Shear-Induced Anisotropy in a Polymer Bicontinuous Microemulsion

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Introduction

Polymer blending is frequently used as an inexpensive route to new materials with synergistic properties. Unfortunately, most pairs of polymers are immiscible and tend to segregate into macroscopically distinct phases. Addition of diblock copolymer as a compatibilizer is a common strategy to enhance the dispersion of the components in polymer blends. It has recently been demonstrated that the addition of block copolymer to an immiscible blend can, under suitable circumstances, lead to an equilibrium bicontinuous microemulsion phase that lies in a region intermediate between swollen lamellar diblock copolymer and macroscopically phase-separated homopolymers in the ternary phase diagram.[1] Examples of polymer bicontinuous microemulsions have now been prepared in several different polymer systems.[2] Here we examine how the microculsion structure is affected by shear flow, using a novel x-ray shear device for studying complex fluid structure in the 1-2 plane.

Methods and Materials

The shear cell is an annular variant of the familiar cone and plate design.[3] The incident x-ray beam is directed through a hole drilled in one side of an annular plate, and then through the gap between the cone and plate on the other side. The cone angle is 5˚, and the beam passes at an angle of 2.5˚ relative to the plate. The path length through the sample is 10 mm, much longer than is typically employed in x-ray studies of polymers. Use of short-wavelength synchrotron radiation reduces absorption and allows adequate flux for time-resolved studies. In these experiments, subambiant temperature control was achieved by circulating cold helium gas through the sample chamber, while using electric heaters to control the temperature of the two fixtures containing the sample. Undulator radiation with an energy of 17 keV (λ = 0.73 Å) was used to reduce absorptive losses within the sample. A two-dimensional CCD detector was used to collect x-ray scattering patterns in both steady-state and transient flows; transient experiments included flow inception, reversal, cessation, and oscillatory shear flow. We studied a bicontinuous polymer microemulsion consisting of poly(dimethylsiloxane) (PDMS) and poly (ethylethylene) (PEE) homopolymers with molecular weights of 2100 and 1700, respectively. These were blended with a symmetric diblock of the two polymers (PDMS-PEE) with molecular weight of 12,700. The sample was formulated to have a symmetric volume fraction (0.5) of each polymer, with a total homopolymer volume fraction of 0.90. This places the sample within the bicontinuous microemulsion phase, as has been previously characterized.[2]

Results and Discussion

Figure 1 presents representative x-ray scattering patterns collected in the 1-2 plane for the PEE-PDMS micromulsion at a temperature of 10˚C. In the quiescent state, the scattering is well described by the Teubner-Strey structure factor for microemulsions.[4] The isotropic scattering is peaked at a scattering vector q = 0.008 1/Å, corresponding to a correlation length of around 78 nm. Under shear, the scattering pattern becomes anisotropic. At low rates, anisotropy initially develops along the principal strain axes of shear flow, orientated at ±45˚ relative to the flow direction. Scattering is enhanced at –45˚, indicating that composition fluctuations with their normals along the compressive axis of shear are enhanced. In addition, the peak wave vector moves outward along this direction, indicating a compression of the length scale of the concentration fluctuations with this orientation. At higher rates, the degree of shear-induced anisotropy increases further, accompanied by a rotation of the peaks towards the velocity gradient direction. At the highest shear rates, the peaks move quite close to the gradient direction and concentration fluctuations become progressively aligned along the flow direction.

These patterns were corrected to remove the intense air scattering at low q, and then analyzed to extract quantitative measurements of anisotropy and orientation angle, present in Fig. 2. The anisotropy grows monotonically with shear rate, while the orientation shows a decrease from an initial value near 45˚ towards the flow direction with increasing shear rate. This is typical behavior for shear-induced anisotropy in complex fluid structure.

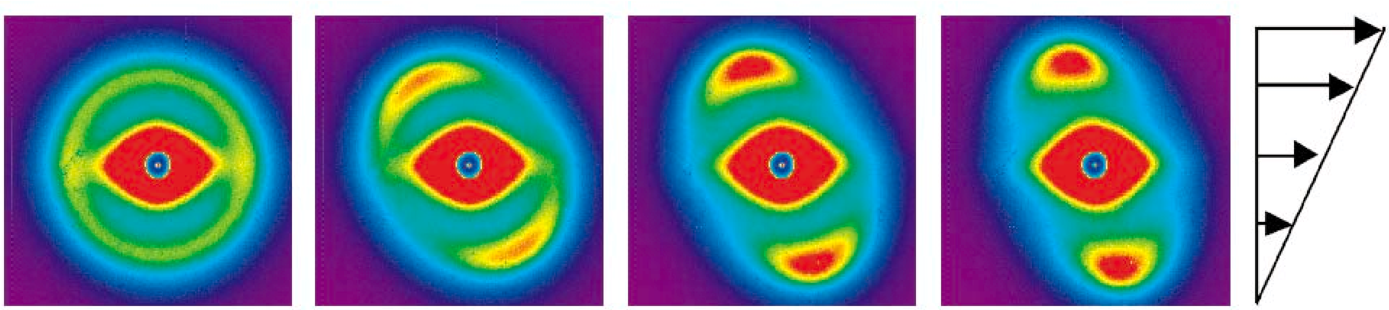

FIG. 1. 1-2-plane SAXS patterns from PDMS-PEE microemulsion at 10˚C, for shear rates of 0, 0.05, 0.1, and 0.2 s^{-1}. Lozenge-shaped feature at low q results from air scatter.

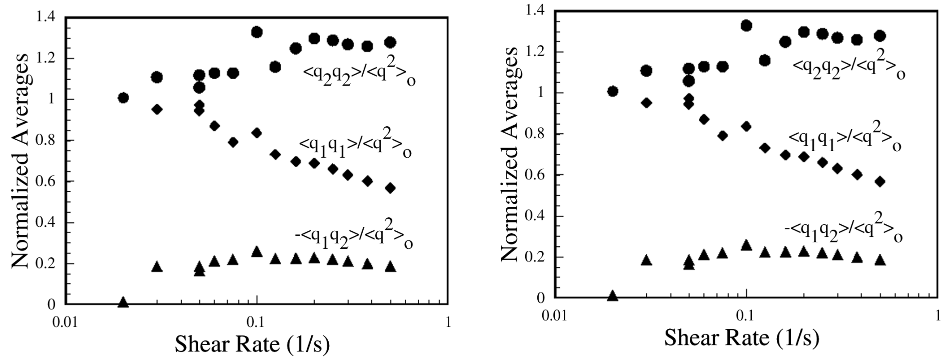

FIG. 2. Steady-state measurements of scattering anisotropy and orientation angle for shear of PDMS-PEE micromulsion at 10°C.

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