Surface-Tension-Gradient-Induced Pattern Formation in Monolayers

Mu Wang,[1,4] G. Wildburg,[2] J. H. van Esch,[2] P. Bennema,[1] R. J. M. Nolte,[3] and H. Rinsdorf[2]

[1]*RIM, Laboratory of Solid State Chemistry, University of Nijmegen, 6525 ED Nijmegen, The Netherlands*
[2]*Institute of Organic Chemistry, University of Mainz, 6500 Mainz, Germany*
[3]*Department of Organic Chemistry, University of Nijmegen, 6525 ED Nijmegen, The Netherlands*
[4]*National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, People's Republic of China*
(Received 16 August 1993)

A surface-tension-gradient-induced growth phenomenon is reported in lipid monolayer films. The surface tension gradient is introduced to the monolayer film by local, subtle heating using the microscope light. This surface tension gradient is responsible for compressing the illuminated area continuously and induces the growth of domains of liquid condensed phase. The evolution of morphology from fractal to faceted and then to dendritic patterns is investigated by *in situ* observations. The mechanism of pattern formation in this system is discussed.

Monolayer films adsorbed on the air-water surface provide an ideal two-dimensional system to study pattern formation processes [1,2]. It has long been known from thermodynamic and spectroscopic data that when a lipid monolayer is compressed isothermally it undergoes a series of phase transitions. The two phase coexistence region in the first-order transition from a liquid expanded phase (LE) to a liquid condensed phase (LC) has been studied intensively, especially after the discovery that the morphology of the LC domains can be imaged by fluorescence microscopy [1–4] and Brewster angle microscopy [5,6]. Some specific features make this system unique from the point of view of pattern formation studies. First, the morphology of LC domains varies from compact to dendritic and fractal patterns [2–4,7], which can now be studied *in situ* experimentally. Second, since this system is truly two dimensional, it is a challenge to interpret the development of the boundaries between LC and LE phases with theories of dendritic growth [7,8] and faceted crystal growth [9]. However, during compression of the film, flows always occur in the water subphase. So in previous studies it was difficult to trace a growing domain over periods longer than 10 s [3]. By introducing an inhomogeneous electric field, it was possible to collect domains under the microscope and study their evolution process [10]. However, the applied electric field in that case may influence the molecular aggregation dynamics, because the electric dipole-dipole interaction is believed to play an important role in LC domain growth. In this Letter, we report for the first time the pattern formation induced by a surface tension gradient in monolayer films. This gradient is introduced by subtle local heating using the illumination of the microscope.

The trough for the monolayer experiment is a conventional one [11]. It consists of a Teflon barrier and a Wilhelmy-type surface tension measuring system. Millipore filtered water is used as a subphase. The thickness of the water subphase is about 1 cm. The temperature of the water subphase is kept at 20 °C by a thermostat. The surfactant R-(-)-N,N-dihexadecy-(2-[1-(1-imidazolyl)-propyl]amine) (DIPA) is dissolved in chloroform and 0.5 mol% fluorescent probe (DPPE-sulforhodamine) is added. The mixture of the compounds is dispersed on the water surface. Monolayers of DIPA are formed spontaneously on the water surface after evaporation of the chloroform. A fluorescence microscope with a mercury arc lamp (100 W) is used to observe the domain growth. This lamp also acts as a heating source to establish a surface tension gradient. A filter is used to generate green light (510–560 nm) for the excitation of fluorescent molecules. The growth process of LC domains is recorded by a microscope-matched video system.

By compressing the monolayer films with the moving barrier, the LE-LC coexistence region is reached. This coexistence region in the DIPA monolayer system is characterized by the formation of dark, fractal-like LC domains. When the LC domains become sufficiently large, the barrier is stopped. The domains cease growing when an equilibrium surface pressure is reached. Because the water flow in the trough is weakened in the meantime, it is easy to keep the cluster under investigation at the center of the view field of the microscope. A typical fractal pattern is shown in Fig. 1(a). On the right corners of this figure, the shade of the optical field diaphragm (OFD) can be seen. The diameter of this OFD shade is about 200 μm. Under the illumination of the microscope light, the morphology of the cluster develops gradually, as shown in Figs. 1(b)–1(e). In the first several tens of seconds, some of the outer arms of the cluster melt and the pattern shrinks. However, this period passes quickly and the cluster begins to grow. As indicated by the arrow in Fig. 1(b), faceted domains are formed on the tips of the fractal branches. However, these faceted tips are not stable. After continuous growth, dendritic patterns are induced, as shown in Figs. 1(c)–1(e). The domains trapped in between the dendritic stems are also growing, but the most outward tips of the domain have a higher probability to develop into a dendritic pattern (screening effect) [Fig. 1(e)]. In the LE-LC coexistence region, nucleation of isolated LC domains
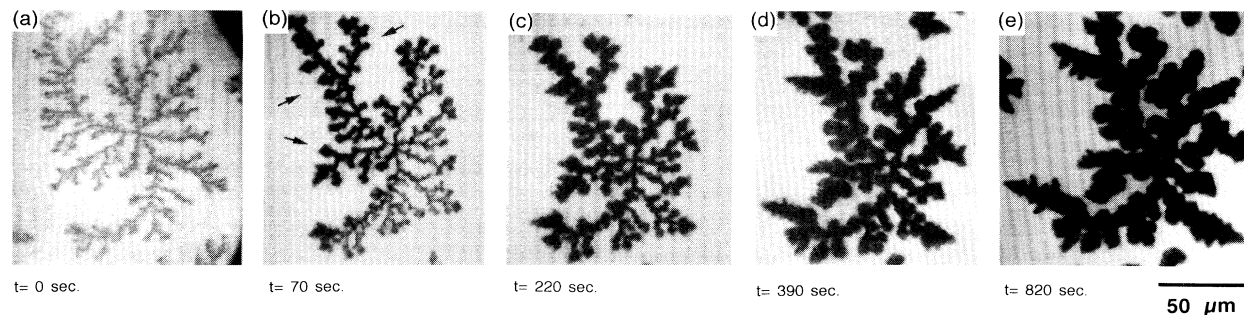
t= 0 sec.   t= 70 sec.   t= 220 sec.   t= 390 sec.   t= 820 sec.

50 μm

FIG. 1. (a) The observed fractal pattern when the monolayer is compressed to the LC-LE coexistence region. (b)-(e) show the evolution of the same pattern from fractal to dendrites under the illumination of the microscope light. At first the tips of the fractal branches become thicker and faceted (b) (see arrows); gradually these tips develop into dendrites with evident main stem and stable tips (c)-(e).

caused by the light illumination has been observed in an area initially free of any LC domains. If the nucleus is formed in the central region of the view field, it develops into dendrites; if the nucleus is induced near the shade of OFD, faceted hexagonal domain will be formed.

The morphologies of the LC domains on the boundary of the area illuminated by the microscope light are shown in Fig. 2. The fractal branches within the illuminated region have developed into many faceted rectangular domains, whereas those outside the illuminated region keep their fractal shape. Some minor branches are even molten. The differences in morphology are evident and the boundary is very sharp between these two regions. The geometric regularity of the faceted domains is shown more clearly in Fig. 3(a), where the domain has sixfold symmetry. The faceted domains are normally formed near the shade of OFD. The light intensity near the shade is supposed to be lower. Hence the driving force for domain growth, as will be discussed below, is smaller in these regions. The evolution of the hexagonal LC

domain to dendritic pattern is shown in Figs. 3(b)-3(d). One can find that the corners of the hexagon are sharpened and dendrites with stable tips and evident main stems are eventually formed.

In order to understand the mechanism of the observed phenomena, the temperature difference between the area directly illuminated by the light of the microscope and the surrounding unilluminated region is measured by two diode thermometers. The result is shown in Fig. 4(a), which indicates that the temperature in the illuminated area is about $0.2\,°C$ higher than in the surrounding regions. A stationary and stable temperature distribution is reached after the area is illuminated for about 1 min. Figure 4(b) illustrates the surface tension (γ) of the DIPA monolayer film as a function of temperature of the water subphase, which indicates that when the tempera-
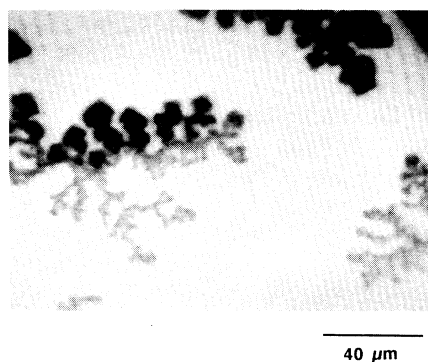

40 μm

FIG. 2. The morphologies of the LC domains on the two sides of the shade of the optical field diaphragm. The branches of the fractals within the illuminated region have developed into connected rectangular domains (the upper parts of the picture), whereas the branches which were outside the field of view almost persist in the fractal-like pattern (the lower parts of the picture). The boundary between these two regions is sharp.

t= 0 sec.   t= 120 sec.

t= 260 sec.   t= 570 sec.

25 μm

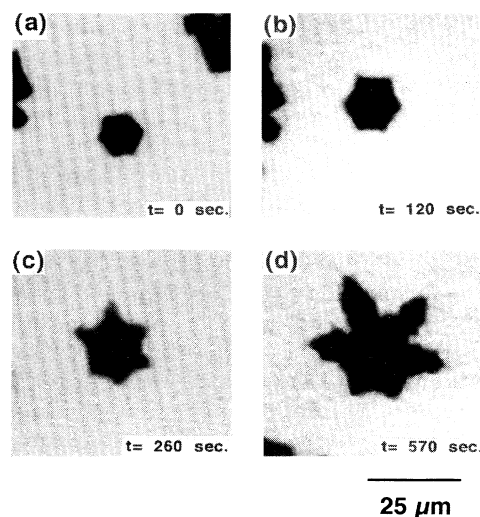FIG. 3. (a) The hexagon domain observed in our system. The faceted domains are usually nucleated near the shade of the optical field diaphragm. (b)-(d) illustrate the evolution of the morphology of the same domain from hexagon to dendritic pattern. The inhomogeneous development of the dendritic branches is due to the influence of the neighboring domains.
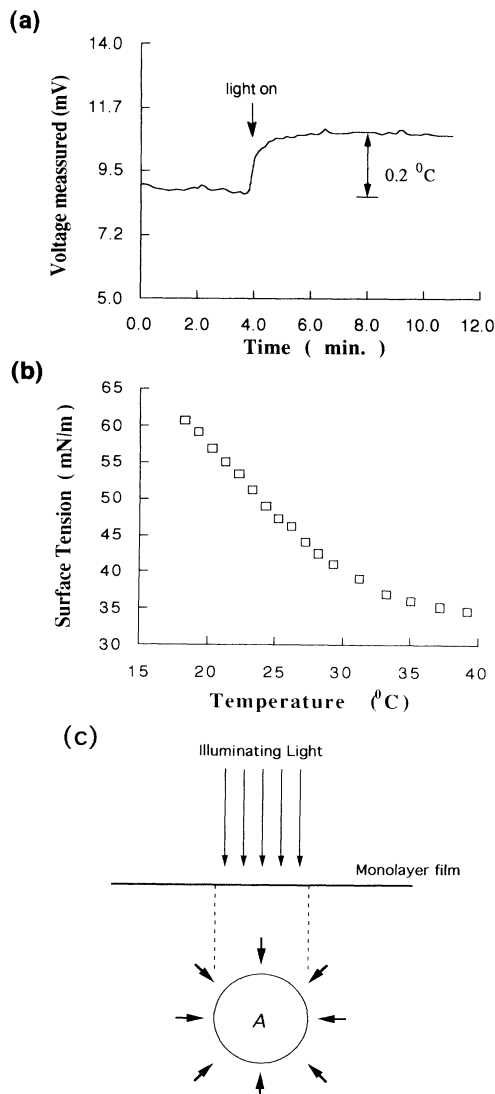
(a)

(b)

(c)

FIG. 4. (a) The temperature difference between the area illuminated by the microscope light and the area outside the shade of the OFD, which is measured by two diode thermometers placed in these two regions, respectively. A stable temperature difference is achieved after illuminating the area for about 1 min. Before the microscope light is turned on, the measured nonzero voltage is due to the fact that the zero points of the thermometers are not identically adjusted. From the time scales on Figs. 1(a) and 1(b), one finds that the time when the fractal pattern shrinks corresponds to the transition period of the temperature increase. (b) The surface tension of a DIPA monolayer film as a function of temperature in the LE-LC two phase coexistence region. The area per molecule is fixed at about 0.5 nm^2/molecule during the measurement. (c) A schematic diagram to illustrate the conditions near the illuminated region A. The temperature within A is higher than the surrounding regions by ΔT. A difference in surface tension is established because of the temperature difference in these two regions (see arrows). The surface tension gradient across the boundary of A is responsible for transporting molecules continuously into A.

ture increases, the surface tension of a monolayer film will decrease.

Our experimental results suggest that the observed growth phenomena are possibly due to the surface tension gradient across the boundary separating the area illuminated by the microscope light and the surrounding region. The microscope light introduces a local temperature increase ΔT within the area viewed by the microscope. According to Fig. 4(b), ΔT causes a decrease of the surface tension. Therefore, a centripetal surface tension difference is established, as illustrated in Fig. 4(c). This surface tension difference transports molecules continuously to area A in Fig. 4(c) from the surrounding regions. Consequently, the LC domains within A will grow. The evolution of the morphology shown in Fig. 1 can be explained as follows. At the beginning of an experiment, a LC domain with fractal shape under equilibrium surface pressure $\Pi_0(T)$ is chosen, where T is the initial temperature (the surface pressure is defined as the difference of the surface tensions of water and monolayer film, $\Pi = \gamma_{\text{water}} - \gamma_{\text{monolayer}}$). By observing the cluster, the heat generated by the microscope light decreases the local equilibrium surface tension from $\gamma_0(T)$ to $\gamma_0(T+\Delta T)$. Correspondingly, the local equilibrium surface pressure increases from $\Pi_0(T)$ to $\Pi_0(T+\Delta T)$. Because the heat diffusion constant is much larger than the mass diffusion constant, it takes a very short period of time for the local equilibrium pressure to change from $\Pi_0(T)$ to $\Pi_0(T+\Delta T)$. However, more time is needed to establish the new molecule concentrations in LC and LE phases, which belong to the new thermodynamic equilibrium determined by the new temperature. During this transitional period, the actual surface pressure is time dependent, i.e., $\Pi(t,T)$ is smaller than $\Pi_0(T+\Delta T)$ but is approaching $\Pi_0(T+\Delta T)$. However, it is noteworthy that the barrier has been stopped in the meantime. The only way to increase the actual local surface pressure in the illuminated region is to increase molecule concentration in the LE phase by dissolving the LC domain and importing molecules from the outside of the illuminated region. Therefore, shrinking of LC domains can be observed during this transitional period. Analogous to crystal growth [12], we define a dimensionless driving force $\Delta\mu/kT$ of pattern formation in this system,

$$\frac{\Delta\mu}{kT} = \ln\left[\frac{\Pi(t,T)}{\Pi_0(T)}\right],$$

where $\Pi(t,T)$ is the time dependent surface pressure and $\Delta\mu$ is the change of chemical potential. The subscript "0" stands for the equilibrium value. From this definition it follows that the driving force for domain growth during the transitional period, $\ln[\Pi(t,T+\Delta T)/\Pi_0(T+\Delta T)]$, is negative. The melting of the fractal pattern stops when the actual surface pressure reaches the new equilibrium value $\Pi_0(T+\Delta T)$. At the same time, the established surface tension gradient at the boundary of area A com-

presses continuously the illuminated region, which is responsible for transporting molecules continuously to area A. Because of the increase of molecular density, the local surface pressure increases. After the equilibrium pressure $\Pi_0(T+\Delta T)$ has been reached, further increasing the surface pressure creates an overpressure, which acts as a positive driving force for LC domain growth. So the LC domains within A will grow in order to dissipate the overpressure and maintain the new local equilibrium pressure $\Pi_0(T+\Delta T)$ [Figs. 1(c)–1(e)]. From Figs. 4(a) and 4(b) we can estimate that $\Delta\mu/kT$ in our system is about 0.8%, which is much smaller than the conventional 5%–10% in compression of a monolayer film by moving the barrier [3,13]. This may explain that the initial fractal-like domains generated by compressing the monolayer film evolve gradually to dendritic patterns (Fig. 1). In our system, by changing the intensity of the microscope light, the value of the equilibrium molecule concentration (equilibrium surface pressure) in the illuminated area can be changed. Hence the driving force for pattern formation can be controlled.

At the corners of a faceted pattern, the concentration gradient is higher than in the middle of the straight edge [12,14]. The mass transfer rate to the corners is higher than at other places. So the corners grow more rapidly than the center region and a dendritic pattern will appear on the corners of the hexagon (Fig. 3). The study of the stability of the faceted domains will be presented elsewhere.

It is well known that the macroscopic morphology of a crystal reflects its microscopic symmetry. We assume that this also holds for the growing LC domains. In Fig. 2 the domains grown from the previous fractal branches possess rectangular shapes. This implies that the molecules therein might be arranged in $\langle 10 \rangle$ directions. Each molecule may have four nearest neighbors. In Fig. 3(a), however, the macroscopic, hexagonal domain suggests that molecules may be aggregated into a more compact structure; i.e., each molecule may have six nearest neighbors. With the same bond energies, we suppose that the structure with the rectangular lattice has higher energy than the hexagonal lattice; i.e., the hexagonal structure is nearer to the thermodynamic equilibrium and hence more stable. In a growth situation far from equilibrium, the aggregation process of the fractal-like domain may be much faster than the relaxation process of the molecules. So the molecules may aggregate with a rectangular lattice. The hexagonal domains, however, are nucleated and grow under a lower driving force. Meanwhile the molecules may have sufficient time to relax to minimum energy positions. The difference in macroscopic morphology implies that the structures of the LC domains may depend on the driving force.

Recently, the microscopic structures of the monolayers have been studied by glancing-angle x-ray diffraction, using the x-ray beam from synchrotron radiation [15,16]. The experiments indicate that the solid domains in monolayers have a microscopically sixfold symmetry. The experimental results presented in this Letter, however, indicate that the light beam used for observation or measurement may cause an inhomogeneous distribution of driving force over the monolayer films. Therefore the structure and the morphology of the domains under observation or measurement may be different from those in the surrounding regions. This situation most probably happens when the light beam is strong and the monolayer is exposed to the light beam for a long time. Therefore, we suggest that it is important to take into account the possible influence of the measuring methods on the structure and morphology of the domains in monolayers.

[1] R. M. Weis and H. M. McConnell, Nature (London) **310**, 47 (1984).

[2] C. M. Knobler, Science **249**, 870 (1990).

[3] A. Miller, W. Knoll, and H. Möhwald, Phys. Rev. Lett. **56**, 2633 (1986).

[4] X. Qiu, J. Ruiz-Garcia, K. J. Stine, and C. M. Knobler, Phys. Rev. Lett. **67**, 703 (1991).

[5] I. R. Peterson and G. J. Russell, Thin Solid Films **134**, 143 (1985).

[6] S. Hènon and J. Meunier, Rev. Sci. Instrum. **62**, 936 (1991).

[7] S. Akamatsu, O. Bouloussa, K. To, and F. Rondelez, Phys. Rev. A **46**, R4504 (1992).

[8] D. A. Kessler and H. Levine, Phys. Rev. Lett. **67**, 3121 (1991).

[9] A. A. Chernov and T. Nishinaga, *Morphology of Crystals* (Terra Scientific, Tokyo, 1987), Pt. A, p. 207.

[10] A. Miller and H. Möhwald, Europhys. Lett. **2**, 67 (1986).

[11] C. M. Knobler, Adv. Chem. Phys. **77**, 397 (1990).

[12] A. A. Chernov, *Modern Crystallography III* (Springer-Verlag, Berlin, 1984).

[13] A. Miller and H. Möhwald, J. Chem. Phys. **86**, 4258 (1987).

[14] R. F. Xiao, J. I. D. Alexander, and F. Rosenberger, Phys. Rev. A **38**, 1447 (1988).

[15] B. Lin, M. C. Shih, T. M. Bohanon, G. E. Ice, and P. Dutta, Phys. Rev. Lett. **65**, 191 (1990).

[16] M. L. Schlossman, D. K. Schwartz, P. S. Pershan, E. H. Kawamoto, G. J. Kellogg, and S. Lee, Phys. Rev. Lett. **66**, 1599 (1991).
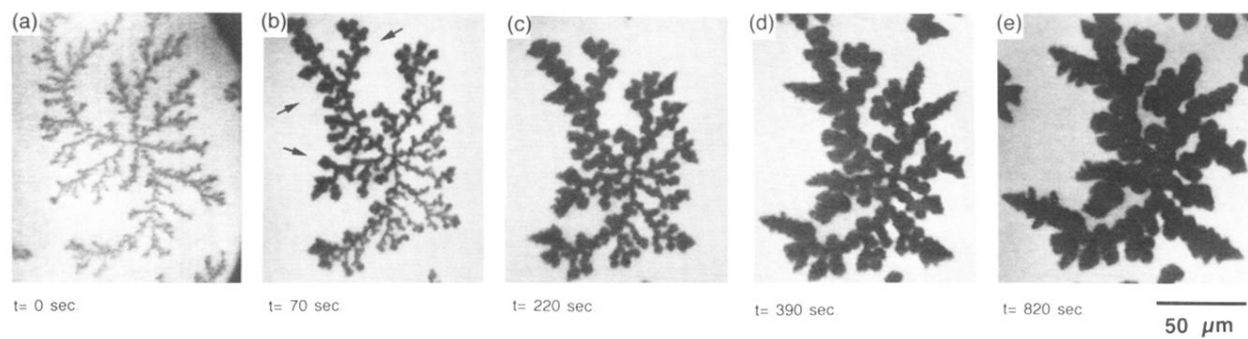
FIG. 1. (a) The observed fractal pattern when the monolayer is compressed to the LC-LE coexistence region. (b)–(e) show the evolution of the same pattern from fractal to dendrites under the illumination of the microscope light. At first the tips of the fractal branches become thicker and faceted (b) (see arrows); gradually these tips develop into dendrites with evident main stem and stable tips (c)–(e).
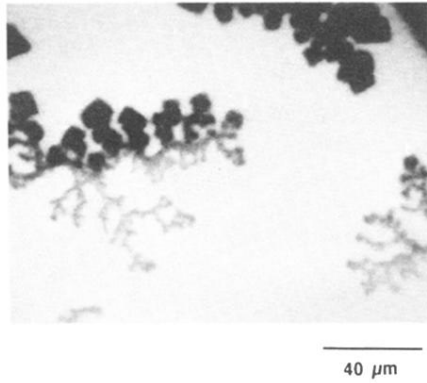
40 µm

FIG. 2. The morphologies of the LC domains on the two sides of the shade of the optical field diaphragm. The branches of the fractals within the illuminated region have developed into connected rectangular domains (the upper parts of the picture), whereas the branches which were outside the field of view almost persist in the fractal-like pattern (the lower parts of the picture). The boundary between these two regions is sharp.
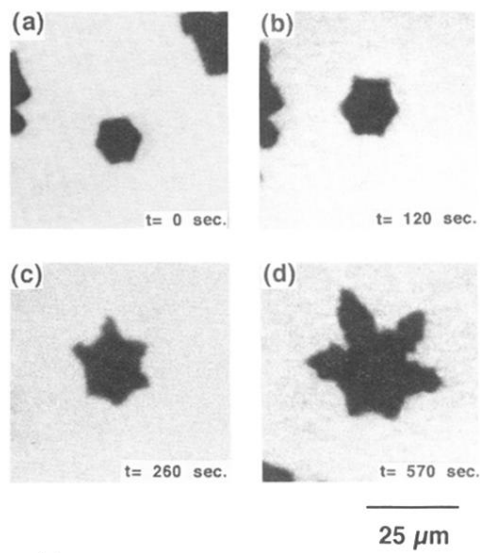
FIG. 3. (a) The hexagon domain observed in our system. The faceted domains are usually nucleated near the shade of the optical field diaphragm. (b)–(d) illustrate the evolution of the morphology of the same domain from hexagon to dendritic pattern. The inhomogeneous development of the dendritic branches is due to the influence of the neighboring domains.