Pattern formations in lipid monolayers under illumination

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In lipid monolayer film we observed that the domains of the liquid-condensed phase may grow under continuous illumination of microscope light. This phenomenon occurred in the coexistence region of liquid-condensed (LC) and liquid-expanded phases. The average area per molecule in the monolayer film remained constant during the domain growth. By analyzing the growth behaviors of the LC domains carefully, we found that the observed domain growth arises from an illumination-related local mass transfer, which can be attributed to the light-induced damage to the fluorescence molecules; our previous explanations [Wang *et al.*, Phys. Rev. Lett. **71**, 4003 (1993)] should be modified. Our results demonstrate the significant effect of the decomposed fluorescence molecules on the growth of the domains in the liquid-condensed phase. This effect may also be used to study the domain growth dynamics.

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I. INTRODUCTION

Monolayers on the air-water interface provide an intriguing model system in which fundamental properties of two-dimensional pattern formation can be studied [1–3]. In this system the amphiphilic molecules that form the monolayers have hydrophilic and hydrophobic portions. The balance between these opposing natures keeps the molecules on the air-water interface. Conventionally, when a monolayer is isothermally compressed, it undergoes a series of phase transitions. By introducing fluorescence microscopy and Brewster angle microscopy [1–4], transition process from a liquid-expanded (LE) phase to a liquid-condensed (LC) phase can be visualized directly. Previous experimental studies have shown that the domains of LC phase may vary from compact faceted patterns [5,6] to dendrites [7] and fractals [3,6,8], and sometimes to even more complicated morphology [9]. Morphology transitions from fractal to dendrite [6], and from fractal to nonfractal [10], etc., have also been found. Therefore, monolayer film is an ideal two-dimensional (2D) system to study pattern formation and pattern selection problems. Normally, monolayers can be characterized by an isotherm of surface pressure (Π) versus area per molecule (A). When the area of the monolayer film is large, the monolayer is in gaseous phase, where the area per molecule is much greater than the molecule dimension. In this case, the hydrocarbon portions of the molecules make a significant contact with water surface. As the area of the monolayer film decreases, a transition from gaseous phase to a liquid-expanded phase (LE) occurs. In LE phase, the hydrocarbon chains lift from the surface but remain largely disordered. Further compression of the monolayer film leads to the appearance of the liquid-condensed (LC) phase, in which hydrocarbon chains lift from the surface and the degree of chain alignment is much higher than in the LE phase. There are evidences of long range orientational order in LC phase. To some extent, we may regard the domains in LC phase as 2D crystals. It is very interesting that Π-A curve of some lipid compounds shows a long, flat plateau in the LC-LE coexistence region. This implies that the LE-LC transition may be a first-order one. Figure 1 shows the measured isotherms of monolayer film of *N*, *N*-dihexadecyl-3-(1-imidazolyl)-propyamine as a function of temperature. When temperature increases, the isotherm shifts upwards, and the flat two phase coexistence region shrinks. Further increase of temperature may lead to the disappearance of the coexistence region, i.e., a critical point is expected. These features resemble very much the phase transition in van der Waals gas, which is a thoroughly studied model system in statistical physics. In Fig. 1, however, we did not observe the critical point, because the monolayer film collapsed when the film was compressed to a certain extent at higher temperature. When collapse happened, the surface pressure did not increase any more even when the film was compressed to a very condensed situation, as indicated by the arrow in Fig. 1. Strong thermofluctuation at high temperature is suggested to be responsible for the collapse of a monolayer film. The first-order-transition-like feature shown in a monolayer system suggests that the concepts and the techniques used in the first-order phase transitions may be applied to the studies of LC domain growth in

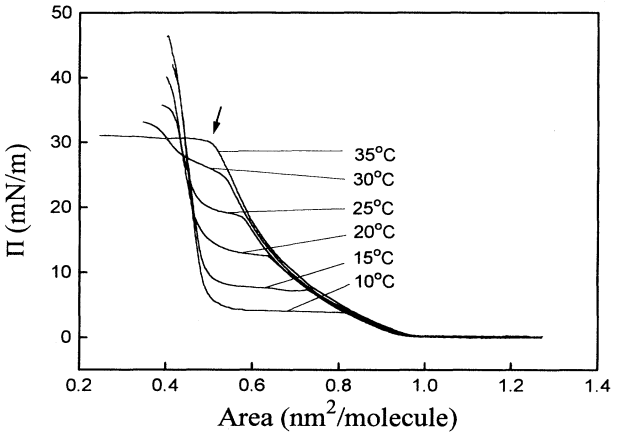

FIG. 1. Π-A isotherms of the monolayer film of *N*,*N*-dihexadecyl-3-(1-imidazolyl)-propyamine as a function of temperature. The LE-LC coexistence region is characterized by the long, flat plateau. We are not able to see the critical point in this figure because the monolayer film collapsed when the area per molecule was decreased to a certain extent at high temperature, as indicated by the arrow.

the LE-LC coexistence region.

Morphology of LC domains in lipid monolayers is rich. Previous experiments have shown that domain morphology may transit from one to another during growth [6]. *In situ* observation is proven to be a useful tool to investigate the mechanism behind these phenomena. However, it was not easy to apply *in situ* observation in a langmuir monolayer system. In conventional langmuir monolayer experiments, LC phase is nucleated by moving a teflon barrier to decrease the area of monolayer film. During the compression, strong convection always occurs in the water subphase. Hence it was normally difficult to trace a growing domain over a long period. By introducing an inhomogeneous electric field, it was possible to collect domains under the microscope and study their evolving process [11]. However, the applied electric field may then influence molecular aggregation dynamics, because the electric dipole-dipole interaction is believed to play an important role in LC domain growth.

In this paper, we report a phenomenon that the LC domains may grow under continuous illumination of microscope light in the LE-LC coexistence region of lipid monolayers. A device is designed to suppress the convection in the water subphase, so we are able to trace the growing process of a specific domain for a period of about 20–30 min and even longer. Technically, the phenomenon reported here implies a system with a controllable driving force to study the development of LC domains. This phenomenon is also enlightening to the domain growth mechanism. Actually, the illumination-related domain growth phenomenon was first reported in 1993 [6]. However, in that paper the role of surface-tension gradient was misinterpreted. Our further investigation indicates that the observed domain growth not only depends on the surface-tension gradient, but also depends on the decomposition of fluorescence molecules upon continuous illumination, which changes the chemical potential in the illuminated region.

II. EXPERIMENT

Imidazole surfactants *R*-(-)-*N*, *N*-dihexadecyl-[2-(1-imidazolyl)propyl]amine (*A*) and *N*, *N*-dihexadecyl-3-(1-imidazolyl)-propylamine (*B*) were synthesized by one of the authors (van Esch) [12]. The synthesized imidazole surfactants were purified by column chromatography. Before doing the experiments, Imidazole surfactant was dissolved in chloroform (P.A. grade, Merck). 0.5 mol% fluorescent probe was added into the solution for fluorescence microscopy. Two different fluorescent probes, DPPE-sulforhodamine and fluorescein-PE (Molecular Probes, USA) were introduced in the experiments separately. Filters were used to generate quasimonochromatic light for the excitation of fluorescent molecules. Green light (510–560 nm) was applied to excite DPPE-sulforhodamine. For fluorescein-PE we utilized blue light (450–480 nm). Monolayer film was formed by carefully spreading the mixed solutions onto the water surface in a teflon-coated trough (350 cm^2), which was thermostatted to 20.0±0.1 °C and placed on the stage of a fluorescence microscope. The water for the monolayer experiments was purified by a Millepore system. The *p*H of the water was 5.5. The trough was equipped with a motorized teflon barrier, allowing compressing monolayers with a controllable rate. In our experiments, this rate was of the order of several $Å^2\,molecule^{-1}\,min^{-1}$. Surface pressure-area (Π-A) isotherm of the monolayers was measured simultaneously. Surface pressures were detected by Wilhelmy balance and were accurate to within 0.1 $mN\,m^{-1}$. The trough, Wilhelmy balance, and temperature measuring system were all interfaced to a personal computer for data acquisition and system control. In order to monitor the behavior of a selected domain, the surface flow in the plane of the monolayer was suppressed greatly by an open circular mask of teflon (diameter 20 mm), which was placed in the subphase under the objective of the microscope. The opening on the mask guaranteed that the surface pressure inside and outside of the mask were identical at equilibrium situation.

The experimental procedure was as follows. First we compressed the lipid monolayer films to the LE-LC coexistence region. In our system, the coexistence region was characterized by the formation of dark, fractal-like LC domains. When the LC domains became sufficiently large, the barrier was stopped and fixed thereafter. The domains ceased growing when an equilibrium surface pressure was reached. Then we chose a LC domain for continuous observation. The water flow in the trough was weakened when compression had been finished for a long time. Also the mask suppressed the convection greatly. So it was easy to keep the domain under investigation at the center of the view field of the microscope. The optical field diaphragm (OFD) of the microscope was

adjusted so that a suitable size of the shade of OFD was achieved. The domains in the shade of OFD were protected from illumination. In the illuminated region the domain growing process was recorded by a microscope-matched video system. Quantitative data about the domain growth, such as the interfacial (interline) growth rate and increasing rate of the fraction of LC domains, etc., were obtained by image analysis.

III. RESULTS AND DISCUSSION

For compound A, typical morphology of LC domain generated by compressing the monolayer film is shown in Fig. 2(a). Because a molecule of compound A is a chiral one, some long branches of the fractal-like domain rotate clockwise. On the right corners of Fig. 2(a), part of the shade of optical field diaphragm can be seen. Continuous illumination of the monolayer film locally by microscope light may induce the growth of the LC domain, as shown in Figs. 2(b)–2(d). It is noteworthy that in the initial period of illumination, some of the outer arms of the LC domain of A melted and the whole pattern shrank [Figs. 2(a) and 2(b)]. Thereafter the cluster started to grow [Figs. 2(b)–(d)]. In the early stage of the illumination-related growth, facets could be formed on the tips of the fractal branches [Fig. 2(b)]. Yet these facets were not stable. As illustrated in Figs. 2(c) and 2(d), dendritic patterns finally emerged after continuous growth. It should be pointed out that although the branches trapped in between the others were growing, the most outward tips grew much faster, as that indicated by the arrows in Figs. 2(b) and 2(c). This phenomena, known as screening effect, was a typical feature in diffusion-limited growth.

Similar growth phenomena happened in the monolayer of compound B, as shown in Figs. 2(a′)–2(d′). In this process, the initial melting of the LC domain upon illumination was not evident. For the domains of compound B, anisotropy during the development of the interface (interline) between LC phase and LE phase is much weaker because B is a nonchiral molecule. According to the microscopic solvability theory [13,14], anisotropy is required in the interfacial dynamics for a stable dendritic growth. If anisotropy is not sufficient, repeated tip splitting occurs and dense branched pattern instead of dendrite may finally be formed. This idea is supported by Fig. 2. From Figs. 2(a′)–2(d′) one may also find that LC domains became more "fat" during the growth. This effect may relate to the positional relaxation of amphiphilic molecules when they incorporated into the LC domain [10].

In the LE-LC coexistence region, we carefully chose an area about 100 micrometers in radius under the microscope, which was free of any LC domains. When we looked under the fluorescence microscope, this area had a homogeneous contrast. By illuminating this area continuously, dendritic LC domains were nucleated, as shown in Fig. 3. Our experiments showed that the illumination-related nucleation process depended on the intensity of the microscope light. If the light intensity was attenuated by adding a polaroid into the optical system, then it took a much longer time to nucleate new LC domains. It had also been observed that the LC domains grew faster when the intensity of the illuminating light became stronger.

As the domains grew in the illuminated region, those branches in the shade of OFD, which were not illumi-

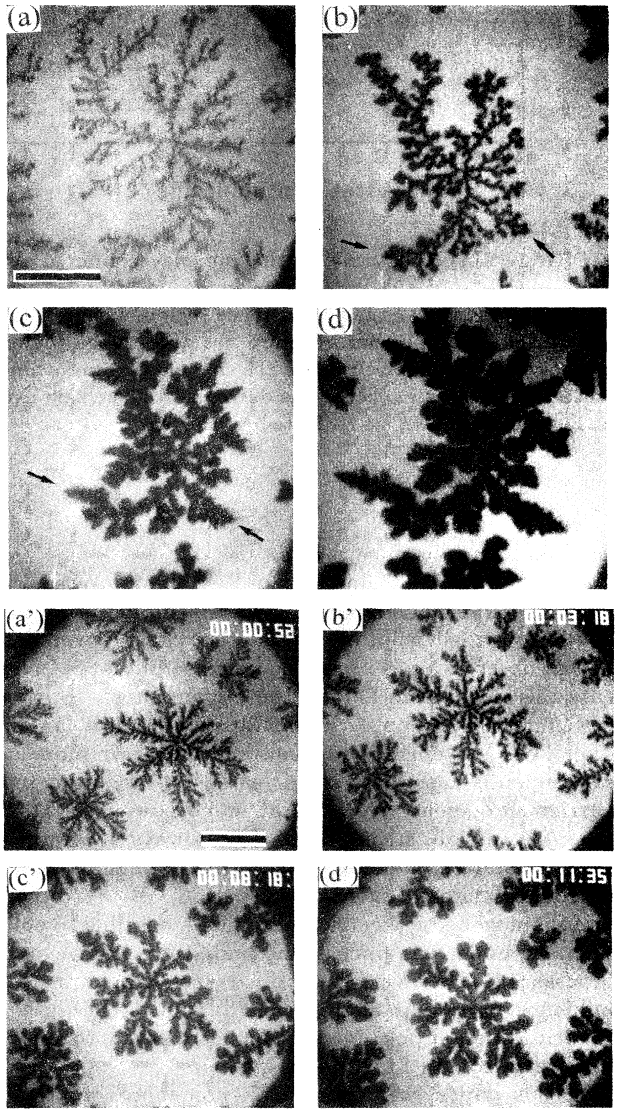

FIG. 2. The successive micrographs to show the illumination-related LC domain growing process. During the domain growth the average area per molecule on the air-water interface remained a constant. (a)–(d) show the growth of LC domain of compound A upon illumination. The fractal-like pattern developed into dendrite after continuous growth [(a)–(d)]. (a′d′) illustrate the illumination-related growth of LC domains of compound B. The initial fractal pattern was thickened during its growth and finally evolved to a fingering pattern (d′). The difference between compound A and B is that compound A has stronger anisotropy. The bars represent 50 μm. On the upper right corners of (a′)–(d′), the codes in the timer represent hours, minutes, and seconds from left to right, respectively.

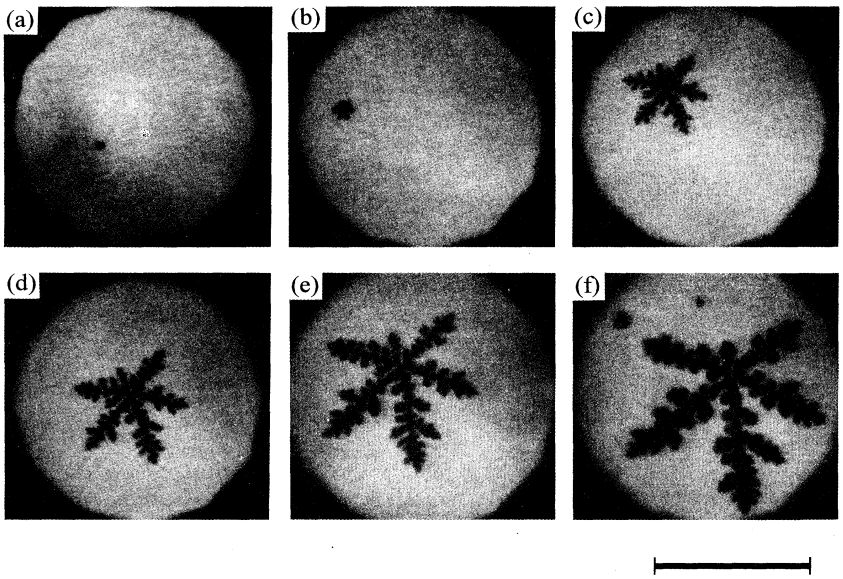

FIG. 3. The successive micrographs to show the illumination-related nucleation process of LC domains of compound A. Initially an area free of any LC domains was selected under the microscope. By illuminating this area continuously, a LC domain was nucleated (a). Continuous illumination made the domain grow. After a long time illumination, new generation of LC domains was induced, as shown in (f). The bar represents 100 μm.

nated, melted gradually in most cases, as indicated by the arrows in Figs. 4(b) and 4(c). The trough on the stage of the microscope was slightly shifted in order to observe these branches in the shade of OFD. It should be pointed out that the process shown in Fig. 4 occurred when the average molecular density in monolayer film remained a constant. The local growth of domains in the illuminated region and melt of domain branches in the surrounding region, as indicated in Fig. 4, suggest that there exists a mass flux moving into the illuminated region from the surrounding areas. The melting of domains in the shade of OFD provides the nutrient needed for the domain growth in the illuminated region. Meanwhile, one may ask what will happen if the mass transfer is blocked by a 2D barrier. Figure 5 gives an example, which demonstrates the domain morphologies near the boundary separating the illuminated area (lower-right part of Fig. 5) and the region protected by the shade of OFD (upper-left corner). There happened to be a long domain branch near the boundary of illumination, which acted as a 2D barrier. On the upper-left corner of the picture, as indicated by the arrow, the initial fractal-like domain morphology has been broken, and a pattern of filaments was formed on one side of the branch. The side branches on the other side, however, have been melted. Faceted patterns have developed in the lower-right part of Fig. 5, which was continuously illuminated. Figure 5 further supports the idea that there exists a local mass transport across the boundary of illumination. If there is not much resistance to the molecular transport, the amphiphilic molecules will move into the illuminated region and support the local domain growth there. If the molecular diffusion is blocked locally, as that shown on the corner of Fig. 5, the molecules will be compressed near the obstacle. Consequently the side of the branch that faces the coming nutrient may grow and form a pattern of filaments. Figure 5 also indicates that the mass transport in this system is really two dimensional.

Concerning the growth phenomena presented above, one may argue that the observed domain growth may result from an inhomogeneous distribution of surface pressure during the compression, for example, local excess surface pressure over the monolayer film after a very quick compression [15]. To avoid the possible inhomogeneous distribution of surface pressure, we left the LC domains on water surface for some time after the compression. During the period waiting for the equilibrium, some minor side branches of the LC domains shrank due to the effect of line tension. We selected a shrinking LC domain for continuous observation. It turned out that the shrinking LC domain also grew upon illumination, as shown in Figs. 6(a)–6(d). If the LC domains were left on the air-water interface for even longer time, those initially fractal-like domains could evolute to a compact circular pattern. The illumination-related growth also occurred to these compact circular domains [16]. We therefore conclude that the observed domain growth does not relate to the possible compression-induced inhomogeneous distribution of surface pressure. One may find that screening effect is clearly demonstrated in Fig. 6. Those branches marked by the arrows grew very slowly comparing to other branches. This means that the domain growth shown here should not be described by a local growth model. Otherwise those marked branches may grow as fast as others.

From a molecular structure point of view, the photochemical reactions of compounds A and B are unlikely. The UV-vis spectra of these two compounds indicated that the absorption band of these two compounds is below 250 nm [17]. On the other hand, however, the fluorescent molecules may decompose upon illumination. When this happens, the illuminated region will become darker. This effect is remarkably illustrated in Fig. 7. The lower part of Fig. 7 has been illuminated for a long period, where well developed compact faceted and dendritic domains can be seen. The upper part of the figure was

protected from illumination by the shade of OFD. In the unilluminated region, the initial fractal-like branches have been broken and many side branches melted. Figure 7 indicates that the chemical environment in the illuminated region was different from that in the unilluminated region due to the decomposition of fluorescent probes.

We found that the growth rate of the illuminated LC domains depends on the concentration of fluorescent dye. We measured the increasing rate of the fraction of the area occupied by the LC domains of compound B over the whole illuminated region. Concentration of fluorescent dye varied from 0.18 mol% to 1.07 mol%. The experimental result is shown in Fig. 8, which indicates that the illumination-related domain growth rate increases when the fluorescence concentration raises.

We also changed the fluorescent probe from DPPE-sulforhodamine to fluorescein-PE to study the behavior of LC domains upon illumination. Meanwhile the wavelength of the illumination light was correspondingly changed to 450–490 nm (blue light). It turned out that the LC domains still grew under continuous illumination. It seems that the illumination-related domain growth does not depend on the wavelength of light. Our previous experiments have shown that the illumination-related domain growth do depend on the amphiphilic molecules which form the monolayer film. As we reported earlier [16], LC domains of L-α-dimyristoyl phosphatidylethanolamine (DMPE) dissolved when they were continuously illuminated.

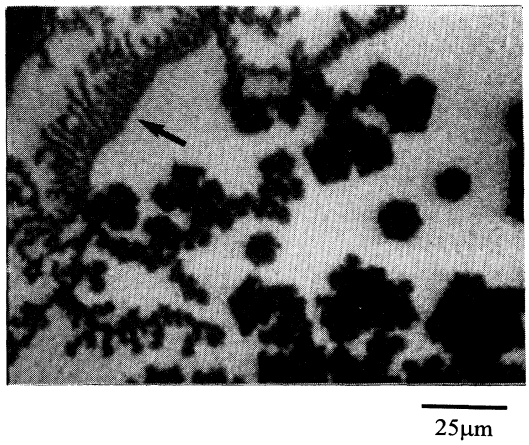

FIG. 5. The luminescence micrograph to show the situations near the boundary of the illuminated region. The lower-right part of the micrograph was continuously illuminated. Faceted LC domains of compound A have developed in this region. The upper-left corner was protected by the shade of OFD. A long domain branch happened to be near the boundary of illumination. As indicated by the arrow, the branches in the previously unilluminated region were broken, and some filaments were formed on one side of the long domain branch.

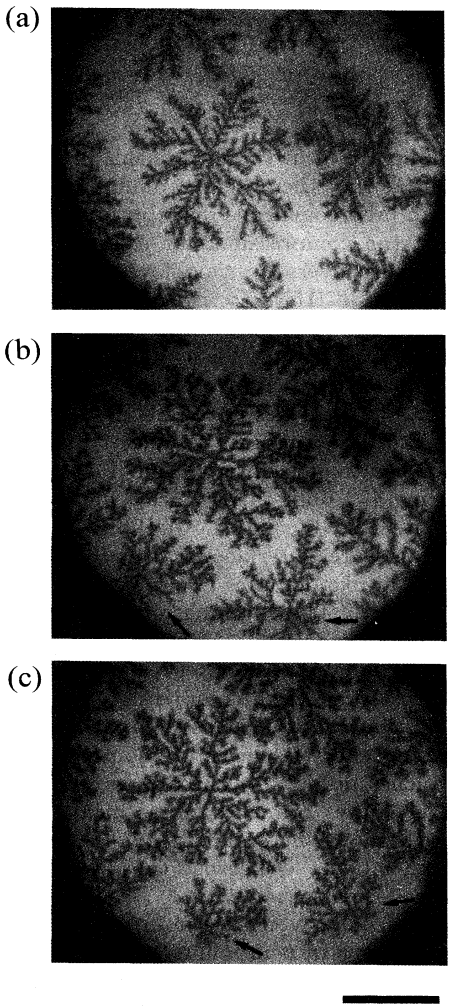

FIG. 4. Corresponding to the growth of LC domains of compound B in the illuminated area, the domain branches in the shade of OFD melted gradually, as indicated by the arrows in (b) and (c). The trough on the stage of the microscope was slightly shifted when the pictures (b) and (c) were taken. The time interval between each micrograph was about 2 min. The bar represents 50 μm.

Rice and McConnell once studied a kind of pattern transition of lipid domains [18], which was attributed to the photochemical effects on the monolayer films. Möbius *et al.* also suggested that photochemical effect may change the local physical property over the monolayer film, for example, local surface pressure [19]. In our case, as we stated above, photochemical reactions on both A and B were unlikely. Moreover, the screening effect in the domain growth suggests that the domain growth should not be the direct result of photochemical reactions. If the observed domain growth were directly resulted from photochemical reaction, all the LC-LE interfaces would grow simultaneously, because the photochemical product should be homogeneously distributed over the illuminated region. Yet what we observed was that the growth usually started from the most outward tips (screening effect).

So far what we learned from the experimental data is as follows. The domain growth upon illumination is independent of the type of fluorescent dye, independent of the illuminating wavelength and the status of the do-

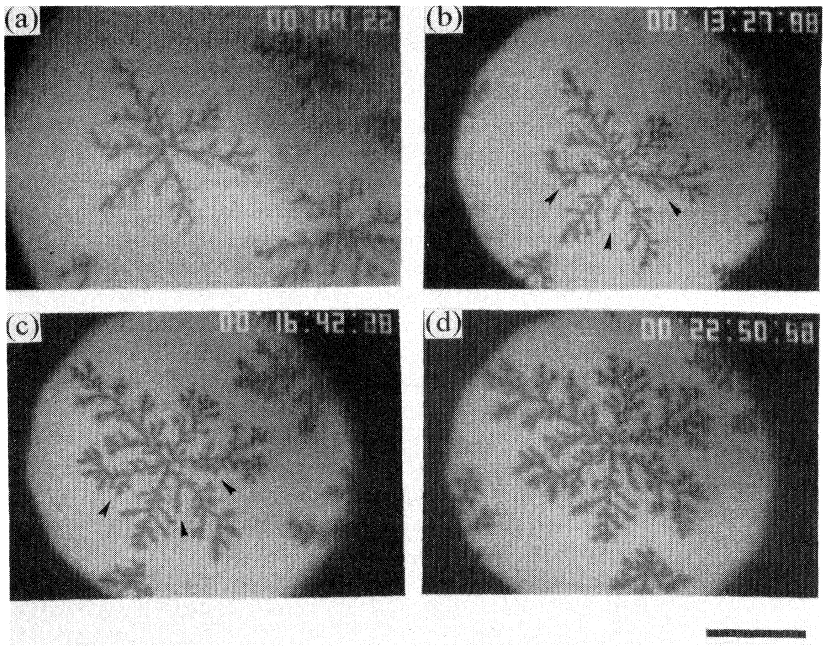

FIG. 6. When the LC domains of compound B were left on air-water interface for some time, the whole pattern shrank under the influence of surface tension. Some minor branches disappeared and only backbones were left (a). It is shown in these micrographs that shrinking LC domain may also grow under continuous illumination. Those branches marked by the arrows grew very slowly comparing to the other branches. This effect is the typical feature of diffusion-limited growth. On the upper right corners of (a)–(d), the first three codes in the timer represent hours, minutes, and seconds, respectively. The bar represents 50 μm.

main. Yet it depends on the amphiphilic compound that forms the monolayer film. In the illuminated region, the chemical environment may be different from the other regions due to the decomposition of fluorescent probes. The evidences of local mass transfer into the illuminated region from surrounding areas have also been observed.

To understand the observed phenomenon, it will be helpful to investigate both the physical and chemical environment on the monolayer film across the illuminated region. The temperature difference between the illuminated area and the surrounding unilluminated region was measured by a pair of identical diode thermometers, which were calibrated before experiments. The sensitivity of the measuring system was about 0.1 °C/mV. Figure 9 shows the result of measurement, which indicates that the temperature in the illuminated area was about 0.2 °C higher [20]. A stable temperature distribution can be reached when the area has been illuminated for about one minute. It is known that surface tension of a monolayer film declines when the temperature increases. Therefore, a centripetal surface-tension gradient is established around the microscope light spot on the

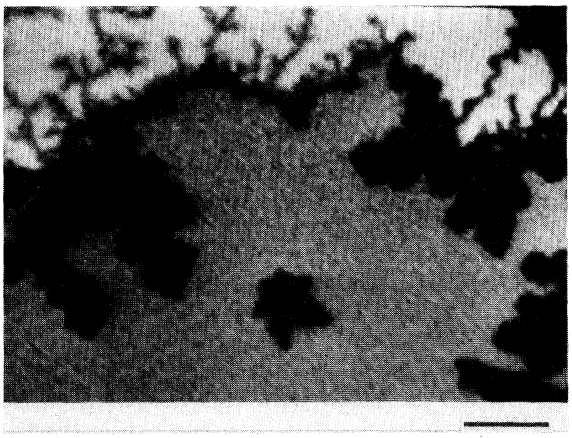

FIG. 7. The luminescence micrograph to illustrate the decomposition of fluorescent probes upon continuous illumination. The up region of the picture was protected by the shade of OFD, where the initial fractal-like domain branches have been melted. The lower part of the picture was continuously illuminated, where LC domains have grown significantly. The darkening of the illuminated region was due to the decomposition of the fluorescent probes. The amphiphile involved in this picture was compound A. The bar represents 25 μm.

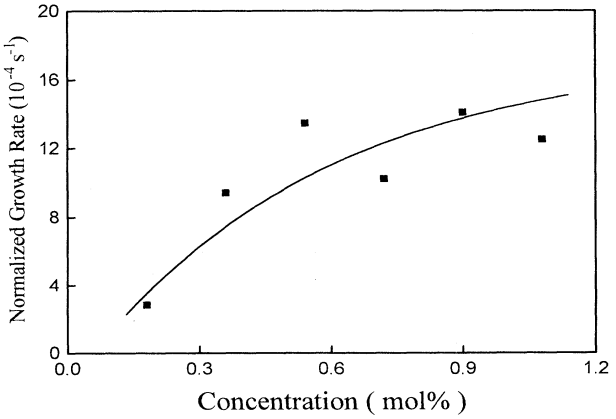

FIG. 8. The plot to show the increasing rate of the fraction of LC domains in the illuminated region as a function of concentration of fluorescent probe. The illumination-related domain growth rate increased with the increase of fluorescent concentration.

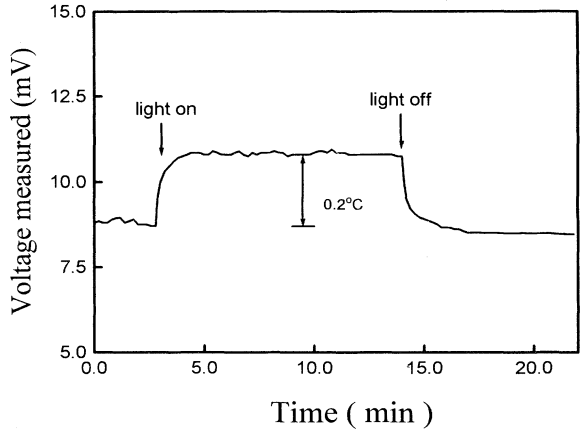

FIG. 9. The plot to show the temperature difference between the area illuminated by the microscope light and the area protected by the shade of OFD, which was measured by two identical diode thermometers placed in these two regions, respectively. One may find that a stable temperature difference can be established after continuous illumination for about 1 min.

monolayer film. This surface-tension gradient, however, does not transport amphiphilic molecules into the illuminated region as what we stated in our previous paper [6]. Contrary, it drives molecules out of the illuminated area. So the effect the surface-tension gradient is to dissolve the LC domains. This effect was experimentally proven by slightly heating a single LC domain with a specially designed device in the water subphase, whereupon we observed the gradual melting of a fractal-like LC domain [21]. On the other hand, as we demonstrated in Fig. 7, continuous illumination may decompose the fluorescent probes in the illuminated region. The decomposed fluorescent molecules in the illuminated area may create a different chemical environment than the surrounding region. This chemical potential difference is responsible for the transport of amphiphilic molecules. The direction and speed of the local molecular transfer, which is determined by molecular interactions, governs the behavior of LC domains in the illuminated region.

Actually, the local temperature build up upon illumination shown in Fig. 9 has two effects. One is local thermoexpansion of the monolayer film, which moves the amphiphile out of the illuminated region. However, thermoexpansion stops as soon as equilibrium is reached. The thickness of a monolayer film is only about several tens of angstrom, so the time required to establish thermoequilibrium in the illuminated region should be very short. Therefore the effect of thermoexpansion is negligible. Another effect comes from the surface-tension gradient around the illuminated region, which also drives molecules out of the illuminated region. So the effects related to the local temperature increase always make the LC domains melt. On the other hand, the decomposed fluorescent probes in the illuminated region may induce a centripetal chemical potential difference. If the chemical potential in the illuminated region becomes lower than that in the surrounding region, a mass flux moving into the illuminated region will be generated. When the flux moving into the illuminated area is stronger than the outward moving flux induced by the surface-tension gradient, the molecular density in the illuminated region will increase continuously. In this case, LC domains in the illuminated region will grow. The growth rate of LC domain depends on the competition between the inward and outward flux. If, however, the chemical potential inside of the illuminated region becomes even higher than that in the surrounding region because of the role of the decomposed fluorescent probes, the amphiphilic molecules will definitely move outward. Meanwhile, LC domain will dissolve upon continuous illumination [16]. Therefore, the behavior of LC domains upon continuous illumination depends on the chemical potential difference across the boundary of the illuminated area, while this potential difference depends on the interactions between amphiphilic molecules and decomposed fluorescent probes. According to solution theory, one may easily write down the relation between molecular interaction and chemical potential. It turns out that a stronger attractive interaction between impurity and compound molecules favors the growth of LC domain [16].

The above picture of domain growth mechanism is supported by our observation of the domain growth rate as a function of fluorescent concentration, as that shown in Fig. 8. When the fluorescent concentration becomes higher, the concentration of the light-decomposed fluorescent molecules will also be high. The effect of impurity will then be more evident. Hence LC domains grow more rapidly at higher fluorescent concentration.

The slight melt of LC domain before the overwhelming growth as that shown in Figs. 2(a) and 2(b) can be understood in the framework of crystal growth theory and solution theory. In fluorescence microscopy, most fluorescence probes are kept out of the LC domain during the domain growth. Only a very small part remains in the LC domain. In LE-LC coexistence region, when equilibrium is reached, chemical potential μ should be equal everywhere, i.e.,

$$\mu^{\mathrm{LE}}(i) = \mu^{\mathrm{LC}}(i) = \mu^{\mathrm{LE}}(o) \tag{1}$$

where "i" and "o" in parentheses stand for "inside" and "outside" of the area that will be illuminated, "LE" and "LC" in superscript stand for the LE phase and LC phase, respectively. Upon illumination decomposed fluorescent probes (impurities) are introduced, which may change the chemical potential. For both the compounds we studied in this paper, chemical potential declines due to the decomposed fluorescence probes. So $\mu^{\mathrm{LE}}(i)$ decreases to $\mu^{\mathrm{LE}'}(i)$. At the same time, $\mu^{\mathrm{LC}}(i)$ decreases to $\mu^{\mathrm{LC}'}(i)$ because the fluorescent probes within the LC domain may also decompose. It is reasonable to expect that the degree of the decline of chemical potential within LC domains is much less than that in the LE phase, because the impurity concentration in LC phase is much lower. So, upon illumination, the following situation holds:

$$\mu^{\mathrm{LE}'}(i) < \mu^{\mathrm{LC}'}(i) < \mu^{\mathrm{LE}}(o). \tag{2}$$

Therefore the LC domains in the illuminated region melt

because $\mu^{\mathrm{LE}'}(i) < \mu^{\mathrm{LC}'}(i)$. At the same time, amphiphilic molecules flow into the illuminated region from the surrounding areas because $\mu^{\mathrm{LE}'}(i) < \mu^{\mathrm{LE}}(o)$. Consequently the amphiphilic molecule concentration in LE phase in the illuminated region increases. According to the solution theory, $\mu^{\mathrm{LE}'}(i)$ will then increase. As soon as $\mu^{\mathrm{LE}'}(i) = \mu^{\mathrm{LC}'}(i)$ is reached, melting of LC domains in the illuminated region stops. Thereafter, because the relation $\mu^{\mathrm{LE}'}(i) < \mu^{\mathrm{LE}}(o)$ still holds, amphiphilic molecules are continuously transported into the illuminated area and the concentration of amphiphilic molecules in LE phase in the illuminated region increases continuously. Therefore $\mu^{\mathrm{LE}'}(i)$ is further increased. Eventually, we may have $\mu^{\mathrm{LC}'}(i) < \mu^{\mathrm{LE}'}(i)$ in the illuminated region, which means that a positive driving force for the growth of LC domain is established. Hence LC domains start to grow.

Whether the initial melting of LC domains upon illumination as that shown in Figs. 2(a) and 2(b) can be observed depends on the initial difference between $\mu^{\mathrm{LE}'}(i)$ and $\mu^{\mathrm{LC}'}(i)$. The degree of this difference relates to the molecular interactions. If $\mu^{\mathrm{LE}'}(i)$ and $\mu^{\mathrm{LC}'}(i)$ do not differ very much, they may become equivalent quickly upon illumination. Meanwhile we are not able to observe obvious melting of LC domains in the initial period of illumination. We suggest this is the situation of compound B [Figs. 2(a′)–2(d′)].

In conventional langmuir monolayer experiments, in order to reach the LE-LC coexistence region, $\rho(\vec{r},t)$ is increased by continuous decreasing of the area of monolayer film. In the illumination-related domain growth, however, $\rho(\vec{r},t)$ is increased by the local mass transport. Whatever the way that $\rho(\vec{r},t)$ is increased, as soon as $\rho(\vec{r},t)$ exceeds the critical value ρ_c, LC domains grow. Corresponding to ρ_c, the surface pressure is $\Pi_0(A_0^{\mathrm{LE}},T)$, where A_0^{LE} is the area per molecules at the critical density ρ_c, T is temperature. When $\rho(\vec{r},t)$ increases, the local surface pressure $\Pi(A^{\mathrm{LE}},T)$ also increases. The locally increased surface pressure is dissipated by the growth of LC domains. Consequently the average surface pressure over the whole monolayer film remains constant. Analog to crystal growth, we suggest that the dimensionless driving force for the domain growth, $\Delta\mu/kT$, be expressed as

$$\frac{\Delta\mu}{kT} \propto \ln\left(\frac{\Pi(A^{\mathrm{LE}},T)}{\Pi_0(A_0^{\mathrm{LE}},T)}\right) \doteq \ln\left(\frac{\rho(\vec{r},t)}{\rho_c}\right). \qquad (3)$$

In the case of illumination-related domain growth, this driving force may be adjusted by changing the concentration of the fluorescent probe, or varying the intensity of the illuminating light.

Briefly, we found in lipid monolayers a growth phenomenon of LC domains, which can be attributed to the light-induced damage of fluorescence molecules. This effect depends on the molecular interactions between amphiphile and decomposed fluorescence molecules, and the illuminating light intensity as well. When studying the domain morphology by fluorescence microscopy, one should be careful of this illumination-related effect. On the other hand, by carefully controlling the illuminating light of the microscope and the concentration of fluorescence molecules, it is possible to create a local growth environment for LC domains with low driving force. One may then investigate the growth dynamics of the 2D faceted crystals and dendrites, as well as 2D morphological instabilities.

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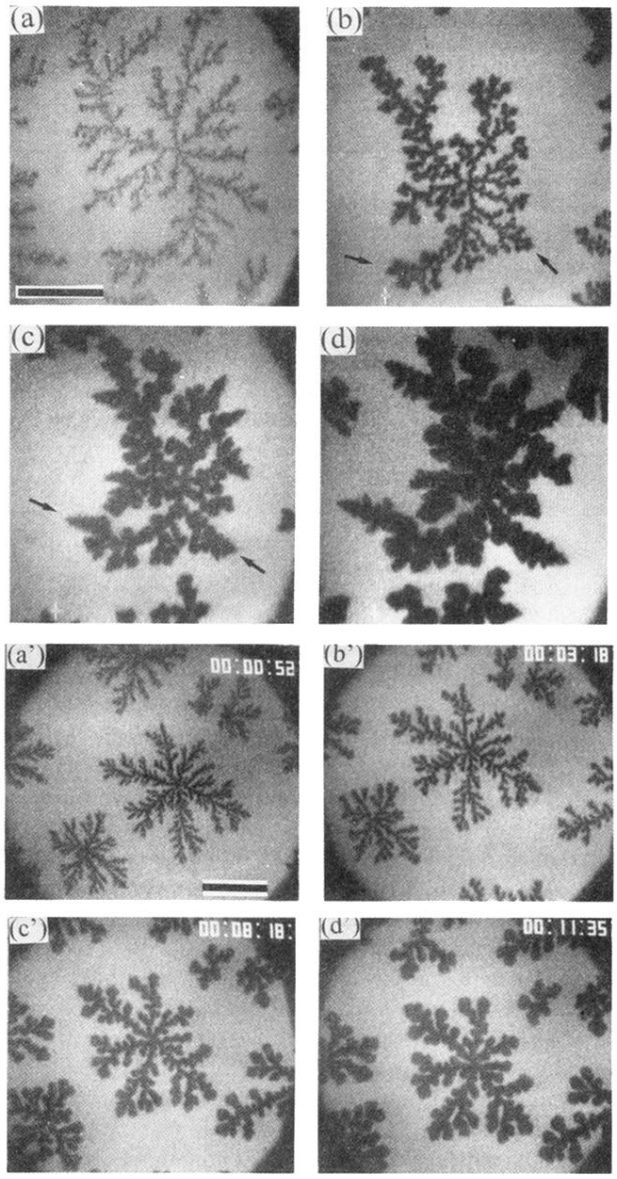

FIG. 2. The successive micrographs to show the illumination-related LC domain growing process. During the domain growth the average area per molecule on the air-water interface remained a constant. (a)–(d) show the growth of LC domain of compound A upon illumination. The fractal-like pattern developed into dendrite after continuous growth [(a)–(d)]. (a′d′) illustrate the illumination-related growth of LC domains of compound B. The initial fractal pattern was thickened during its growth and finally evolved to a fingering pattern (d′). The difference between compound A and B is that compound A has stronger anisotropy. The bars represent 50 μm. On the upper right corners of (a′)–(d′), the codes in the timer represent hours, minutes, and seconds from left to right, respectively.

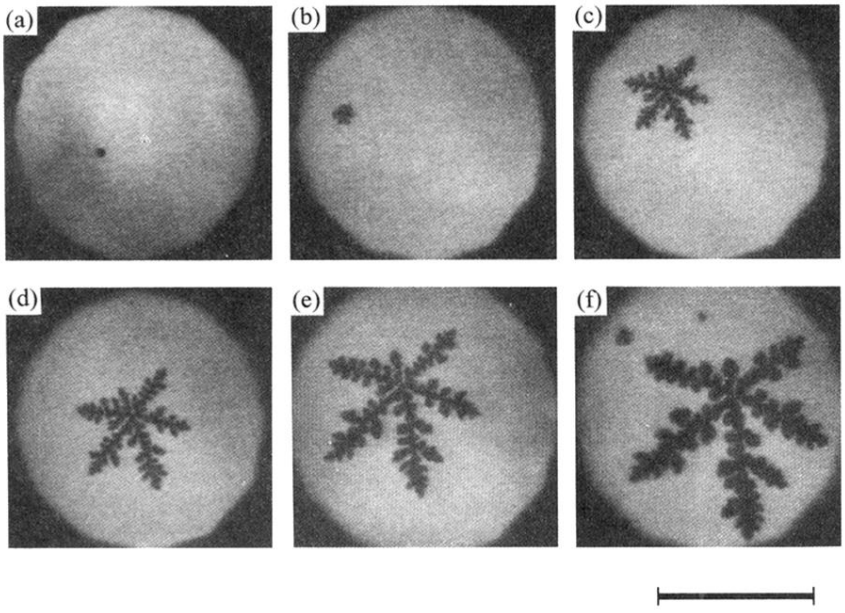

FIG. 3. The successive micrographs to show the illumination-related nucleation process of LC domains of compound *A*. Initially an area free of any LC domains was selected under the microscope. By illuminating this area continuously, a LC domain was nucleated (a). Continuous illumination made the domain grow. After a long time illumination, new generation of LC domains was induced, as shown in (f). The bar represents 100 μm.

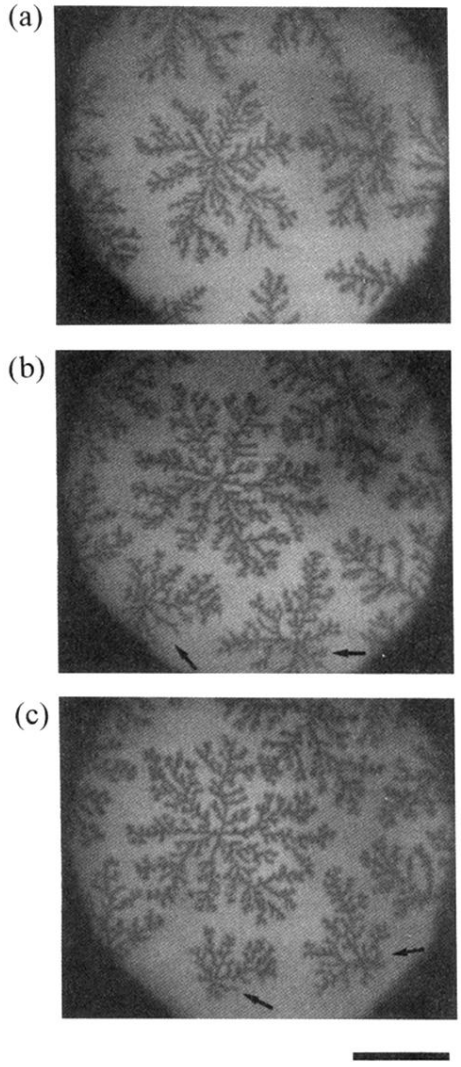

FIG. 4. Corresponding to the growth of LC domains of compound B in the illuminated area, the domain branches in the shade of OFD melted gradually, as indicated by the arrows in (b) and (c). The trough on the stage of the microscope was slightly shifted when the pictures (b) and (c) were taken. The time interval between each micrograph was about 2 min. The bar represents 50 μm.

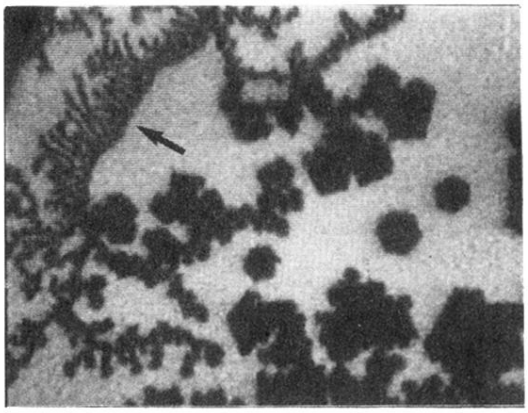

FIG. 5. The luminescence micrograph to show the situations near the boundary of the illuminated region. The lower-right part of the micrograph was continuously illuminated. Faceted LC domains of compound *A* have developed in this region. The upper-left corner was protected by the shade of OFD. A long domain branch happened to be near the boundary of illumination. As indicated by the arrow, the branches in the previously unilluminated region were broken, and some filaments were formed on one side of the long domain branch.

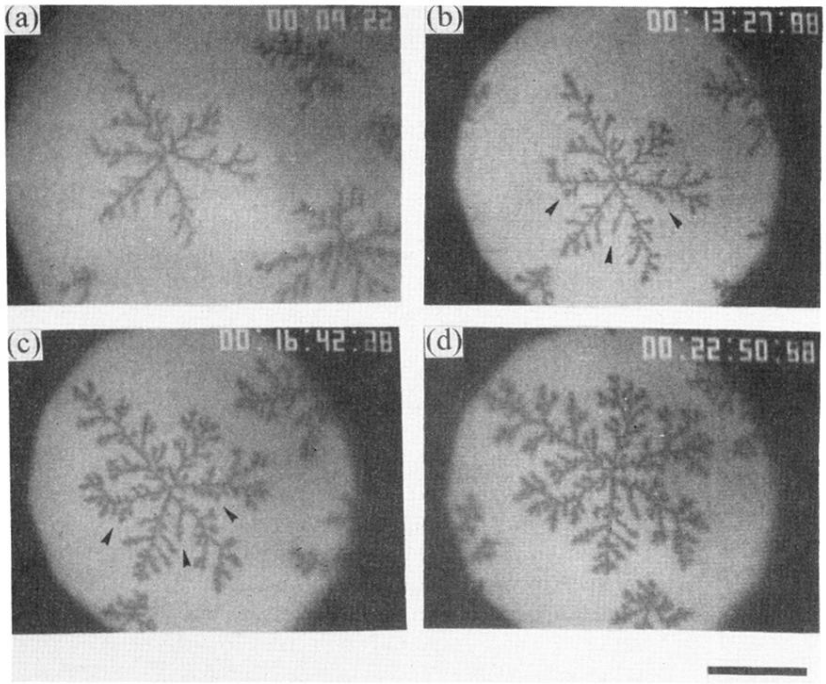

FIG. 6. When the LC domains of compound B were left on air-water interface for some time, the whole pattern shrank under the influence of surface tension. Some minor branches disappeared and only backbones were left (a). It is shown in these micrographs that shrinking LC domain may also grow under continuous illumination. Those branches marked by the arrows grew very slowly comparing to the other branches. This effect is the typical feature of diffusion-limited growth. On the upper right corners of (a)–(d), the first three codes in the timer represent hours, minutes, and seconds, respectively. The bar represents 50 μm.

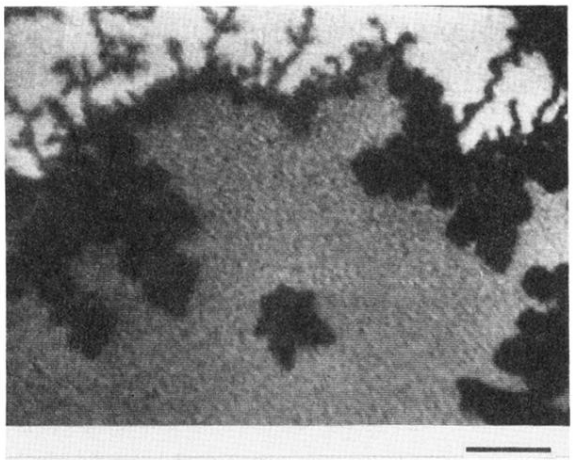

FIG. 7. The luminescence micrograph to illustrate the decomposition of fluorescent probes upon continuous illumination. The up region of the picture was protected by the shade of OFD, where the initial fractal-like domain branches have been melted. The lower part of the picture was continuously illuminated, where LC domains have grown significantly. The darkening of the illuminated region was due to the decomposition of the fluorescent probes. The amphiphile involved in this picture was compound *A*. The bar represents 25 μm.