

Solution rheology of hydrophobically modified associative polymers: Effects of backbone composition and hydrophobe concentration

Ahmed A. Abdala

*Department of Chemical Engineering, North Carolina State University, Raleigh,
North Carolina 27695-7905*

Wenjun Wu, Keith R. Olesen, and Richard D. Jenkins

*The Dow Chemical Company, UCAR Emulsion Systems, 410 Gregson Drive,
Cary, North Carolina 27511*

Alan E. Tonelli

*Fiber and Polymer Science Program, North Carolina State University, Raleigh
North Carolina 27695-8301*

Saad A. Khan^{a)}

*Department of Chemical Engineering, North Carolina State University, Raleigh,
North Carolina 27695-7905*

(Received 8 May 2003; final revision received 9 February 2004)

Synopsis

We investigate the effects of polymer molecular structure on the solution rheology of a hydrophobically modified associative polymer comprised of macromonomers with alkyl hydrophobes attached to a poly(ethyl acrylate-co-methacrylic acid) backbone. In particular, the effect of polymer backbone composition with variable proportions of methacrylic acid (MAA) and ethyl acrylate (EA) are examined. We find that the concentration of the MAA monomer has a large impact on polymer viscoelasticity. Polymers with low MAA content have smaller hydrodynamic size that result in lower viscosities and dynamic elastic moduli compared to polymers with high MAA content. Moreover, the balance between the polymer hydrodynamic size, the chain flexibility, and the aggregation of the EA blocks yield maxima in these material functions with respect to the MAA concentration. The scaling of shear viscosity, high frequency elastic modulus, and creep compliance with polymer concentration exhibits power-law behavior with different exponents. In all cases, three power-law regimes, regardless of the MAA content, are observed that can be attributed to the presence of different modes of hydrophobic interaction. However, the transitions shift to lower concentrations as the MAA content increases. With regards to the effects of the macromonomer side-chain concentration, we observe a substantial increase in viscosity at intermediate macromonomer content (1 mol %), possibly due to an increase in the number of intermolecular junctions as the number of hydrophobes per chain increases. This is in contrast to (i) low macromonomer concentration (0.3 mol %) behavior that reveals low viscosity due to weak

^{a)}Author to whom all correspondence should be addressed; electronic mail: khan@eos.ncsu.edu

hydrophobic associations, and (ii) high macromonomer concentration (1.9 mol %) behavior that favors more intramolecular association resulting in lower viscoelastic properties compared to intermediate macromonomer concentrations. © 2004 The Society of Rheology.

[DOI: 10.1122/1.1773781]

I. INTRODUCTION

Alkali soluble emulsion (ASE) polymers are carboxylic functional copolymers produced by free-radical emulsion polymerization of ethylenically unsaturated monomers. The ASE polymers are insoluble in water at low *pH*, but exhibit chain expansion and concomitant dissolution at *pH* greater than 6 upon neutralization with a base [Shay (1989)]. These nonassociative polymers can be hydrophobically modified by the incorporation of a small number of hydrophobic macromonomers, usually nonionic surfactants that have been endcapped with an unsaturated double bond [Jenkins *et al.* (1996)]. The hydrophobically modified alkali-soluble emulsion (HASE) polymers exhibit characteristics of both the ASE polymers, swelling upon neutralization, and that of the hydrophobically modified ethoxylate urethane polymers, forming transient networks through molecular associations. Due to their hybrid nature, HASE polymers have been increasingly used as rheology modifiers in a variety of applications including cosmetic and personal care products, paints, paper coating, and anti-icing fluids. However, optimal use of these polymers requires control of their structures and compositions.

The structure of a typical HASE polymer is shown in Fig. 1, and can be described as a polyelectrolyte backbone with a number of hydrophobic macromonomers randomly distributed along the backbone. The backbone is composed of a copolymer of hydrophilic segments that provide solubility, and, slightly water insoluble segments that enhance the thickening performance and promote adsorption of the polymer to hydrophobic latex in many applications. The hydrophilic segments are usually acrylic acid or alkyl acrylic acid, while the water insoluble segments are usually acrylates. In most studies of HASE polymers, including the present one, the hydrophilic segment is methacrylic acid (MAA), whereas the other segment is ethyl acrylate (EA). The hydrophobic side chains are attached to the polymer backbone through urethane linkages to unsaturated alkyl or aryl groups that are separated from the backbone by 5–100 ethylene oxide (PEO) units. The complexity of the HASE polymers is depicted in Fig. 1, which shows the chemical structure of the polymers used in this study. With such a complex architecture, the association behavior of these polymers would be expected to be quite diverse and dependent on many factors, such as the structure of the backbone that dictates their water solubility and flexibility, and concentration and the structure of the macromonomer, that includes the type of hydrophobic groups and the length of the PEO spacers [Jenkins *et al.* (1996)].

The effects of polymer-architectural parameters, such as the PEO spacer length, and the type and concentration of the hydrophobic groups, on the solution behavior have been the subject of many recent studies [Jenkins *et al.* (1996); Lau *et al.* (2001); Seng *et al.* (2000); Tan *et al.* (2000b; 2001); English *et al.* (1997, 1999); Olesen *et al.* (1999); Tirtaatmadja *et al.* (1997); Tam *et al.* (1998, 2000a)]. However, the effects of the composition of the polymer backbone have received little attention [Jenkins *et al.* (1996); Gupta *et al.* (2000)]. An understanding of how the polymer backbone composition affects polymer flexibility, hydrophobic associations, and rheological properties is important not only from a fundamental standpoint, but also for tailoring polymers with controlled solution properties. In this study, we examine this issue utilizing polymers that contain different proportions of MAA and EA in their backbones and with macromonomer side chains containing hydrophobes and PEO spacers of different lengths.

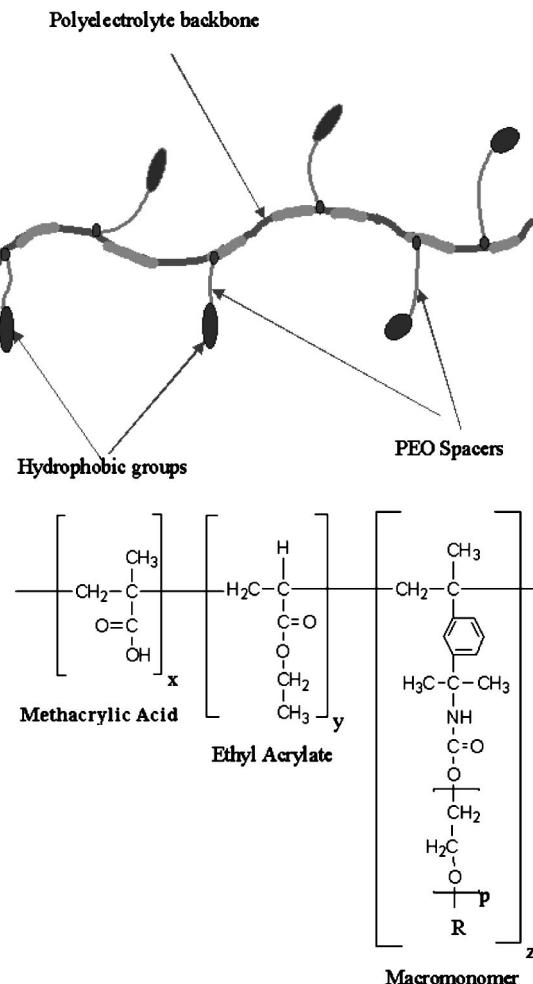


FIG. 1. Schematic representation of a typical HASE polymer together with the molecular constitution of the HASE polymers used in this study. R refers to the hydrophobic groups. x , y , z , p are structural parameters.

II. EXPERIMENTAL MATERIALS AND METHODS

A. Polymers

Two sets of model HASE polymers (DOW Chemical Company) were used in this study. The macromonomers on the first set of polymers have C_{20} hydrophobes with PEO spacers of 32–35 units. The second set of samples has macromonomers with C_{18} hydrophobes and 40 EO unit spacers. The composition of these polymers is shown in Fig. 2. The MAA content was varied between 18 and 73 mol %. The lower limit of MAA, 18%, is bound by the solubility of the polymer. On the other hand, the upper limit, 73%, was chosen to maintain the colloidal stability of the polymer in the latex form. The macromonomer level was varied from 0.2 to 1.9 mol % and was chosen based on the colloidal stability and thickening performance of the polymer.

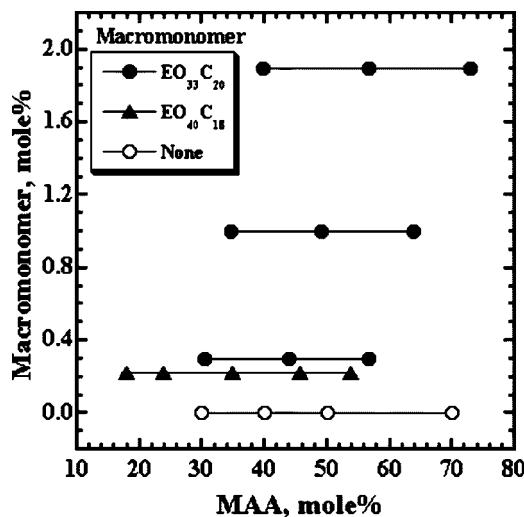


FIG. 2. Composition of the polymers used in this study. A total of 18 samples have been used, including four nonassociative ASE samples having no macromonomers.

B. Solution preparation

The polymer latex was dialyzed against de-ionized water using cellulosic tubular membranes for at least 3 weeks with a daily change of water. After dialysis, the polymer was freeze-dried, and 5% solutions were prepared and neutralized to *pH* of 9.0 ± 0.1 with NaOH, and the ionic strength was adjusted to either 10^{-4} or 0.1 M with KCl. These salt concentrations ensured controlled/negligible polyelectrolyte effect. Other polymer concentrations were subsequently prepared by dilution of the 5% solution, while maintaining both *pH* and ionic strength.

C. Rheological measurements

The rheological properties of the polymer solution were measured using stress-controlled rheometers (Rheometrics DSR II or TA Advanced Rheometer AR2000) fitted with appropriate cone and plate or couette geometries. The rheological properties of HASE polymers have been shown to be dependent on their previous shear history; therefore, a preshear protocol was necessary. Prior to any measurement, the sample was subjected to a shear rate of 1 s^{-1} for 5 min followed by a 10 min rest period. This protocol was found to be sufficient for structure recovery of the sample as noticed from dynamic time sweep experiments [English *et al.* (1997, 1999, 2000, 2002); Abdala *et al.* (2003)]. In this study, we conducted three types of experiments, steady shear, dynamic oscillatory shear, and transient creep. Both the dynamic oscillatory and the transient creep experiments were carried out using small stresses so that the sample was within the linear viscoelastic region, where the properties are independent of the applied stress.

The intrinsic viscosities of the polymer solutions were measured with Ubbelohde dilution viscometers situated in a thermostatic-control water bath at 25°C . The efflux times of the polymer solutions were converted to reduced and inherent viscosities according to the following definitions:

$$\eta_{\text{reduced}} = \frac{\eta_{\text{specific}}}{c} = \frac{t - t_s}{ct_s}; \quad (1)$$

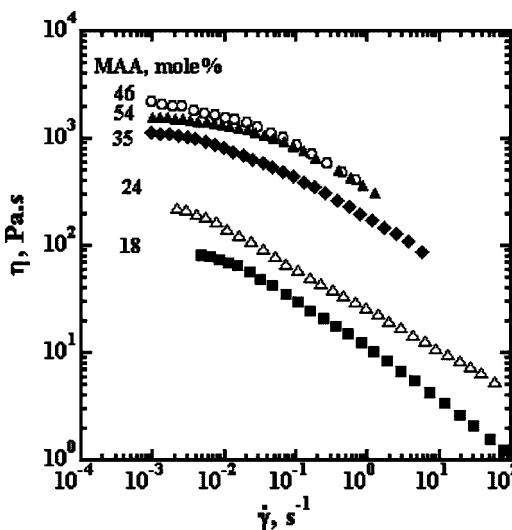


FIG. 3. Steady shear data for 3% solution of HASE polymers with different MAA concentration. Polymers have 0.22 mol % macromonomers with C18 hydrophobes and 40 EO units: Viscosity is shown as a function of shear rate.

$$\eta_{\text{inherent}} = \frac{\ln(\eta_{\text{relative}})}{c} = \frac{\ln(t/t_s)}{c}, \quad (2)$$

where t_s is the solvent efflux time. Using the familiar Huggins and Kraemer equations

$$\eta_{\text{reduced}} = [\eta] + K_H [\eta]^2 c, \quad (3)$$

$$\eta_{\text{inherent}} = [\eta] + K_K [\eta]^2 c, \quad (4)$$

the intrinsic viscosity $[\eta]$ was obtained by plotting the resulting reduced and inherent viscosities against concentration and extrapolating to zero concentration.

D. Glass transition temperature (T_g) measurements

The second order transition temperature, T_g , was measured for the bulk polymer samples using a Perkin-Elmer DSC-7 thermal analyzer equipped with a cooler system. Measurements were carried out on 3–8 mg samples at a heating rate of 10 °C/min and an indium standard was used for calibration. Before each scan, samples were annealed at 200 °C for 3 min to erase thermal history, followed by a flash quenching to –100 °C at 500 °C/min. T_g was taken as the midpoint of the second order transition.

III. RESULTS AND DISCUSSION

A. Effect of MAA content

The steady shear viscosity profiles of polymers with different MAA mol % at a fixed level of macromonomer are shown in Fig. 3. We find the samples to exhibit strong shear thinning with a small or nominal zero shear plateau indicating that all samples maintain their associative behavior. One of the functions of the MAA group is to render the polymer soluble (not a latex), and we find that even at the lowest MAA content of 18 mol % the polymer is sufficiently soluble and expanded to allow hydrophobic associations. Figure 3 also reveals a large increase in the steady shear viscosity as the MAA

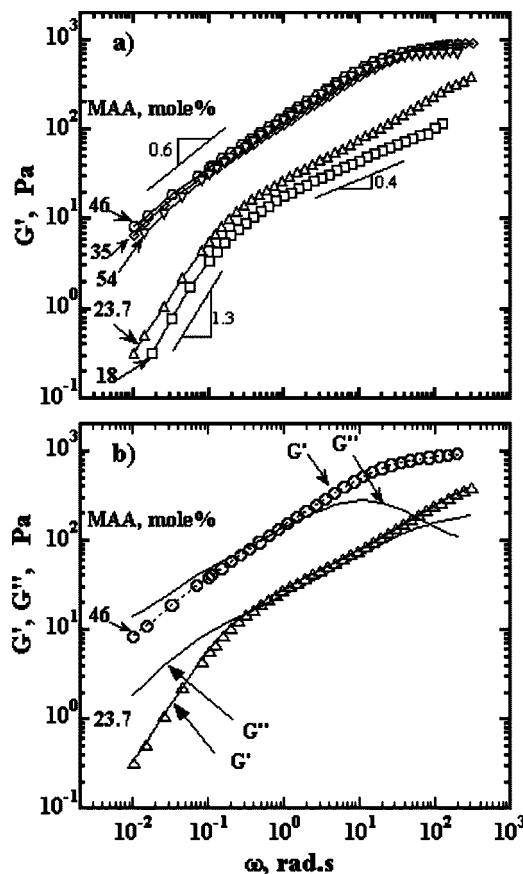


FIG. 4. Dynamic frequency spectrum of 3% solutions of HASE polymers: (a) elastic modulus (G') of polymers with different MAA content and (b) elastic and viscous moduli of two polymers with different MAA content.

content is increased from 18 to 35 mol %, with a substantial jump observed between 24 and 35 mol %. Further increase of the MAA content to 46% shows a moderate increase in viscosity. For MAA contents higher than 46 mol %, the viscosity shows a slight decrease. A maximum in Brookfield viscosity has been reported previously for an analogous polymer system at a MAA composition of 40 mol % [Jenkins *et al.* (1996)].

Similar behavior is observed when we examine the dynamic behavior of these samples as probed by an oscillatory shear experiment. Figure 4(a) shows the elastic modulus (G') as a function of frequency for samples with different MAA content. There is a significant increase in G' as the MAA content increases up to 35% followed by a slight increase as the MAA content is increased to 46%. Further increase in the MAA acid content to 54% leads to a slight decrease in G' . In addition, a jump in G' is observed when the MAA concentration is increased from 25% to 35%. All these characteristics are reminiscent of the steady shear behavior. Moreover, there is a change in the dependence of G' on frequency as the MAA content increase. With low MAA, the elastic modulus scales as $G' \sim \omega^{1.3}$ in the terminal region followed by a weaker dependence, $G' \sim \omega^{0.4}$, at high frequencies. In contrast, at high MAA content, the elastic modulus shows a weaker dependence on frequency in the terminal region, $G' \sim \omega^{0.6}$, and reaches a plateau at higher frequencies. It is very interesting that the slope in the terminal region for the

sample with 54% MAA increases to 0.7, which suggests the presence of an optimum MAA concentration that yields the lowest dependence on frequency. Details on the power-law exponents of these types of polymers, together with their deviation from the Cox-Merz rule are presented elsewhere [English *et al.* (1997; 2002); Tam *et al.* (1998; 2000a); Tan *et al.* (2000b; 2001)].

Another interesting behavior observed is the change in the longest relaxation time (taken as the reciprocal of the angular frequency where G' and G'' are equal) with the MAA content. Figure 4(b) shows the dynamic frequency spectrum of two samples with low (23%) and high (46%) MAA content. The G' , G'' crossover shifts to higher frequency as the MAA increases. The slower dynamics for the samples with low MAA is unexpected, because of their relatively weaker network structures, *vis a vis* lower G' . A likely explanation for this could be that polymers with low and high MAA contents have different relaxation mechanisms. A close examination of the moduli profiles in Figs. 4(a) and 4(b) show that samples with high MAA content exhibit features typical of common associative polymers: terminal region with cross over of G' and G'' followed by a near plateau in G' and a maxima in G'' . In contrast, low MAA samples show both G' and G'' to have the same scaling exponent ($\sim \omega^{0.4}$) at intermediate frequencies, and absence of a G' plateau or, no plateau or maximum in G'' . Such behavior has been reported for HASE polymer samples with different hydrophobe sizes and attributed to the formation of microgel formation rather than the formation of a true solution [English *et al.* (1999)]. Due to the smaller hydrodynamic size of samples with low MAA, the accessibility of the hydrophobic groups could be reduced leading to formation of swellable aggregates rather than completely soluble particles. In this case, the relaxation mechanism will involve both deformation and diffusion of the swollen aggregates rather than the relaxation associated with the soluble polymer solution formed with high MAA.

The large increase in the viscosities and moduli observed as the MAA content increases from 18 to 35 mol % may be attributed to the increase in the hydrodynamic size of the polymer chains caused by increased hydrophilicity of the polymer backbone and increased charge density (polyelectrolyte effect). To verify this increase in chain dimension, experiments were conducted to measure the intrinsic viscosity [η] of various samples. Figure 5 shows a representative plot of polymers with different MAA proportions for fixed macromonomer content. This change in the hydrodynamic size is evident from the observed increase in the intrinsic viscosity [η]. The values of $k_H - k_K$ for the samples with different MAA content lie between 0.57 and 0.77, which is higher than the expected theoretical value of 0.4. This deviation from the hard sphere value is perhaps an indication of the samples possessing an associative nature, regardless of the MAA content. To further examine how changes in hydrodynamic size alone would affect viscosity; we measured the viscosity of a 5% solution of the nonassociative ASE polymers, which are copolymers of MAA and EA. We find the viscosity of such polymers, shown in Fig. 6, to increase with MAA content and plateau at large MAA concentration, similar to the behavior observed in the associative HASE polymers.

For associative polymers, we envision other factors to play a role as well, in dictating their rheology as the MAA content is increased. At low MAA concentrations, the smaller chain size will limit the hydrophobic interactions to predominantly intramolecular association. As the MAA content is increased, the polymer hydrophilicity increases and the chains become more extended. The solution viscosity and viscoelastic properties could therefore be further enhanced by the ability of the hydrophobes to form intermolecular associations. On the other hand, increasing the MAA content could increase the inherent chain stiffness and hinder accessibility of the hydrophobic groups. This suggested loss of chain flexibility as a result of increasing the MAA content may be consistent with the

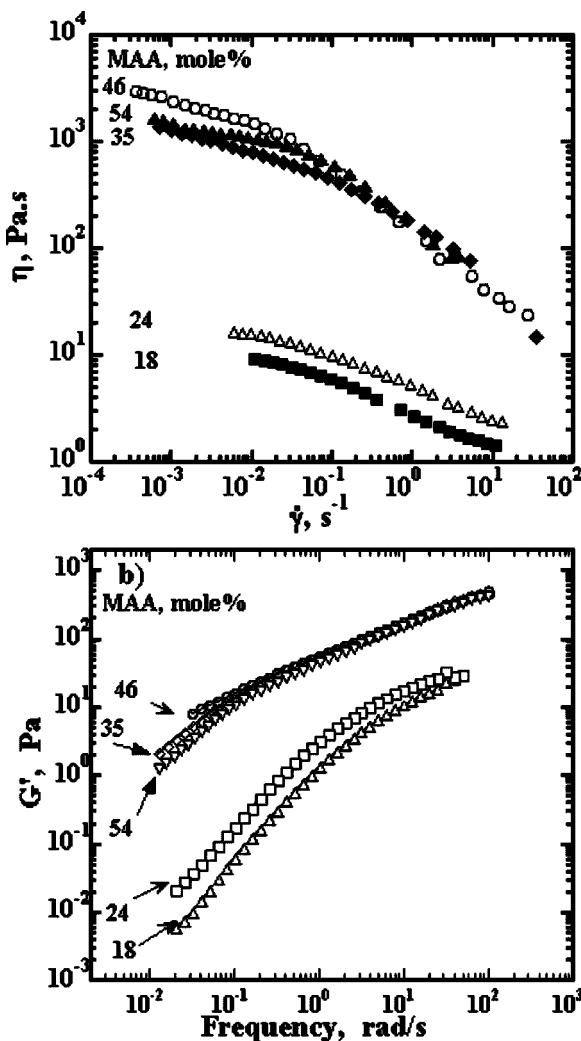


FIG. 5. Steady shear viscosity (a) and elastic modulus (b) for 3% solution of HASE polymers with different MAA concentration at 0.1 M KCl. Polymers have 0.22 mol % macromonomers with C₁₈ hydrophobes and 40 EO units.

increase in the glass temperature (T_g) values observed as MAA content increases in Fig. 5 for undiluted HASE polymer samples. Another factor that could contribute to the solution rheology of HASE copolymers would be the aggregation of the EA blocks [Dai *et al.* (2000); Seng *et al.* (2000); Ng *et al.* (2001); Tan *et al.* (2001)]. The contribution from the aggregation of EA blocks would diminish due to a decrease in their relative amount as the MAA content increases. A balance among these three factors (hydrodynamic size, chain flexibility, and aggregation of EA blocks) could possibly lead to maxima in G' and η as the MAA content is increased.

An issue to address at this stage is the relative importance of the hydrophobic and electrostatic interactions in dictating our rheological results. Since the salt concentration used in our study thus far has been substantially lower than the carboxylic group concentration, one may expect electrostatic effects to dominate. However, the rheology of

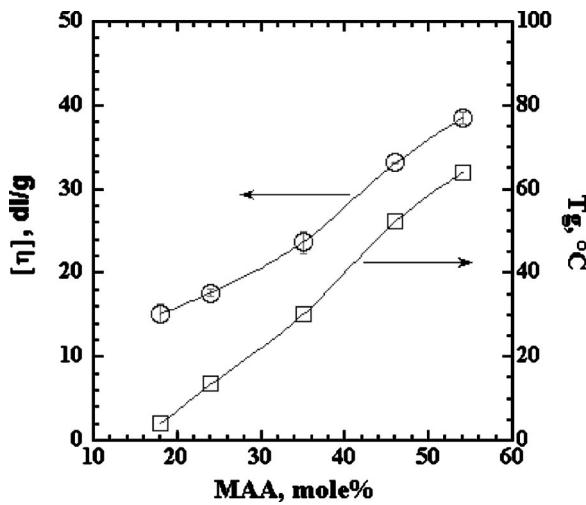


FIG. 6. Intrinsic viscosity ($[\eta]$) and glass transition temperature (T_g) for polymers with different MAA content. All polymers have 0.22 mol % macromonomer with C₁₈ hydrophobes and 40 EO units.

our system is primarily controlled by hydrophobic interactions. This is supported from three sources. First, several studies on the effects of salt concentration on similar HASE polymers [Ng *et al.* (1999); Dai *et al.* (2001, 2002)] indicate that electrostatic interactions (polyelectrolyte effect) are influential in the dilute regime whereas hydrophobic effects are dominant in the concentrated or semi concentrated regime. The salt concentration, *vis a vis* electrostatic interactions, would have more of an impact on the dilute solution properties as it would effect the chain size. At higher concentrations, however, once the chains are able to engage in hydrophobic interactions, the electrostatic effect becomes minimal. Second, comparison of the steady shear viscosity of a 5% solution of the parent polymers with no hydrophobic groups (Fig. 7) to a 3% solution of the hydrophobically

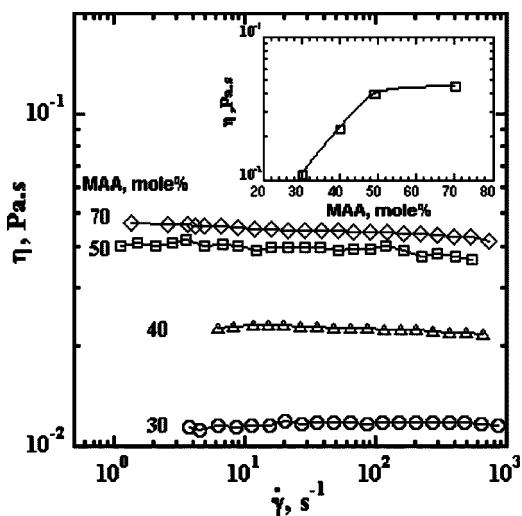


FIG. 7. Steady shear viscosity vs shear rate for the nonassociative ASE polymers with different MAA content. Inset shows the zero shear viscosity as a function of MAA mol %.

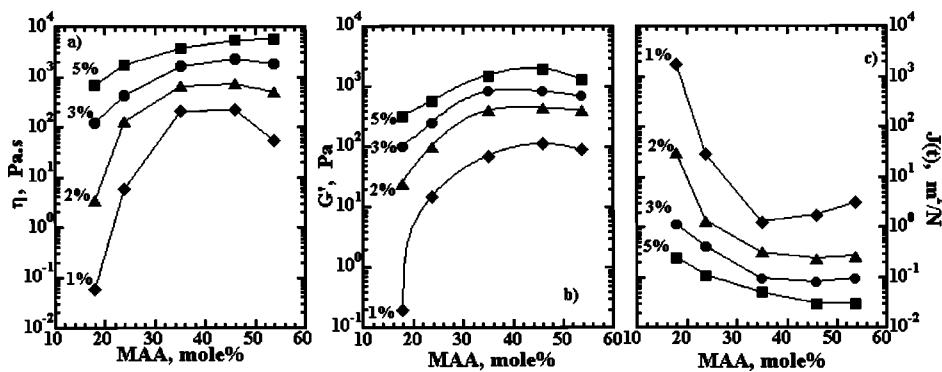


FIG. 8. Effect of MAA content and polymer concentration on (a) the steady shear viscosity at shear rate = 0.01 s^{-1} , (b) the elastic modulus at angular frequency = 100 rad/s , and (c) the creep compliance at $t = 100\text{ s}$. All polymers have 0.22 mol % macromonomer with C_{18} hydrophobes and 40 EO units.

modified sample (Fig. 3) reveals that addition of hydrophobes to the parent polymer increases the viscosity by more than three orders of magnitude. This, clearly, shows the overriding role of hydrophobic interactions. Finally, examination of samples prepared at a much higher salt concentration (0.1 M KCl) reveal the same trend in viscosity and elastic modulus with increasing MAA content (Fig. 5) as that observed at the low salt concentration of 10^{-4} M KCl (Figs. 3 and 4). This unambiguously suggests that the behavior pattern observed in our system is not a manifestation of polyelectrolyte effects but rather of hydrophobic interactions. The magnitude of η and G' are, however, different than those at the low salt concentration, as expected, due to the different chain size at the high salt concentration.

B. Concentration effects

To determine if the observed trends in viscosity and modulus with increasing MAA content carries over to other polymer concentrations, we examine in Fig. 8 the viscoelastic characteristics of polymers at four different concentrations (1%, 2%, 3%, and 5%). Figure 8(a) shows the steady shear viscosity at a fixed shear rate of 0.01 s^{-1} as a function of MAA mol % for the different polymer concentrations. We find all four-polymer concentrations to show the same dependence on MAA content with a broad maximum around 40 mol % MAA. Similar results are obtained when the high frequency elastic modulus (G' at $\omega = 100\text{ rad/s}$) is plotted versus MAA content for the different polymer concentrations, as shown in Fig. 8(b). On the other hand, a broad minimum is observed when the creep compliance at $t = 100\text{ s}$ is plotted versus the MAA content for different concentrations [Fig. 8(c)]. It is interesting to point out that all three material functions are consistent in that the maxima or minimum occur at the same MAA content of approximately 40 mol %.

The difference in the polymer behavior at low and high MAA (e.g., Fig. 4) should manifest themselves in different concentration dependence of the rheological material functions. Figure 9 shows the concentration dependence of the low shear viscosity (shear rate = 0.01 s^{-1}), the high-frequency elastic modulus ($\omega = 100\text{ rad/s}$), and the creep compliance ($t = 100\text{ s}$) for two representative polymers with different MAA content. In both cases we find η , G' , and $J(t)$ to exhibit power-law behavior, albeit with different exponents. In fact, the data suggest the presence of three distinct power-law regimes for all three material functions regardless of the MAA content. However, the concentration at

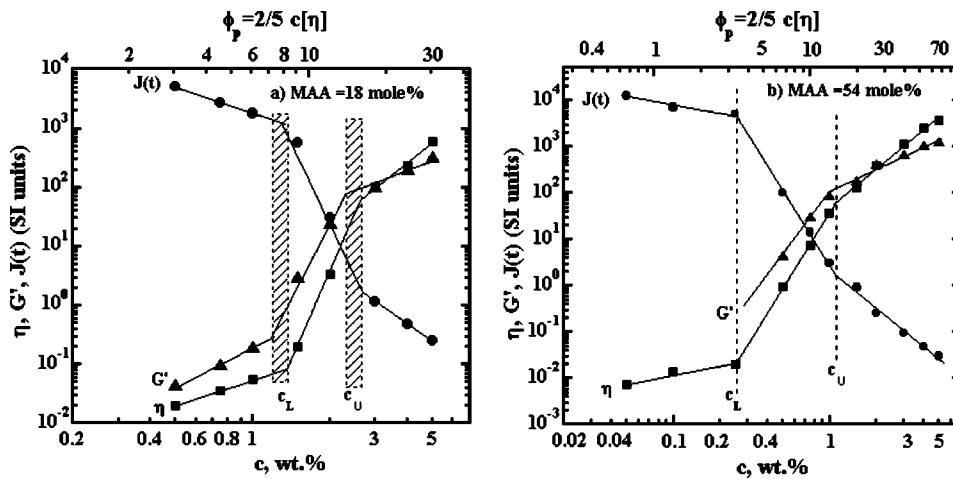


FIG. 9. Concentration dependence of steady shear viscosity (η) at 0.01 s^{-1} , elastic modulus (G') at 100 rad/s , and the creep compliance $J(t)$ at $t = 100\text{ s}$ for polymer with (a) 18 and (b) 54 mol % MAA.

which these transitions occur shifts to lower values as the MAA content increases. Interestingly, three concentration regimes have been observed recently for a similar HASE polymer [Knaebel *et al.* (2002)] and other hydrophobically modified polymers [Regalado *et al.* (1999)]. It has also been predicted by the sticky Rouse model [Rubinstein *et al.* (2001)]. Figures 9(a) and 9(b) show η , G' , and $J(t)$ as a function of the coil overlap of the polymer, $\phi = 2/5 c[\eta]$. In this case, the transitions seem to take place at somewhat similar ϕ . The lower transition occurs at a ϕ of about 3–7 whereas the upper transition takes place at $\phi \sim 12$ –15. The ϕ value for the upper transition is slightly higher than the expected value for the onset of entanglement of 5–10 [English *et al.* (2002)]. However, this should not be construed as being a polyelectrolyte effect as the entanglement concentration for a polyelectrolyte solution is about 10^3 – $10^4 c^*$ [Dobrynin *et al.* (1995)] whereas in our case this occurs at about 36–46 c^* (Fig. 10).

Concentration transitions for conventional polymers are typically attributed to a change from dilute, to unentangled and entangled semidilute regimes and occur at concentrations related to the overlap concentration, c^* . For associative polymers, on the other hand, the overlap concentration c^* is not a relevant variable [Abdala *et al.* (2003); Regalado *et al.* (1999)]. This can be demonstrated by comparing the concentration at which the transitions occur as shown in Fig. 9. For simplicity we denote the lower transition concentration as c_L and the upper transition concentration c_U . Figure 10 shows the transition concentrations c_L and c_U for samples with different MAA content; c_L ranges between 1.2 and 0.25 whereas c_U ranges from 2.5 to 1.1. To compare the transition concentrations with the overlap concentration (c^*), Fig. 10 also includes data for 10 times c^* , where c^* is taken as the reciprocal of the intrinsic viscosity. We find all transition concentrations to shift to lower values as the MAA content increases. This is expected based on the higher intrinsic viscosity values observed for samples with higher MAA content (Fig. 6). However, the shape and magnitude of the c_L and c_U curves show no correlation with the c^* curve indicating it to be not a pertinent parameter.

We believe that the three concentration regimes observed in Fig. 9 can be explained in terms of different modes of hydrophobic association. Figure 11 shows schematically the expected hydrophobic associations possible in these different regions. In regime 1 ($c < c_L$), the polymer chains are isolated and, as a result, only intramolecular associations

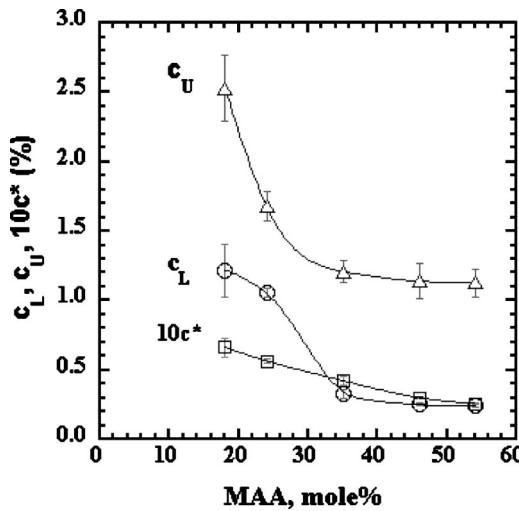


FIG. 10. Effect of MAA content on the transition concentrations (c_L and c_U), and the overlap concentration (c^*).

are possible. The solution viscosity in this region is similar to that of unmodified polymer analogs. In this regime, the scaling exponent for each material function varied with MAA. At low MAA content (18 mol %), scaling exponents of 1.2, 2.0, and -1.3 are observed for η , G' , and $J(t)$, respectively. These exponents decrease with MAA content and reach values of 0.60 and -0.65 corresponding to viscosity and creep compliance, respectively. The variation of the scaling exponents can be attributed to the changes in the polymer-solvent interactions. There is an increase in the polymer hydrophilicity as the MAA content increases, which leads to a relative change in solvent quality towards being a good solvent. The scaling exponent for η for low MAA content samples is also in agreement with an exponent of 1.34 observed for hydrophobically modified polyacrylic acid [Lochhead and Rulison (1994)].

In regime 2 ($c_L < c < c_U$), the polymer chains become overlapped and the hydrophobes are engaged in intra- and intermolecular associations. Therefore, this region is characterized by a very rapid increase in viscosity due to the transformation from intra- to intermolecular association with an expected strong dependence on concentration. In fact, η , G' , and $J(t)$ exhibit very large dependences on concentration for all samples. The scaling exponents, however, change as the MAA content changes. For samples with low

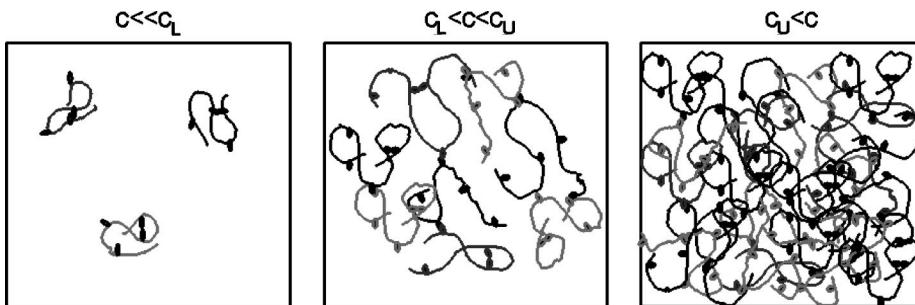


FIG. 11. Schematic of possible hydrophobic interaction modes in different concentration regimes.

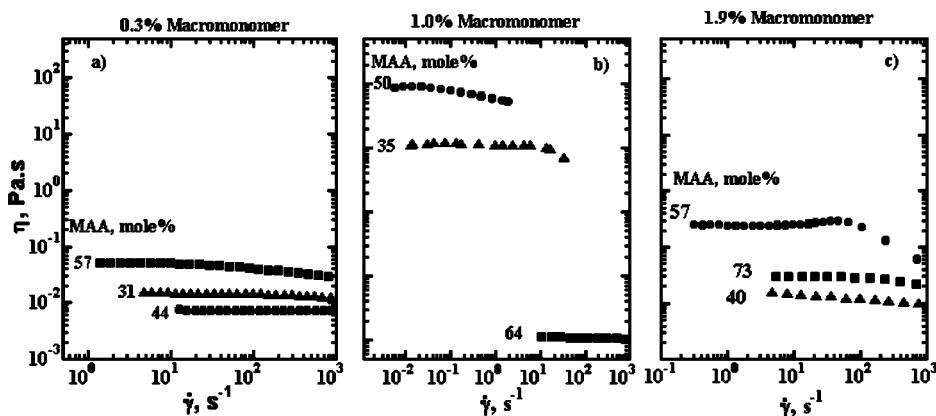


FIG. 12. Effect of MAA content on the steady shear viscosity of 3% solutions of polymers with (a) 0.3, (b) 1.0, and (c) 1.9 mol % macromonomer content.

MAA content (18 mol %), exponent factors as high as 9.0 for η , 4.6 for G' and -8.9 for $J(t)$ are obtained, as compared to 4.4 for G' , 5.4 for η , and -5.3 for $J(t)$ for the sample with 54% MAA. Regaldo *et al.* (1999) also obtained varied scaling exponents in this region for solutions of hydrophobically modified polyacrylamide polymers. Scaling exponents varied below and above 4.3 based on the number of stickers (hydrophobes) per chain. The large variation on scaling exponent values for samples with high and low MAA supports our earlier conclusion about the difference in the microstructure of samples with high and low MAA. Our result of a viscosity exponent (5.4) at high MAA is in good agreement with the theoretical value of 4.2 based on the sticky Rouse model for an associative polymer in a good solvent [Rubeinstein *et al.* (2001)]. On the other hand, the higher value (9.0) at low MAA content is in good agreement with the exponent (7.9) reported for similar HASE polymers [English *et al.* (1999, 2002)].

In regime 3 ($c > c_U$) the hydrophobes are mainly engaged in intermolecular interactions. Thus, a weaker dependence on concentration is expected. We obtained scaling exponents of 2.6, 1.8, and -2.4 for η , G' , and $J(t)$, respectively. The viscosity scaling-exponent is in full agreement with the value 2.7 reported for similar HASE polymers [English *et al.* (2002)]. However, it is lower than the 3.75 predicted by Rubeinstein *et al.* (2001) and observed experimentally for hydrophobically modified polyacrylamide [Regaldo *et al.* (1999)]. Since all our data were taken at a fixed shear rate, frequency or time and not under zero shear or plateau modulus conditions, we make no attempt to compare our exponents with theory as this would be inappropriate and beyond the scope of this work.

C. Effect of macromonomer concentration

To examine the effect of macromonomer concentration on rheology, we used nine polymers each having macromonomers with C₂₀ hydrophobes and a degree of ethoxylation of 33 EO spacer units. Every three polymers in this set have the same macromonomer concentration with varied MAA and EA content, as shown in Fig. 2. Figure 12 compares the viscosity versus shear rate profiles for 3% polymer solutions using samples with different MAA content. The results of Figs. 12(b) and 12(c), together with our earlier discussion (Figs. 3 and 8), seem to indicate that there is an optimum MAA concentration that leads to a maximum in steady shear viscosity, regardless of macromonomer concentration. This optimum concentration lies between 43 and 60 mol %

MAA. For the sample in Fig. 12(a), which does not exhibit a viscosity maximum, we believe that such a maximum would be observed if samples with MAA content higher than 57% were synthesized and examined.

The effect of the concentration of macromonomers on the steady shear data can also be observed from Fig. 12. It is clear that the highest viscosity in this set of samples is obtained with 1.0 mol % macromonomers, Fig. 12(b). The steady shear viscosity of a 3% solution of samples with 1.0% macromonomers and low or moderate contents of MAA is about two orders of magnitude higher than that of any of the other samples. This indicates that there is also an optimum macromonomer concentration that yields the highest enhancement in viscosity. At a low macromonomer concentration (0.3%), we observe the viscosity to be low and almost Newtonian indicating the presence of minimal hydrophobic associations [Fig. 12(a)]. In particular, the very low viscosity of samples with 44% and 31% MAA suggests the absence of hydrophobic interactions. Only the chain expansion and aggregation of the blocky EA groups contribute to the solution rheology. The chain expansion contribution is larger for the sample with 44% MAA while the EA aggregation is larger for sample with 31%. The sum of these two contributions leads to a higher viscosity for the sample with 31% MAA. This is in contrast to samples with higher macromonomer contents, Figs. 12(b) and 12(c), where the increase in MAA contribute to the chain size as well as hydrophobic associations.

The higher steady shear viscosity of the samples with 1% macromonomer concentration compared to those with 0.3% macromonomer can be attributed to the increase in the number of intermolecular junctions as the number of hydrophobes per chain increases. On the other hand, if there are too many hydrophobes per chain such that the distance between hydrophobes is less than the PEO spacer length, larger numbers of the hydrophobes will engage in intramolecular association rather than form active junctions through intermolecular association [McCormick *et al.* (1992); Chang and McCormick (1994a; 1994b); Petit *et al.* (1997); Yamamoto *et al.* (1998); Yamamoto and Morishima (1999)]. This would lead to a decrease in viscosity [Fig. 12(c) with 1.9% macromonomer] as the steady shear viscosity and the viscoelastic properties of this polymer system are largely dependent on the number of active intermolecular associations. The transient network theory [Tanaka *et al.* (1992)] predicts that the plateau modulus is proportional to the number of active junctions and the steady shear viscosity is the product of the plateau modulus and the microscopic relaxation time corresponding to the reciprocal of the bond breaking and reformation rate. Thus increasing the number of active junctions will increase the steady shear viscosity by both increasing the plateau modulus and slowing the relaxation process.

IV. SUMMARY

This study provides a comprehensive analysis of the effects of polymer composition on the rheology of associative polymers. The effects of the polymer backbone composition is elucidated by varying the relative proportion of MAA and EA while that of the pendant macromonomer is examined by varying its concentration. An increase in the proportion of MAA in the backbone leads to a higher viscosity and enhancement in viscoelastic characteristics (G', J) consistent with a concomitant increase in chain size. At higher MAA concentrations, maxima in viscosity and viscoelastic properties are observed. Such a behavior can be attributed to the combined effects of increased chain dimension, possible loss of chain flexibility, and reduced contributions from the aggregation of blocky EA groups that occurs with increased MAA content. The scaling of viscosity, elastic modulus, and creep compliance with polymer concentration reveal the

presence of three transitional regimes, each with power-law dependence. These regimes are attributed to changes in the hydrophobic interactions with concentration.

The macromonomer concentration also has a strong influence on polymer rheological behavior, with a maximum in viscosity observed at intermediate macromonomer concentrations. At low macromonomer concentration, low viscosity resulting from weak associative behavior is observed. On the other hand, high concentration favors the formation of intra- over intermolecular associations leading to a reduction in solution viscosity from that observed at intermediate macromonomer concentrations.

ACKNOWLEDGMENT

The authors gratefully acknowledge the comments and suggestions of Robert J. English (Northeast Wales Institute) during the preparation of the manuscript.

References

- Abdala, A. A., K. Olesen, and S. A. Khan, "Solution rheology of hydrophobically modified associative polymers: Solvent quality and hydrophobic interactions," *J. Rheol.* **47**, 497–511 (2003).
- Chang, Y., and C. L. McCormick, "Water-soluble copolymers. 58. Associative interactions and photophysical behavior of amphiphilic terpolymers prepared by modification of maleic anhydride/ethyl vinyl ether copolymers," *Macromolecules* **27**, 2151–2158 (1994a).
- Chang, Y., and C. L. McCormick, "Water-soluble copolymers: 57. Amphiphilic cyclocopolymers of diallylalkoxybenzyl-methylammonium chloride and diallyl-dimethylammonium chloride," *Polymer* **35**, 3503–3512 (1994b).
- Dai, S. T., K. C. Tam, and R. D. Jenkins, "Light scattering of hydrophobically modified alkali-soluble emulsion (HASE) polymer: Ionic strength and temperature effects," *Macromol. Chem. Phys.* **202**, 335–342 (2001).
- Dai, S. T., K. C. Tam, R. D. Jenkins, and D. R. Bassett, "Light scattering of dilute hydrophobically modified alkali-soluble emulsion solutions: Effect of hydrophobicity and spacer length of macromonomer," *Macromolecules* **33**, 7021–7028 (2000).
- Dai, S. T., K. C. Tam, and R. D. Jenkins, "Dynamic light scattering of semi-dilute hydrophobically modified alkali-soluble emulsion solutions with varying length of hydrophobic alkyl chains," *Macromol. Chem. Phys.* **203**, 2312–2321 (2002).
- Dobrynin, A. V., R. H. Colby, and M. Rubinstein, "Scaling theory of polyelectrolyte solutions," *Macromolecules* **28**, 1859–1871 (1995).
- English, R. J., H. S. Gulati, R. D. Jenkins, and S. A. Khan, "Solution rheology of a hydrophobically modified alkali-soluble associative polymer," *J. Rheol.* **41**, 427–444 (1997).
- English, R. J., S. R. Raghavan, R. D. Jenkins, and S. A. Khan, "Associative polymers bearing n-alkyl hydrophobes: Rheological evidence for microgel-like behavior," *J. Rheol.* **43**, 1175–1194 (1999).
- English, R. J., R. D. Jenkins, D. R. Bassett, and S. A. Khan, "Rheology of a HASE associative polymer and its interaction with non-ionic surfactants," in *Associative Polymers in Aqueous Media*, ACS Advanced in Chemistry Series No. 765, edited by J. E. Glass (American Chemical Society, Washington, DC, 2000), pp. 369–380.
- English, R. J., J. H. Laurer, R. J. Spontak, and S. A. Khan, "Hydrophobically modified associative polymer solutions: Rheology and microstructure in the presence of nonionic surfactant," *Ind. Eng. Chem. Res.* **41**, 6425–6435 (2002).
- Gupta, R. K., K. C. Tam, and R. D. Jenkins, "Rheological properties of model alkali soluble associative (HASE) polymers: Effect of varying acid monomer and macromonomer composition," Proc. 13th Int. Congr. Rheol, Cambridge, UK, 2000, Vol. 1, pp. 340–342.
- Jenkins, R. D., L. M. Delong, and D. R. Bassett, "Influence of alkali-soluble associative emulsion polymer architecture on rheology," in *Hydrophilic Polymers: Performance with Environmental Acceptance*, ACS Advances in Chemistry Series No. 248, edited by J. E. Glass (American Chemical Society, Washington, DC, 1996), pp. 425–447.
- Knaebel, A., R. Skouri, J. P. Munch, and S. J. Candau, "Structural and rheological properties of hydrophobically modified alkali-soluble emulsion solutions," *J. Polym. Sci., Part B: Polym. Phys.* **40**, 1985–1994 (2002).
- Lau, A. K. M., C. Tiu, and K. C. Tam, "Rheology of hydrophobically-alkali-soluble-emulsions (HASE)," 6th World Congress of Chemical Engineering, Melbourne, Australia, 2001.

- Lochhead, R. Y., and C. J. Rulison, "An investigation of the mechanism by which hydrophobically modified hydrophilic polymers act as primary emulsifiers for oil-in-water emulsions. 1. Poly(acrylic acids) and hydroxyethyl celluloses," *Colloids Surf. A* **88**, 27–32 (1994).
- McCormick, C. L., C. E. Hoyle, and M. D. Clark, "Water-soluble copolymers: 26. Fluorescence probe studies of hydrophobically modified maleic acid-ethyl vinyl ether copolymers," *Polymer* **33**, 243–247 (1992).
- Ng, W. K., K. C. Tam, and R. D. Jenkins, "Evaluation of intrinsic viscosity measurements of hydrophobically modified polyelectrolyte solutions," *Eur. Polym. J.* **35**, 1245–1252 (1999).
- Ng, W. K., K. C. Tam, and R. D. Jenkins, "Rheological properties of methacrylic acid/ethyl acrylate copolymer: Comparison between unmodified and hydrophobically modified system," *Polymer* **42**, 249–259 (2001).
- Olesen, K. R., D. R. Bassett, and C. L. Wilkerson, "Surfactant co-thickening in model associative polymers," *Prog. Org. Coat.* **35**, 165–170 (1999).
- Petit, F., I. Iliopoulos, R. Audebert, and S. Szonyi, "Associating polyelectrolytes with perfluoroalkyl side chains: Aggregation in aqueous solution, association with surfactants, and comparison with hydrogenated analogues," *Langmuir* **13**, 4229–4233 (1997).
- Regalado, E. J., J. Selb, and F. Canadu, "Viscoelastic behavior of semidilute solutions of multisticker polymer chains," *Macromolecules* **32**, 8580–8588 (1999).
- Rubinstein, M., and A. N. Semenov, "Dynamic of entangled solution of associating polymers," *Macromolecules* **34**, 1058–1068 (2001).
- Seng, W. P., K. C. Tam, R. D. Jenkins, and D. R. Bassett, "Calorimetric studies of model hydrophobically modified alkali-soluble emulsion polymers with varying spacer chain length in ionic surfactant solutions," *Macromolecules* **33**, 1727–1733 (2000).
- Shay, G. D., "Alkali-swellable and alkali-soluble thickener technology—A review," *Adv. Chem. Ser.* **223**, 457–49 (1989).
- Tam, K. C., M. L. Farmer, R. D. Jenkins, and D. R. Bassett, "Rheological properties of hydrophobically modified alkali-soluble polymers: Effects of ethylene-oxide chain length," *J. Polym. Sci., Part B: Polym. Phys.* **36**, 2275–2290 (1998).
- Tam, K. C., W. P. Seng, R. D. Jenkins, and D. R. Bassett, "Rheological and microcalorimetric studies of a model alkali-soluble associative polymer (HASE) in nonionic surfactant solutions," *J. Polym. Sci., Part B: Polym. Phys.* **38**, 2019–2032 (2000).
- Tan, H., K. C. Tam, V. Tirtaatmadja, R. D. Jenkins, and D. R. Bassett, "Extensional properties of model hydrophobically modified alkali-soluble associative (HASE) polymer solutions," *J. Non-Newtonian Fluid Mech.* **92**, 167–185 (2000b).
- Tan, H. T., K. C. Tam, and R. D. Jenkins, "Network structures of a model HASE polymer in semidilute salt solutions," *J. Appl. Polym. Sci.* **79**, 1486–1496 (2001).
- Tirtaatmadja, V., K. C. Tam, and R. D. Jenkins, "Rheological properties of model alkali-soluble associative (HASE) polymers: Effect of varying hydrophobe chain length," *Macromolecules* **30**, 3271–3282 (1997).
- Tanaka, F., and S. F. Edwards, "Viscoelastic properties of physically crosslinked networks. 1. Transient network theory," *Macromolecules* **25**, 1516–1523 (1992).
- Yamamoto, H. M., M. Mizusaki, K. Yoda, and Y. Morishima, "Fluorescence studies of hydrophobic association of random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate and n-dodecylmethacrylamide in water," *Macromolecules* **31**, 3588–3594 (1998).
- Yamamoto, H., and Y. Morishima, "Effect of hydrophobe content on intra- and interpolymer self-associations of hydrophobically modified poly[sodium 2-(acrylamido)-2-methylpropanesulfonate] in water," *Macromolecules* **32**, 7469–747 (1999).