Rheological Behavior of Ph-Responsive Associating Ionic Polymers of Diallyammonium Salts and Sulfur Dioxide

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ABSTRACT: In this study, the viscoelastic behavior of hydrophobically modified polyelectrolytes obtained from the hydrolysis of cationic acid salts (CAS's) as a function of their zwitterion fraction (x) and anion fraction (z) was studied. The dynamic viscosity (η') dependence on frequency of polymer solutions of polybetaine/anionic polyelectrolyte (APE) with various compositions of x and z in $0.1N$ NaCl showed typical shear thinning behavior. η' of a solution of CAS **4** (M_2-4 (4 mol % hydrophobe)) attained a maximum value in the presence of 1.67 equiv of NaOH (corresponding to an $x : z$ ratio of 33 : 67) and decreased with any further addition of NaOH. We suggest this maximum to be a result of a combined effect of coil expansion and hydrophobic association. The influence of the temperature and concentration on η' of CAS **4** (M_2-4) treated with 1.67 equiv of NaOH was also investigated. The rheology of CAS **4** (M_2-4) samples treated with 1.67, 1.81, and 2.0 equiv of NaOH suggested a reversible network. However, for APE **7** (M_2-5 (5 mol % hydrophobe)), elastic behavior was dominant, and the formation of highly interconnected three-dimensional networks was suggested. At lower $x : z$ ratios, the effect of coil expansion due to a higher APE fraction was more than counterbalanced by the lower degree of intermolecular hydrophobic associations, whereas at higher $x : z$ ratios, coil contraction became the predominant effect. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 125–131, 2009

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INTRODUCTION

Associating water-soluble polymers have been the subject of extensive research during the past decades because of their interesting rheological behaviors in aqueous solution.[1–3] These are amphiphilic polymers containing a small proportion of hydrophobic groups incorporated in hydrophilic polymer chains. Above a certain polymer concentration [the concentration required for hydrophobic association (C^*_{HA})], the intermolecular association of the hydrophobic groups leads to the reversible formation of three-dimensional physical crosslinks of polymer chains in aqueous solution. Whereas regular polymers build viscosity through a combination of concentration and molecular weight, associating polymers depend on the formation of physical networks. The most salient features of such networks are their significant enhancements of viscosity and elastic behavior compared to those of polymers without associating groups. One reason for using associative polymers as rheology modifiers is that their mechanical degradation is reversible. The physical links in the networks may be disrupted when the strain rate is high and sustained but may reform when the imposed stress drops. The primary advantage of associative polymers is that they contribute less elasticity than regular linear high-molecular-weight polymers, which is desirable in some coating processes.[4] The shear thinning feature associated with the reversible nature of these physical crosslinks has led to their application as rheology modifiers (particularly as thickening agents), especially in aqueous-based formulations within numerous industrial domains, such as waterborne coatings, paints, cosmetics, and enhanced oil recovery.[5–8]

The increase in viscosity can be enhanced with charged monomers because intermolecular charge repulsions lead to coil expansion. In contrast to polymers containing neutral hydrophilic and neutral hydrophobic groups, the presence of ionic sites of similar charges along the hydrophilic backbone of associating polyelectrolytes leads to a great variety of interesting behaviors.[9] In partially hydrolyzed, hydrophobically modified polyacrylamide, the electrostatic repulsion between the negative charges of carboxylate groups causes the polymer chains to extend, and this extension can effectively enlarge the

Scheme 1
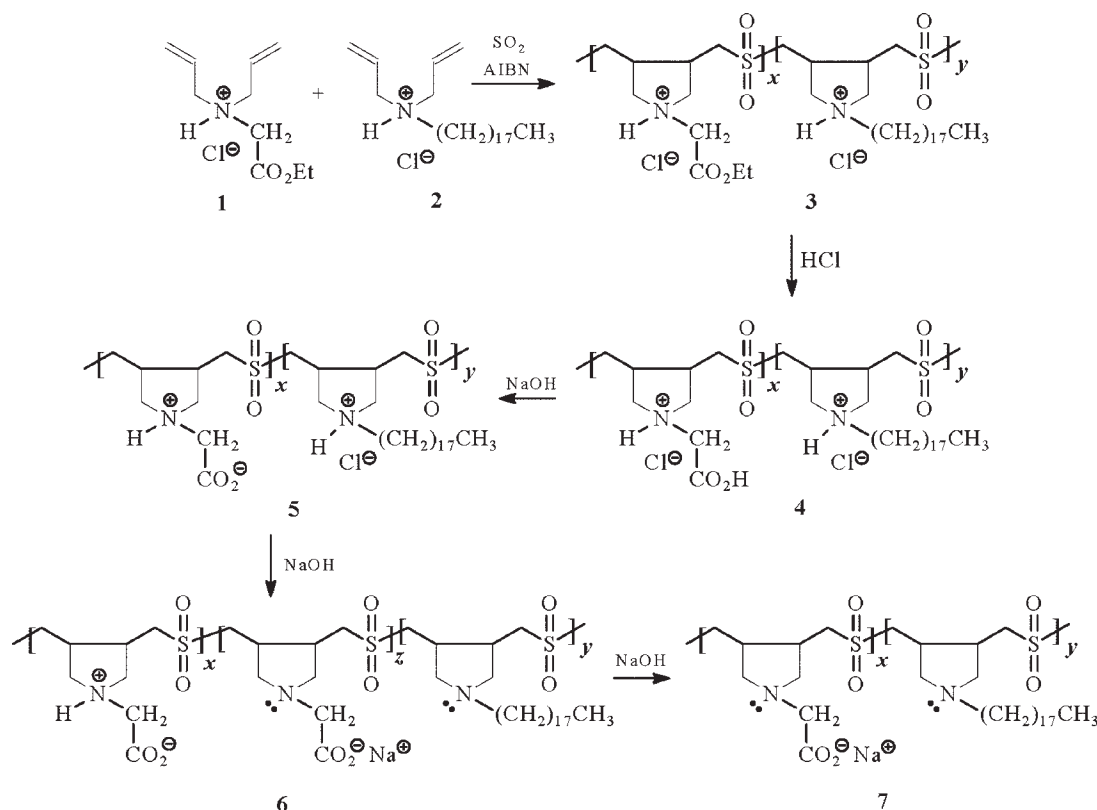
hydrodynamic volume of the polymer chain and, hence, increase the viscosity.[10] The physics behind hydrophobic self-association in hydrophobically associating ionic polymers is that hydrophobic interactions compete with electrostatic repulsion within the same polymer chain and/or between different polymer chains. Thus, the balance between hydrophobic interactions and electrostatic repulsions determines whether the polymer will undergo hydrophobic self-association or not. Primarily, this balance is a function of the charge density and hydrophobe concentration in the polymer as well as the size and arrangement of the hydrophobe.[11]

In addition to forming highly viscous solutions, aqueous systems containing hydrophobically modified water-soluble polymers may organize into viscoelastic hydrogels. The hallmark of viscoelastic materials is the presence of a so-called rubbery plateau in its dynamic rheological spectra. This means that under oscillatory applied shear, there exists some range of applied frequency [ω (s^{-1})], over which the material behaves more like an elastic solid than a viscous fluid, and its response is independent of ω. Thus the dynamic storage modulus (G', or elastic modulus) exceeds the dynamic loss modulus (G'', or viscous modulus), and G' is invariant with ω. In contrast, in polymer solutions, G'' is greater than G' over the entire frequency range. Thus, the physical

distinction between a hydrogel and a polymer solution is that the intermolecular linkage points in a gelled network are mechanically stable over some range of applied shear stress, whereas those in a solution are not.[12]

Since the discovery that the free-radical polymerization of diallyl quaternary ammonium salt yields water-soluble cyclopolymers instead of crosslinked polymers,[13] numerous homopolymers and cocyclopolymers of scientific and technological interest have been synthesized from various diallyamine compounds.[14–21] There are, however, only a few reports, that describe the synthesis of associating ionic copolymers prepared by Butler's cyclopolymerization technique.[22–24]

Recently, we reported[25] the synthesis and solution properties of a series of cycloterpolymers of sulfur dioxide [N,N-diallyl-N-carboethoxymethylammonium chloride (1)] with varying amounts of hydrophobic monomers [N,N-diallyl-N-alkylammonium choloride (2; with alkyl lengths of 12 and 18 carbons; Scheme 1). The incorporation of small amounts of the hydrophobic comonomer dramatically enhanced the viscosity values in the C$_{18}$ polymer series, whereas the presence of even a large amount of C$_{12}$ (0–10 mol %) failed to achieve association in the studied concentration range (0.0625–2 g/dL). The electrostatic repulsive forces between the chains did

not permit them to approach each other to a safe distance required for the dodecyl pendents ($C_{12}H_{25}$) to manifest interchain association. The octadecyl pendents ($C_{18}H_{37}$) could associate intermolecularly because the extended length of the pendents allowed them to mingle with each other without exposing the chains to the adverse effect of electrostatic repulsions. The low C^*_{HA} (~ 1 g/dL) observed for the C_{18} polymer series was indeed a notable improvement over the C^*_{HA} of 15–17 g/dL for the similar cyclopolymers with about C_{11} pendents.[26]

In this study, we examined the viscoelastic behavior of hydrophobically modified polyelectrolytes obtained from the hydrolysis of cationic acid salt (CAS) **4** as a function of zwitterion fraction (x) and anion fraction (z). The CAS **4** samples were completely converted to corresponding anionic polyelectrolyte (APE) **7** in the presence of 2.0 equiv of NaOH, whereas the treatments of CAS **4** (M_2-4, containing 4 mol % hydrophobe) with 1.5, 1.67, and 1.8 equiv of NaOH afforded the corresponding polybetaine (PB)/APE **6** with different x and z values (Scheme 1). The rheological behavior of this system was pH sensitive. The dynamic rheology of APE **7** as function of hydrophobe content was also examined. In addition, influence of the concentration of CAS **4** (M_2-4) treated with 1.67 equiv of NaOH was studied in the range 2–3 g/dL.

EXPERIMENTAL

Materials

The polymers used in this study were prepared by the free-radical cycloterpolymerization of sulfur dioxide and **1** with the hydrophobic comonomer N,N-diallyl-octdecylammonium choloride (**2**) to afford water-soluble cationic polyelectrolyte (CPE) **3**. CPE **3**, upon acidic (HCl) hydrolysis of the pendent ester groups, gave the corresponding CAS **4**, which was hydrolyzed with NaOH to introduce a carboxylate pendent on the polymer backbone. Details of the synthesis, characterization, and aqueous solution properties were reported elsewhere.[25] All of the polymers used in this study had linear alkyl side chains composed of 18 carbons and hydrophobe levels of 4 and 5 mol %, and the weight-average molecular weight was $3.7 \pm 0.4 \times 10^5$ g/mol for the 4 mol % hydrophobe polymer. The molecular weight was determined with a Wyatt static light-scattering DAWN instrument with 18-angle detection. The molecular weight measurement was carried out in methanol to minimize electrostatic interactions. Hydrolysis levels ranged from 1.5 to 2.0 equiv of NaOH for CAS **4** (M_2-4) and 2.0 equiv of NaOH for CAS **4** (M_2-5).

## Conversion of CAS 4 to PB/APE 6 and APE 7 by basification and its use in rheology measurements

The CAS **4** (M_2-4, which contained 4 mol % hydrophobe) were converted to the corresponding PB/APE **6** ($x = z = 0.48$, $y = 0.04$) by the addition of 1.5 equiv of aqueous NaOH, and the resultant solutions were used for rheology measurements in $0.1N$ NaCl. A solution of the above PB/APE **6** (M_2-4) was prepared by the dissolution of 0.400 g (1.418 mmol) of CAS **4** (M_2-4) in a NaOH solution containing 2.099 mmol (i.e., $1.418 + 1.418 \times 0.96 \times 0.5$ mmol) of NaOH (9.8 cm³ of $0.2137N$ NaOH was used for this purpose). The release of 1.418 mmol of NaCl thus made the system $0.144N$ NaCl. The solution was then diluted to 14.2 cm³ with deionized distilled water to make the solution $0.1N$ NaCl. Further dilution with $0.1N$ NaCl to 20 cm³ made the concentration of CAS **4** (M_2-4) in the presence of 1.5 equiv of NaOH as 2 g/dL in $0.1N$ NaCl. [CAS ($4.1H_2O$) and APE ($7.2H_2O$) had very similar molar masses of 273.73 and 277.27, respectively, for the repeating units.]

Likewise, the solutions of 2 g/dL of CAS **4** (M_2-4) in the presence of 1.67, 1.8, and 2.0 equiv of NaOH were prepared by the treatment of 0.400 g (1.418 mmol) of CAS **4** (M_2-4), as done previously, with $1.418 + 1.418 \times 0.96 \times 0.67$, $1.418 + 1.418 \times 0.96 \times 0.80$, and $1.418 + 1.418 \times 0.96 \times 1$ equiv of NaOH to obtain solutions of APE/PB **6** ($x = 0.32$, $z = 0.64$, $y = 0.04$), APE/PB **6** ($x = 0.19$, $z = 0.77$, $y = 0.04$), and APE **7** ($x = 0.96$, $y = 0.04$), respectively. A stock solution of 3-g/dL CAS **4** (M_2-4) and a 2-g/dL solution of CAS **4** (M_2-5, derived from CPE **3** M_2-5) in the presence of 1.67 and 2.0 equiv of NaOH, respectively, were prepared in a similar way. To ensure complete dissolution, the solutions were left at room temperature for 24 h and vigorously stirred with a magnetic stirring bar for 1 h to obtain a homogeneous solution.

Rheological measurements

Dynamic shear measurements of polymer solutions over a wide range of oscillation frequencies were conducted with a constant strain advanced rheometric expansion system fitted with a stainless steel cone and a plate sample cell operating in oscillatory mode. The radius of the plate was 50 mm, the cone angle was 0.1 rad, and the gap between the cone and plate was set to 0.0483 mm. A shear strain amplitude of 10% was used after a strain sweep test on selected samples showed that this shear strain amplitude was sufficiently small to produce dynamic properties in the linear viscoelastic region. The reproducibility of the frequency sweep measurements is shown in Figure 1 for the CAS **4** (M_2-5) sample. The displayed results represent two independent measurements of fresh loadings of the same
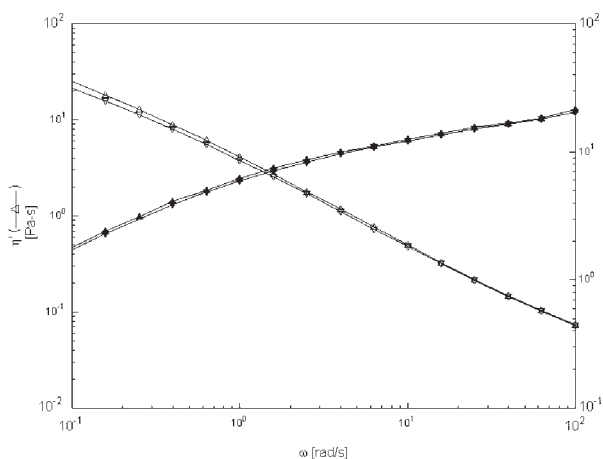
Figure 1 Reproducibility of the $\eta'(\omega)$ and $G'(\omega)$ data of CAS **4** (M$_2$-4) treated with 1.67 equiv of NaOH.

sample. Excellent agreement of both the dynamic viscosity (η') and G' showed the degree of reproducibility of these measurements. All experiments were conducted at 25 ± 0.1°C and were performed in a descending ω order from 10^2 to 10^{-2} rad/s.

RESULTS AND DISCUSSION

CPE **3** was synthesized via the cycloterpolymerization of sulfur dioxide, **1,** and the hydrophobic monomer **2** according a procedure reported earlier.[25] CPE **3** was hydrolyzed in 6N HCl to produce the water-insoluble CAS **4** (M$_2$-4), which on treatment with 1.5, 1.67, 1.80, and 2.0 equiv of NaOH, afforded solutions of PB/APE **6** and APE **7** in approximate PB:APE ratios of 50 : 50, 33 : 67, 20 : 80, and about 0 : 100, respectively. Before the addition of alkali, the CAS **4** polymer contained insoluble carboxylic acid groups in the form of latex particles. The addition of NaOH solution neutralized the acid groups (—COOH) on the polymer chain, and as a result, the carboxylic acid groups were converted to the ionized carboxylate form, which had a higher solubility in water.

The CAS **4** (M$_2$-4) terpolymer containing 4.0 mol % hydrophobe and its corresponding PB **5** [obtained by the treatment of CAS **4** (M$_2$-4) with 1 equiv of NaOH] was found to be insoluble in salt-free and salt-added solutions.[27] The critical NaOH equivalent required for the solubility of CAS **4** (M$_2$-4) was around 1.25; this amount of NaOH resulted in the formation of PB/APE **6** with a $x : z$ ratio of approximately 75 : 25 (Scheme 1). As for the CAS **4** (M$_2$-5) terpolymer containing 5.0 mol % hydrophobe, the critical NaOH equivalent was around 1.50, with treatment with 1.67 equiv of NaOH giving a cloudy solution.

Figure 2 shows the η' dependence on frequency of a 2-g/dL polymer solution of PB/APE **6** (M$_2$-4) with various compositions of PB (x) and APE (z) fractions
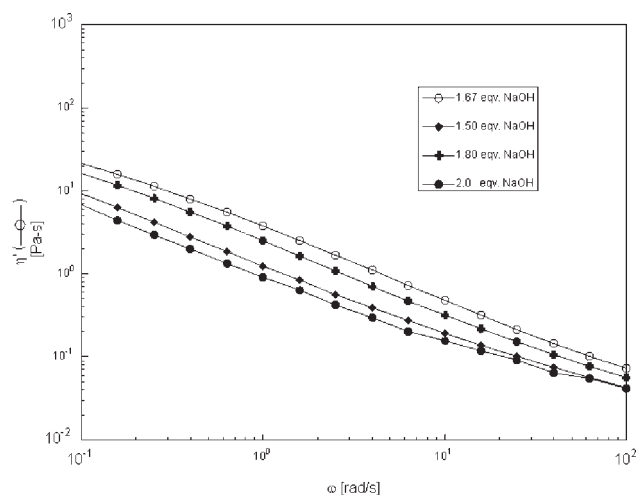

Figure 2 η' as a function of frequency for CAS samples treated with different equivalents of NaOH at 25°C.

in 0.1N NaCl. The viscosity values generally decreased with increasing oscillation frequency, a typical shear thinning behavior of associative polymers. As the oscillation frequency increased, the intermolecular hydrophobic associations were disrupted, and this resulted in a decrease in the viscosity. It is interesting to note that no Newtonian plateau was observed, even at very low frequencies. This indicated that the network links were very sensitive and were disrupted under the slightest shear. This might have been caused by the high electrostatic repulsion, the highly swollen nature of the network, and the slight hydrophobic overlap resulting from the strong repulsion. The variation of η' of a 2-g/dL solution of CAS **4** (M$_2$-4) at various oscillation frequencies in the presence of various equivalents of NaOH in 0.1N NaCl is shown in Figure 3. η' attained its maximum value in the presence of 1.67 equiv of NaOH and decreased upon further addition of NaOH. The addition of 1.67 equiv of NaOH
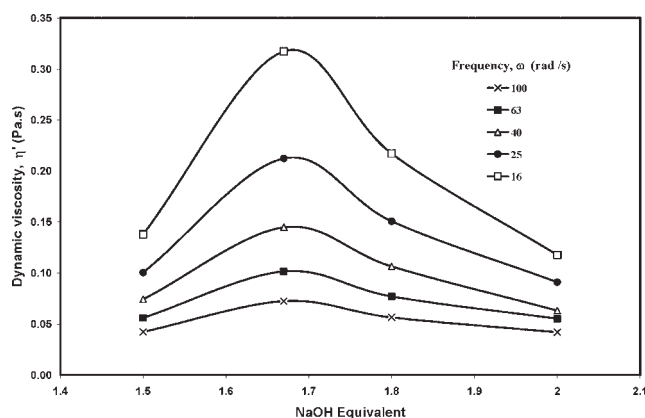
Figure 3 Variation of η' of 2-g/dL solutions of CAS **4** (M$_2$-4) at various oscillation frequencies in the presence of various equivalents of NaOH in 0.1N NaCl at 25°C.
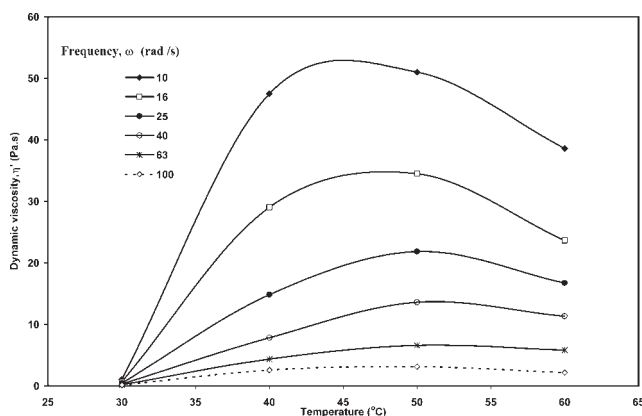
Figure 4 Variation of η' with temperature of 3-g/dL solutions of CAS **4** (M$_2$-4) treated with 1.67 equiv of NaOH in 0.1N NaCl at various oscillation frequencies.

transformed the CAS **4** (M$_2$-4) to its corresponding PB/APE **6,** with an approximate composition of 33 : 67 for x and z, respectively. As mentioned earlier, CAS **4** and PB **5** (obtained from CAS 4 on treatment with 1 equiv of NaOH) were insoluble in water. The internal neutralization of the charges in PBs is known to lead the polymer backbone to adapt a collapsed coil conformation as a result of intrachain interactions.[28,29] When the net charge of an ionic polymer approaches zero, attraction between oppositely charged units lead to a globulelike conformation and most often to insolubility in pure water. As the pH increases, the anionic fraction increases and the PB fraction decreases, as a result the intramolecular aggregates are progressively destroyed because the anionic charge density on the polymer backbone is increased. Although the presence of ionic sites of similar charges (CO$_2^-$ groups in the APE fraction) along the hydrophilic backbone can lead to better solubility in water and a stronger thickening efficiency due to coil expansion, intermolecular electrostatic repulsions lead to a lowering of the degree of hydrophobic association. A synergistic effect may be observed where the electrostatic repulsions can result in chain expansion, and the hydrophobic groups may also maintain interpolymer association. At an $x : z$ ratio of 33 : 67, the combined effect of coil expansion and hydrophobic association led to a maximum viscosity value (Fig. 3). At high pH, the CAS samples were completely converted to APE, and the electrostatic repulsion caused the chain to loose flexibility; thus, hydrophobic groups were less capable of associating with each other to form a viscoelastic network. Thus, at lower $x : z$ ratios, the effect of coil expansion due to a higher APE fraction was more than counterbalanced by the lower degree of intermolecular hydrophobic associations, whereas at higher $x : z$ ratios, coil contraction became the predominant effect.

Figure 4 displays the effect of temperature on η' of a 3-g/dL solution in 0.1N NaCl of CAS **4** (M$_2$-4) treated with 1.67 equiv of NaOH. Over the entire frequency range studied, η' increased gradually as the temperature increased. The hydrophobic effect can be regarded as a process of entropy increase, which means that as the temperature increases, the hydrophobic effect increases. The η' increase observed upon heating was consistent with an entropy-driven increase in hydrophobic bonding.[30,31] On the other hand, the association effect was retarded at high temperatures, presumably as a result of changes in the hydration spheres of the hydrophobic groups and the strong thermal vibration of water molecules.

The viscoelastic properties of concentrated or semidilute polymer solutions are described by two functions: G', which represents the elasticity of the network, and G'', which accounts for the local friction of the polymer chain. Figures 5–7 show the frequency dependence of G' and G'', respectively, for a 2-g/dL polymer solutions of the CAS **4** (M$_2$-4) samples treated with 1.50 and 1.67 equiv of NaOH obtained at 25°C. The G' of CAS **4** (M$_2$-4) treated with 1.5 equiv of NaOH was consistently lower than G'' over the entire frequency range studied. Both moduli were highly frequency dependent and increased in a parallel manner with increasing ω; thus, no crossover frequency (ω_{cross}) was obtained. On the other hand, the CAS **4** (M$_2$-4) samples treated with 1.67, 1.81, and 2.0 equiv of NaOH showed a transition from an elastic-dominated response ($G' > G''$) at high frequencies to a viscous-dominated response at lower frequencies. These data were reminiscent of a reversible network, wherein interchain interactions are transient.[32] A weak gel-like system was obtained with a high-frequency dependence of
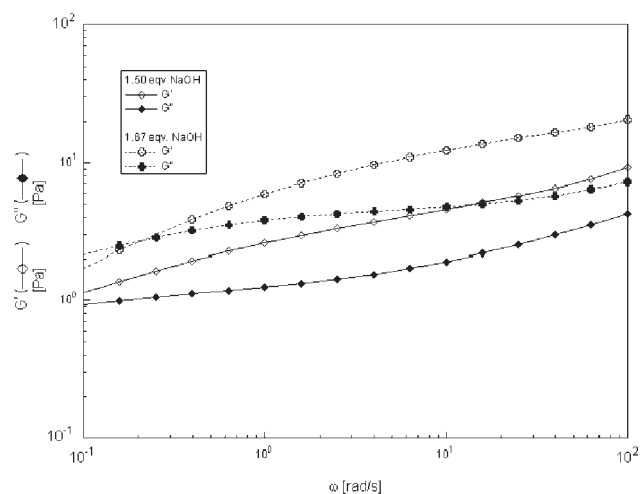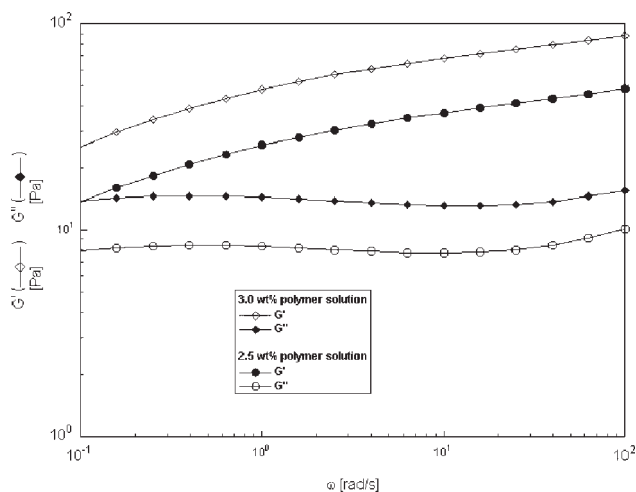

Figure 5 G' and G'' as a function of frequency for the CAS **4** (M$_2$-4) samples treated with 1.5 and 1.67 equiv of NaOH at 25°C.
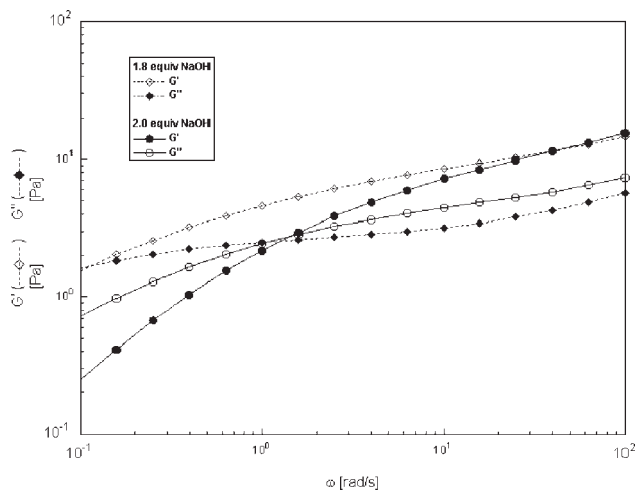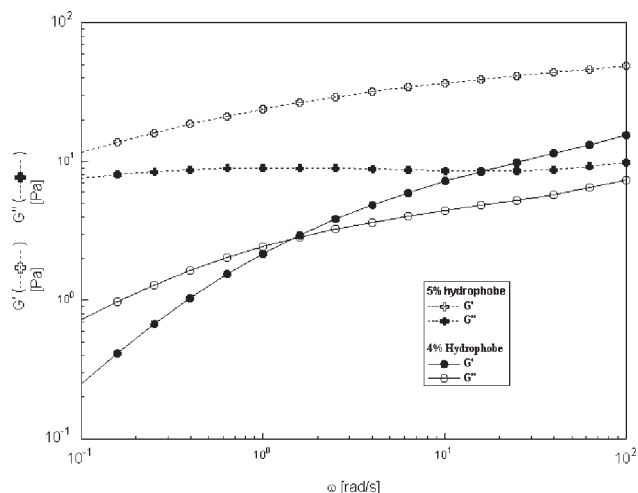
Figure 6 G' and G'' as a function of frequency for the CAS **4** (M$_2$-4) samples treated with 1.80 and 2.0 equiv of NaOH at 25°C.

G' and up to the ω_{cross} beyond which G'' was relatively less frequency-dependent, whereas G' showed a progressive increase with frequency, and no plateau value was obtained in either case. The lack of a plateau was attributed to the rapid relaxation process.[33] Hydrophobically modified polymers, such as galactomannam ether,[34] galactomannam/borate,[35] and polyvinylalcohol/borate,[36] have been reported to exhibit similar viscoelastic behaviors. The $G'(\omega)$ and $G''(\omega)$ curves crossed each other at a particular frequency, designated as ω_{cross}, and at a critical modulus. The critical moduli of the CAS **4** samples treated with 1.67, 1.80, and 2.0 equiv of NaOH were found to be 2.7, 1.7, and 2.8, respectively.

The frequency dependence of G' and G'' obtained at 20°C for 2.5- and 3-g/dL polymer solutions of the CAS **4** (M$_2$-4) samples treated with 1.67 equiv of NaOH showed an elastic behavior in which G' was

Figure 7 G' and G'' as a function of frequency for the CAS **4** (M$_2$-4) samples treated with 1.67 equiv of NaOH at 25°C.

Figure 8 G' and G'' as a function of frequency for the CAS **4** (M$_2$-4) and CAS **4** (M$_2$-5) samples treated with 2.0 equiv of NaOH at 25°C.

consistently greater than G'' across the frequency range studied, which suggests the formation of a highly interconnected three-dimensional network. G' showed a high frequency dependence at low frequencies and a relatively lower frequency dependence at high frequencies with no plateau value, whereas G'' remained relatively constant and reached a plateau, which denoted a constant viscous relaxation. No ω_{cross} was obtained for the 2.5- and 3-g/dL polymer solutions of the CAS **4** (M$_2$-4) samples treated with 1.67 equiv of NaOH.

In addition to the previously mentioned ionic charge density effect, the polymer concentration and hydrophobe content were certainly other factors that affected the rheological properties of the polymer solutions. Figure 8 shows G' and G'' as a function of frequency for 2.0-g/dL APE **7** (M$_2$-4) and APE **7** (M$_2$-5). The APEs were obtained by the treatment of the corresponding CAS **4** with 2.0 equiv of NaOH. As mentioned earlier, APE **7** (M$_2$-4) showed a transition from an elastic-dominated response ($G' > G''$) at high frequencies to a viscous-dominated response at lower frequencies, which suggested a reversible network behavior wherein interchain interactions were transient, whereas APE **7** (M$_2$-5) clearly exhibited elastic behavior, in which G' was consistently greater than G'' across the frequency range studied, which suggested the formation of highly interconnected three-dimensional networks.

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