

Non-linear shear deformation of hydrophobically modified polyelectrolyte systems

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Abstract

The shear imposed oscillation technique was employed to probe the shear-induced structural changes of 3 wt% hydrophobically modified polyelectrolyte solutions that possess shear-thinning and shear-thickening behavior. The shear-thickening behavior is related to the transformation of predominantly intra-molecular to inter-molecular associations. On the other hand, the shear-thinning behavior under moderate shear deformation is caused by the re-organization of the transient network structure. Under high shear deformation, the shear-thinning behavior is solely caused by the shear-induced effect that increases the chain-end exit rate, which reduces the mechanically active chains and lifetime of the hydrophobe in the micellar junctions.

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1. Introduction

Hydrophobically modified alkali-soluble emulsion (HASE) polymers have received considerable attention in recent years [1–12]. This class of hydrophobically modified anionic polyelectrolyte system is prepared by emulsion polymerization at low pH to yield an acid-rich co-polymer in the form of a dispersion of latex particles. Each particle may contain as many as 10–50 polymer chains. When a base is added to the dispersion, the –COOH groups of the polymer are neutralized. The particles swell and dissolve, releasing charged polymeric chains into the solution [12]. The polymer solution thickens by an associative mechanism (intra- or inter-molecular) and by the expansion of the high-molecular-weight polymer backbone [7,10]. The creation of the polymer network commences when the hydrophobes attached to its polymer backbone begin to associate, which produces a network structure consisting of numerous polymeric chains.

The grafting of hydrophobic groups to the water-soluble polymer backbone enhances the rheological properties when compared to those without hydrophobic groups. The increase in the viscosity profile is caused by the self-association of the hydrophobic groups, yielding inter-molecular networks in solution [11,13–17]. Volpert et al. [18] and Aubry and Moan [19] observed lower rheological properties for the modified hydrophobic system at low polymer concentrations. They attributed this behavior to the formation of intra-molecular associations between the hydrophobes along the same polymer chain. As a result, the dimension of the polymer coil is reduced, yielding a lower radius of gyration that corresponds to a lower viscosity.

The structure of the associative polymer with hydrophobes attached as pendant side chain is much more complex when compared to end-capped hydrophobic systems. This is due to the steric hindrance of the polymer backbone that prevents the formation of hydrophobic junctions, yielding hydrophobic junctions/clusters with a poly-dispersed aggregation number [8,14,20–23]. On the other hand, the comb-type polymer exhibits a better viscosity enhancement than the end-capped

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system [21,24]. This is because the combed system is more efficient in creating bridges between micelles, yielding larger number of inter-molecular associative junctions compared to HEUR system. Moreover, the rheological properties of the associative polymer can be further enhanced by the extension of the branched alkyl chain and by increasing the hydrophobicity of the hydrophobic moieties [20,25–27]. This will slow down the dynamic exchange rate between the micellar junctions, which increases the relaxation time of the polymer system. Leibler et al. [28] presented a relaxation model of a polymer system with reversible network, where the relaxation behavior was divided into two different processes. The slower process is related to the reptation motion of polymer chains by coherent breaking of a few cross-links at a time, which is dependent on the degree of association, while the faster process is due to the relaxation of segments between entanglement points and related to the average lifetime of the association.

As a result of the hydrophobic side chain, which gives rise to multiple relaxation times, the polymer system can no longer be described by a single Maxwell model. Therefore, the prediction of the lifetime of the polymer using the dynamic cross-over frequency and onset of steady rate viscosity may not be applicable [19]. Alternative technique for determining the characteristic lifetimes of the comb polymer is to measure N_1 (first Normal stress) at low shear [21] and the relaxation time was calculated to be ~ 0.01 s. Recent studies by Tirtaatmadja et al. [20] and Seng et al. [29] showed that with the addition of non-ionic surfactant, a sharp discontinuity in viscosity was observed at high shear stresses. The shear-thickening behavior observed is commonly due to (i) the stretching of elastic polymeric segments beyond its linear viscoelastic region [1], (ii) a change from intra-molecular to inter-molecular hydrophobic association brought about by the unfolding of polymer chains at high shear rates [2,18,29], (iii) dangling segments being recaptured by the network before they have the opportunity to fully relax to the equilibrium state [10,30]. The shear-thinning is generally believed to be caused by shear-induced disruption of the network formed by the weak associating hydrophobic groups.

The viscoelasticity of the polymer can be differentiated into two regions, linear and non-linear viscoelastic regions. On application of a small strain, $\gamma < \gamma_c$, the relaxation modulus will collapse onto a master curve indicating linear viscoelastic behavior. Often, the master curve may be obtained by shifting the horizontal and vertical axes. As the applied strain is larger than the critical strain, $\gamma > \gamma_c$, the relaxation modulus is no longer independent of strain yielding the non-linear viscoelastic behavior. If the stress relaxation modulus in the non-linear behavior is parallel to those in the linear viscoelastic region, it means that the time dependence of $\tau(\gamma, t)$ is factorable from the strain dependence [31,32],

$$\tau(\gamma, t) = G_o(t)h(\gamma)\gamma$$

$$G(\gamma, t) = G_o(t)h(\gamma) \quad (1)$$

where $h(\gamma)$ is the damping coefficient (shift factor) at strain γ , $G_o(t)$ is the relaxation modulus in linear viscoelastic region.

The structural behaviors of the associative polymers under the application of shear and strain deformations were investigated using the superposition of oscillation on steady shear flow and stress relaxation. Such information provides insights into the structure under deformation that is relevant to many processes. The polymer systems used are 3 wt% HASE05-20 and HASE40-20. These polymers were chosen because they exhibit different shear deformation behaviors. HASE05-20 exhibits a continuous shear-thinning behavior while HASE40-20 possesses shear-thickening behavior at moderate shear rate.

2. Experimental

The model associative polymers studied are hydrophobically modified, alkali-soluble (HASE) polymers synthesized by Dow Chemicals (formerly Union Carbide), via the emulsion polymerization of methacrylic acid (MAA), ethyl acrylate (EA) and a macromonomer that had been capped with a hydrophobic group. The polymer examined in the present work has a chemical structure shown in Fig. 1, where R is C_nH_{2n+1} alkyl chain, and the ratio of $x:y:z$ in mol% is 50:49:1.

The polymer examined is designated as HASE05-20 and HASE40-20, where the ethylene-oxide spacer chain length of HASE40-20 is 40 mol while HASE05-20 is 5 mol. The hydrophobes of the polymers consist of the $C_{20}H_{41}$ alkyl chain. A brief description of the synthetic route of the model polymer has been previously reported [1,3] and will not be presented here. It has an average molecular weight of approximately 200,000–250,000 g/mol determined by intrinsic viscosity [2] and static light scattering measurements [33,34]. The molecular weight and monomer sequence distribution of these polymers are believed to be quite similar since the process used to produce them was held constant [34]. Recently, Sprong and co-workers synthesized HASE polymers with well-controlled molar masses and narrow molar mass distributions using the reversible addition–fragmentation chain transfer

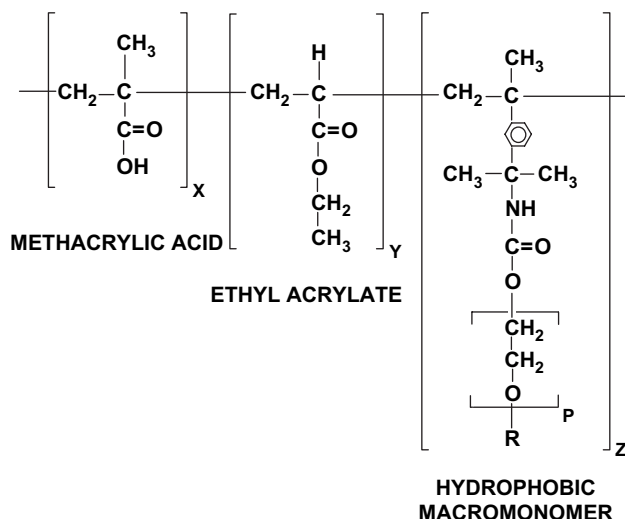


Fig. 1. Chemical structure of model HASE polymers.

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