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SHORT COMMUNICATION

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Rheology of an aqueous solution of an end-capped poly(ethylene glycol) polymer at high concentration

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Abstract Generally it is observed that the viscosity of an aqueous solution of a hydrophobically modified polymer increases with concentration; however, here it is shown that the viscosity profile of an end-capped poly(ethylene glycol) polymer passes through a maximum. Thus, a substantial decrease in viscosity is observed at high concentrations (≥50 wt%). The observation is suggested to be due to a gradual change, on the molecular level, from a structure containing micellelike structures that are interconnected via polymer bridges to a more meltlike state, where micro segregation in hydrophilic and hydrophobic regions is less pronounced.

Key words End-capped poly(ethylene glycol) · Viscosity · Rheology · Phase behavior · Microstructure

Introduction

End-capped poly(ethylene glycol) polymers (HM-PEG) belong to a family of associative thickeners that find frequent use in paint formulations [1]. Due to shipping costs the most efficient way is to transport the product as a dry powder from manufacturer to user. However, due to slow dissolution kinetics, which is a complication for the user, a trade-off has to be made and the thickener is generally shipped in an aqueous solution. It is generally found that such a solution has a high viscosity [2–4], and to have a solution that is easy to handle the high viscosity has to be reduced. A reduction can be obtained in various ways, where addition of a less polar solvent or addition of a surfactant can be noticed [5, 6]. As a complication, the added cosolute may disturb the final paint formulation, and for this reason it is desirable to reduce its concentration. In the present investigation it is shown that the viscosity as a function of HM-PEG concentration passes through a maximum and decreases strongly at concentrations above about 50 wt%. This suggests that a method to reduce the viscosity compatible with the demands is simply to increase the dry content.

Experimental

Materials and sample preparation

The preparation of the HM-PEG, which has a triblock structure (TB), was started by ethoxylation of a mixture of unsaturated alcohol chains (C_{16}-C_{18}). The reaction continued until each of them contained, on average, 140 repeating ethylene oxide (EO) units. This compound ($C_{18}EO_{140}$), which has a diblock structure (DB), may be viewed as a surfactant molecule with a polymeric-sized headgroup (Fig. 1). In a reaction between isophoronediisocyanate (IPDI) and $C_{18}EO_{140}$, two entities of $C_{18}EO_{140}$ were connected head-to-head to obtain one HM-PEG polymer ($C_{18}EO_{140}$-IPDU-$EO_{140}C_{18}$). During the reaction IPDI was present in small excess and dibutyltindilaurate was used as a catalyst. Unreacted IPDI was eliminated by termination with small amounts of ethanol.

In the following, HM-PEG will be referred to as the TB polymer or TB, and DB will be the term used for the $C_{18}EO_{140}$ compound.

By using size-exclusion chromatography with well-characterized PEG fractions as calibration standards the weight-average molecular weight (M_w = 11 000) and the polydispersity index (M_w/M_n = 1.1) of the TB polymer could be determined. The TB was used without any further purification.

Samples for rheology and phase studies, each containing a volume of about 10 ml, were prepared by weighing the components directly into glass tubes. These were sealed with Teflon tightened screw caps. Because the dry TB material has a fluffy structure and the water in which this powder should be dissolved had a much smaller volume, the dissolution process was sometimes

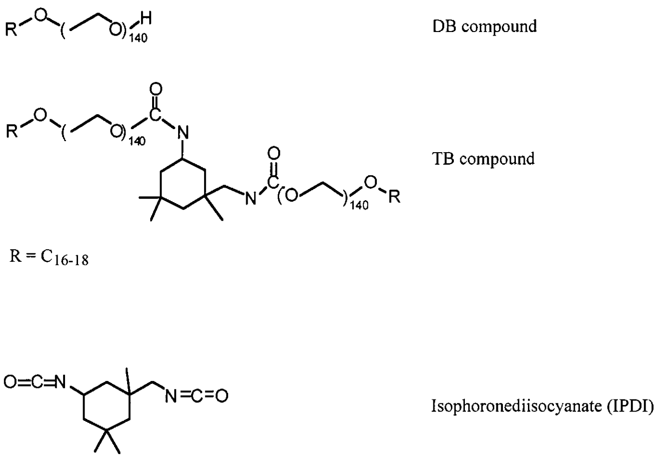

Fig. 1 The chemical structure of the end-capped poly(ethylene glycol) (*TB*) investigated together with the structure of the building blocks (*DB* and *IPDI*) from which the TB polymer was synthesized

complicated, especially for samples with a high concentration of the TB polymer; however, by using a centrifuge the process could be sped up and after a few hours of centrifugation all samples appeared homogeneous. After completed dissolution the samples were left to stand overnight before any measurements were performed.

Phase behavior

In the present investigation only a brief study of the phase behavior was performed. This was done in order to ensure that the viscosity was determined under conditions where the solution was a single phase. The cloud-point-curve data (defining the border between the one- and two-phase regions at low TB concentration, cf. Fig. 2) is reproduced from an earlier publication [4]. By using X-ray diffraction it has been found that at high concentrations of the TB polymer a crystalline phase appears at low temperatures. This phase border was determined by decreasing the temperature of each sample in steps of 2 °C. The temperature of the samples was controlled to within ±0.1 °C by immersion in a jacketed glass vessel connected to a temperature-controlled water bath. At each temperature the samples were allowed to equilibrate for at least 12 h before visual inspection. Phase separation which led to the formation of a crystalline phase in equilibrium with the micellar phase was observed as small white "regions" due to scattered light from the crystallites which were formed within the sample.

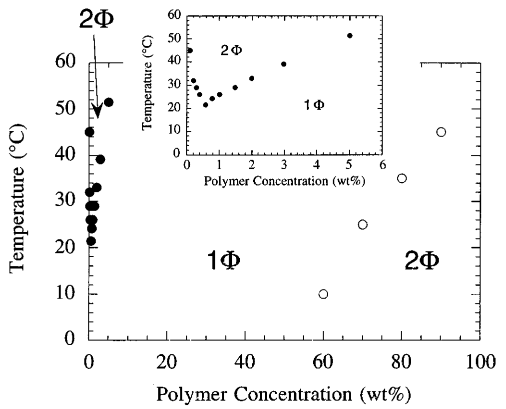

Fig. 2 Partial phase diagram for the TB polymer. The *inset* shows a blow-up of the two-phase region (*2Φ*) at low concentrations. Here the two liquid phases in equilibrium are isotropic with one phase enriched in polymers, while the other is depleted. In the two-phase region at high concentrations a crystalline phase containing only small amounts of water is balanced by an isotropic phase containing a fairly high concentration of the TB polymer. The phase diagram is dominated by a micellar one-phase region (*1Φ*)

Rheological experiments

Oscillatory-shear and steady-shear experiments were conducted in a Physica UDS 200 rheometer that was equipped with an automatic gap setting and a plate–plate geometry with a diameter of 25 mm. The temperature was controlled to within 0.1 °C with a Peltier plate and the samples were protected from water evaporation by using a solvent trap during the measurements. Before carrying out any oscillatory-shear measurements each sample was checked to ensure it was within the linear viscoelastic region where the storage (G') and the loss (G'') moduli are independent of the applied stress. In the samples investigated this regime was easily identified because it was typically found to extend over a rather wide shear-stress range (Fig. 3). While the data presented in Fig. 3 were obtained for one sample at one temperature (20 wt% at 40 °C), similar behavior was observed for all samples investigated. The complex viscosity was calculated using $\eta^* = \sqrt{G'^2 + G''^2}/\omega$, where $\omega = 2\pi f$ is the angular frequency, and f is the frequency of the oscillation in hertz.

The viscosity, η, of the samples was also obtained with steady-shear measurements. It was found that by increasing the shear rate the tendency increased for air to enter the measuring gap and replace a significant volume fraction of the sample. This effect became more pronounced when the TB concentration was increased. If the viscosity is presented as a function of the shear rate this artifact is observed as a pronounced shear-thinning behavior. An alternative method to identify unphysical data is to plot the viscosity as a function of the shear stress, σ (Fig. 4b). In this representation a certain shear stress sometimes corresponds to two different viscosity values. In Fig. 4a, for each measurement we have chosen to omit viscosity data obtained at shear rates exceeding the maximum shear stress (Fig. 4b). The maximum shear rate given by this method agreed with that determined by careful examination of when fluid was exiting the measuring gap. Therefore, for the data presented in Fig. 4a, the shear-rate range decreases when the TB concentration increases.

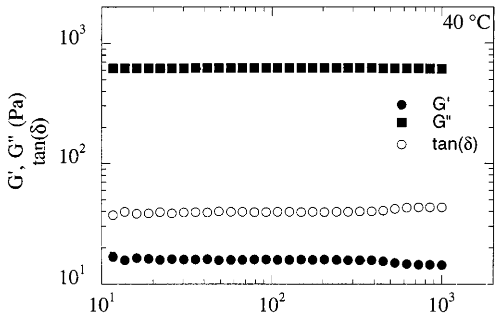

Fig. 3 The storage (G') and loss (G'') moduli, and the damping factor $\tan(\delta) = G''/G'$ given as a function of the applied stress (σ). The data were obtained at a TB concentration of 20 wt%, the frequency was 1 Hz, and the temperature was kept constant at 40 °C

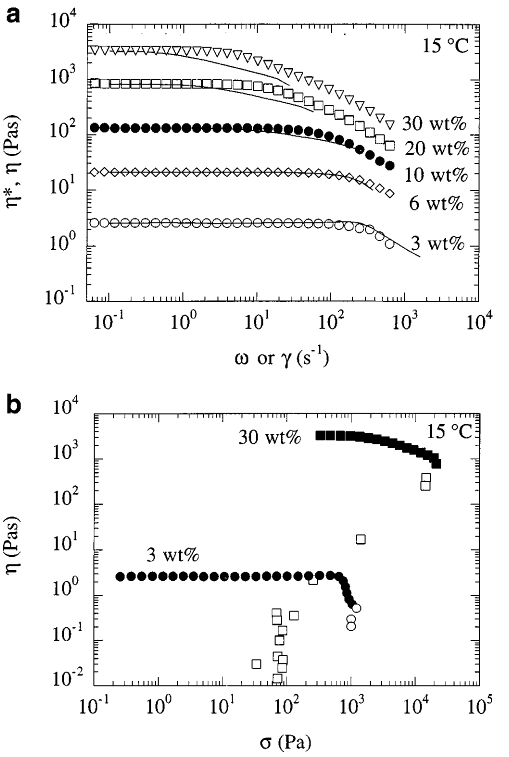

Fig. 4 a The viscosity for five different TB concentrations obtained from oscillatory-shear experiments and from steady-shear experiments. The complex viscosity, η^* , (*symbols*) and the steady shear viscosity, η, (*thin lines*) are shown. The temperature was 15 °C. **b** The steady-shear viscosity for samples containing 3 wt% (*circles*) and 30 wt% (*squares*) TB polymer as a function of the applied stress, σ. *Filled symbols* refer to the data points used in Fig. 4a, while the *open data points* have been dropped as being erroneous (see text)

Results and discussion

In this investigation rheology measurements were conducted at two different temperatures (15 and 40 °C); however, at low TB concentrations only the temperature slightly below room temperature (15 °C) could be used, while at high concentrations the measurements could only be performed at the high temperature (40 °C). The reason for this is the phase behavior of the aqueous TB solution. Generally, PEG-based compounds in aqueous solution have a reversed temperature dependency and a phase separation into one phase rich and one phase depleted in PEG-containing molecules is induced by increasing the temperature [7]. This is also the case with the present TB polymer, and the phase-separation temperature passes through a minimum corresponding to about 20 °C at a TB concentration of about 0.6 wt% (Fig. 2) [4]. On the other hand, at high concentrations the solution separates into one phase very concentrated in TB polymer (virtually 100%) which is in equilibrium with a phase of a lower concentration. The concentration of the TB polymer in the lower-concentration phase is still relatively high (65 wt% at 15 °C and 85 wt% at 40 °C). The very concentrated phase contains TB polymer in the crystalline state. The crystalline structure of this phase has been detected by X-ray diffraction measurements. By increasing the temperature the tendency of this latter phase separation can be decreased so that the one-phase region extends to higher concentrations (Fig. 2). A deeper examination of the phase behavior was beyond the scope of the present investigation.

Steady-shear measurements versus oscillatory-shear measurements

At sufficiently low frequencies or shear rates all samples obeyed the Cox–Mertz rule [8] and, consequently, η^* had the same numerical value as η (Fig. 4a). At higher frequencies or shear rates this was not the case, and the two methods gave different results. As indicated in the Experimental section one reason for such an observation may be the penetration of air bubbles into the measuring gap; however, great care was taken to only present data that represent material properties of the polymer solution. In contrast to the oscillatory-shear measurements, which all were performed at small deformations (linear viscoelastic region), the steady-shear mode results in a more severe perturbation of the sample [9]. At rest, the equilibrium situation may be pictured in the following way. Virtually all polymer chains are associated in aggregated structures of various sizes, and provided the concentration is sufficiently high, a percolated dynamic network structure reaches throughout the solution [4, 9]. The effect of the flow may be that the percolated network is fragmented into smaller aggregated structures [9]; however, the fragments, which are oriented in the flow profile, may still contain many associated polymer chains. This process may be seen as a virtual reduction of the polymer concentration (i.e. the number of polymer chains contributing to the viscosity via intermolecular associations within the percolated dynamic network is decreased). Another effect of the flow may be that polymer chains, which are due to hydrophobic associations serving as links in the network, are stretched. The stretched-chain conformations provide energy to overcome the potential barrier for disengagement. In this way the exit rate from a polymer–polymer junction is increased (i.e. higher dynamics) [10]. Both these effects are expected to decrease the viscosity and, thus, the shear-thinning region should first be detected in the steady-shear mode; however, at the lowest concentration (3 wt%) the opposite was observed, and the shear-thinning region was first detected with the rheometer put in the oscillatory-shear mode (Fig. 4a). A tendency for shear-thickening can also be discerned from the steady-shear measurement in an intermediate shear-rate range at this concentration. Others have reported similar observations for solutions of associating polymers, with a shear-thickening region before the shear-thinning part [9, 11–13]. This may be rationalized along the same lines as Witten and Cohen [14, 15] used to explain the shear-thickening behavior of ionomers in organic solvents. They concluded that the effect was due to a rearrangement from intra- to interaggregation when individual polymer chains were stretched in the flow profile (i.e. the number of polymer chains contributing to the viscosity via intermolecular associations is increased). Recently Tam et al. [9] argued that flow-induced interaggregation also increases the fraction of polymers that participate in the percolation network; however, at even higher shear rates the normal shear-thinning behavior is always observed (Fig. 4a). We note that in the unperturbed state the fraction of polymer chains in the loop conformation (i.e. both ends of the polymer chain bind to the same hydrophobic domain) is expected to increase when the concentration decreases. Therefore, in a limited concentration interval the shear-thickening effect is expected to increase with decreasing concentration.

Influence of dynamics on the viscosity

Figure 5 reports η^* from the low-frequency limit ($\omega \rightarrow 0$), where all solutions had Newtonian behavior (frequency-independent viscosity). At 15 °C the viscosity seems to reach a plateau, and within the concentration range investigated, no significant decrease can be observed; however, at this temperature the concentration range is limited, while at 40 °C, where higher concentrations are accessible, the Newtonian viscosity passes through a maximum, and a decrease corresponding to more than one decade can be observed at high TB concentrations. In order to rationalize these observations it may be valuable to follow the concentration dependency of the evolution of G' and G'' (as a function of frequency) (Fig. 6). An indirect way to probe polymer dynamics is to determine the inverse angular frequency, $\tau^* = 1/2\pi f^*$, where G' and G'' intersect. At times shorter than this characteristic time a solution has a response which is mainly elastic (this may be interpreted as the polymer chains not having the time to relax to their new equilibrium positions), while at longer times viscous behavior prevails. However, it is important to realize that τ^* is not expected to correspond to any characteristic time on a molecular level, but rather it should be used to indicate differences between samples. It is likely that τ^* is influenced by factors such as entanglements and intermolecular associations. The

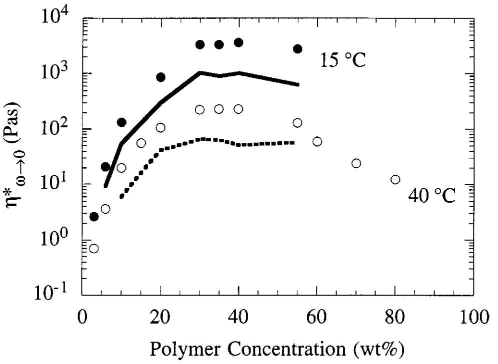

Fig. 5 The Newtonian viscosity as a function of TB polymer concentration. The data points were obtained from oscillatory-shear experiments via the complex viscosity, η^*, when the angular frequency, ω, approached 0 s^{-1}. The *lines* are calculated as the product of G^* and τ^* (see text). *Dots* (●) and the *full line* refer to 15 °C, while *open circles* (○) and the *dashed line* were obtained at 40 °C

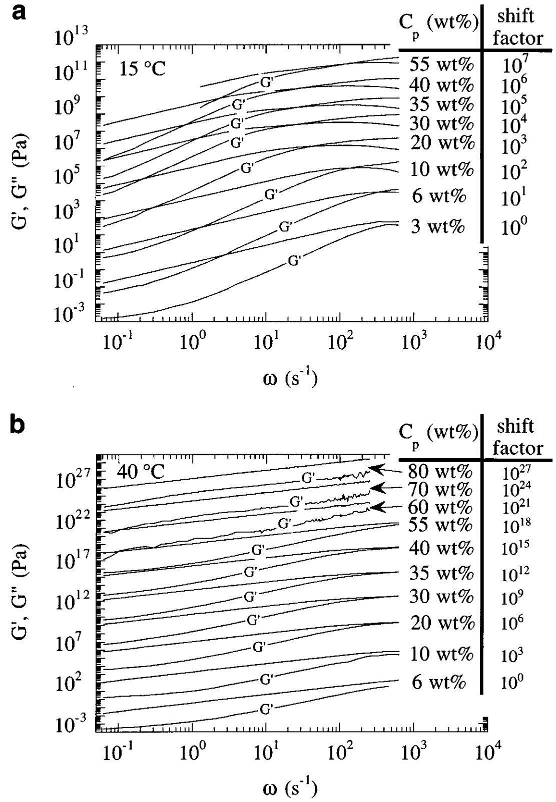

Fig. 6 a Storage, G', and loss, G'', moduli as a function of angular frequency, ω. Measurements at eight different concentrations of the TB polymer are given, and in order to have a separation between the different measurements the curves were vertically shifted by the shift factors given. For each TB concentration the storage modulus is indicated, and the line above each G' curve represents the corresponding loss modulus. The concentration corresponding to each pair (of G' and G'') is given in the table. From *bottom* to *top* the TB concentration is 3, 6, 10, 20, 30, 35, 40, and 55 wt%. The temperature was kept constant at 15 °C. **b** The same as in **a** but the measurements were performed at 40 °C. Each pair of G' and G'' curves corresponds to the concentrations given in the table. Note the shift factors coordinates (τ^* and G^*) of the intersection points of G' and G'' for the different samples at the two temperatures are shown in Fig. 7. Generally, for polymer solutions the expectation is that the dynamics and the viscosity of the solution are coupled. For solutions containing nonassociating polymers the normal case is that an increased entanglement situation follows an increasing polymer concentration. Thus, an increase both in the Newtonian viscosity as well as in τ^* is anticipated with increasing concentration. This is indeed the case at low-to-intermediate TB concentrations, while in line with what was observed from the viscosity (Fig. 5), Fig. 7 clearly shows that, with the present TB polymer, τ^* passes through a maximum, and a decrease is observed at high concentrations; however, the concentration corresponding to the onset of the decrease differs somewhat for the two parameters (with the decrease in τ^* located at a lower concentration). Figure 7 also shows that G^* increases in the concentration range investigated. In a system where the rheological response is determined by a single relaxation process the product of the characteristic time of that process, τ, and the value of the storage modulus in the high-frequency limit, G_∞, is proportional to the Newtonian viscosity [16]: $\eta = \tau G_\infty$. In Fig. 5, together with the data of the Newtonian viscosity, we have included the product $\tau^* G^*$. Despite the absolute values differing, the evolution with concentration is similar. Here we notice that a difference is expected since $G^* \neq G_\infty$ and, furthermore, it is reasonable that, at least at high concentrations, this system is associated with more than one relaxation process. This would in turn imply that $\tau^* \neq \tau$.

Influence of structure on the viscosity

Here a more thorough discussion regarding the microstructure of the solution is valuable. Relative-viscosity measurements on the corresponding DB system (from which the TB polymer is produced – see Material and sample preparation section and Fig. 1) and a nonlinear least-squares fit of a hard-sphere model to that data, suggest that this solution approaches maximum packing at a DB concentration of about 5–6 wt%. Of course one has to be careful with absolute values given by the hard-sphere model since the micelles definitely have a soft potential; however, it should be without doubt that at fairly low concentrations the solution is filled with micelles. This conclusion is also suggested by the intrinsic viscosity, $[\eta] = 47\ \mathrm{cm}^3/\mathrm{g}$, of the DB system, which suggests that the micelles overlap at a concentration of 2.1 wt% (calculated from the reciprocal intrinsic viscosity $[\eta]^{-1} = 0.021\ \mathrm{g/cm}^3$). The intrinsic viscosity was extracted from measurements in the concentration range 0.1–5 wt% of the DB polymer. Because the critical micelle concentration, (cmc) of this compound is expected to be very small, $[\eta]$ refers to a solution containing DB micelles. (The cmc of a similar DB compound, $C_{18}EO_{84}$, was reported to be 10^{-3} wt% [17].) We note that the different numerical values from the two different methods (5–6 and 2.1 wt%, respectively) are to be expected. The hard-sphere model results in a smaller radius of the micelles than that given by intrinsic viscosity data, which give the hydrodynamic radius. Furthermore, the suggestion that the solution is filled with micelles at rather low concentrations is in line with a recent investigation regarding structural and dynamic properties of aqueous solutions of the related compound $C_{17}EO_{84}$ [18]. It was found that the micellar phase at low concentration was followed by a close-packed micellar phase at higher concentration (transition region 10–20 wt%). From an earlier publication it is known that the present TB compound also assembles in self-aggregated structures [4]; these are expected to have a strong resemblance to the DB micelles. At very low TB concentrations the average distance between "polymeric micelles" is long, and there is a high probability that a TB polymer has both ends in the same micelle, with the PEG middle block being in a loop conformation; however, this is not the case in the present investigation because higher concentrations are employed. With increasing concentration intermicellar bridges become increasingly important, and this is the main reason for an increased viscosity with increasing TB concentration. At even higher concentrations the bridges are expected to reach not only nearest micelles but also micelles further away [19]; thus, at intermediate concentrations the solution may be viewed as consisting of polymeric micelles connected via these bridges to "clusters", and at higher concentrations the solution becomes more entangled with "interpenetrating clusters". We conclude that the observation that τ^* and the viscosity increase with increasing concentration at low-to-intermediate TB concentrations is reasonable.

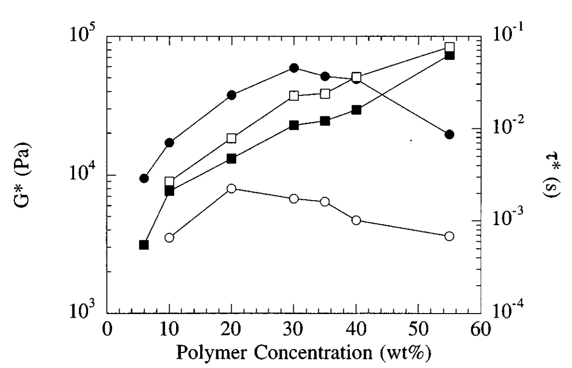

Fig. 7 τ^* (*circles* and *dots*) and G^* (*open* and *filled squares*) given from the "cross-over" points in Fig. 6a. *Filled symbols* refer to 15 °C, while *open symbols* refer to 40 °C. The "cross-over" points in the 10 and 55 wt% solutions at 40 °C were determined by extrapolating G' and G''

If the increase in τ^* and the viscosity is straightforward to explain, it is more difficult to rationalize the decrease in these parameters at high concentrations. The first alternative which comes to mind is a transition from a close-packed micellar phase containing spherical aggregates in cubic symmetry, to a hexagonal phase, and later a lamellar phase. This is the normal behavior when increasing the concentration in systems containing amphiphilic compounds [20]. The structural change is expected to reduce the viscosity because the symmetry in the solution changes. Rods in hexagonal symmetry and lamellas can slide relative to each other. One example of where the viscosity has been reported to decrease by passing the phase border from cubic micellar to hexagonal is in aqueous solutions of Pluronic polymers [21, 22]. [A Pluronic polymer has the structure $(EO)_n$(propylene oxide)$_m(EO)_n$.] In these investigations increasing the temperature while keeping the concentration fixed changed the microstructure in the Pluronic solution; however, such a phase transition should also result in birefringence of the samples when observing them between crossed-polarized glass plates. No birefringence could be detected for any of the TB samples. Perhaps the lack of less-curved aggregates (hexagonal and lamellar structures) could be anticipated taking into account the large middle block of the TB molecules. The associated big headgroup area at the polar/nonpolar interface should tend to give a high spontaneous curvature towards oil favoring spherical aggregates. This is a general trend with increasing headgroups that has been observed both experimentally and in mean-field calculations in systems containing the Pluronic type of polymer [23, 24]. At the present stage we do not have an unambiguous explanation for the decreased τ^* and viscosity at high TB concentrations, but we believe that the observation can be ascribed to the fact that the solution approaches a "meltlike" state. Thus, the border between polar and nonpolar regions becomes blurred, and the solution becomes more homogeneous on a molecular level. In this view, and referring to Figs. 5 and 7, the viscosity decreases as a result of a gradual change, starting with a decreased lifetime of the hydrophobic moieties in the polymeric micelles and ending with vanishing interpenetrating clusters, clusters, and micelles.

Conclusions

In this paper we have shown that the viscosity changes in a nonmonotonous way with increasing concentration of an HM-PEG polymer (TB) in aqueous solution, and at high concentrations the viscosity decreases substantially. At low and intermediate TB concentrations the increase in viscosity was interpreted in terms of the formation of polymeric micelles, which were connected to clusters and later, at higher concentrations, interpenetrating clusters. The decrease in viscosity at high concentrations was suggested to be due to a gradual transformation towards a meltlike state, and at this stage the organization of the solution into polar and nonpolar regions should be less pronounced.

The observation should be important, for instance, for manufacturers of polymers of the TB type. Such polymers are generally shipped to consumers in aqueous solution, and a low viscosity solution with a high dry content is desired. This has, for instance, been obtained by adding different cosolutes (as exemplified by nonpolar solvents and surfactants) to solutions containing a moderate TB concentration. The observation in this investigation suggests that a high dry content and a relatively low viscosity may be obtained by simply increasing the TB concentration; however, with the present TB polymer the highest concentrations (and thus the lowest viscosity) are not easily accessible due to the formation of a crystalline phase at low-to-intermediate temperatures. Here we note that the latter property may also be of interest. Under conditions where the concentrated sample phase-separates, it follows that the viscosity of the micellar phase (which is the main part of the sample) increases substantially due to a decrease in the HM-PEG concentration in that phase. By lowering the temperature of a solution containing at least 80 wt% HM-PEG to below 10 °C an increase in the viscosity corresponding to about one decade can be expected (as suggested by Figs. 2, 5 in combination). This is a property that may be useful in applications where a "gelation" by lowering the temperature is sought.

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