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Rheo-SAXS Study on Lamellar-Onion-Lamellar Transition with Varying Temperature under Shear Flow in a Nonionic Surfactant ($C_{14}E_5$) /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]. We have also found reentrant lamellar-onion (lamellar → onion →lamellar) transition with increasing temperature for a $C_{14}E_4$/$C_{14}E_6$/water system [3]. In this study, we report the reentrant transition in a binary system of $C_{14}E_5$ and water.

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 15A. The scattered beam was recorded using the CCD area detector covering the scattering vector range from 0.15 to 2.5 nm^{-1}.

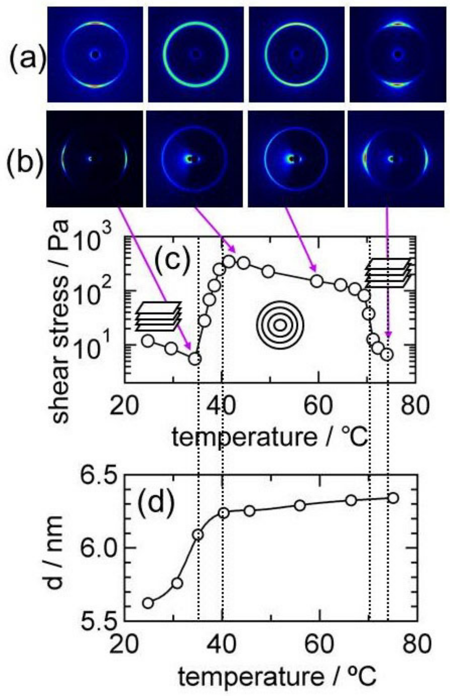

Fig. 1 Time evolutions of 2D SAXS pattern for the radial (a) and tangential (b) configurations and shear stress (c) at the shear rate of 3 s^{-1} and the repeat distance at rest (d) in a $C_{14}E_5$/water system (50 wt%).

Results

Figure 1 shows Time evolutions of 2D SAXS pattern for the radial (a) and tangential (b) configurations and shear stress (c) at the shear rate of 3 s^{-1} and the repeat distance at rest (d) in a $C_{14}E_5$/water system (50 wt%). In the lower temperature less than 23°C, the lamellae are oriented to the neutral direction. When the temperature exceeds 35°C, the shear stress increases steeply. Between 40°C and 70°C, the shear stress remains high and isotropic SAXS patterns are observed. As the temperature exceeds 70°C, the shear stress abruptly decreases and again the lamellae are orientated to the neutral direction. These results suggest lamellar→onion →lamellar transition with increasing temperature under a constant shear rate.

Figure 1(d) shows temperature dependence of the lamellar repeat distance at rest. Near the lower transition temperature (~35°C), the repeat distance increases with increasing temperature. Such a change in the repeat distance is not observed near the upper transition temperature (~70°C). In the C_nE_m/water systems, the spontaneous curvature of monolayers decreases and hence the saddle-splay modulus of bilayers decreases with increasing temperature. This may cause the onion-to-lamellar transition with increasing temperature, which can explain the upper transition. On the other hand, the lower transition may be caused by the increase in the repeat distance.

References

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