Shear Thickening in Aqueous Solutions of Hydrocarbon End-Capped Poly(ethylene oxide)

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ABSTRACT: The shear thickening behavior in aqueous solutions of model hydrophobically end-capped poly(ethylene oxide) was examined. Poly(ethylene oxide) fully end-capped with C_{12}, C_{16}, or C_{18} alkanes was prepared by direct addition of monoisocyanate to poly(ethylene glycol). The response of these polymers in aqueous solution to both steady shear and oscillatory shear was determined. The effects of polymer concentration, temperature, association strength, and polymer chain length on shear thickening have been investigated. PEO with higher molecular weight (35 000) shows only shear thinning behavior whereas PEOs with lower molecular weights (10 000 and 20 000) show mild shear thickening over a range of concentrations. The magnitude of shear thickening was found to increase with association strength and to decrease with temperature. The critical shear rate at which onset of shear thickening occurs shifted to lower shear rate as the association strength or concentration increases or as temperature decreases. The scaling factors of the magnitude of shear thickening, the critical shear rate, and the critical shear stress have been interpreted in terms of the free path model proposed by Marrucci et al.,[1] which suggests that shear thickening is due to non-Gaussian chain stretching and fast recapture of dissociated end groups.

Introduction

Over the past decade, associating polymers have attracted widespread interest both theoretically and experimentally. Winnik and Yekta[2] gave a detailed survey of literature on this subject in a recent review. Associating polymers are polymers that contain a small amount of functional groups that are capable of forming multiplets or clusters in a selective solvent. These materials are industrially important since they can be tailored to exhibit specific rheological properties and have found wide applications in coatings, paper manufacture, oil production and transportation, water treatments, and thickeners for food and health care products.

Not only do associating polymers find wide industrial applications, such polymers are also ideal systems for fundamental studies, especially telelchelic associating polymers, where associating groups are located only at both ends of the polymer chain. One class of polymers which is of particular interest is telechelic hydrophobically modified poly(ethylene oxide). These polymers consist of poly(ethylene oxide) end-capped with a long hydrocarbon or fluorocarbon alkyl chain. Aqueous solutions of these polymers often show enhanced zero-shear viscosity and elastic behavior. Under flow, the solution exhibits Newtonian behavior at low shear rates (i.e., viscosity is independent of shear rate). Above some critical shear rate, the solution shows shear thickening behavior (i.e., viscosity increases with shear rate), and then at higher shear rates, the solution shows shear thinning behavior. Compared to the complex flow properties, the viscoelastic response of these materials is relatively simple. In general, they can be described by the Maxwell model, using one or two relaxation times.[3,4]

It is generally accepted that the unusual rheological properties of associating polymers originate from the formation of a physically cross-linked network. When the water-soluble polymer chain has a hydrophobic moiety along the backbone, the hydrophobic groups aggregate into micelles at very low concentration in the same way as surfactants do. If each polymer chain contains at least two associating groups, at sufficiently high concentration, a three-dimensional transient network is formed by bridging the neighboring micelles, in which junctions continuously break and recombine in thermal fluctuations. Not all of the polymer chains participate in bridge formation. A significant fraction of the polymers are looped, with both hydrophobic chain ends located in the same micelle. These looped chains are assumed to be mechanically inactive. Although the structure of associating polymers in solution has been extensively studied by various scattering and spectroscopy methods,[5−8] there is still a dearth of information concerning the size, the shape, and the connectivity of the micelle-like hydrophobic microdomains that function as dynamic cross-links in the transient network.

The rheological behavior of associating polymers is often interpreted using transient network models. Two clearly distinct categories of systems have been considered. The first describes unentangled networks in which the molecular weight between neighboring junctions is smaller than the entanglement molecular weight so that each chain obeys Rouse dynamics modified by sticky trapping centers.[9] The second model is meant for entangled networks made up of linear chains with many temporary cross-links. The chain motion is described by a sticky reptation controlled by the concentration and the lifetime of junctions.[10] Recently, Pham et al. used an adhesive hard-sphere model together with the entropic attraction between micelles to interpret the association and rheology of aqueous solutions of associating polymers.[11,12]

Shear-thickening behavior has been reported in associating polymer solutions since the 1950s and has attracted considerable attention in recent years. Despite such efforts, the molecular origin of shear thickening remains a subject of controversy. Although different mechanisms have been proposed to account for shear

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thickening behavior in associating polymer solutions, there has been little effort made to quantitatively compare experimental data to the predictions of the various theories.

Most of studies on shear thickening of associating polymer solutions have been focused on ionomers in nonpolar solvents since they exhibit large shear thickening effects.[13−18] Bhargava and Cooper studied the effect of water on magnesium neutralized dicarboxypolybutadiene in toluene.[17] The study has shown that the rheological behavior of this system is profoundly influenced by moisture content. For example, a content of 300 ppm of water reduces the zero-shear viscosity by 2 orders of magnitude. The onset of shear thickening shifts to a lower shear rate, and the magnitude of shear thickening is reduced as well. Since water is always present at the time of neutralization and can be easily absorbed from the atmosphere, their study suggests that ionomers in nonpolar solvents are difficult systems to study. An alternative candidate for the study of shear thickening is the hydrophobically modified water-soluble associating polymer in aqueous solution. It has been reported that mild shear thickening was observed in hydrophobically modified ethoxylated urethanes (HEURs) in aqueous solutions.[3,19−22] The drawback of this system is that the association strength is much weaker compared to that of ionomer solutions due to the intrinsically weaker hydrophobic interactions, and consequently only mild shear thickening is observed over a limited concentration range.

In this paper, the shear thickening behavior of hydrocarbon end-capped PEO in aqueous solutions is described. The experimental results are compared to the free path model proposed by Marrucci et al.[1] which suggests that shear thickening is due to non-Gaussian chain stretching and fast recapture of dissociated end groups. In the following section, different theories that have been proposed to explain shear thickening are briefly reviewed.

Shear Thickening Theory

Although rarely observed in common polymer melts or solutions, shear thickening effects have been observed in complex fluids including dense suspensions, wormlike micelles, and associating polymers solutions. The shear thickening seems to be caused by shear-induced structural changes in all of these systems. However, despite this “universality”, the details of mechanism of shear thickening in various systems are quite different and often poorly understood.

Several theoretical models have been proposed to describe the shear thickening behavior in associating polymer solutions.[1,9,23−31] These theories differ in the mechanisms they propose for chain conformation or in how aggregation changes under deformation. They fall into three main categories: (1) shear-induced “cross-linking”, (2) shear-induced non-Gaussian chain stretching, and (3) network reorganization.

Witten and Cohen first proposed a mechanism of shear thickening in the framework of a mean-field approximation.[23] They showed in their calculation that the shear flow can increase the probability of interchain association at the expense of intrachain association, thus leading to the viscosity increase. Ballard et al. extended Flory’s theory of the expansion parameter to self-associating polymers and predicted that shear thickening will occur in a flow field of sufficiently high strain rate.[25] Their proposed mechanism for shear thickening is similar to that of Witten and Cohen. Wang[28] introduced free chains into the transient network model first proposed by Tanaka and Edwards[9,26,27] and predicted that shear thickening is the result of coagulation of free chains into the existing network.

Marrucci et al. explored the possibility of shear thickening as arising due to a non-Gaussian chain stretching effect.[1] On the basis of Tanaka and Edwards transient network model, they argued that under flow conditions polymer chains may elongate considerably, well into the non-Gaussian regime. By replacing the linear force law with an inverse Langevin function, small shear thickening was found as a result of non-Gaussian chain stretching.

In an extension, termed the free path model, Marrucci et al. further assumed that when the chain end dissociates from a network junction, it can only partially relax its extended conformation since it is soon recaptured by the network again. As a consequence, the maximum in the viscosity occurs at a critical shear rate when the ratio of the detachment frequency to the shear rate (which decreases monotonically with increasing shear rate) has not dropped to its asymptotic lower bound, and yet the polymer chains are already stretched close to their maximum extension. The tension in the highly stretched polymer chain is close to the highest value (nearly E/b, where E is the activation energy and b is the persistent length of polymer chain). The maximum in the viscosity is estimated to be higher by a factor of E/kT than the zero-shear viscosity. Van den Brule and Hoogerbrugge formulated a Brownian dynamics simulation of reversible polymeric networks, taking the topology of the network into account.[31] It was found that significant shear thickening can occur if dangling segments are recaptured by the network before they had the opportunity to fully relax to the equilibrium state, even in systems with Gaussian chains and fixed association and dissociation rates.

The experimental data that could quantitatively support various theories are scarce, and therefore the actual mechanisms that lead to the observed behavior are still unknown. Success in the development of an accurate analytical description of the shear-thickening phenomenon lies in closer examination of the existing experimental data and further experimental data collection. In the following sections, a systematic study on hydrophobically end-capped poly(ethylene oxide) (PEO) in aqueous solution is reported and quantitatively compared to the free path model’s predictions.

Experimental Section

Materials. Hydroxyl-terminated poly(ethylene glycol)s (PEG) were obtained with molecular weights of 10 000, 20 000 (Shearwater Polymers, Inc.), and 35 000 (Fluka) with polydispersity of 1.02, 1.03, and 1.15, respectively. Three hydrophobic end groups—dodecyl isocyanate ($C_{12}H_{25}NCO$), hexadecyl isocyanate ($C_{16}H_{33}NCO$), and octadecyl isocyanate ($C_{18}H_{37}NCO$) (Aldrich)—were used without any further purification. Anhydrous chloroform ($CHCl_3$, Aldrich) was distilled through calcium hydride (CaH_2, Aldrich).

Synthesis of the Model System. Detailed discussion on synthesis of hydrophobically modified PEO has been reviewed elsewhere.[32] In this study, we chose the direct addition of monoisocyanate to guarantee the telechelic structure (shown in Figure 1). Although the reaction involves straightforward urethane chemistry, the quantitative reaction of an exact stoichiometric amount of PEG and monoisocyanate is difficult to achieve due to the large difference in molecular weights of

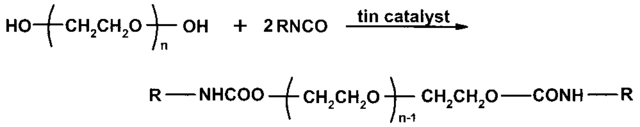

Figure 1. Synthesis of telechelic hydrophobically end-capped PEO.

Table 1. Extent of End-Capping Efficiency (^{1}H NMR)

PEOs	end group	designation	$(CH_2)/(OCH_2CH_2)$ theor	$(CH_2)/(OCH_2CH_2)$ exptl	hydrophobe per chain
PEO(10K)	$C_{18}H_{37}$	PEO(10K)-C18	0.0704	0.0698	1.98
PEO(20K)	$C_{18}H_{37}$	PEO(20K)-C18	0.0352	0.0354	2.00
PEO(35K)	$C_{18}H_{37}$	PEO(35K)-C18	0.0201	0.0201	2.00
PEO(10K)	$C_{16}H_{33}$	PEO(10K)-C16	0.0616	0.0618	2.00
PEO(20K)	$C_{16}H_{33}$	PEO(20K)-C16	0.0308	0.0302	1.96
PEO(35K)	$C_{16}H_{33}$	PEO(35K)-C16	0.0176	0.0193	2.00
PEO(10K)	$C_{12}H_{25}$	PEO(10K)-C12	0.0440	0.0439	1.99
PEO(20K)	$C_{12}H_{25}$	PEO(20K)-C12	0.0220	0.0222	2.00

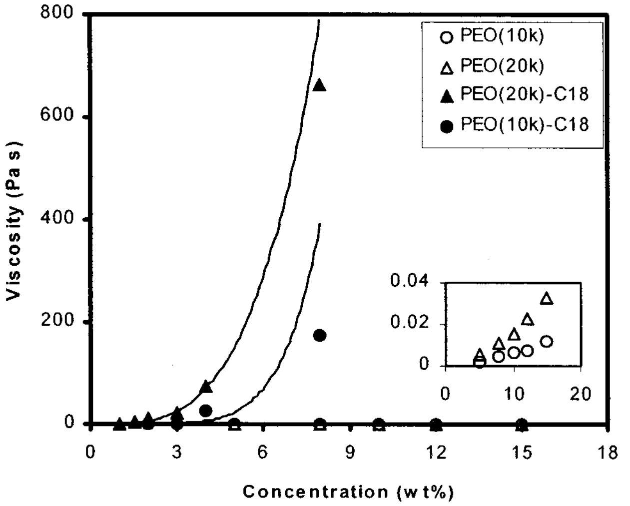

Figure 2. Concentration dependence of zero-shear viscosity of hydrophobically end-capped PEOs (PEO(10K)-C18 and PEO(20K)-C18) and unmodified PEOs with the same molecular weight. The inset shows the same data for unmodified PEOs.

the two reactants. Another complicating factor is the side reaction of isocyanate functional group with water. Water readily reacts with isocyanate group to form amine, and amine can further react with isocyanate to form urea. The hygroscopic nature of PEG and water tightly bound to the PEG chain makes it difficult to have a completely moisture-free reaction environment. Precautions were taken to eliminate the moisture in the reaction system as much as possible. These include (1) vacuum-drying PEG above its melting temperature overnight, (2) freshly distilling the solvent through calcium hydride (CaH_2, Aldrich), and (3) purging the reaction with dry argon. All other chemicals are used as received. The general procedure of making hydrocarbon end-capped PEO is as follows.

Predried PEG was dissolved into dry $CHCl_3$ (freshly distilled thorough CaH_2) at concentration of 10 wt %. The solution was heated in a water bath at 60 °C. When PEG was completely dissolved into $CHCl_3$, a stoichiometric amount of monoisocyanate RNCO (where R = $C_{12}H_{25}$−, $C_{16}H_{33}$−, or $C_{18}H_{37}$−) was added to the mixture. Ten drops of dibutyltin laurate (Aldrich) was then added as catalyst. The reaction mixture was purged by dry argon throughout the reaction. After 12 h, 3 times the stoichiometric amount of monoisocyanate was added to the reaction mixture again. An addition of the large excess of monoisocyanate ensured 100% end-capping. The reaction was kept at 60 °C for another 24 h.

Purification and Characterization of the Model System. The product was precipitated into an excess of hexane. The white powder like precipitate was then filtered and dried under vacuum. The white powder was then redissolved into warm acetone. The solution was filtered through a 1 μm syringe filter and slowly precipitated into hexane again. The second step was repeated several times until the desired purity was achieved. The aqueous solution of the final product was optically clear. Purified polymer was stored in the refrigerator to minimize air oxidation.

The end-capping efficiency was determined from ^{1}H NMR spectrum (δ = 0.8, hydrophobe methyl group; δ = 1.2, hydrophobe methylene groups; δ = 3.6, oxyethylene methylene group). The results are summarized in Table 1. ^{1}H NMR experimental results indicate that each polymer chain contained two hydrophobes. It should be noted that for the higher molecular weight, because the molar ratio of proton in hydrophobe and polymer monomer unit is so small, there is some uncertainty in the end-capping efficiency.

Sample Preparation. Aqueous solutions of hydrocarbon end-capped PEO at different concentration levels were prepared by directly dissolving a known amount of polymer into deionized distilled H_2O. Each solution was gently stirred until the solution was homogeneous. If the viscosity of solution was too high to be efficiently stirred, it was gently rotated for 2 or 3 days, depending on the viscosity.

Rheological Measurements. The rheological properties of the polymer solutions were measured using a Bohlin VOR strain-controlled rheometer with a Couette flow geometry (C14, 14 mm o.d. with a gap of 1 mm) or cone-and-plate (CP5/30, 3 cm, 5° cone) at temperatures ranging from 5 to 40 °C. Both steady and oscillatory shear tests were conducted on freshly made samples at each temperature. An hour was given to reach thermal equilibrium at each temperature. A standard procedure was used for all rheological measurements. After loading, the sample was sheared at 1 s^{-1} for 2 min, followed by 15 min of rest. This preconditioning procedure ensured that all samples have the same shear history. A strain sweep experiment was performed prior to each oscillatory experiment to determine the linear viscoelasticity regime. For the steady shear experiment, an equilibration time of 90 s was given at each shear rate to allow the system to reach steady state.

Results

General Observations. It is well-known that the solution viscosity of telechelic hydrophobically end-capped PEO is much higher than that of an unmodified PEO solution at the same concentration and depends strongly on the polymer concentration. Figure 2 shows typical viscosity−concentration profiles for octadecyl end-capped PEOs in water at 20 °C. The solution viscosities of PEO(10K)-C18 and PEO(20K)-C18 are about 4 orders of magnitude higher than those of unmodified PEOs with the same molecular weight and increases exponentially with concentration, in contrast to the linear dependence for the unmodified PEO. A similar trend was observed in hexadecyl end-capped PEOs as well. This large viscosity enhancement is convincing evidence of the association of the hydrophobic end groups in water.

Figure 3 shows a typical viscosity profile for a 3 wt % aqueous solution of PEO(10K)-C18 as a function of shear rate. Although the steady shear viscosity of unmodified PEO is independent of shear rate, three regimes can be identified in the shear response of the hydrophobically end-capped PEO solution. Below a characteristic shear rate ($\dot{\gamma}_{crit}$), viscosity is independent of shear rate (Newtonian regime). Above $\dot{\gamma}_{crit}$, viscosity increases with shear rate (shear thickening regime), until it reaches a maximum at another characteristic shear rate ($\dot{\gamma}_{cross}$). Above $\dot{\gamma}_{cross}$, viscosity rapidly decreases with shear rate (shear thinning regime).

It is worth noting that the whole spectrum of shear response shown in Figure 3 can only be obtained if the

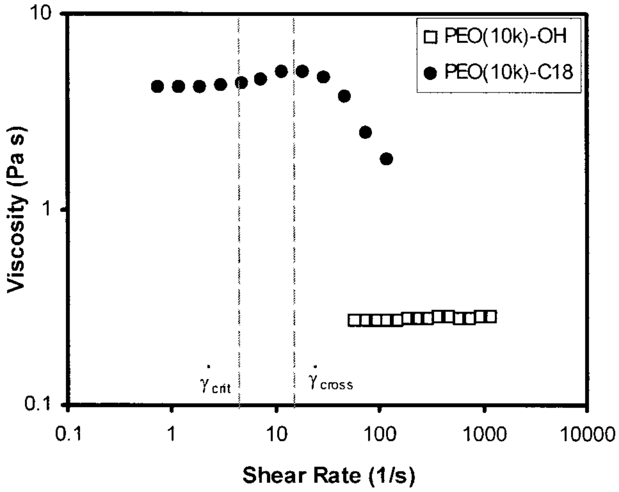

Figure 3. Steady shear viscosity as a function of shear rate for a 3 wt % aqueous solution of PEO(10K)-C18 at 15 °C. The open symbols are an 8 wt % aqueous solution of unmodified PEO at the same molecular weight (unmodified PEO has been scaled up by a factor of 100).

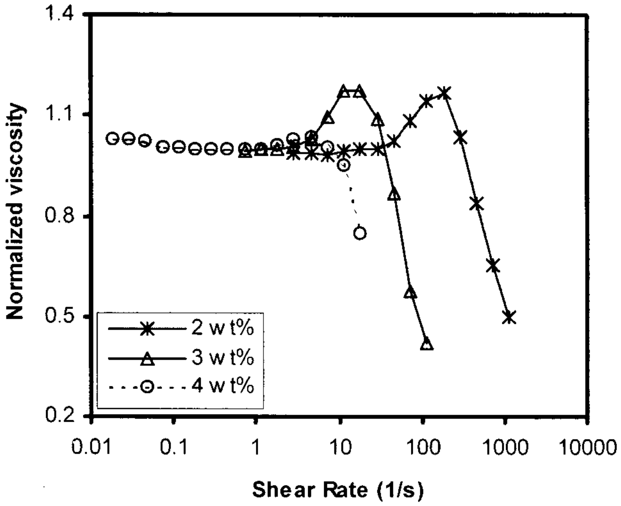

Figure 4. Effect of concentration on shear thickening of PEO (10K)-C18 at 15 °C. The viscosity is normalized by the zero-shear viscosity.

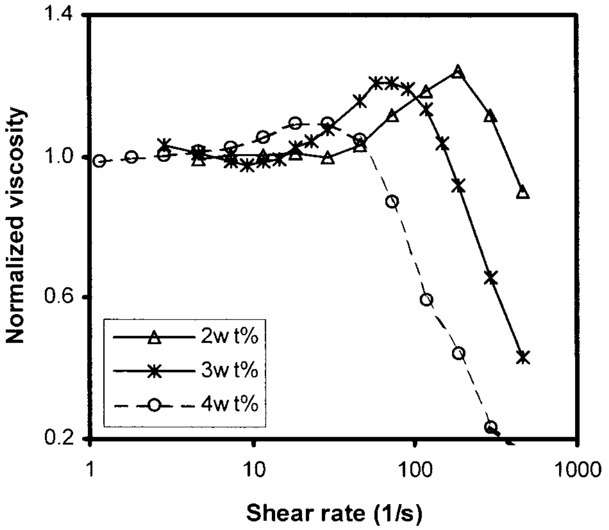

Figure 5. Effect of concentration on shear thickening of PEO (20K)-C18 at 15 °C. The viscosity is normalized by the zero-shear viscosity.

available rheometer covers the appropriate range of shear rates and torques. At higher concentration, the viscosity of solution becomes so high that shear thickening and/or shear thinning regime is not accessible due to either the limitation of torques available to rheometer or the onset of flow instability. Even though all the samples remain perfectly clear during and after shear, samples at higher concentration show the Weisenberg effect or fractures at high shear rates.

Effect of Concentration. Figure 4 shows viscosity profile of PEO(10K)-C18 at three concentrations. As concentration increases, the onset of shear thickening and shear thinning shift to the lower shear rates. The magnitude of shear thickening does not appear to have a strong dependence on concentration. Similar behavior was observed for PEO(20K)-C18 (Figure 5).

Shear thickening behavior was also reported in telechelic ionomers in nonpolar solvents. The two systems behave qualitatively in a similar fashion. As concentration increases, both systems show a viscosity enhancement and a shift to lower shear rates for the onset of shear thickening and shear thinning. However, the shear thickening effect is much more pronounced in ionomer solutions. Some ionomer solutions flow when gently rocked but form gels when vigorously shaken.[33] The shear thickening behavior of telechelic ionomer solutions was also reported to depend strongly on polymer concentration. Maus et al. have reported that the magnitude of shear thickening increased by a factor of 2 when concentration increased from 2.51 to 2.56 g dL^{-1} for magnesium neutralized carboxylatopolyisoprene in toluene.[16] However, this apparent strong effect of polymer concentration might be combining effects of polymer concentration and moisture content, since the rheological experiments reported above were not conducted in a moisture-controlled environment.

Shear thickening was also observed in a hydrophobically modified alkali-swellable polymer (HASE) system.[34] An alkali-swellable associating polymer is a hydrophobically modified carboxylic acid containing copolymer, with a molecular weight of usually several hundred thousand, which swells in aqueous media upon neutralization. The hydrophobes are usually randomly distributed along the polymer backbone. The shear thickening effect is weaker than that observed in hydrophobically end-capped PEO, primarily due to the competing effect of topological entanglement and hydrophobic association at moderate shear rates. English et al. have studied the solution behavior of comblike HASE polymers.[34] Using fluorescence measurements, they showed evidence of a shear-induced structuring associated with shear thickening at low polymer concentrations. However, as concentration increases, intermolecular interactions dominate, and shear-induced transition from intra- to intermolecular association no longer plays an important role in shear thickening.

Effect of Temperature. Figures 6 and 7 show the steady shear viscosity profiles of 2 wt % of octadecyl end-capped PEO solutions with molecular weight of 10 000 and 20 000 at different temperatures. Similar effects were observed: the zero-shear viscosity increases with decreasing temperature, and the shear thickening as well as shear thinning occurs at lower shear rates. In addition, the magnitude of shear thickening increases as temperature decreases.

As temperature increases, the network junctions become weaker, and the hydrophobic end groups dissociate from the junctions more easily. As a result, the

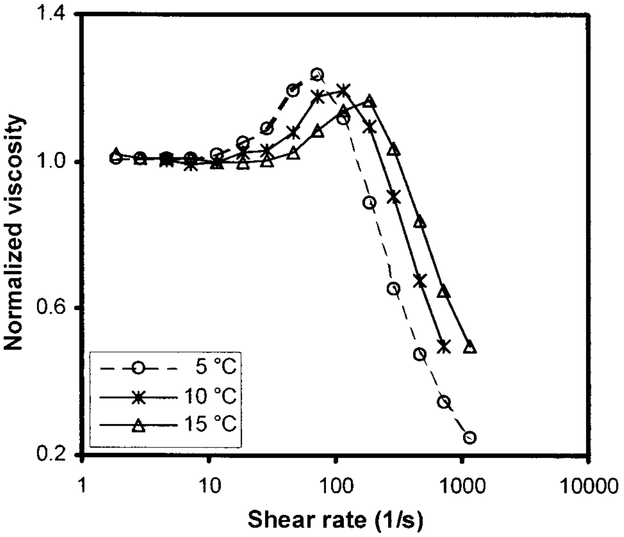

Figure 6. Effect of temperature on shear thickening of PEO(10K)-C18 at 2 wt %. The viscosity is normalized by the zero-shear viscosity.

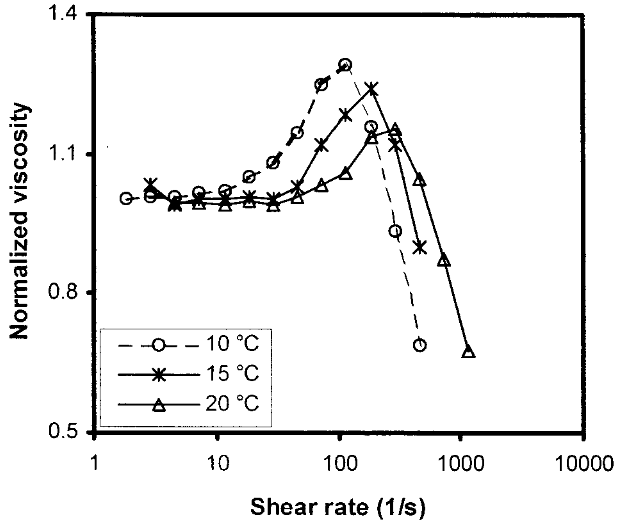

Figure 7. Effect of temperature on shear thickening of PEO(20K)-C18 at 2 wt %. The viscosity is normalized by the zero-shear viscosity.

network relaxation time decreases as well as the number of elastically active chains. For a system with a transient network, the viscosity is the product of plateau modulus and network relaxation time. Reduction in plateau modulus (or the number of elastically active chains) and network relaxation time will result in a reduction in zero-shear viscosity. Furthermore, as relaxation time decreases with increasing temperature, the shear rate at which the polymer chain reaches the non-Gaussian deformation increases. Thus, the onset of shear thickening shifts to higher shear rate as temperature increases.

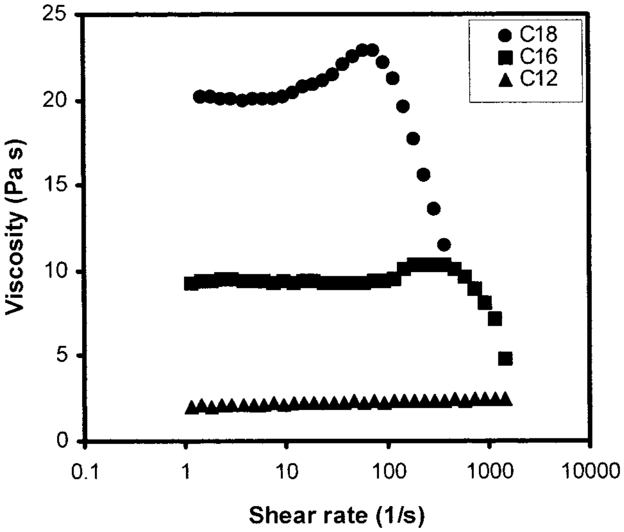

Figure 8. Effect of association strength (varied by changing the hydrophobe length) on shear thickening of hydrophobically end-capped PEO(20K) at 20 °C. The polymer concentrations were fixed at 2 wt %. For clarity, the viscosity of PEO(20K)-C18, PEO(20K)-C16, and PEO(20K)-C12 has been scaled up by a factor of 2, 10, and 100, respectively.

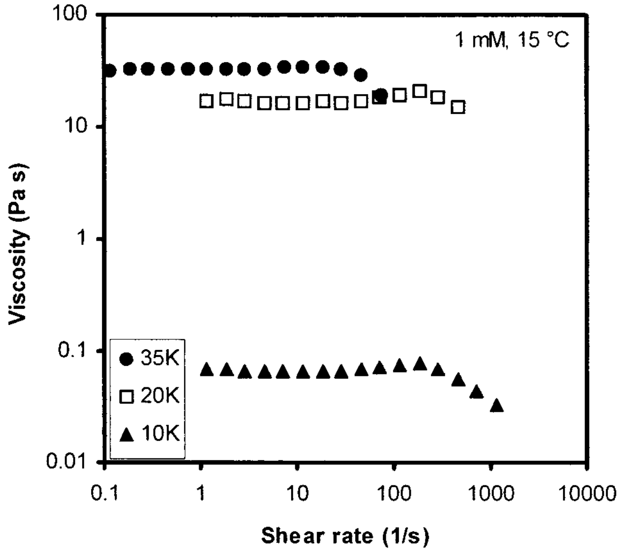

Figure 9. Effect of chain length on shear thickening of C18 end-capped PEO.

Effect of Association Strength. Association strength can be varied by changing the length of the hydrophobe. The greater the length of the hydrophobe, the stronger the association strength. In Figure 8, it shows that, by increasing six carbons in the hydrophobe, the zero-shear viscosity increases by nearly 2 orders of magnitude. For dodecyl end-capped PEO, there is no obvious shear thickening observed. As the association strength increases, as a result of a longer hydrophobe, significant shear thickening can be observed. As the association strength increases, the magnitude of shear thickening increases and onset of shear thickening shifts to lower shear rates since the relaxation time increases. Qualitatively, when the polymer chains are under shear, shear flow moves the junctions affinely, causing the elastically active chains to stretch. When the tension in the stretched chain reaches a critical value, the chain end dissociates from the junction, decreasing both the overall lifetime and number of elastically active chains. As a result, shear thinning occurs. To exhibit shear thickening, the association strength has to be strong enough to withstand the stress so that the polymer chain can be stretched into to the non-Gaussian regime.

Effect of Polymer Chain Length. Figure 9 shows the response of octadecyl end-capped PEO with various polymer chain lengths under steady shear. All systems show Newtonian behavior at low shear rates. At higher shear rates, the system with the longest chain (35 000) shows only shear thinning behavior, while shear thickening was observed in the polymers containing the

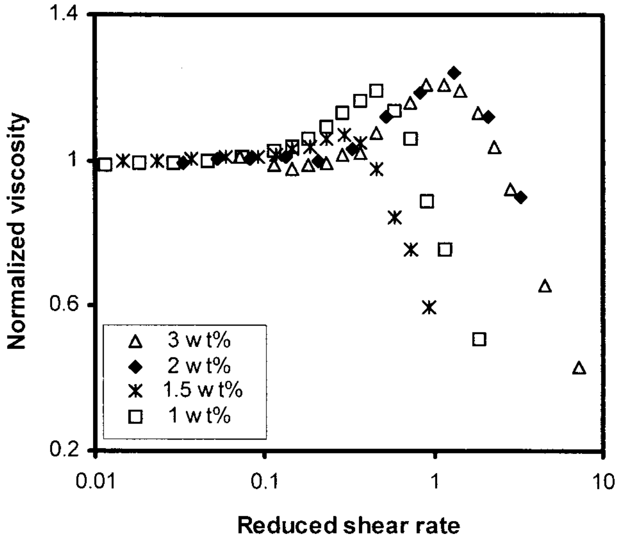

Figure 10. Shear thickening of PEO(20K)-C18 as a function of reduced shear rate at concentrations below and above the overlap concentration. The viscosity is normalized by the zero-shear viscosity.

shorter polymer chains (10 000, 20 000). This is qualitatively consistent with the non-Gaussian chain stretching as the origin of shear thickening. As the elastically active chain is being progressively stretched, a point will be reached where the linear force law no longer holds. Further stretching the chain requires an exceedingly large amount of work, and the system exhibits shear thickening. The longer the polymer chain is, the larger the deformation required to stretch the polymer chain into the non-Gaussian regime. The absence of shear thickening in the 35 000 samples may be due to insufficient deformation being applied to the system. The apparent shear thinning in these samples results from either the chain end being pulled out of the junctions at high deformation or the onset of flow instability. The same effect of polymer chain length was observed in similar systems (hexadecyl end-capped PEOs).[35]

Discussion

Critical Shear Rate. In the free path model, the critical shear rate is estimated assuming that the elastically active chains reach full extension at the onset of shear thickening.[1] The mean-square distance of the polymer chain is then on the order of molecular weight (N), and the critical shear rate is approximately

$$\dot{\gamma}_{\mathrm{crit}} \approx N^{1/2}/\tau \qquad (1)$$

where $\dot{\gamma}_{\mathrm{crit}}$ is critical shear rate (onset of shear thickening) and τ is the network relaxation time. The network relaxation time can be estimated by fitting dynamic experiment data to the Maxwell model with a single relaxation time. Since network relaxation time depends on concentration, temperature, and polymer chain length, the reduced shear rate ($\dot{\gamma}\tau$) is a better parameter to compare different systems. Figure 10 plots the viscosity of PEO(20K)-C18 as a function of reduced shear rate at four different concentrations. The critical reduced shear rate is about 0.2 for all concentrations above the overlap concentration (estimated to be ~2 wt %). At concentrations below the overlap concentration, the critical reduced shear rates are lower than those of solutions above overlap concentration. The plateau moduli of 1 and 1.5 wt % solutions from dynamic experiments indicate that less than 10% of chains are elastically active. This implies that below the overlap concentration the transient network has not yet fully developed, and shear thickening is more likely due to the shear-induced transition from intra- to intermolecular association. However, above the overlap concentration, where intermolecular association dominates, this mechanism no longer plays an important role, and the non-Gaussian chain stretching mechanism prevails.

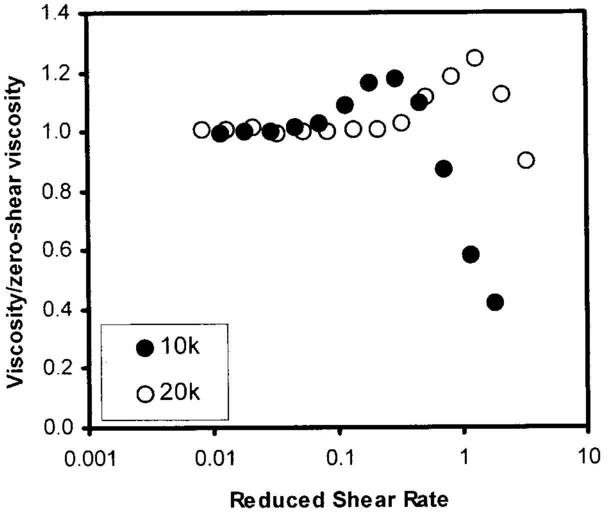

Figure 11. Effect of molecular weight on reduced critical shear rate.

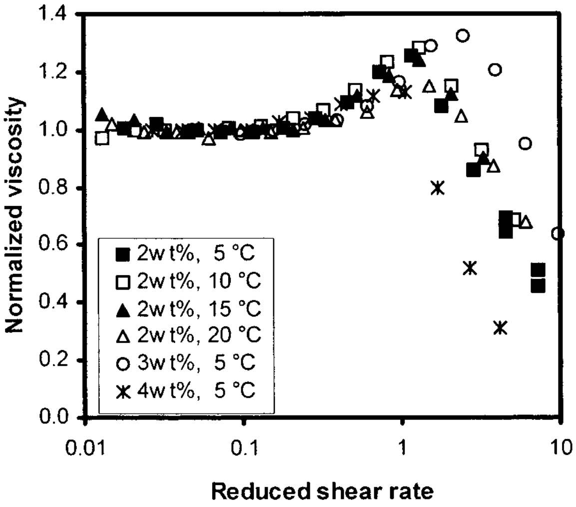

Figure 12. Shear thickening of PEO(20K)-C18 as a function of reduced shear rate.

For the non-Gaussian chain stretching mechanism, the critical reduced shear rate increases with molecular weight. Figure 11 shows viscosity as a function of the reduced shear rate. The viscosity is normalized by the zero-shear viscosity. It is clear that the critical reduced shear rate of lower molecular weight (PEO(10K)-C18) is smaller than that of higher molecular weight (PEO(20K)-C18).

For systems with the same molecular weight, the reduced critical shear rate should be roughly the same, regardless of concentration or temperature. Figure 12 plots the viscosity of PEO(20K)-C18 as a function of reduced shear rate at different concentrations and temperatures. As can be readily seen in Figure 12, the reduced critical shear rates are between 0.1 and 0.3 for all samples plotted.

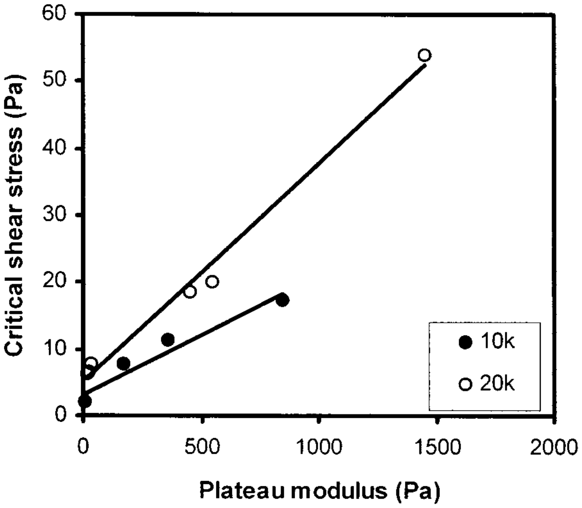

Figure 13. Effect of molecular weight on critical shear stress.

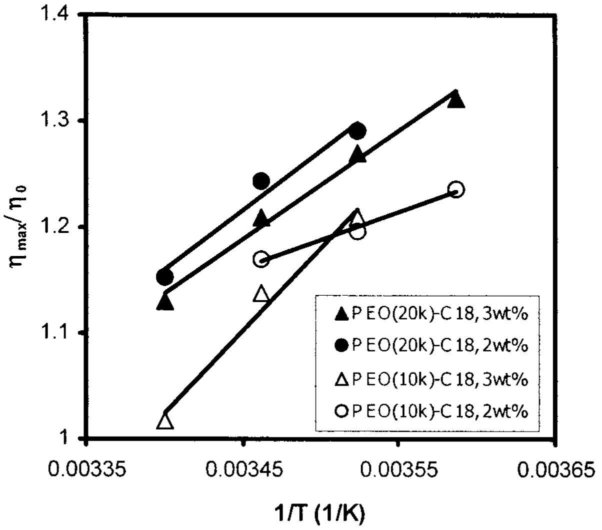

Figure 14. Effect of temperature on magnitude of shear thickening.

Critical Shear Stress. In the free path model, the critical shear stress is estimated to be

$$\sigma_{\mathrm{crit}} \approx \nu k T N^{1/2} = G_{\infty} N^{1/2} \tag{2}$$

where ν is the number of elastically active chains. The latter equality is based on simple rubber elasticity.[36] Figure 13 plots the critical shear stress as a function of plateau modulus at two different molecular weights. For the same molecular weight, σ_{crit} linearly increases with the plateau modulus. At comparable plateau modulus, σ_{crit} of PEO(20K)-C18 is larger than that of PEO(10K)-C18 as predicted in eq 2.

Magnitude of Shear Thickening. The free path model predicts that the viscosity attains a maximum value given by

$$\eta_{\max} \approx \nu E \tau = \frac{E}{kT}\eta_0 \tag{3}$$

where E is the activation energy. The value of the viscosity maximum depends directly on the energy barrier E/kT. Figure 14 plots the magnitude of shear thickening ($\eta_{\max}/\eta_0$) against $1/T$. A linear relationship was observed, and the activation energy estimated from the slope is similar to the value estimated from the relaxation time.

In summary, our experimental results are consistent with the free path model, where shear thickening is due to the non-Gaussian chain stretching. It should be noted that the rheological experiments do not give direct evidence of chain stretching. Such evidence can be obtained through flow birefringence. Chassenieux et al. have studied the solution of lithium neutralized sulfonatopolystyrene in toluene.[18] It was found that the onset of shear thickening is associated with a strong increase of birefringence. Taking into account the fraction of looped chains, the chain extension ratio was estimated on the order of 4 for the bridging chains.

Another system that forms similar structure as in the aqueous solution of hydrophobically end-capped PEO is suspensions flocculated by reversible bridging of polymer with weak affinity to the particle surface. Otsubo has studied suspensions of styrene−methyl acrylate compolymer particles with poly(acrylic acid).[37] The suspensions also show shear thickening in a narrow range of shear rates. It was found that the flexible bridges are fully extended, and the critical strain is approximately constant at the onset of shear thickening. The shear thickening was thus attributed to the nonlinear elasticity due to the entropy effect of extended polymer bridges. Using a nonlinear viscoelastic model with a single relaxation time, Otsubo was able to describe the main features of shear thickening behavior observed in the experiment.

Conclusions

The effect of deformation on the structure and chain stretching of hydrophobically end-capped PEO in aqueous solution was investigated through rheological studies. Effects of concentration, temperature, association strength, and polymer chain length on shear thickening were studied and compared to the free path model proposed by Marrucci et al. Hydrophobically end-capped PEO of high molecular weight (35 000) shows only shear thinning behavior whereas PEO of lower molecular weights (10 000, 20 000) shows mild shear thickening over a range of concentrations. The onset of shear thickening decreases with concentration as predicted by theory of Marrucci et al. Longer polymer chains or larger distances between junctions requires larger deformation (or higher shear rate) to stretch the chain into the non-Gaussian regime, in which the shear thickening effect is observable. Higher shear rates however tend to destroy the transient network, resulting in shear thinning behavior. Unless the association strength is very strong, where the shear thinning effect can be postponed to much higher shear rate, the two competing effects dictate that, in systems with moderate association strength such as hydrophobically end-capped PEO, only mild shear thickening occurs over a limited concentration and molecular weight range. However small the effect is, shear thickening observed in our experiments is in semiquantitative agreement with the free path model predictions. Above the overlap concentration, the onset of shear thickening was found to decrease as concentration increases, temperature decreases, or association strength increases. The critical reduced shear rate depends only on molecular weight. The critical shear stress increases with molecular weight and plateau modulus. The magnitude of shear thickening increases inversely with temperature.

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References and Notes

(1) Marrucci, G.; Bhargava, S.; Cooper, S. L. *Macromolecules* **1993**, *26*, 6483.
(2) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424.
(3) Annable, T.; Buscall, R.; Ettelaie, R.; Whittlestone, D. *J. Rheol.* **1993**, *37*, 695.
(4) Ng, W. K.; Tam, K. C.; Jenkins, R. D. *J. Rheol.* **2000**, *44*, 137.
(5) Alami, E.; Almgren, M.; Brown, W.; Francois, J. *Macromolecules* **1996**, *29*, 2229.
(6) Chassenieux, C.; Nicolai, T.; Durand, D. *Macromolecules* **1997**, *30*, 4952.
(7) Chassenieux, C.; Nicolai, T.; Durand, D.; Francois, J. *Macromolecules* **1998**, *31*, 4035.
(8) Francois, J.; Maitre, S.; Rawiso, M.; Sarazin, D.; Beinert, G.; Isel, F. *Colloids Surf. A: Physicochem. Eng. Aspects* **1996**, *112*, 251.
(9) Tanaka, F.; Edwards, S. F. *J. Non-Newtonian Fluid Mech.* **1992**, *43*, 247.
(10) Rubinstein, M.; Dobrynin, A. V. *TRIP* **1997**, *5*, 181.
(11) Pham, Q. T.; Russel, W. B.; Thibeault, J. C.; Lau, W. *Macromolecules* **1999**, *32*, 2996.
(12) Pham, Q. T.; Russel, W. B.; Thibeault, J. C.; Lau, W. *Macromolecules* **1999**, *32*, 5139.
(13) Broze, G.; Jerome, R.; Teyssie, P.; Marco, C. *Macromolecules* **1983**, *16*, 996.
(14) Peiffer, D. G.; Lundberg, R. D.; Duvdevani, I. *Polymer* **1986**, *27*, 1457.
(15) Lundberg, R. D.; Duvdevani, I. Shear-Thickening Behavior of Ionomers and Their Complexes. In *Polymers as Rheology Modifiers*; Schulz, D. N., Glass, J. E., Eds.; 1991; p 155.
(16) Maus, C.; Fayt, R.; Jerome, R.; Teyssie, P. *Polymer* **1995**, *36*, 2083.
(17) Bhagarva, S.; Cooper, S. L. *Macromolecules* **1998**, *31*, 508.
(18) Chassenieus, C.; Tassin, J.-F.; Gohy, J.-F.; Jerome, R. *Macromolecules* **2000**, *33*, 1796.
(19) Jenkins, R. D. Thesis, Lehigh University, 1991.
(20) Lundberg, D. J.; Glass, J. E.; Eley, R. R. *J. Rheol.* **1991**, *35*, 1255.
(21) Kaczmarski, J. P.; Glass, J. E. *Macromolecules* **1993**, *26*, 5149.
(22) Tam, K. C.; Jenkins, R. D.; Winnik, M. A.; Bassett, D. R. *Macromolecules* **1998**, *31*, 4149.
(23) Witten, T. A.; Cohen, M. H. *Macromolecules* **1985**, *18*, 1915.
(24) Vrahopoulou, E. P.; McHugh, A. J. *J. Rheol.* **1987**, *31*, 371.
(25) Ballard, M. J.; Buscall, R.; Waite, F. A. *Polymer* **1988**, *29*, 1287.
(26) Tanaka, F.; Edwards, S. F. *J. Non-Newtonian Fluid Mech.* **1992**, 273.
(27) Tanaka, F.; Edwards, S. F. *J. Non-Newtonian Fluid Mech.* **1992**, *43*, 289.
(28) Wang, S. Q. *Macromolecules* **1992**, *25*, 7003.
(29) Groot, R. D.; Agterhof, W. G. M. *J. Chem. Phys.* **1994**, *100*, 1649.
(30) Ahn, K. H.; Osaki, K. *J. Non-Newtonian Fluid Mech.* **1995**, *56*, 267.
(31) van den Brule, B.; Hoogerbrugge, P. *J. Non-Newtonian Fluid Mech.* **1995**, *60*, 303.
(32) Wetzel, W. H.; Chen, M.; Glass, J. E. Associative Thickener: An Overview with an Emphasis on Synthetic Procedures. In *Hydrophilic Polymers: Perfomance with Environmental Acceptability*; Glass, J. E., Ed.; American Chemical Society: Washington, DC, 1996; p 163.
(33) Witten, T. A. *J. Phys. (Paris)* **1990**, *2*, 1.
(34) English, R. J.; Gulati, H. S.; Jenkins, R. D.; Khan, S. A. *J. Rheol.* **1997**, *41*, 427.
(35) Nomula, S.; Ma, S. X.; Cooper, S. Solution Structure and Shear Thickening Behavior of Ionomers and Hydrophobically Associating Polymers. In *Associative Polymers in Aqueous Media*; Glass, J., Ed.; American Chemical Society: Washington, DC, 2000; p 127.
(36) Green, M. S.; Tobolsky, A. V. *J. Chem. Phys.* **1946**, *14*, 80.
(37) Otsubo, Y. *Langmuir* **1999**, *15*, 1960.

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