Macromolecules **2001,** *34,* 2641−2647

Shear-Induced Phase Separation in an Associating Polymer Solution

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Received July 27, 2000; Revised Manuscript Received January 2, 2001

ABSTRACT: Rheological and rheo-optical experiments have been performed under shear flow on 1% solution of an hydrophobic ethoxylated urethane (HEUR) with a molecular weight of 35 000 and a C18 hydrophobic end-cap. After a Newtonian behavior at low shear rates, followed by a slight shear thickening, a pronounced drop in viscosity is observed above a given shear rate. Creep experiments confirms, that above a critical stress a rather long time is required to reach a steady state with a rather low viscosity. Under steady-state conditions at 20 °C, birefringence first increases with shear rate until $\dot{\gamma} \approx 5\ \mathrm{s}^{-1}$, then decreases until $\dot{\gamma} \approx 50\ \mathrm{s}^{-1}$ and increases upward again. The decrease in molecular orientation is accompanied by a decrease of the transmitted light intensity. On cessation of shear flow, the transmitted intensity increases back to its initial value. This behavior is interpreted in terms of a reversible shear-induced phase separation.

Introduction

Associating polymers can be used as rheology modifiers, thanks to their ability to self-associate forming thereby large scales temporary networks which can significantly increase the low shear viscosity of an aqueous medium.[1] The increase in viscosity can be controlled by the concentration of the associating polymer, but also by the hydrophilic−lipophilic balance (HLB). With this respect, hydrophobically end-capped linear polymers, such as the so-called HEUR (hydrophobically modified ethoxylated urethanes), offer a rather simple way to control this parameter by varying the length of the hydrophobic group or the molecular weight of the polymer backbone. Indeed, increasing with a given backbone the association energy through the length of the hydrophobic groups or their chemical nature, increases the corresponding relaxation time and the zero-shear viscosity.[2]

The commonly accepted description of these telechelic polymers in solution involves at low concentrations the formation of flowerlike micelles consisting of looped chains in which both hydrophobic end groups are located in the core of the same micelle.[3] As concentration increases, a secondary association process occurs leading to the formation of bridges between micelles until finally a network is formed from the percolation of bridges leading to a large increase in viscosity.[4] In some cases, a phase separation between a dilute solution of essentially separated flowers and a dense phase of aggregated micelles can be observed.[5−7] The existence of a phase separation depends strongly on the length of polymer backbone, the chemical nature of the hydrophobic terminal group as well as the extent of modification of the parent polymer. For instance, Alami et al.[8] report an homogeneous solution at room temperature for octadecyl end-capped POE chains of molecular weight 35 000, specially synthesized to avoid the introduction of an urethane rotule, whereas phase separation has been observed by Pham et al.[7] on the same type of polymers but containing an urethane group. With less substituted polymers or larger molecular weight distribution due to condensation reactions during synthesis, phase separation is apparently not observed.[9,10] This sensitivity to the molecular details of the polymer structure is also responsible for the variations in the zero-shear viscosity or the relaxation time reported in the literature.

The phase separation has been predicted on the basis of theories of interacting polymer brushes. It originates from an entropic attraction of chain ends in neighboring micelles which leads to bridging between micelles.[11] Experimental investigations on hydrophobically modified polyoxyethylene chains confirm the validity of the theoretical prediction.[6,7] The influence of the hydrophobic−hydrophilic balance on the phase diagram has been studied. Apparently, in the dilute regime, the phase separation can be seen as a first-order gas−liquid transition which does not seem much affected by temperature, although the quality of the solvent decreases with an increase in temperature, emphasizing the entropic origin of the attraction mechanism.[7]

The linear viscoelastic behavior of telechelic associative polymer solutions can be described with a good approximation by a Maxwell model (single relaxation time t_0 and an elastic plateau modulus G_0)[2,4,9] although a stretched exponential[12] or a log-normal distribution of relaxation times[13] may sometimes improve the fit. The viscoelastic parameters (t_0 and G_0) vary with the details of the chemistry for a given backbone length and hydrophobic end group. The relaxation time increases exponentially with the number of carbon atoms in the hydrophobic group[2,12,14] and with the concentration[2]. This relaxation time is commonly attributed to the lifetime of an end group in a given micelle[4] although this interpretation has been recently debated.[10]

Under shear flow, the steady state behavior of these systems shows a Newtonian behavior at low shear rates, followed by a more or less pronounced shear thickening region and a strongly shear thinning one.[2,9] Fluorescence quenching experiments under flow indicate that the number of hydrophobic groups per micelle does not change with shear rate. On the basis of these observations, Yetka et al.[15] proposed a qualitative model in which the shear thickening is explained by the deforma-

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10.1021/ma001324a CCC: $20.00

tion and stretching of chains between micelles with a constant aggregation number. At larger shear rates, a bridge to loop transition is though as responsible for the shear thinning behavior.

More recently, Tam et al.[9] have used superposition of dynamic oscillations on steady shear flow to probe the structure of the material under flow. They proposed a slightly different view of the same rheological behavior. The shear thickening is attributed to a rearrangement of the network which induces an increase in the number of bridges between micelles at the expense of the number of loops. The shear thinning is ascribed to a stress-induced decrease of the relaxation time of the chain segments leading to an increased rate of rupture of bridges as the shear rate increases. Eventually, at higher shear rates, smaller aggregates of bridged micelles can be formed, accounting for additional shear thinning.

Beside this molecular behavior, specific to telechelic-associating polymers, classical polymer solutions may undergo structural changes under shear or elongational flow fields, leading to the appearance of turbidity.[16,17] This phenomenon is explained theoretically by a shear-induced enhancement of concentration fluctuations due to the coupling between concentration and stress.[18] Large effects are observed in semidilute solutions at temperatures slightly above the binodal curve[19] (i.e., in the one phase region in the quiescent state). Shear induced phase separation leads to shear thinning eventually followed by shear thickening at very high shear rates.[20] Numerous experimental investigations have been carried out by several groups involving a variety of experimental techniques like small angle light or neutron scattering, flow dichroism and birefringence.[21]

To our knowledge, anomalous behavior under flow of associative polymers that were homogeneous at rest has only been briefly mentioned in a study by François et al. [6] where an opacification of the solution is noted together with the appearance at low angle of an excess intensity in neutron scattering and more recently by Pham et al. [22] where shear-induced phase separation has been suspected from creep experiments as well as from visual observation of the fluid after shear flow.

In this paper we report on the rheological and rheo-optical behavior under shear flow of a solution of HEUR which is homogeneous at rest. We demonstrate that microscopic shear-induced phase separation occurs under specific conditions by comparing the evolution of the shear stress and that of optical quantities like birefringence, orientation angle and turbidity vs shear rate. We also point out the fact that, after cessation of shear, the system returns to an isotropic and homogeneous state showing the reversibility of the phenomena induced by the shear flow. We also offer a speculative view of the molecular behavior under shear.

Experimental Section

Materials. The associative polymer is a modified polyoxyethylene of molecular weight $M_w = 35\,000$ (Fluka Chemicals) containing C18 alkyl groups at both ends (POE35C18). It has been synthesized according to the work of Xu et al.[23] by modification of the hydroxyl end groups with isophorone diisocyanate (IDPI, Aldrich) and further addition of an excess of octadecylamine (Aldrich). The resulting polymer was purified by many dissolution−crystallization experiments in order to eliminate POE aggregates, the existence of which strongly modifies the optical response under shear flow.[24] The extent of modification has been calculated through UV spectroscopic titration of the residual hydroxyl groups after addition of large excess of phenylisocyanate to be above 80%.

Solutions were prepared by dissolution under gentle stirring of the solid polymer into distilled water, with sodium azide at a typical level of 0.2% in w/w, to avoid bacterial degradation. It was checked, by preparing solutions without sodium azide, that this salt, at such a low concentration, does not affect rheological properties of the solutions. In this work, concentrations are expressed as a percentage in weight.

Rheological Measurements. Several types of rheological experiments were performed. A Haake RS 100 stress controlled rheometer equipped, for most of the experiments, with a 35 mm diameter, 2° angle cone and plate geometry has been used to determine shear stress and viscosity vs shear rate curves under steady state conditions. For this purpose, shear stress sweeps with an equilibration time of 200 s per point and a stability criterion of the shear rate better than 2%/s were applied to the sample. In some relevant cases, creep experiments were carried out to follow the evolution of the instantaneous shear rate and corresponding viscosity vs time. These experiments ensure whether steady state is reached or not. A Contraves LS 40 strain controlled rheometer using a concentric cylinder Couette geometry (inner bob radius bob length = 9 mm; gap = 0.25 mm) has also been used for these studies, especially at the lowest shear rates.

Rheo-Optical measurements. The rheo-optical measurements were performed on a ROA (Rheometrics Optical analyzer) operating with an He−Ne laser ($\lambda = 632.8$ nm). A Couette flow cell was used with light propagating along the vorticity axis (inner bob radius = 15 mm, length = 12 mm, gap = 1 mm). The ROA equipment allows us to characterize several properties of the complex refractive index tensor using a polarization modulation method. Owing to the geometry of the experiment using a Couette cell, the birefringence and dichroism are measured in the velocity−gradient plane of the shear flow. Here we will be mostly concerned by the flow induced birefringence Δn, the average orientation angle χ, as well as the possible variation of the transmitted unmodulated light intensity, which detects appearance of turbidity inside the cell.

Optical experiments consist in start-up shear flow at a given shear rate until a steady state is reached followed by cessation of shear, where the optical quantities mentioned above are monitored.

Unless specified, rheo-optical and rheological experiments were carried out at a controlled temperature of 20 °C.

Results

Linear Viscoelastic Measurements. A 1 wt % solution of the POE35C18 shows the usual Maxwellian behavior for this type of system. The characteristic relaxation time obtained from a fitting of the dynamic moduli as a function of frequency using a Maxwell model is 0.45 s. It is associated with the lifetime of an hydrophobic end group inside a given micelle. This order of magnitude is close to that reported by other authors[2,14] but significantly larger than those evaluated on rather similar systems by Pham et al.[22] The differences might be due to the absence of the coupling agent in the case of this latter study. According to them, the presence of the isophoronediisocyanate is almost equivalent to adding two carbons to the aliphatic chain. A careful examination of the data shows that a shorter time relaxation process (0.01 s) exists in this system[25] as recently noted by Ng et al.[10]

Nonlinear Rheological Measurements. The steady-state viscosity and shear stress vs shear rate curves for a 1% solution of polymer obtained with the RS 100 are given in Figure 1. The values corresponding to the steady-state viscosity as obtained from creep experiments are added as open symbols.

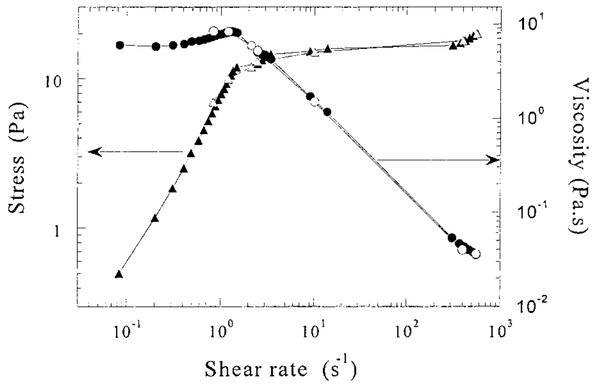

Figure 1. Shear stress and viscosity vs shear rate under steady-state shear flow: stress ramp (filled symbols) and creep experiments (open symbols); (△) Shear stress; (○) viscosity (1% solution, 20 °C).

Under increasing shear rate, a Newtonian plateau associated with a zero-shear viscosity of 6 Pa•s is followed by a slightly shear thickening regime with a maximum viscosity at 9 Pa•s. For shear rates above 1.5 s^{-1} a strong drop in viscosity is observed, as stated by a plateau value of the shear stress within a large domain of shear rates. This behavior has been often observed in surfactant solutions and is commonly ascribed to an inhomogeneous shear rate inside the gap due to a purely mechanical instability or a partial transition toward a nematic state.[26,27]

Since a stress plateau can also result from wall slip or fracturing of the material, we performed the same experiments using different geometries (2 cm diameter, 4° angle; 6 cm diameter, 1° angle), and the same results were obtained. We also cross-checked through visual observation with a video camera that this behavior was not due to wall slip or fracturing. Neither were we able to observe shear banding structures between crossed polars. The same experiments were repeated at various temperatures above and below 20 °C. The behavior is qualitatively similar. The stress plateau is slightly increasing as temperature decreases (15 Pa at 30 °C up to 25 Pa at 5 °C), but the drop of viscosity is observed at a critical shear rate which increases significantly as temperature increases (1 s^{-1} at 5 °C up to 30 s^{-1} at 30 °C). This suggests the existence of a critical Weissenberg number ($\dot{\gamma}\tau$) where τ is a molecular relaxation time with a strong temperature dependence.

This unusual behavior led us to study the transient behavior using creep experiments at shear stresses slightly lower or above the plateau value. Between two experiments, the sample was allowed to relax for at least 10 mn. The time dependence of the viscosity is plotted in Figure 2 for various stresses. Until a value of 10 Pa, which nearly corresponds to the critical shear stress, the viscosity reaches its steady state rapidly and does not seems time-dependent. However for higher shear stresses, after a pseudo-equilibrium or metastable state which might, depending on the applied stress, be longer than 100 s, an unexpected drop of viscosity is observed after a sufficiently long shearing time, t_d. Figure 2 suggests that this behavior involves at least two metastable states. One is related to the viscosity plateau at short times. The other one appears between the first drop in viscosity and the second one where a steady value is finally observed. The time associated with the second drop in viscosity decreases with increasing shear stress and seems also to decrease if the resting time between two consecutive experiments is decreased. It must be noted that t_d is orders of magnitude longer than the Maxwell relaxation time.

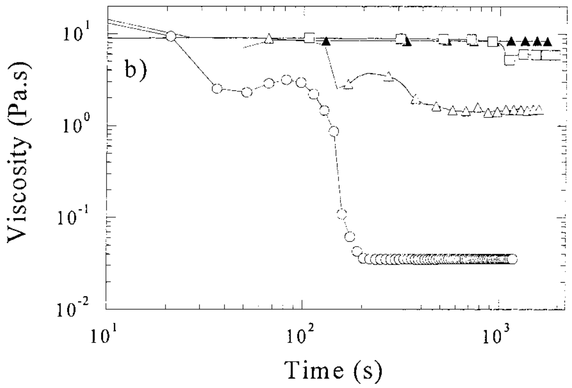

Figure 2. Viscosity vs time during creep experiments: (○) 20 Pa; (△) 15 Pa, (□) 12 Pa; (♦) 7 Pa (1% solution, 20 °C).

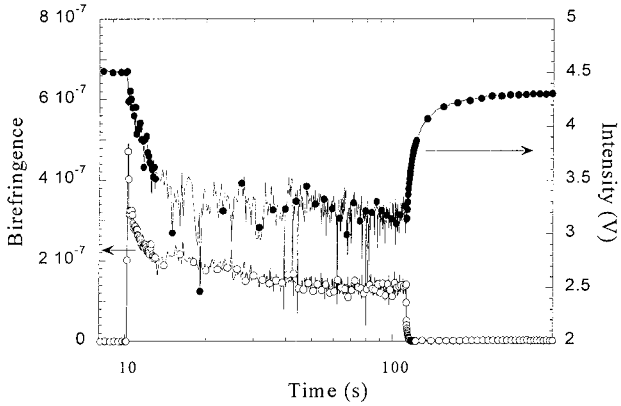

Figure 3. Birefringence and transmitted light intensity vs time during a shear flow experiment. Shear rate = 20 s^{-1}. (○) birefringence; (●) intensity (V) (1% solution, 20 °C).

At steady state, the viscosity obtained from creep experiments agrees well (see Figure 1) with that measured from stress sweeps, provide the parameters of the rheological protocol (especially the equilibration time) are conveniently set.

Rheo-Optical Measurements. The evolution of birefringence and transmitted light intensity as a function of time during a start-up experiment at $\dot{\gamma} = 20$ s^{-1} are represented in Figure 3. The intensity decreases until a steady value is reached within roughly 60 s. The birefringence shows a strong overshoot (as high as 4 times the steady state value) at the beginning of the shear flow. The observation of the flowing solution using a large light field and a video camera showed that the decrease in intensity could not be attributed to air bubbles generated during shear flow and could not be possibly favored by the nonionic surfactant character of the hydrophobically modified POE.

After cessation of shear flow, the intensity increases back slowly to its initial value (strictly speaking 3.5% below after 250 s resting time) and the birefringence relaxes down to the isotropic state. The relaxation of birefringence is significantly more rapid than that of the transmitted intensity as shown in Figure 4. The typical relaxation time for birefringence is on the order of 0.6 s (i.e., the linear viscoelastic relaxation time) whereas relaxation of transmitted intensity requires longer characteristic times (on the order of 6 s).

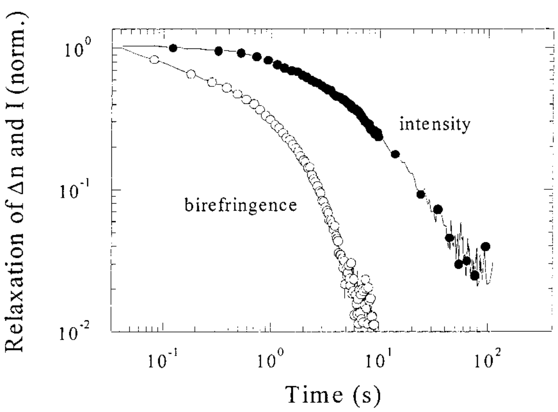

Figure 4. Normalized relaxation of birefringence (○) and transmitted intensity (●) after steady shear flow at 20 s^{-1} (1% solution, 20 °C).

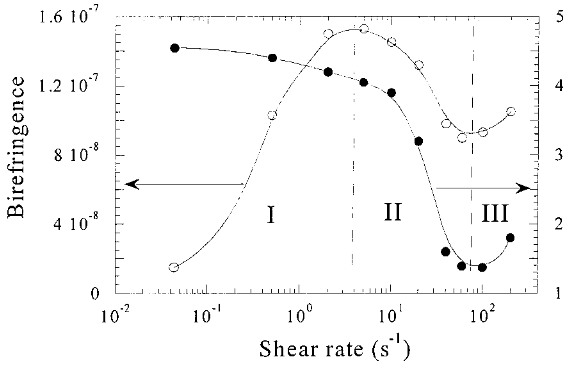

Figure 5. Steady-state birefringence (○) and transmitted light intensity (●) vs shear rate. The various regimes are indicated as I, II, and III. Lines are smooth curves through the data (1% solution, 20 °C).

To the first order, the relaxation kinetics of the transmitted intensity and of the birefringence are independent of the preceding shear rate, except at the highest shear rates where a slightly more rapid relaxation is observed.

The evolution of the steady state birefringence and transmitted light intensity is represented vs the applied shear rate in Figure 5. It must be emphasized that each point corresponds to a different experiment where flow is started at a given shear rate, the sample being initially at rest. Obviously, the birefringence does not vary monotonically with the shear rate, as it is usually observed for polymer solutions. Upon increasing $\dot{\gamma}$, birefringence first increases until $\dot{\gamma} \approx 5\ s^{-1}$ (regime I), then decreases until $\dot{\gamma} \approx 50\ s^{-1}$ (regime II) and increases again at higher shear rates (regime III). The transmitted intensity decreases smoothly at low shear rates and more significantly as birefringence starts to decrease. In regime III, the turbidity of the sample seems to decrease and a small dichroism, on the order of 10^{-8}, slightly increasing with shear rate has been detected.

The behavior of the average orientation angle depicted in Figure 6 also shows an unusual shape. In classical polymer solutions, it decreases continuously from 45° as the shear rate is increased. This behavior is observed with our 1% POE35C18 solution but only at low shear rates (regime I). Than, the orientation angle goes through a minimum value and increases again when the molecular deformation as deduced from birefringence decreases (regime II). In the third regime, the increase of the orientation angle with shear rate appears less pronounced.

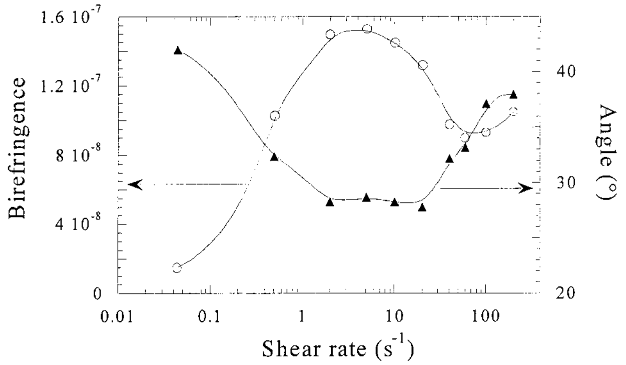

Figure 6. Steady-state birefringence (○) and orientation angle (▲) vs shear rate (1% solution, 20 °C).

Figure 6 shows that the birefringence and the orientation angle are closely coupled. Indeed, the minimum value of the orientation angle is observed in the same shear rate ranges as the maximum of birefringence, and an increase of one of these quantities is accompanied by a decrease of the other one.

Since the presence of dichroism can alter the optical response when birefringence is thought to be measured, several measurements with an optical train suitable for dichroism were also carried out. The dichroism was on the order of a few 10^{-9} (i.e., in the noise level of the equipment) and was not changed upon increasing shear rate, except in regime III where it increases up to a few 10^{-8}. It is, however, by 1 decade lower than the birefringence and therefore does not contribute significantly to the signal detected in the birefringence mode. We thus deduce that the anisotropy of the large scale structures, formed under shear flow and responsible for light scattering, is almost negligible, except in regime III.

This peculiar behavior has been observed at other concentrations (1.2 and 1.48%), but no special effort has been made to explore the eventually limiting concentrations. It has also been observed at all the other investigated temperatures in the range 5−30 °C. As the temperature is decreased, the shear rate corresponding to the maximum of birefringence is decreasing toward lower values, implying that temperature-dependent relaxation times may play an important role. Figure 7a illustrates the behavior of the birefringence vs the reduced shear rate defined as $\dot{\gamma}\tau$, where τ is the Maxwell relaxation time at the relevant temperature. A master curve is obtained within the accuracy of the experiments, showing that the minimum and the maximum values of the birefringence are almost independent of temperature and that the reduced shear rate is the relevant parameter, at least for the appearance of regime II. The critical Weissenberg number, related to the appearance of regime III is slightly increasing as temperature decreases.

The minimum value of the orientation angle seems temperature dependent but also appears at around the same reduced shear rate as shown in Figure 7b.

The behavior of the transmitted intensity is also similar whatever the temperature, showing a slight decrease of the turbidity in regime III, which is best seen at low temperatures.

The plateau in the stress vs shear rate curve, as well as the S-shaped curve of the birefringence (which would be almost the equivalent of the shear stress if stress optical law applies [28]) can be a signature of mechanical

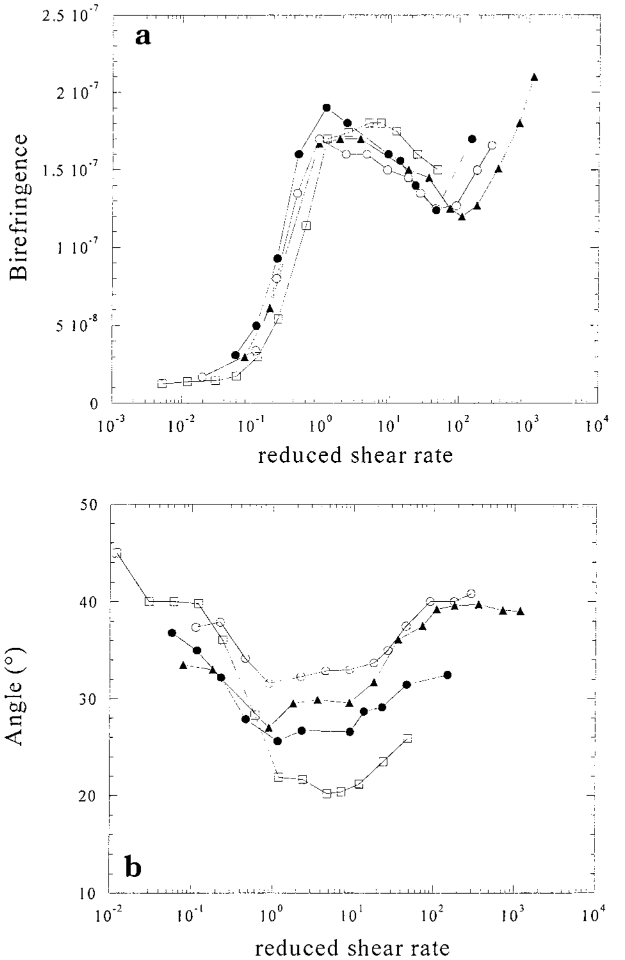

Figure 7. Steady-state birefringence (Figure 7a) and steady-state angle (Figure 7b) at various temperatures vs the reduced shear rate $\dot{\gamma}$ where τ is the Maxwell relaxation time at the considered temperature: (▲) 10 °C; (○) 20 °C; (●) 25 °C; (□) 30 °C (1% solution).

instability.[29] Again, in our case, no shear banding structures were detected using a cross polarizers set up as described by Makhloufi et al.[30]

Discussion

The rheological and rheo-optical behaviors observed in this work are rather unusual and cannot be simply interpreted in terms of the current ideas of the molecular behavior of associating telechelic polymers.[2,4,9,15] It must be pointed out that observation of these phenomena requires well-defined steady-state conditions and that rapid shear rate or shear stress ramps may hide partially the experimental observations presented above. Nevertheless, some rheological experiments reported on HEUR's also reveal a strong shear thinning.[9,22,31]

The shear thinning phenomenon is accompanied by various experimental facts, detected using rheo-optical tools, which lead us to a quite different interpretation than that recalled in the Introduction. First, the creep experiments clearly show that, after a shearing time t_d, in a shear stress range corresponding to the shear thinning regime, a transition in the structure occurs, characterized by metastable states occurring before a sharp drop of viscosity. The higher the shear stress, the lower the shearing time required to induce the new structure.

Second, a maximum value of birefringence together with a minimum in the orientation angle is observed at a given shear rate associated with the maximum of the viscosity. At the same time, the sheared sample becomes slightly turbid and turbidity increases with shear rate. The optical behavior observed at higher shear rates, more precisely the decreasing birefringence and the increasing orientation angle, is compatible with either a decrease in the number of the stretched polymer chains or a lower degree of extension.

It must be noted that this decrease in birefringence is completely different from what is observed in polystyrene/dioctylphthalate (PS/DOP) semidilute solutions undergoing shear-induced phase separation, where an increase in the absolute value of Δn is observed especially in the high shear rate regime.[21]

In our case, both the light-scattering phenomenon and the behavior of the birefringence and the orientation angle can be attributed to a shear-induced phase separation. Indeed, creation of large structures would obviously lead to light scattering and decrease the number of polymer chains undergoing a significant deformation under flow. The absence of dichroism proves that the large structures are not oriented under flow. From the theoretical picture of the phase separation at rest in associative polymer solutions, the large structures can be though as domains of strongly connected micelles forming submicrometer gels. Their formation leads to a decrease in the connectivity of the physical network explaining the decrease of birefringence. The strong decrease of viscosity is at first order explained by the large change in the connectivity of the system.

The reversibility of this flow-induced structure must be pointed out. Upon cessation of shear the transmitted intensity increases back to the initial value. Moreover, the relaxation of intensity is roughly 10 times slower than that of the birefringence, justifying the existence of two different species in the sheared solution. Since the relaxation time associated with each of these species is not affected by shear rate, we believe that the number of densely packed micelles rather than their size increases with shear rate. Furthermore, since the birefringence relaxation time is also independent of shear rate and almost equal to the Maxwell relaxation time, we attribute it to the same origin as under linear viscoelastic conditions, i.e., the lifetime of an hydrophobic group inside a micelle. Thus, the flowing solution can essentially be viewed as a suspension of strongly connected and densely packed micelles in a suspending medium made of much less connected micelles.

At rest, phase separation in associative telechelic polymers has been predicted theoretically[11] and experimentally observed and studied.[6,7] Clearly, experimental data show that the phase separation conditions are strongly linked to the HLB balance of the polymer.[7] From a theoretical point of view, phase separation results from an entropic attraction due to the bridging between isolated flowers. The depth of the attractive free energy increases with the square root of the aggregation number, making the phase separation conditions strongly dependent on the molecular characteristics of the associative polymers (molecular weight, length of the hydrophobic group and exact functionality). The concentrated phase consists of densely packed bridged flowers, whereas the dilute phase can be seen as a gas of isolated flowers. Experimental evidence of

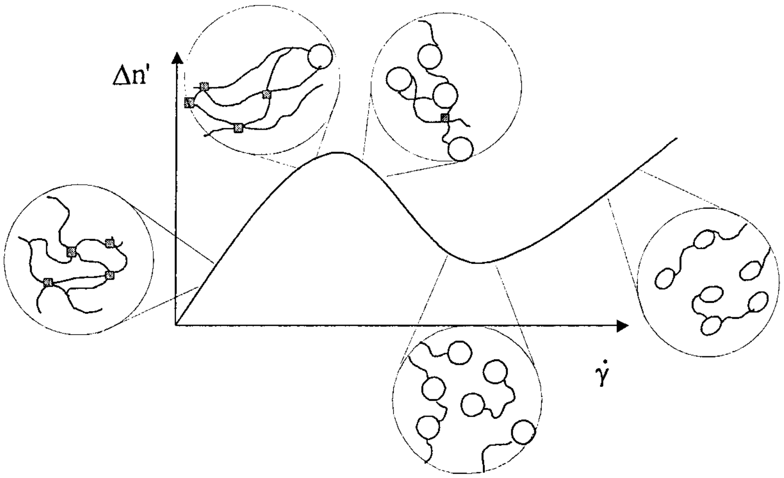

Figure 8. Schematic picture of the polymer solution in the various regimes. The circles represent particles of densely packed and bridged micelles (drawn to a much smaller scale) and squares are junction points consisting in micelles (loops are not represented for clarity).

the major points of the theoretical predictions has been reported recently.[7]

However, these theories consider a thermodynamical and mechanical equilibrium and do not take into account the possible influence of shear flow, which is known to be able to bring in the biphasic region homogeneous systems,[18] especially when they are taken within a short distance from the phase separation conditions. This might be the situation with our POE35C18 sample, which is only 80% end-capped by hydrophobic groups. In the work of Pham et al.,[7] an almost fully modified POE of the same molecular weight and with the same hydrophobic groups (but without the isophorone group) shows a biphasic region for concentrations between ca. 0.2 and 2.7 wt %. Existence of a fraction of chains bearing an hydrophobic group at only one end might favors steric repulsion between micelles, acting against the attraction arising from the formation of bridges. Indeed, we observed that a POE of molecular weight 20000 fully capped (>95%) with C16 hydrophobes was undergoing a phase separation whereas a lower degree of substitution (70%) yielded an homogeneous solution.[25]

Our results point out that phase separation appears after the shear thickening regime (see Figure 7a). According to the work of Tam et al.,[9] in addition to chain stretching and molecular orientation which might strongly increase the shear stress,[32] shear thickening is linked to an increasing number of bridges between neighboring micelles. This additional bridging might favors the phase separation. It can also be considered that chain stretching tends to increase the mean distance between the core of neighboring micelles along the principal direction (corresponding to the measured orientation angle) but also to decrease it along the perpendicular direction in the plane of the flow. This can also favors bridging by decreasing the steric repulsion along this latter direction.

Our final view of the molecular and mesoscopic behavior of POE35C18 is given in Figure 8 where the molecular behavior in the different regimes of the birefringence vs shear rate is sketched. During the Newtonian regime and the beginning of shear thickening, the chains bridging flowerlike micelles are stretched and oriented along the flow direction. During the shear thickening regime a rather rapid decrease of the orientation angle is observed as in other telechelic polymeric systems.[33] It is most probable that phase separation already starts in this regime, as seen by the slight decrease of transmitted intensity. However, the volume fraction of the dense phase is probably very small, so that the connectivity of the network is not much affected. During the stress plateau, a decrease of birefringence is noted which is attributed to a direct consequence of the phase separation. The volume fraction of the dense phase increases during this regime and the fraction of extended bridges decreases. In the high shear rate branch of the curve, the increase in birefringence is ascribed to a slight stretching of the dense phase particles, the size of which might be somewhat decreasing as seen from the upturn in the transmitted intensity as well as from the slight shortening of the relaxation time of the transmitted intensity upon cessation of shear.

As a last remark, we mention that this kind of behavior, might be rather specific to systems that are in the one phase regime at rest, but that are close to the two phase region because of their hydrophilic–lipophilic balance. Indeed, the same type of rheological behavior (strong drop of viscosity at a given shear stress) has been reported for F–HEUR (containing hydrophobic CF_2 groups instead of CH_2 for HEUR).[31] However, the same type of rheo-optical studies carried out in our group on less hydrophobic associative polymers (thus further away from the phase separation conditions at equilibrium) show a rather different behavior. There is no evidence for a significant decrease in the transmitted intensity, neither for an S-shaped curve nor for birefringence vs shear rate.[25] A comparison between these two different cases will be reported in a forthcoming paper.

Conclusion

We reported in this paper, that solutions of associating polymers, for given conditions of the hydrophilic–lipophilic balance, may show an unusual rheological behavior under shear flow with a strong drop of viscosity above a critical Weissenberg number. This rheological behavior is associated with the appearance of turbidity and a decrease in birefringence with increasing shear rate. This is at variance with the observations on the shear-induced phase separation in semidilute polymer solutions just above the binodal curve, where birefringence increases with shear rate. Obviously, a light-scattering characterization of our system under flow would be helpful to confirm our assumptions and such studies are currently underway.

Acknowledgment. J.-F.L.M. gratefully acknowledges the FSE "Fond Structurel Europien" for financial support.

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MA001324A