Effect of a Nonionic Surfactant on the Flow Dynamics of a Model HASE Associative Polymer

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The interaction between a model hydrophobically modified alkali soluble emulsion polymer and a nonionic surfactant $C_{12}EO_4$ is investigated. A huge synergistic increase in the viscosity over 10,000-fold is demonstrated when the surfactant concentration is increased to 0.1 M, due to the formation of mixed micelles of surfactant hydrophobic tails and polymer hydrophobic groups. Incorporating surfactant molecules increases the number of mechanically active junctions in the polymer network and thus reduces the functionality of the hydrophobic groups. In the intermediate range of surfactant concentrations (0.001–0.01 M), the parallel superposition of steady shear and dynamic testings reveal that the microstructure of the network is affected by stress even in the low-shear plateau region of the flow curves. The number of network junctions increases substantially with applied shear stress within the low-shear viscosity region, although the longest relaxation time of the polymer–surfactant systems is greatly reduced. At very high surfactant concentrations (> 0.01 M), polymer hydrophobes interact with the surfactant to form a stiff gel-like structure. Surfactant molecules form a mixed bilayer structure with the polymer hydrophobes. These stronger network junctions cause a larger increase in both the viscosity and longest relaxation time of the system. Thus, adding a nonionic surfactant can effectively enhance flow properties of the associative polymer depending on the amount of surfactant used.

Introduction

Water-soluble associative polymers are currently gaining importance as thickeners, or viscosity modifiers, in a number of waterborne applications in technology ranging from paints to paper coatings. The recently developed hydrophobically modified alkali-soluble emulsion (HASE) polymers (Shay et al., 1985, 1989a,b; Jenkins et al., 1996) are increasingly being used to replace the long-chain cellulosic polymers due to their enhanced performance and economic advantages. HASE polymers generally offer excellent viscosity building, wide formulation latitude, excellent biostability, and ease of dosing and are supplied as a high solids latex, free of organic cosolvents. In the coating applications, the addition of surfactants can be potentially beneficial in formulating high performance systems, or in reducing formulating cost by improving thickener efficiency (Jenkins and Bassett, 1997).

Hydrophobically modified alkali-soluble associative polymers generally consist of a poly(methacrylic acid) backbone, onto which hydrophobic macromonomers are attached in a random or comblike structure. In an alkaline solution, the hydrophobic moieties of the polymers associate dynamically with one another to form transient or reversible hydrophobic junctions. Beyond the overlap concentration, the polymer formsa network consisting of both intra- and intermolecular hydrophobic associations, yielding a large increase in the solution viscosity as compared to the unmodified polymers without the hydrophobic groups (Aubry and Moan, 1994).

The interactions of surfactants and polymeric systems have been a subject of interest in recent times and a number of review articles have appeared in the literature: see, for example, Goddard and Ananthapadmananbhan (1993) and Winnik and Regismond (1996). Other studies, such as those by

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Petit et al. (1997), Jenkins and Bassett (1997), English et al. (1996), Persson et al. (1996), Aubry and Moan (1996), Loyen et al. (1995a,b), Zhou (1995), Annable et al. (1994), Hulden (1994), and Senan et al. (1994), are aimed specifically at associative polymer–surfactant systems. For the alkali-soluble hydrophobically modified associative polymers, the amount of research done is still very limited; nonetheless, it is known that the addition of surfactants can affect the flow dynamics of associative polymers to a different extent. Surfactants can either increase, increase to a maximum and subsequently decrease, or decrease the viscosity of associative polymers, depending on the structure. The interactions of the comblike associative polymers with ionic surfactants generally result in an increase in the rheological properties of the solution to a maximum, followed by a decrease to the surfactant concentration increases beyond its critical micelle concentration (CMC) (Seng, 1997; Petit et al., 1997; Senan et al., 1994). This observation is similar to that found for the telechelic-type (or HEUR) associative polymers with hydrophobic groups attached to both ends of the long polyethylene oxide backbone (Tarng et al., 1996; Annable et al., 1994; Hulden, 1994). The increase in viscosity and moduli at low surfactant concentrations is known to be due to the strengthening of the polymer hydrophobic junctions by the binding of the surfactant hydrophobic tails. At surfactant concentrations beyond the CMC, the polymer hydrophobes are saturated by the surfactant molecules forming small micelles around them, thus hindering the hydrophobic groups from associating with others. Hence the network structure is destroyed, resulting in a dramatic decrease in the solution viscosity. In extreme cases, where all the associative junctions are disrupted, the polymer network is broken into small clusters or individual chains and the solution viscosity is the same as that of polymer without association (Tarng et al., 1996).

However, the interactions of HASE polymers with nonionic surfactants have generally exhibited a more complex behavior. (Tanaka et al., 1992; Jenkins and Bassett, 1997). Nonionic surfactants can either cothicken or lower the viscosity of HASE polymers, depending on the hydrophilic–lipophilic balance (HLB) of the surfactant, as well as on the structure of the hydrophobic tail of the surfactant relative to the polymer hydrophobic group (Jenkins and Bassett, 1997; Petit et al., 1997). The dramatic difference in the flow dynamics of the polymer must come either from changes in the functionality of the network junctions, the strength of the associative junctions, or from an increase/decrease in the average number of these junctions, or a combination of any of these factors (Rubenstein and Dobrynin, 1997).

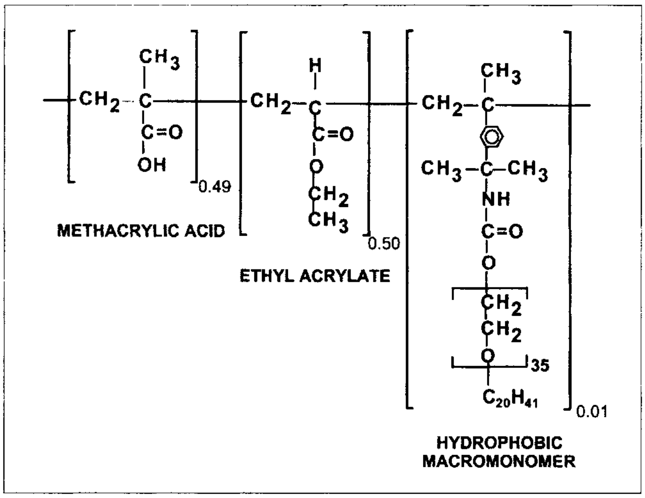

Figure 1. Chemical structure of model HASE polymer, with mole ratio of $X/Y/Z = 49.1/50.0/0.9$ and $m = 35$.

The present work investigates the interaction between a well-characterized model associative HASE polymer and a nonionic surfactant of the alkyl poly(oxyethylene) glycol type. The polymer–surfactant interaction is studied in terms of the solution's rheological properties. The effects of surfactant concentration on the flow properties are investigated, and the effect of applied shear stress on the viscoelastic properties are examined as a means of elucidating the network structure of the polymer–surfactant systems.

Theory

The theory of transient networks was first introduced by Green and Tobolsky (1946). It was an extension of classic rubber elasticity theories that account for entanglements or reversible physical bonds. The theory predicts a constant steady-shear viscosity of

$$\eta(\dot{\gamma}) = \eta_0 = \tau G_\infty, \tag{1}$$

where the relaxation time τ is the reciprocal of the bond breaking and reformation rate, and G_∞ is the high-frequency or plateau modulus. The plateau modulus is related to the number density of effective or elastic chains, υ_{eff}, by the relationship

$$G_\infty = \upsilon_{\text{eff}} RT, \tag{2}$$

where R is the gas constant and T the absolute temperature. Thus if the plateau modulus is known, the mechanically active junctions in the system can be estimated.

Experimental Studies

Material used

The associative polymer used (designated RDJ35-20) is a HASE polymer consisting of a backbone of ethyl acrylate and methacrylic acid. Attached to this backbone by a urethane linkage (through an unsaturated isocyanate) are associative macromonomers consisting of a 35-mol ethoxylate chain end-capped with an eicosanyl ($C_{20}H_{41}$) hydrocarbon group. The incorporation of the associative macromonomers along the polymer chain is expected to be random, as discussed in Tirtaatmadja et al. (1997b). The chemical structure of the $C_{20}H_{41}$-hydrophobe HASE polymer is given in Figure 1, with the mole percentages of the ethyl acrylate/methacrylic acid/macromonomer, that is, the ratio $X/Y/Z$, being 49.1/50.0/0.9. The polymer was synthesized from the emulsion copolymerization process detailed in Jenkins et al. (1996) and Tirtaatmadja et al. (1997b). The only difference from the described procedure is that the present series of HASE polymers has been synthesized at a total solids content of 10 wt.

% (instead of the 30 wt. % used previously). Determining the molecular weight of the polymer is a difficult task due to the association of the hydrophobic end groups even in very dilute solutions (Jenkins et al., 1996). Seery et al. (1992) conducted light scattering studies on solutions of a polyacrylamide containing small amounts of the comonomer, 2-(*N*-ethylperfluorooctanesulfonamido)ethyl acrylate, in which the addition of a surfactant enabled them to observe single-chain behavior. We are exploring this phenomenon together with Winnik and Macdonald's group at the University of Toronto, using light scattering, fluorescence spectroscopy, and pulse gradient NMR. Some success has been achieved in removing the associations by using cyclodextrin (Ou-Yang, personal communication, 1997), and more work is in progress at our laboratory. From the intrinsic viscosity value, however, the nominal molecular weight of the polymer has been estimated to be of the order of 200,000. Based on this value and the mole percentages just given, the number of hydrophobes is estimated to be between 18 and 20 per polymer chain (Tirtaatmadja et al., 1997b).

After synthesis, the polymer latex was cleaned by dialysis and final samples containing 0.5 wt. % polymer and various concentrations of the nonionic surfactant were prepared in a 10^{-4}-M KCl solution. The polymer, either in its pure state or in the presence of the surfactant, was solubilized in an alkaline aqueous solution using 2-amino-2-methyl-1-propanol, AMP-95 (supplied by Angus Chemical Co.), at a level of 0.006 mol/g of polymer, the final pH of all solutions being between 9 and 9.5. The nonionic surfactant used was a polyethoxylated dodecanol, containing a nominal 4-mole ethylene oxide, that is, $C_{12}H_{25}O(CH_2CH_2O)_4H$ (supplied by Rhone-Poulenc under the tradename Rhodasurf L-4), referred to here as RL-4. The surfactant is generally designated $C_{12}EO_4$, but it possibly contains a fairly broad distribution of the ethylene oxide consisting of between 3 and 6 mol of CH_2CH_2O per surfactant. The $C_{12}EO_4$ surfactant has a low CMC of about $4\text{-}8 \times 10^{-5}$ mol·L^{-1} (Rosen, 1978; Van Os et al., 1993). Solutions containing the 0.5 wt. % model HASE polymer, with concentrations of the nonionic surfactant from 10^{-4} M to 0.1 M, have been prepared and used in this work.

Rheological measurements

Two rheometers were used to measure the properties of the associative polymer–surfactant systems: a Contraves Low-shear LS40 and a controlled stress Carri-Med CSL500. For the Contraves LS40, a concentric cylinder (with an outer cup diameter of 12 mm and a gap of 0.5 mm) was used. For the Carri-Med CLS500, three different geometries were used: a 2-cm- and a 4-cm-diameter cone-and-plate system and a double concentric cylinder (with an inner cup diameter of 40 mm and both radial gaps of 0.34 mm). In the controlled stress rheometer, a specific stress was applied to the test sample, and the strain was measured over a 5-s interval, from which the strain rate was computed. This value was compared with the previous strain rate, and when the average strain rate over three consecutive intervals did not deviate by more than 5%, it was assumed that an equilibrium viscosity condition had been reached. For the polymer in the 0.1-M RL-4 solution, however, its viscosities in the low shear conditions are very high, and hence the measured shear rates are usually very low and subject to large uncertainties. Its shear viscosity was determined by conducting creep experiments at each applied stress for 10 min, and the slope of the strain vs. time curve was taken as the average shear rate from which the viscosity was determined.

In addition to conventional steady shear and dynamic measurements, superposition of oscillation onto steady shear flows (Tirtaatmadja et al., 1997a,b) has been used. In this technique, an oscillatory stress of frequency ω is superimposed onto a steady shear stress of magnitude σ_s, and the output strain measured. By resolving the strain into its steady shear and oscillatory components, the viscoelastic storage and loss moduli at any applied shear stress of σ_s, such as $G'(\sigma_s, \omega)$ and $G''(\sigma_s, \omega)$, can be determined in the usual manner. From the measured dynamic properties, an estimate of the longest relaxation time τ_x of the associative polymer–surfactant systems at any applied stress can be determined from the relaxation time function, which is given by

$$\tau_X(\sigma_s, \omega) = \frac{G'(\sigma_s, \omega)}{\omega^2 \eta'(\sigma_s, \omega)}, \tag{3}$$

where $\eta'(\sigma_s, \omega)$ is the dynamic viscosity at the applied stress of σ_s, or $= G''(\sigma_s, \omega)/\omega$. The maximum in the $\tau_X(\sigma_s, \omega)$ curve, which corresponds to the terminal region in the G' and G'' plots, gives an estimate of the longest relaxation time of the solution at the applied stress σ_s.

In addition to parallel superposition, orthogonal superposition can also be used to study the microstructural evolution of the materials under shear. Vermant et al. (1998) have recently reported a comparison between both techniques and concluded that orthogonal superposition can be related more directly to the microstructure than the parallel superposition technique. They also showed that the experimental values of the moduli obtained from the parallel and orthogonal superposition measurements were related to each other as derived using the K-BKZ model. Despite the fact that the main and the imposed parallel shear fields are coupled for parallel superposition measurement, qualitative information on the structural evolution under shear can still be inferred from such studies.

For cases where no terminal region is detected within the experimental frequency range, the relaxation time is taken to be the inverse of the frequency at the point of interception between the G' and G'' curves. This is true for Maxwell-type viscoelastic behavior, but for the systems that do not follow Maxwell behavior, the treatment will probably lead to lower values of the longest relaxation time, but the value obtained should be adequate for the comparison of different solutions.

The equilibrium shear modulus G_N^0 or plateau modulus G_∞ can be determined from the plateau value in the $G'(\omega)$ curve at high frequencies (Ferry, 1989). The number of mechanically active junctions υ_{eff} can then be determined from the G_N^0 value via the relationship (Eq. 2):

$$G_N^0 = \upsilon_{\text{eff}} RT. \tag{4}$$

For all the samples tested, strain-amplitude sweep experiments were carried out to determine the range of amplitude for which the dynamic response is within the linear viscoelastic region. All dynamic property measurements were then conducted using a strain amplitude within this region. The rheological properties of all associative polymer–surfactant systems have been measured at 25°C.

Results and Discussion

In an alkaline solution, the methacrylic acid of the HASE polymer is ionized and the electrostatic repulsive force caused by negative charges along the chain backbone makes the polymer molecules expand. The model HASE polymer becomes solubilized in the aqueous solution at a pH of approximately 6. At concentrations above the overlap value, that is, approximately 0.35 wt. % for the polymer with $C_{20}H_{41}$ hydrophobe (Seng, private communication, 1997), the solution viscosity increases significantly upon solubilization and remains constant between pH 7 and 13 (Kumacheva et al., 1997). At the high pH condition, the hydrophobic groups of the expanded polymer chains interact with those of neighboring chains to form temporary or reversible hydrophobic junctions that may involve several polymer chains. This is depicted and shown later in Figure 6a. The polymer forms a 3-D network, which may span the whole volume if the concentration is sufficiently high.

At a concentration slightly above the overlap value, the 0.5 wt. % HASE polymer displays a slight shear-thinning characteristic in its flow curve, with a low shear viscosity of 0.18 Pa·s (see Figure 2). This viscosity is almost two orders of magnitude higher than the polymer without hydrophobe, that is, with a Newtonian viscosity of 0.004 Pa·s (Seng, 1997), and must be due to the formation of a network of hydrophobic junctions, as discussed earlier.

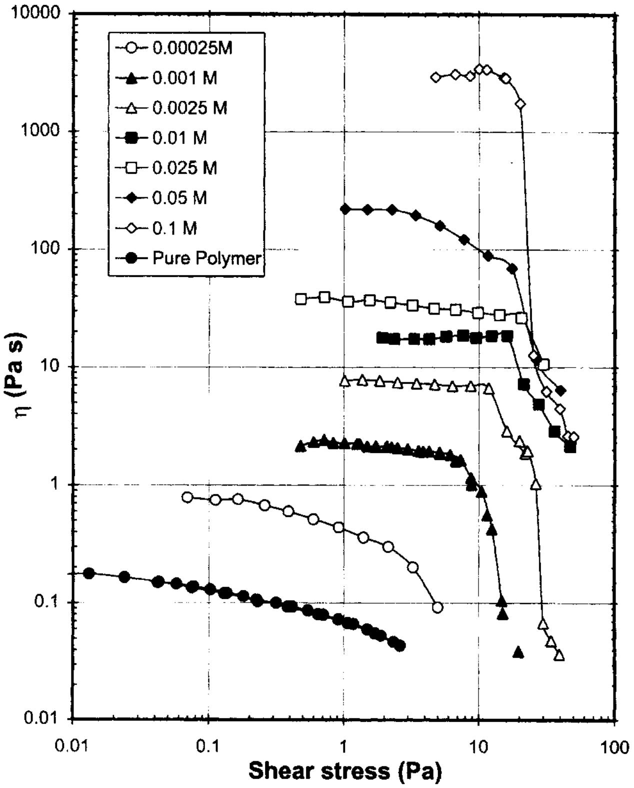

Figure 2. Steady shear viscosity as a function of shear stress of the 0.5 wt. % HASE polymer in different concentrations of the nonionic surfactant (RL-4).

Effects of surfactant concentration

The steady shear viscosity and dynamic (storage and loss) moduli of the model HASE polymer with increasing surfactant (RL-4) concentrations are shown in Figures 2 and 3, respectively. The addition of the nonionic surfactant (RL-4) to the HASE polymer causes a monotonic increase in both the viscosity and moduli of the solution up to the surfactant concentration of 0.1 M. There is an increase of up to some five orders of magnitude in the low-shear viscosity of the HASE polymer as the concentration increases to 0.1 M. This monotonic increase in viscosity with surfactant concentration is also found for the interaction of a HASE polymer (containing complex hydrophobes) with a nonionic surfactant containing two nonylphenyl substituents in its hydrophobic tail (Jenkins and Bassett, 1997) and a 6-mole ethoxylated nonylphenyl surfactant (English et al., 1996). In the mixed polymer–surfactant system, the surfactant hydrophobic tails combine with

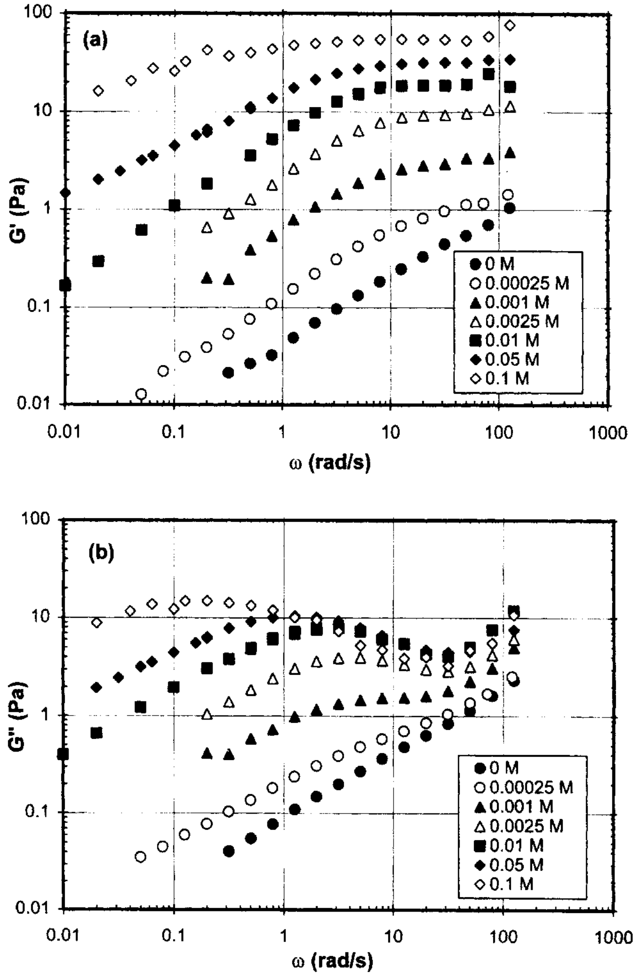

Figure 3. Dynamic moduli as a function of frequency of the 0.5 wt. % HASE polymer in different concentrations of the nonionic surfactant (RL-4): (a) storage modulus; (b) loss modulus.

the polymer hydrophobes to form mixed aggregates or junctions (see Figure 6b). Due to steric hindrances and entropic considerations, however, these network junctions must rearrange themselves in such a way that, as the surfactant concentration increases, there is an increase in the number of junctions. Hence the strength of the polymer network is enhanced, as demonstrated by the increase in activation energy from 50 to 75 kJ/mol when the nonionic surfactant concentration was increased from 0 to 0.01 M (Tirtaatmadja et al., 1997c). In addition, it was observed that both the steady shear viscosity (Figure 2) and moduli (Figure 3) of the solutions increased significantly. Despite its high viscosity level, however, the polymer–surfactant system does not exhibit a yield stress; this is attributable to the dynamic nature of the network junctions. Mast et al. (1993) have reported a study on the behavior of a low molecular weight model HEUR associative polymer in concentrated surfactant systems. They observed that the low shear viscosity and the moduli are all higher for low molecular weight HEUR than with a polymer of high molecular weight. Based on their results, they concluded that the thickening and viscoelastic behavior are related to the increase in hydrodynamic volume and not in a network, which is contrary to the results obtained for our present HASE polymer in a nonionic surfactant system.

Figure 2 shows that at surfactant concentrations in excess of 0.001 M, the flow curves show a distinct region of almost constant viscosity at low shear stress, followed by a drastic drop at higher stresses. The polymer network is totally destroyed when subjected to a certain applied stress, the value of which increases with increasing surfactant concentration. This reinforced the fact that the strength of the network must increase as the concentration of the nonionic surfactant is increased to the maximum value investigated.

The catastrophic drop in the viscosity at a certain shear stress is similar to that observed by Aubry and Moan (1996) for the solutions of hydrophobically modified (hydroxypropyl) guar in the presence of a nonionic surfactant (polyoxethylated octyl phenol–Triton X-100). However, the general trend of Aubry and Moan's results showed that there is a maximum in the viscosity at a surfactant concentration slightly above its CMC, followed by a decrease in the viscosity level of the unmodified polymer at higher concentrations. This is similar to the observations of the interactions of HASE polymers with ionic surfactants, such as SDS (Seng, private communication, 1997). The decrease in the viscosity above the CMC is due to the formation of small spherical surfactant micelles surrounding the polymer hydrophobic groups, preventing them from associating with others to form network junctions; hence, the drop in viscosity at higher concentrations.

On the other hand, the $C_{12}EO_4$ nonionic surfactant used, as well as others that have short ethylene oxide length in comparison with the hydrophobic groups, generally have a limited solubility in aqueous solution, and are known to form a lamellar structure above room temperature (Mitchell et al., 1983). With the addition of the $C_{12}EO_4$ nonionic surfactant up to many orders of magnitude in excess of its CMC, the viscosity of the polymer–surfactant systems continues to increase up to the highest concentration of 0.1 M. Hence the mechanics of association of this surfactant with the HASE polymer must be different from that of the ionic surfactants.

The storage and loss moduli of the HASE polymer with a varying amount of RL-4 surfactant are also shown in Figures 4a to 4d, where the G' and G'' curves for each solution are plotted together. The pure HASE polymer solution (Figure 4a) displays a viscoelastic fluid behavior, with G' being lower than G'' for the whole frequency range measured. With increasing surfactant concentrations (Figures 4b and 4c), the polymer–surfactant systems become more like a physical gel, with the G' values being higher than G'' at high frequencies, and G' also displaying a broader constant plateau of increasing value. At the highest surfactant concentration of 0.1 M (Figure 4d), G' is always higher than G'' and both remain almost constant over the entire range of frequencies measured. This behavior is characteristic of a strong gel and is observed as long as the characteristic relaxation time of the system is longer than the process time, that is, time per cycle of oscillation.

The observed viscoelastic behavior of the HASE polymer (Figures 3 and 4) is very different from those of the telechelic type of associative polymers, that is, the HEUR polymers with poly(ethylene oxide) chain end-capped with a hydrophobic group. For these latter polymers, the polymer chains exist either in the loop formation wherein both ends reside within the same aggregate of hydrophobic junction or as a bridge joining two junctions. The network dynamics of the HEUR system can be represented by a single Maxwell relaxation time; this time is related to the dissociation time of the hydrophobes from the aggregates (Annable et al., 1993; Jenkins, 1990; Tanaka and Edwards, 1992).

For the HASE polymer, the viscoelastic behavior clearly indicates a spectrum of relaxation times, with the longest time expected to be much larger than the Maxwell values found for the HEUR polymers. Hydrophobic associations are likely to exist at several sites along the HASE chains due to the larger number of hydrophobic groups attached randomly along the backbone. The mechanics of the associations and the dynamics of network relaxation when subjected to shear are thus expected to be more complicated compared to the HEUR system. The hindered reptation model introduced by Leibler et al. (1991) with two main relaxation times may be more appropriate for the HASE polymers (English et al., 1997; Tirtaatmadja et al., 1997b; Aubry and Moan, 1994). In this model, the terminal or longest relaxation may be interpreted as the time for a polymer chain to disengage from the network by letting go at several aggregated points. The second and much shorter relaxation time of the hindered reptation model is related to the dissociation of individual hydrophobes from the associative junctions, and the value can be determined from the second intercept of the G' and G'' curves at higher frequency, in the transition region. Experimentally this frequency is probably too high to be measured by the available instruments.

Aubry and Moan (1994) contended that the dissociation time of the hydrophobes from the junctions can be determined at the point where the catastrophic drop in the shear viscosity occurs, that is, t_c = ratio of the viscosity just before the catastrophic drop to the shear stress where the drop occurs, which is when the rate of junction destruction is faster than the rate at which it can be reformed. The authors found t_c to be proportional to the polymer concentration to the power of 1.7 (Aubry and Moan, 1994), but it is independent

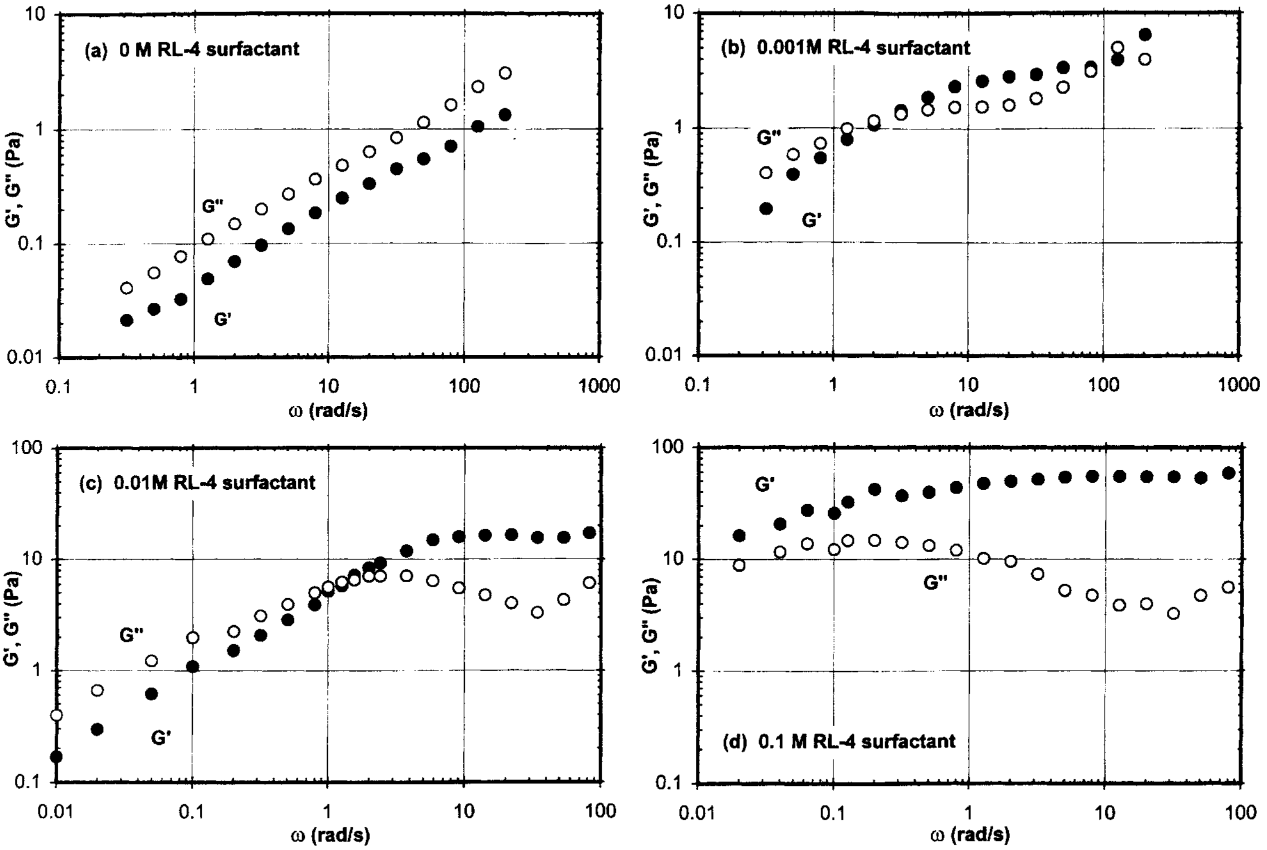

Figure 4. Storage and loss moduli of the 0.5 wt. % HASE polymer in: (a) 0 M surfactant; (b) 0.001 M; (c) 0.01 M; (d) 0.1 M nonionic surfactant (RL-4).

of the added nonionic surfactant concentration (Aubry and Moan, 1996). For our systems, the values of t_c cannot be determined very accurately because of the uncertainty in identifying both the viscosity and stress where the drop in viscosity occurs. It has been estimated, however, that for our HASE–nonionic surfactant systems between the concentrations of 0.001 and 0.01 M, t_c is of the right order of magnitude, that is, 0.05 s compared to a value of 0.1 s found for the modified (hydroxypropyl) guar of Aubry and Moan (1996). This value seems to increase with surfactant concentration.

The low shear viscosity η_0, plateau modulus G_N^0, and the longest relaxation time τ_X of the polymer–surfactant systems are plotted as a function of surfactant concentration in Figure 5a, and as a function of υ_{eff}, the effective junction density, in Figure 5b. The plateau modulus, or G_N^0, was determined from the plateau value of the G' curves at high frequency in the cases where such a plateau exists, or else it is estimated from the inflection point in the G' curves. The longest relaxation time τ_X was obtained from the inverse of the frequency at which the G' and G'' curves intercept. For non-Maxwellian fluids, the τ_X values determined this way are generally much lower than the values obtained from the terminal values of the G' and G'' curves. This fact was confirmed for the cases of HASE polymer–surfactant systems with superimposed shear stress wherein the terminal regions are within the experimental frequency range. However, the τ_X values obtained from the G' and G'' intercepts should be adequate for comparisons between the HASE-surfactant systems with different surfactant concentrations.

From Figure 5a, it is apparent that both the η_0 and G_N^0 curves are linearly proportional to surfactant concentration, C_S, up to 0.01 M. From Eq. 4, the number of mechanically active junctions, υ_{eff}, must also be proportional to the surfactant concentration at a constant temperature. This is depicted in Figure 5b where η_0 increases linearly with υ_{eff} up to a value of approximately 10 mmol/m^3. The longest relaxation time, on the other hand, is less dependent on surfactant concentration, that is, $\tau_X \propto C_S^{1/3}$, and hence also $\propto \upsilon_{\mathrm{eff}}^{1/3}$. Thus with increasing surfactant concentration, and hence number of active junctions, the average aggregation number of the surfactant molecules in the micellar junction must remain approximately constant, while the number of polymer hydrophobes in each junction decreases in order to accommodate the increase in the number of junctions. It is the balance between the functionality of the hydrophobes—the number of hydrophobes involved in the junctions—and the number of bound surfactant molecules that determines the strength of the hydrophobic junctions.

Above 0.01 M surfactant, the viscosity and relaxation time both show a much stronger dependence on surfactant concentration, that is, $\propto C_S^3$, while G_N^0 and hence υ_{eff} are less dependent on C_S. In the region of high surfactant concentrations, the number of active junctions no longer increases linearly with surfactant concentration, and either the surfactant

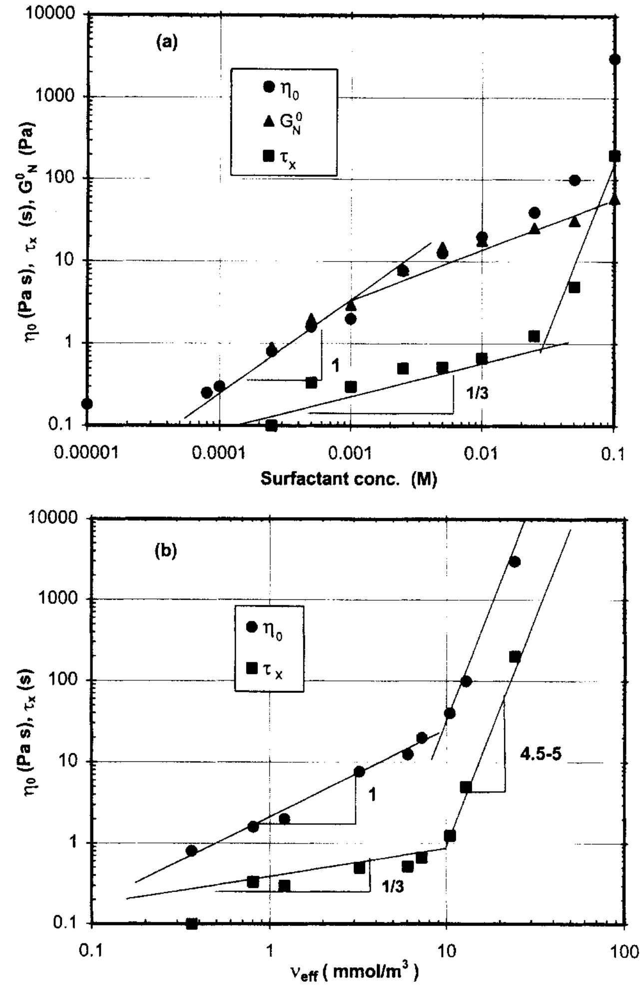

Figure 5. Zero-shear viscosity, plateau modulus and the longest relaxation time of the 0.5 wt. % HASE polymer: (a) as a function of the nonionic surfactant (RL-4) concentration; (b) as a function of the number of mechanically active junctions.

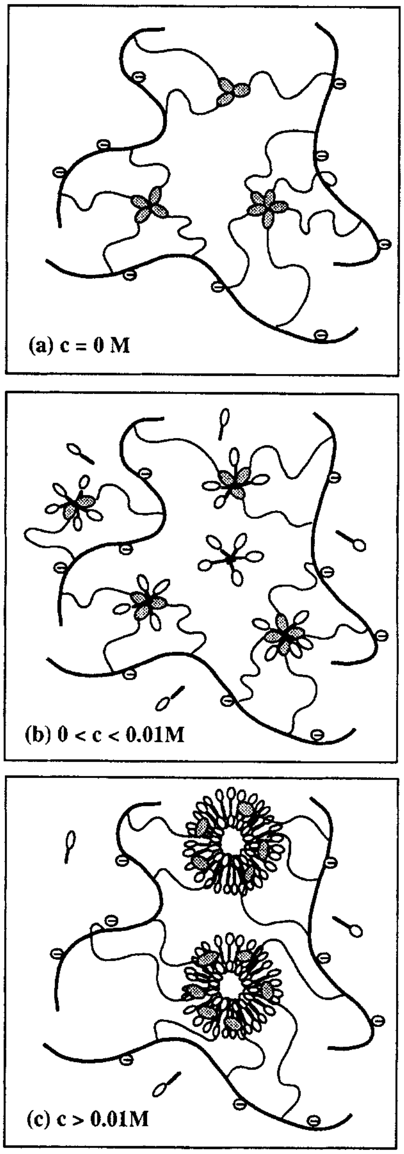

Figure 6. Network topology of the HASE polymer–nonionic surfactant system: (a) without surfactant; (b) at intermediate surfactant concentrations, that is, 0.0001 to 0.01 M; (c) at surfactant concentrations above 0.01 M.

forms larger mixed aggregates with polymer hydrophobes or a larger number of free surfactant micelles are present in solution. For the C_{12} nonionic surfactants of relatively short EO length, that is, from 3 to 6 mol EO (CH_2CH_2O-group), the surfactants are known to exist above room temperature in a bilayer lamellar phase (Jonstromer and Strey, 1992; Hofland et al., 1993). Loyen et al. (1995a,b) found that in the presence of a hydrophobically modified poly(sodium acrylate), the nonionic $C_{12}EO_{3\text{-}6}$ surfactants form large vesicles onto which the polymer hydrophobes bind; this is the cause of the stiff gel structure above the phase transition temperature. A similar structure probably exists in our HASE polymer–surfactant systems at high surfactant concentrations, where large vesicles or cylindrical bilayers are formed, each providing a possible binding site for a large number of polymer hydrophobes (see Figure 6c). Thus hydrophobic junctions of much greater strength are present, and this results in the huge increase in both the viscosity and elastic property of the system, as can be seen in the sharp rise in both the η_0 and τ_X values with υ_{eff} to the power of 4.5–5 at high surfactant concentrations.

Effect of applied shear stress

Using the technique of superposing oscillation onto steady shear flows, the viscoelastic properties of the associative polymer–nonionic surfactant systems can be determined at different shear stresses. The storage moduli of the HASE polymer with a different amount of added surfactant when subjected to shear are distinctly different, as shown in Figures 7a to 7d. In general, as the polymer–surfactant systems are subjected to increasing stress, it is the longest relaxation time that is being curtailed (Tirtaatmadja et al., 1997a,b); this is evident from the fact that the terminal regions have shifted to higher frequencies. For the low to intermediate surfactant concentrations, that is, between 0.0001 and 0.01 M, the application of a small amount of shear stress, in the range where the viscosity remains within the low shear plateau values, causes a significant increase in the plateau modulus G_N^0 (see Figures 7b and 7c). That is, there is an increase in the number of hydrophobic junctions when the network is perturbed slightly from its equilibrium state. With increasing applied shear stress, the network junctions underwent rearrangement such that there was an increase in the number of hydrophobic junctions; this was achieved by reducing the number of hydrophobes and surfactant molecules per junction. The overall result is that the viscosity of the system remains constant under shear, while the relaxation time is significantly reduced. At stresses beyond the low shear viscosity region, the associative polymer network is totally disrupted and the viscoelastic properties cannot be measured.

At a surfactant concentration in excess of 0.01 M (see Figure 7d for 0.1 M surfactant), the application of a small amount of stress within the low-shear viscosity region does not noticeably increase the G_N^0 of the polymer–surfactant systems. That is, the number of network junctions is not affected by the applied stress, as was the case with the lower surfactant concentrations. At these high concentrations, the surfactant probably forms large vesicles or cylindrical bilayers, onto which a large number of polymer hydrophobes can bind. The strength of these junctions is sufficiently large, compared to those at lower concentrations, that they are able to resist deformation at moderate values of applied stress. However, a complete breakdown of the network occurs at higher stresses, that is, in excess of 30 Pa for the 0.1-M surfactant. This is apparent as a shift from the strong gel-like structure, with an almost flat G' curve, to a viscoelastic liquid behavior, with G' being proportional to ω^2 at all frequencies measured when the applied stress is above 30 Pa. The change from gel-like solid to viscoelastic liquid coincides with the drastic drop in the viscosity of the system.

The terminal relaxation time and the normalized plateau modulus for the 0.5 wt. % associative polymer are shown in Figures 8a and 8b, respectively, as a function of applied stress for different surfactant concentrations. The relaxation times are the terminal values obtained from the relaxation time function calculated using Eq. 3. All the G_N^0 were determined from the plateau region of the G' curves, except for the pure HASE polymer solution, where the G' values at a frequency of 20 rad s^{-1} have been used, and these values have been normalized against the values at zero applied stress, that is, $G_N^0(\sigma_S)/G_N^0(0)$. Comparing Figure 8a with the viscosity profile curves shown in Figure 2, it is apparent that the terminal relaxation times of these polymer–surfactant systems are sig-

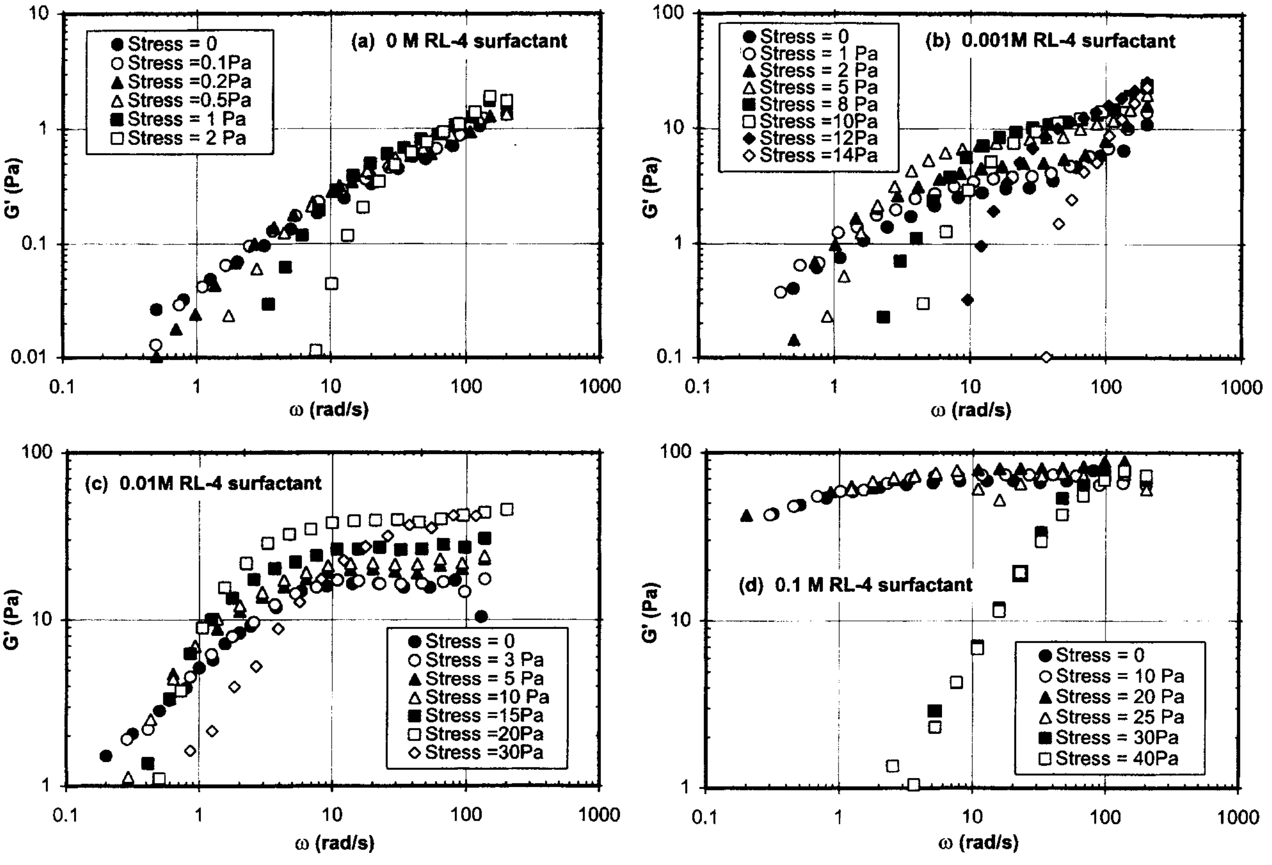

Figure 7. Effect of applied shear stress on the storage modulus of the 0.5 wt. % HASE polymer in: (a) 0 M; (b) 0.001 M; (c) 0.01 M; (d) 0.1 M nonionic surfactant (RL-4).

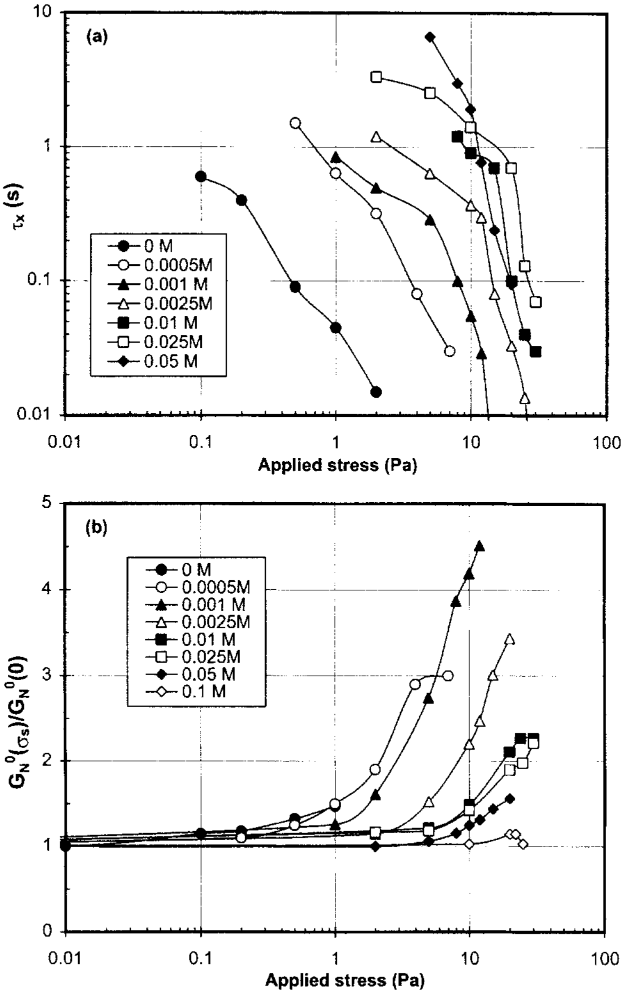

Figure 8. (a) Longest relaxation time, τ_X, and (b) reduced plateau modulus, $G_N^0(\sigma_S)/G_N^0(0)$, as a function of applied shear stress of the 0.5 wt. % HASE polymer in different concentrations of the nonionic surfactant (RL-4).

nificantly reduced, even when subjected to relatively low stresses within the low-shear plateau region of viscosities. The reduction in the relaxation times is probably a consequence of the shear-induced decrease in the functionality of the hydrophobes in the junctions. This is offset by the increase in the junction density, as seen in the accompanying increase in the G_N^0 values, shown in Figure 8b. Consider, for example, that in the system with 0.001 M RL-4 (filled triangles) within the shear stress regime of 1 to 10 Pa, the viscosity remains essentially constant even though the relaxation time decreases by more than an order of magnitude (from 0.8 to 0.05 s). This is offset by the almost fourfold increase in the plateau modulus, giving rise to very little change in the viscosity according to the relationship: $\eta = G_N^0 \tau$.

From Figure 8b, it can be seen that the increase in the network junction density due to shear is most prominent in the intermediate surfactant concentration between 0.0005 and 0.01 M, where small spherical-type mixed micelles exist. At the applied stress of 10 Pa, the shear-induced increase in the junction density, that is, the normalized plateau modulus, is the greatest for the lowest surfactant concentration of 0.001 M, and the value decreases with increasing surfactant concentration. As the overall strength of the network increases due to increasing surfactant concentrations, the amount of network junction rearrangement as a result of applied stress is reduced. However, at the higher applied stress, where the complete destruction of the network occurs, the number of active junctions must drop drastically with an accompanying drastic decrease in both the viscosity and relaxation time. The G_N^0 values at this condition cannot be measured experimentally, as the system behaves like a viscoelastic fluid with a very low elastic component.

At the highest surfactant concentrations of 0.05 and 0.1 M (open and filled diamonds, respectively), moderate shear stress causes very little rearrangement of the network, and hence very little increase in the normalized plateau modulus with increasing shear stress. This is due to an increase in the strength of the larger micellar aggregates, in the form of vesicles or bilayers, present.

Conclusions

The addition of a nonionic surfactant consisting of mainly $C_{12}EO_4$ to the 0.5 wt. % HASE polymer causes a monotonic increase in the solution shear viscosity and elastic modulus up to the highest concentration investigated, 0.1 M. At low to intermediate surfactant concentrations, that is, up to 0.01 M, the network junction density increases linearly with surfactant concentration. In this region, the viscosity also increases linearly with the increase in the number of network junctions, while the longest relaxation time shows a lower dependency. The surfactant molecules form mixed aggregates in the form of small spherical-shaped micelles with the polymer hydrophobic groups. The increase in the number of these mixed aggregates with increasing surfactant concentration is achieved through a reduction in the number of hydrophobes in the junctions. Applying shear stress in the region where the viscosity remains within the low shear plateau values results in a rearrangement of the network and its junctions, such that the number of junctions increases. This must be accommodated through a reduction in the functionality of the polymer hydrophobes, with a subsequent drop in its strength, hence a drastic decrease in the relaxation time.

At surfactant concentrations above 0.01 M, the number of hydrophobic junctions no longer increases linearly with surfactant concentration; this is possibly due to the formation of large cylindrical bilayers or vesicles, onto which a large number of polymer hydrophobes are bound. These relatively large junction sites thus exert greater strength on the network, resulting in an enhanced increase in both the viscosity and relaxation time.

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