Influence of hydrophobe content on the solution rheology of hydrophobically modified terpolymer of SO₂, *N,N*-diallyl-*N*-carboethoxymethylammonium chloride

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Abstract

Rheological properties of hydrophobically modified copolymer of SO₂, *N,N*-diallyl-*N*-carboethoxymethylammonium chloride and the hydrophobic monomer *N,N*-diallyl-*N*-octadecylammonium chloride were studied. The influence of hydrophobe content (HP) and polymer concentration was investigated. Polymers with HP content in the range 1.5–5% were examined and the concentration was varied in the range 2–5 wt%. Both dynamic and steady-shear experiments were performed in ARES rheometer. Copolymers were observed to exhibit typical viscoelastic behavior even with low HP content. Both the dynamic viscosity, η' and storage modulus, G', increase with the increase of both the polymer concentration and the HP content of the system. The viscosity of the high HP content polymer showed a strong shear dependency, while G' was a weak function of frequency and gel-like behavior was observed. The zero-shear viscosity, η_0, showed a strong concentration dependency ($\eta_0 \sim \phi^{\alpha}$; $1.1 < \alpha < 5.9$). The concentration dependency of η_0 suggests that intermolecular association is dominant in the high HP content polymer. Control of the HP content and polymer concentration of this class of polymers can lead to a wide range of interesting rheological properties.
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1. Introduction

Macromolecules that possess charges as well as hydrophobes (HPs) along with or pendent to the polymer backbone are one of the most important classes of polyelectrolytes [1]. This class of polyelectrolytes is often termed as 'amphiphilic polyelectrolytes' (APs) or 'hydrophobically modified polyelectrolytes' (HMPs). APs show self-association behavior in aqueous solution due to non-covalent forces, such as, electrostatic, hydrogen bonding, van der Waals and hydrophobic interactions. The physics behind hydrophobic self-association in HMPs is that hydrophobic interactions compete with electrostatic repulsion within the same polymer chain and/or between different polymer chains. Thus, the balance of hydrophobic interaction and electrostatic repulsion determines whether the polymer undergoes

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hydrophobic self-association. Primarily, this balance is a function of the number of charges and hydrophobes in the polymer as well as the size of the HP. HMPs can form micelle-like aggregates of different morphologies. At concentrations above the critical association concentration, the self-association of such charged polymers leads to the formation of aggregates consisting of a dense hydrophobic core and the extended charged corona [1,2].

Subsequent copolymerization of *N,N*-diallyl quaternary ammonium salts [3] with sulphur dioxide [4–6] led to the synthesis of an array of water-soluble cationic polyelectrolytes [7–10]. A particularly successful approach for controlling the rheology of such polyelectrolytes exploits the association characteristics of hydrophobically modified water-soluble polymers [11]. Viscosity enhancement and elastic responses are considerably stronger for solutions of HMPs than in the solution of unmodified polyelectrolytes [12–14]. Interaction of nonionic, anionic surfactants and oppositely charged polyelectrolytes with HMPs has been extensively studied [15–19].

Recently, Xue et al. [20] studied the effect of the type of hydrophobic comonomer and the number and length of hydrophobic units on the rheological properties of hydrophobically modified polyacrylamides synthesized from the copolymerization of di-*n*-propylacrylamide (DPAM) and di-*n*-octylacrylamide (DOAM). Incorporation of DOAM into PAM caused a dramatic enhancement in viscosity due to hydrophobic interactions [20]. Viscosity increase can probably be attributed to a combined effect of electrostatic interactions and hydrophobic associations [18]. Similar studies on solution rheology of hydrophobically modified alkali-soluble emulsion (HASE) were performed during the last few years [21–23]. Jimenez-Regalado et al. [24] and Caputo et al. [25] investigated the viscoelastic properties of multi-block associating hydrophobically modified polyacrylamides.

Over the past two decades, APs attracted considerable attention due to their potential use in a variety of commercial applications, such as associative thickeners, rheology modifiers, polymer-based surfactants, emulsifiers, solubilizers, coagulants/flocculants, colloids and enhanced oil recovery applications [26–34]. Aqueous systems containing APs are an excellent candidate for environmentally benign substitutes for organic solvent

systems being currently used in various commercial processes [35,36]. The inherent propensity of HMPs to self-assemble in aqueous media due to the presence of both ionizable and hydrophobic groups and thus change viscosity making HMPs an ideal tool for designing smart drug delivery vehicles and protein stabilizing constituents of pharmaceutical formulations [1].

In this paper, we report the rheology of a novel class of HMPs containing varying percentage of HP content, which is expected to play vital role in the self-assembling phenomena of HMPs. HMPs used in experiment are copolymers of SO_2, *N,N*-diallyl-*N*-carboethoxymethyl-ammonium chloride and *N,N*-diallyl-*N*-octadecylammonium chloride (hydrophobic monomer). The synthesis of this class of polymers through cyclopolymerization made it possible to study the influence of HP content on the solution rheology of water-soluble polymers. The synthesis and characterization of the polymers used in this study has just been reported [37]. In that study, only viscometric techniques were used to measure the intrinsic and apparent viscosities. Here, viscoelastic properties of such class of polymers are investigated. Dynamic and oscillatory shear rheology of the copolymer were examined for polymers with 5%, 2.5% and 1.5% HP content. The influence of polymer concentration was studied in the range 2–5 wt%. Finally, the viscoelastic properties were fitted to rheological models and the influence of the HP content and polymer concentration on the viscoelastic properties was reported.

2. Experimental

2.1. Materials and sample preparation

As shown in Fig. 1, a mixture of 97.5% electrolytic monomer (1) and 2.5% electrolytic monomer (2) was added in di-methyl sulphoxide (DMSO) and SO_2 was absorbed in the solution. The initiator (2,2′-Azobisisobutonitrile, AIBN) was supplied by Fluka Chemie AG (Buchs, Switzerland). The required amount of AIBN was then added under N_2 and the closed flask was stirred using magnetic stir-bar at 56 °C for 21 h. After few hours, the magnetic bar stopped stirring and initial reaction mixture (slurry) became a solid mass of white cationic polyelectrolyte (CPE) polymer (3). At the end of
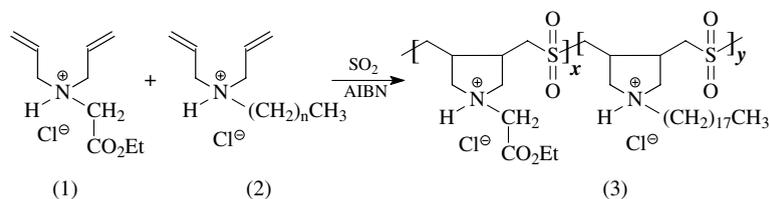

Fig. 1. Synthesis of amphiphilic polyelectrolytes by free-radical copolymerization.

Table 1
Terpolymerization[a] of the hydrophilic and hydrophobic monomers with SO_2[a] (Umar et al., 2004)

	Sample	Hydrophilic monomer (M_1) (mmol)	C_{18} (M_2) (mmol)	Feed M_1:M_2	Polymer M_1:M_2[b]	Yield (%)	Intrinsic viscosity (dl g^{-1}) polymer
1	M_2–0	30		100:0	100:0	85.6	0.600
6	C_{18}–1.5	29.55	0.45	98.5:1.5	98.5:1.5	93.2	0.514
7	C_{18}–2.5	29.25	0.75	97.5:2.5	97.3:2.7	87.2	0.501
8	C_{18}–3.5	28.95	1.05	96.5:3.5	96:4	86.8	0.581
9	C_{18}–5	28.5	1.5	95:5	94.8:5.2	90.1	0.446[c]

[a] Polymerization reactions were carried out in DMSO (7.85 g) containing 30 mmol of SO_2 in the presence of AIBN (145 mg) at 57 °C for 20 h.

[b] Mol% in the feed and polymer (as determined by ^{1}H NMR).

[c] Cloudy solution throughout the concentration range.

the elapsed time, the hard polymeric mass was crushed to form powder, soaked in methanol, filtered and washed with liberal excess of hot (50 °C) methanol to ensure the complete removal of the unreacted monomer (as indicated by ^{1}H NMR). The copolymer was then dried to maintain a constant weight at 55 °C under vacuum. Details of the synthesis of the CPE were given elsewhere [37] and summarized in Table 1. The CPE (3) was then stored in a desiccator.

Polymer solutions were prepared with different percentage of HP content (1.5%, 2.5% and 5%). Five percent stock solutions of all samples were prepared by dissolving the polymer in deionized water and the solutions were homogenized by stirring at room temperature for three days. Special precautions were taken during stirring to prevent air bubbles formation and the stirring speed was varied depending on the viscosity of the solution. Different concentrations (2 wt%, 3 wt% and 4 wt%) were subsequently prepared by the dilution of the 5 wt% stock solution with deionized water. All water used was MilliQ quality. Continuous stirring ensured homogeneity of the solutions. For viscous samples, air bubbles of the solution were removed by centrifugation in alternating directions for several hours at room temperature.

2.2. Methods

The rheological properties of HMPs were measured in ARES constant-strain rheometer equipped with a normal force transducer (2–2000 g). Cone-and-plate geometry (50 mm radius and 0.1 rad angle) was used for all rheological measurements. Each sample was loaded in the plate with extreme care to prevent the formation of air bubbles and was allowed to rest for 5 min prior to the measurement. Both the steady-shear and oscillatory experiments were carried out at room temperature (24 °C).

The linear viscoelastic range was determined from strain sweep measurements as 15–30% strain, depending on the concentration of the sample. Then, the frequency sweep tests were conducted with the frequency varied from 0.1–100 rad/s with the strain constant and in the linear viscoelastic range. In frequency sweep tests, the displayed results represent two independent measurements on fresh loadings of the same sample to ensure the reproducibility of the results. At very low frequency, data was not shown since the torque is lower than the sensitivity limit of the transducer. In addition to dynamic shear measurements, transient steady-shear experiments were performed at two different shear rates (0.1 and 1.0 s^{-1}) for all polymer samples.

3. Results and discussion

3.1. Dynamic shear measurements

The results of the rheological measurements for the 5%, the 2.5% and the 1.5% HP content polymers are shown in Fig. 2a–c, respectively. The dynamic shear viscosity, η', represents the viscous component, while the storage modulus G' reflects the elasticity of the polymer. The measurements were performed in the frequency, ω, range 100–0.1 rad/s. In Fig. 2a–c, the influence of polymer concentration on η' and G' was displayed as a function of ω. The results show that both η' and G' increase with the increase of polymer concentration. For the 5% HP content polymer, η' and G' increase evenly in the concentration range 2–4%. For the 5% concentration, values of η' and G' do not increase in the same proportion as the 4% solution. This suggests pronounced association between the polymer molecules. This is due to the increased intermolecular association with increasing concentration. The intermolecular association hypothesis is later confirmed by the concentration dependency of the zero-shear viscosity. Also, no entanglements are expected at such low concentrations. However, there is a saturation concentration above which no new network junctions generate to increase the dynamic viscosity significantly. This is indicated by the small difference observed in η' and G' for the solutions containing 4% and 5% polymer.
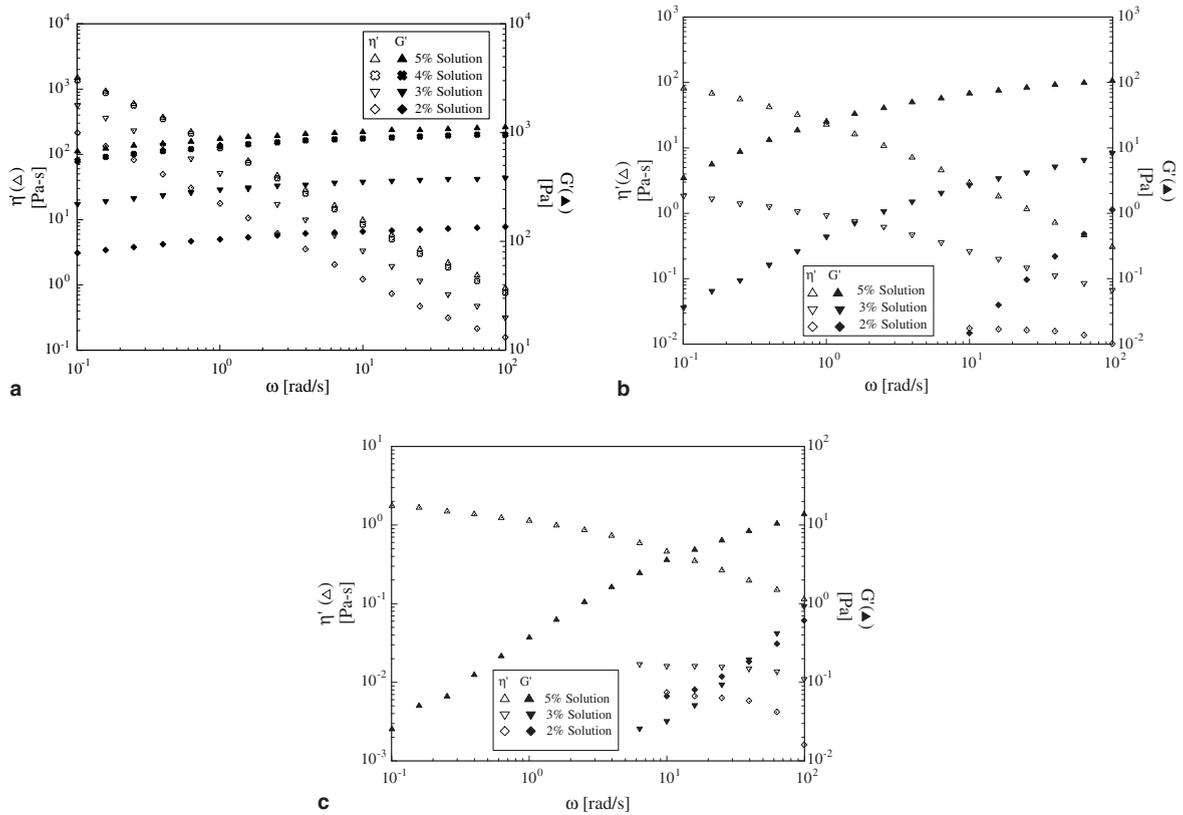
Fig. 2. (a) $\eta'(\omega)$ and $G'(\omega)$ for the 5% HP sample as a function of concentration; (b) $\eta'(\omega)$ and $G'(\omega)$ for the 2.5% HP sample as a function of concentration and (c) $\eta'(\omega)$ and $G'(\omega)$ for the 1.5% HP sample as a function of concentration.
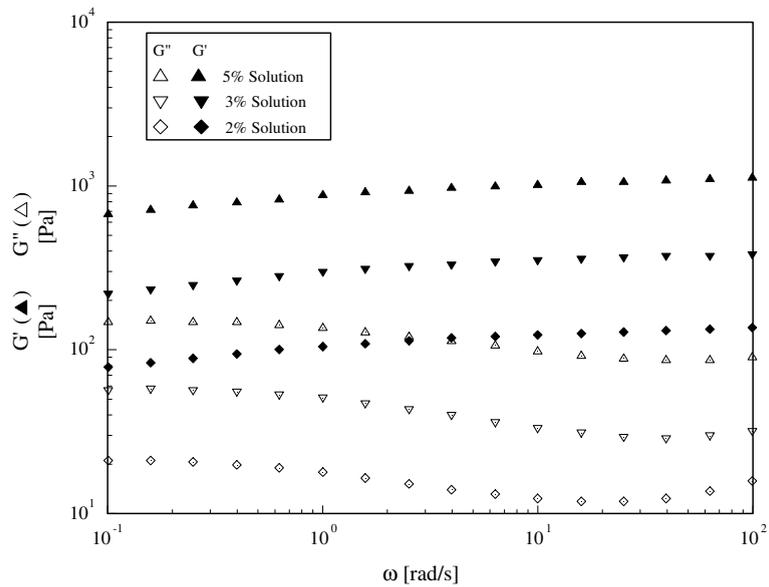

Fig. 3. $G'(\omega)$ and $G''(\omega)$ for the 5% HP sample at different concentrations.
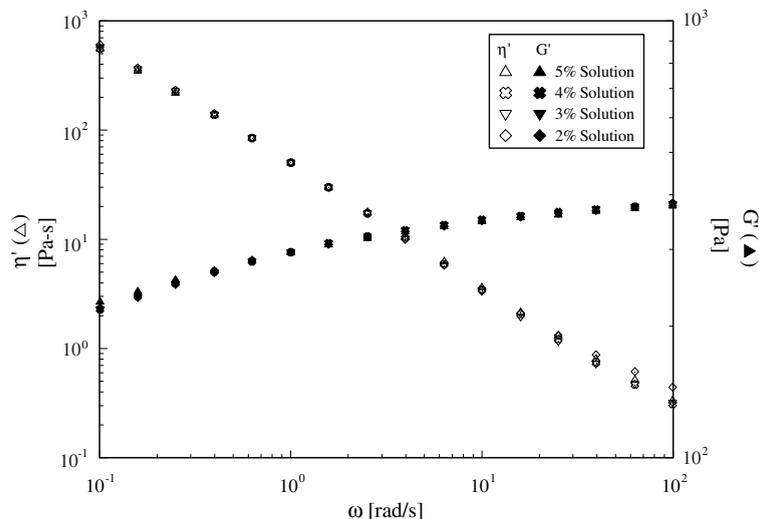
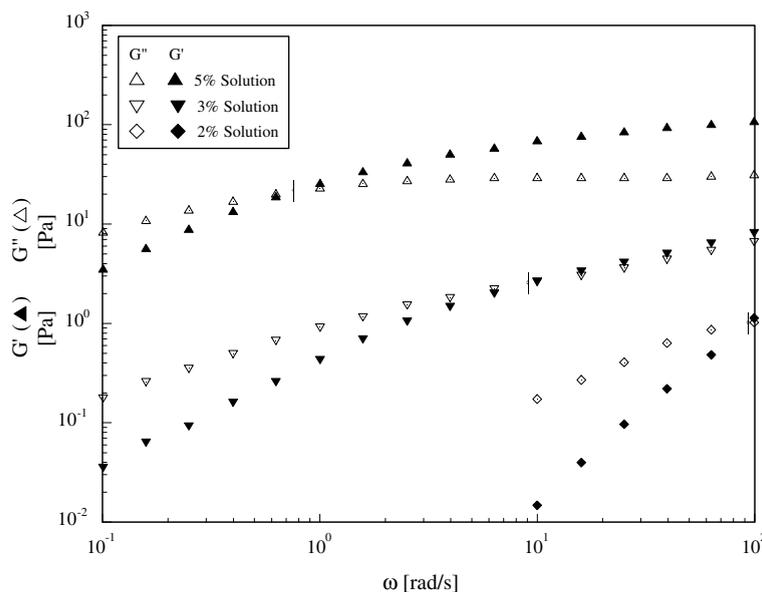Fig. 4. Master curve for the 5% HP sample.

Fig. 5. $G'(\omega)$ and $G''(\omega)$ for the 2.5% HP sample at different concentrations.

Fig. 2b shows similar pattern of η' and G' curves for the 2.5% HP content polymer. The 2% solution was too dilute; hence, data collected at $\omega < 10$ rad/s was below the instrument sensitivity. Similarly, for the 1.5% HP content system (Fig. 2c) both the 2% and the 3% concentrations had very low viscosity and the torque values were rejected for ω less than 10 and 6.3 rad/s, respectively. However, the 1.5% and the 2.5% HP content polymers show typical power-law relation between G' and ω ($G' \alpha \omega^n$) that depends on polymer concentration and HP content. For the low HP content (1.5%) sample,

the slope of the curve of G' vs. ω was found to be high at low polymer concentrations and low at high polymer

Table 2
G_c and ω_c of the 5% solution as a function of HP

HP content of HMPs system	G_c	ω_c
5	No crossover	No crossover
2.5	21.457	0.757
1.5	7.2356	30.427

concentration. Also, this relation holds over a wide range of ω especially at low concentrations or low HP contents. The behavior of the 1.5% and the 2.5% HP polymers suggests the presence of a reversible network wherein inter-chain interactions are transient and the system does not behave like a physical gel [22]. In addition, strong shear dependence of η' was observed especially at high HP content and high polymer concentrations. At higher polymer concentrations, the solution becomes more viscoelastic; hence, more shear thinning leading eventually to gel-like structures.

Fig. 2a–c also indicate the shear thinning behavior of all polymer solutions of different HP contents. In addition, the high HP content polymers showed yield stress behavior, because they contain more physical network-

ing points that are broken under high shear. This observation is typical of yield stress fluids, where η' represents the apparent viscosity. The 1.5% HP content showed typical Newtonian behavior at low ω at all concentrations (2–5%). On the other hand, the 2.5% HP polymer showed Newtonian behavior at 2% concentration only, while the 3% and the 5% solutions will likely approach the Newtonian limit at $\omega < 0.1$ rad/s. For the 5% HP polymer, strong shear thinning was observed at all concentrations and the polymer is expected to show a yield stress due to the observed gel-like nature of the polymer solution.

The storage modulus of the 5% HP content sample showed weak dependency on ω over the entire ω-range and G' approached a plateau modulus (Fig. 2a). This
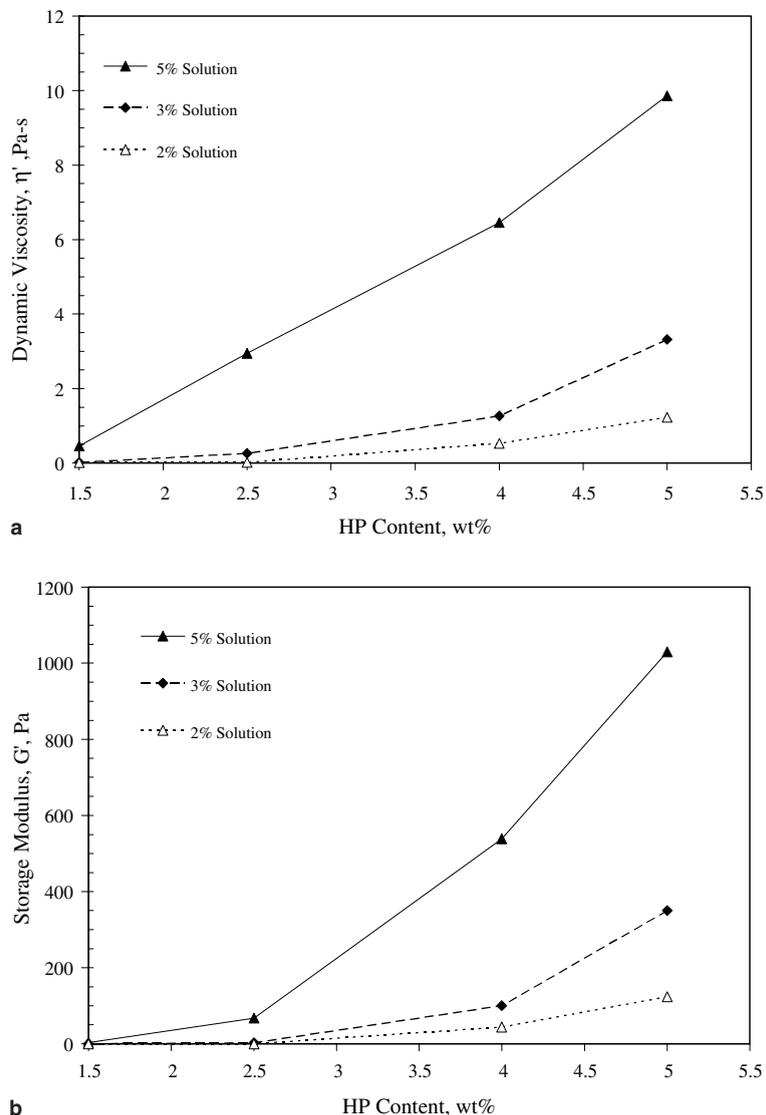

Fig. 6. (a) η'(HP) at different polymer concentrations ($\omega = 10$ rad/s) and (b) G'(HP) for different polymer concentrations ($\omega = 10$ rad/s).

solid-like behavior of the high HP polymer is likely due to the presence of strong intermolecular association, which increases the number of elastically active junctions [38]. At fixed polymer concentrations, the increase in molecular size and hydrodynamic volume is likely the reason behind the increase in η' with the increase in HP content. The strong shear thinning of η' (no Newtonian limit) and the very weak dependency of G' on ω (slope of log G' vs. log $\omega \ll 1$) are strong evidence of the presence of yield stress associated with gel-like fluids.

The gel nature of the 5% HP polymer was further examined by comparing the storage and loss (G'') moduli at different polymer concentrations. Results are given in Fig. 3. G' and G'' values increase with increasing polymer concentration and show weak dependency on ω. At all ω, the magnitudes of G' of the 5% solution is at least 5 times as that of G'', which is a reflection of the solid-like behavior of the 5% solution. Also, G' of the 5% solution is ~10 times that of the 2% solution. At all concentrations of the 5% HP polymer, G' is always higher than G'' over the whole ω domain. This suggests the dominant elastic behavior of the 5% HP content system. It was also evident that no crossover point (where $G' = G'' = G_c$) is found at any concentration of the 5% HP system. This is a typical feature of physical gels [39].

In Fig. 4, a master curve [$\eta'(\omega)$ and $G'(\omega)$] is shown for the 5% HP content sample. Here, the 3% solution is taken as a reference and the data for the 5%, the 4% and the 2% concentrations were shifted. The shift factor, a_ϕ, was obtained as 0.33705, 0.395381 and 2.808836 for the 5%, 4% and 2% solutions, respectively. For the 2%, 3% and 4% concentrations, log a_ϕ correlates to polymer weight fraction, ϕ, through a linear relation (log a_ϕ 1.2925–0.9803ϕ; $r^2 = 0.999$). For these concentrations,

both $\eta'(\omega)$ and $G'(\omega)$ perfectly superimposed on each other. The shift factor for the 5% solution deviates from linear behavior. At higher $\omega(\omega > 30$ rad/s), there are some dispersed viscosity data for the 2% solution as shown in Fig. 4. This master curve can be used to predict η' and G' data for the 5% HP content system up to 4% polymer concentration. This confirms our previous suggestion that the 5% polymer solution represents a critical concentration.

For the 2.5% HP content polymer, results of $G'(\omega)$ and $G''(\omega)$ are shown in Fig. 5 for different polymer concentrations. Fig. 5 shows that the 2% solution does not behave like a classical Newtonian fluid with $G' \sim \omega^2$ and $G'' \sim \omega^1$ [19,23] and G'' dominates G' especially at low concentrations. For both the 5% and the 3% solutions of the 2.5% HP system, G'' dominates G' at low $\omega(\omega < 1$ rad/s) indicating the liquid-like behavior of this system. It is also evident from Fig. 5 that the crossover modulus, G_c, increases with decreasing polymer concentration, reflecting the transient network formation of hydrophobically modified polymer molecules [11].

For the 2.5% HP content polymer, the concentration dependence of log G_c is linear (log $G_c = 1.0288\phi -$ 0.9108; $r^2 = 0.999$). Also, log ω_c was almost linear (log $\omega_c = -1.5541\phi + 3.19988$; $r^2 = 0.971$). Thus relaxation time or time of intersection, λ_c, of the polymer system can be calculated from $\lambda_c = 1/\omega_c$. The relaxation time decreases with decreasing polymer concentration, which again justifies the formation of short-lived transient network at low concentration of this system. From Table 2, it can be concluded that high HP content system take longer times to relax the applied stress. This observation from dynamic shear data was later confirmed by independent steady-shear transient measurements.
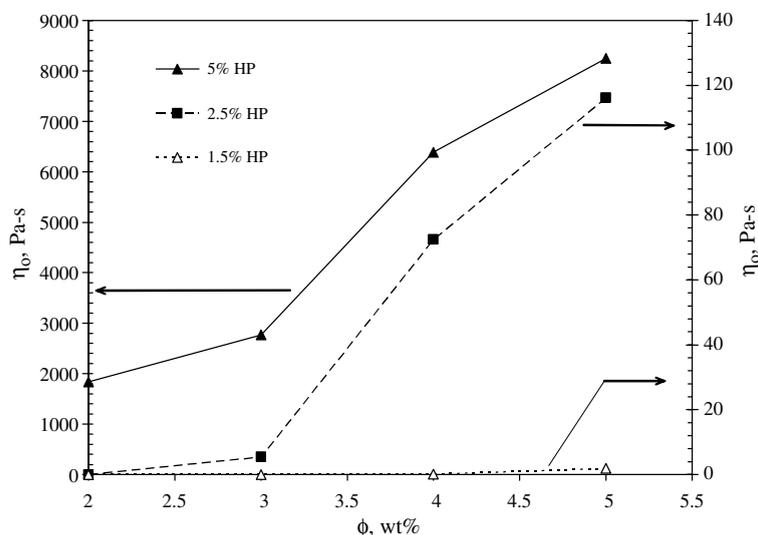

Fig. 7. $\eta_0(\phi)$ for different polymer solutions containing different HP content.

Furthermore, η'(HP) and G'(HP) at different concentrations and a fixed frequency of 10 rad/s are shown in Fig. 6a and b, respectively. At a fixed ω, both η' and G' increase with increasing HP content and polymer concentration.

Dynamic viscosity data for all sets of different HP content systems were fitted with Ellis model and the zero-shear viscosity, η_0, was obtained at different polymer concentrations (see Fig. 7). For all of the three systems, η_0 jumps appreciably after exceeding a concentration of 3%, which is likely due to intermolecular asso-

ciation. If the data for the 2.5% and the 5% HP polymers is fitted to $\eta_0 \sim \phi^\alpha$, the value of α has a physical significance. The concentration dependency of η_0 reflects whether the polymer molecules are undergoing intramolecular, intermolecular or topological entanglements. For entangled systems α is 15/4, while for intermolecular association $5.9 < \alpha < 1.1$ [22,40–42]. For both the 2.5% and the 5% HP content polymers, α is ~5.8 and 2, respectively. Hence, intermolecular association is dominant and concentrations up to 5% do not result in entanglements.
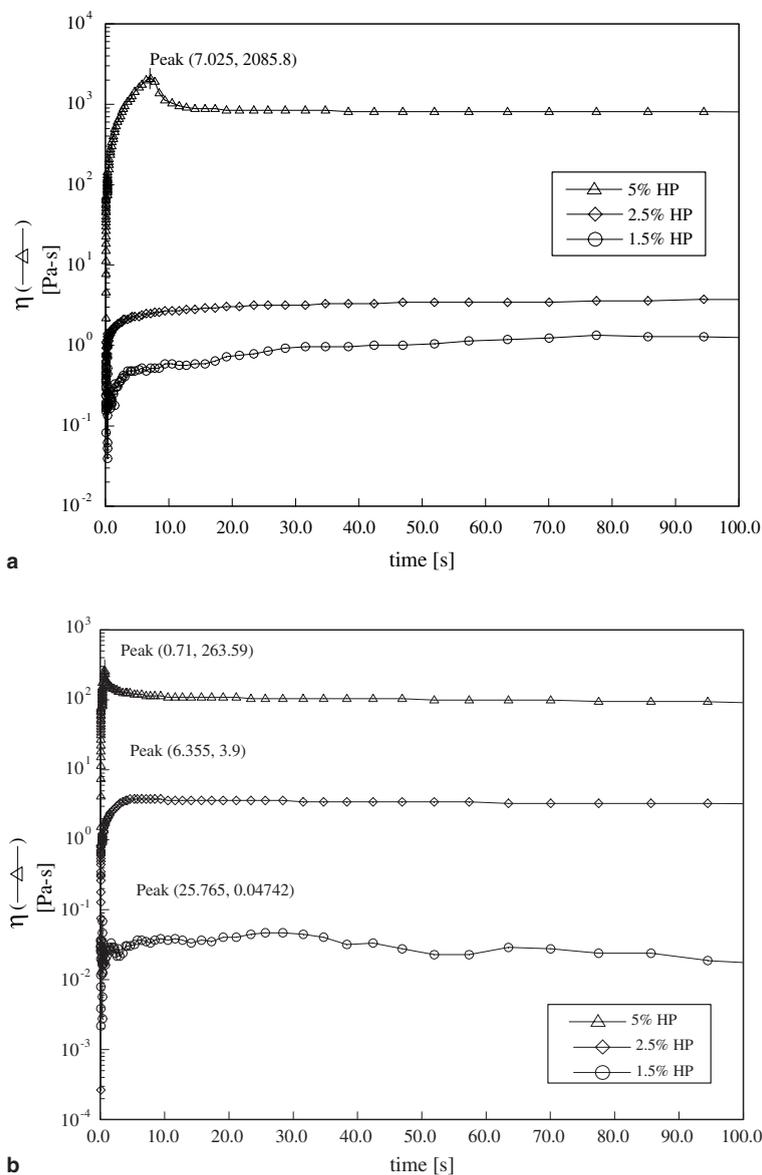

Fig. 8. (a) $\eta(t)$ for the 3% solution at different HP content ($\dot{\gamma} = 0.1\ \text{s}^{-1}$) and (b) $\eta(t)$ for the 3% solution at different HP content ($\dot{\gamma} = 1.0\ \text{s}^{-1}$).

3.2. Transient steady-shear measurements

Steady-shear transient measurements were made with unidirectional platen rotation (counterclockwise). The transient steady-shear viscosity $\eta(t)$ was obtained at constant rates of 0.1 and 1 s^{-1}. Fig. 8a,b shows $\eta(t)$ for the 3% polymer solution as a function of HP. At 0.1 s^{-1}, the 5% HP content sample yields considerably high viscosity as compared to the 2.5% and the 1.5% HP content system (Fig. 8a). The steady-state value of η for the 5% HP sample is ∼400 and 1000 times that of the 2.5% and the 1.5% HP samples, respectively. This result indicates the higher degree of intermolecular association in the 5% HP sample. It is also evident from Fig. 8a that higher HP content systems require longer time to reach steady-state, which suggests that high HP content polymers are characterized by longer relaxation time. This supports the previous findings from the dynamic shear measurements. Fig. 8b shows similar pattern of $\eta(t)$ at a rate of 1.0 s^{-1}. The magnitude of η of the 5% HP polymer is ∼65 and 4000 times that of the 2.5% and the 1.5% HP content samples, respectively.

It is clear that the high HP content polymer is strongly influenced by high shear leading to substantial
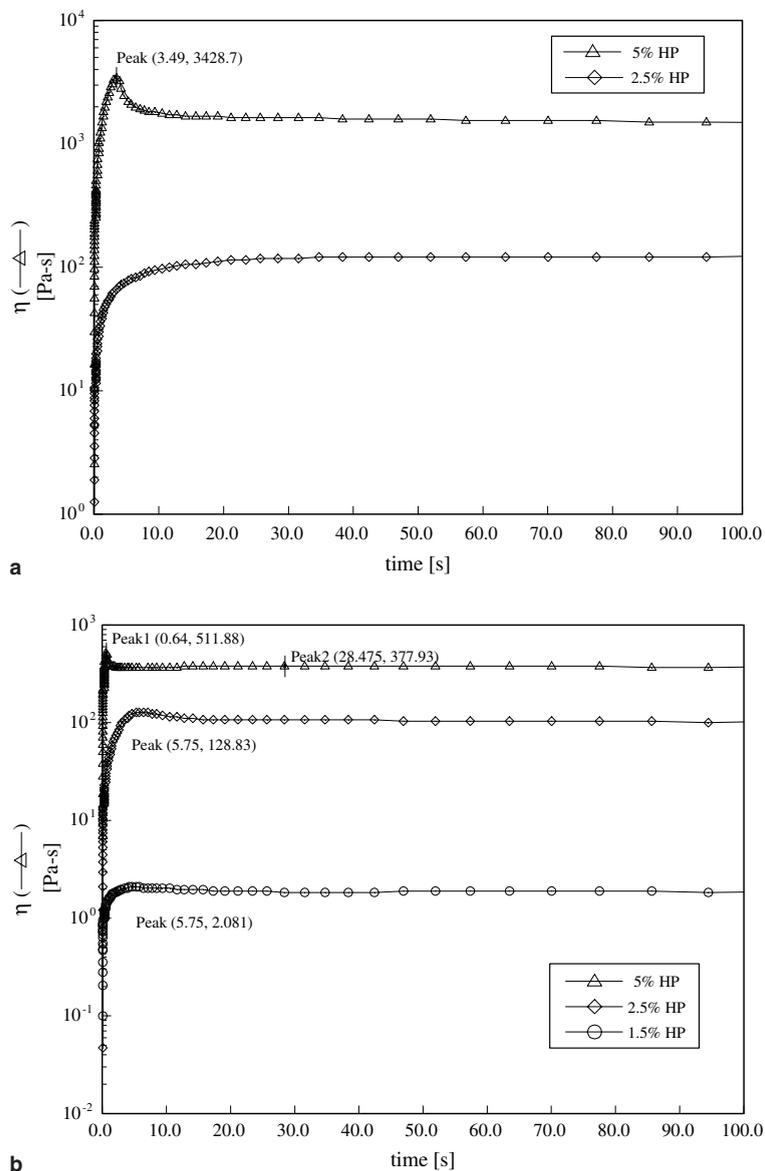

Fig. 9. (a) $\eta(t)$ for the 5% solution at different HP content ($\dot{\gamma} = 0.1\ s^{-1}$) and (b) $\eta(t)$ for the 5% solution at different HP content ($\dot{\gamma} = 1.0\ s^{-1}$).

decrease in viscosity. Increased shear rate disrupts the intermolecular network of the high HP content system. Low HP polymers were less sensitive to shear. Again, this result supports the previous observations on the strong shear thinning of the high HP polymer obtained from dynamic shear measurements.

Fig. 9a,b present similar results for the 5% solution as a function of HP content. The 5% HP content sample yields significantly higher viscosity at both shear rates used in the experiment. As the shear rate increases from 0.1 to $1.0\ \mathrm{s}^{-1}$, the viscosity of the 5% HP content system decreases from 3428 Pa s to 511 Pa s. On the other hand, the viscosity of the 2.5% HP content system remains almost unchanged. Since, elastic response dominates in the 5% HP content sample (see Fig. 4), increased shear rate influences the viscosity of the system by breaking network structure and eventually decreases the viscosity of the system. It was interestingly observed in Fig. 8b that at $1.0\ \mathrm{s}^{-1}$ shear rate the 5% solution of the 5% HP content system yields two peaks. This double yield phenomenon was previously reported for structured materials such as liquid crystalline polymers that have equally complex rheology.

4. Conclusion

Rheological properties of a copolymer of SO_2, N,N-diallyl-N-carboethoxymethylammonium chloride and the hydrophobic monomer N,N-diallyl-N-octadecylammonium chloride were measured. Both dynamic and steady-shear measurements were performed. Dynamic viscosity and storage modulus increased significantly with increasing both polymer concentration and HP content of the polymer system. At high HP content (5%), G' was found to be independent of frequency and the polymer solution behaved like a gel ($G' \gg G''$). The shear dependence of the dynamic viscosity increases with increasing both HP content and polymer concentration. The system containing moderate percentages of HP (2.5%) behaves like a liquid ($G'' > G'$) at very low frequency and later a crossover point ($G'' = G' = G_c$) was observed. Crossover points shift to the higher frequency with decreasing polymer concentration. At low concentration (2%), the system shows typical Newtonian behavior over the entire frequency domain (0.1–100 rad/s).

Dynamic viscosity data fits perfectly to Ellis model leading to zero-shear viscosity, η_0, which was found to be a strong function of polymer concentration. The concentration dependency of η_0 ($\eta_0 \sim \phi^\alpha$ with $1.1 < \alpha < 5.9$) indicated intermolecular association [22]. Steady-shear viscosity was found to be appreciably high (order of 3 kPa) for the high HP content system. With increasing shear rate, η of the 5% HP content sample decreases significantly while the shear viscosity of the low HP content

polymer remains almost unchanged. Steady-shear experiments were also used to estimate the time needed to reach the steady-state. Both dynamic and steady-shear measurements suggest that relaxation time increases with increasing HP content and polymer concentration.

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