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Polymer 42 (2001) 249–259

polymer

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Rheological properties of methacrylic acid/ethyl acrylate co-polymer: comparison between an unmodified and hydrophobically modified system

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Received 10 December 1999; received in revised form 27 March 2000; accepted 31 March 2000

Abstract

Earlier experimental studies on the emulsion polymerized methacrylic acid/ethyl acrylate co-polymer indicated that the ethyl acrylate (EA) segments are sufficiently blocky to induce hydrophobic association between the EA blocks once the methacrylic acid groups are neutralized by a base. Detailed rheological characterization on semi-dilute solutions suggests that the viscoelastic property is caused by the transient network assembled through hydrophobic associations, rather than by physical chain entanglements. In the semi-dilute solution regime, the hydrophobically modified associative polymer exhibits higher viscosities when compared to the unmodified analogue. This is due to the formation of higher proportion of intermolecular association between the polymer clusters, which enhances the hydrophobic interaction between the hydrophobic macromonomers of different polymer chains. A mechanistic model is proposed to describe the nature of associations between the blocky EA and the hydrophobic segments of the polymer. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Ethyl acrylate; Rheological properties; Hydrophobically modified systems

1. Introduction

Water-soluble hydrophobically modified alkali soluble associative polymers (HASE) have attracted significant research interests in recent years [1–13]. This class of hydrophobically modified anionic polyelectrolytes associative polymer is prepared by emulsion polymerization at low pH to yield an acid-rich co-polymer in the form of latex dispersions. Each particle may contain as many as 10–50 polymer chains. When a base is added to the dispersion, the –COOH groups of the polymer are neutralized. The particles swell and then dissolve, releasing charged polymer chains into the solution [8,14]. The polymer solution thickens by an associative mechanism (intra- or intermolecular) and by the expansion of the high-molecular-weight polymer backbone [8,11]. The creation of the polymer network commences when the hydrophobes attached to its polymer backbone begin to aggregate, which produces a network structure consisting of numerous polymer chains.

The grafting of hydrophobic groups to the water-soluble polymer backbone enhances the rheological properties when compared to those without hydrophobic groups. The increase in the viscosity profile is caused by the self-association of the hydrophobic groups, yielding intermolecular networks in solution [6,11,15–20]. Volpert et al. [21,22] and Aubry and Moan [23] observed lower rheological properties of the modified hydrophobic system at low polymer concentrations. They attributed this behavior to the formation of intramolecular associations between the hydrophobes along the same polymer chain. As a result, the dimensions of the polymer coil is reduced, yielding a lower radius of gyration that corresponds to a lower viscosity.

Most of the previous studies focused on incorporating 1–5 mol% of hydrophobic moiety to a homopolymer (e.g. polyacrylamide [21,22,24] and polyacrylic acid [25–27]) instead of a co-polymer. In addition, Candau and co-workers reported on the behavior of acrylic acid–acrylamide–styrene copolymers containing only 1–2 mol% styrene [28,29]. In their study, an individual styrene unit was incorporated to the acrylic acid–acrylamide backbone, producing blocky styrene sequences (blocky hydrophobic bunches), which produces a very strong hydrophobic association. The rheological properties of a series of acrylic acid–acrylamide copolymers with C_{16} alkyl chains were examined, where strong association was observed that gave rise to a large increase in the viscosity. Hydrophobically modified associative polymers containing blocky ethyl acrylate segments on the polymer backbone has not been reported by other research groups. The associative mechanism that

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PII: S0032-3861(00)00280-9

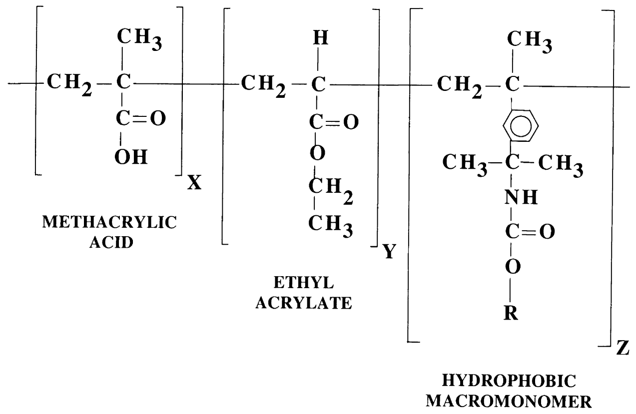

Fig. 1. Chemical structure of the model HASE polymers.

controls the rheological properties for this complex polymer system is not clear at this point in time.

This paper describes the rheological behavior of the hydrophobically modified and unmodified co-polymers of methacrylic acid/ethyl acrylate in dilute and semi-dilute solutions. A comparative study between the hydrophobically modified and unmodified samples will provide a clearer insight into the associative mechanism and how it affects the polymer chain dynamics.

2. Material and experimental methods

The model associative polymers are the hydrophobically modified, alkali-soluble (HASE) polymers synthesized by Union Carbide, via the emulsion polymerization of methacrylic acid (MAA), ethyl acrylate (EA) and a macromonomer capped with a hydrophobic group. The polymer examined in the present work has a structure as shown in Fig. 1, where R is C_nH_{2n+1}. HASE 00-20 contains 1 mol% of a $C_{20}H_{41}$ alkyl group distributed along the charged polymer backbone while HASE 107 is a control polymer consisting of a co-polymer of MAA/EA with no macromonomer attached to its polymer backbone.

A brief description of the synthesis route of the model polymer has been previously reported [1,5] and will not be presented here. The characteristics of the model polymer are given in Table 1. The molecular weight of the model associative polymer is in the order of 100,000–200,000 as determined by intrinsic viscosity [3] and static light scattering [30]. The molecular weight and monomer sequence distribution is believed to be quite similar since the process used to produce them was held constant.

Table 1
Details on chemical composition of model HASE polymers

Name of HASE	Moles of EO	Hydrophobes name	Hydrophobes formula	Molar ratio of MAA/ EA/macromonomer
RDJ 107	0	–	None	50:50:0
RDJ 00-20	0	Eicosanyl	$C_{20}H_{41}$	49:50:1

The samples were prepared from a stock solution of 3 wt% of polymer dispersions in 10^{-4} M KCl. For higher concentrations of up to 5 wt%, the stock solution was concentrated by slow evaporation of the water under constant stirring. The alkaline used to neutralize the polymer to the required pH of ~9.0 is 2-amino-2-methyl-1-propanol (AMP-95, Angus Chemical). This is to ensure complete neutralization of the polymer where maximum enhancement of the rheological properties was observed [8,11].

2.1. Dilute solution

The viscosities of the polymer solution at low concentration were measured using a Ubbeldohe capillary viscometer at a temperature of 25 ^ 0.02°C. The detailed experimental procedures for ensuring high accuracy, repeatability and reliability was previously reported by Ng et al. [10].

The intrinsic viscosities were obtained by extrapolating the reduced and inherent viscosity data to zero polymer concentration using Huggins [31] and Kraemer [32] equations as shown below:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c \tag{1}$$

where K_H is the Huggins coefficient and

$$\frac{\ln \eta_r}{c} = [\eta] + (K_K)[\eta]^2 c \tag{2}$$

where K_H is the Kraemer coefficient and theoretically, $K_H - K_K = 1/2$.

2.2. Semi-dilute solution

The steady shear and dynamic properties of semi-dilute associative polymer solutions were measured using a Rheometric Scientific ARES fluids rheometer. The ARES system is fitted with a double concentric cylinder geometry with an inner cup diameter of 27.94 mm, outer cup diameter of 34 mm, inner bob diameter of 29.5 mm, outer bob diameter of 32 mm and bob length of 31.9 mm. All the dynamic rheological data were checked as a function of strain amplitude to ensure that the shear oscillatory measurements were performed in the linear viscoelastic region. In order to ensure that the dynamic data reflects the true material properties, the data from the ARES rheometer were compared with those obtained from the controlled rate Contraves LS40 rheometer. The dynamic data obtained from the LS40 and ARES rheometers are identical. This gives us some confidence that the dynamic properties of the low-viscosity polymer solution using the couette geometry in the ARES fluids rheometer are real material properties and not caused by fluid inertia.

In addition, the relaxation spectrum obtained from the Orchestrator software is found to be identical to those generated from the PolySoft software [33]. Hence, the

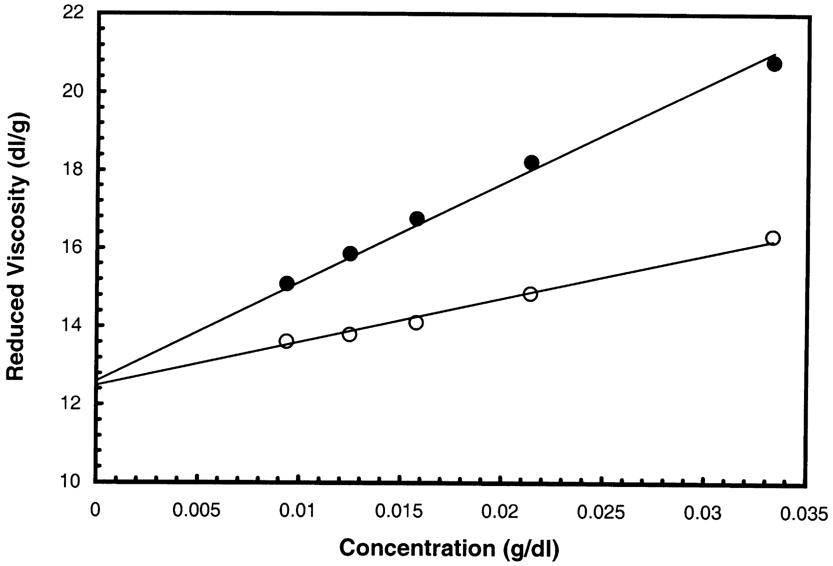

Fig. 2. Reduced viscosities of model polymers HASE 107 (X) and HASE 00-20 (W) at 25°C.

accuracy of the transformed relaxation spectra for the determination of the relaxation time is reliable.

3. Results and discussion

3.1. Dilute solution properties

The intrinsic viscosity plot as described by Eq. (1) for the model polymer systems, HASE107 (control) and HASE 00-20, in controlled pH and conductivity environment is shown in Fig. 2. It is interesting to observe that the polyelectrolyte co-polymer system (HASE 107) in low salt obeys the Huggins relationship, rather than the Fuoss and Strauss relationship [34,35]. The reason for this behavior is as follows. The chemical structure of the unmodified polymer as shown in Fig. 1 (HASE 107) shows that it is a co-polymer

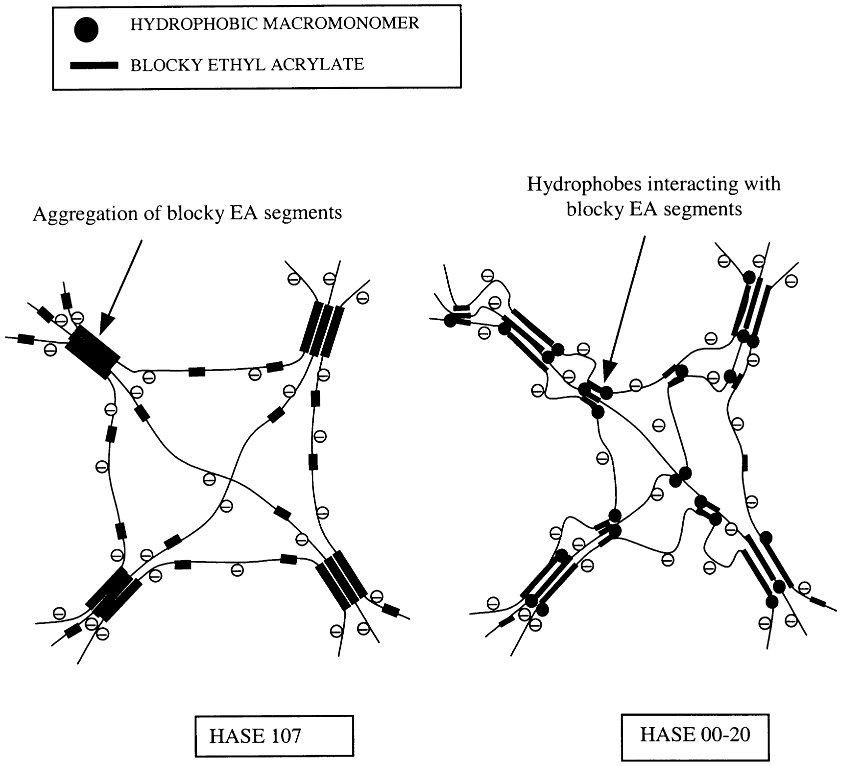

Fig. 3. Proposed associating mechanism for unmodified (HASE 107) and hydrophobically modified (HASE 00-20) in the dilute solution regime.

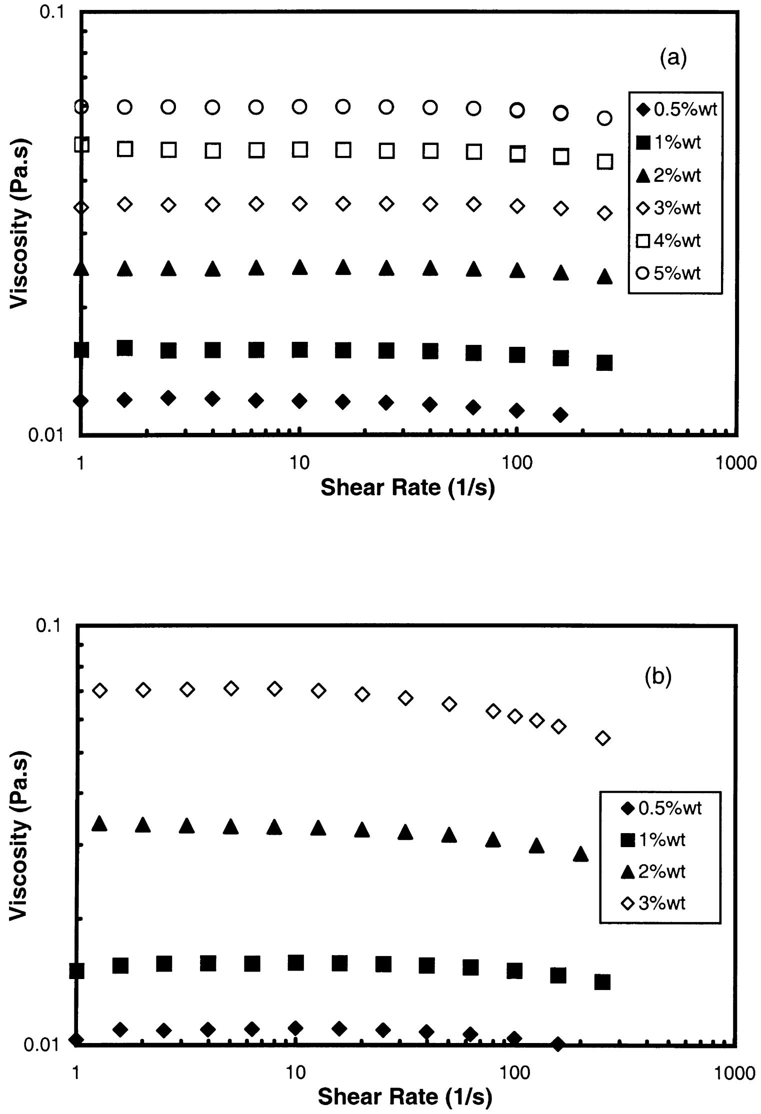

Fig. 4. Steady shear viscosity profiles of various concentrations of: (a) HASE 107; (b) HASE 00-20 (pH ~ 9.5).

containing methacrylic acid (MAA) and ethyl acrylate (EA). The backbone of the co-polymer is predominantly hydrophilic because it contains sufficient carboxyl anions to render it water soluble at elevated pH. However, ethyl acrylate (EA) is slightly hydrophobic. Thus, when the ethyl acrylate is sufficiently blocky, it will induce hydrophobic association. Recent studies by Dai et al. [36] on the HASE system using dynamic light scattering technique showed that the EA blocks along the polymer chain is hydrophobic enough to form hydrophobic association in water. Aggregates consisting of a few polymer chains occur in solution and the hydrophobic sites in HASE 107 suppresses the electrostatic intramolecular repulsion of the polyelectrolyte chains, which gives rise to a linear relationship in the reduced viscosity in the dilute solution regime.

The intrinsic viscosity of the two polymer systems shown in Fig. 2 is found to be identical ($[\eta] = 12.6$ dl/g). This implies that the size of the associative polymer cluster in water, as described by Flory [37,38] is similar. The theories on frictional properties of polymer molecules in solution demonstrate that the intrinsic viscosity is proportional to the effective hydrodynamic volume of the molecule in solution divided by its molecular weight. The effective volume is proportional to the cube of a linear dimension of the randomly coiled chain. If the root mean square end–end distant $\langle r^2\rangle^{1/2}$ of the polymer is chosen, then

$$[\eta] = \frac{\Phi\langle r^2\rangle^{3/2}}{M_w} \tag{3}$$

where Φ is a constant that does not depend on the constitution or configuration of the polymer or solvent, but on the relative expansion of the coil in solution.

Although both systems possess significant difference in their hydrophobicity, the presence of their hydrophobic associating sites along the stiff polymeric backbones [39]

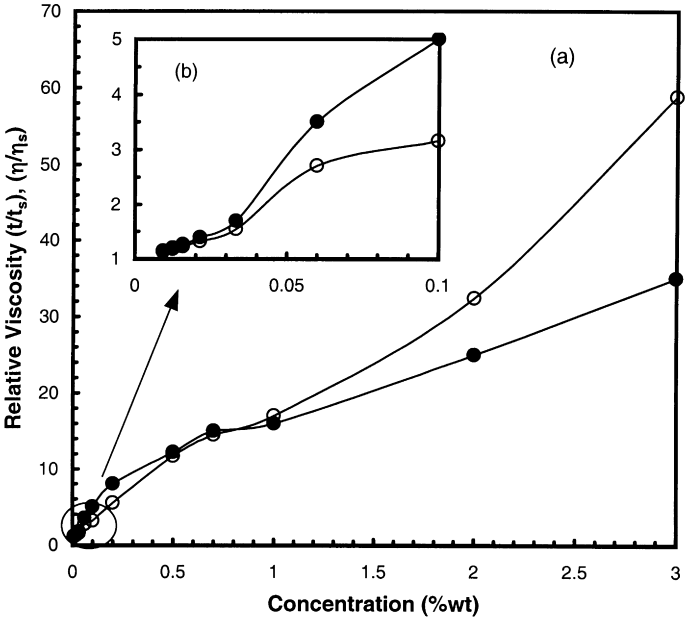

Fig. 5. (a) Dependence relative viscosity on concentration of unmodified (HASE 107) (X) and hydrophobically modified (HASE 00-20) (W) HASE polymers (pH $\sim$ 9.5). (b) Inset for concentrations of 0–0.1 wt%.

are expected to produce identical associating behavior. This may explain the similarity in the effective hydrodynamic volume between the hydrophobically modified (HASE 00-20) and unmodified (HASE 107) system.

Although the effective hydrodynamic volume of the polymer systems is similar, their polymer–solvent interaction as described by the slope of the reduced viscosity curve is different (see Fig. 2). The slope of the reduced viscosity is described by the Huggins coefficient as indicated by Eq. (4). A low Huggins coefficient (less than 0.5) means that polymer–solvent interactions are good. Due to the presence of hydrophobic domains in the aqueous environment, the interaction between the polymer and solvent is usually poor. Hence the Huggins coefficient for such a system is usually much higher [11,19,22]. As observed from Fig. 2, the Huggins coefficient K_H of the polymer systems, HASE 107 and HASE 00-20, is 1.32 and 0.713, respectively. A relatively lower value of K_H for hydrophobically modified HASE polymer (HASE 00-20) indicates that the polymer–solvent interaction of the hydrophobically modified system is better than the unmodified system. Intuitively, we should expect to observe higher K_H values for polymer molecules with more hydrophobic character, i.e. in this case HASE 00-20 when compared with HASE 107. However, a reverse trend was observed. The only explanation to account for this usual trend is that the hydrophobic macromonomer interacts with the blocky ethyl acrylate, thereby minimizing the exposure of hydrophobic sites of the polymer system to the surrounding aqueous environment and hence improves the polymer–solvent interaction. One such associating mechanism of unmodified and hydrophobically modified system is proposed, as shown in Fig. 3. For the unmodified system (HASE 107), the blocky EA segments aggregate to form hydrophobic domains incorporating several polymer chains. In contrast, for HASE 00-20, in addition to the interaction between the blocky EA segments, the C20 hydrophobes associate with the EA segments to yield two different types of hydrophobic domains.

3.2. Semi-dilute solution properties

3.2.1. Equilibrium shear viscosity behavior

It has been widely reported that by grafting hydrophobic blocks to the water-soluble polymer, the rheological properties are enhanced. However, at low polymer concentrations and depending on the stiffness and steric hindrance of the polymeric backbone, the rheological properties of the hydrophobically modified associative (HASE) polymer can either be higher or lower than the unmodified analogue (ASE).

Fig. 4a and b shows the steady shear properties of the unmodified and hydrophobically modified HASE polymers. The zero shear viscosity was extracted from the figures and plotted in Fig. 5. At extremely low concentration of $C < 0.01$ wt% (see inset), the viscosity of HASE 107 and HASE 00-20 approaches one another, which is in agreement with the intrinsic viscosity data observed earlier. Two distinct regimes can be observed. At the concentration from 0.01 to 0.5 wt%, the unmodified analogue displays higher relative viscosity than the hydrophobically modified system. Between the concentration range of 0.5 and 0.8 wt%, there is no significant difference in the viscosity between the two polymers. However beyond 0.8 wt%, the viscosity of the hydrophobically modified system exceeds the unmodified analogue. Such trends are also observed in

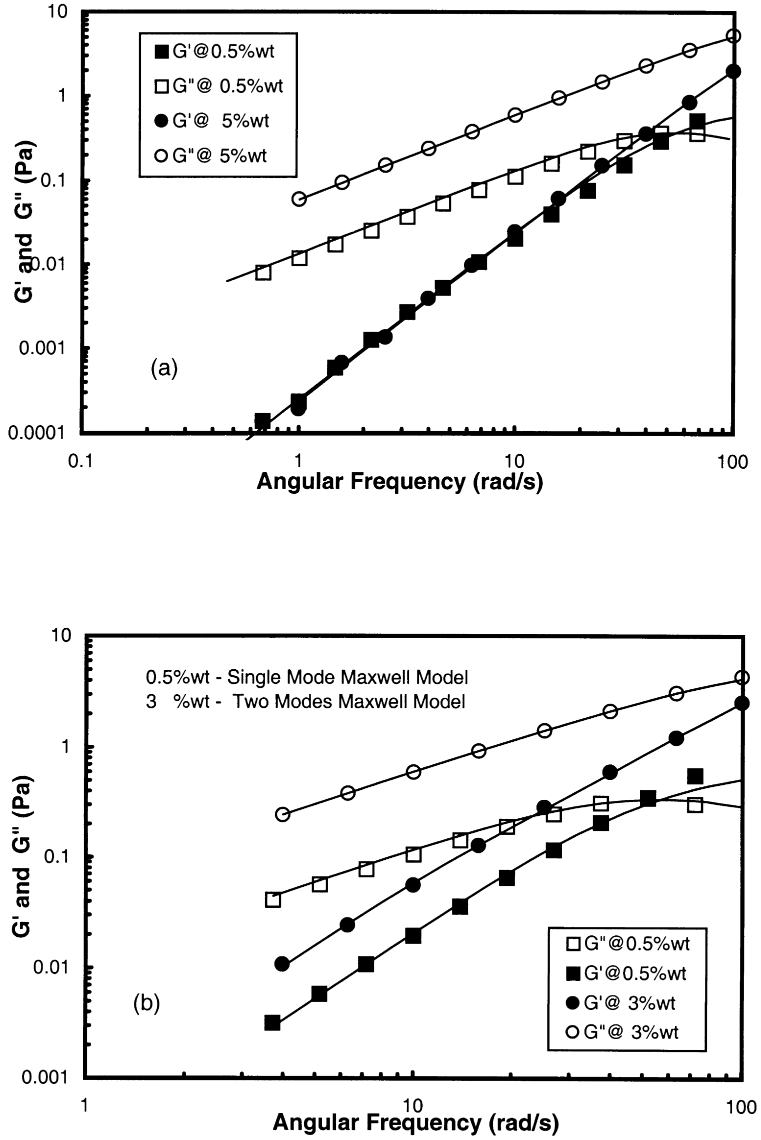

Fig. 6. Fitting of the Maxwell model equation to the dynamic properties: of (a) HASE 107; (b) HASE 00-20.

the storage modulus and the activation energy of the systems, which will be discussed later.

Aubry and Moan [23] and Volpert et al. [21,22] reported a lower viscosity behavior for the hydrophobic modified polymer system at low polymer concentration. They attributed this to the increasing hydrophobicity that leads to the formation of intramolecular interactions between the hydrophobic sites along the same polymer chain. Although the viscosity behavior between HASE and ASE in Fig. 5 bears strong resemblance to the rheological behavior described above, the concept of intramolecular interaction cannot be applied. This is because the presence of negative charges (COO^-) in the HASE and ASE systems introduces high stiffness to the polymer backbone [3]. This increases the rigidity of the polymer chains that hinders the association of hydrophobic sites along the same polymer chain [3,19].

As discussed earlier, the polymer–solvent interaction (Huggins coefficient, K_H) between the hydrophobically modified and unmodified analogues shows that HASE 107 has more hydrophobic sites exposed to the aqueous environment compared to HASE 00-20. In a dilute solution regime and with increasing polymer concentrations, the larger number of exposed hydrophobic sites in aqueous environment will cause more polymer chains to associate in a single polymer cluster, leading to a larger cluster size and higher viscosity. In order to test this hypothesis, an independent dynamic light scattering experiment was conducted. The experiment shows that the particle size of HASE 107 is larger than HASE 0020 in the dilute solution regime [40] and this information confirms the validity of the above hypothesis. Between 0.01 and 0.1 wt%, the size of HASE 107 clusters grows faster than HASE 00-20 due to the incorporation of more polymer chains in the cluster, resulting in a higher viscosity, as evident from Fig. 5,

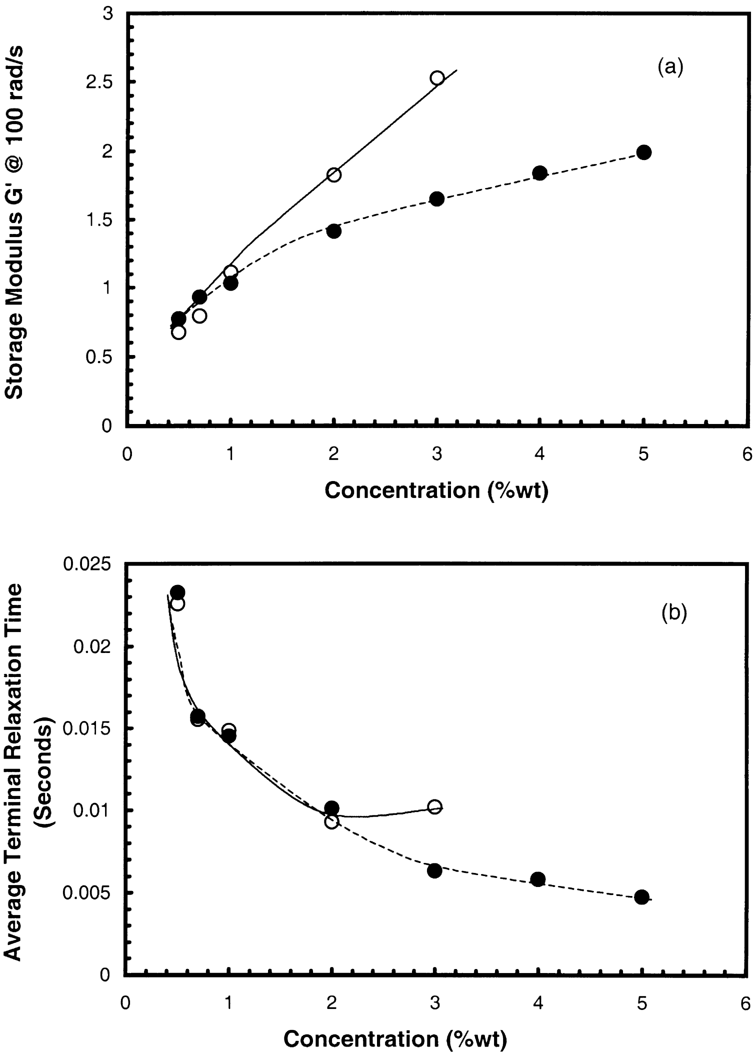

Fig. 7. Dependence of: (a) storage modulus; and (b) relaxation time on polymer concentration of unmodified (HASE 107) (X) and hydrophobically modified (HASE 00-20) (W) HASE polymers at pH 9.5.

over the concentration ranges from 0.01 to ~0.5 wt% (Fig. 5b).

At low polymer concentrations, each HASE 00-20 cluster contains fewer numbers of polymer chains compared to HASE 107. Hence, for a given polymer concentration, HASE 00-20 is expected to contain a larger number of polymer clusters in solution. Above the cluster overlapping concentration ($c^* \sim 0.08$ wt%) as determined from $c^*[\eta] = 1$, the polymer cluster begins to interact with one another and with increasing concentration, larger clusters and eventually a polymer network is formed at high polymer concentration. Due to the larger number of clusters and hence associating junction points, HASE 00-20 forms stronger polymer networks, which correspond to the larger viscosity at $c > 1.0$ wt% (Fig. 5a).

3.2.2. Dynamic and relaxation behavior

The dynamic frequency plots for the polymer systems in semi-dilute solutions are shown in Fig. 6a and b. Both figures show that the longest relaxation behavior of the material, as indicated by G' vs. ω^2, could be attained within the measuring range of the equipment. Therefore, the terminal relaxation time can be determined from the expression:

$$\lambda = \lim_{\omega \to 0} \left(\frac{G'}{\omega^2 \eta'} \right) \tag{4}$$

where η' is the dynamic viscosity, and the plateau region in λ vs. ω curve, which corresponds to the terminal region in the G' and G'' plot gives an estimate of the average terminal relaxation time. The average terminal relaxation time of both systems is plotted in Fig. 7b.

The dynamic data can be fitted with the generalized Maxwell Model/Maxwell–Wiechert model, given by the

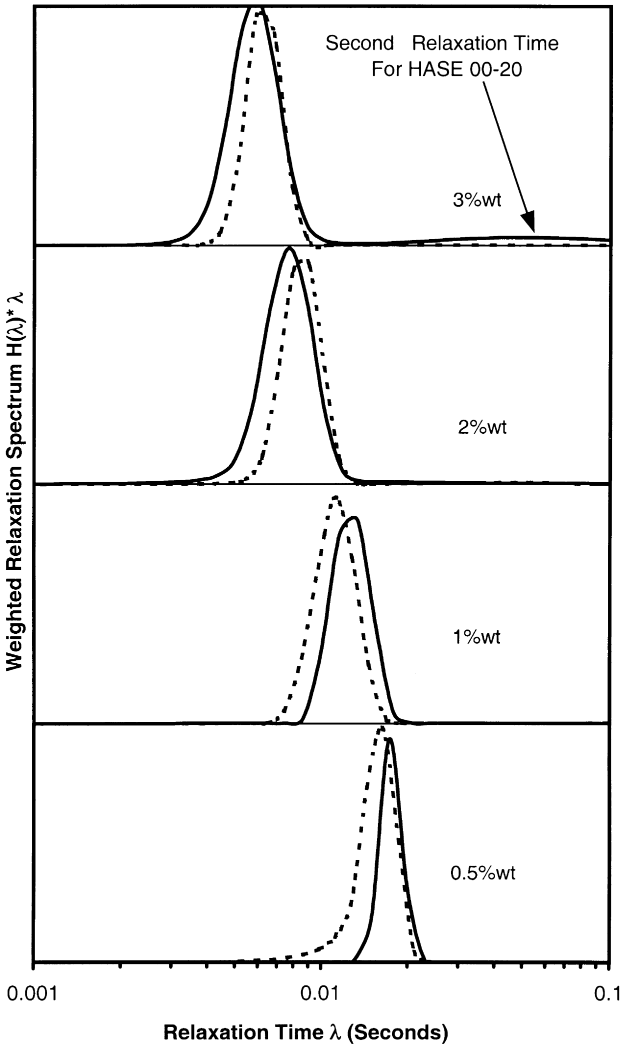

Fig. 8. Relaxation spectra for unmodified (HASE 107) (dotted line) and hydrophobically modified (HASE 00-20) (continuous line) HASE polymers at pH 9.5.

expressions:

$$G'(\omega)=\sum_{i=1}^{N}\frac{G_i\omega_i^2\lambda_i^2}{1+\omega_i^2\lambda_i^2},\qquad G''(\omega)=\sum_{i=1}^{N}\frac{G_i\omega_i\lambda_i}{1+\omega_i^2\lambda_i^2}\tag{5}$$

where the subscript "i" is used to denote the number of repeated simple Maxwell elements. Although the plateau modulus, G_n^0 cannot be determined at high frequency, the high frequency storage modulus G' was used to represent the strength of the network as shown in Fig. 7a. Based on the Green and Tobolosky theory [41] on rubber elasticity, the G' at high frequency can be used to represent the junction densities in the transient network system. Green–Tobolsky [41] extended the simple theory of rubber elasticity to transient networks where the magnitude of the plateau modulus G_n^0 is related to the number of the effective chains per unit volume ν:

$$G_{\mathrm{N}}^0=g\nu\mathrm{R}T\tag{6}$$

where g is a correction factor whose magnitude is unity [42].

Fig. 7a shows that the junction densities (as given by the moduli) and thus the strength of the polymeric network, represented by E_{a} in Fig. 9b, increase with polymer concentrations. However, the rate of junction density increment (as represented by G') is lower for HASE 107 when compared to HASE 00-20. This eventually leads to higher junction densities for HASE compared to ASE at higher concentrations, which correlates well with the observed higher viscosity for the HASE00-20 system.

In order to have a clearer understanding on the relaxation behavior of the polymer system, the determination of the distinct relaxation time, λ, is important. The viscoelastic response of the polymer can be better described by examining the distribution of the relaxation times [42–44]. Information on the relaxation spectrum $H(\lambda)$ can be derived by the transformation of data obtained in the frequency domain according to the expressions:

$$\begin{aligned}G'(\omega)&=\int_{-\infty}^{\infty}H(\lambda)\left[\frac{\omega^2\lambda^2}{1+\omega^2\lambda^2}\right]\mathrm{d}(\ln\lambda),\\G''(\omega)&=\int_{-\infty}^{\infty}H(\lambda)\left[\frac{\omega\lambda}{1+\omega^2\lambda^2}\right]\mathrm{d}(\ln\lambda).\end{aligned}\tag{7}$$

The calculation of the relaxation spectrum from the material functions such as storage and loss modulus requires the inversion of the type of equation as shown in Eq. (7). The relaxation time spectrum was computed using the commercial software provided by Rheometric Scientific Inc. (Orchestrator software). The spectra obtained from the storage and loss modulus at different concentrations are plotted as $H(\lambda)\lambda$ vs. λ, as shown in Fig. 8.

The relaxation spectra shown in Fig. 8 reveal that both polymer systems exhibit similar relaxation time over a wide range of polymer concentrations up to 3 wt%. The lifetime (as represented by the fast peak in the relaxation spectrum) [44] for both systems are fairly similar. However, the average terminal relaxation time of 3 wt% HASE 00-20 is larger than HASE 107 (Fig. 7b). This is due to higher degree of intermolecular association in the polymeric network as shown in Fig. 7a, which slows down the network relaxation. Such a hypothesis can be justified from the relaxation spectrum (see Fig. 8), where the transformations from a single to double relaxation times for HASE 00-20 is observed when the concentration increases from 2 to 3 wt%.

From Fig. 7b, the average terminal relaxation time decreases with increasing polymer concentration. This behavior may be explained by the competition of hydrophobic moieties to form more hydrophobic junctions (Fig. 7a) with fewer hydrophobes per junction. Independent measurements using fluorescence spectroscopy may provide important results to confirm this hypothesis. Winnik's group at the

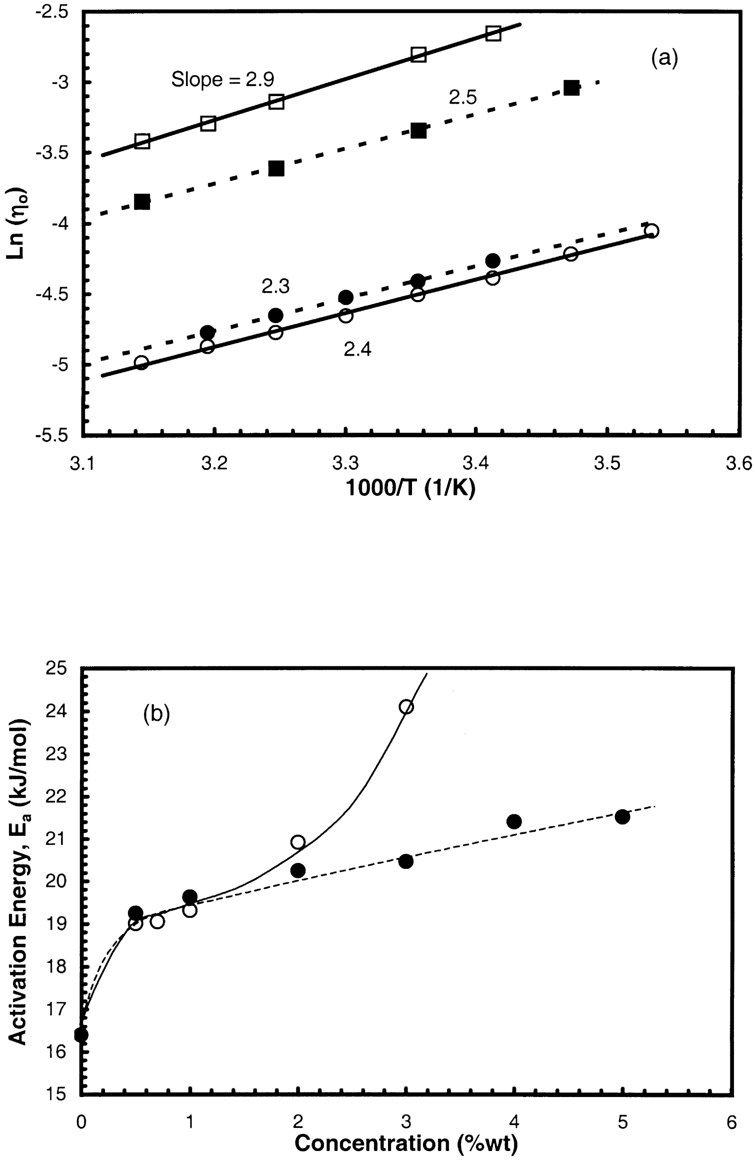

Fig. 9. (a) Determination of activation energy from $\ln(\eta_0)$ vs. $1/T$: HASE 107 (X —0.5 wt%; B —3 wt%); HASE 00-20 (W —0.5 wt%; A —3 wt%). (b) Dependence of activation energy on polymer concentrations for unmodified (HASE 107) (X) and hydrophobic modified (HASE 00-20) (W) HASE polymers at pH 9.5.

University of Toronto is currently performing fluorescence spectroscopy measurements on similar HASE polymers. However, it should be pointed out that quantifying the aggregation number of systems that form multiple hydrophobic domains in a polymer aggregate is not trivial. Some success has recently been reported where the mean aggregation number in a aggregate is found to be approximately 55 [45]. This contributes to a slight increase in the average lifetime of the polymer systems as observed from the fast peak in the relaxation spectrum shown in Fig. 8. Such behavior was also detected by independent dynamic light scattering measurements on HASE systems [36] where the correlation length between the hydrophobic junctions decreases with increasing polymer concentration. Furthermore, the low relaxation time (<0.1 s) and decreasing trend of the relaxation behavior with increasing concentrations suggests that there is no chain entanglement in the polymeric network. Instead, the relaxation behavior is governed by the dynamics of the associative junctions.

3.2.3. Activation energy

The activation energy can be used to quantify the strength of the polymer network, where E_a is the total energy contributed by lifetime of the hydrophobic junction and junction densities in the network [44–47]. The Arrhenius expression of the viscosity can be described by the following equation:

$$\eta_0 = \frac{\nu kT}{\omega_0}\exp(E/kT) = \frac{\nu kT}{\beta_0}. \qquad (8)$$

The activation energies of HASE 107 and HASE 00-20 at

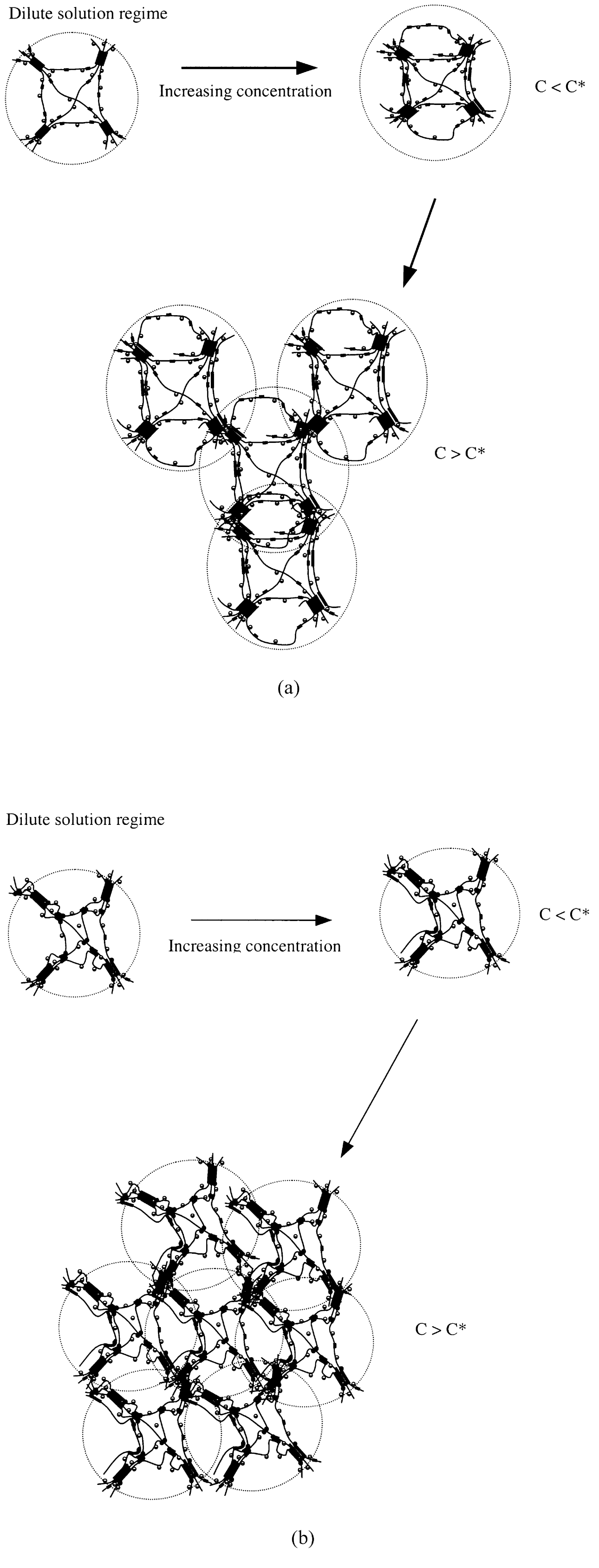

Fig. 10. Proposed associating mechanism in the semi-dilute solution regime for: (a) HASE 107; (b) HASE 00-20.

concentrations from 0.5 to 5 wt% (semi-dilute region), obtained from the temperature–viscosity plot (Fig. 9a), are summarized in Fig. 9b. Fig. 9b shows that both systems possess similar activation energies at the concentration ranges from 0.5 to 1.5 wt%. This behavior is due to the similarity in the junction densities and relaxation time of both systems as shown in Figs. 7a,b and 8, respectively. When the concentration exceeds 1.5 wt%, the activation enthalpy of the hydrophobic modified system (HASE 00-20) is greater than that of the unmodified analogue. The higher network strength of the hydrophobically modified system is mainly due to more effective “bridging” between the polymer clusters, which contributes to higher number of active junction densities and relaxation times.

4. Proposed associating mechanism in semi-dilute solution regime

In order to provide an overview of the associating behavior between the hydrophobically modified and unmodified system, a proposed model describing the associative mechanism of HASE 107 and HASE 00-20 at various concentrations are shown in Fig. 10a and b. As more hydrophobic sites are exposed to the aqueous environment in HASE 107, more polymer chains will associate to the single polymer cluster. This produces a larger cluster size, which enhances the rheological properties of HASE 107 (compared to HASE 00-20) at low polymer concentration ($c < c^*$). Beyond c^*, these clusters begin to interact with each other and reorganize to form a temporary network.

For HASE 00-20, the microstructure at dilute solution regime is similar to HASE 107 except that the size of the cluster is smaller due to the additional association between the C_{20} hydrophobes and the blocky EA segments (Fig. 10b). Beyond the cluster overlapping concentration (c^*), the presence of a smaller size but larger number of polymer clusters in HASE 00-20 system provides more associating sites for possible linkage between the clusters. The higher intermolecular interaction forces cause more polymer clusters to associate, which strengthens the polymer network as depicted in Fig. 9b, leading to the enhancement of rheological properties of HASE 00-20 over the unmodified analogue. Such behaviors are pictorially illustrated in Fig. 10a and b.

5. Conclusions

Our study has shown that ethyl acrylate (EA) is blocky enough to induce hydrophobic association. This results in the formation of association in the unmodified polymer system. The hydrophobically modified HASE polymer exhibits better polymer–solvent interaction compared to its unmodified analogue due to the association between the EA and hydrophobic macromonomer, which minimizes the exposure of the hydrophobic sites to the aqueous environment.

The rheological properties of semi-dilute solutions is not influenced by the physical entanglement of the polymer chains. Instead, the formation of a transient network through hydrophobic association contributes to the enhancement of the rheological properties. In the semi-dilute solution regime, the hydrophobically modified associative polymer exhibits higher viscosities compared to the unmodified analogue. This is due to the formation of higher degree of intermolecular association between the polymer clusters, which enhances the hydrophobic interaction between the hydrophobic macromononers of different polymer chains.

Acknowledgements

We are grateful to Dr David Bassett of Union Carbide Corporation for his enthusiasm and support in this research collaboration. One of the authors (N.W.K.) would like to acknowledge the financial support provided by the University. We would also like to acknowledge the financial support provided by the National Science and Technology Board of Singapore, the Ministry of Education and the Singapore–Ontario Collaborative research program.

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