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Orientation Control of the Inverse Bicontinuous Cubic Phase by using Shear Alone: Effects of Grain-Refinement Processes.

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1 Introduction

The inverse bicontinuous cubic phase (V_2 phase) is one of the lyotropic phases consisting 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 application of the large amplitude oscillatory shear (LAOS) with the strain amplitude (γ_0) of about 20 induces grain refinement, whereas orientation occurs by applying the "medium" amplitude oscillatory shear ("MAOS") whose strain amplitude is much smaller than the LAOS but still in the nonlinear regime just after the LAOS. The lattice constant does not change throughout all the shearing processes and equal to that at rest. In the present study, we have studied effects of grain-refinement processes on the orientation processes caused by the MAOS. First we have examined effects of reduction in the strain amplitude of the LAOS. Then we have investigated effects of replacement of the LAOS by the stead shear. In both experiments, the MAOS with the same conditions was applied after the LAOS or the steady shear.

2 Experiment

Rheo-SAXS measurements were performed on the beamline 15A2 by using a stress-controlled rheometer AR550 (TA Instruments). The details of the shear cell have been reported previously [2]. The scattered beam was recorded with the camera length of 2.6 m using the PILATUS 2M.

3 Results and Discussion

Figure 1 shows typical 2-D SAXS patterns in the tangential configuration for the shear conditions shown in the table. In the steps ① and ③, we applied the LAOS with the same angular frequency (ω) but different γ_0 whereas in the steps ②, ④, and ⑥, the MAOS with the same ω and γ_0 was applied. In the step ⑤, the steady shear was applied instead of the LAOS. All the diffraction patterns for the steps ①, ③, and ⑤ are powder like whereas those for steps ②, ④, and ⑥ shows that the [111] axis is directed to the flow direction and that the normal vector of one of the (211) planes is directed to the velocity gradient direction. For quantitative discussion, we use the degree of the orientation α defined by

$$\alpha \equiv \frac{\dfrac{1}{12\delta\phi}\displaystyle\sum_{n=0}^{5}\int_{(n\pi/3)-\delta\phi}^{(n\pi/3)+\delta\phi} I(\phi)\,\mathrm{d}\phi}{\dfrac{1}{2\pi}\displaystyle\int_0^{2\pi} I(\phi)\,\mathrm{d}\phi} \qquad (1)$$

where $I(\phi)$ is the peak intensity of the (211) reflection at the azimuthal angle ϕ. For the "ideal" powder sample, α becomes 1. When all the peaks are included within $(n\pi/3) \pm \delta\phi$, on the other hand, α should be $6\pi/\delta\phi = 3$ because we set $\delta\phi = \pi/18$. Time evolution of α is shown in Figure 1. For the steps ① and ⑤, α is 1 as expected. For the step ③, on the other hand, α is slightly larger than 1, which may be due to the reduction of the strain amplitude of the LAOS. However, the maximum α value for the steps ④ is nearly equal to that for the step ②. For the step⑥, the maximum α value is slightly less than those for the steps ② and ④. However, the α value in the end of the step is larger than those in the steps ② and ④.

Figure 1also shows time evolution of the grain size (L) estimated from the line-width of the (211) reflection. For the step ②, the grain size increases with time as expected from the increase of α. However, such an increase of L does not occur for the step ④, which may be due to the fact that grain refining in the step ③ is not enough compared to the step ①. It should be noted that steep increase of L occurs for the step ⑥. These results indicate that grain refining processes are important for the grain growth caused by the MAOS.

	①	②	③	④	⑤	⑥
	LAOS	MAOS	LAOS	MAOS	steady shear	MAOS
ω /rad s^{-1}	0.1	6.28	0.1	6.28	shear rate 0.5s^{-1}	6.28
γ_0	~20	~0.04	~6	~0.04		~0.04

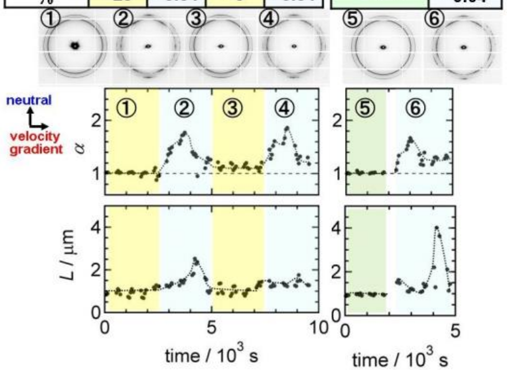

Fig. 1 Time evolution of 2-D SAXS patters in the tangential configuration, the degree of orientation obtained from the peak intensity of the (211) reflection using Eq. 1, and the grain size estimated from the line-width of the peak from the (211) reflection with the change in the shear conditions shown in the table where ω and γ_0 are the angular frequency and the strain amplitude of the oscillatory shear, respectively.

References

[1] M. Yamanoi et al., *Langmuir* , **32**, 2863 (2016).
[2] Y. Kosaka et al., *Langmuir*, **26**, 3835 (2010).

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