

Thermal Properties of Hydrophobically Modified Methacrylic Acid–Ethyl Acrylate Copolymer Solutions

K. C. Tam,¹ W. K. Ng,¹ R. D. Jenkins²

¹*School of Mechanical and Production Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798*

²*The Dow Chemical Company, UCAR Emulsion Systems, 410 Gregson Drive, Cary, North Carolina 27511, USA*

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ABSTRACT: The thermal behavior of a water-soluble associating polymer system, hydrophobically modified alkali-soluble emulsion (HASE) polymer, was investigated. This polymer contains a methacrylic acid–ethyl acrylate copolymer backbone with 1 mol % of pendant hydrophobic groups grafted to it. The thermal behavior of the HASE polymer exhibits different trends compared to the hydrophobic ethoxylated urethane (HEUR) system. The lifetime of the hydrophobic junction of the HASE polymer increases with temperature due to the increase in the entropy of the system. However, the structural relaxation time decreases with temperature, caused by the enhanced Brownian dynamics of

polymer chains. The relaxation behavior of HASE polymers is either governed by the lifetime of the hydrophobic junction, the structural relaxation time, or a combination of both, depending on the degree of network formation and temperature. Temperature studies indicated that the transient network theory proposed by Tanaka and Edwards is inadequate for describing the activation process of hydrophobic junctions in the HASE associative polymer. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 604–612, 2004

Key words: association; activation energy; thermal properties

INTRODUCTION

Complex water-based systems containing hydrophobically modified polymers and surfactants find important practical applications in various formulations found in detergents, paints, cosmetics, etc. These polymers contain long-chain hydrophilic backbones, where small fractions of hydrophobic moieties are incorporated in the polymer chains.¹ Hence, these polymers contain both hydrophobic and hydrophilic segments that induce an amphiphilic character to the polymer. When dissolved in aqueous solutions, where the hydrophobic groups aggregate to minimize their exposure to water, in a manner analogous to surfactant at concentrations exceeding the critical micelle concentration.^{2–5}

Hydrophobically modified alkali-soluble emulsion (HASE) polymers have received considerable attention in recent years.^{6–20} Some studies on the thermal behavior of associative polymers have been reported previously,^{21–28} but detailed studies on the HASE system are scarce.^{19,29} Based on our understanding of the behavior of pure nonionic surfactants,^{5,30} the association of hydrophobic residues in aqueous solution is known to be endothermic (entropy driven), hence it

increases with temperature. At an elevated temperature, the water structures surrounding the hydrophobic segments are disrupted, producing a poorer solvent environment that drives the hydrophobes to form aggregates, whose number increases with temperature.^{25,31} The thermal behavior of the associative polymer is complicated by the fact that the relaxation time of the system is dependent on the lifetime of the hydrophobic junction and the Brownian dynamic of the network structure.^{22,26}

The temperature dependence of the HEUR polymer has been extensively studied by Annable et al.³² They observed an increase in viscosity and relaxation time (lifetime) with decreasing temperatures. The thermal properties (viscosity and relaxation time/lifetime) of the HEUR system were found to obey the Arrhenius relationship. These results corresponded to a model developed separately by Jenkins³³ and Tanaka and Edwards,^{34,35} based on the transient network theory originally developed by Green and Tobolsky.³⁶ However, this transient network model seems to be inconsistent with the behavior of micelles. It only predicts the energy potential barrier required for the dissociation of hydrophobes from the hydrophobic junction based either on its own thermal motion or by the thermal motion of connecting chains. It, however, does not predict the growth of micelles with increasing temperature that leads to the increase in the lifetime of the hydrophobic cluster. In addition, recent

Correspondence to: K. C. Tam (mkctam@ntu.edu.sg).

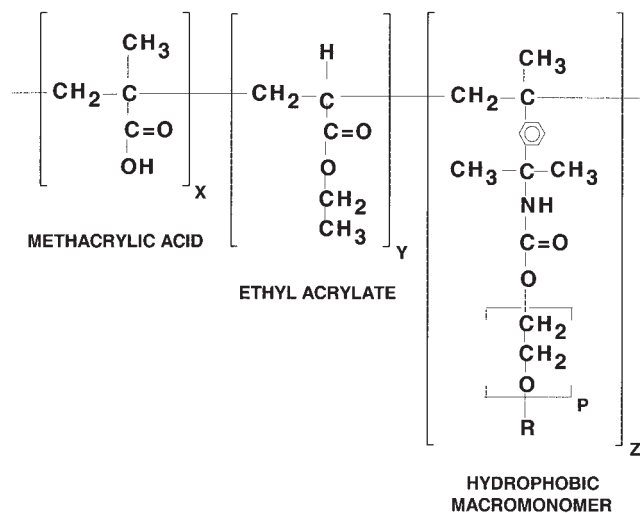


Figure 1 Chemical structure of HASE polymer system.

laboratory studies showed that the HEUR system exhibits multiple relaxation times at low temperatures.³⁷ This further complicates the analysis of the activation enthalpy, which is the summation of the energy contributed by the lifetime of the micelle and the number of hydrophobic junctions in the network.³⁷

Recent studies by Thuresson et al.²⁶ on EHEC-SDS and HM-EHEC-SDS systems showed some interesting thermal properties. The viscosities of both systems exhibit an Arrhenius behavior. However, the trends of characteristic relaxation time λ_{exp} (based on the crossover frequency) of the two systems are totally different. The HM-EHEC-SDS system exhibits a reduction in λ_{exp} with increasing temperature, while the EHEC-SDS system shows an opposite trend. They attributed the trend of the EHEC-SDS system to the increasing hydrophobicity of the polymer with increasing temperature giving rise to the enhanced hydrophobic association. The reduction of λ_{exp} with increasing temperature for the HM-EHEC-SDS system is caused by the increase in the Brownian dynamic of polymer chains as well as the polymer hydrophobes. It should be noted that the HM-EHEC-SDS system possesses multiple relaxation times. Therefore, the τ_{exp} may only reflect the Brownian dynamic of the polymer chain rather than the character of the hydrophobic junction.

Light scattering technique on associating polymers such as the HM-chitosan system²² showed that the

cooperative diffusion coefficient decreases with increasing temperature. This behavior is related to the increasing flexibility of the polymer chains, which leads to the participation of a larger number of hydrophobes in an associative junction. The structural relaxation time was found to be weakly dependent on the temperature, nevertheless a reduction in the relaxation time was observed with increasing temperatures. This trend may be due to the increased mobility of polymer chains that disrupts intermolecular association when the temperature increases.

In the present study we explore the effect of temperature on the characteristics of hydrophobic junctions and its implication on the rheological properties, which have not been fully addressed.

EXPERIMENTAL

The model associative polymers studied are HASE polymers synthesized by Dow Chemicals (previously Union Carbide), via the emulsion polymerization of methacrylic acid, ethyl acrylate, and a macromonomer that had been capped with a hydrophobic group. The polymer examined in the present work has a structure shown in Figure 1, where R is $\text{C}_n\text{H}_{2n+1}$. The difference between the polymeric systems is the length of the poly(ethylene-oxide) spacer, which varied from 0 to 23.5 monomer residues. The hydrophobe of the polymers is a $\text{C}_{20}\text{H}_{41}$ alkyl chain.

A brief description of the synthesis methodology of the model polymer has been reported previously.^{6,12} The characteristics of the model polymer are given in Table I; its molecular weight was $\sim 200,000$ Daltons.^{38,39} The monomer sequence distributions of these polymers were believed to be quite similar, since the process used to produce them was held constant.

Samples with the desired concentration were prepared from a stock solution of 3 wt % polymer in 10^{-4}M KCl. The base used to neutralize the polymer to pH 9.0 is 2-amino methylpropanol (AMP). This is to ensure complete neutralization of the polymer where maximum enhancement of the rheological properties was observed.^{15,18}

The rheological characterization of the thermal behavior of the HASE polymer systems was performed in Rheometric ARES at pH 9.0. A double concentric cylinder geometry (inner cup diameter 27.94 mm,

TABLE I
Characteristics of HASE Polymer Systems

Name of HASE	Moles of EO (p)	Hydrophobes name	Hydrophobes formula	Molar ratio of MAA/EA/macromonomer (X/Y/Z)
HASE0020	0	Eicosanyl	$\text{C}_{20}\text{H}_{41}$	49/50/1
HASE0520	4.2	Eicosanyl	$\text{C}_{20}\text{H}_{41}$	49/50/1

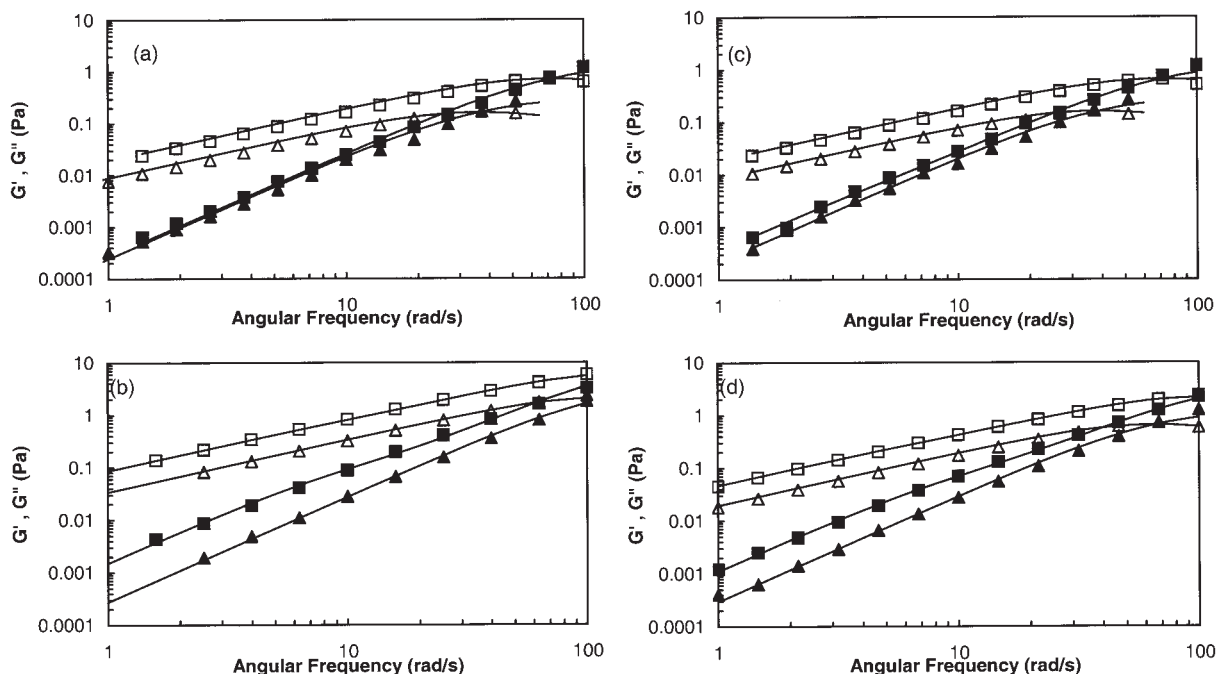


Figure 2 Dynamic properties of (a) 0.5 wt % HASE0020; (b) 3 wt % HASE0020; (c) 0.5 wt % HASE0520; and (d) 1 wt % HASE0520, at 10°C (squares) and 40°C (triangles). [Note: filled symbols are for G' and unfilled symbols are for G''].

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 polymeric systems. The thermal expansion of the measuring geometries was compensated when experiments were conducted at temperatures other than 25°C.

RESULTS AND DISCUSSION

Dynamic behavior and relaxation times

The thermal behavior of linear viscoelastic properties of the model polymer systems (HASE 0020, HASE 0520) are shown in Figures 2(a–d). These figures demonstrate that the storage (G') and loss (G'') moduli increase with decreasing temperatures. To identify the basis of such thermal behavior, the high frequency storage moduli were extracted from the figures and replotted in Figure 3. The results show that the storage and loss moduli decrease with increasing temperatures. Based on the Green and Tobolsky theory of rubber elasticity, the G' at high frequency can be used to represent the junction densities of the transient network system. Green and Tobolsky³⁶ 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 effective chains per unit volume ν :

$$G_N^0 = g\nu RT \quad (1)$$

where $g \sim 1$ and ν is the number of mechanically active junctions.³³

The reduction in the storage modulus at high frequency (see Fig. 3) indicates that the number of hydrophobic junctions in the network decrease with increasing temperatures. At elevated temperature, the water “cage” structures surrounding the hydrophobes are being disrupted by the increase in thermal energies. This disturbs the thermodynamic equilibrium of hydrophobic junctions in water, making the medium a poorer solvent for the hydrophobic segments. This forces more hydrophobes into a junction to minimize their exposure to the aqueous environment.^{5,30} The increase in the number of hydrophobes in a junction with increasing temperature will lead to a reduction of junction densities of the polymeric network, which will also lead to an increase in the lifetime of the junction, analogous to the behavior of surfactants^{5,27,30} To provide evidence to support this observation, the relaxation times of the model polymer system were examined.

The average terminal relaxation time can be determined from the expression

$$\lambda = \lim_{\omega \rightarrow 0} \left(\frac{G'}{\omega^2 \eta'} \right) \quad (2)$$

where η' is the dynamic viscosity, and the plateau in λ versus ω curve, which corresponds to the terminal

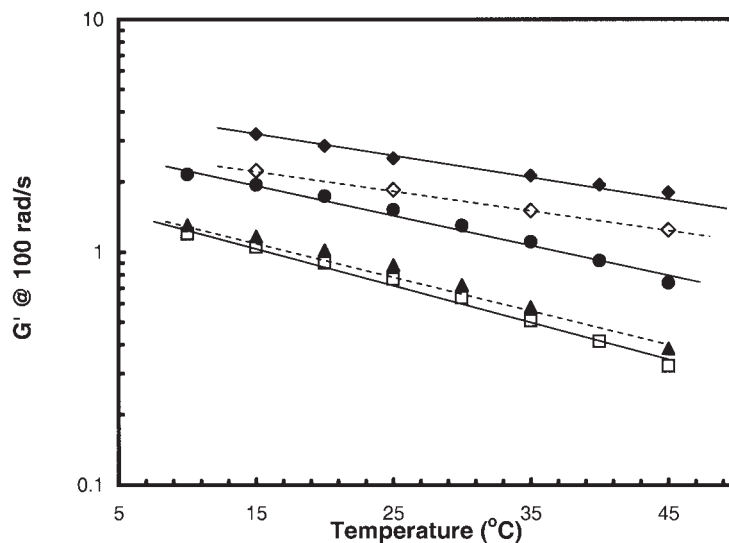


Figure 3 Dependence of storage modulus at 100 rad/s of various HASE polymers and concentrations on temperatures. □, HASE0020–0.5 wt %; ◆, HASE0020–3.0 wt %; ▲, HASE0520–0.5 wt %; ◇, HASE0520–1.0 wt %; ●, HASE2520–0.5 wt %.

region in the G' and G'' plot gives an estimate of the average terminal relaxation time. Figure 4 shows the relaxation times of the polymer systems (HASE 0020 and HASE 0520) at different temperatures. The average terminal relaxation time plotted in Figure 4 exhibits two distinct characteristics. An increase in relaxation time with increasing temperature was observed for HASE0020 (0.5 wt %). On the other hand, a decline in the relaxation time was observed for HASE0020 (3 wt %) and HASE0520 (1 wt %), but a slower rate of decrease was observed above 30°C. The 0.5 wt % HASE0520 displays both characteristics with increasing temperatures. To understand the complex relax-

ation behavior of the polymer systems, the relaxation spectra shown in Figures 5(a–d) are presented.^{17,40}

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

$$G'(\omega) = \int_{-\infty}^{\infty} H(\lambda) \left[\frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \right] d(\ln \lambda) \quad (3)$$

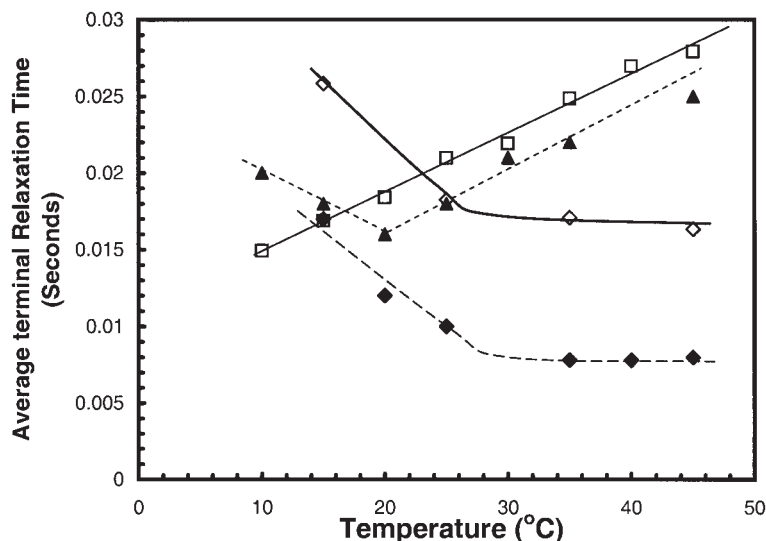


Figure 4 Average terminal relaxation time of various HASE polymers as a function of temperature. □, HASE0020–0.5 wt %; ◆, HASE0020–3.0 wt %; ▲, HASE0520–0.5 wt %; ◇, HASE0520–1.0 wt %.

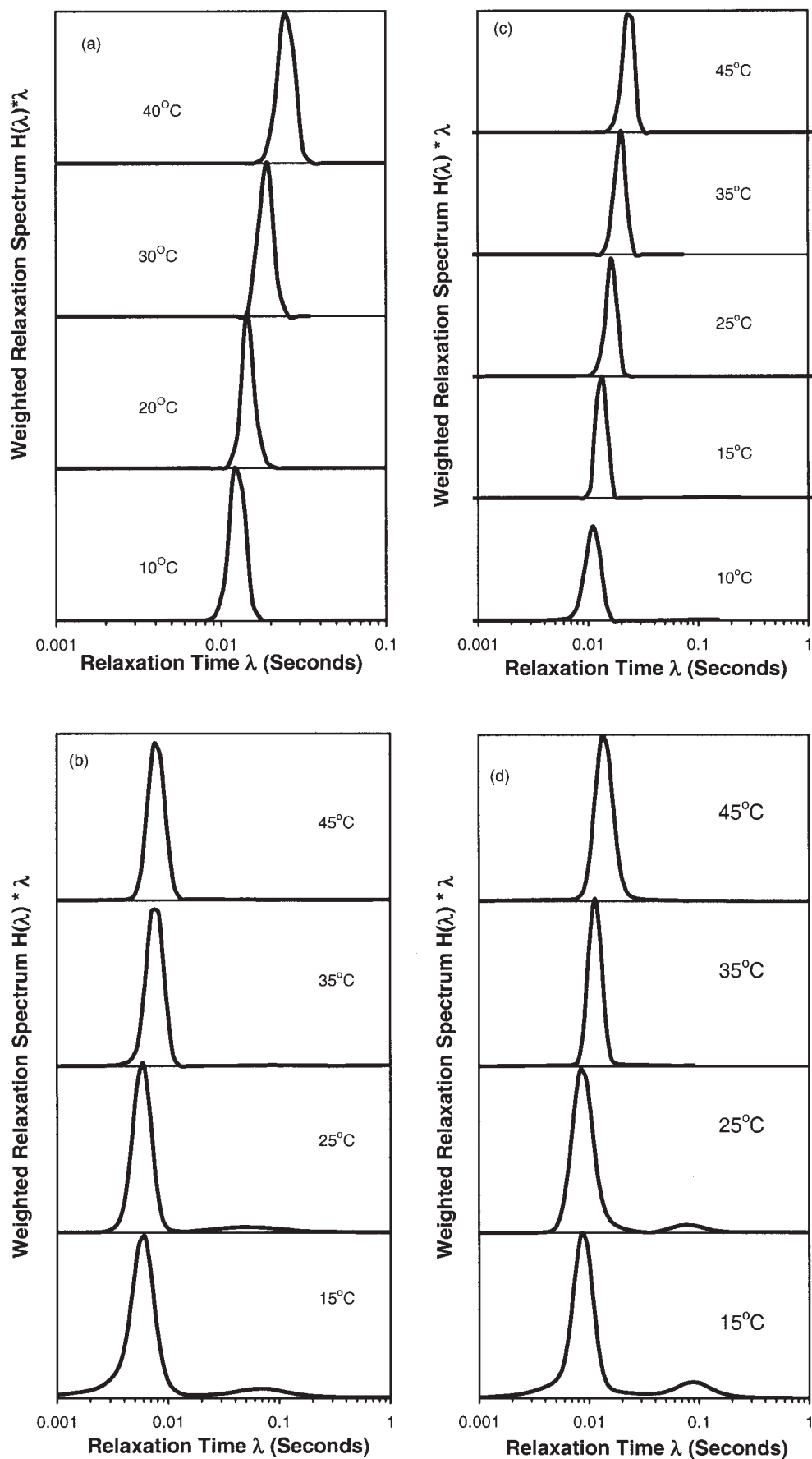


Figure 5 Weighted relaxation spectra of (a) 0.5 wt % HASE0020; (b) 3 wt % HASE0020, (c) 0.5 wt % HASE0520; and (d) 1 wt % HASE0520 at 10 to 45°C.

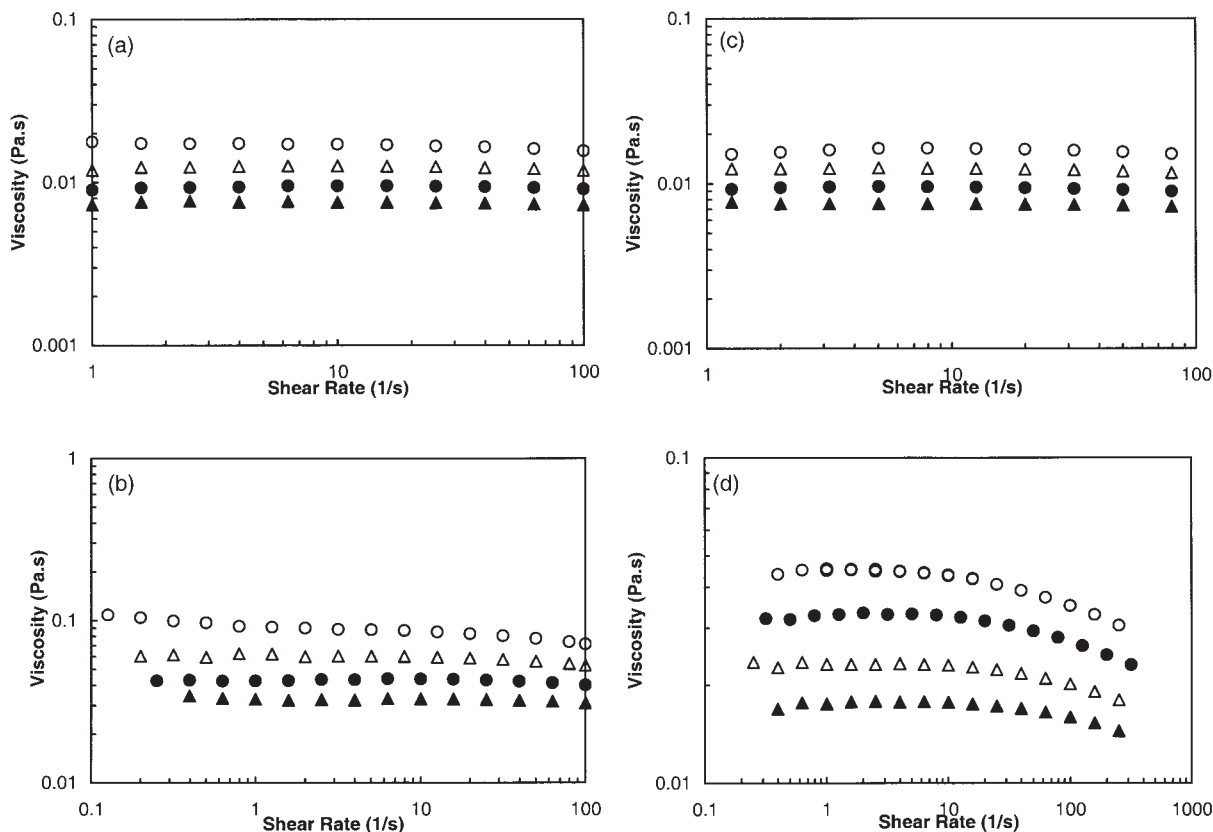


Figure 6 Steady shear viscosity profiles of (a) 0.5 wt % HASE0020; (b) 3 wt % HASE0020; (c) 0.5 wt % HASE0520; and (d) 1 wt % HASE0520 at 10 to 45°C. ○, 10°C; ◇, 20°C; ●, 30°C; ▲, 40°C.

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

The relaxation time spectrum was computed using Rheometric Scientific Inc. Orchestrator[®] software. The spectra obtained from the storage and loss moduli at different temperatures were plotted as $H(\lambda)\lambda$ versus λ as shown in Figures 5(a–d).

The relaxation spectra [Figs. 5(a–d)] show that, as the temperature increases, the fast relaxation time shifts to longer times. The increase in the relaxation time with increasing temperature resembles the characteristics of nonionic surfactants. The magnitude of this relaxation time lies in the range of 0.01 to 0.05 s, which Xu et al.,⁴¹ Tirtaatmadja et al.,²⁹ and Tam et al.¹⁹ identified as the exit rate or lifetime of the hydrophobic junction. Therefore, we believe that the fast peak represents the lifetime or dynamic exchange rate of the hydrophobic junctions. The increase in the lifetime of a hydrophobic junction is proportional to the increase in the hydrophobic aggregation number.^{42,43} This is a further confirmation that the formation of a larger aggregation number at elevated temperature

reduces the junction densities in the network. The slower relaxation peaks as shown in the spectrum [Fig. 5(d)] shifts to shorter times with increasing temperatures. They represent the structural/network relaxation times since the relaxation behavior is strongly influenced by the Brownian dynamics of polymer chains, where the rate of polymer chain rearrangement increases with increasing temperature, leading to shorter relaxation times.⁴⁴

By comparing the average terminal relaxation time of the polymer systems (Fig. 4) with the relaxation spectra [Figs. 5(a–d)], the following conclusions can be drawn:

1. The increases in the average terminal relaxation behavior with temperature for the 0.5 wt % HASE0020 (open circles in Fig. 4), indicates that the relaxation behavior is dominated by the junction lifetime, since, in the semidilute solution regime, the density of the polymer network is not sufficient for the reptation behavior of the polymer chain to dominate.⁴⁵ The increase in the lifetime with temperature is attributed to the increase of hydrophobic aggregation number as also observed for surfactant systems.

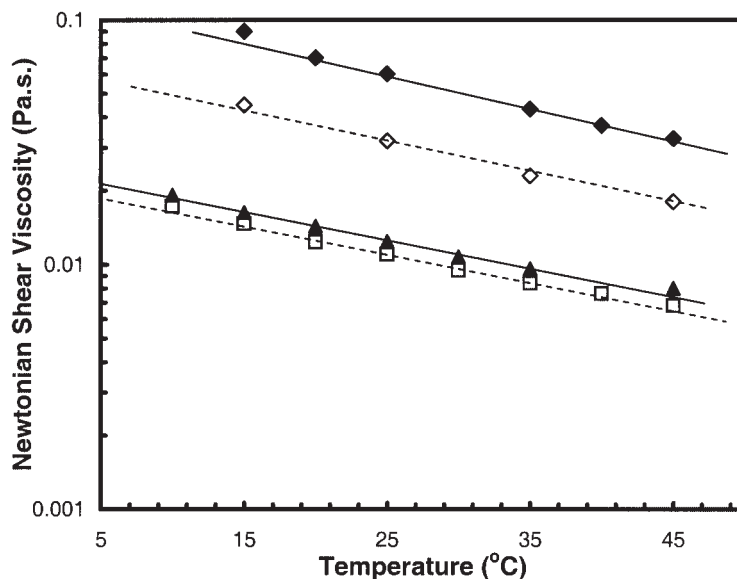


Figure 7 Dependence of Newtonian viscosities on temperatures of HASE polymer solutions. \square , HASE0020–0.5 wt %; \blacklozenge , HASE0020–3.0 wt %; \blacktriangle , HASE0520–0.5 wt %; \diamond , HASE0520–1.0 wt %.

- The decreasing trend of the average terminal relaxation time with increasing temperature for 1 wt % HASE0520 (open triangles in Fig. 4 at temperatures between 15 and 30°C) and 3 wt % HASE0020 (filled diamonds in Fig. 4 at temperatures between 15 and 30°C) suggests that the structural/network relaxation time dominates the relaxation behavior. With increasing polymer concentrations, network formation becomes dominant. This slows the reptation motion of polymer chains, leading to a longer overall relaxation time. The decreasing relaxation behavior (Fig. 4) with increasing temperature implies that the rate of diffusion and reptation motion of the polymer chains increases with temperature, leading to a faster relaxation time.
- A slower rate of decline of the relaxation time with increasing temperatures was observed for the 1 wt % HASE0520 and 3 wt % HASE0020. This suggests that, with increasing temperatures, the relaxation behavior is dominated by the lifetime of the junctions. This mixture of relaxation behavior is clearly demonstrated in the 1.0 wt % HASE0520 [see Figs. 4 and 5(d)], where two relaxation peaks were observed at 15 and 25°C.

Based on the above observations, it can be deduced that the overall relaxation behavior of the HASE polymer is governed by the lifetime of the hydrophobic junction, structural relaxation time, or a combination of both, depending on the degree of network formation and temperature.

Equilibrium shear viscosity behavior and activation energy

The thermal behavior based on the steady shear viscosity of the model polymer systems HASE0020 and HASE0520 was plotted in Figures 6(a–d). The Newtonian viscosity was extracted from the above plots and summarized in Figure 7. These figures clearly show that, as the temperature of the polymer solutions increases, the shear viscosity decreases. The trend is identical to the dynamic modulus–temperature plot as shown in Figure 3, where the reduction in the viscosity with increasing temperature is predominantly caused by the reduction in the mechanically active junction densities based on $\eta_0 = G_\infty \lambda$. The viscosity–temperature behavior shown in Figures 7 and 8 follows the Arrhenius relationship described as follows:

$$\eta_0 = \frac{\nu k T}{\omega_0} \exp(E/kT) = \frac{\nu k T}{\beta_0} \quad (4)$$

where ω_0 is the natural frequency of thermal vibration of the reactive group in an isolated state, k the Boltzmann constant, T is the absolute temperature, and η_0 is the zero shear viscosity.

The viscosity–temperature behavior of the HASE polymer as shown in Figures 7 and 8 obeys the Arrhenius relationship as given by eq. (4). However, the lifetime–temperature behavior of the polymer systems plotted in Figure 8 exhibits a negative slope, in contrast with the results for viscosity, where a positive slope was observed.³² This difference can be understood by the transient network theory of Tanaka and Edwards.^{34,35} It only predicts the energy potential bar-

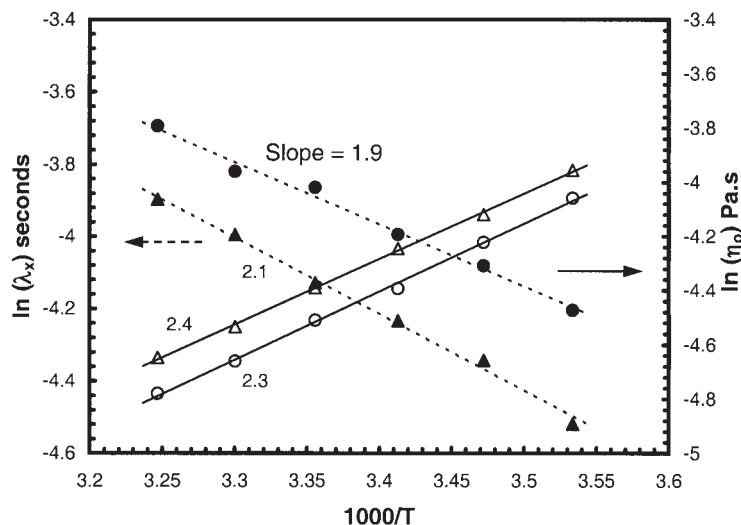


Figure 8 Arrhenius plots of Newtonian viscosities and lifetimes for HASE0020 and HASE0520. Relaxation time: ●, HASE0020–0.5 wt %; ▲, HASE0520–0.5 wt %. Zero shear viscosity: ○, HASE0020–0.5 wt %; △, HASE0520–0.5 wt %.

rier required for dissociation of hydrophobes from the hydrophobic junction based on either its own thermal motion or the thermal motion of connecting chains. Hence, with increasing temperature, the depth of the energy well and the bonding potential for a hydrophobe in a junction decreases. This results in the increase in the dynamic exchange rate of a hydrophobe in a hydrophobic junction. However, this model does not predict the behavior of the hydrophobic system where the aggregation number in a hydrophobic associating site increases with temperature, which leads to an increase in the lifetime of the hydrophobic junction. This may then explain the discrepancy between the transient network model and the experimental results observed for the lifetimes. Recently, we³⁷ identified a dual relaxation behavior in the HEUR polymer system. The lifetime of the system increases with temperature, while the reverse is true for the network relaxation time. This may suggest that the interpretation proposed by Annable et al.³² may not be adequate to fully explain the thermal effects on the relaxation process observed in the HEUR system.

Comparison of the activation energy based on the lifetime and viscosity was tabulated in Table II. The Arrhenius equation based on the lifetime is slightly modified to provide an absolute number for the activation energy, where

$$\tau_x = \omega_0^{-1} \exp(-E/kT) \tag{5}$$

From Table II, the activation energy based on Newtonian viscosity and relaxation time increases with increasing spacer chain length. The viscosity-based activation energy is a measure of the macroscopic strength of the system, while the lifetime-based activation energy measures the microscopic strength of the system, i.e., the strength of the hydrophobic junction, whereas the macroscopic strength of the system is based on both the strength and the densities of the hydrophobic junction in the network.³⁷ Table II also shows that the viscosity-based activation energy is always higher than the lifetime-based energy. Since the lifetime-based activation energy is a measure of the strength of the hydrophobic junction, the net difference between the two energies reflects the junction densities in the network.

We conclude that the lifetime from the Arrhenius equation proposed by Tanaka and Edwards is not applicable for describing the activation process of the HASE associative polymer. This is because Tanaka and Edwards³⁴ do not consider the thermal behavior of hydrophobic junctions, whose aggregation number increases with temperature.

TABLE II
Comparison of Activation Energies based on Lifetime and Viscosity at 0.5 wt % of HASE Polymer Solutions

Polymer designation	Activation energy based on Newtonian viscosity (kJ/mol)	Activation energy based on lifetime (kJ/mol)
HASE0020	19.00	16.25
HASE0520	20.11	17.65

CONCLUSION

With increasing temperatures, the aggregation number in the hydrophobic junction increases. Hence, the lifetime of the associative polymer shifts to longer times due to the increase in the hydrophobicity of the macromonomer. The structural relaxation time decreases with increasing temperatures. This is caused by the Brownian dynamics of polymer chains, which enable the chains to relax at a faster rate. Therefore, the overall relaxation time of the HASE polymer is either governed by the lifetime of the hydrophobic junction, the structural relaxation time, or a combination of both, depending on the degree of network formation and temperature.

The temperature studies also show that the transient network theory proposed by Tanaka and Edwards cannot fully describe the activation energy process of the hydrophobic junctions in a HASE associative polymer.

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