Linear Viscoelasticity of a Polymeric Bicontinuous Microemulsion

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ABSTRACT: Ternary polymer blends of immiscible homopolymers and the corresponding diblock copolymer are useful models for studying equilibrium and nonequilibrium behavior of self-assembled fluids. We report linear viscoelastic data for a polymeric bicontinuous microemulsion, experiments that are possible due to the comparatively high viscosities of the principal components. After subtracting a viscous background contribution from the pure constituents, the microemulsion exhibits “excess” viscoelastic behavior similar in character to that resulting from the Rouse model of polymer dynamics. The data are compared to the predictions of a time-dependent Landau–Ginzburg model developed by Pätzold and Dawson, using structural parameters derived from neutron scattering as input. This model captures the essential characteristics of the viscoelastic behavior very well. However, using independent dynamic light scattering measurements of the Onsager coefficient for these blends, it appears that the model fails to predict either the magnitude or the temperature dependence of the zero shear viscosity and relaxation time of the microemulsion accurately. Possible origins for these discrepancies are discussed.

Introduction

Self-assembling fluids exhibit a rich diversity of equilibrium and nonequilibrium phenomena. The supramolecular organization of surfactants, liquid crystals, and block copolymers reflects a subtle balance of energetic and entropic effects. In the case of typical surfactant mesophases, the presence of water complicates the phase behavior significantly, owing to its specific and highly temperature-dependent interactions with both hydrophilic and hydrophobic moieties. Ternary polymer blends, composed of two immiscible homopolymers with the corresponding diblock copolymer, can be very useful as model surfactants since their thermodynamic interactions are better understood, exhibit a simpler temperature dependence, and may be easily manipulated through choice of monomer and molecular weight.

In this work we consider the rheology of bicontinuous microemulsions (B_{tE}). While many surfactant systems are known to exhibit B_{tE} phases, they typically occur over a narrow temperature range. It has now been established that B_{tE} phases may be routinely accessed in ternary polymer blends through suitable selection of molecular weight and blend composition. The wider temperature range accessible to polymeric B_{tE} phases has facilitated detailed studies of their underlying thermodynamics and dynamics, drawing heavily upon the phenomenological Landau–Ginzburg free energy description of Teubner and Strey. The effects of shear flow on microemulsion structure and rheology have been analyzed theoretically using nonequilibrium generalizations of this approach. However, there are very few rheological data available for this class of fluids, due to the low viscosity and associated fast dynamics of surfactant-based B_{tE} phases. Here again, polymeric systems offer substantial advantages, in that their higher viscosity slows structural relaxation processes to a more readily accessible time scale. Indeed, we have recently documented a diverse range of rheological and structural phenomena in a polymeric bicontinuous microemulsion subjected to steady shear flow. In this paper, we examine the linear viscoelastic response of this system. By combining rheological measurements with small-angle neutron scattering (SANS) and dynamic light scattering (DLS), we perform the first direct tests of theoretical descriptions of microemulsion rheology.

Theoretical Background

Pätzold and Dawson have analyzed shear-induced structural changes and rheology in self-assembling fluids. While Teubner and Strey demonstrated that the quiescent scattering from bicontinuous microemulsions could be well-represented using only quadratic terms in the free energy expansion, Pätzold and Dawson retained higher-order terms in their analysis. Although these terms may play a role under strong flow conditions, in the equilibrium state they merely lead to a renormalization of the quadratic coefficients, so that the structure factor has the same form as given by Teubner and Strey:

\[ S(q) = \frac{KT}{a_2 + c_1q^2 + c_2q^4} \]

where T is temperature, k is the Boltzmann constant, q is the scattering vector, and \(a_2\), \(c_1\), and \(c_2\) are coefficients of the free energy expansion. In particular, \(a_2\) is the coefficient of the leading term in fluctuations of the order parameter (i.e., the local deviation from the average composition), and \(c_1\) is the coefficient of the leading gradient term. At a certain temperature the system may cross the Lifshitz line, where \(c_2 = 0\), and at lower temperatures the spontaneous formation of
interface is favored \((C_2 < 0)\). In this regime the structure factor exhibits a maximum at \(q = q_{\text{max}} = \sqrt{-C_2/2C_1}\).

Two characteristic lengths may be extracted from this form of the structure factor, a periodicity, \(d\), and a correlation length, \(\xi\), given by

\[
d = 2\pi \left[ \frac{1}{2} \left( \frac{a_2}{2c_2} \right)^{1/2} \right] \left[ \frac{1}{4} \left( \frac{c_1}{2c_2} \right) \right]^{-1/2}
\]

\[
\xi = \left[ \frac{1}{2} \left( \frac{a_2}{2c_2} \right)^{1/2} \right] \left[ \frac{1}{4} \left( \frac{c_1}{2c_2} \right) \right]^{-1/2}
\]

The periodicity, \(d\), describes the natural length scale of the B/rE structure, namely the average distance between A-rich and B-rich domains. The correlation length reflects the coherence of the structure. Given the presence of extensive interfacial structure within the B/rE, it is reasonable to expect an enhanced viscoelastic response, above that associated with a completely disordered mixture of the components themselves. In the slow-flow limit, Pätzold and Dawson showed that the "excess" viscosity associated with deformation of the self-assembled fluid structure is given by \(\eta_{\text{excess}} \approx \eta_{\text{viscous}} \times \Delta q^{3/2}\).

\(\eta_{\text{excess}}\) may be obtained from \(\eta_{\text{viscous}}\) according to the methodologies described elsewhere, as noted above, only treating the component viscous dissipation. The behavior predicted by eqs 5 and 6 is, in broad terms, Rouse-like: terminal viscoelastic behavior at low frequencies, crossing over to \(\eta'' = \eta''_0 \sim \omega^{-1/2}\) in the limit of high frequencies. However, the details of the frequency dependence are somewhat distinctive, in that the viscoelastic phase angle, \(\delta = \tan^{-1}(\lambda_1'/\lambda_1'')\), exhibits a mild undershoot on its way to the high-frequency asymptote of \(\pi/4\). We reemphasize that the above expressions do not include the background pure component viscous dissipation.

**Experimental Section**

Poly(ethylene) (PEE), poly(dimethylsiloxane) (PDMS), and a PEE–PDMS block copolymer were synthesized using methods described elsewhere, and the samples used here have molecular weights of 1710, 2130, and 10 400 \((M_{\text{PEE}} = 0.52)\), respectively, with low polydispersities \((M_{\text{PEE}}/M_{\text{PDMS}} = 11)\). In both homopolymer and copolymer, the PEE was partially deuterated by saturating the precursor \(1,2\)-polybutadiene with deuterium. The microemulsion sample was prepared with volume composition 10% copolymer, 45% PEE, and 45% PDMS. Both the molecular weights and volumetric compositions of this sample render it highly symmetric in a thermodynamic sense, a condition which facilitates formation of the bicontinuous microemulsion phase. However, the sample is very asymmetric dynamically; for instance, at 20 °C, the viscosities of the PEE and PDMS homopolymers are 26 and 0.026 Pa·s, respectively. Due to their low molecular weights, the measurable rheological response of the homopolymers is entirely Newtonian.

Neutron scattering experiments were performed using the 30m NSF/CHNRS SANS instrument NG-3 at NIST (Gaithersburg, MD). The data presented here were collected in a quartz Couette shear cell; however, only quiescent data are used in this work. The incident neutron beam \((\lambda = 12 \AA, \lambda \Delta \lambda = 0.11)\) passes radially through the cell, with a total sample thickness of 1 mm. Rheological characterization of the microemulsion sample was performed using a Rheometrics Scientific ARES controlled-strain rheometer, using cone and plate fixtures and a convection oven with dry nitrogen atmosphere for temperature control.

**Results and Discussion**

Equation 1 describes the SANS data obtained in the PEE–PDMS microemulsion very well (Figure 1) over a range of temperatures. Table 1 presents the structural variables extracted from the fits to these data; the parameters and general trends agree well with prior experiments covering a wider temperature range. As temperature decreases from 30 to 10 °C, both \(d\) and \(\xi\) increase, reflecting the increasingly segregated and organized state of the microemulsion; these changes are rather modest over this limited temperature range. For this sample the Lifshitz line is crossed at 72 °C.

Krisnan and co-workers have recently reported both the linear and nonlinear rheological response of this PEE–PDMS microemulsion sample. The analysis of Pätzold and Dawson, as noted above, only treats the "excess" rheological properties associated with the self-assembled fluid structure. To make comparisons to this theory, therefore, it is necessary to subtract the background viscous response arising from the pure components. In light of (i) the extreme viscosity contrast
between the two homopolymers, (ii) the spatially heterogeneous state of mixing between PEE and PDMS, and (iii) the unknown viscosity of the PEE–PDMS block copolymer (at these temperatures the pure diblock is in the lamellar ordered state), there seem to be no prospects for estimating this purely viscous contribution from first principles. However, in fitting a discrete relaxation spectrum to linear viscoelastic data on this sample, it was determined that a purely viscous contribution must be included to properly represent the relative magnitudes of the elastic and viscous moduli.\(^{15}\) We believe that this may be taken as a reasonable estimate of the sought-after pure-component contribution to the rheology of the microemulsion sample and denote it the "background" viscosity, \(\eta_b\). (This plays a role analogous to the solvent viscosity in polymer solution rheology.) Figure 2 presents the excess viscoelastic properties, \(\Delta\eta' = \eta' - \eta_b\) and \(\eta''\), measured in the PEE–PDMS microemulsion. For data collected at 10 °C, Figure 2 also presents the full measured \(\eta''\) to illustrate the effects of subtracting the background contribution. The remarkable shift in the position of the \(\eta''\) maximum, in particular, reflects a very strong temperature dependence in the average viscoelastic relaxation time.\(^{15}\) The rheological properties of the microemulsion are summarized in Table 2.

Apart from large changes in zero-shear viscosity and relaxation time, the complex viscosity components have similar shapes at all temperatures studied. This is emphasized in Figure 3, in which the data are plotted in reduced form, using the zero-shear excess viscosity and the average relaxation time as scaling factors. The data reduce well to a master curve, and the main features agree well with the qualitative behavior predicted by Pätzold and Dawson.\(^{11}\) The solid curves in Figure 3 are the predictions of eqs 5 and 6, computed using parameters derived from neutron scattering data collected at 20 °C. The data cover the full temperature range 10 to 30 °C, consistent with the data.)

A more sensitive test of the model is provided by considering the phase angle, \(\delta\) (Figure 4). There is an obvious discrepancy between the data, which fall off at high frequency within each data set, and the model prediction, which plateaus toward the high frequency asymptote of 45°. The theory will naturally break down at sufficiently high frequencies where the elastic character of the polymer constituents comes into play. However, recognizing that no elastic character was detectable in the pure homopolymers at these frequencies, the disagreement in Figure 4 may partly be an

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Table 1. Parameters Derived from Teubner–Strey Fits to Neutron Scattering Data

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>d (nm)</th>
<th>(\xi) (nm)</th>
<th>(\beta)</th>
<th>(I(0)) (cm(^{-1}))</th>
<th>(q_{\text{max}}) (nm(^{-1}))</th>
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<td>0.0791</td>
<td>0.0796</td>
</tr>
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</table>

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Table 2. Viscoelastic Properties of PEE–PDMS Microemulsion

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(\eta_b) (Pa s)</th>
<th>(\Delta\eta\eta_0) (Pa s)</th>
<th>(\lambda) (s)</th>
<th>(\Delta\eta\eta_0\lambda) (Pa)</th>
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<tr>
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<td>5.58</td>
<td>0.148</td>
<td>37.7</td>
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</tbody>
</table>

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Figure 1. Quiescent neutron scattering from PEE–PDMS microemulsion. Curves represent fits of eq 1 to the data.

Figure 2. Complex viscosity components, \(\Delta\eta' = \eta' - \eta_b\) (filled symbols) and \(\eta''\) (open symbols), vs angular frequency. For clarity, curves have been shifted vertically by a factor \(C = 9\) (10 °C), 3 (15 °C), 1 (20 °C), \(\lambda_b\) (25 °C), and \(1/3\) (30 °C). In the case of the 10 °C data, the symbol (iii) denotes the raw \(\eta'\) data, prior to subtraction of the background viscosity.

Figure 3. Data from Figure 2 plotted in reduced form. Solid curves represent predictions of eqs 5 and 6, computed using parameters derived from neutron scattering data collected at 20 °C.

Figure 4. Data from Figure 2 plotted in reduced form. Solid curves represent predictions of eqs 5 and 6, computed using parameters derived from neutron scattering data collected at 20 °C.
artifact of the way in which the background viscosity term was estimated. Since data were not available at frequencies greater than 100 rad/s, the discrete relaxation time spectrum fit to the viscoelastic portion of the response used a shortest relaxation time of 0.01 s. While theory suggests the existence of faster viscoelastic modes, the lack of high-frequency data means that any such contributions in the data are lumped into the viscous background term, \( \eta_b \), which thus is most likely an overestimate of the actual dissipative contributions from the pure components. When subtracted from the experimental \( \eta' \) data, this would artificially suppress the viscous component of the microemulsion viscoelasticity, particularly at high frequency. Given these experimental limitations, the best case for comparison with the theory should be the data at 10 °C, where a greater portion of the microemulsion relaxation spectrum occurs within the accessible frequency range. These data are qualitatively similar to the theoretical predictions, including a distinct undershoot in phase angle with increasing frequency. The theory underpredicts the phase angle slightly in the high-frequency range. If \( \eta_b \) is indeed overestimated as described above, this discrepancy would actually be larger than it appears in Figure 4, since adding viscous character to the microemulsion viscoelasticity would elevate the phase angle.

Although the viscoelastic data collected at different temperatures collapse extremely well in Figure 3, this sample is not thermorheologically simple in the usual sense. As may be seen in Table 2, the average relaxation time depends more strongly on temperature than does the zero-shear viscosity. Considering eqs 4 and 7, the major source of temperature dependence is expected to be the microscopic mobility, \( \Lambda \), which affects both \( \Delta \eta_0 \) and \( \lambda \). Quantitative tests of the absolute predictive capabilities of the Pätzold and Dawson analysis require independent data on the temperature dependence of the Onsager coefficient of the microemulsion sample. Morkved and co-workers have studied this microemulsion sample using dynamic light scattering. Over a wide temperature range, they found that the autocorrelation function was dominated by a single diffusive mode. The diffusivity measured in dynamic light scattering may be expressed in terms of the Onsager coefficient and the static structure factor (independently measured by SANS) according to

\[
D = \frac{kT}{S(q=0) \Lambda}
\]  

(9)

where \( S \) is evaluated as \( q \to 0 \), owing to the large length scales probed in dynamic light scattering relative to neutron scattering. Using the known deuterium labeling content of the PEE in the sample, the appropriate neutron contrast factors may be calculated, allowing \( S(0) \) to be determined by

\[
I(q) = V\langle \Delta \rho \rangle^2 S(q)
\]

(10)

Figure 5 presents the Onsager coefficients computed by combining the dynamic light scattering and quiescent neutron scattering data on the microemulsion sample. As expected, \( \Lambda \) is highly temperature dependent.

Using the results in Figure 5, eqs 4 and 7 may be tested against the experimental data in an absolute fashion, since all parameters have been independently measured. Both the zero shear viscosity (Figure 6a) and the average relaxation time (Figure 6b) are significantly underpredicted by the analysis of Pätzold and Dawson, and the temperature dependence of neither quantity is precisely captured. A somewhat more constrained test may be made by considering the ratio \( \Delta \eta_0 / \lambda \). Combining eqs 4 and 7 shows that this quantity no longer involves the Onsager coefficient and hence should be unaffected by any uncertainty in the data in Figure 5:

\[
\frac{\Delta \eta_0}{\lambda} = \frac{2}{15\pi} \frac{kT \xi_1 f_1^2(\alpha)}{d^4 f_2(\alpha)}
\]

(11)

Figure 6c shows that this quantity is more highly temperature dependent than \( \lambda \) predicts.

Several factors might contribute to the discrepancies between theory and experiment evident in Figure 6. First, we consider the aforementioned uncertainty in the bare viscosity. Given that \( \Delta \eta' \) must remain positive, an upper bound estimate of \( \eta_b \) may be obtained from the smallest value of \( \eta' \) measured in the microemulsion at high frequency. At 10 °C, for instance, \( \eta'(100 \text{ rad/s}) = 20.5 \text{ Pa s}, \) slightly larger than \( \eta_b = 16.4 \text{ Pa s}. \) Using this larger value could only account for about 2% of the discrepancy between the predicted and measured \( \Delta \eta_0 \). Further, subtracting the larger background value would warp the high frequency \( \Delta \eta' \) data so that they would no longer exhibit the Rouse-like \(-1/2 \) power law at high frequency predicted by the theory. We may conclude that the uncertainty in the background term plays at...
and cannot even speculate as to whether ever, we have no experimental access to this quantity that the relevant microemulsion dynamics occur. How-

viscosity to relaxation time as a function of temperature. (c) Ratio of excess zero-shear viscosity as a function of temperature. (b) Average for viscoelastic properties of the microemulsion. (a) Excess q factor, rather than at

Experimental data. (c) Predictions of eqs 4, 7, and 11 using parameters from Table 1 and Figure 5.

Figure 6. Absolute tests of Pätzold and Dawson predictions for viscoelastic properties of the microemulsion. (a) Excess zero-shear viscosity as a function of temperature. (b) Average relaxation time as a function of temperature. (c) Ratio of excess viscosity to relaxation time as a function of temperature. (●) Experimental data. (○) Predictions of eqs 4, 7, and 11 using parameters from Table 1 and Figure 5.

most a minor role. A second issue concerns the Onsager coefficient. It would presumably be more appropriate to employ \( \lambda \) evaluated at the peak of the structure factor, rather than at \( q = 0 \), as it is on that length scale that the relevant microemulsion dynamics occur. However, we have no experimental access to this quantity and cannot even speculate as to whether \( \lambda(q_{\text{max}}) \) is greater than, equal to, or less than \( \lambda(0) \). However, in Figure 6c the Onsager coefficient has been factored out, and yet a significant discrepancy remains; therefore, we conclude that this cannot be the main explanation.

We suspect that the main origin of the difference between experiment and theory lies with the theory and in particular with its assumption of a homogeneous strain field. For a system with such a large viscosity contrast between the components—such as the one employed here—it is not difficult to envision an inho-
mogeneous strain field at the length scale of the microemulsion, d. Unfortunately, it is not a trivial matter to incorporate this possibility into the framework of Pätzold and Dawson’s model. Further, since these modifications would lead to a full coupling of a complex fluid mechanics problem with the Langevin equation for the order parameter field, it is difficult to anticipate how the theoretical predictions would be affected. However, from the experimental perspective it should be possible to construct a bicontinuous microemulsion from polymer components with nearly identical viscosities. Since oil/water/surfactant bicontinuous microemulsions may not exhibit the extreme viscosity contrast of the PEE–PDMS system considered here, a viscosity-matched polymer system might also be a more faithful model of surfactant-based systems.

Conclusions

The linear viscoelastic properties of a polymeric bicontinuous microemulsion have been described. The presence of the microemulsion structure confers a substantial frequency dependence to the components of the dynamic viscosity and an excess viscosity over that of the pure components. Furthermore, the microemulsion exhibits a strongly temperature-dependent relaxation time, which is well within the experimentally accessible frequency range. This may be contrasted with oil/water/surfactant microemulsions, where any viscoelastic response typically lies outside the experimental window.

The results have been compared to the model of Pätzold and Dawson, which describes the excess viscoelasticity based on a Landau–Ginzburg free energy expansion, and the coupling of the order parameter and velocity fields under shear. The theory captures the main features of the viscoelastic response very well, including an approximately Rouse-like frequency dependence at high frequencies, and even a small undershoot in the phase angle with increasing frequency. However, by employing parameters obtained from previous SANS and DLS measurements on the same microemulsion, it is possible to compare the data with the Pätzold and Dawson theory quantitatively. In this case it emerges that the theory tends to systematically underestimate the excess viscoelasticity. Among the possible contributing factors, the most likely candidate is the assumption of a locally homogeneous strain (or velocity) field, given that the pure homopolymer components have viscosities that differ by a factor of approximately 1000.

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References and Notes

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