Rheological Properties of Hydrophobically Modified Polyelectrolyte Systems: Concentration Effects

K. C. Tam,[1] W. K. Ng,[1] R. D. Jenkins[2]

[1]School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798
[2]The Dow Chemical Company, UCAR Emulsion Systems, 410 Gregson Drive, Cary, North Carolina 27511

ABSTRACT: The behavior of hydrophobically modified alkali-soluble associative polymer (HASE) at various polymer concentrations was investigated. The results showed that the formation of network structure, which enhances the rheological behavior, depends on two critical polymer concentrations, namely the critical cluster overlapping concentration (C^*) and the established network concentration (C^{**}). C^* is defined as the critical concentration for the transformation of individual cluster to a transient network structure. C^{**} represents the critical concentration in the semidilute regime where the formation of transient network is completely established. Experimental results demonstrated that the polymer solutions transformed from a predominantly viscous behavior below C^* to one with dominant elastic properties above C^{**}. Because of the formation of larger aggregation number above C^{**}, the relaxation times of the polymer systems shift to longer times. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5166–5173, 2006

Key words: association; hydrophilic polymers; polyelectrolytes; solution properties; rheology

INTRODUCTION

The better enhancement in the rheological properties of combed-type hydrophobically modified associative polymer (HASE) over the end-terminated associative polymer (HEUR)[1–6] has attracted significant research interests in recent years. Several important experiments on the rheological properties have revealed interesting features of the HASE polymer.[7–14]

The complexity in the rheological properties of the associative polymer with hydrophobes attached as pendant side groups compared to the end-capped hydrophobic system is related to the steric hindrance of the polymer backbone that prevents the formation of hydrophobic junctions, yielding hydrophobic clusters with a polydispersed associative junctions.[3,9,11,15–18] On the other hand, the combed-type polymer possesses a better viscosity enhancement characteristic than the end-capped system.[15,19] This is because the combed system is more efficient in creating bridges between micelles, yielding higher intermolecular associative junctions compared to HEUR system. Moreover, the rheological properties of associative polymer can be further enhanced by the extension of the branched alkyl chain and by increasing the hydrophobicity of the hydrophobic moieties.[1–4] This will slow

down the dynamic exchange rates between the micellar junctions, which increase the relaxation times of the polymeric system. Leibler et al.[20] presented a model, which demonstrated that the relaxation behavior of a polymeric system with reversible network is governed by two processes. The slower process is related to the reptation motion of polymer chains by coherent breakage of a few crosslinked points at a time, which is dependent on the degree of association. The faster process is due to the relaxation between entanglement points, which is related to the average lifetime of association.

As a result of the hydrophobic side chain, which gives rise to multiple relaxation times, the polymeric system can no longer be described by a single Maxwell model. In HASE polymer, the second order region of the storage modulus was often not attainable even at a frequency of 0.01 rad/s.[9,11,13,21] The relaxation of the polymer network is governed by the combined effects of disengagement rate of hydrophobes and the physical constraints arising from chain entanglements, which slow the relaxation rate.[11] On the other hand, Tritaatmadja et al.[3] suggested that the long relaxation time in the relaxation spectrum was caused by hydrophobic junctions having lower dynamic micellar exchange rate rather than chain entanglements. This is due to the low molecular weight (as compared to HEUR system) of the polymer where chain entanglements are negligible at low to moderate concentrations. Several models such as the exponential stretch and multiple modes Maxwell model[15,16,22] were used
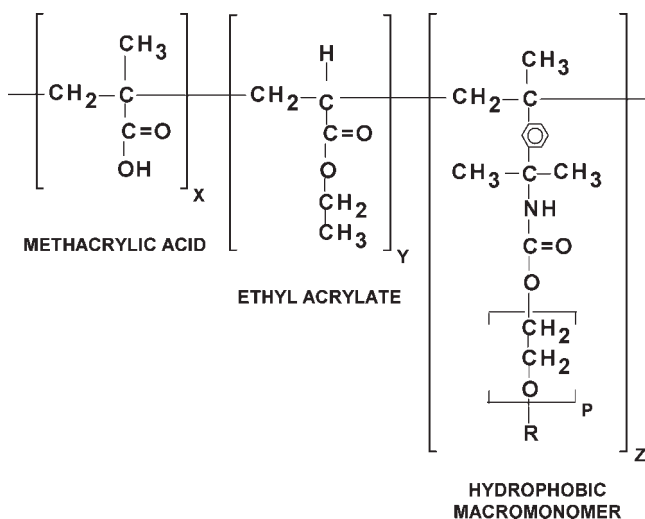
Figure 1 Chemical structure of model HASE polymers.

to describe the behavior of such combed polymer system. However, they are unable to provide the qualitative and quantitative description of polymer system.

In this article, rheological experiments were designed to investigate the effect of polymer concentration on the rheological and structural behavior of HASE polymers. This characterization is accompanied by relaxation spectrum analysis, which provides both qualitative and quantitative description of the associative polymer network.

MATERIAL AND EXPERIMENTAL METHODS

The model associative polymers studied are hydrophobically modified, alkali-soluble (HASE) polymers synthesized by Dow Chemicals (formerly Union Carbide), via the emulsion polymerization product of methacrylic acid (MAA), ethyl acrylate (EA), and a macromonomer that had been capped with a hydrophobic group. The polymer examined in the present work has a chemical structure shown in Figure 1, where R is C_nH_{2n+1} alkyl chain. It has an average molecular weight of $\sim$ 200,000–250,000 determined by intrinsic viscosity[8] and static light scattering measurements.[23,24] The polymer examined is designated as HASE05-20, and HASE15-20, where the ethylene-oxide spacer chain length of HASE15-20 is 15 mol while HASE05-20 is 5 mol. The hydrophobes of the polymers consist of the $C_{20}H_{41}$ alkyl chain.

A brief description of the synthesis route of the model polymer has been previously reported[3,7] and will not be presented here. The characteristics of the model polymer are given in Table I. Although the distribution of the molecular weights of the model associative polymer remains unknown, the molecular weight and monomer sequence distribution of these polymers are believed to be quite similar, since the process used to produce them was held constant.[23] Recently, Sprong et al. synthesized HASE polymers with well-controlled molar masses and narrow molar mass distributions using the reversible addition-fragmentation chain transfer polymerization of methyl methacrylate, and methacrylic acid. Molecular weights ranging from 27,000 to 50,000 g/mol with polydispersity index of 1.2–1.5 were reported.[25,26]

The samples of a desired concentrations were prepared from a stock solution of 3 wt % polymer by diluting with $10^{-4}M$ KCl solution. The alkaline used to neutralize the polymer to the required pH of 9.0 is 2-aminomethylpropanol (AMP). This is to ensure complete neutralization of the polymer where maximum enhancement of the rheological properties was observed.[13,27]

Dilute solution

The rheological properties of associative polymer solutions in dilute solution regime were measured using a Ubbeldohe capillary viscometer at temperature of $(25 \pm 0.02)°C$ maintained with a thermostatic bath. Careful sample preparation was adopted based on our earlier findings, and the experimental procedures for ensuring high accuracy, repeatability, and reliability were previously reported by Ng et al.[28]

The efflux time measured from the capillary viscometer is related to the reduced and inherent viscosity by assuming the density of the polymer solution is similar to the solvent. When the solution concentration approaches zero, both the reduced and inherent viscosities approach the intrinsic viscosity:

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{\ln \eta_r}{c} \tag{1}$$

The intrinsic viscosities were obtained by the extrapolation of reduced and inherent viscosity data to zero

TABLE I
Details on Chemical Composition of Model HASE Polymers

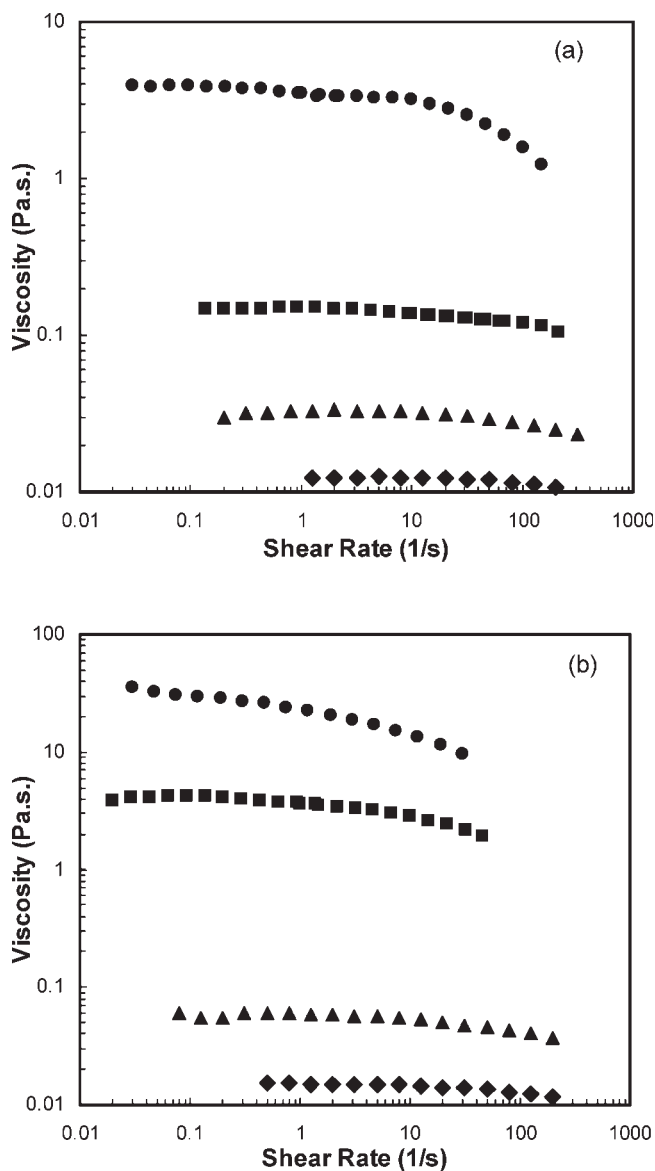| Polymer	Moles of EO	Hydrophobes name	Hydrophobes formula	Molar ratio of MAA/EA/macromonomer
HASE05-20	4.2	Eicosanyl	$C_{20}H_{41}$	49/50/1
HASE15-20	15.4	Eicosanyl	$C_{20}H_{41}$	49/50/1

Figure 2 Steady shear viscosity profiles for aqueous (a) HASE05-20 and (b) HASE15-20 solutions at pH 9.5. (◆) 0.5 wt %; (▲) 1 wt %; (■) 2 wt %; (●) 3 wt %.

polymer concentration using Huggins[29] equation as shown below:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c \qquad (2)$$

where K_H is the Huggins coefficient, a constant for a series of polymer of different molecular weights in a given solvent and temperature.

Semidilute solution

The rheological characterization of the thermal behavior of the HASE polymer systems was performed in the Rheometric ARES rheometer at a pH of 9.5. A double concentric cylinder geometry (inner cup diameter

27.94 mm, outer cup diameter 34 mm, inner bob diameter 29.5 mm, outer bob diameter 32 mm, and bob length 31.9 mm), and cone and plate geometry (diameter 50 mm, 0.04 radian) were used to measure the viscoelastic properties of the model polymers systems. Characterization of the polymer solutions was carried out under well-controlled thermal environment using a circulating water bath.

RESULTS AND DISCUSSION

Equilibrium shear viscosity and activation energy behavior

The steady shear viscosity is a measure of the ability of the material to resist shear deformation. This enables the understanding of the nonlinear viscoelastic properties, which is important in the field of coating applications. Figure 2 displays the shear viscosity behavior of the polymer systems at different concentrations. When the time scale of the imposed deformation is larger than the relaxation time of the polymeric chains, the
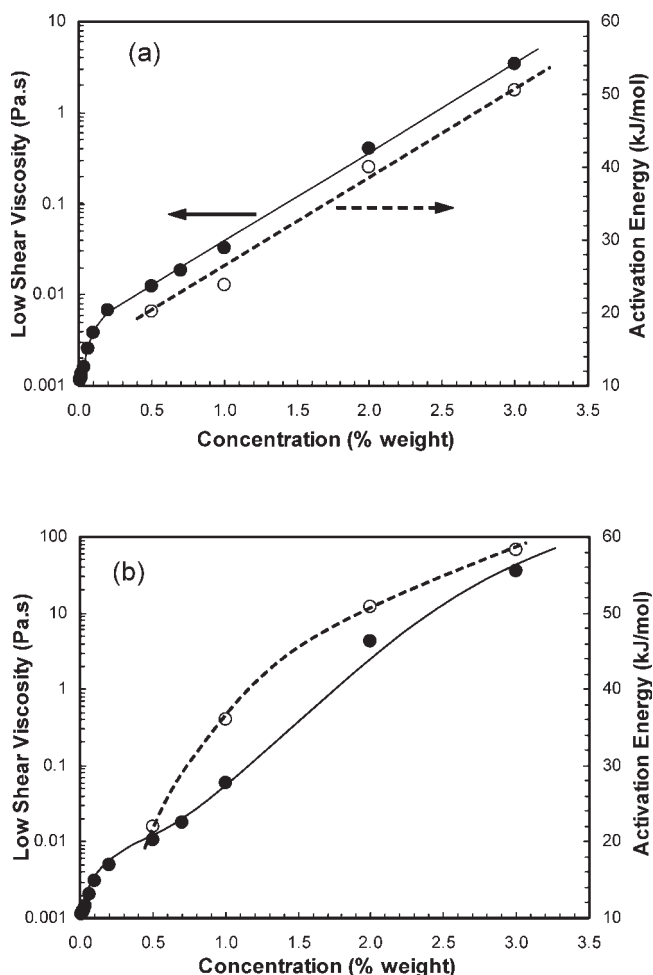

Figure 3 Viscosities and activation energies as a function of polymer concentration for (a) HASE05-20 and (b) HASE15-20 at pH 9.5 (shear rate of 0.1 s^{-1}).

deformed chains can fully relax to its unperturbed state. This allows the dissociated hydrophobes to reassociate to form hydrophobic junctions, where the balance of inter and intramolecular junctions is restored. Thus, Newtonian behavior can be achieved at low rate of deformation as shown in Figure 2. At higher rate of deformation, a continuous shear-thinning behavior is observed without an abrupt change in the viscosity that was observed for some systems, such as the HEUR. By comparing the shear-thinning behavior of HASE and hydrophobically modified (hydroxyropropyl) guar system,[30] it can be deduced that the continuous thinning behavior observed for the HASE polymer is due to the disruption and rearrangement of the polydispersed hydrophobic junctions (i.e., junctions of varying aggregation numbers). The presence of multiple hydrophobic associative junctions in such polymeric systems is responsible for the increase and broadening of the relaxation time spectrum.[3,11,15] Under shear, the presence of these mechanically active hydrophobic junctions hinders and delays the complete breakdown of the transient network structure, which slows down the destruction of the polymeric network.[12,31]

It is evident from Figure 2 that at higher polymer concentration, the onset of shear thinning behavior occurs at lower shear rates. With increasing polymer concentration, the formations of higher number of mechanically active hydrophobic junctions and aggregation number in the network are expected to retard the relaxation behavior of the polymeric chains.[20] When the relaxation time of the polymer chains is slower than the time scale of imposed deformation, the dissociated hydrophobes are not able to reassociate to restore the network junctions. Instead, they reorganize
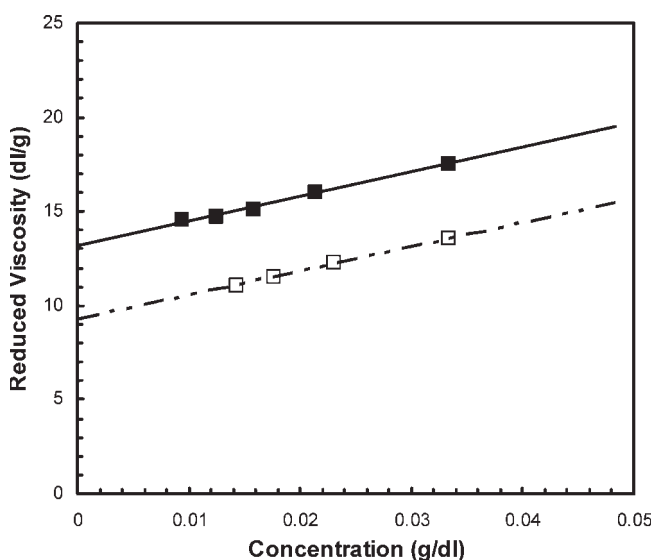
TABLE II
Comparison of Cluster Overlapping Concentration (C^*) Based on Intrinsic Viscosity and Viscosity Onset's Concentration

Polymer	$C^* = 1/[\eta]$ (wt %)	C^* based on onset of viscosity (wt %)
HASE05-20	0.13	0.15
HASE15-20	0.10	0.15

to form a network structure containing junctions with lower aggregation number, which contributes to a reduction in the strength of the network and overall resistance to shear deformation. A consequence of this is the shifting of shear-thinning behavior to lower shear rates with increasing polymer concentration.

To have a complete overview on the changes in the viscosity with polymer concentration, the viscosities in the dilute and semidilute solution regime were measured and summarized in Figure 3. The general trend of the viscosity for the model polymeric systems is that the viscosity increases continuously with concentration ranging from 0.01 to 3 wt %. The increase is rapid within the first region up to 0.30 wt %, and it continues to increase with concentration reaching a significantly high viscosity of 4–30 Pa s for HASE05-20 and HASE15-20, respectively. Such behavior was recently reported for pyrene-modified HASE polymeric system.[6] This trend is related to the increase in the number of mechanically active hydrophobic junctions and aggregation number, which enhances the strength of the network structure, making it more resistant to shear deformation. This explanation can be further supported by the viscosity-based activation energy plotted on the same figure.

The viscosity form of Arrhenius Equation can be determined from the following equation,

$$\eta_0 = \frac{\upsilon kT}{\omega_0} \exp\left(E/kT\right) = \frac{\upsilon kT}{\beta_0} \tag{3}$$

where ω_o is the natural frequency of thermal vibration of the reactive group in an isolated state, k the Boltzmann constant, T the absolute temperature, and η_0 is the zero shear viscosity. The increase in the activation enthalpy correlates with the increase in the strength of

Figure 4 Reduced viscosities for HASE05-20 and HASE15-20 in aqueous solutions.

TABLE III
Comparison of Second Onset Concentration (C^{**}) Determined from Viscosity and Relaxation Times

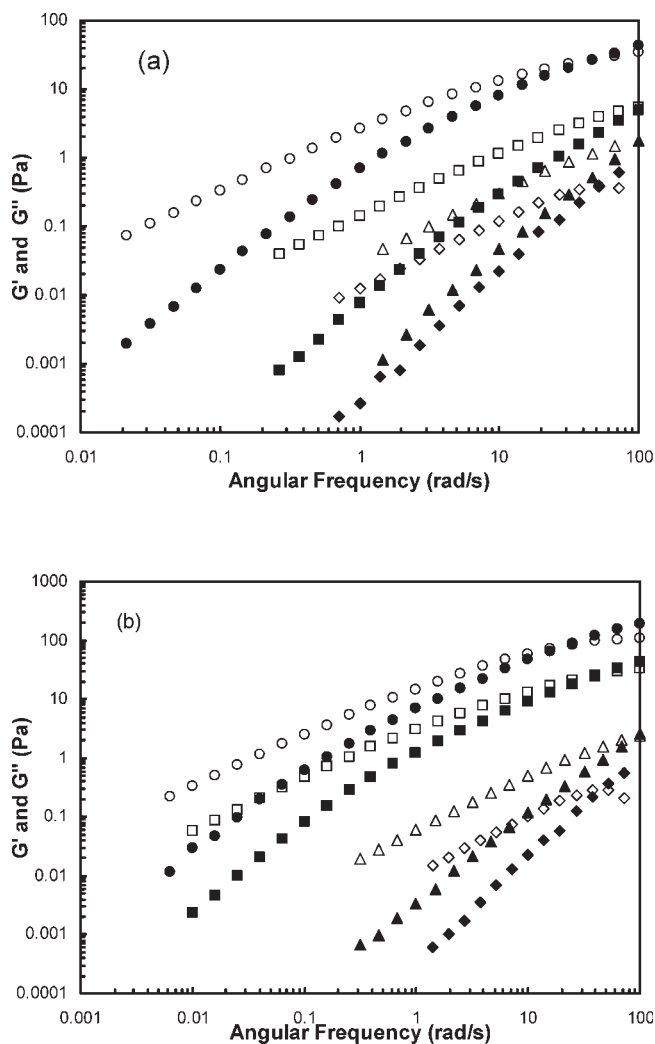| Polymer	Second viscosity onset concentration C^{**} (wt %)	Onset concentration from average terminal relaxation time C^{**} (wt %)
HASE05-20	1.0	1.0
HASE15-20	0.7	0.6

Figure 5 Dynamic shear moduli versus frequency for aqueous (a) HASE05-20 and (b) HASE15-20 solutions at pH 9.5. ($\diamond$, $\blacklozenge$) 0.5 wt %; ($\triangle$, $\blacktriangle$) 1 wt %; ($\square$, $\blacksquare$) 2 wt %; ($\bigcirc$, $\bullet$) 3 wt % (filled symbols, G'; open symbols, G'').

the polymer network.[12] The viscosity plots in Figure 3 also display an onset in the concentration, ranging from 0.1 to 0.3 wt %. Comparison of this onset with those obtained from the inverse of the intrinsic viscosity determined from Figure 4, demonstrates that these values are fairly similar (see Tables II and III). As $C^* = 1/[\eta]$ defines the cluster overlapping concentration, hence the onset concentration observed in Figure 3 represents the onset point where individual cluster associates to form a transient network structure. This was recently confirmed by fluorescence study on a pyrene-modified HASE polymer system.[6]

Dynamic and relaxation behavior

The determination of the linear viscoelastic properties of model-associating polymer systems was carried out in the semidilute solution regime. This solution regime

begins from $\sim$ 0.15 wt %, on the polymer systems as determined from the intrinsic viscosity measurements. The dynamic measurements were conducted from 0.5 to 3.0 wt % as the elastic properties lower than 0.5 wt % lie outside the lower limits of the rheometer. The storage and loss moduli as a function of angular frequency at different polymer concentrations are shown in Figure 5. The general trends of the dynamic modulus plots are that the high frequency storage modulus and terminal region shift to higher modulus and lower frequency with increasing polymer concentrations. To have a better overview of the rheological behavior, the storage modulus at 100 rad/s and the terminal relaxation time were extracted and summarized in Figure 6.

The high frequency storage modulus plots in Figure 6 shows that the modulus increases with concentrations (0.5–3 wt %). Based on Green and Tobolsky theory,[32] the increase in the dynamic modulus with concentrations is interpreted to correspond to the increase in hydrophobic intermolecular junction densities.
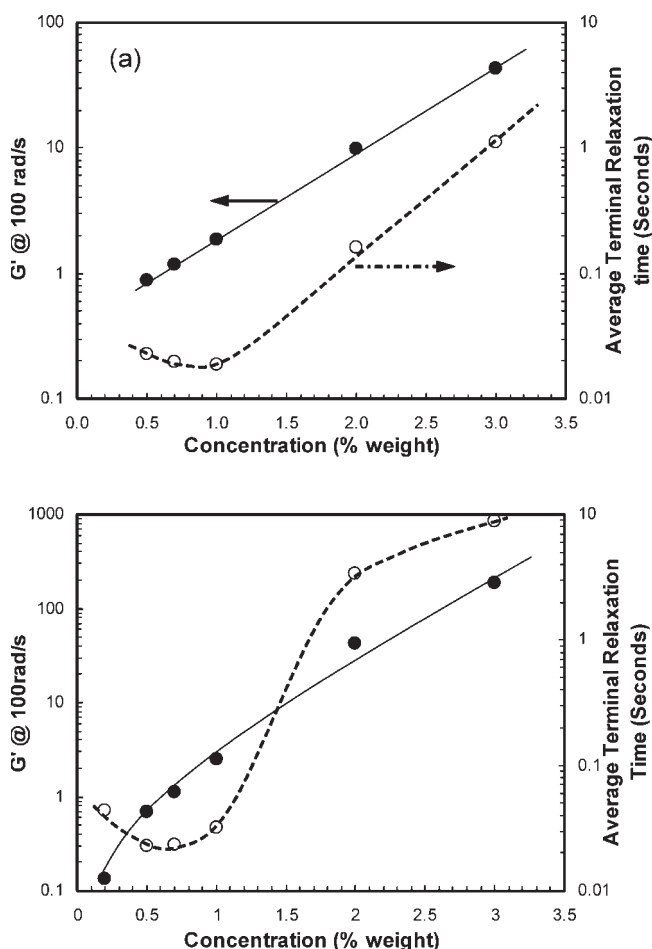

Figure 6 Storage modulus at 100 rad/s and average terminal relaxation time versus polymer concentration at pH 9.5 for (a) HASE05-20 and (b) HASE15-20.
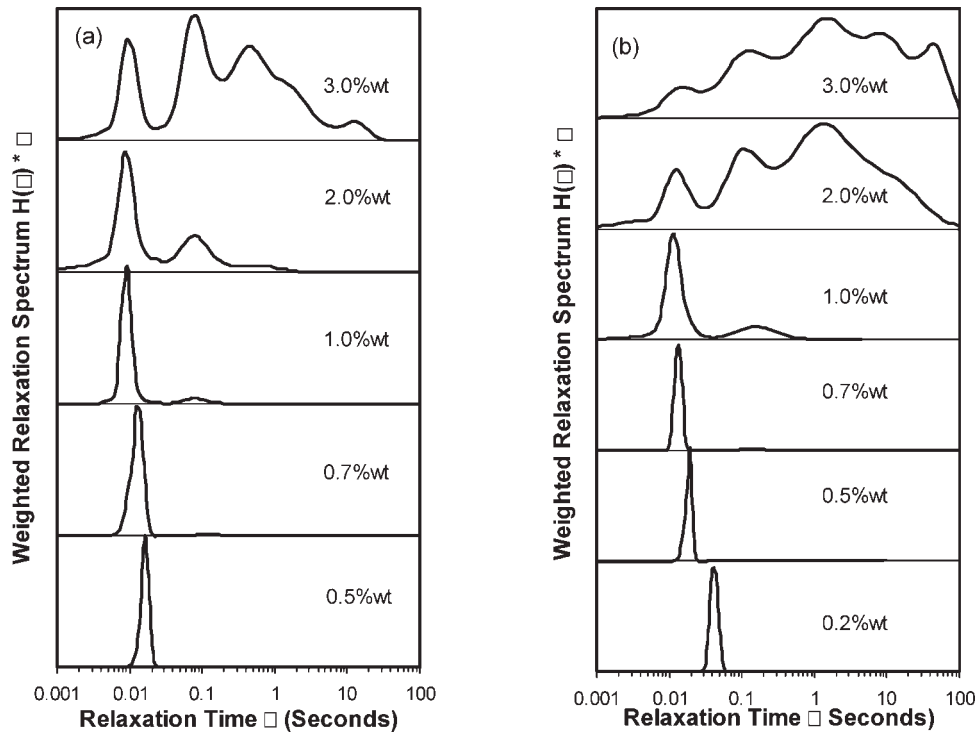
Figure 7 Weighted relaxation spectra for (a) HASE05-20 and (b) HASE15-20 at varying polymer concentrations at pH of 9.5.

The average terminal relaxation time can be determined from the expression:

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

where η' is the dynamic viscosity, and the plateau in λ versus ω curve, which corresponds to the terminal region in the G' and G'' plot, gives an estimate of the average terminal relaxation time of the system. The average terminal relaxation time in the concentration ranging from 0.1 to 3 wt % exhibits two types of behavior (Fig. 6). At the lower concentration region, the relaxation time decreases with increasing concentration and the reverse is true for the higher concentration regime. To understand these relaxation behaviors, the analysis of the relaxation spectrum was conducted.

Information on the relaxation spectrum $H(\lambda)$ can be derived by the transformation of data obtained in the frequency domain according to the expressions below:

$$G'(\omega) = \int_{-\infty}^{\infty} H(\lambda)\left[\frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2}\right] d(\ln \lambda)$$

$$G''(\omega) = \int_{-\infty}^{\infty} H(\lambda)\left[\frac{\omega \lambda}{1 + \omega^2 \lambda^2}\right] d(\ln \lambda) \qquad (5)$$

The relaxation time spectrum was mathematically computed using commercial software provided by Rheometric Scientific Inc. (Orchestrator software). The spectra obtained from the storage and loss modulus at different concentrations for HASE05-20 and HASE15-20 were plotted as $H(\lambda)\lambda$ versus λ in Figure 7(a and b), respectively.

Analysis of the relaxation spectra [Fig. 7(a and b)] shows that the fast peak or lifetimes of the polymer system at low concentration decreases with increasing polymer concentration.[12,33] In low concentration regime where the formation of the basic polymeric network is not fully established, the micellar junctions rearrange to maximize the hydrophobic junction densities, which lead to higher junction densities containing lower hydrophobic aggregation number. The reduction in the aggregation number in this low concentration regime reduces the lifetime of the polymer system as indicated by the shifting of fast relaxation peak to lower time as depicted in Figure 7(a and b). Such behavior was also detected by dynamic light scattering technique performed on HASE systems,[34,35] where the correlation length between the hydrophobic junctions decreases with increasing polymer concentration. This behavior was pictorially presented in Figure 8, where the concentration is increased from cluster overlapping concentration, C^*, to established network concentration, C^{**}.

At higher polymer concentration, the relaxation times of the polymer system, shown in Figures 6 and 7, increase with polymer concentration. This is caused by the increase in the aggregation number of the intermolecular junction and junction densities. The difference
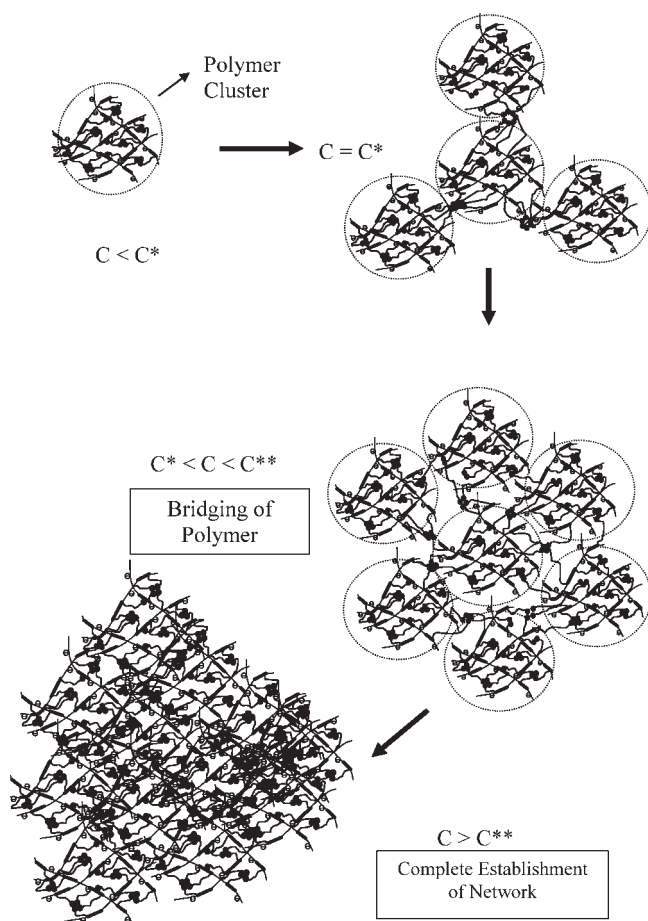
Figure 8 Proposed associating mechanism for model associative polymers at varying polymer concentrations.

in the relaxation behavior compared to the lower polymer concentrations signifies that their associating behaviors are different. Since the reduction in the lifetime at lower polymer concentration is due to incomplete formation of the polymer network, the increase in the relaxation time at higher concentration indicates that the basic network structure has been established. Therefore, any further increase in the polymer concentrations will not only maximize the junction densities, but also gradually increases the hydrophobic aggregation number of the associating junctions. Higher hydrophobic aggregation number increases the lifetime of the network, which slows the reptation motion of the polymer chains. The slower chain reptation will lead to the formation of longer multiple relaxation times observed in the polymer system as shown in the relaxation spectra. This behavior is proposed in Figure 8[34,35] for concentration greater than the established network concentration C^{**}.

To identify the established network concentration for the polymer systems, the transition in the viscosity and average terminal relaxation versus concentration plots as shown in Figures 3 and 6 was extracted and tabulated in Table III. The magnitude of the transition

or "onset" concentration is fairly identical. This suggests that there are two important critical concentrations in the polymer systems; namely, the critical cluster overlapping concentration (C^*) and established network concentration (C^{**}). The C^* is defined as the critical concentration where individual cluster is transformed into a transient network structure. The second critical concentration C^{**} is defined as the critical concentration in the semidilute solution regime where the formation of the transient network becomes fully established. Therefore, any increase in the polymer concentration above C^{**} will result in an increase of junction densities and hydrophobic aggregation number, leading to the increase of overall relaxation times and strength of the network.

CONCLUSIONS

Our studies on the rheological properties of associative polymer from dilute to semidilute solution regime show that the formation of network structure depends on two critical polymer concentrations. They are the critical cluster overlapping concentration (C^*) and established network concentration (C^{**}). C^* is defined as the critical concentration where individual clusters are transformed to a transient network structure. C^{**} is defined as the critical concentration in the semidilute regime where the formation of transient network is fully established. Experimental results demonstrated that the polymer solutions transformed from a predominantly viscous behavior below C^* to one with dominant elastic properties above the C^{**}. Because of the formation of higher hydrophobic aggregation number above the C^{**}, the relaxation times of the polymer systems shift to longer times.

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