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Orientation of the Inverse Bicontinuous Cubic Phase Induced by Combination of Oscillatory Shears with Different Strain Amplitudes

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1 Introduction

The Inverse bicontinuous cubic (V_2) phase consists of bilayer networks with a long-range order. Recently, we have studied effects of oscillatory shear on the orientation of the V_2 phase with a space group Ia3d formed in a nonionic surfactant ($C_{12}E_2$)/water system by using simultaneous measurements of rheology/small-angle X-ray scattering (rheo-SAXS) [1]. We have found that the grain refinement occurs by applying large amplitude oscillatory shear (LAOS) with the strain amplitude (γ_0) of about 20, whereas oriented sample can be obtained when small amplitude (γ_0 ~ 0.0004) oscillatory shear (SAOS) in the linear regime is applied just after the LAOS. Interestingly, the grain growth is strongly enhanced by the "medium amplitude" (γ_0 ~ 0.05) oscillatory shear ("MAOS") after the SAOS. The lattice constant does not change throughout all the shearing processes and equal to that at rest. These results suggest a possibility to control the grain size only by changing the conditions of oscillatory shear.

Although preparation of orientated samples has been reported for the normal [2] and inverse [3] cubic phases in the amphiphilic systems and the gyroid phase of the block copolymers [4] by using epitaxial phase transition from other anisotropic phases oriented by shear, or shear melting from the cubic to the sponge phase, no nobody have succeeded alignment of the bicontinuous cubic phase by shear flow alone except for the very recent study for the block copolymer [5]. In the present study, we have studied effects of the frequency and the strain amplitude of the MAOS applied just after the LAOS.

2 Experiment

Rheo-SAXS measurements were performed on the beamline 6A by using a stress-controlled rheometer AR550 (TA Instruments) modified for SAXS experiments [6]. 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 23°C (lamellar phase). Then the temperature was raised to 30°C (corresponding to the Ia3d phase) without shear.

3 Results and Discussion

Figure 1 shows time evolution of 2-D SAXS patters for the tangential configuration, γ_0, and storage (G') and loss (G'') modulus with the change in the stress amplitude (σ_0) and the angular frequency (ω). It should be noted that the steps ②, ④, and ⑥ are the LAOS with the same σ_0 and ω and that the steps ①, ③, ⑤, and ⑦ are the MAOS with the same ω but different σ_0. All the diffraction patterns under the LAOS are powder like whereas those under the MAOS after the LAOS indicate that the [111] axis is directed to the flow direction and that the normal vector of one of the (211) plane is directed to the velocity gradient direction. Such an orientation cannot be seen from the pattern for the step ① in spite that σ_0 and ω are the same as those for the step ③, which indicates that the grain refining process under the LAOS is necessary for the orientation under the MAOS. Figure 1 also shows that the sample for the step ③is more oriented than for the steps ⑤ and ⑦, suggesting that the degree of the orientation depends on the strain amplitude of the oscillatory under the same frequency. We have also investigated the frequency dependence of the orientation under the same σ_0.

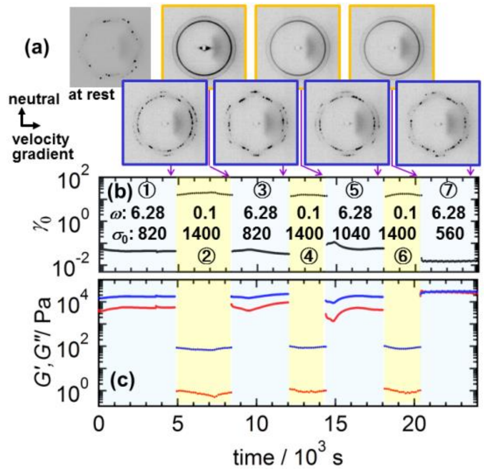

Fig. 1 Time evolution of 2-D SAXS patters in the tangential configuration (a), strain amplitude (γ_0) of the oscillatory shear, and storage (G', red lines) and loss (G'', blue lines) modulus (c) with the change in the stress amplitude (σ_0) and the angular frequency (ω) (indicated in the panel (b)) for $C_{12}E_2$/water system (63 wt%, 30°C).

References

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