Shear-Induced Sponge-to-Lamellar Transition in a Hyperswollen Lyotropic System

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We demonstrate here experimental evidence of the shear-induced sponge-to-lamellar transition in a hyperswollen lyotropic system. We also show that shear flow suppresses the first-order nature of the transition, especially above a critical shear rate. The phenomena are probably caused by two effects: (i) Symmetry-breaking shear field reduces large fluctuation effects associated with the degeneracy of the possible orientations of the ordered state. (ii) Shear flow favors the lamellar phase more than the sponge phase because the interconnected membrane structure obstructs flow. The sponge structure is destabilized for shear flow strong enough to tear off the passage of the membrane. [S0031-9007(96)01698-5]

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Recently, shear effects on complex fluids including polymer and surfactant solutions have attracted much attention [1]. The coupling between shear flow and the large internal degrees of freedom of complex fluids leads to the so-called Reynolds effect, which is unique to complex fluids and never exists in simple fluids. A typical example is a shear-induced phase separation in polymer mixtures. Among various kinds of shear effects on complex fluids, the shear effects on anisotropic complex fluids having lamellar order include a new physical problem that has a universal nature relating to the fluctuations coming from the Landau-Peierls instability intrinsic to the low-dimensional systems.

From this aspect, the effects of the symmetry-breaking field, such as shear flow field, on the phase behavior of anisotropic complex fluids [2] have recently been intensively studied, both theoretically and experimentally, for smectic thermotropic liquid crystals [3] and the lamellar phase of block copolymers [4–6]. We focus here on another kind of smectic phase, namely, lyotropic smectic phase, which is often observed in aqueous solutions of amphiphiles. This phase is different from the others on the following points: (i) The lamellar phase (L_α phase) is composed of the membranes and intermembrane fluids. (ii) The corresponding isotropic phase (L_3 phase, or "sponge phase") has an internal structure of interconnected membranes. Since both phases are constructed by the same bilayers, they can be distinguished only by way of the packing of the bilayers into space.

On the lyotropic liquid crystals, shear effects to the lamellar phase itself have recently been investigated both theoretically [7,8] and experimentally [9,10]. However, there have so far been few experimental studies on the shear effects on sponge-to-lamellar transition. Recently, Cates and Milner [2] theoretically studied this problem on the basis of a physical picture that the sponge-to-lamellar transition in a lyotropic system also belongs to the category of the fluctuation-induced first-order phase transition [11]. They predicted (i) shear-induced sponge-to-lamellar phase transition and (ii) the decrease in the first-order nature of the transition with an increase in the shear rate, based on the idea that symmetry-breaking shear field suppresses the origin of the first-order nature, namely, large fluctuation effects associated with the degeneracy of the possible orientations of the ordered state. Experimentally, it is widely known that the sponge phase becomes birefringent under shear field [12,13]. However, there have not been any systematic studies or experimental evidence of the shear-induced sponge-to-lamellar phase transition [13]. In this Letter, we demonstrate the first clear experimental evidence of shear-induced sponge-to-lamellar transition.

The lyotropic liquid crystal system studied here is a two component mixture of pentaethylenglychol *n*-dodecyl ether ($C_{12}E_5$) and water [14]. The weight fraction of $C_{12}E_5$ was 1.8 wt. % in this study. The temperature resolution and stability were ± 0.05 K and ± 0.01 K, respectively. With an increase in the temperature, the system changes from the L_α to the L_α-L_3 coexisting phase at $T_\alpha = 62.0\,^\circ$C, and farther from the coexisting phase to the L_3 phase at $T_3 = 62.8\,^\circ$C. The existence of the two-phase coexisting region between sponge and lamellar phase indicates a weak first-order character of the transition [14].

Since the characteristic length of the structure can be expanded to the visible light wavelength by dilution with water in the hyperswollen L_α phase, light scattering provides us with information on the lamellar order in the L_α phase via optical Bragg reflection. For studying the shear-induced phase transition, we have thus constructed the time-resolved light scattering measurement system under oscillatory shear flow field. A sample is introduced into a flow cell that is composed of two parallel fused-quartz flat plates with a gap of 1 mm. Thus, the membranes are oriented in parallel with the plates in the L_α phase. Oscillatory motion of a piston produces periodic Poiseuille's flow in the flow cell. The oscillation frequency f is fixed to 5 Hz in this study.

First, we show simple, but direct, experimental evidence of shear-induced sponge-to-lamellar transition. We measured the scattered light intensity under shear flow in the

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L_3 phase near T_3. Without shear flow, the scattered light intensity is almost zero in the whole range of the observed wavelength, which indicates that the system is in the L_3 phase. When we apply the shear flow to the sample, an evident Bragg peak appears, as shown in Fig. 1. This unambiguously demonstrates that the sponge-to-lamellar transition is induced by the shear flow. This transition is confirmed to be reversible since, after stopping the shear flow, the Bragg peak completely disappears.

Next, we show the dynamic response of the lyotropic system to the oscillatory shear flow ($f = 5$ Hz). In Fig. 2 we plot the temporal change in the peak intensity and the peak wavelength against the past time after switching on the shear flow for the following two cases: (i) One is the measurement performed in the sponge phase near the sponge-to-lamellar transition. In this case, the sponge phase is transformed into the lamellar phase by applying the oscillatory shear. (ii) The other is the measurement performed in the sponge phase far above the transition. In this case, on the other hand, the system remains to be sponge phase even under shear flow. The behavior of the peak intensity (open circles in Fig. 2) for case (i) evidently shows that the sponge-to-lamellar transition is induced by the shear. We also notice from the dynamic behavior that there exist two kinds of fluctuation modes in the lamellar phase which respond to shear with quite different time scales: The fast mode has a characteristic rheological time much faster than the oscillation period of 0.2 s, while the slow mode responds only to the switching on of shear flow very slowly and likely feels only the average shear rate of the oscillatory flow. For case (ii), where a sponge phase is preserved even under the shear flow, the slow mode is clearly observed while the fast mode is observed only weakly (see Fig. 2). In contrast to the behavior of the peak intensity, we can observe only the slow mode in the behavior of the peak wavelength for both cases (i) and (ii), namely, the peak wavelength cannot follow a quick change of a frequency of 5 Hz. This indicates that the fast mode is associated to the local change in membrane fluctuations and is not coupled with the average global structure.

Relating to these two types of modes, the following experimental facts should also be recalled: Porte *et al.* [12] found that the slow topological relaxation mode [15] exists in the L_3 phase. On the other hand, we have also confirmed experimentally that, for the lamellar phase, there exists a slow mode responding to shear, which is related to the undulation fluctuation of the membrane [10]. Including the results shown in Fig. 3 and the above facts, we conclude that (i) the fast mode newly found in this study is likely related to the local suppression of undulation fluctuations of a single membrane by shear, and (ii) the slow mode is attributed to the fluctuation of the average characteristic length. The above assignment is consistent with the fact that the fast mode is observed only weakly in the L_3 phase.

Since we focus our attention only on the shear-induced phase transition in this Letter, we discuss hereafter only the final steady state under an oscillatory shear, and not the dynamic process. In this periodic steady state under oscillatory shear characterized by $\dot{\gamma} = \langle\dot{\gamma}\rangle \sin(\omega t)$ ($\langle\dot{\gamma}\rangle$: the average shear rate of the Poiseuille's flow field in the flow cell), the peak intensity I and the peak wavelength ξ can be described by the following expressions: $I = I_0(\langle\dot{\gamma}\rangle, T) + I_1(\langle\dot{\gamma}\rangle, T) \sin(2\omega t)$ and $\xi = \xi_0(\langle\dot{\gamma}\rangle, T)$. As described previously, I reflects the response of the fast mode to shear, while ξ does not.

First, we show the temperature and the shear-rate dependences of the average peak intensity I_0 in Fig. 3(a). For weak shear, I_0 decreases steeply at T_α. We can clearly see that T_α increases with an increase in $\langle\dot{\gamma}\rangle$. Furthermore, I_0 in the L_α phase decreases with an increase in $\langle\dot{\gamma}\rangle$, while that in the L_3 phase increases. Thus, the discontinuity in I_0 at $T_\alpha(\dot{\gamma})$ becomes weaker with an increase in $\langle\dot{\gamma}\rangle$, and the change in I_0 at $T_\alpha(\dot{\gamma})$ eventually becomes continuous. This result strongly suggests that the L_α and

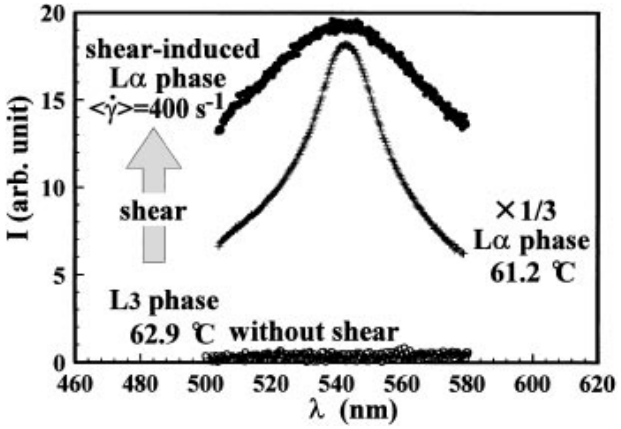

FIG. 1. Scattering profiles before (open circles) and after applying shear field (closed circles). $T = 62.9\,^{\circ}\mathrm{C}$ just above T_3 and the average shear rate $\langle\dot{\gamma}\rangle = 400\ \mathrm{s}^{-1}$. We also show the scattering profile below T_α without shear, for comparison.

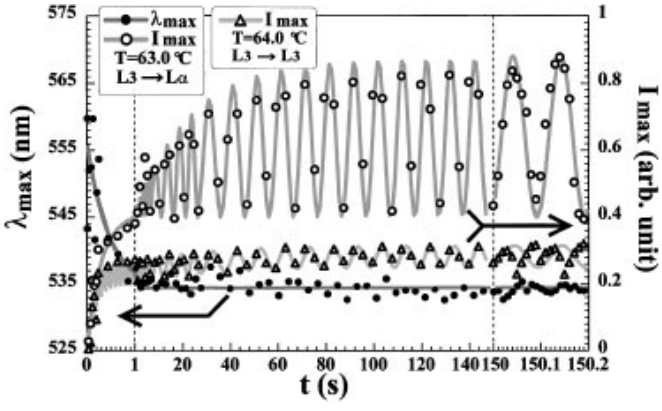

FIG. 2. Transient and steady state responses of the peak intensity and the peak wavelength of the Bragg peak to the oscillatory shear flow, plotted against the past time after switching on the shear flow ($f = 5$ Hz, $\langle\dot{\gamma}\rangle = 440\ \mathrm{s}^{-1}$). Note that the scale of the time axis is changed twice.

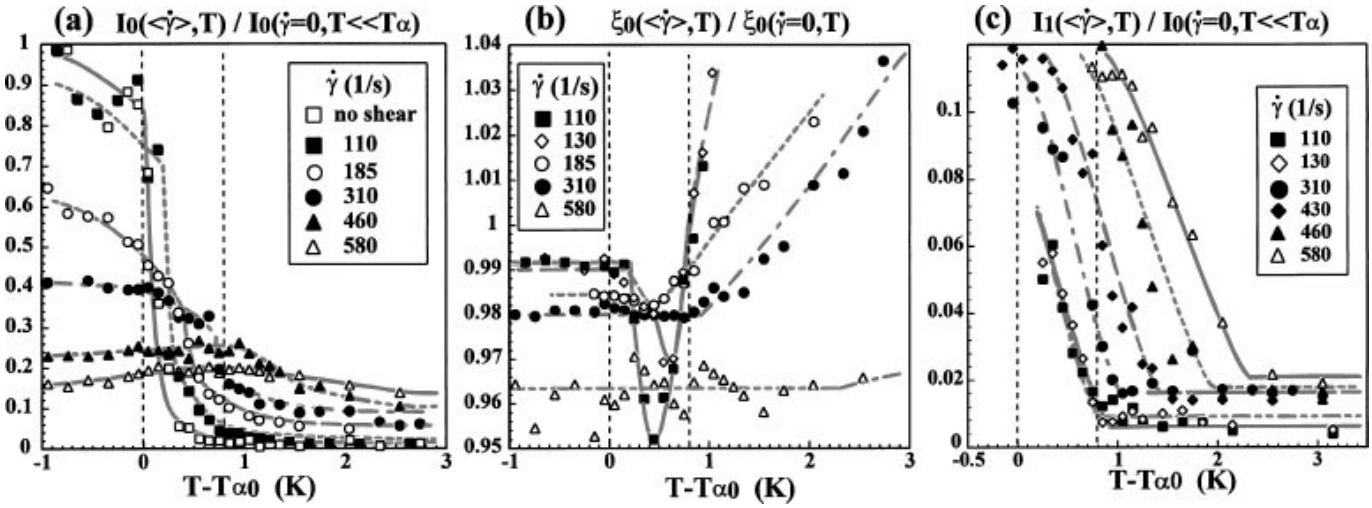

FIG. 3. Temperature dependences of (a) $I_0(\langle\dot{\gamma}\rangle, T)$, (b) $\xi_0(\langle\dot{\gamma}\rangle, T)$, and (c) $I_1(\langle\dot{\gamma}\rangle, T)$ under various average shear rates $\langle\dot{\gamma}\rangle$. I_0 and I_1 are normalized by I_0 at the temperature far below T_α without shear, $I_0(\dot{\gamma} = 0, T \ll T_\alpha)$, while ξ_0 is normalized by ξ_0 at the same temperature without shear, $\xi_0(\dot{\gamma} = 0, T)$. $T_{\alpha 0}$ is the T_α without shear.

L_3 coexistence region is narrowed by applying the shear flow, and the shear flow suppresses the first-order nature of the phase transition.

Next we show the shear-rate dependence of $\xi_0(T, \langle\dot{\gamma}\rangle)$ in Fig. 3(b). For a weak shear, ξ_0 suddenly decreases at T_α. This condensation of the L_α phase is a natural result of its coexistence with the dilute L_3 phase above T_α. The dip of the wavelength change around the coexistence region becomes shallower with an increase in $\langle\dot{\gamma}\rangle$. Above the critical shear rate $\langle\dot{\gamma}\rangle_c$, the peak wavelength starts to increase almost continuously at the phase-transition point and approaches the characteristic length of the unperturbed sponge structure which is larger than that of the lamellar phase by a factor of $\sim$1.5 [14]. The value of $\langle\dot{\gamma}\rangle_c$ is very close to the one determined in Fig. 3(a) from the shear rate at which the discontinuity in the peak intensity change apparently disappears. This indicates that the first-order nature of the transition is strongly suppressed rather discontinuously above $\langle\dot{\gamma}\rangle_c$.

Figure 3(c) indicates the temperature dependence of $I_1(T, \langle\dot{\gamma}\rangle)$, which corresponds to the amplitude of the fast mode of undulation fluctuations. I_1 is clearly independent of temperature and very small in the L_3 phase. On the other hand, I_1 increases drastically below T_3. As explained previously, the fast mode can be observed only in the L_α phase. Using this fact, we can unambiguously determine the shear-rate dependence of T_3 from Fig. 3(c).

Using all the above results on the shear-rate dependences of T_α and T_3, we construct the "dynamic phase diagram" [2,6] under shear flow. The phase-transition temperatures T_α and T_3 are plotted against the shear rate in Fig. 4. Please note that all the transitions are confirmed to be reversible. For a weak shear, T_α increases with an increase in the shear rate, but the sponge-to-lamellar transition still remains to be first order, and the coexistent region exists. With an increase in the shear rate, the coexistence temperature range becomes narrower. Finally, the first-order nature of the sponge-to-lamellar transition becomes extremely weak above the critical shear rate of $\langle\dot{\gamma}\rangle_c \sim 300\ \mathrm{s}^{-1}$ (see Fig. 4). A further increase in the shear rate increases this phase-transition temperature.

Our experimental findings can be summarized as follows: (i) There exists the shear-induced sponge-to-lamellar phase transition, (ii) shear flow suppresses the first-order nature of the transition, and (iii) there exists the critical shear rate $\langle\dot{\gamma}\rangle_c$ separating the weak and strong shear regime. In the strong shear regime above $\langle\dot{\gamma}\rangle_c$, the transition looks almost continuous, and it is almost impossible to judge experimentally whether the transition is discontinuous (first order) or continuous. All these facts can be mostly explained by the theory of Cates and Milner [2]. According to their theory, there is a critical shear rate given by $\langle\dot{\gamma}\rangle_c \sim k_B T/\eta\xi^3$, where k_B is Boltzmann's constant and η is the viscosity. Using $\xi \sim 250$ nm and $\eta \sim 1$ cP, we get for our system $\langle\dot{\gamma}\rangle_c \sim 270\ \mathrm{s}^{-1}$, which

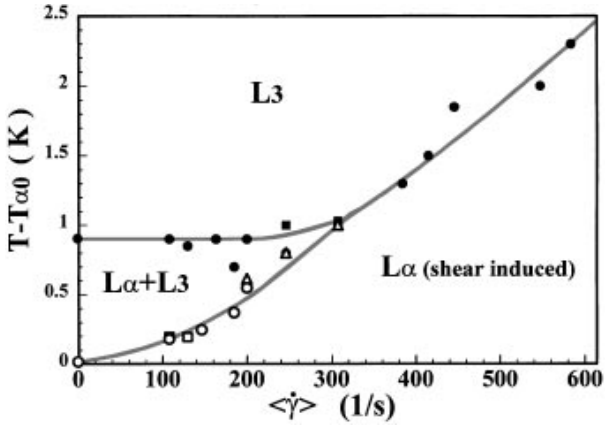

FIG. 4. Dynamic phase diagram. Open circles and triangles, T_α determined from Fig. 3(a); open squares, T_α determined from Fig. 3(b); closed squares, T_3 determined from Fig. 3(b); closed circles, T_3 determined from Fig. 3(c).

coincides quite well with the experimental value of $\langle\dot{\gamma}\rangle_c$ ($\sim$300). It should be noted that Koppi *et al.* [6] found that the theory [2] is consistent with their experimental results of the shear effects on isotropic-lamellar transition in block copolymers, although their shear rate is limited below the critical one. Thus, the phenomenon is probably universal to any isotropic-lamellar phase transition [2]. However, there is an important discrepancy from the prediction: In our system, lamella is formed perpendicularly to the velocity gradient, in contrast to the theoretical prediction [2] that lamellar ordering occurs with the wave vector normal to both the velocity and the velocity gradient, which was confirmed for block copolymers [6]. This is probably the unique feature of lyotropic systems relating to the fact that *membrane systems should be described by a two-fluid model* [7].

Relating to the origin of the shear-induced phase transition, note that the viscosity of the L_3 phase is a few times higher than that of the L_α phase [10,16]. This high viscosity of sponge phase is likely due to the fact that the passage of the membrane disturbs the shear flow fields. However, there is probably little disturbance to shear flow fields in the L_α phase. This fact is probably also responsible in part for the shear-induced transition, as well as the mechanism proposed by Cates and Milner [2].

Although both sponge and lamellar phases are constructed by the same membranes, they have no permanent structure and can be easily reconstructed even by a weak perturbation [12,13,15]. Thus, in the sponge phase, shear flow tears off selectively the passage of the membrane that is not along the flow direction, if it is strong enough [12,13,15], and the sponge phase starts to have *anisotropy* with an increase in the shear rate. This likely leads to the shortening of the characteristic length of the system. When the shear rate becomes strong enough to erase all the passages, the characteristic length becomes equal to that of the lamellar phase, and thus the shear-induced sponge-to-lamellar transition takes place. This is supported by the following experimental results: In the strong shear regime above $\langle\dot{\gamma}\rangle_c$, we observe the weak Bragg peak even in the L_3 phase near the phase transition [see Fig. 3(a)]. Its peak wavelength keeps decreasing with decreasing T and eventually becomes equal to that of the L_α phase at the transition [see Fig. 3(b)]. It should be noted that Koppi *et al.* also mentioned that shear induces weak anisotropy in the disordered phase [6].

This intuitive scenario of the appearance of anisotropy even in the disordered phase is probably related to the fact that shear flow selects the fluctuations having the specific wave vector because of its symmetry-breaking feature [2]. However, we point out one important difference between lyotropic surfactant solutions and block copolymers: The characteristic length of the isotropic sponge phase is roughly the $3/2$ of the lamellar repeat distance, from the consideration on the packing of membranes under the membrane mass conservation. This makes a marked contrast to block copolymers [2,6], where both disordered and ordered phases have fluctuations with about the same wave number. Thus, the behavior shown in Fig. 3(b) is probably unique to lyotropic surfactant solutions.

Finally, we point out another characteristic feature of a lyotropic system that is related to the energetic factor stabilizing the isotropic sponge phase. Two types of physical pictures have so far been proposed for the lamellar-sponge transition: (i) entropy-driven order-disorder phase transition [17,18] and (ii) Gaussian-curvature-driven topological transition [12,19–22]. If we do not consider the contribution of the Gaussian curvature, the transition is described purely by the fluctuation-induced first-order transition [2,11]. However, the elastic energy associated with the Gaussian curvature may modify the character of the transition since the sponge phase also has some order.

In summary, we show experimental evidence of the shear-induced sponge-to-lamellar phase transition in lyotropic liquid crystals. The behavior is consistent with the predictions of Cates and Milner [2] and the results on block copolymer [6], suggesting the universal nature of the shear effects on isotropic-lamellar transition. However, there remains some unsolved problems likely specific to membrane systems. Thus, we need further quantitative study focusing on the special characteristics of the sponge phase (such as the membrane configuration, the associated elastic energy, and the two-fluid nature).

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