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Effects of Oscillatory Shear on the Orientation of the Inverse Bicontinuous Cubic Phase in a Nonionic Surfactant/Water System

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1 Introduction

The bicontinuous inverse cubic phase (V_2 phase) consists of bilayer networks with a long-range order. Although several reports have been published on the effects of shear flow in the bicontinuous (normal) cubic phase (V_1 phase) [1, 2], there has been no report in the V_2 phase except for the recent study of Seddon *et al.* [3] in a monoolein/1,4-butanediol/water system. They have shown that an oriented V_2 (Pn3m) phase can be obtained by applying the large-amplitude oscillatory shear (LAOS) to the L_3 phase durig addition of water to transform from the L_3 phase to the V_2 phase. To the authors´ knowledge, however, there has been no report on making highly oriented sample by applying shear directly to the V_2 phase. Moreover, the relation between the rheological properties and the grain growth under shear is unclear. In the present study, we have performed simultaneous measurements of rheology/small-angle X-ray scattering (rheo-SAXS) on the V_2 phase of a nonionic surfactant ($C_{12}E_2$)/water system.

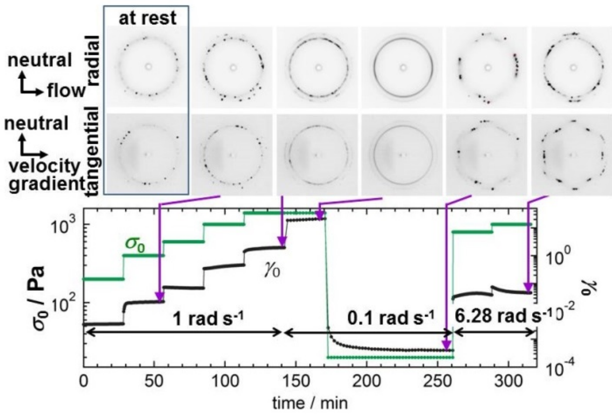

Fig. 1: Time evolution of 2-D SAXS patterns, stress amplitude (σ_0) and strain amplitude (γ_0) of the oscillatory shear for $C_{12}E_2$/water system (63 wt%, 30°C).

2 Experiment

The $C_{12}E_2$/water system exhibits two kinds of V_2 phase whose symmetries are different, i.e., Pn3m and Ia3d. We chose the latter which extends more wide temperature and concentration range than the former. Rheo-SAXS Measurements were performed on the beamline 6A by using a stress-controlled rheometer AR550 (TA Instruments) modified for SAXS experiments. Details of the cell have been reported previously [4]. The scattered beam was recorded using the CCD area detector covering the scattering vector range from 0.2 to 2.8 nm^{-1}. Before the rheo-SAXS experiments, the sample containing 63 wt% $C_{12}E_2$ was presheared at 20°C (lamellar phase). Then the temperature was raised to 30°C without shear corresponding to the Ia3d phase.

3 Results and Discussion

Figure 1 shows time evolution of 2-D SAXS patters for the radial and tangential configurations and strain amplitude (γ_0) with the change in the stress amplitude (σ_0) and the angular frequency (ω).

First we increased σ_0 stepwise from 200 Pa to 1400 Pa for $\omega = 1$ rad s^{-1}. With increasing σ_0, γ_0 increases and the 2-D SAXS pattern was changed from the spotty pattern to the powder pattern. After the application of the oscillatory shear for $\sigma_0 = 1400$ Pa, we changed ω from 1 rad s^{-1} to 0.1 rad s^{-1} keeping σ_0. This decrease of ω enabled us to increase γ_0 from 2 to 20, which made the diffraction pattern complete powder (isotropic) ring.

Next, we changed σ_0 from 1400 Pa to 20 Pa keeping ω to 0.1 rad s^{-1}, which led to the rapid relaxation of γ_0 from 20 to 0.002 followed by the slow relaxation to the steady state (~ 0.0004). At the same time, the spotty pattern reappeared. With the elapse of time, the peak intensity at a particular azimuthal angle increases, suggesting grain growth. After the application of the oscillatory shear under these conditions for 90 minutes, we changed σ_0 and ω to 800 Pa and 6.28 rad s^{-1} (1 Hz), respectively, and then, σ_0 to 1000 Pa keeping ω, leading increase of γ_0 up to ~0.05. Interestingly, this change of γ_0 enhanced the orientation of the sample as can be seen from the SAXS pattern in the tangential configuration.

These results indicate that the grain refinement occurs by LAOS (γ_0 ~ 20) whereas the small amplitude (γ_0 ~ 0.001) oscillatory shear just after the LAOS induces the grain growth. Furthermore, the grain growth is enhanced by the medium amplitude (γ_0 ~ 0.05) oscillatory shear. Thus, it may be possible to control the grain size only by changing the conditions of oscillatory shear.

References

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