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Lamellar-to-Onion and Onion-to-lamellar Transition Processes with Varying Temperature under Shear Flow in a Nonionic Surfactant/Water System

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Introduction

In the past 20 years, much attention has been paid to 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 reentrant lamellar-onion (lamellar → onion →lamellar) transition with increasing temperature for a $C_{14}E_5$/water system [4]. In the present study, we have performed rheo-SAXS experiments near the the lower transition temperature to compare the transition processes of the lamellar-to-onion transition with increasing temperature and onion-to-lamellar transition with decreasing temperature.

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

Figure 1 shows temperature dependences of the diffraction-peak intensity in each direction and shear stress at the shear rate of 3 s^{-1} in heating (upper panel) and cooling (lower panel) processes in a $C_{14}E_5$/water system (50 wt%). In the heating process, the most lamellae are oriented with the layer normal along the velocity gradient direction at 32 °C. As the temperature exceeds 34 °C, the peak intensity in the velocity gradient direction abruptly increases and takes a maximum at 35°C, just before the increase in the shear stress. As the temperature increases by 0.5 K, the intensity in the gradient direction rapidly decreases and instead, the intensity in the neutral direction increases. As the temperature increases further, the intensities in all the directions become equal, corresponding to the formation of onions. These results are similar to the results for the $C_{16}E_7$/water system [3].

In the cooling process, the temperature dependences

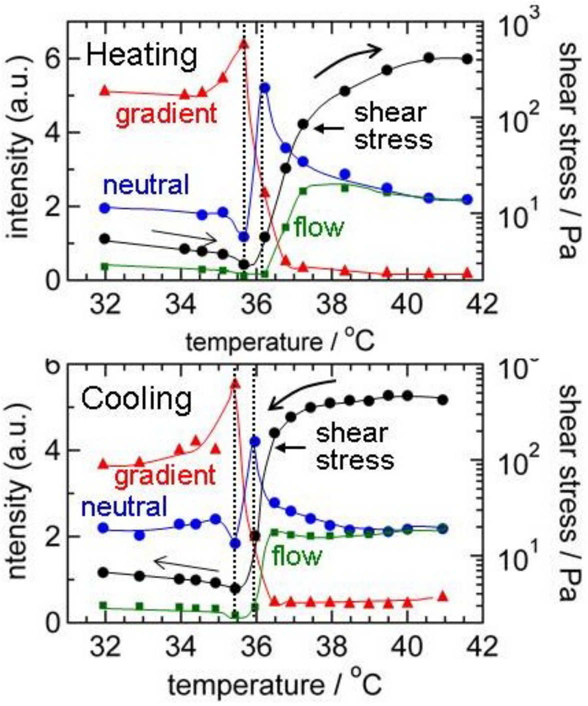

Fig. 1 Temperature dependences of the diffraction-peak intensity for each direction and shear stress at the shear rate of 3 s^{-1} in heating (upper panel) and cooling (lower panel) processes in a $C_{14}E_5$/water system (50 wt%).

in the peak intensity and the shear stress are very similar to those in the heating process although the slight hysteresis (~0.3 K) is observed. This suggests that the onion-to-lamellar transition process is a reverse process of the lamellar-to-onion transition process and that the intermediate structures are not transient but characteristic to temperature.

References

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