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Viscoelastic properties of hydrophobically modified alkali-soluble emulsion in salt solutions

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Abstract

An experimental study was carried out to examine the effects of added salt on the rheology of four model hydrophobic alkali-soluble associative polymer (HASE) solutions. With increasing salt concentrations, the solution viscosities of all the model polymers decreased continuously and the viscoelastic properties of the hydrophobe-containing polymer solutions changed from predominantly elastic to viscous behavior. Model polymers with stronger hydrophobic associations were more susceptible to the presence of added salt, however such effects were weakened at high shear stresses. At a certain level of added salt, the model polymer with hydrophobes consisting of C20 alkyl chain demonstrated a unique shear-thickening behavior at high shear stresses. The critical shear stress at which the shear-thickened viscosity reached the maximum value was independent of the salt concentration, but was proportional to the polymer concentration. The shear superimposed oscillation technique was employed to probe the shear-induced structural changes of the model polymer that contributed to the shear-thickening behavior. With increasing applied shear stresses, a corresponding increase in the storage modulus (G') was observed at the shear-thickening region where the viscosity increased with applied stresses. This observation indicated that the shear-thickening behavior is caused by the formation of a larger number of network junctions. The increase in the network junction densities was attributed to the conversion of intra- to inter-molecular associations. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrophobic polyelectrolyte; Shear-thickening; Salt

1. Introduction

Associative polymers are a new class of thickeners developed in recent years to minimize the shortcomings of conventional non-associative thickeners. This class of thickener is motivated by the need to control the rheology of water-borne coating products. The current trend is to use associative polymers instead of the conventional non-associative thickeners in applications such as paints and coatings, water treatment and enhanced oil recovery. The three most popular types of commercial associative polymers are: (a) non-ionic hydrophobically modified ethylene oxide urethane (HEUR) block copolymers [1–6]; (b) hydrophobically modified hydroxyethyl cellulose (HMHEC) [7–9]; and (c) hydrophobically modified alkali-soluble emulsions (HASE) [2,5,10,11]. Although other types of associative polymers have been synthesized and studied by various researchers, they have not been introduced for commercial applications. Systems based on the polyacrylamide family have been synthesized and studied by various research groups [12–15].

The aqueous solution properties of associative polymers, in particular, the steady shear and dynamic properties, have been extensively studied over the last 10–15 years. These properties are very important in that they are directly related to the thickening efficiency of the polymers. Information obtained from such studies can be used to identify microscopic interactions that contribute to the observed thickening behavior. Such studies can also be used to analyze the effects of other constituents, such as surfactants, cosolvents, and latex particles on the overall rheological properties of the polymer systems. In addition, a detailed understanding of the relationship between the aqueous solution rheology and the molecular architecture of associative polymers provide the necessary feedback for the synthesis of better performance materials.

Previous research activities on associative polymers have largely been focused on the HEUR and HMHEC systems [16–20]. Relatively few studies have been carried out on the

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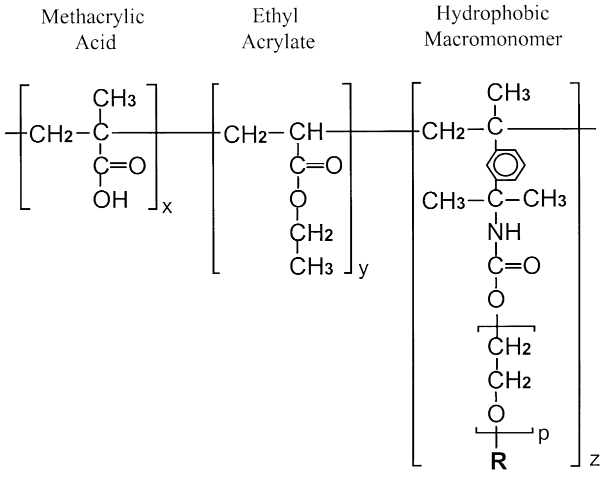

Fig. 1. Molecular structure of model HASE associative polymers.

HASE system owing to its recent introduction. Hence, there is a lack of fundamental understanding of the role of the molecular architecture of the HASE system on its rheological properties.

Associative polymers of the HASE system can be classified as hydrophobically modified anionic polyelectrolytes. When neutralized in aqueous solution with a suitable base, the latex particles are ionized as a result of the acid–base reaction. The partially neutralized polymer becomes water soluble and the polymer chains expand owing to the mutual repulsion of the negative charges along the polymer backbones. Beyond a certain polymer concentration, the hydrophobic moieties along the polymer backbones associate inter-molecularly to form a network structure. This network structure greatly increases the solution viscosity and thickens the solution significantly. As a result of these unique effects, it has become a very attractive system for many industrial applications. Being polyelectrolytes, associative polymers of the HASE system are sensitive to the salts present in the solution. The concentration of the salt in the solution has a profound effect on the network structure and hence its solution properties.

Despite the numerous publications on salt effects in polyelectrolyte systems [21–27], only a few studies have been reported for hydrophobically modified associative polymer systems. One reason is that most of the associative polymer research has been concentrated on the HEUR system, which is a non-ionic polymer. Some studies on the effect of salt on the phase behavior have also been reported [28,29]. The studies on the effects of salt on the rheology of associative polymers have largely been focused on hydrophobically modified polyacrylic acid (HMPAA) [30,31], hydrophobically modified partially hydrolyzed polyacrylamide (HMPAM) [32,33] and hydrophobically modified cellulose (HMHEC) [8]. In the study on modified polyacrylic acid, Wang et al. [30] observed that the addition of salt at the appropriate level can enhance the viscosity of C18 modified PAA as a result of conformational changes and enhanced inter-chain aggregation owing to hydrophobic interactions. A later study by the same group indicated that intra-chain aggregation occurred in the dilute solution regime, resulting in a decrease in the viscosity. Upon the addition of NaCl, the polymer exhibited a transition from a non-aggregated coil to an aggregated one. The transition occurred above a critical salt concentration which was dependent on the length and content of the hydrophobic alkyl groups. The intrinsic viscosity studies on the model HASE polymers in NaCl solutions have shown that the addition of salt tended to increase the Huggins coefficient as the polymers became less soluble and the solvent quality was reduced and thus more intramolecular associations were promoted [15,32,34]. In contrast, the stiffness of the polymer backbone tended to decrease as a result of charged shielding effects and this enhanced the intra-molecular associations of the hydrophobes.

In the present article, an experimental study was conducted to examine the salt effects on a novel series of model associative polymers of the HASE type developed by Union Carbide. The steady shear viscosity and dynamic shear viscoelastic properties were measured for the model polymers in different amounts of salt. In addition, the shear super-imposed oscillation technique was used to probe the structural changes of the network under various stress or shear conditions.

2. Materials

The four model HASE emulsion polymers designated RDJ31-1, RDJ31-2, RDJ31-4, and RDJ31-5, respectively, were emulsion copolymerization products of methacrylic acid (MAA), ethyl acrylate (EA), and a macromonomer

Table 1
Characteristics of model HASE associative polymers

Polymer name	Hydrophobe name	Calculated macro. M_n	GPC M_n/M_w for macro.	Mole composition MAA/EA/ Macro.
RDJ31-1	None			49/51/0
RDJ31-2	Octyl	1765	1884/1936	49/50/1
RDJ31-4	Hexadecyl	1962	2197/2257	49/50/1
RDJ31-5	Eicosanyl	2036	2023/2077	49/50/1

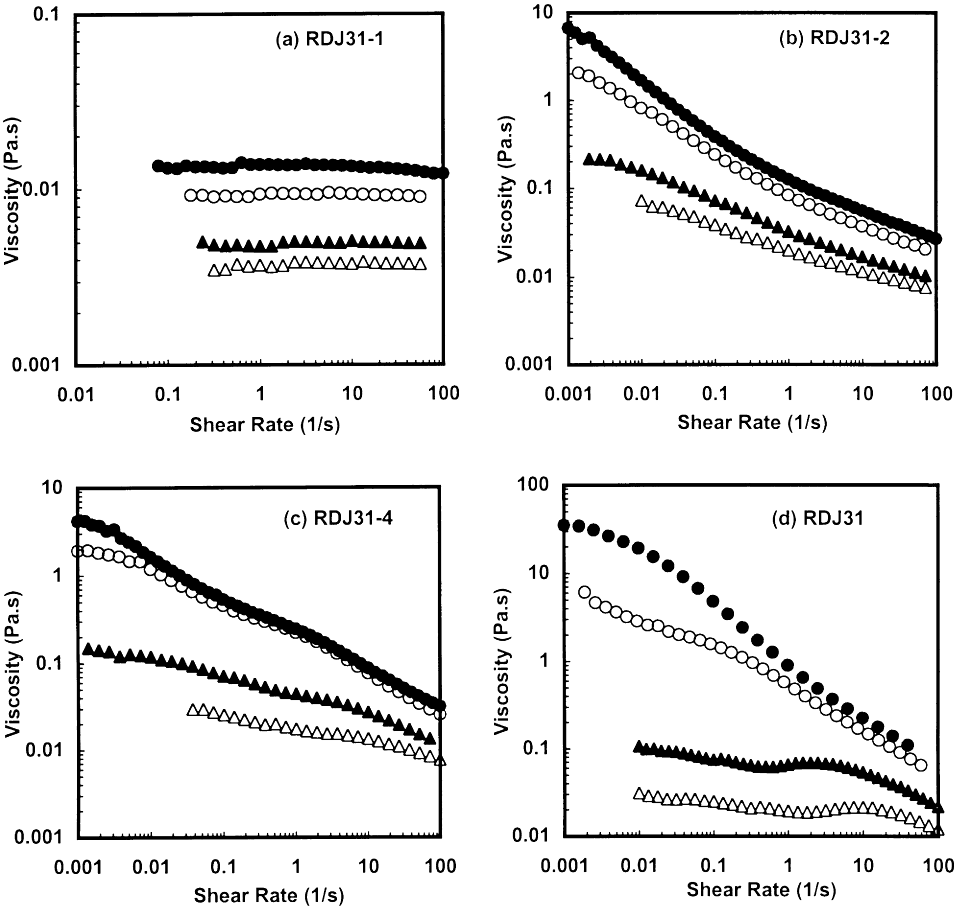

Fig. 2. Salt effect on steady shear viscosity of 0.5 wt.%: (a) RDJ31-1; (b) 31-2; (c) 31-4; and (d) 31-5 solutions in 0 M NaCl (●); 0.01 M NaCl (○); 0.05 M NaCl (▲); 0.1 M NaCl (△).

that had been capped with a hydrophobic group. These model polymers differed from each other only in the length of their hydrophobes. The hydrophobes of RDJ31-2, RDJ31-4, and RDJ31-5 are octyl (C_8H_{17}), hexadecyl ($C_{16}H_{33}$), and eicosanyl ($C_{20}H_{41}$), respectively. RDJ31-1 had no macromonomer and acts as the control. The hydrophobes were ethoxylated with ethylene oxide to approximately 35 mol. Fig. 1 shows the molecular structure of these polymers, where R represents the hydrophobe, the number of ethoxylation $p = 35$, the molar composition ratio $x/y/z$ for MAA/EA/macromonomer is 49/50/1 for RDJ31-2, RDJ31-4 and RDJ31-5, and 49/51/0 for RDJ31-1. It is believed that MAA, EA, and the macromonomer are randomly distributed along the polymer backbones. A brief description of the synthesis route of the model polymers has been previously reported [35,36] and will not be presented here. The characteristics of the model polymers are given in Table 1.

The exact molecular weight of the model polymers is still unknown, but they are believed to be quite similar, as the process used to synthesize the polymers was identical. Based on the intrinsic viscosity study of these polymers in 0.01 and 0.1 M NaCl solution, the molecular weight of the polymers was estimated to be in the range of 170 000–190 000 Da. Hence the average number of hydrophobes on each polymer chain is estimated to be 16–18. The intrinsic viscosity of RDJ31-1 in 0.1 M NaCl was found to be 3.3 dl/g [34], hence at 0.5 wt.%, $c[\eta] = 1.65$, which suggests that the polymer solutions are in the semi-dilute region.

3. Experiments

These model HASE polymers were dialyzed in deionized distilled water for one month using the regenerated cellulose tubular membrane. The water was replaced twice every week. After this treatment, stock solutions were prepared at a concentration of 5.0 wt.% in 10^{-4} M KCl solution. The stock solutions were kept in the refrigerator at 5°C. Various samples of 0.5 wt.% polymer in 0–0.1 M NaCl were prepared by diluting the stock solution with an appropriate amount of sodium chloride solution. Solutions of the RDJ31-5 polymer at 0.5, 1.0 and 2.0 wt.% in NaCl concentrations up to 2 M were prepared for the shear superimposed oscillation experiments. All of the polymer solutions were neutralized to a pH in the range from 8.5 to 9.0. Preliminary experiments have shown that the model

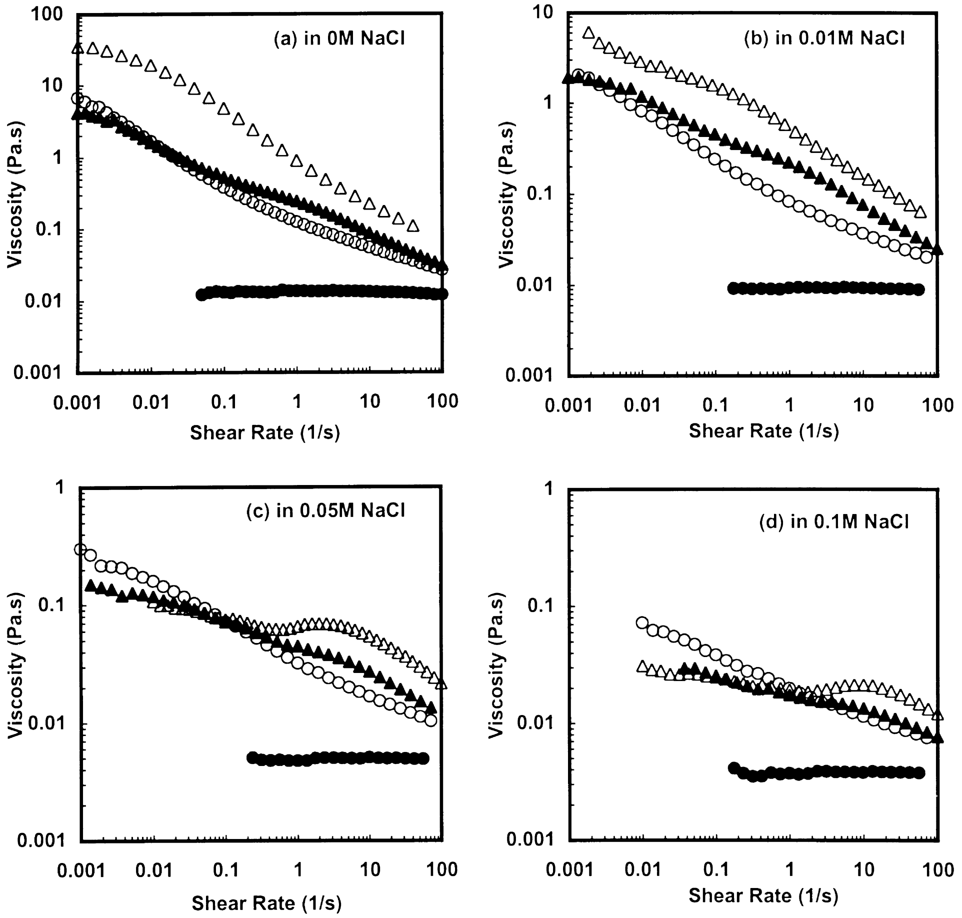

Fig. 3. Steady shear viscosity of 0.5 wt.% model HASE polymer in (a) 0 M; (b) 0.01 M; (c) 0.05 M; and (d) 0.1 M NaCl solutions: RDJ31-1 (●); RDJ31-2 (○); RDJ31-4 (▲); RDJ31-5 (△).

associative polymers developed a full thickening efficiency and maintained constant rheological properties within the pH range of 8–11.5.

Experiments for the present study were carried out using the Contraves LS40 controlled rate rheometer fitted with the MS 41S/1S concentric cylinder measuring system consisting of a cup with a diameter of 12 mm and a bob with a diameter of 11 mm and length of 8 mm. The Carri-Med CSL500 controlled stress rheometer was also used for more viscous solutions and also to conduct shear superimposed oscillation experiments. A 4 cm, 2° cone and plate and a double concentric cylinder measuring system were used. A detailed description of this technique has been described in our previous publication [36]. All of the experiments were carried out at a temperature of 25 ± 0.1°C.

4. Results and discussion

4.1. Steady shear and dynamic properties

Fig. 2 shows the effects of varying NaCl concentrations on the steady shear viscosity of the 0.5 wt.% model polymer solutions. It can be seen that the RDJ31-1 solution exhibited a Newtonian behavior at all salt levels. RDJ31-1 does not contain hydrophobes on its polymer backbone and the Newtonian viscosity profile is largely the results of hydrodynamic volume effects of the polymer chains. There may be some possible chain entanglement as the viscosity data of the 0 M NaCl exhibited a slight shear-thinning behavior at high shear rates, as can be observed in Fig. 2(a). Unlike the RDJ31-1 solution, solutions of the hydrophobe-containing polymers demonstrated an obvious shear-thinning behavior. As the molecular weight of the four model associative polymers are fairly similar (estimated from intrinsic viscosity data), the difference in the rheology profiles between RDJ31-2, 31-4, 31-5 and RDJ31-1 can be attributed to the presence of a network structure. These network structures were continuously being disrupted at higher and higher shear rates or stresses, resulting in a reduction in the viscosity of the solution.

It could clearly be seen from Fig. 2 that the viscosity of all the polymer solutions decreased when the salt concentration was increased. The viscosity reduction of the RDJ31-1 solution was in line with the typical behavior of polyelectrolyte

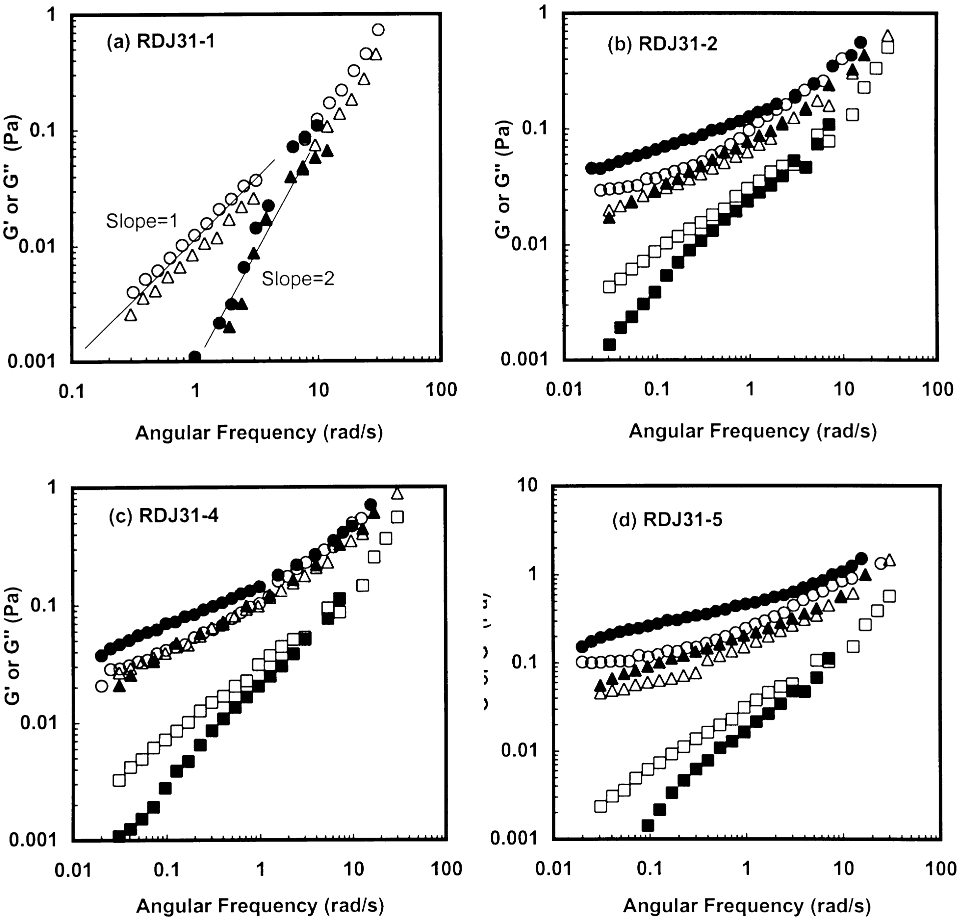

Fig. 4. Salt effect on dynamic shear moduli of 0.5 wt.% (a) RDJ31-1; (b) 31-2; (c) 31-4; and (d) 31-5 solutions in 0 M NaCl (●○); 0.01 M NaCl (▲ △); 0.05 M NaCl (■□) (filled = G'; open = G'').

solutions. The most common and widely accepted interpretation [37] for this behavior is based on conformational changes of the polymer coils. With an increase in salt content, the intra-macro-ion electrostatic repulsion becomes shielded, causing the polyion chains to shrink, resulting in a reduction in the hydrodynamic volume. It has been observed from intrinsic viscosity measurement that the molecular coil size of the model polymers decreased with increasing salt level in the solution [31,34]. The viscosity reduction of the RDJ31-1 solution is hence the result of a decrease in the hydrodynamic volume. The shrinkage of the polymer backbones also reduced the probability of molecular entanglement and this to a certain degree, caused the solution viscosity to decrease.

Besides reducing the hydrodynamic volume, the shrinkage of the polymer backbones rendered it easier for the hydrophobes of the other three model polymers to form intra-molecular associations. As a result, the junction density of inter-molecular networks decreased and accordingly, the network structure became weaker. The number of intra-molecular hydrophobic junctions increased at the expense of inter-molecular associations when the salt level was increased. In addition to the reduction of the hydrodynamic volume, the weakening of the network structure also accounted for the drastic drop in the solution viscosity of the hydrophobe-containing polymers.

Fig. 3 shows a comparison of the solution viscosity of the model polymers at each salt level. For the hydrophobe-containing polymers, it could be seen that when the salt level was increased from 0 to 0.1 M, the viscosity reduction of the RDJ31-5 solution (unfilled triangle) at low shear rates showed the largest drop, from being the highest (Fig. 3(a)) to being the lowest (Fig. 3(d)) among the three polymers, while the viscosity reduction of the RDJ31-2 solution (unfilled circle) showed the lowest reduction, from being almost equal to (Fig. 3(a)) that of the RDJ31-4 solution to being the highest (Fig. 3(d)). This phenomenon can be explained as follows: For the polymer solutions with no salt, the carboxylate repulsion caused the polymer backbones to open and expand to the maximum degree. The density of inter-molecular hydrophobic junctions was at its optimum. As the hydrophobes of the RDJ31-5 polymer contained more carbon atoms, the clusters formed by the hydrophobes were stronger than that of the other model polymers (i.e., RDJ31-2 and 31-4). This suggests that the network structure of the RDJ31-5 solution was the strongest,

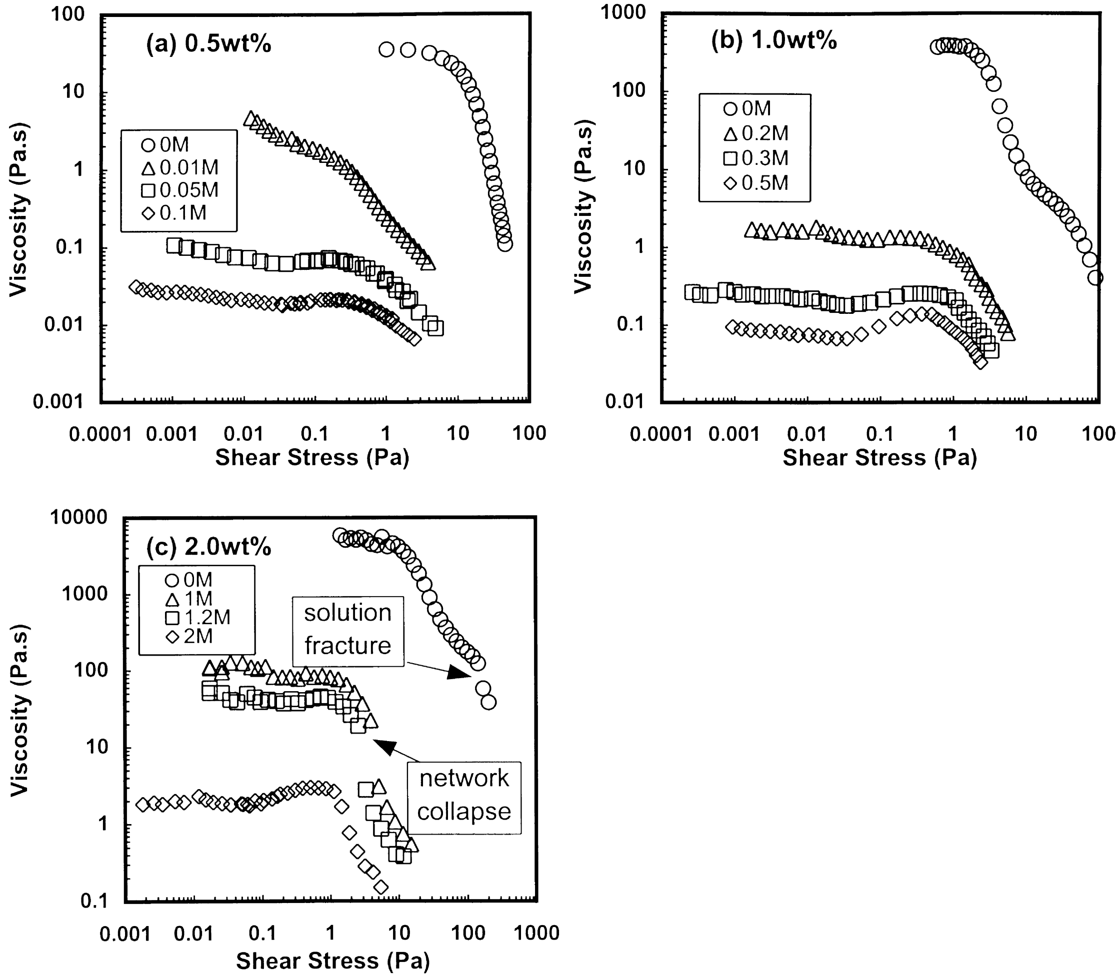

Fig. 5. Effects of NaCl concentrations on the viscosity of (a) 0.5 wt.%; (b) 1.0 wt.%; (c) 2.0 wt.% RDJ31-5 solutions.

giving rise to the highest viscosity. When the salt content was increased, the polymer backbones shrank more, resulting in the destruction of the inter-molecular hydrophobic junctions which led to the formation of a larger number of intra-molecular junctions. As a result of the difference in the bonding strength of hydrophobes, the RDJ31-5 solution experienced the maximum change in the inter- and intra-molecular junction densities. Hence the viscosity reduction of the RDJ31-5 solution was significantly larger than that of the other polymers.

At high shear rates, the model polymer solutions did not exhibit a significant difference in their viscosity profiles. However, shear-thickening behavior was observed for RDJ31-5 at salt concentrations greater than 0.05 M. This suggests that at high shear rates, some structural changes in the polymer network must have occurred as a result of the presence of salt in the polymer solution when subjected to a high deformation flow field. The imposition of applied shear stress on the polymer solution disrupted the network structure, which caused the polymer solutions to exhibit a shear-thinning behavior. However, the applied shear stress had an opposite effect to that of added salts; i.e., it opened and expanded the coiled polymer backbones. As observed from Fig. 2, the viscosity of the RDJ31-5 solution at $\dot{\gamma} = 0.01\ \mathrm{s}^{-1}$ decreased by three orders of magnitude while it decreased by less than one order of magnitude at higher shear rate, $\dot{\gamma} = 50\ \mathrm{s}^{-1}$. Thus the effects of salt on the network structure was greatly reduced at high shear rates. The combined effects of added salt and applied shear stress was to shift the property of the polymer solution to a viscosity profile with a lower viscosity and shear-thinning characteristics. However, the applied shear stress, had negligible effects on the polymer backbones of the RDJ31-1 solution, as this solution exhibited Newtonian behavior at all salt concentrations. The observed shear-thickening behavior of the RDJ31-5 solution at high shear rates was interesting and will be discussed in detail in Section 4.2. Similar behavior had been reported for non-associating systems such as hydrolyzed polyacrylamide in salt/glycerol solutions [23,38,39], polystyrene in toulene [40] and polyethyleneoxide at very high shear rates as measured in a capillary viscometer [41].

The dynamic shear moduli of the model polymer solutions are shown in Fig. 4. The experiments were carried out within the linear viscoelastic region. For the RDJ31-1 solution (Fig. 4(a)), it was observed that the storage modulus $G'(\omega)$ had a slope of 2 and the loss modulus $G''(\omega)$ a slope of 1 at low frequencies. It was also noted that $G''(\omega)$ was higher than $G'(\omega)$. This type of properties is typical of solutions that exhibit a dominant viscous behavior.

Fig. 4(b)–(d) shows the viscoelastic properties of the hydrophobe-containing polymer solutions. It was observed that for these polymer solutions in a salt free environment, the elastic property was more dominant than the viscous property i.e., G' was greater than G''. This suggests that there was a significant buildup of network structure that was responsible for imparting a significant elasticity to the polymer solutions. However, when the salt level was increased, the storage modulus $G'(\omega)$ decreased faster than the loss modulus $G''(\omega)$, leading to a situation where at a salt level of 0.05 M, the storage modulus $G'(\omega)$ became lower than the loss modulus $G''(\omega)$. This meant that when the salt level was increased, the viscoelastic properties of the hydrophobe-containing polymer solutions changed from a pseudo-gel like behavior to one representing more of a viscoelastic solution. Such changes may be attributed to the collapse of the network structure, caused by the shrinkage of the polymer backbones owing to the shielding effects of the positive sodium ions.

4.2. Shear-thickening behavior of RDJ31-5 solutions

In this section, the shear-thickening behavior of RDJ31-5 solutions under the influence of added salt will be discussed. The focus of the discussion will be on the mechanism that causes the observed thickening property of some of the RDJ31-5 solutions.

Fig. 5 shows the dependence of viscosity on shear stress of 0.5, 1.0 and 2.0 wt.% RDJ31-5 solutions in salt concentrations ranging from 0 to 2.0 M. In all the three polymer concentrations, the shear-thickening phenomenon was observed at moderate to high salt levels. The amount of salts required to effect a shear-thickening behavior increases with polymer concentration. As previously discussed, the added salt tended to shrink the polymer backbones, while the applied shear stress reduced this effect by expanding the polymer backbones through the deformation of the network structure. At moderate to high level of salts, the backbone shrinkage led to the reduction in the density of inter-molecular hydrophobic junctions, which weakened the network structure. When the shear stress was increased further, the deformation of the network structure caused the polymer backbones to uncoil. The process of uncoiling the polymer backbone by the applied stress results in the destruction of some intra-molecular and inter-molecular associations. At the same time, the "free" hydrophobes are able to re-associate to form new inter-molecular junctions. If the net number of inter-molecular junctions increased with increasing shear stress, then the network structure will be strengthened and the viscosity will increase. However, the polymer backbones cannot expand infinitely, a limit will be reached when a significant number of inter-molecular junctions will be destroyed. This corresponds to the large decrease in the viscosity beyond the optimum viscosity values. The concept of the intra- to inter-molecular network formations is only a conjecture at the present moment and further experimental evidence will be presented in the discussion on super-imposed oscillation on shear studies. An assumption implicit in invoking the conversion of intra- to inter-molecular associations is that an increase in the association junction density is the only explanation for the shear-thickening behavior. However, as polymer chains are stretched to large extensions, the relationship between force and strain can become non-linear [42]. This non-linear behavior of the polymer chains which undergo large deformations may be responsible for the shear-thickening properties observed.

It can be noted from Fig. 5 that the critical shear stress at which the solution exhibited the maximum viscosity was almost independent of the salt level but slightly dependent on the polymer concentration. The higher the polymer concentration, the higher the critical shear stress. This implied that the critical shear stress might be directly related to the number of polymer backbones per unit volume of the solution. It appeared that the rheological properties of the model polymers were shear stress controlled rather than shear rate controlled.

As observed in Fig. 5, shear-thickening did not occur at low salt levels. At these low levels of salt, the polymer chains existed in their expanded form and were generally stiffer. The network formed by the hydrophobic junctions was predominantly inter-molecular which was responsible for the high viscosity and elasticity. One would speculate that the ratio of intra- to inter-molecular junctions was low and hence the probability of a conversion of intra- to inter-molecular junctions would be low, which accounted for the absence of shear-thickening behavior at low salt levels.

An obvious question that arose from the previous discussion was, "why did the RDJ31-5 solution exhibit a shear-thickening phenomenon, while the other polymer solutions did not?" Comparing the macromonomers of the three model polymer systems (RDJ31-5, 31-4 and 31-2), it was clear that RDJ31-5 contained the most hydrophobic macromonomer as the hydrophobe had 20 carbon atoms compared with 16 and eight for the other two model systems. As previously discussed, the most likely reason for the shear-thickening behavior was the conversion of intra- to inter-molecular associations, resulting in an increase in the association junction density. This is naturally a function of the hydrophobicity of the macromonomer. Similarly, invoking the concept that the non-linear deformation of the polymer chains could cause shear-thickening behavior, it was expected that junctions formed by the C20 hydrophobes were strong enough to support the stress before rupturing. Hence, one should expect to see shear-thickening in the C20 hydrophobe and not the C16 or C8 hydrophobes as the network junctions formed with these "shorter" hydrophobes

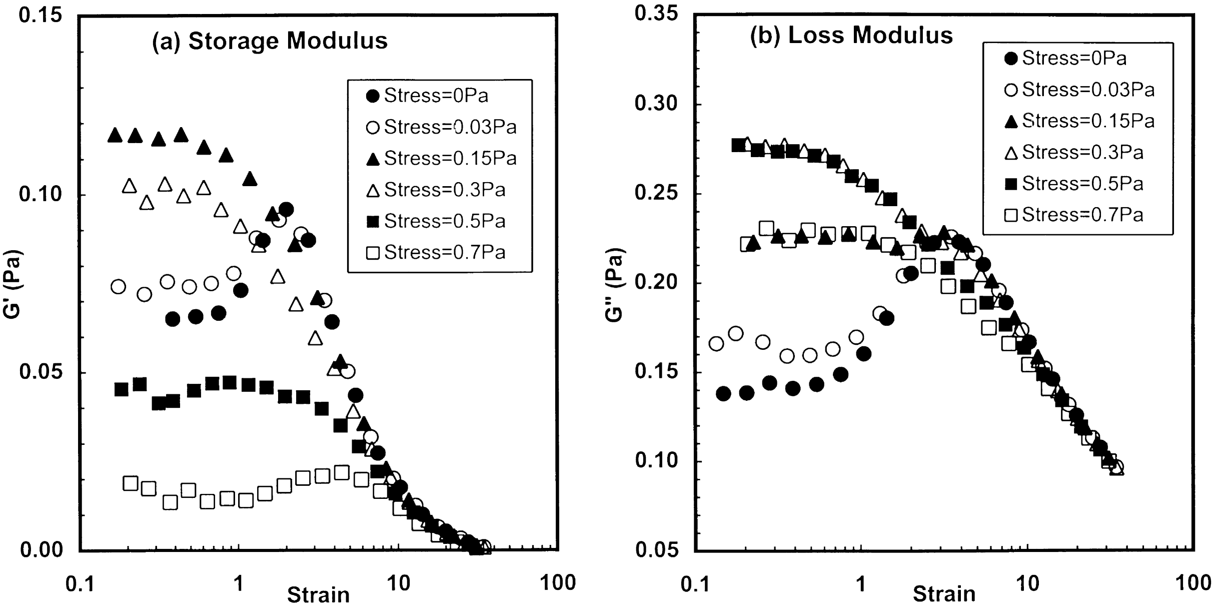

Fig. 6. (a) Storage and (b) loss moduli vs. strain at 1 Hz of 0.5 wt.% RDJ31-5 solution in 0.05 M NaCl solution at varying applied stresses.

would rupture at a smaller extension and hence did not experience a non-linear deformation.

It was observed that the 2.0 wt.% RDJ31-5 solution in 0 M NaCl fractured when shear stress was increased to about 140 Pa (Fig. 5(c)). This behavior could clearly be observed during the testing where the fluid became unstable and fractured at the edge of the cone and plate geometry. The output signals (strain in this case) became fairly erratic. Fracture occurred as the test solution was very viscous and to some extent "solid like" and hence could not be subjected to large deformations. However, a sample fracture was not observed for the solution in 1 or 1.2 M NaCl solutions, where a large drop in viscosity occurred at a shear stress of between 2–5 Pa. This behavior was usually attributed to a sudden collapse of the network structure at the critical shear stress. Aubry and Moan [43] also observed such a discontinuity for their hydrophobically modified (hydroxypropyl) guar polymer system. The discontinuity in the viscosity curve for their polymer system appeared almost at the same shear rate over a wide range of solution concentrations. They interpreted this discontinuity to be the result of "total destruction of the hydrophobic junctions network which had no time to reform when the applied stress was maintained at a certain level". The phrase "had no time to

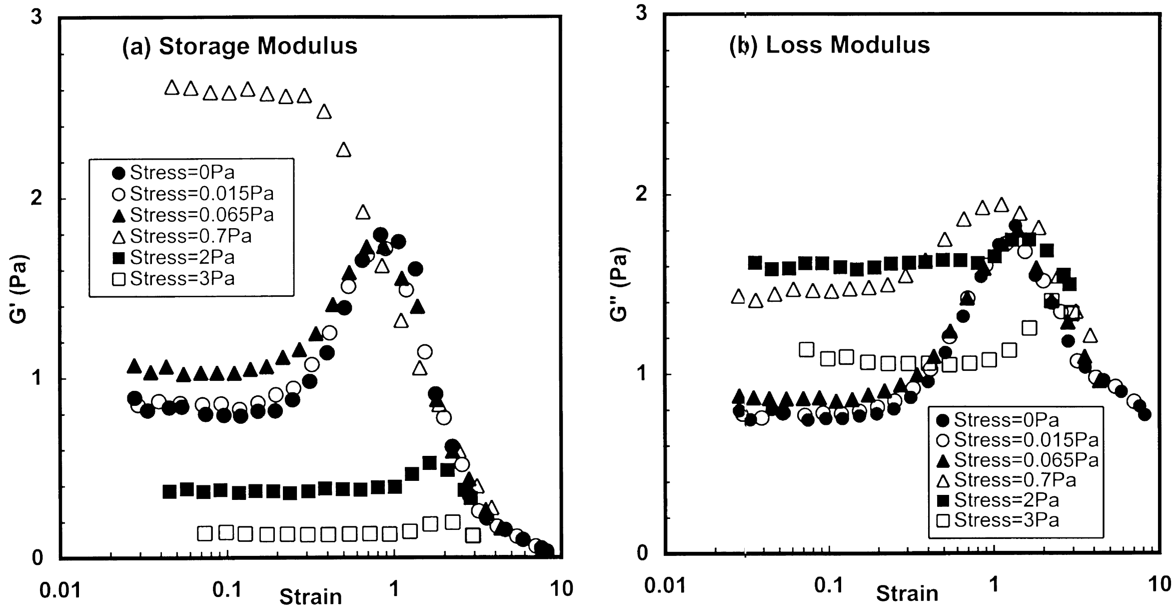

Fig. 7. (a) Storage and (b) loss moduli vs. strain at 1 Hz of 2.0 wt.% RDJ31-5 solution in 2.0 M NaCl solution at varying applied stresses.

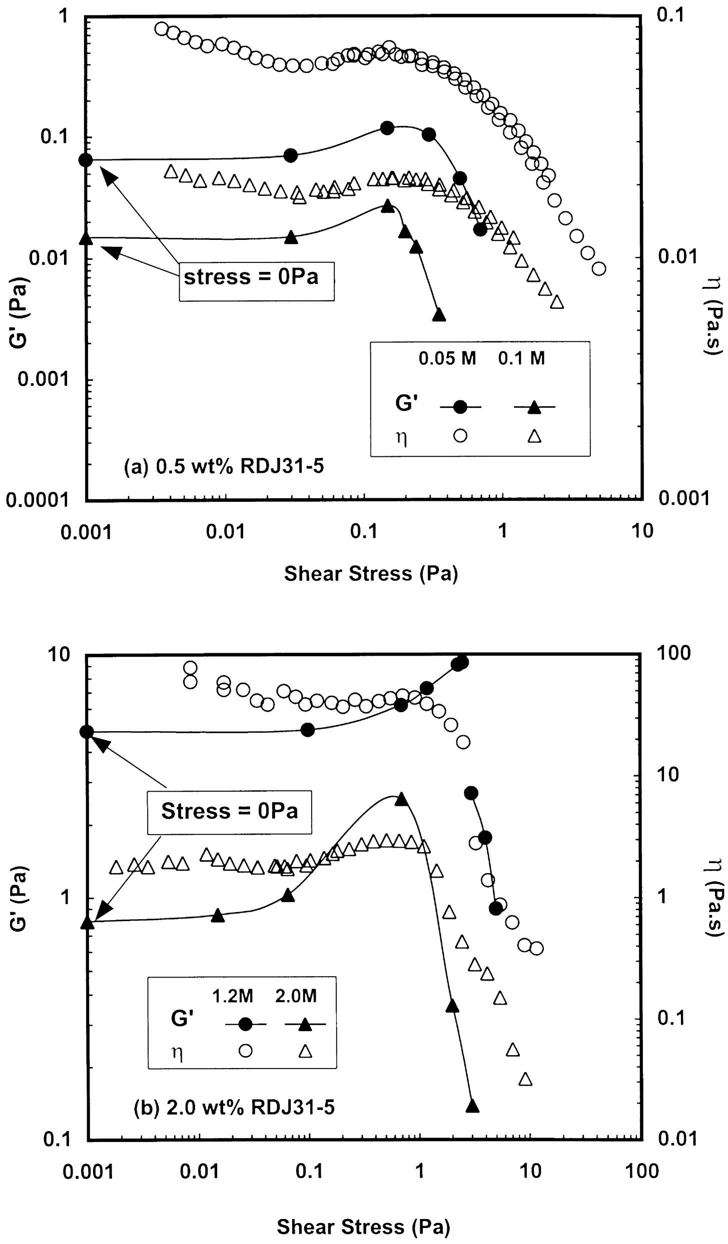

Fig. 8. Comparison between storage modulus obtained from super-imposed oscillation test with steady shear viscosity of (a) 0.5 wt.% RDJ31-5 in 0.05 and 0.1 M NaCl solutions; (b) 2.0 wt.% RDJ31-5 in 1.2 and 2.0 M NaCl solutions.

reform" has the meaning that the rate of deformation is too quick for the junctions to rebuild. Their arguments do not seem to be applicable to our system. Firstly, the discontinuity in our viscosity curve only occurred within a very narrow concentration range. Secondly, the discontinuity in the viscosity curve at different salt levels (including the level of 0 M) did not occur at the same shear rate.

4.3. Viscoelastic strain sweep behavior

Figs. 6 and 7 show the results of the oscillation strain sweep test at various applied stresses of 0.5 wt.% RDJ31-5 in 0.05 M NaCl and 2.0 wt.% in 2.0 M NaCl solutions respectively. These solutions exhibited shear-thickening behavior. The tests were performed at a moderate frequency of 1 Hz (6.28 rad/s). A number of observations can be made from the results.

1. At low applied stresses, strain-thickening was observed in both the storage and loss modulus. A linear region occurred at strains of less than 1, and 0.2 for the 0.5 and 2.0 wt.% RDJ31-5 solutions respectively.
2. The strain thickening vanished over the range where the applied stresses yield a shear thickened viscosity in the steady shear viscosity curves.
3. At stresses greater that the stress where the optimum

viscosity was observed, the storage modulus at the linear viscoelastic region decreased sharply to values below that at zero applied stress. However, the magnitude of the loss modulus was greater than that at zero applied stress. It was observed that at high strains, the data at all the various applied stresses collapsed onto a single curve.

From these figures it can be seen that with increasing levels of imposed shear stress, the linear viscoelastic moduli (G' and G'') increased initially and then decreased again. The imposed shear stress at which the storage modulus G' achieved a maximum value corresponded to the stress at the maximum viscosity observed in the steady shear viscosity data. As can be observed from the results in Fig. 8 for 0.5 and 2.0 wt.% RDJ31-5 solutions respectively, the storage modulus data followed the same trend as that of the steady shear viscosity. The storage modulus at a moderate frequency can be used to provide an indication of the network junction density based on the Green–Tobolsky relationship [44] ($G_0 = \nu kT$), where ν is the network junction density. Hence the results shown in Fig. 8 suggested that at the onset of the shear-thickening observed in the steady shear test, the increase in the viscosity corresponded to an increase in the network junction density. One would then ask, “Where did this additional junction density come from?” The main source of the increase in the junction density must have come from the conversion of intra- to inter-molecular associations. As the applied stress was increased, the polymer backbone of a coiled chain at high salt concentrations deformed first. Such an unfolding of the backbone caused the intra-molecular bonds to break, making available more “free” hydrophobes which could then form inter-molecular junctions with other hydrophobes in the system. The net result was an apparent increase in the network junction density as the results suggested. It is important to note that the moduli data plotted in Fig. 8 were obtained from the linear viscoelastic region. Hence, the increase in the network junction density was not a consequence of the non-linear deformations. It could be concluded that the most likely cause for the shear-thickening in our system of HASE polymers in high salt concentrations was a result of the conversion of intra- to inter-molecular junctions and not owing to the non-linear deformation.

5. Conclusions

The presence of a simple salt strongly influenced the rheological properties of the model associative polymers in semi-dilute to concentrated solutions. With increasing salt concentration, the solution viscosity of all the model polymers decreased progressively, and the viscoelastic properties of the hydrophobe-containing polymer solutions changed from predominantly elastic to viscous behavior. The variation of the rheological properties was attributed to the shrinkage of the polymer backbones and the breaking down of the network structure. For model polymers with stronger hydrophobic associations, the influence of the added salt was more profound. The effects of added salt, however, were weakened at high shear stresses because of the disruptive effects of the imposed shear stress. The combined effect of added salt and imposed shear stress led to a tendency of the viscosity curve to exhibit a Newtonian behavior. At a certain level of added salt, the model polymer with the strongest hydrophobic associations, namely the RDJY31-5 polymer, demonstrated a unique shear-thickening behavior at high shear stresses. The critical shear stress at which the thickened viscosity reached the maximum was independent of the salt concentration, but was proportional to the polymer concentration.

The super-imposed oscillation on steady shear flow technique provided additional information on the specific shear-induced network structural change of the salt containing RDJY31-5 solutions. With increasing level of imposed shear stress, an initial rise and subsequent drop was observed for the linear dynamic shear moduli G' and G'' at 1 Hz in the strain sweep tests. The same corresponding trend, according to the increase of applied shear stress, was observed for the storage modulus and the steady shear viscosity. The maximum of the storage modulus and viscosity occurred at the same applied stress. The shear-thickening observed in RDJ31-5 in salt solutions was attributed to the conversion of intra- to inter-molecular junctions under shear or stress.

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References

[1] Glass JE, Fernando RH, England-Jongewaard SK, Brown RG. J Oil Colors Chemists Assoc 1984;67:256.

[2] Schaller EJ. Surf Coatings Aust 1985;22:6.

[3] Glass JE. In: Glass JE, editor. Water soluble polymers: beauty with performance. Advances in chemical series, vol. 213. Washington DC: American Chemical Society, 1986. p. 375.

[4] Schwab FG. In: Glass JE, editor. Advances in chemical series, vol. 213. Washington, DC: American Chemical Society, 1986. p. 369.

[5] Thibeault JC, Sperry PR, Schaller EJ. In: Glass JE, editor. Water soluble polymers: beauty with performance. Advances in chemical series, vol. 213. Washington DC: American Chemical Society, 1986. p. 375.

[6] Karunasena A, Brown RG, Glass JE. In: Glass JE, editor. Polymers in aqueous media: performance through association. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 495.

[7] Gelman RA, Barth HG. In: Glass JE, editor. Water soluble polymers: beauty with performance. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1986. p. 101.

[8] Goodwin JW, Hughes RW, Lam CK, Miles JA, Warren BCH. In: Glass JE, editor. Polymers in aqueous media: performance through

association. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 365.
[9] Sau AC, Landoll LM. In: Glass JE, editor. Polymers in aqueous media: performance through association. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 343.
[10] LeSota S, Lewandowski EW, Schaller EJ. Polymers in aqueous media: performance through association. In: Glass JE, editor. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 543.
[11] Shay GD. Polymers in aqueous media: performance through association. In: Glass JE, editor. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 543.
[12] Kramer MC, Stefer JR, Hu Y, McCormick CL. Macromolecules 1996;29:1992.
[13] Selb J, Biggs S, Renoux D, Candau F. In: Glass JE, editor. Hydrophilic polymers: performance with environmental acceptability. Advances in chemical series, vol. 248. Washington DC: American Chemical Society, 1996. p. 251.
[14] Volpert E, Selb J, Candau F. Macromolecules 1996;29:1452.
[15] Volpert E, Selb J, Candau F. Polymer 1998;39:1025.
[16] Jenkins RD. The fundamental thickening mechanism of associative polymers in latex systems: a rheological study. PhD Thesis. Bethlehem, PA: Lehigh University, 1991.
[17] Lundberg DJ, Glass JE, Eley RR. J Rheol 1991;35:1255.
[18] Richey B, Kirk AB, Eisenhart EK, Fitzwater S, Hook J. J Coat Technol 1991;63:31.
[19] Annable T, Buscall R, Ettelaie R, Whittlestone D. J Rheol 1993;37:695.
[20] Hulden M. Colloids and Surf A: Physicochem and Eng Aspects 1994;82:263.
[21] Durst F, Haas R, Kaczmar BU. J Appl Polym Sci 1981;26:3125.
[22] Rochefort WE, Middleman SM. J Rheol 1987;31:337.
[23] Ait-Kadi A, Carreau PJ, Chauveteau G. J Rheol 1987;31:537.
[24] Yamaguchi M, Wakutsu M, Takahashi Y, Noda I. Macromolecules 1992;25:470.
[25] Tam KC, Tiu C. Colloid Polym Sci 1990;268:911.
[26] Tam KC, Tiu C. J Non-Newt Fluid Mech 1993;46:275.
[27] Tam KC, Tiu C. Colloid Polym Sci 1994;272:5161.
[28] Nwankwo I, Xia DW, Smid J. J Polym Sci Part B: Polym Phys 1988;26:581.
[29] Zhou G, Chen X, Smid J. In: Glass JE, editor. Hydrophilic polymers: performance with environmental acceptability. Advances in chemical series, vol. 248. Washington DC: American Chemical Society, 1996. p. 31.
[30] Wang TK, Iliopoulos I, Audebert R. In: Shalaby SW, McCormick CL, Butler GB, editors. Water-soluble polymers: synthesis, solution properties and applications. ACS symposium series, vol. 467. Washington DC: American Chemical Society, 1991. p. 218.
[31] Magny B, Iliopoulos I, Audebert R. In: Dubin P, Bock J, Davis R, Schulz DN, Thies C, editors. Macromolecular complexes in chemistry and biology, Berlin: Springer-Verlag, 1994. p. 51.
[32] Bock J, Siano DB, Valint PL, Pace CJ. Polymers in aqueous media: performance through association. In: Glass JE, editor. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 411.
[33] McCormick CL, Johnson CB. Polymers in aqueous media: performance through association. In: Glass JE, editor. Advances in chemical series, vol. 223. Washington DC: American Chemical Society, 1989. p. 437.
[34] Guo L, Tam KC, Jenkins RD. Macromol Chem Phys 1998;199:1175.
[35] Jenkins RD, DeLong LM, Basset DR. In: Glass JE, editor. Hydrophilic polymers: performance with environmental acceptability. Advances in chemical series, vol. 248. Washington DC: American Chemical Society, 1996. p. 425.
[36] Tirtaatmadja V, Tam KC, Jenkins RD. Macromolecules 1997;30: 3271.
[37] Basu S, Gupta PCD. J Colloid Sci 1952;7:53.
[38] Choplin L, Sabatie J. Rheolog Acta 1986;25:570.
[39] Bradna P, Quadrat O, Dupuis D. Colloid Polym Sci 1995;273:642.
[40] Georgelos PN, Torkelson JM. Rheolog Acta 1988;27:369.
[41] Vrahopoulou V, McHugh AJ. J Non-Newt Fluids Mech 1987;25:157.
[42] Schultz JM. The mechanics of amorphous polymers, ch. 7. Polymer Materials Science. Englewood, New Jersey: Prentice-Hall, 1974.
[43] Aubry T, Moan M. J Rheol 1994;38:1681.
[44] Green MS, Tobolsky AV. J Chem Phys 1946;14:80.