

Network Structure of a Model HASE Polymer in Semidilute Salt Solutions

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ABSTRACT: The effects of salt and temperature on a model hydrophobically modified alkali-soluble emulsion (HASE) associative polymer were investigated. The shear viscosities and viscoelastic properties decrease continuously as the salt concentration is increased. The decrease is attributed to the shielding of charged polyelectrolyte backbones by excess cations, which causes the “stiff” polymer backbone to shrink, leading to the destruction of intermolecular junctions. Smaller individual polymer clusters with predominantly intramolecular associations are then formed. At moderate deformation rates, the solutions exhibit a shear-thickening behavior, which is attributed to the conversion of intramolecular to intermolecular junctions [Tam et al. *Polymer* 1999, 40, 6369]. The activation energy determined from the zero-shear viscosity decreases with the salt concentrations, while that obtained from the maximum viscosity increases until 0.6M NaCl, beyond which it decreases. This trend indicates that the strength of the network is greater in the shear-thickening region due to the larger proportion of intermolecular junctions. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1486–1496, 2001

Key words: associative polymers; salt; charged shielding; shear-thickening

INTRODUCTION

The HASE polymer is classified as a hydrophobically modified associative polymer with charged backbones. Upon neutralization to a pH of greater than 7, the polymer chains solubilize and expand due to repulsion of the negative charges distributed along the polymer backbones. The interactions between hydrophobic groups distributed

along the polymer backbones yield both intra- and intermolecular junctions, which gives rise to a large viscosity enhancement. The addition of salt to the solution shields the electrostatic repulsion between charges on the polymer chains. The removal of electrostatic repulsion by salt addition reduces the stiffness of the polymer backbone, causing the chain to coil, thereby disrupting the intermolecular junctions. The rupture of the polymer network brought about by the contraction of the polymer backbone results in a significant reduction in the viscosity and elasticity. The addition of salt can transform the polymer solution from a semidilute to a dilute solution regime. The critical salt concentration in which the polymer backbone changes from a “stiff” to a flexibility

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chain is dependent on the characteristics of the hydrophobic alkyl groups.¹

Studies on the effects of salt on the behavior of polyelectrolyte solutions are numerous and they have been described extensively in a number of monographs.²⁻⁶ However, only a limited number of studies on hydrophobically modified associative polymers in salt solutions have been reported in the literature. The effects of salt on the phase behavior and the viscoelastic properties of hydrophobically modified polyacrylic acid (HMPAA),⁷⁻¹⁰ hydrophobically modified partially hydrolyzed polyacrylamide (HMPAM),^{11,12} and hydrophobically modified cellulose (HMHEC)¹³ systems have recently appeared. In the study on hydrophobically modified polyacrylic acid, Wang et al.⁹ observed that the addition of salt at the appropriate level can enhance the viscosity of C₁₈-modified PAA, due to the conformational changes and the enhanced interchain aggregation resulting from hydrophobic interactions. A later study by the same group indicated that intrachain aggregation occurs in the dilute solution regime, which causes a reduction in the viscosity. Upon the addition of NaCl, the polymer exhibits a transition from a nonaggregated to an aggregated polymer cluster. This transition occurs above a critical salt concentration, which is dependent on the length and content of the hydrophobic alkyl groups. The intrinsic viscosity studies on the model HASE polymers in NaCl solutions indicated that the addition of salt increases the Huggins coefficient, which means that the polymers are becoming less soluble. The solvent quality is reduced, which promotes more intramolecular associations.^{11,14,15} On the other hand, the stiffness of the polymer backbone tends to decrease due to charged shielding and the enhanced intramolecular associations of the hydrophobes.

The objective of this work was to examine the effects of salt on a hydrophobically modified polyelectrolyte solution to further elucidate the mechanism on the conversion of intra- to intermolecular associations. The scope includes investigating the effects of salt concentrations on the steady shear and viscoelastic properties of a 1 wt % model HASE polymer with a C₂₀ hydrophobe (designated as RDJ31-5). The choice of this system is based on the earlier study by Tam et al.,¹⁶ where the interesting shear-thickening behavior of 1 wt % RDJ31-5 in different salt solutions was observed. The strength of the associative junctions will be quantified by examining the Arrhenius dependence of viscosity on temperatures. The

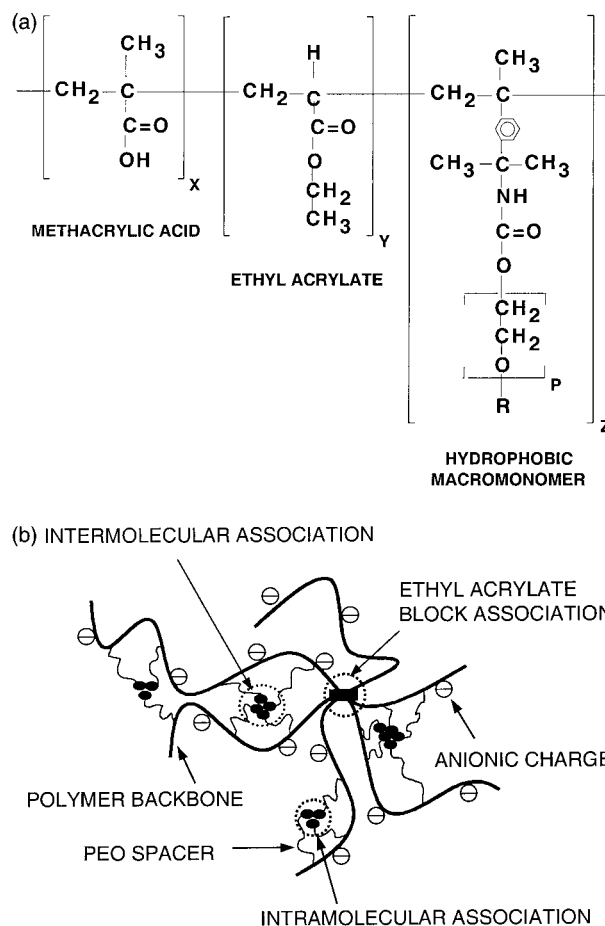


Figure 1 (a) Chemical structure of model HASE associative polymer. (b) Network structure of model HASE polymer in aqueous solution.

stiffness of the polymer chain is altered by the addition of salt, and its effects on the hydrodynamic volume, aggregation number of the junction, and network structure can be examined by conducting careful rheological experiments.

EXPERIMENTAL

Materials

The model associative polymer used is an emulsion copolymerization product of methacrylic acid (MAA), ethyl acrylate (EA), and a macromonomer capped with a hydrophobic group through poly(ethylene oxide) (PEO) chains. The general chemical structure of the HASE polymer is shown in Figure 1(a). X,Y,Z represents the mol fraction of each segment of the polymer chain corresponding to the ratio of 50/49/1. The HASE polymer is des-

ignated as RDJ31-5. This nomenclature is similar to the ones used in previous publications.^{17,18} The PEO chains, p , and the hydrophobic alkyl group, R , were kept constant at 31 mol and 20 carbons, respectively. The network structure of the model HASE polymer in an aqueous solution is described in Figure 1(b). The molecular weights of the macromonomers were calculated by adding the molecular weight of meta-TMI (MW = 201.25) to the hydroxyl number-average molecular weights of the surfactant precursors. The synthesis procedure and GPC output of the macromonomer was described elsewhere.^{17,19} The exact molecular weight of these model polymers was determined by capping the hydrophobe with cyclodextrin. For RDJ31-5, the molecular weight as determined by static light scattering is $\sim 180,000$.²⁰ This result agrees with that determined from the intrinsic viscosity for the polymer in 0.01 and 0.1M NaCl solutions, where the molecular weight was estimated to be in the range of 170,000 to 190,000 daltons. Hence, the average number of hydrophobes on each polymer chain is estimated to be 16–18. The intrinsic viscosity of RDJ31-5 in 0.1M NaCl was found to be 3.3 dL/g¹⁵; hence, at 1.0 wt %, $c[\eta] = 3.3$, which suggests that the polymer solutions are in the semidilute region.

Measurement Techniques

A stock solution containing 8.27 wt % polymer latex dispersion was diluted with an appropriate amount of sodium chloride (NaCl) to a concentration of 1 wt %, whose pH was then adjusted to 9–9.5 by adding 2-amino-2-methyl-1-propanol (AMP). The samples were kept for 3 days prior to testing to allow the solutions to come to an equilibrium.

Experiments were carried out using a Contraves LS40 controlled-rate rheometer. It was fitted with the MS 41S/1S concentric cylinder measuring system consisting of a cup with the diameter of 12 mm and a bob with the diameter of 11 mm and length of 8 mm. The Carri-Med CSL500 controlled stress rheometer was used for more viscous solutions and to perform shear superimposed oscillation experiments. A 4-cm, 2° cone and plate and a double concentric cylinder measuring system was used. All the experiments were carried out over a temperature range of 10–35 \pm 0.1°C.

The dynamic light scattering experiments were carried out in a Brookhaven BI-200SM goniometer

system equipped with a 522-channel BI9000AT digital multiple τ correlator. A power-adjustable vertically polarized argon ion laser with a wavelength of 488 nm was used as the light source. The 1 wt % RDJ31-5, in various NaCl concentrations, was centrifuged for 5–6 h and subsequently placed in the measuring cell. Autocorrelation functions were obtained and the data analyzed using the Inverse Laplace Transform routine (REPES) supplied with the GENDIST software package to determine to relaxation time. A detailed description of the analysis and the theory of dynamic light scattering was described by an excellent monograph edited by Brown.²¹

RESULTS AND DISCUSSION

Effect of Salt on Steady Shear and Viscoelastic Properties of RDJ31-5

From the previous study by Guo,¹ it was observed that the HASE polymer with longer hydrophobic groups exhibits a unique behavior when shear is applied. At moderate shear stress (10–100 Pa), the viscosity profile departs from the shear-thinning behavior and shows an upward curvature as depicted in Figure 2(b). Such a response is commonly referred to as the shear-thickening behavior. This behavior is attributed to the conversion to intermolecular associations at the expense of intramolecular associations. A progressive increase in the salt concentration significantly alters the shear viscosity profile of RDJ31-5.¹⁶ However, a detailed study on the nature of the network structure and its strength has not been carried out. The addition of salt provides an electrostatic shield between charges along the polymer backbones. The polymer backbone contracts, which disrupts the intermolecular associative junctions, yielding smaller clusters with predominantly intramolecular associations. The reduction in the active junctions has a significant impact on the rheological properties.

Figure 2(a) depicts the shear viscosity profile of 1 wt % RDJ31-5 at salt concentrations ranging from 0.2 to 1.0M. Typically, a constant zero-shear viscosity region at small deformation rates is observed, followed by a shear-thickening behavior at moderate deformation rates and, finally, a shear-thinning region. Increasing the salt from 0.2 to 1.0M reduces the shear viscosity by approximately two orders of magnitude. The reduction in the mechanically active junctions is responsi-

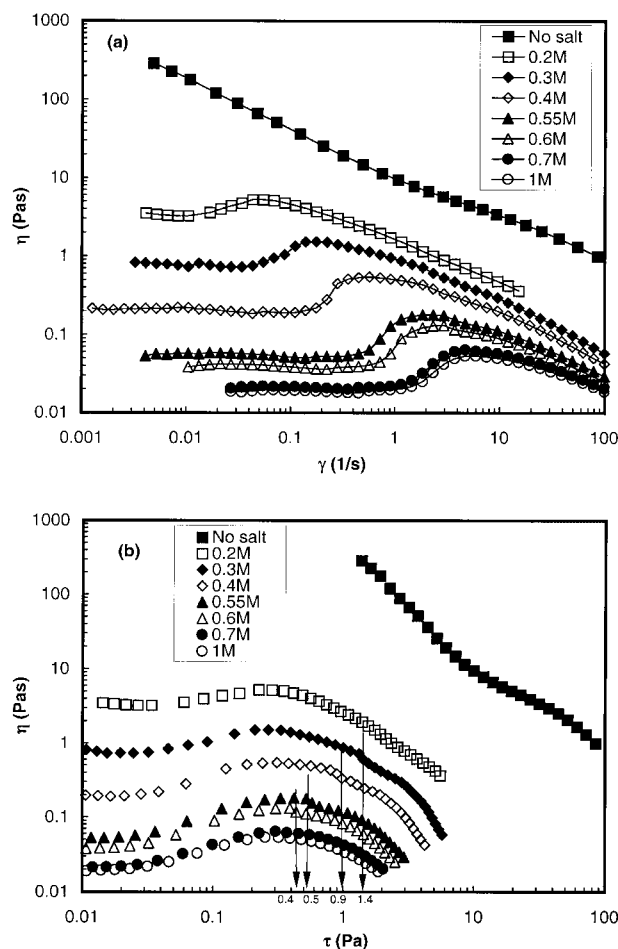


Figure 2 Effects of salt on (a) η versus $\dot{\gamma}$ and (b) η versus τ of 1 wt % RDJ31-5 at 25°C.

ble for the large decrease in the shear viscosity. As indicated in Figure 2(a), the maximum viscosity shifts to higher deformation rates as the salt concentration increases. However, beyond 0.7M NaCl, no significant change in the viscosity is evident, which means that any further addition of salt does not change the cluster size. This is also an indication that the intramolecular association induced by network disruption by salt addition is at its optimum at approximately 0.7M NaCl. The constant viscosity region is related to the balance between the creation and destruction of intermolecular associative junctions under low shear deformations. The implication of this steady shear behavior is that the overall number of mechanically active junctions remains constant. With increasing salt content, the location of the maximum viscosity in the shear-thickening region shifts to higher shear rates, which suggests that the equilibrium is shifted to favor more formation

than disruption of intermolecular associative junctions. The applied shear gradient has the dual effects of (a) disrupting the intramolecular associative junctions and (b) increasing the probability of collisions between micellar clusters. The sum of these two effects yields an increase in the number of mechanically active junctions.¹⁶ Beyond the shear-thickening region, the viscosity decreases, indicating that the deformation stresses have exceeded the overall strength of the network junctions, causing a large proportion of the active junctions to break [Fig. 2(a,b)].

The shear-thickening phenomenon is not evident at low salt concentrations, and this is attributed to two possible factors:

1. At low salt concentration, the proportion of intermolecular junctions is significantly higher compared to intramolecular junctions. Hence, any contribution from the conversion of small fractions of intramolecular junctions to intermolecular junctions would have an insignificant effect on the viscosity.
2. Due to the strong electrostatic repulsion between charges along the polymer backbone, the polymer chains are extended with large numbers of micellar junctions containing fewer hydrophobes. When stress is applied, the micellar junctions break in a continuous fashion and could not reassociate due to the stiff backbone.

From Figure 2(a), it is evident that shear thickening becomes more prominent when the salt concentration increases. At high salt concentrations, charged shielding effectively removes the electrostatic repulsion between negative charges located along the polymer backbone. This leads to the collapse of the polymer chains, which facilitates the formation of a larger proportion of intramolecular associations with a larger aggregation number. When the solutions are deformed, the intraassociative junctions are disrupted, freeing more hydrophobes, which reassociate with neighboring hydrophobes to form a larger number of intermolecular associative junctions. The aggregation number of the hydrophobic clusters is larger as the hydrophobes are more accessible to associate with each other since the steric hindrance of the stiff polymer backbone is removed by charged shielding of the salt ions. This enhances the strength of the intermolecular associative junctions, which are now more resistant to

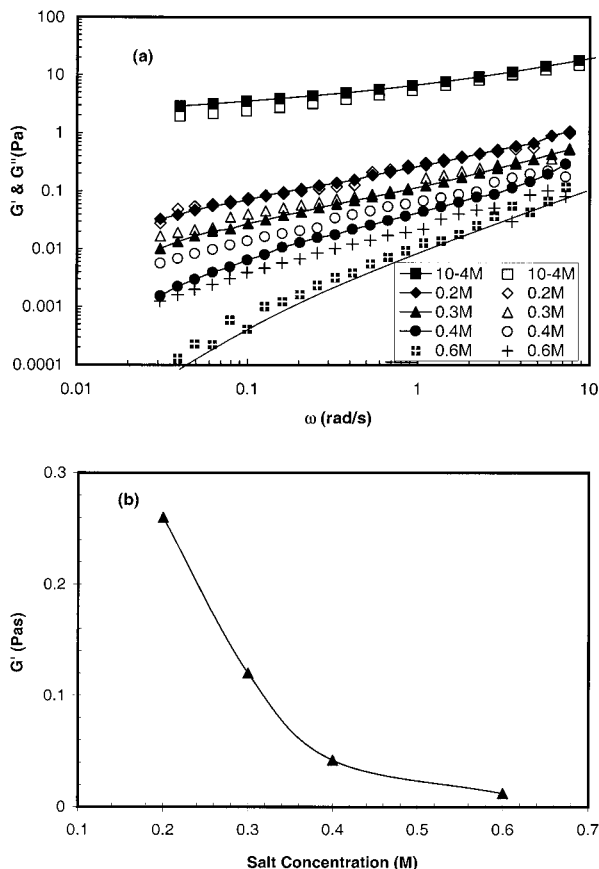


Figure 3 (a) Effects of salt on G' and G'' of 1 wt % RDJ31-5 at 25°C (filled symbol for G'). (b) Dependence of G' ($\omega = 1$ rad/s) on salt concentrations for 1 wt % RDJ31-5.

shear deformation. However, the overall network structure of the HASE polymer with a low salt content is stronger than that at a large amount of salt since the number of mechanically active junctions as depicted by the storage modulus decreases with increasing salt concentrations [Fig. 3(b)]. The meaning of the mechanically active junctions can be analyzed based on the transient network theory proposed in 1946 by Green and Tobolsky.²² The theory was based on the extension of classical rubber elasticity theories for transient networks, which was first introduced to account for entanglements or reversible physical bonds. The theory predicts a constant steady-shear viscosity of

$$\eta(\dot{\gamma}) = \eta_0 = \lambda G_\infty \quad (1)$$

where the relaxation time λ is the reciprocal of the bond-breaking and reformation rate, and G_∞ is the high-frequency or plateau modulus given by

$$G_\infty = \nu_{\text{eff}} RT \quad (2)$$

where ν_{eff} is the number density of effective or elastic chains; R , the gas constant; and T , the absolute temperature. Thus, from the knowledge of the plateau modulus, the mechanically active junctions in the system may be estimated. A consequence of this is that the viscosity decreases with increasing salt concentration based on eq. (1). At low shear rates, the viscosity of the RDJ31-5 in the $10^{-4}M$ salt solution is larger by almost five orders of magnitude when compared to that in the $1.0M$ salt solution. However, the difference in the shear viscosity is reduced to two decades at high shear rates. The stiffness of polyelectrolyte backbones plays an important role in controlling the nature and the number of intermolecular associative junctions. The onset of the shear-thickening behavior and the maximum viscosity is shifted to higher shear rates as the salt concentration is increased. This trend is a natural consequence arising from the decrease in the viscosity when the salt concentration is increased. The shear viscosity plotted against shear stress in Figure 2(b) shows that the maximum viscosity is roughly independent of the shear stress. The maximum shear viscosities occur at a constant shear stress of approximately 0.3 Pa. The viscosity profile shows a slight kink at a critical stress τ^* of 1.4, 0.9, 0.5, and 0.4 Pa for the polymer in 0.3, 0.4, 0.55, and 0.6M NaCl solutions, respectively. Such behavior may be attributed to the rupture of junction points with similar strength.

The dependence of the storage and loss modulus, G' and G'' , on the frequency are plotted in Figure 3(a). At low salt concentration, the modulus shows a slight dependence on the frequency. Both moduli decrease with the addition of salt. When the salt concentration exceeds 0.4M, the storage modulus, G' , displays a second-order region, and the longest relaxation time can be determined from the expression

$$\lambda = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2 \eta_0} \quad (3)$$

The relaxation time measures the time required for the network to relax after an imposed deformation. At salt concentrations exceeding 0.7M, the elastic property of the fluid decreases to a limiting value, which is not detectable with the rheometer. The magnitude of the storage modulus at a fixed frequency can be correlated to the

plateau modulus, which gives a measure of the number of mechanically active junctions as indicated by eq. (2). With increasing salt concentrations, the number of mechanically active junctions decreases as represented by the reduction in G' shown in Figure 3(b). It is thus evident that the addition of salt induces intramolecular associations at the expense of intermolecular junctions, resulting in the decrease in the number of mechanically active junctions. At 0.2M NaCl, the storage and loss modulus superimposes onto the same curve but the difference increases with increasing salt concentrations. This suggests that the viscoelastic properties of the polymer are dominated by the viscous behavior at high salt concentrations.

Figure 4(a) shows the effects of salt on two different characteristic times of the HASE polymer. The characteristic time curves, t_0 and t_m , were obtained from the inverse of the shear rate at the onset point of shear thickening and maximum shear viscosities, respectively. t_0 is always higher than is t_m , but the magnitude decreases with increasing salt concentrations. Addition of salt drastically reduces the magnitude of the characteristic times. The relationship between the ratio of maximum-to-zero shear viscosity against salt concentrations is shown in Figure 4(b). The results show a rapid increase in the ratio until it reaches a maximum at 0.6M NaCl; thereafter, it decreases to an equilibrium value of approximately 3. The ratio of maximum to zero shear viscosity is directly related to the overall net increase in the intermolecular associative junctions. Similarly, this ratio could be correlated to the overall strength of intermolecular associative junctions.

Temperature Effects

The viscosity and dynamic properties of 1 wt % RDJ31-5 in various salt solutions were determined at different temperatures, ranging from 10 to 35°C. Figure 5(a–d) depicts the shear viscosity profiles of 1.0 wt % RDJ31-5 in 0.2–0.6M NaCl, respectively. Similar trends are observed for other salt concentrations. The maximum shear viscosities are shifted to higher deformation rates when the temperature is increased. The extent of shear thickening is most significant at approximately 0.6M NaCl and this may indicate that the conversion of an intra- to intermolecular association produced by a shear-induced phenomenon is at its optimum. Based on similar observations by

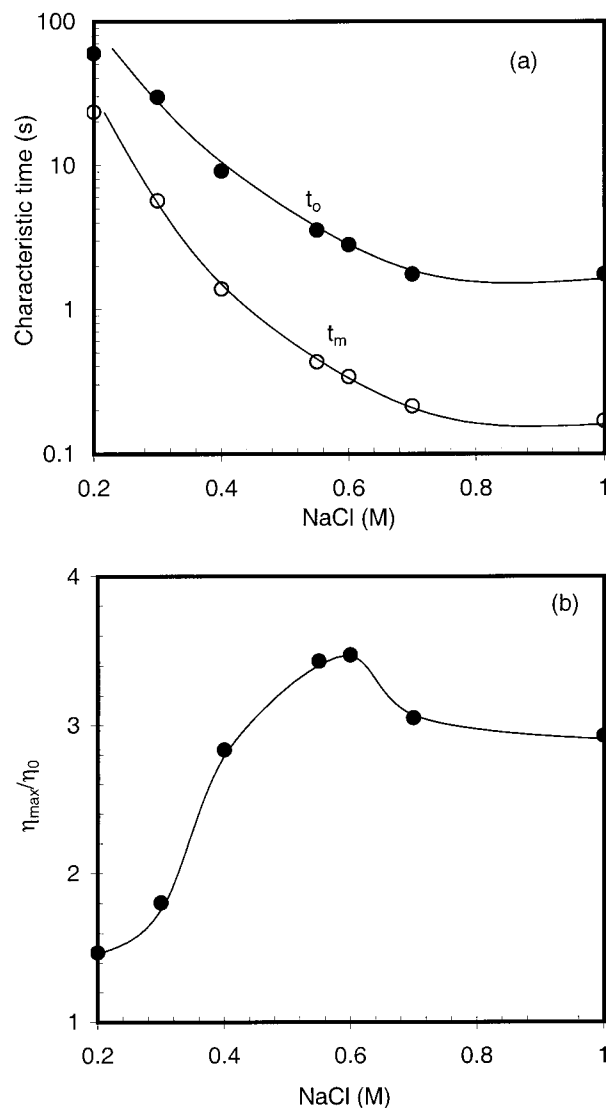


Figure 4 Effects of salt on the (a) characteristic times and (b) ratio of maximum to zero shear viscosity of 1 wt % RDJ31-5.

Aubry and Moan,²³ the slight kink after the maximum viscosity as evident in Figure 5(d) is related to the disruption of junctions with similar size or strength. By decreasing the temperature, the kink becomes even more apparent due to the slower Brownian dynamics of the hydrophobic clusters.

The critical stress, τ_0 , at which the shear viscosities start to exhibit shear-thickening behavior is plotted against salt concentrations as shown in Figure 6. There is a significant drop in τ_0 beyond 0.3M NaCl; thereafter, it remains constant at 0.01 Pa. This trend suggests that at 0.4–0.6M NaCl the size of the polymer clusters have de-

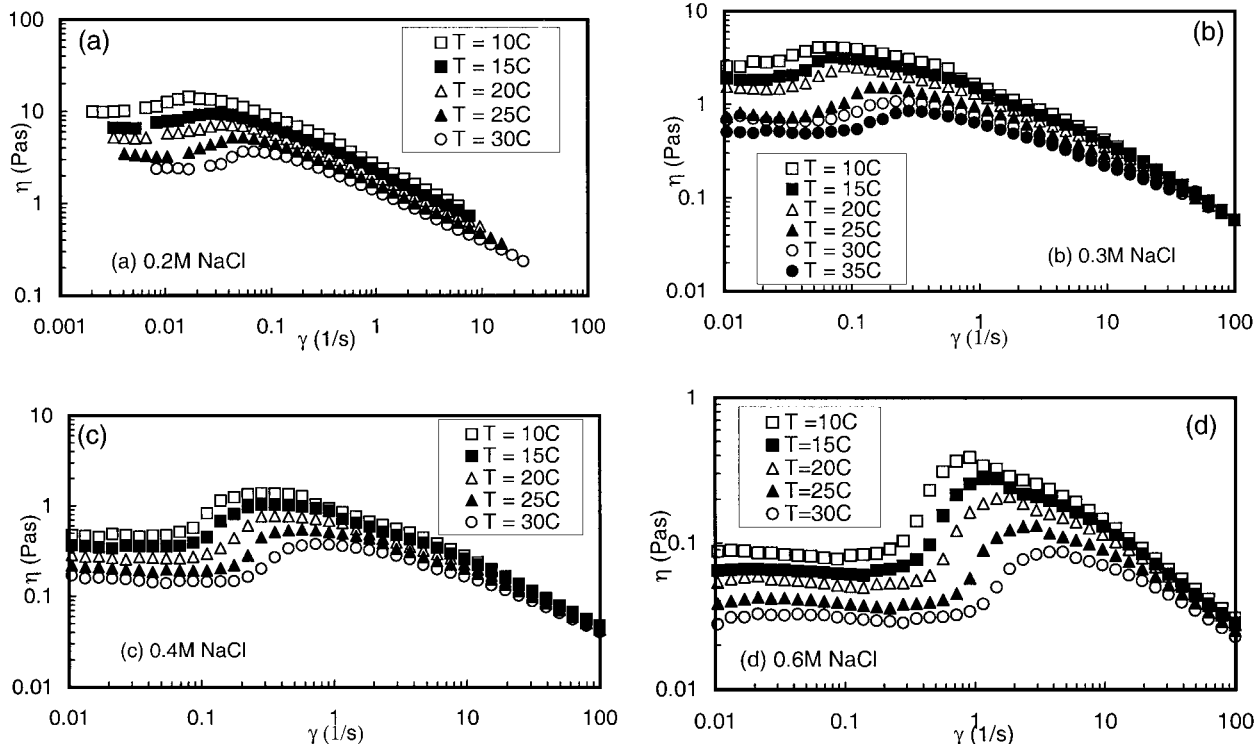


Figure 5 Effects of temperature on η versus $\dot{\gamma}$ of 1 wt % RDJ31-5 in (a) 0.2M, (b) 0.3M, (c) 0.4M, and (d) 0.6M NaCl.

creased to a stable-limiting value. This observation is further confirmed by dynamic light scattering experiments where the relaxation time of the cluster (indicated by a filled circle) exhibits identical trends. The relaxation time of the cluster

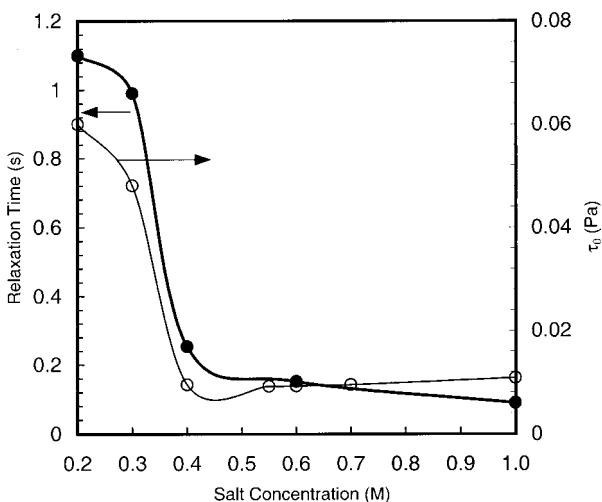


Figure 6 Relaxation time determined from dynamic light scattering and critical stress of 1 wt % RDJ31-5 in various salt concentrations (at 25°C).

is directly related to the diffusion of the cluster in solution, which corresponds to the size of the cluster. Hence, it can be concluded that the critical stress is directly proportional to the nature of the polymer clusters, that is, the proportion of intra- and intermolecular junctions.

The ratio of maximum-to-zero shear viscosity is related to the formation of intermolecular associations at the expense of intramolecular associations. The viscosity ratio was determined at different temperatures and salt concentrations and is shown in Figure 7. The results are tabulated in Table I. The graph shows that at low salt concentrations of 0.2 and 0.3M the ratio is independent of temperature. This implies that at this salt content the proportion of intra and intermolecular junctions does not change with the temperature. One interpretation for this is that the Brownian dynamics arising from a temperature change could not disrupt the associative junctions. However, at $C_s > 0.3M$, the viscosity ratio decreases with temperature. At higher salt concentrations, the number of mechanically active junctions decreases; hence, the viscosity ratio tends to be more sensitive to temperature. Another possible explanation for the decrease in the

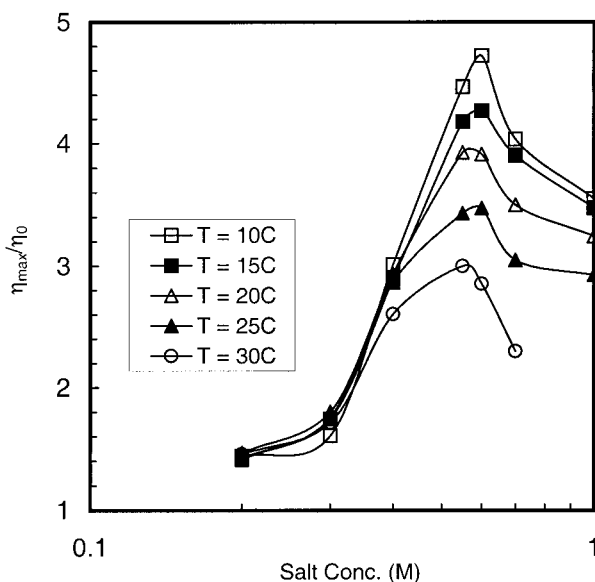


Figure 7 Dependence of η_{\max}/η_0 on temperature for 1 wt % RDJ31-5 in 0.2–1.0M NaCl.

viscosity ratio is the reduced solubility of the HASE polymer at high salt content and temperatures. Further study using microcalorimetry to determine the phase behavior of the polymer solution will be carried out to elucidate this possible phenomenon. From Figure 7, it is evident that the viscosity ratio at all temperatures ranging from 10 to 30°C increases with the salt content, reaching a maximum at 0.6M, beyond which the viscosity ratio decreases to a second limiting value. The decrease is possibly due to other possible effects such as charged shielding and rearrangement of the hydrophobic clusters.

Activation Energies of 1 wt % RDJ31-5 in Salt Solutions

The activation energy, E_a , was determined to provide information on the strength of the overall net-

work junction at various salt concentrations. E_a was calculated according to the following steps:

1. Shear stress was corrected to the reference shear stress at room temperature (25°C) using the expression below:

$$\tau = \tau_r \times \frac{T}{T_r} \quad (4)$$

where τ and τ_r are the applied shear stress at temperature T and T_r .

2. The corresponding shear viscosity was used to determine the activation energy, E_a , based on the Arrhenius equation:

$$\eta_0 = Ae^{-(E_a/RT)} \quad (5)$$

where η_0 is the shear viscosity at very low shear stress (Pa s); A , the Arrhenius constant; E_a , the activation energy (J/mol); R , the gas constant (8.314 J mol⁻¹ K⁻¹); and T , the temperature (K).

The activation energy of the 1 wt % HASE polymer without hydrophobic groups, RDJ31-1, is approximately 20 kJ/mol (~ 8.1 RT), while that of RDJ31-5 (C20 hydrophobe) at a very low salt concentration (10⁻⁴M KCl) is approximately 51 kJ/mol (~ 20.7 RT).²⁴ By increasing the hydrophobic alkyl chain to 20 carbon atoms, the activation energy increases dramatically to more than twice the value of the controlled polymer with no hydrophobic groups.

Two activation energies, one determined from the plateau viscosity (E_{a0}) and the other from the maximum viscosity ($E_{a,\max}$) at various salt concentrations, were determined from the viscosity data and plotted in Figure 8. The activation energy determined from the zero shear viscosity

Table I Numerical Values of the Ratio of Maximum to Zero Shear Viscosity of 1 wt % RDJ31-5 in Different Salt Concentrations and Temperatures

Salt Concentration (M)	η_{\max}/η_0 at Various Temperatures				
	10°C	15°C	20°C	25°C	30°C
0.20	1.44	1.43	1.41	1.47	1.46
0.30	1.61	1.75	1.76	1.80	1.72
0.40	3.01	2.90	2.94	2.87	2.61
0.55	4.47	4.18	3.93	3.43	3.00
0.60	4.72	4.27	3.91	3.47	2.86
0.70	4.04	3.90	3.50	3.05	2.30
1.00	3.55	3.47	3.24	2.93	—

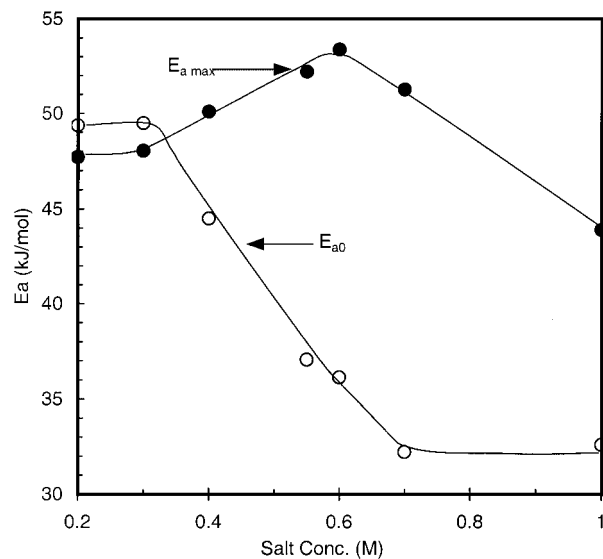


Figure 8 Dependence of activation energies determined from zero shear and maximum viscosity of 1 wt % RDJ31-5 on salt concentrations.

($E_{a,0}$) remains constant up to a C_s of $0.3M$. It then decreases continuously from a value of 49 to 32 kJ/mol at $0.7M$ NaCl and remains essentially constant thereafter. The continuous decrease in the activation energy at C_s greater than $0.3M$ is attributed to the disruption of the intermolecular associative junctions. However, at $C_s > 0.7M$ NaCl, no further disruption of the intermolecular junctions occurs. On the other hand, $E_{a,max}$ increases with salt concentrations until $0.6M$ and then decreases. The magnitude of $E_{a,max}$ is larger than $E_{a,0}$ at $C_s > 0.3M$ due to formation of a larger proportion of intermolecular junctions under moderate shear, which strengthens the network junctions. This corresponds to the higher energy required to disrupt the associative junctions. The activation energy reaches a maximum value of 54 kJ/mol at $0.6M$ NaCl, suggesting that the conversion of intra- to intermolecular junctions is at its optimum. However, at a salt concentration higher than $0.6M$, charged shielding becomes significant, causing a consequential reduction in the intermolecular junctions and, hence, a large reduction in the activation energy. Under such conditions, the destruction of active junctions becomes more significant than the creation of these junctions.

Mechanism of HASE Polymers in Salt Solutions at Various Shear Deformations

From the present study on the HASE polymer in shear flows, the addition of salt drastically alters

the rheological properties. Based on our understanding of the microstructure of the HASE polymer in solution, the evolution of the network structure with added salt during deformation is proposed. The pictorial representation of the network structure in the shear flows is summarized in Figure 9:

- (a) *Zero-shear region and without the addition of salt.* In this unperturbed condition, the HASE polymer forms a stable and extended network through the intermolecular association between hydrophobes of neighboring polymer chains. The association of the blocky ethyl acrylate also exists but is weak compared to the association between the hydrophobes.
- (b) *Zero-shear region with the addition of large amount of salt.* The addition of a moderate to a large amount of salts to the polymer system shields the ionic charges along the polymer backbones, which transforms the backbone from a stiff to a flexible chain. As a result, the polymer backbones collapse and, consequently, disrupt the hydrophobic intermolecular junctions. This condition favors the formation of intramolecular junctions at the expense of intermolecular associations.
- (c) *Low-to-moderate deformation stresses on polymer in high salt content.* When a small deformation stress is applied to the system, the balance between the creation and destruction of intermolecular associative junctions does not significantly change the amount of mechanically active junctions. Since the destruction and reformation of intra-association does not contribute to the viscosity profile, the shear viscosity is independent of the shear stress. Further increase in the shear stress causes the hydrophobic junctions to fragment. The “free” hydrophobes reassociate with hydrophobes of neighboring polymer clusters to produce more mechanically active junctions. The conversion of intra- to intermolecular associations is responsible for the shear-thickening behavior observed at moderate deformation rates.
- (d) *High deformation stresses on polymer in high salt content.* When the stress is further increased, the intermolecular junctions can no longer resist the detachment force and, consequently, the junctions frag-

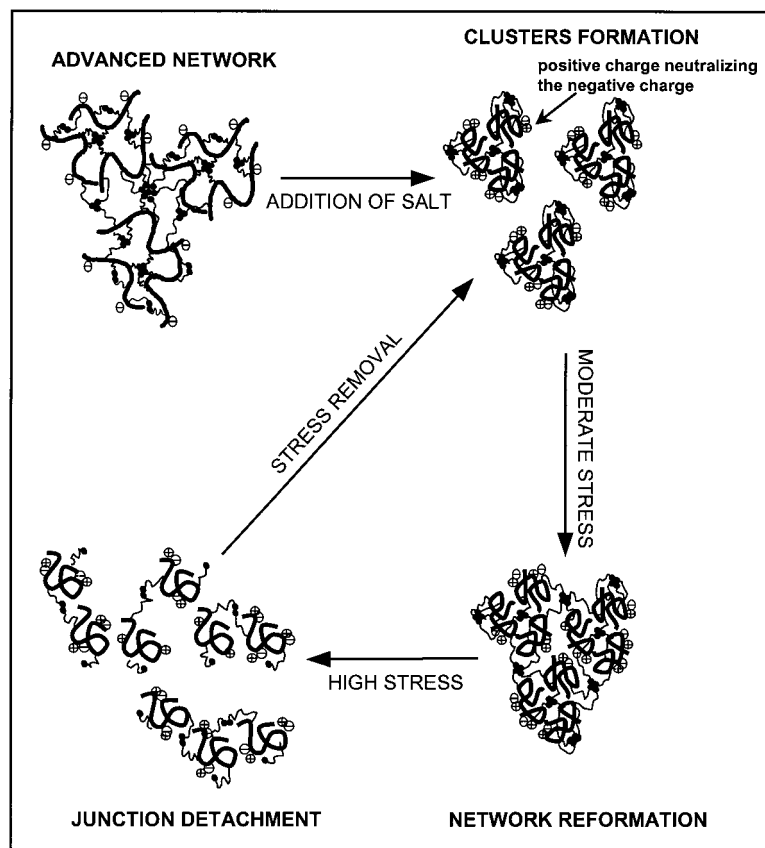


Figure 9 Pictorial representation of the network structure of HASE polymer in salt solution under the shear deformation.

ment to yield isolated clusters. When the stress is removed, the reversible process occurs where the isolated micellar clusters reassociate and the original polymer network is restored.

CONCLUSIONS

The shear viscosity profile is highly sensitive to the presence of salts. When the amount of salt is increased, the shear-thickening behavior of 1 wt % RDJ31-5 becomes more dominant. The shear-thickening behavior is attributed to the conversion of intra- to intermolecular associations, and this is reflected by the larger activation energies. A critical salt concentration of approximately $0.6M$ can be defined, where the magnitude of the ratio of maximum to zero shear viscosity reaches an optimum value and is proportional to the amount of mechanically active junctions produced in moderate shear flows. The maximum shear

viscosity shifts to higher shear rates as the temperature and salt concentrations increases. They are, however, independent of shear stresses.

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