Hydrophobic interactions in associative polymer/nonionic surfactant systems: Effects of surfactant architecture and system parameters

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Synopsis

The rheological behavior of a comb-like associative polymer with pendant hydrophobes in the presence of nonylphenol polyethoxylate (NPe) nonionic surfactants is examined. In particular, the effects of surfactant concentration, polymer concentration, and surfactant’s hydrophilic–lipophilic balance (HLB) are investigated with the latter being varied by using surfactants with different number of ethoxylate units (e = 6, 8, 12, and 15). Steady shear and dynamic measurements are performed and the zero/low shear viscosity ($\eta_0$), the number and average life time of the hydrophobic junctions, and the numbers of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction are determined. The trend of zero/low shear viscosity with increasing NP8 surfactant concentration exhibits four distinct regions, each of them related to molecular-level changes: (1) surfactant addition to the hydrophobic junctions (no change in $\eta_0$ from that of pure hydrophobically modified alkali–soluble emulsion polymer solution); (2) formation of mixed micelles containing surfactants and several polymer hydrophobes ($\eta_0$ increases); (3) saturation of each polymer hydrophobe by individual surfactant micelles ($\eta_0$ decreases); and (4) formation of free surfactant micelles ($\eta_0$ is constant). The viscosity trend of the polymer/NP8 surfactant systems with increasing surfactant concentration does not change upon increasing polymer concentration from 0.5 to 1 wt %. Moreover, the number of surfactant molecules bound to polymer hydrophobes at the viscosity maximum is the same for both polymer concentrations. In terms of the effects of surfactant HLB on polymer/NPe surfactants systems, we find essentially similar trends of zero/low shear viscosity with increasing surfactant concentration for systems containing surfactants of higher HLB (NP12 and NP15). However, the viscosity maximum is lower, and viscosity in the fourth region gradually decreases for systems containing higher HLB surfactant. In contrast, systems containing a surfactant with lower HLB (NP6) exhibit a different behavior with a continuous increase in zero/low shear viscosity with increasing surfactant concentration. © 2006 The Society of Rheology. [DOI: 10.1122/1.2355530]

I. INTRODUCTION

Hydrophobically associating polymers are macromolecules consisting of a polymer backbone with hydrophobic groups attached either at the ends (telechelic associating polymers) or along the polymer backbone (comb-like associating polymers) [English et al. (1997), Jenkins et al. (1996), Jenkins et al. (1991a, 1991b), Kumacheva et al. (1997),

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Semenov et al. (1995)]. In aqueous formulations, the hydrophobic groups interact to form a transient network giving unique rheological properties to the solutions. As such, these polymers are typically used as thickeners in many industrial applications that include paint formulations, paper coatings, adhesives, agrochemicals, ceramics, pharmaceuticals, and personal care products [Glass (1996)]. Their scope has further broadened with their potential applications in oil recovery (e.g., drilling fluids, mobility control, and profile modification) [Taylor and Nasr-El-Din (1998)], triggered drug delivery [Tonge and Tighe (2001)], and glycol based anti-icing aircraft fluids [Carder et al. (1998), Jenkins et al. (1993, 1997)]. The wide industrial and also potential applications of associative polymers, coupled with their environmentally benign nature create an obvious research interest.

Hydrophobically modified alkali-soluble emulsion (HASE) polymers are one class of comb-like associating polymers. They consist of a copolymer backbone with pendant hydrophobic groups, also named polymer hydrophobes. The polymer hydrophobes are alkyl groups attached to the backbone through a urethane linkage and separated from it by a polyoxyethylene (PEO) spacer; the entire structure is referred to as a macromonomer as applied to the monomer used in polymerization [Tirtaatmadja et al. (1997a; 1997b)]. The transient network formed in the solution will hereon be referred to as an associative network. Over the past decade, HASE polymers have drawn considerable research interest due to their significant advantages in terms of cost, biostability and wide formulation latitude [Tirtaatmadja et al. (1999a)] over other hydrophobically associating polymers with simpler architectures such as telechelic polymers [Annable et al. (1993, 1996), Groot and Agterof (1995), Lundberg et al. (1991), Semenov et al. (1995)]. Studies on HASE polymers include their synthesis [Mrkvickova et al. (2000), Quadrat and Snuparek (1990), Snuparek et al. (1993)], their flow behavior in parallel superposed steady and dynamic shear [Tirtaatmadja et al. (1997b)], their nonlinear rheology [Pellens et al. (2004)], the effects of the backbone composition on flow dynamics [Abdala et al. (2004), Gupta et al. (2000)], and the influence of the hydrophobic size and side-chain length [Dai et al. (2002), English et al. (1999), Tirtaatmadja et al. (1997a)], and of the ethylene oxide (EO) group number and ionic strength [Dai et al. (2000, 2001), Guo et al. (1998), Seng et al. (2000), Tam et al. (1998)] on solution rheology.

Since most hydrophobically associating polymers are employed in formulations containing surfactants or other amphiphilic species, the interactions of HASE polymers with surfactants have also received considerable attention. HASE polymer/surfactant systems exhibit a range of interesting and complex behavior, controlled by a number of variables, thereby providing a powerful and potent tool to manipulate further the rheology of these systems. The variables can be: (i) component related, i.e., the polymer itself particularly its macromonomer composition, and the surfactant type; and/or (ii) composition or condition related, i.e., the component concentration and the temperature. Experimental studies [Seng et al. (1999), Tirtaatmadja et al. (1998), Wu et al. (2001)] have shown that the presence of surfactants can affect the dynamics of the solutions by monotonically increasing, decreasing, or exhibiting a maximum in the system viscosity depending on the surfactant concentration and type. Surfactant induced factors that change the number and strength of hydrophobic junctions as well as their functionality (or the number of polymer hydrophobes in a hydrophobic junction) thus play a major role in changing the solution rheology.

The interaction of HASE polymers with ionic surfactants generally result in an increase in solution viscosity to a maximum at a critical surfactant concentration $c^*$, followed by a decrease in viscosity. Although the reasons for viscosity enhancement upon addition of surfactants up to $c^*$ have been debated, it is well accepted now that such an
increase is related to an increase in both the number of intermolecular hydrophobic junctions and the average lifetime of these junctions [Seng et al. (1999)]. The viscosity decrease upon further addition of ionic surfactants is associated with decrease in both the number of intermolecular hydrophobic junctions and the associative network strength.

HASE polymer/nonionic surfactant systems exhibit a more complex behavior depending on the surfactant hydrophilic–lipophilic balance (HLB) and the structure of the surfactant hydrophobic tail relative to that of the polymer hydrophobe. HLB value gives a quantitative measure of the amphiphilicity of the surfactants. For the case of nonionic surfactants, it is generally defined as

$$\text{HLB} = 20 \times \frac{M_H}{M_H + M_L}$$

where $M_H$ is the molecular weight of the hydrophilic portion of the surfactant molecule while $M_L$ is the molecular weight of the hydrophobic or lipophilic portion [Rosen (2004)]. A higher HLB value thus indicates higher water solubility and a higher critical micelle concentration (CMC), and vice versa. The concentration effect of nonionic surfactant Rhodasurf L-4 ($C_{12}EO_4$, HLB = 9.7) on a 0.5 wt % solution of associative polymer, with macromonomer hydrophilic and hydrophobic parts consisting of approximately 35 EO units and a $C_{20}H_{41}$ chain, respectively, have been studied [Tirtaatmadja et al. (1998)]. In contrast to the effect of ionic surfactant concentration, a monotonic increase in low-shear viscosity by up to five orders of magnitude was observed as the nonionic surfactant concentration was increased to 0.1 M. The authors attributed the viscosity enhancement at high surfactant concentration to the formation of mixed cylindrical bilayers or vesicles which considerably reinforce the associative network. The morphological transition of the surfactants from spherical micelles to large vesicles results in a stronger associative network and hence, a higher solution viscosity has also been observed [Tirtaatmadja et al. (1999a)] for the same HASE polymer–nonionic surfactant system with increasing temperature. The effect of temperature on nonionic surfactant co-thickening has been further explored by Wu et al. (2001) using Brij 97 surfactant ($C_{12}EO_{10}$, HLB = 12.4) and 0.5 wt % associative polymer with macromonomer composed of 40 EO units and a $C_{16}H_{37}$ chain. A maximum in solution viscosity with increasing temperature was observed at 45 °C. The authors attributed the trend in solution viscosity to changes in size and structure of surfactant micelles, which in turn affect the number and strength of hydrophobic junctions.

Tam et al. (2000) studied the rheological properties of a 1 wt % HASE polymer (macromonomer with 25 EO units and $C_{20}H_{41}$ alkyl hydrophobe) with nonionic Brij 35 surfactant ($C_{12}EO_{23}$, HLB = 16.9) and observed that both the low shear viscosity and the dynamic moduli initially increase with surfactant concentration, $c >$ CMC, reach a maximum at a critical concentration $c^m$ (about 17 times the CMC of $C_{12}EO_{23}$ surfactant) and then decrease with increasing surfactant concentration. According to the authors, an increase in the number of hydrophobic junctions and a strengthening of the associative network were the dominant mechanisms responsible for the viscosity increase with increasing surfactant concentration while the disruption of the associative network caused by decrease of both the number and strength of hydrophobic junctions was responsible for the viscosity decrease. English et al. (2002) studied the effects of two nonylphenol ethoxylate surfactants NP6 ($C_6\Phi EO_6$, HLB = 10.9) and NP10 ($C_6\Phi EO_{10}$, HLB = 13.2)—where $\Phi$ stands for phenol group—on the rheological properties of 0.6 wt % and 1 wt % HASE polymer solutions. The HASE polymer used in this study was vastly different in its macromonomer composition and structure from that in the
above mentioned studies, i.e., the macromonomer hydrophilic and hydrophobic parts consisted of approximately 80 EO and bis-nonylphenol units, respectively. The authors observed a decrease in low shear viscosity with increasing NP10 surfactant concentration from 0.3 to 0.8 g dL$^{-1}$ but an increase in low shear viscosity with increasing NP6 surfactant concentration from 0.1 to 1.5 g dL$^{-1}$. They attributed the decrease in solution viscosity with increasing NP10 surfactant concentration to the formation of NP10 surfactant micelles surrounding the hydrophobic junction concurrently decreasing the number of polymer hydrophobes present in a given hydrophobic junction. The increase in solution viscosity with increasing NP6 surfactant concentration was explained by the formation of complex microstructure of partially water-soluble surfactant in HASE polymer solution.

Studies on HASE polymer–nonionic surfactant systems to date have thus dealt with either a complex macromonomer HASE polymer and nonionic surfactant having intermediate to high HLB [English et al. (2002)], or a simpler macromonomer HASE polymer and nonionic surfactants having either a high [Tam et al. (2000)] or a low HLB [Tirtaatmadja et al. (1998)]. In the latter case involving polymers with simpler macromonomer, the polymer–surfactant combinations used are different in each case making it difficult to generalize the results. To the best of our knowledge, no systematic attempt has been made to obtain a detailed account of the effects of surfactants with different HLB on the rheological behavior of HASE polymers. The goal of this study is to examine how the interactions between HASE polymer and nonionic surfactants vary with changes in the surfactant HLB. We first describe the effect of increasing surfactant concentration on the rheology of HASE polymer/NP8 nonylphenol ethoxylate surfactant (C$_9$ΦEO$_8$, HLB =12.6) systems. Subsequently, the effects of increasing polymer concentration in the former system are investigated. Finally, we explore how the effects of increasing surfactant concentration on the system rheology vary with increasing surfactant HLB from 10.9 to 15. An attempt is made to provide a molecular level explanation of the different phenomena observed in the aforesaid systems.

II. MATERIALS AND METHODS

The polymer used in this study was obtained from UCAR emulsion systems (Dow Chemicals, N.C.). A schematic of its chemical structure is shown in Fig. 1; the ratio of methacrylic acid, ethylacrylate and macromonomer is 43.57/56.21/0.22, respectively, in terms of mole percent. The macromonomer, which is linked to the backbone via a urethane linkage, is composed of a PEO spacer with 40 EO units and a C$_{22}$ alkyl group. The HASE polymer was supplied in the form of aqueous latex at a solid concentration of approximately 26 wt %. All impurities and unreacted chemicals were removed from the aqueous latex by dialyzing it against deionized water using a Spectrapore cellulose membrane (cut off MW = 10 000) for 3 weeks. The dialyzed latex was then lyophilized for 2 days under a vacuum of 100 mTorr to obtain the HASE polymer in a powder form. The pH of the subsequently prepared polymer solution was adjusted between 9 and 9.5 by adding 0.1 M NaOH. The polymer was dissolved in 0.05 M NaCl solution to ensure controlled/negligible polyelectrolyte effect [Abdala et al. (2004)]. Details on the protocol to purify and prepare the polymer solution can also be found in several previous publications [Abdala et al. (2003, 2004), English et al. (1999, 2002), Tam et al. (2000)]. Nonylphenol ethoxylates (NPe) nonionic surfactants, Tergitol® were supplied by Dow Chemicals (N.C.) and used as received. The name and chemical specifications of the surfactants used in this study are listed in Table I. Once the polymer/surfactant samples were prepared by combining the requisite amounts of HASE polymer and NPe surfactant
solutions, they were put in a water bath overnight at 50 °C to remove entrained air and subsequently left for 48 h prior to rheological measurements. Rheology of the samples was measured within 3 weeks of the preparation to avoid possible polymer degradation in the presence of NaOH [Tirtaatmadja et al. (1999b)].

All rheological experiments were performed at pH=9 and T=25 °C in a TA Instruments AR-2000 stress controlled rheometer using primarily cone and plate geometry. Both steady and dynamic shear experiments were conducted on each sample. Since the steady shear response of HASE polymer/surfactant systems is sensitive to shear history [Tirtaatmadja et al. (1999b)], a preshear was applied at a strain rate of 5 s⁻¹ for 180 s followed by a rest period of 120 s. A dynamic stress sweep test was performed to determine the limit of linear viscoelastic regime, which was thereafter utilized to perform the dynamic frequency sweep test. Zero or low shear viscosity was determined from the steady shear viscosity profiles by averaging over the first ten points of the Newtonian region. Each experiment reported in this study was performed at least twice and all experiments were reproducible within ±5%. The error is included in the symbol size.

III. RESULTS AND DISCUSSION

A. Effect of NP8 surfactant concentration

The steady shear viscosity profiles of a 0.5 wt % polymer solution (equivalent to 0.11 mM polymer hydrophobes) in the presence of NP8 surfactants at concentrations C_{NP8} varying from 0 to 27 mM are shown in Fig. 2. For ease of viewing, only selected

<table>
<thead>
<tr>
<th>Surfactant name</th>
<th>EO moles (average number)</th>
<th>HLB</th>
<th>CMC (mM)</th>
</tr>
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<tbody>
<tr>
<td>NP6</td>
<td>6</td>
<td>10.9</td>
<td>—</td>
</tr>
<tr>
<td>NP8</td>
<td>8</td>
<td>12.6</td>
<td>0.068</td>
</tr>
<tr>
<td>NP12</td>
<td>12</td>
<td>13.8</td>
<td>0.082</td>
</tr>
<tr>
<td>NP15</td>
<td>15</td>
<td>15</td>
<td>0.11</td>
</tr>
</tbody>
</table>
polymer/NP8 surfactant systems studied are presented in Fig. 2. For polymer solutions containing NP8 surfactants at $C_{NP8}/H_{33355}^{1.7 \text{ mM}}$, the steady shear viscosity is higher than that of the polymer itself. We observe a Newtonian region at low shear stresses followed by an abrupt drop at higher shear stresses. The drastic drop in steady shear viscosity with increasing shear stress is related to the disruption of the associative network in associative polymer/surfactant systems [Tam et al. (2000)]. In contrast, we observe no drastic decrease in steady shear viscosity for the pure polymer solution or for polymer solutions containing NP8 surfactants at $C_{NP8}/H_{33356}^{3.4 \text{ mM}}$. In this surfactant concentration regime, the steady shear viscosity is lower than that of the pure polymer solution.

The effect of surfactant concentration on system viscosity is seen more clearly in Fig. 3, in which we plot the zero/low shear viscosity from Fig. 1 as a function of NP8 surfactant concentration. Four distinct regimes can be observed in Fig. 3. The first region corresponds to very low NP8 surfactant concentration ($C_{NP8}/H_{33355}^{\leq 0.1 \text{ mM}}$) in which the viscosity is nearly constant and equal to the viscosity of the pure polymer solution. In the second region, the viscosity of the polymer/NP8 surfactant solution increases with in-

FIG. 2. Steady shear viscosity ($\eta$) as a function of shear stress for 0.5 wt % HASE polymer solution in the presence of NP8 surfactants at concentrations $C_{NP8}$ varying from 0 to 27 mM.

FIG. 3. Low shear viscosity ($\eta_0$) as a function of NP8 surfactant concentration ($C_{NP8}$) for 0.5 wt % HASE polymer/NP8 surfactant systems.
creasing NP8 surfactant concentration up to a maximum at $C_{\text{NP8}} \approx 0.85$ mM. The viscosity at this point is more than an order of magnitude higher than the viscosity of the pure polymer. In the third region ($0.85 \leq C_{\text{NP8}} \leq 10$ mM), the viscosity of polymer/surfactant systems decreases with increasing NP8 surfactant concentration up to 10 mM, and then finally reaches the fourth region of constant low shear viscosity hereon referred to as the plateau region. We find the viscosity in the last regime to be approximately a factor of 30 lower than the viscosity of the pure polymer solution. To the best of our knowledge, a plateau region at high surfactant concentrations has not been reported before for HASE polymer/nonionic surfactant systems.

Figure 4 shows the effects of NP8 surfactant on the dynamic moduli of the HASE polymer solution for three representative NP8 concentrations: 0, 0.85, and 27 mM. Surfactant concentrations of 0.85 and 27 mM correspond to the maximum and low viscosity regime observed in Fig. 3. Compared to the pure polymer, the dynamic moduli show a substantial increase at $C_{\text{NP8}} = 0.85$ mM. The “characteristic” relaxation time, denoted by the crossover point, also increases by an order of magnitude. Further addition of NP8 to $C_{\text{NP8}} = 27$ mM not only drops the moduli to below that of the pure polymer but also decreases the relaxation time by about two orders of magnitude. Such behavior, suggesting enhancement of association followed by disruption upon surfactant addition, is consistent with the observed changes in viscosity.

To better understand the possible mechanisms responsible for the different zero/low shear viscosity trends with increasing NP8 surfactant concentration, we first discuss the effect of increasing NP8 surfactant concentration both on the number and average lifetime of the hydrophobic junctions, and on the number of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction. Based on the theory by Green and Tobolsky (1946) on transient networks, the number of mechanically active hydrophobic junctions, $\nu_{\text{eff}}$ in a polymer/surfactant system, can be related to the high frequency plateau modulus $G_\infty$ through the following expression:

$$G_\infty = \nu_{\text{eff}} RT,$$

where $R$ is the gas constant and $T$ is the absolute temperature. Figure 5 shows the effects of increasing NP8 surfactant concentration on $G_\infty$, which is proportional to the number of hydrophobic junctions. We find that the number of hydrophobic junctions initially decreases slightly for $C_{\text{NP8}} \leq 0.025$ mM, increases to reach a maximum at $C_{\text{NP8}}$...
=0.85 mM and then decreases with increasing NP8 surfactant concentration. We also observe that the maximum number of hydrophobic junctions is reached at the same NP8 surfactant concentration as the low shear viscosity maximum (cf. Fig. 3). It should be noted that $G_\infty$ could not be determined for polymer/NP8 surfactant systems at surfactant concentrations $C_{NP8} > 1.7$ mM because of the presence of inertial effects at higher frequencies; nevertheless, most of the relevant features are captured in the concentration regime shown in Fig. 5.

Figure 5 also shows the average junction lifetime of our system as a function of surfactant concentration. Aubry and Moan (1996) proposed that the average lifetime of the hydrophobic junctions, $T_c$, can be calculated as the ratio of the steady shear viscosity to shear stress at the point where a drastic drop in steady shear viscosity occurs, that is when the associative network disrupts. Because of the uncertainty in accurately identifying such a point, we determine $T_c$ to be the point at which straight lines drawn through the Newtonian region and through the region after the steady shear viscosity drop intersect. Although $T_c$ is an approximate value of the average junction lifetime, it is a useful parameter to compare for the different HASE polymer/NP8 surfactant systems which exhibit a disruption of the associative network, i.e., for concentration range $0.025 \leq C_{NP8} \leq 1.7$ mM. We find from Fig. 5 that as the NP8 surfactant concentration increases, the average junction lifetime initially increases, and then decreases after achieving a maximum at $C_{NP8} = 0.85$ mM.

We have also estimated the numbers of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction by dividing the molar density of polymer hydrophobes in a 0.5 wt % (0.11 mM) HASE polymer solution and the number of surfactant molecules at a given NP8 surfactant concentration respectively by the number of hydrophobic junctions, $r_{eff}$. These calculations hold true only in the surfactant concentration range in which the NP8 surfactant molecules systematically bind onto the hydrophobic junctions up to $C_{NP8} = 0.85$ mM and assuming that all NP8 surfactant molecules and polymer hydrophobes present in the system participate in hydrophobic junctions. The numbers of polymer hydrophobes and NP8 surfactant molecules per hydrophobic junction are plotted against NP8 surfactant concentration in Fig. 6. We observe that the number of polymer hydrophobes per hydrophobic junction continuously decreases while the number of surfactant molecules per hydrophobic junction monotonically increases.

**FIG. 5.** Plateau modulus $G_\infty$ (■) and average lifetime of hydrophobic junctions $T_c$ (▲) as a function of NP8 surfactant concentration ($C_{NP8}$) for 0.5 wt % HASE polymer/NP8 surfactant systems.
with increasing NP8 surfactant concentration, in agreement with fluorescence studies on similar systems containing hydrophobically modified hydroxycellulose and cationic surfactants [Panmai et al. (2002)].

In the light of the observations made in Figs. 5 and 6, the low shear viscosity trend of the polymer/surfactant system observed in Fig. 3 with increasing NP8 surfactant concentration can be explained in terms of the schematic representations of the polymer/NP8 surfactant interactions shown in Fig. 7. Figure 7 also includes the zero/low shear viscosity with increasing NP8 surfactant concentration replotted from Fig. 3. In the first region ($C_{NP8} \leq 0.1$ mM), although NP8 surfactant molecules may be binding to the hydrophobic junctions, its contribution is not large enough to be reflected on the rheology of the polymer/surfactant systems. Such observation is consistent with results obtained in a previous study by Tam et al. (2000). In the second region ($0.1 < C_{NP8} \leq 0.85$ mM), the surfactant molecules bind to the hydrophobic junctions to form mixed micelles with the polymer hydrophobes. The strength of the hydrophobic junctions increases further as shown by the increase in $T_c$ with increasing $C_{NP8}$ from 0.1 to 0.85 mM (cf. Fig. 5).

**FIG. 6.** Number of NP8 surfactant molecules per hydrophobic junction (NP8/HJ) (■) and number of polymer hydrophobes per hydrophobic junction (hydrophobes/HJ) (△) as a function of NP8 surfactant concentration ($C_{NP8}$) for 0.5 wt % HASE polymer/NP8 surfactant systems.

**FIG. 7.** Schematic representation of HASE polymer–NP8 surfactant interactions and low shear viscosity as a function of NP8 surfactant concentration ($C_{NP8}$).
However, to accommodate the increasing number of surfactant molecules (Fig. 7), the polymer hydrophobes rearrange to create more hydrophobic junctions as shown by the increase in $G_\infty$ and the decrease in polymer hydrophobes per hydrophobic junctions with increasing NP8 surfactant concentration. As a result the associative network is stronger and hence the low shear viscosity increases. At $C_{NP8} = 0.85$ mM, both the number of hydrophobic junctions and the low shear viscosity reach a maximum at which approximately eight molecules of NP8 surfactant are bound to each polymer hydrophobe. The strength of hydrophobic junctions which is determined by the balance between the polymer hydrophobe number and the surfactant molecule number per hydrophobic junctions [Tirtaatmadja et al. (1998)] also exhibits a maximum at $C_{NP8} = 0.85$ mM. In the third region, increasing NP8 surfactant concentration from 0.85 to 10 mM leads to: (i) some individually surfactant-saturated polymer hydrophobes, i.e., fewer hydrophobic junctions consistent with the observed decrease in $G_\infty$ for $C_{NP8} > 0.85$ mM (Fig. 5); and (ii) shorter average lifetime of the hydrophobic junctions to a point that no disruption of the associative network is observed for HASE polymer/NP8 surfactant systems at $C_{NP8} \geq 3.4$ mM (Fig. 2). Consequently, the low shear viscosity decreases. At $C_{NP8} \approx 10$ mM all the polymer hydrophobes are individually surfactant saturated; there is no more associative network as shown by the low shear viscosity plateau which is lower than the low shear viscosity of the pure polymer. This notion of the absence of hydrophobic interaction is consistent with the fact the viscosity of the polymer/surfactant systems in the plateau region ($\sim 0.3$ Pa s) is similar to that observed for the same polymer but with no hydrophobes attached [Abdala et al. (2003)]. Assuming that at $C_{NP8} \approx 10$ mM, all NP8 surfactant molecules present in the system form mixed micelles around each polymer hydrophobe, the aggregation number of the mixed micelles is approximately 94, which is less than the aggregation number of pure NP8 surfactant micelles in water. Although the aggregation number of NP8 surfactant is not reported in the literature to our knowledge, it can be safely assumed to be greater than 350, the aggregation number of NP9 surfactant [Van Os et al. (1993)] as the aggregation number decreases with increasing HLB for nonionic surfactants. Finally, additional NP8 surfactant molecules form free micelles which do not affect the rheology of the polymer/surfactant system since its low shear viscosity remains constant (plateau region).

An important issue to examine is the role of polymer concentration on the trends observed thus far with surfactant addition. Figure 8(a) shows the zero/low shear viscosity of polymer/surfactant systems as a function of NP8 surfactant for two different HASE polymer concentrations, 0.5 wt % (0.11 mM) and 1 wt %. (0.22 mM) The viscosity trend of the polymer/surfactant systems with increasing NP8 surfactant concentration, the presence of an initial plateau followed by a maximum and finally another low viscosity plateau, remains unchanged for the two polymer concentration. However, the initial plateau with no viscosity change seems to extend to a higher surfactant concentration for the 1 wt % polymer solution. In addition, the viscosity curve for the higher polymer concentration is always higher, and for some surfactant concentrations by more than an order of magnitude. Finally, we observe the viscosity maximum for the 1 wt % polymer/surfactant system to occur at twice the surfactant concentration than that for the 0.5 wt % polymer/surfactant system. As expected, the molar ratio of NP8 surfactant to polymer hydrophobes at the viscosity maximum is the same for both systems and approximately equal to 8 as can be seen in Fig. 8(b) wherein the viscosity data in Fig. 8(a) have been replotted against moles of NP8 surfactant per mole of polymer hydrophobe. In effect, the number of surfactant molecules able to bind onto a hydrophobic junction depends on the surfactant architecture (as will be shown later) and not on the polymer concentration, i.e., the number of hydrophobic junctions in the system.
B. Effect of surfactant hydrophilic–lipophilic balance (HLB)

To explore the effect of varying surfactant HLB on the rheology of polymer/surfactant systems, four different surfactants were considered: NP6, NP8, NP12, and NP15. The HLB of these surfactants is reported in Table I and ranges from 10.9 for NP6, the most hydrophobic surfactant studied, to 15 for NP15. As mentioned earlier, increasing HLB increases the CMC and decreases the aggregation number of the surfactants. The surfactant concentration studied for systems containing NP8, NP12, or NP15 surfactants ranged between 0.1 and 34 mM while the maximum concentration studied for systems containing NP6 surfactant was limited to 10 mM as higher concentrations of NP6 surfactant in the HASE polymer solution resulted in a non-homogeneous system. Figure 9 shows the zero/low shear viscosity of polymer/NP6 surfactant systems as a function of NPe surfactant concentration (CNP6) and (b) moles of NP8 per mole of polymer hydrophobe.

FIG. 8. Low shear viscosity (η₀) for 0.5 wt % (●) and 1 wt % (▲) HASE polymer/NP8 surfactant system as a function of: (a) NP8 surfactant concentration (CNP8) and (b) moles of NP8 per mole of polymer hydrophobe.
Third, the viscosity trend observed for systems containing NP8, NP12, or NP15 surfactants are similar in that they all exhibit a viscosity maxima in region II ($0.1 \text{ mM} \leq C_{NP12} \leq 0.85 \text{ mM}$). In the case of NP15 containing system, no sharp maximum is observed but rather a plateau extending from $C_{NP15} = 0.25 \text{ mM}$ to $C_{NP15} = 1 \text{ mM}$. Finally, for NP12 and NP15 containing systems at high surfactant concentrations (region IV), we observe a gradual drop in viscosity instead of the viscosity plateau observed for NP8 containing system. Additionally, the viscosity of both systems is essentially the same in this region.

In order to obtain further insights on how the molecular interactions between HASE polymer and NPe surfactants vary with the surfactant HLB, we examine in Fig. 10 the number ($G_o$) and average lifetime ($T_c$) of hydrophobic junctions as a function of NPe surfactant concentration for the above mentioned systems. For any surfactant system, the behavior observed for $G_o$ and $T_c$ with increasing surfactant concentration is qualitatively similar to that observed for the corresponding viscosity. For HASE polymer/NP6 surfactant systems, the number and average lifetime of the hydrophobic junctions continuously increase with increasing surfactant concentration, whereas for HASE/NPe surfactant systems containing NP8, NP12, or NP15 surfactants, the number and average lifetime of hydrophobic junctions exhibit a maximum (broad in one case) followed by a drop with increasing surfactant concentration. We note that for HASE polymer/NP15 surfactant system, the average lifetime of hydrophobic junctions slightly increases from $C_{NP15} = 0.1$ to $1 \text{ mM}$ instead of showing a plateau as for the zero/low shear viscosity and the number of hydrophobic junction. $G_o$ and $T_c$ values for NP8- NP12- and NP15-based systems could not be determined for region IV because of frequency constraints of the rheometer.

Based on the observations made in Figs. 9 and 10, and our explanation of the viscosity trend for polymer/NP8 surfactant systems (cf. Fig. 7), we attempt to explain the various observed behavior, particularly the differences between the various NPe systems in terms of molecular interactions. For polymer/NP6 surfactant systems in region II, the surfactant molecules bind onto the hydrophobic junctions strengthening the average lifetime of the associative network ($T_c$ increases) and forces the polymer hydrophobes to rearrange and
form more hydrophobic junctions ($G_\infty$ increases). The zero/low shear viscosity strongly increases in this region. Due to the ability of NP6 surfactant to form lamellar structures in solution instead of spherical micelles [Tirtaatmadja et al. (1999a)], the associative network is further strengthened with NP6 addition in region III, consistent with the continuous increase in the number and average lifetime of hydrophobic junctions as well as the low shear viscosity.

The molecular interactions in region II for systems containing NP8 or NP12 are essentially the same as that for NP6, i.e., surfactant molecules bind to the polymer hydrophobes, and polymer hydrophobes rearrange to form more hydrophobic junctions. For NP15 surfactant system, we believe that in addition to these hydrophobic interactions between the surfactant tail and the polymer hydrophobes, the EO chain in NP15 is long enough to create a hydrophilic corona with the PEO spacer of the HASE polymer by analogy to the corona formed by the surfactant hydrophilic parts of a micelle in water. Therefore the polymer hydrophobes are stabilized by both hydrophobic and hydrophilic interactions, and the thermodynamic energy penalty for a polymer hydrophobe to leave a hydrophobic junction and form a new one is high. Consequently, the number of hydrophobic junctions ($G_\infty$) increases at low surfactant concentration ($C_{NP15} \leq 0.25$ mM) but then remains essentially constant over a range of surfactant concentration such as

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**FIG. 10.** Plateau modulus $G_\infty$ (a) and average lifetime of hydrophobic junctions $T_c$ (b) as a function of NPe ($e=6, 8, 12,$ and $15$) surfactant concentration ($C_{NPe}$) for 0.5% HASE polymer/NPe surfactant systems.
0.25 mM \leq C_{NP15} \leq 1\, mM. Addition of surfactant molecules to the existent hydrophobic junctions strengthens the associative network and the average lifetime of the hydrophobic junctions ($T_c$) slightly increases.

As for region IV, we earlier hypothesized in Sec. III A for NP8 surfactants that all the polymer hydrophobes are screened by the surfactant micelles and further addition of surfactant leads to the formation of free surfactant micelles in solution. Based on the aggregation number of NPe surfactants in water, the number of free micelles formed at a given surfactant concentration is approximately three and six times greater [Van Os et al. (1993)] than that of NP8 in the case of NP12 and NP15 surfactants, respectively. We believe that the presence of much higher number of free micelles causes a further breakdown of the associative network. In the case of NP12 or NP15 containing systems, the formation of additional micelles with increasing surfactant concentration act to align the polymer chains; consequently, the zero/low shear viscosity exhibits a gradual decline with increasing surfactant concentration in region IV as seen in Fig. 9. It should be noted that we have based our hypothesis from rheological data but scope remains to further investigate these systems using other techniques such as light scattering or dye solubilization.

IV. SUMMARY

In this study, we examined the rheological behavior of HASE polymer/nonylphenol polyethoxylate (NPe) nonionic surfactant systems under different conditions related either to the system such as the surfactant and polymer concentration, or to the surfactant architecture itself through the HLB. An effort was made to explain the rheological behavior in terms of the molecular interactions between polymer hydrophobes and surfactants. We first examined the effect of NP8 surfactant concentration on the rheology of HASE polymer/NP8 surfactant systems and found that the trend of zero/low shear viscosity with increasing NP8 surfactant concentration can be divided into four distinct regions. The rheological behavior in each of them was explained in terms of surfactant addition to the hydrophobic junctions formed by the polymer hydrophobes, formation of mixed micelles containing surfactants and several polymer hydrophobes, saturation of each polymer hydrophobe by individual surfactant micelles, and finally formation of free surfactant micelles. To our knowledge, the fourth or plateau region observed at high NP8 surfactant concentrations has not been reported earlier for similar associative polymer/surfactant systems. A change in the polymer concentration for the HASE polymer / NP8 surfactant systems did not affect the viscosity trend with increasing NP8 surfactant concentration and the number of surfactant molecules bound to the polymer hydrophobes at the viscosity maximum was the same for both polymer concentrations.

We also examined the effect of surfactant HLB on the rheology of HASE polymer/NPe surfactants systems. The trends of zero/low shear viscosity were essentially similar for systems containing surfactants with higher HLB (NP8, NP12, and NP15) barring two differences. The viscosity maximum for NP15 surfactant systems showed a broad plateau. The viscosity curve for NP12 and NP15 surfactant-containing systems exhibited a gradual drop in viscosity instead of a plateau (seen for NP8 systems) in the fourth region; we attributed this to the presence of a much higher number of free surfactant micelles in these systems. Systems containing a surfactant with lower HLB (NP6), in contrast, showed a continuous increase in zero/low shear viscosity with increasing surfactant concentration which can possibly be ascribed to the formation of large lamellar structures by surfactant molecules.
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References


