, i.e., the lifetime of a typical cluster is long relative to its hydrodynamic relaxation time. Upon increasing the polymer concentration further, a polydisperse ensemble of larger "dynamic" clusters ensues. The lifetime of a cluster is much shorter than its relaxation time, in which case the structure of the cluster fluctuates, constantly breaking and reforming. This regime of dynamic clusters persists through the percolation concentration, ϕ^* , where a sample-spanning network forms. At yet higher concentrations, all the chains are incorporated into the network, but the connectivity remains low, with only a few critical bonds supporting an imposed stress. Under these conditions, many of the chains are not multiply-connected to the network, and association occurs predominantly between stickers located on the same chain. Only at very high concentrations do most chains become multiply-connected to the network.

Each of the concentration regimes described above can be identified by a different viscosity scaling relationship of the same format as the η_0 data shown in Figure 3. At polymer concentrations in slight excess of ϕ^* , a pronounced change in the concentration dependence of the zero-shear viscosity is predicted.^{42,47} In this unentangled regime, this change reflects a transition from predominantly intramolecular to intermolecular association as the polymer concentration is increased. Such a trend is analogous to the loop-bridge transition presumed to occur in solutions of telechelic associating polymers with alkyl end caps.^{7,8} A transition from intramolecular to intermolecular association with increasing polymer concentration has been previously suggested²⁰ for the polymer considered in the present study on the basis of the extent of shear-induced structuring achieved during nonlinear deformation.

If the concentration of polymer in the system is increased to a level such that the strands between stickers overlap, then most of the association interactions should occur between stickers on different chains. A network of this structure results at a volume fraction of ϕ_s .⁴² In this case, a much reduced concentration (c) dependence of the zero-shear viscosity is expected: $\eta_0 \sim c^{5.9}$ in the region of conversion of intramolecular to intermolecular association, and $\eta_0 \sim c^{1.1}$ once stickers associate exclusively between different chains. Such behavior has been observed⁴⁶ experimentally for solutions of graft copolymers composed of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) with acrylic acid. In the case of solutions consisting of entangled associating polymers, a similar change in the scaling behavior of η_0 becomes evident once the strands between intermolecularly associated stickers overlap. In this regime, further viscosification accompanies increasing polymer concentration because of an increase in entanglement density, and a scaling exponent of $15/4$ is anticipated.⁴² This scaling behavior has recently been observed⁴³ in the case of hydrophobically modified poly-(acrylamide)s possessing blocky hydrophobic sequences. At polymer concentrations below that required for strand overlap in entangled systems, a sharply pronounced change in the concentration dependence of the zero-shear viscosity is predicted,⁴² with $\eta_0 \sim c^{8.5}$.

It is interesting to note that the scaling exponents derived from Figure 3, 7.9 and 2.7, are reasonably close to those predicted for solutions of entangled associating polymers below and above the polymer concentration for strand overlap (ϕ_s): 8.5 and 3.75, respectively.⁴²

Careful consideration of the data, however, precludes entanglement as a mechanism for viscosification. Most notably, the effective volume fraction of the polymer $\phi_p = {}^2/5 c[\eta]$ in the concentration range examined (0.4–1.2 g dL⁻¹) does not exceed 2.5. In the case of solvated chains, ϕ_p is a measure of coil overlap and can be interpreted as the number of neighboring chains whose center of mass falls within the volume occupied by a given coil. Thus, in this concentration range, the polymer coils are only slightly interpenetrated, and entanglements are not expected to develop to a significant extent.

Further verification of unentangled HASE chains is obtained from the magnitude of G_N . The quantity G_N/kT is related to the chain contour concentration, ν_{eff} , a measure of the number density of elastically active strands in the network or, equivalently, the mechanical interaction density. The plateau modulus is also related to the number of steps in the primitive path of the chain (L/a), that is, the number of tube segments, by the following expression:⁴⁴

$$G_N = N_c \frac{L}{a} kT \quad (2)$$

Here L is the chain contour length, a is a dimension on the order of the mesh size of the network, and N_c is the number density of chains. The concept of a confining tube is valid only for values of $L/a \gg 1$. At the highest concentrations studied, L/a is estimated to be about 0.1 for the HASE polymer. Currently unreported results for HASE polymers prepared under similar conditions suggest that the \bar{M}_w of these polymers can typically be 2.5×10^6 Da. If this were the case, L/a would be ~ 1 at most, which would still be too low a value for reptation to occur. If the system were entangled, however, it would be impossible to distinguish rheologically between hydrophobic associations and topological entanglements, as both these types of interaction would contribute to G_N .

Our above estimates of coil occupancy and mechanical interaction density appear to preclude the possibility of entanglements in the system under study, in contrast to our previous interpretation of the behavior of this polymer.²⁰ In this respect, the change in viscosity scaling behavior (Figure 3) cannot be attributed to the overlap of strands between hydrophobes.⁴² It is also useful to note that EA/MAA copolymers for which \bar{M}_w is similar to that of the polymer of the present study exhibit a viscosity scaling relationship of the form $\eta_0 \sim c^{1.5}$ at similar levels of coil occupancy.³⁶ This would again preclude the existence of chain entanglements. Polymers without hydrophobes would be expected to show a scaling exponent close to the predicted value of $15/4$ in the entangled regime, the onset of which should occur at a value of ϕ_p in the range 5–10. Further work is therefore required to elucidate the changes in network structure underpinning the observed change in viscosity scaling.

B. Nonlinear Viscoelastic Response of the HASE Polymer. The nonlinear response of the HASE polymer solutions is illustrated in Figure 4. A series of sequential transitions from a linear response through weak shear thinning to shear-induced structuring is observed with increasing strain rate. The origin of shear-induced structuring in HASE polymers has previously been considered in detail elsewhere.²⁰ A noteworthy feature of Figure 4 is evident at high polymer concentrations (c

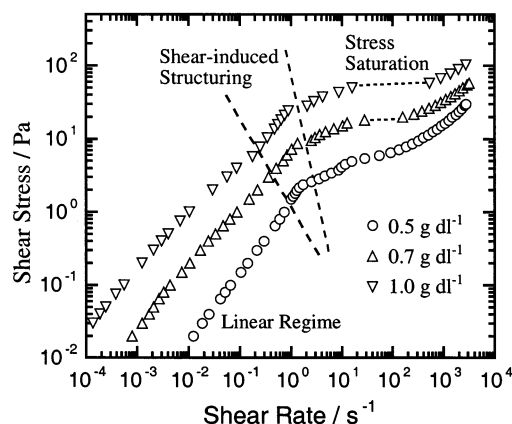


Figure 4. Nonlinear response of solutions of the HASE polymer expressed in terms of the shear stress as a function of the rate of deformation.

> 0.7 g dL⁻¹). In this regime, the flow curve exhibits a marked discontinuity. Because these data were acquired with a controlled-stress instrument, such a discontinuity demonstrates that flow occurs at constant stress. This behavior implies the onset of stress saturation wherein $\eta \sim \dot{\gamma}^{-1}$. These tests have been repeated on a controlled-strain instrument (RMS800), in which case a time delay of 45 s was applied at each strain rate prior to measurement of the shear stress (torque). Consistent with the data shown in Figure 4, the measured shear stress saturates to a constant plateau value, σ_p , at polymer concentrations above ~ 0.6 g dL⁻¹. This behavior is strikingly similar to that of wormlike surfactant micelles, for which a stress plateau is often observed^{51–53} in the flow curve.

Pronounced shear thinning at high strain rates in associating polymer solutions has been attributed to several phenomena. Previous studies have interpreted this characteristic in terms of nonaffine network deformation.⁵⁴ Alternatively, it has been related to the point at which the time scale of the imposed deformation becomes shorter than the rate of association formation, suggesting that the number of hydrophobic associations becomes depleted.³⁹ In this regard, it is again interesting to consider the similarities between the rheological response of HASE polymer solutions and that of wormlike surfactant micelles.^{51–53} Catastrophic shear thinning or stress saturation observed in these systems has been attributed to the development of shear-banding flow instabilities. Thus, in the constant-stress plateau, the system becomes heterogeneous, phase-separating into zones with different velocity gradients. This phenomenon is theoretically predicted for a purely mechanical flow instability by McLeish and co-workers,⁵³ who propose that the plateau shear stress, σ_p , and the plateau modulus measured in oscillatory shear, G_p' , are generally related by

$$\sigma_p = 0.67 G_p' \quad (3)$$

Equation 3 has been verified experimentally.^{51–53} Whereas the plateau stress is proportional to the steady-shear plateau modulus for the HASE polymer solutions in Figure 5, the relationship established here is $\sigma_p \sim 6G_N$, which deviates considerably from the predicted relationship above. The reason for this difference is presently unclear, but rheo-optical studies of wormlike micelles have detected⁵⁵ additional flow instabilities due to the formation of elongated microstructural elements

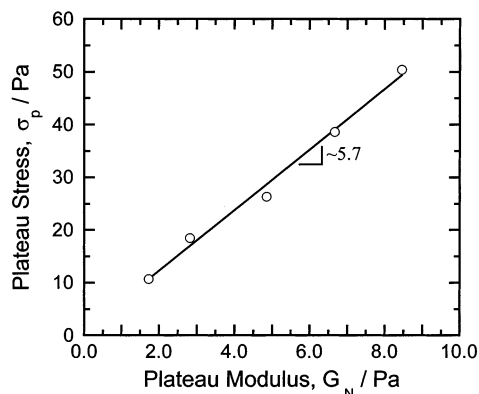


Figure 5. Variation of the plateau stress (measured in the region of stress saturation attained at high strain rates) with the plateau modulus determined under conditions of linearity.

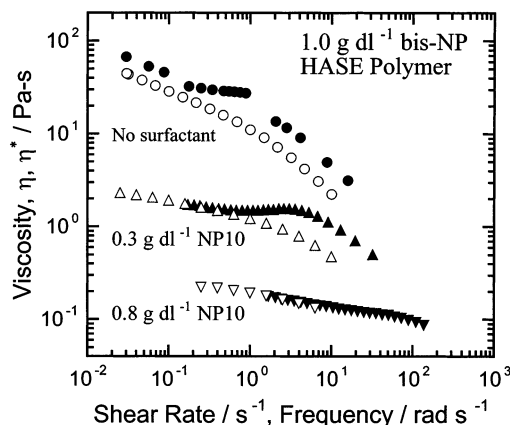


Figure 6. Cox-Merz plots for solutions of the HASE polymer containing various concentrations of the NP10 surfactant. Solid symbols correspond to the steady-shear viscosity (η), whereas open symbols correspond to the complex viscosity (η^*).

that align with the flow field. These oriented elements are presumed to form when the characteristic flow time is shorter than the micellar breaking time. Although it is difficult to provide a detailed mechanistic explanation for shear thinning in HASE polymer systems, possible considerations include (i) the persistence of hydrophobic associations at high strain rates,³⁹ (ii) mechanical and/or microstructure-induced flow instabilities,^{51–53,55} and (iii) nonaffine network deformation.⁵⁴ It is also interesting to note here that stress saturation has likewise been observed in solutions of poly(vinyl alcohol) and borate, another polymer system that exhibits transient associations.⁴¹ Flow instabilities have also been reported in oil-in-water microemulsions composed of a telechelic associating polymer,⁵⁶ as well as in cubic phases of block copolymer micelles.⁵⁷

C. Viscoelastic Response of the HASE Polymer with Nonionic Surfactants. Rheological data for solutions of the HASE polymer in the presence of the water-soluble surfactant NP10 are presented in Figures 6 and 7, whereas data collected from comparable solutions containing NP6, which exhibits limited water solubility, are provided in Figures 8–10. An increase in the concentration of the hydrophilic NP10 surfactant is accompanied by a pronounced reduction in the magnitude of the zero-shear viscosity, which is seen in Figure 6 to decrease by ~ 3 orders of magnitude over the range of surfactant concentration explored. Previous studies^{8,58,59} of hydrophobically associating polymers in the presence of anionic and nonionic surfactants at

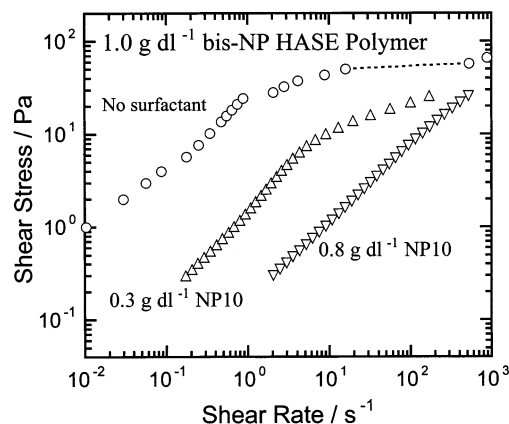


Figure 7. Effect of the addition of NP10 on the nonlinear response of the HASE polymer.

concentrations well above their critical micelle concentration (cmc) also report substantial viscosity reduction. Above its cmc, NP10 is anticipated to form small, spherical micelles. It immediately follows that polymer-bound hydrophobes might become incorporated in these micelles, forming mixed junction domains.^{8,58,59} Consequently, as the concentration of surfactant micelles in the system is increased, the overall functionality of the junction domains (i.e., the mean number of polymer-bound hydrophobes present in a given junction domain) is concurrently reduced. This loss in connectivity is reflected macroscopically as decreases in the magnitudes of G_N and η_0 .⁵⁹

Another apparent effect that occurs upon increasing the concentration of NP10 is a marked reduction in shear-induced structuring (see Figure 6). This observation is again consistent with the formation of mixed junction domains, as described above. Low concentrations of surfactant in solutions of comblike associative polymers can, in some cases, induce an entropically driven change in network topology, yielding an increase in intermolecular hydrophobic associations at the expense of intramolecular ones.^{8,58} This scenario is expected to promote an overall increase in the connectivity of the dynamic network and a corresponding increase in η_0 , as reported by Aubry and Moan⁵⁹ for a hydrophobically modified galactomannan ether with nonionic surfactant. Our previous photophysical study²⁰ indicates that the cmc of NP10 is well below the range of concentrations employed in the current study. In fact, the concentration of NP10 is over 2 orders of magnitude higher than the concentration of polymer-bound hydrophobes in the system, which results in the depleted network connectivity discussed above. Thus, a surfactant-mediated reduction in intramolecular polymer-polymer associations is consistent with the data in Figure 6 and the apparent elimination of shear-induced structuring. In similar fashion, high concentrations of the NP10 amphiphile effectively reduce intermolecular associations. This accounts for (i) the steady-shear response becoming more linear and (ii) the disappearance of the surfactant-free shear thinning/stress saturation regimes apparent in Figure 7. Therefore, interactions of the HASE polymer with the NP10 surfactant reveal a profound effect of hydrophobic interactions on network connectivity and molecular dynamics in associative polymer systems. We note here that, at high NP10 concentrations, the steady-shear response of HASE/NP10 solutions is surprisingly analo-

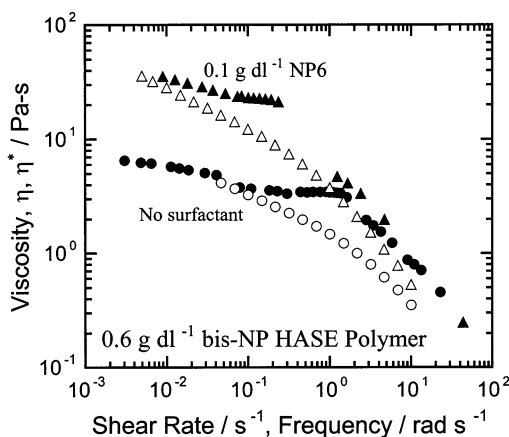


Figure 8. Cox–Merz plots for solutions of the HASE polymer with and without the addition of the NP6 surfactant. Solid symbols correspond to the steady-shear viscosity (η), whereas open symbols correspond to the complex viscosity (η^*).

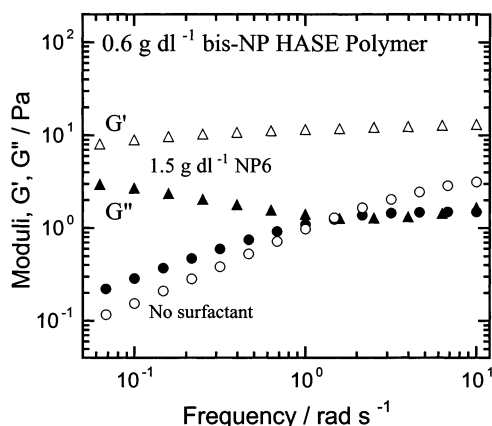


Figure 9. Frequency spectra of the dynamic moduli [$G'(\omega)$, $G''(\omega)$] measured for the HASE polymer solutions with and without the addition of NP6.

gous to that of alkali-swallowable poly(ethyl acrylate-*co*-methacrylic acid) latex prepared without macromer.^{17,19}

Selected steady-shear data for the HASE polymer with and without the NP6 surfactant are compared in Figure 8 and demonstrate that NP6 affects the HASE solution differently than its NP10 counterpart: η_0 is increased, and shear-induced structuring is preserved. At higher concentrations of NP6 shown in Figure 8 (1.5 g dL⁻¹), the system becomes progressively more structured and gel-like. Under these conditions, the possibility of shear fracture and the generation of flow instabilities preclude reliable characterization in steady shear, in which case we now turn our attention to dynamic experiments as a means of providing additional microstructural information. The NP6-induced behavior seen in Figure 8 is likewise evident in the frequency spectra of the dynamic moduli shown in Figure 9. Values of G_N derived from Figure 9 are included in Figure 10 and confirm that an increase in NP6 concentration promotes a systematic increase in G_N and, hence, network connectivity. An increase in NP6 content is also accompanied by a concurrent increase in the characteristic time, τ_{network} , which reflects a shift of the terminal region to progressively lower frequencies.

According to the data displayed in Figure 10, G_N increases nearly 2-fold as the concentration of NP6 is increased from 0.1 to 1.5 g dL⁻¹. More importantly, τ_{network} is observed to increase by about 2 orders of magnitude over the same concentration regime. This

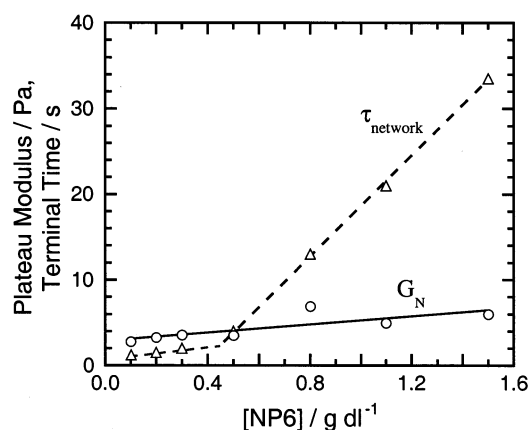


Figure 10. Influence of the addition of NP6 on the plateau modulus and network relaxation time of HASE polymer solutions.

surfactant-induced change appears to be principally responsible for the increase in viscosity achieved upon addition of this surfactant. These trends might, however, be underpinned by more complex phase changes induced by incorporation of an amphiphilic species of relatively low aqueous solubility.^{30,34,60} Surfactant phase behavior has been previously considered²⁴ regarding microstructural development in HASE polymer solutions containing a primary alcohol ethoxylate of low HLB (C₁₂EO₄). Nonionic surfactants with little ethoxylation can exhibit a rich variety of complex microstructures in the presence of water-soluble polymers. Specifically, dispersed uni/multilamellar vesicles (L_α^+) or “sponge”-type (L_3) bicontinuous microstructures can be produced.^{30,60} The thermodynamically stable microstructure will be influenced by such design considerations as the polymer and surfactant concentrations, as well as the surfactant HLB.

D. Microstructural Characteristics of the HASE Polymer with Nonionic Surfactants. Figure 11a is a TEM image of diluted HASE latex particles prior to dissolution in the presence of alkali. The discrete particles appear nonspherical, exhibiting an irregular “raspberry-like” morphology. Because only small numbers of particles are evident in this and complementary images, the particle size distribution cannot be ascertained. Rather, we note that several particles exhibit diameters of 300–400 nm, whereas smaller particles typically measure ca. 100 nm across. This difference in size scale might, however, reflect differences in the location of the fracture front as it propagated around the particles during specimen preparation. The fine internal structure of these particles appears complex and suggests that the particles grow by a coagulative mechanism in which large particles form by aggregation of numerous smaller particles measuring about 30 nm in diameter. In similar fashion, the influence of particle coagulation on the growth of latex particles has recently been explored in the copolymerization of ethyl acrylate and methacrylic acid.^{13,14}

Coagulation in an emulsion polymerization is augmented by the use of persulfate salts as free-radical initiators. If the initiator feed is continuous throughout the polymerization, the tendency for particle coagulation increases as the ionic strength of the aqueous medium increases, because the electrostatic double layers surrounding the growing particles become compressed. Such instability in the present work is corroborated by the observation that the concentrated HASE latex

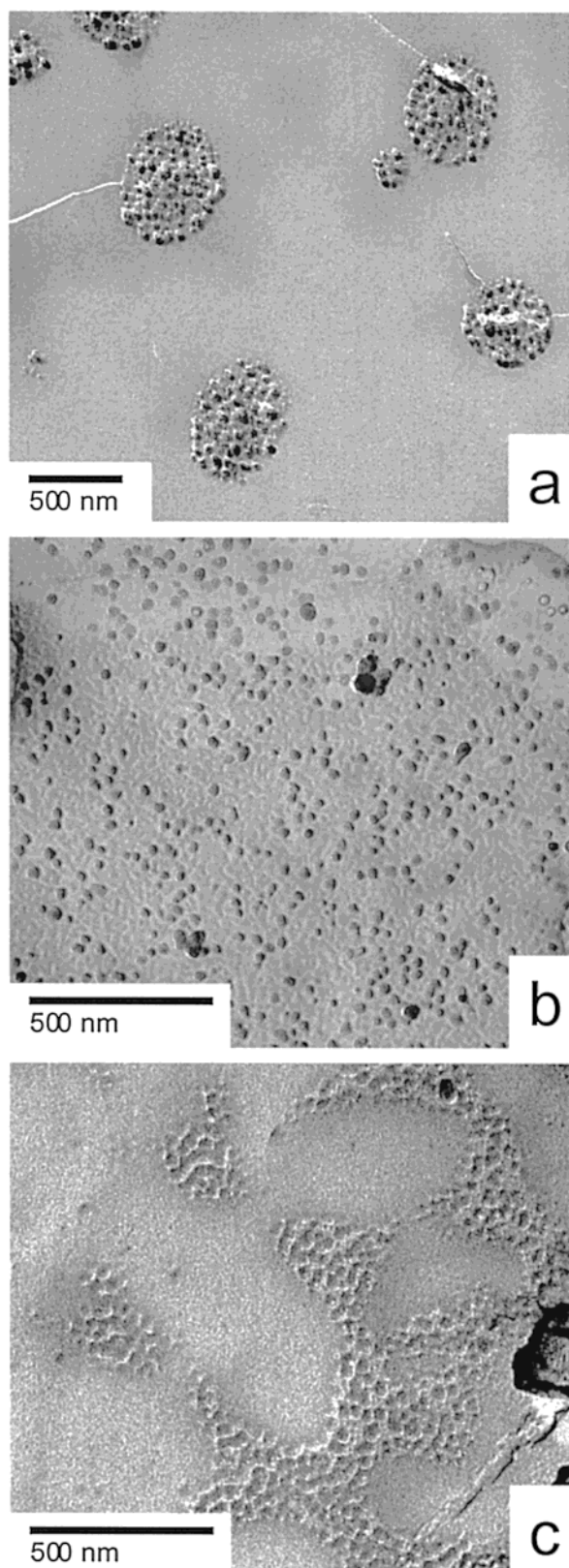


Figure 11. Cryofracture-replication TEM images of HASE polymer solutions with and without surfactant: (a) HASE latex prior to solubilization, (b) 1.0 g dL⁻¹ solution of the solubilized HASE polymer with 0.5 g dL⁻¹ NP10, (c) 0.6 g dL⁻¹ solution of the solubilized HASE polymer with 0.8 g dL⁻¹ NP6.

undergoes sedimentation upon storage. Samples in which excess serum electrolyte is removed by dialysis exhibit no such instability. While the present HASE polymer was prepared at a solids content of ~30%,

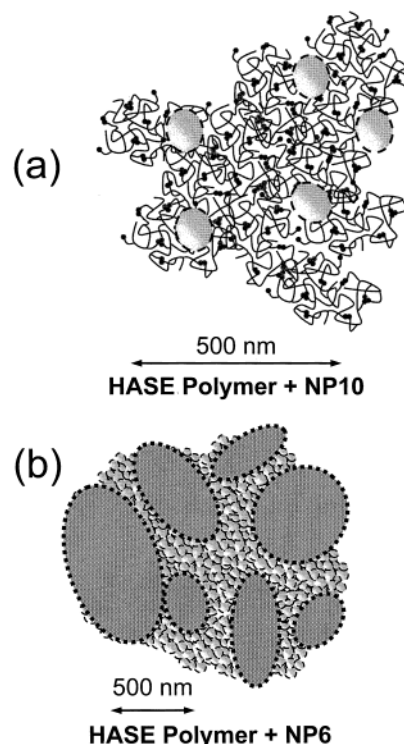


Figure 12. Schematic illustrations relating to the TEM micrographs displayed in Figure 11b and c: (a) HASE polymer with NP10 and (b) HASE polymer with NP6. In (a), aggregates measuring about 30 nm across and composed of an EA/macromer-rich polymer fraction develop in a matrix of a solubilized MAA-rich polymer fraction. In this case, NP10 is miscible and forms mixed junction domains with the polymer hydrophobes. In (b), the presence of polymer promotes depletion flocculation of NP6 micellar aggregates, in which case the system segregates into polymer-rich and surfactant-rich phases.

which is common in industrial practice, polymers with increased colloidal stability and smaller particle diameters (70–100 nm) can be prepared by reducing the solids content to ~15%.³⁶ Coagulative particle growth can be confirmed by recognizing that clusters of this type exhibit a distinct tendency to degenerate into smaller particles upon alkalization.^{13,14} By increasing the degree of neutralization, α , of the backbone carboxyl groups upon addition of alkali, the hydrodynamic radius (R_H) of the particles increases to a maximum of ~200 nm at $\alpha = 0.35$ –0.4. At higher α (~0.60), the swollen particles disintegrate into numerous smaller ones with $R_H \approx 90$ nm.⁶¹ In contrast, longer reaction times and increased solids levels hinder particle dissolution, presumably due to increased cross-linking, which can arise via chain-transfer reactions.¹³

Figure 11b displays the microstructure of a 1.0 g dL⁻¹ solution composed of solubilized HASE polymer in the presence of 0.5 g dL⁻¹ NP10. This image provides information regarding the microstructure of the solubilized polymer and confirms that the polymer and surfactant do not phase-separate. This observation is consistent with the rheological data presented earlier, in which NP10 is surmised to reduce molecular connectivity via the formation of mixed junction domains with the polymer hydrophobes. The image shown in Figure 11b reveals that considerable heterogeneity exists in systems consisting of solubilized HASE polymers, as a relatively large number of compact objects measuring about ~30 nm across are clearly visible. A schematic diagram of the microstructure is shown in

Figure 12a. Recall that the contrast in this image is provided by shadowing a fresh fracture surface with evaporated Pt. To enhance contrast prior to shadowing, the specimen has been briefly etched at $-100\text{ }^{\circ}\text{C}$ to remove (by sublimation) the top layer of vitreous ice from the fracture surface, consequently exposing microstructural features of interest. To assign the features evident in Figure 11b, it is instructive to consider prior morphological studies of solubilized HASE polymer conducted by complementary techniques, such as dynamic light scattering and pulsed gradient spin-echo (PGSE) NMR spectroscopy.

Several dynamic light scattering studies of HASE polymers indicate the existence of two populations of particles differing in their translational diffusion coefficients (D_0).⁴⁵ The "fast" particles are characterized by a D_0 value of about $1.2\text{--}1.5 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$, which corresponds to $R_H = 15\text{--}20\text{ nm}$. The slower population exhibits a hydrodynamic relaxation time at least an order of magnitude smaller, with D_0 decreasing to $(2\text{--}3) \times 10^{-12}\text{ m}^2\text{ s}^{-1}$ and R_H increasing to $80\text{--}100\text{ nm}$. These populations have been ascribed to single HASE polymer chains and clusters with up to ~ 5 chains, respectively. The latter result is derived from static and dynamic light scattering on the assumption that the refractive index gradients of the two particle populations are identical. Supporting studies of HASE polymer systems by PGSE NMR spectroscopy confirm the presence of two particle populations exhibiting translational diffusion characteristics similar to those listed above.³ However, NMR data also yield information about chemical constitution. Although the mean composition of purified HASE polymers determined by ^1H NMR spectroscopy is comparable to that of the monomer feed employed in the polymerization,³⁶ the faster particles are enriched in both macromer and ethyl acrylate. The slow particles, on the other hand, tend to be rich in methacrylic acid and depleted in macromer.

Such compositional heterogeneity has been verified by sample fractionation via precipitation from tetrahydrofuran (THF)/hydrochloric acid. Fractions similar in composition to the fast- and slow-diffusing particle populations exhibit diffusion characteristics similar to those identified above.³ Thus, it is reasonable to conclude that the fast species most likely represents hydrophobic chains exhibiting a compact conformation, which is consistent with heightened levels of macromer and ethyl acrylate. Moreover, the hydrodynamic size of the fast-diffusing species is in favorable agreement with the ca. 30-nm objects visible in the TEM image of the solubilized HASE polymer (see Figure 11b). Such compact, highly hydrophobic dispersions are anticipated to withstand fracture and subsequent surface etching. If the slow particles consist of highly swollen hydrophobic chains that are rich in methacrylic acid and depleted in macromer, it is less likely that these objects would be as clearly discernible (if detectable at all) as the more compact particles. This expectation is supported by Figure 11b, in which large particles possessing a hydrodynamic size of $\sim 200\text{ nm}$ are not visible, as well as recent attempts to image the mesoscopic structure in aqueous solutions of guar galactomannan. In this case, the guar galactomannan solutions, which exhibit rheological characteristics comparable to those of the present HASE polymer solutions (including complex modes of stress relaxation that persist over long time scales⁴⁴), appear homogeneous when imaged by cryo-

racture-replication TEM. The compositional heterogeneity deemed responsible for different particle populations reflects the synthesis of HASE polymers in a complex multiphase environment.^{3,15} In addition to generating fractions differing in overall composition, it is plausible that unexpected sequence distributions develop upon macroradical transfer from the aqueous phase.¹⁵ Recent photophysical studies, for instance, suggest that the distribution of ethyl acrylate in HASE polymers is "blocky."¹⁶

The TEM image provided in Figure 11c illustrates the microstructure of a solution of solubilized HASE polymer in the presence of 0.8 g dL^{-1} NP6. In this image, a textured semicontinuous, rather than dispersed, morphology is evident. Phase separation of mixtures composed of water-soluble polymers and surfactants is well documented^{62,63} as a consequence of depletion-type interactions. Depletion flocculation and phase separation in the case of surfactant micelles occur via a mechanism that is similar to that responsible for the flocculation of colloidal particles. Thus, the large globular features measuring up to ca. $1\text{ }\mu\text{m}$ across are believed to constitute a surfactant-rich phase, whose precise microstructure is ill-defined. Although bilayered dispersions (vesicles, designated L_v) might develop when nonionic surfactants interact with linear alkyl hydrophobes at relatively high concentrations,⁶⁴ the surfactant-rich phase seen in Figure 11c most likely consists of flocculated micelles.⁶⁵

Micelle flocculation has been observed⁶⁵ to occur at low concentrations of ethoxylated nonionic surfactants at temperatures above the cloud point. Unfortunately, no complete phase diagram for NP6 currently exists to the best of our knowledge. However, at low concentrations (as in the present study), the polymer-free microstructure of C_{12}EO_8 consists of large micellar aggregates (W phase) coexisting with spherical micelles (L_1 phase), according to cryo-TEM.⁶⁵ In general, the addition of polymeric species to aqueous solutions of nonionic surfactants serves to lower the cloud point,⁶³ but the microstructure of the surfactant-rich phase formed upon such mixing is usually similar to that of the pure surfactant.⁶² Associative polymers, which can bind surfactants within their junction domains, are less intrusive in terms of depletion flocculation. Since the cloud point of NP6 in water is most likely well below the temperature at which the present analysis was conducted ($20\text{ }^{\circ}\text{C}$), we conclude that the addition of HASE polymer promotes extensive flocculation of the micellar aggregates and that viscosification ensues through phase segregation into polymer- and surfactant-rich phases (see Figure 11c). A schematic diagram illustrating the proposed microstructure of HASE/NP6 derived from combined rheological and morphological considerations is provided in Figure 12b.

Conclusions

The present study illustrates the complex nature of HASE polymers, alone and in combination with nonionic surfactants. Regarding the polymer solutions alone, such behavior most likely reflects a complex interplay between compositional heterogeneity within the polymer and the mechanism of particle growth during synthesis. Compositional heterogeneity in polymers of this type is consistent with differences in the water solubility of methacrylic acid and ethyl acrylate, which is further complicated by coagulative particle growth. Propagation

of macroradicals within particles generates a relatively hydrophobic fraction enriched in ethyl acrylate, which promotes the formation of compact aggregates upon solubilization in an alkaline medium. Existence of slow modes of stress relaxation implies the existence of HASE polymer aggregates, which can be visualized by TEM. The concentration-dependent linear rheological response of HASE polymer solutions can be compared, at least qualitatively, to predictions from contemporary theoretical treatments. Of particular interest is the scaling behavior of the zero-shear viscosity, which is described by two regimes across the concentration range examined. The first is most likely attributed to the conversion of intramolecular to intermolecular associations, whereas the physical origin of the second regime is not yet firmly established.

Upon addition of a nonionic surfactant, the rheological and morphological characteristics of the HASE polymer solutions are substantially altered, depending on the compositions of the surfactant and solution. In this work, we have examined the effects of two ethoxylated surfactants that exhibit different degrees of solubility in water. Addition of the surfactant that is partially water-soluble to a HASE solution results in not only an increase in shear stress with increasing surfactant concentration and shear rate, but also an increase in the shear rate range over which shear-induced structuring and stress saturation occur. In marked contrast, the completely soluble surfactant systematically reduces the shear stress of the solution with increasing surfactant concentration and shear rate. Moreover, at high surfactant concentrations, evidence for shear-induced structuring and stress saturation is completely eliminated. These unexpected results are interpreted in terms of differences in mixed micellization of the HASE polymer and surfactant. Examination of these HASE/surfactant solutions by TEM reveals that the HASE particles aggregate into discrete particles in the presence of the fully soluble surfactant but form a semicontinuous microstructure suggestive of phase separation in the presence of the partially soluble surfactant. By simultaneously probing the rheological behavior and real-space morphology of these highly associative polymer solutions, we have demonstrated that an improved physicochemical understanding of these complex systems can be achieved, which is of paramount importance in establishing design paradigms.

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