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Lamellar to Onion Transitions with Increasing Temperature under Shear Flow in a Nonionic Surfactant System Studied by Rheo-SAXS

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Introduction

In the past 15 years, much attention has been paid to the effects of shear flow on the structure of the lyotropic phase of surfactant systems, especially on 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]. Although this type of transition has been reported both for various systems, transition mechanism has not yet been established. Recently, we have found the lamellar-to-onion transition with *increasing* temperature under shear flow in the lamellar phase of a nonionic surfactant $C_{16}E_7$/water system (C_nE_m is abbreviation of $C_nH_{2n+1}(OC_2H_4)_mOH$) by using simultaneous measurements of shear stress and small-angle light scattering (Rheo-SALS) and small-angle X-ray scattering (Rheo-SAXS). The lamellar-to-onion transition with *decreasing* temperature has been reported for several homologues which is explained in terms of increase (less negative) in the saddle-spray modulus of bilayers with the temperature elevation [2]. Our findings are apparently controversial with these results. In the present study, we investigate the transition processes in more detail and discuss the mechanisms of the transition.

Experimental

A rheometer AR550 (TA Instruments) is modified for rheo-SAXS experiments. Details of the cell have been reported previously [3]. Measurements were performed on the beamline 15A. The scattered beam was recorded using the CCD area detector covering the scattering vector range from 0.015 to 0.25 $Å^{-1}$.

Results

Figure 1 shows temperature dependences of the shear stress and the diffraction-peak intensities for the radial and tangential configurations for the lamellar phase of a $C_{16}E_7$/water system (48 wt%) for the shear rate of 3 s^{-1}. In this experiment, the sample temperature was increased by 0.1 K/15 min. As the temperature increases from 67°C to 68°C, the shear stress increases more than one order of magnitude. Just before the increase in the shear stress, the peak intensity for the velocity-gradient direction is suddenly increased. The subsequent increase in shear stress accompanies enhancement of the neutral peak as well as suppress of the gradient peak. These results support transition mechanism proposed by Zilman and Granek [5] where the coherent buckling of lamellae induces the lamellar-to-onion transition. We have also observed abrupt increase in the lamellar spacing during the transition. When the sample temperature is increased rapidly, such a change in the spacing has not observed.

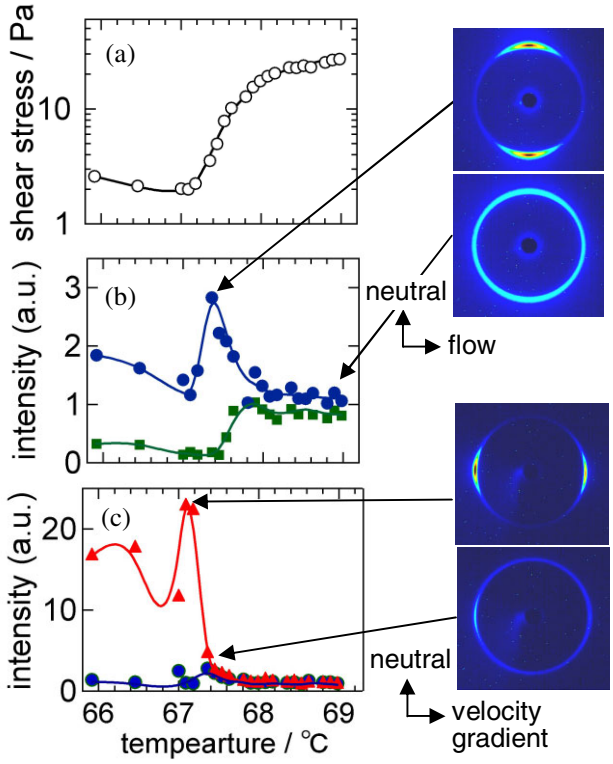

Fig. 1 Temperature dependence of the shear stress (a), and the peak intensities for the radial (b) and tangential (c) configurations for the lamellar phase of a $C_{16}E_7$/water system (48 wt%) at 3 s^{-1}. The circles, squares, and triangles in (b) and (c) indicate the neutral, flow, and velocity-gradient directions, respectively.

References

[1] D. Roux, in "Nonequilibrium Dynamics, Metastability and Flow" ed. by M. E. Cates, M. R. Evans, and P. Osborne, Institute of Physics Publishing, Bristol (2000).
[2] T. D. Le et al. *Langmuir* **17**, 999 (2001).
[3] T. Kato, K. Miyazaki, Y. Kosaka, and Y. Kawabata, *PF Activity Report 2005,* **23**, Part B (2006).
[4] F. Nettesheim et al. *Langmuir* **19**, 3618 (2003).
[5] A.G. Zilman and R. Granek *Eur. Phys. J. B* **11**, 593 (1999).

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