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 (V₂ 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 (V₁ phase) [1, 2], there has been no report in the V₂ 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 V₂ (Pn3m) phase can be obtained by applying the large-amplitude oscillatory shear (LAOS) to the L₃ phase during addition of water to transform from the L₃ phase to the V₂ phase. To the authors’ knowledge, however, there has been no report on 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 V₂ phase of a nonionic surfactant (C₁₂E₂)/water system.

2 Experiment
The C₁₂E₂/water system exhibits two kinds of V₂ 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% C₁₂E₂ 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 patterns for the radial and tangential configurations and strain amplitude (γ) with the change in the stress amplitude (σ₀) and the angular frequency (ω).

First we increased σ₀ stepwise from 200 Pa to 1400 Pa for ω = 1 rad s⁻¹. With increasing σ₀, γ increasing and the 2-D SAXS pattern was changed from the spotty pattern to the powder pattern. After the application of the oscillatory shear for σ₀ = 1400 Pa, we changed ω from 1 rad s⁻¹ to 0.1 rad s⁻¹ keeping σ₀. This decrease of ω enhanced the orientation of γ, 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 σ₀ and ω to 800 Pa and 6.28 rad s⁻¹ (1 Hz), respectively, and then, σ₀ to 1000 Pa keeping ω, leading increase of γ up to ~0.05. Interestingly, this change of γ 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 ~ 20) whereas the small amplitude (γ ~ 0.001) oscillatory shear just after the LAOS induces the grain growth. Furthermore, the grain growth is enhanced by the medium amplitude (γ ~ 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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