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Re-entrant Lamellar/Onion Transition with Varying Shear Rate in a Nonionic Surfactant ($C_{14}E_5$)/Water System

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Introduction

There have been reported many studies concerning the effects of shear flow on the structure of the lamellar phase. Among them, the most striking result may be the transition from the lamellar phase to the "onion phase" where all the space is filled by multilamellar vesicles alone [1]. Recently, we have reported the lamellar-to-onion transition with *increasing* temperature under a constant shear rate in the lamellar phase of a nonionic surfactant $C_{16}E_7$/water system (C_nE_m is an abbreviation of $C_nH_{2n+1}(OC_2H_4)_mOH$) by using simultaneous measurements of shear stress/small-angle light scattering and shear stress/small angle X-ray scattering (rheo-SAXS) [2, 3]. We have also found the re-entrant lamellar/onion (lamellar-onion-lamellar) transition with varying temperature at the shear rate of 3 s^{-1} in a $C_{14}E_5$/water system [4]. In the present study, we have performed rheo-SAXS experiments with a stepwise increase and decrease in the shear rate at constant temperature in the same system ($C_{14}E_5$/water) to find the re-entrant transition along another path.

Experimental

A rheometer AR550 (TA Instruments) is modified for rheo-SAXS experiments. Details of the cell have been reported previously [2]. Measurements were performed on the beamline 6A. The scattered beam was recorded using the CCD area detector covering the scattering vector range from 0.15 to 2.5 nm^{-1}.

Results and Discussion

Figure 1 shows time evolution of 2D SAXS patters for the radial configuration (we have also measured SAXS in the tangential configuration), shear stress (a), and the diffraction-peak intensity for each direction (b) with a stepwise increase in the shear rate in a $C_{14}E_5$/water system (35 wt%, 36°C). At the shear rate of 1 s^{-1}, first the most lamellae are oriented with the layer normal along the velocity gradient direction. After 300 s, the peak intensity in the velocity gradient direction takes a small maximum just before the increase in the shear stress and then rapidly decreases. On the other hand, the neutral peak abruptly increases and takes a maximum at about 800 s. As the time elapses further, the intensities in all the directions become equal, corresponding to the formation of onions.

When the shear rate exceeds 200 s^{-1}, the intensities in the velocity gradient and flow directions again deviate from the intensity in the neutral direction. These results suggest that the onion-to-lamellar transition with increasing shear rate. We have also performed rheo-SAXS experiments with a stepwise *decrease* in the shear rate from 1000 to 20 s^{-1} and confirmed that the SAXS pattern becomes isotropic below 200 s^{-1} indicating lamellar-to-onion transition with *decreasing* shear rate.

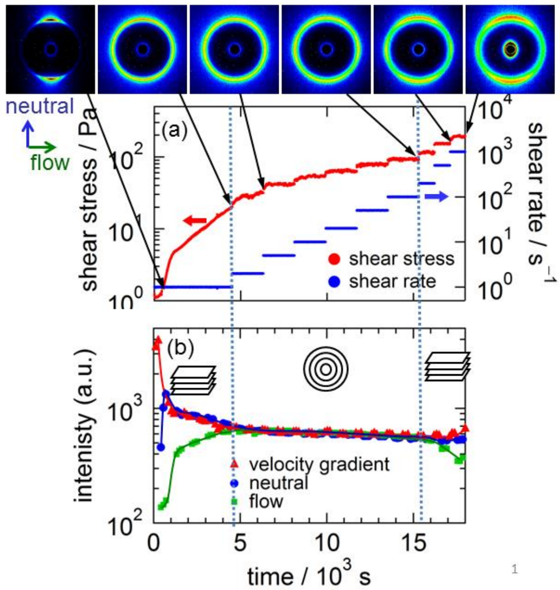

Fig. 1 Time evolution of 2D SAXS patters for the radial configuration, shear stress (a), and the diffraction-peak intensity for each direction (b) with a stepwise increase in the shear rate (see the scales on the right axis of (a)) in a $C_{14}E_5$/water system (35 wt%, 36°C).

These results suggest the re-entrant lamellar/onion transition, i.e., lamellar-onion-lamellar transition with varying shear rate. Taking into account the results of our previous studies, we can infer that the onion formation occurs only in the closed region in the temperature-concentration-shear rate diagram.

References

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