

## Observation of Pattern Evolution during Homeotropic-Focal Conic Transition in Cholesteric Liquid Crystals

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We have observed an interesting pattern evolution of cholesteric liquid crystals during the homeotropic-focal conic transition in a dispersed polymer network. From the electrical field induced homeotropic state, if the field is reduced to an appropriate bias level focal conics grow at a constant speed, being an open or compact structure depending on the field strength. When the field is increased, these patterns change to ramified structures. We phenomenologically explained the observation. [S0031-9007(99)09387-4]

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Pattern formation is a rapidly developing area in statistical physics [1–3]. Liquid crystals (LCs) are generally composed of rodlike molecules [4], and they are a rich source of materials for the study of pattern formation in nonequilibrium systems [3,5–10] due to their anisotropic shape and interactions. Usually, when external conditions change, some interesting pattern begins to grow in a uniform background. This pattern growing process attracted a lot of research attention in the past years. However, few addressed how the pattern would shrink if the external conditions were reversed to their original state [6]. Whether the pattern growing process is reversible is an interesting question, not only for LCs but also for pattern formation in general. Although the nature of the growing as well as the shrinking processes may depend upon the system in question, the study of some specific systems can shed light on this general problem.

LCs have different phases such as nematic, smectic, cholesteric *et al.* [4]. The rodlike molecules can be oriented and the orientation is called the director. Cholesteric LCs are chiral nematics. In the undistorted state, their director is uniformly twisted around an axis called a helical axis. If the helical axis is perpendicular to the substrate surface, the state is called a planar state; if the helical axis is more or less parallel to the substrate surface, the state is called a fingerprint. A focal conic (FC) state is a multidomain state of fingerprints. In an external electrical field, if the field is higher than a critical value and the material has a positive dielectric anisotropy, the twisted structure can be unwound to a state called homeotropic ( $H$ ); the director becomes uniform in space and follows the direction of the field. We denote that threshold voltage as  $V_{fh}$ . From the  $H$  state, if the voltage is decreased below another critical value ( $V_{hf}$ ), the LCs change to the FC state again.  $V_{hf} < V_{fh}$  and the difference is called hysteresis. In this paper, we employ a cholesteric system to study the pattern growing and shrinking processes. In particular, we focus

on the pattern evolution during the  $H$ -FC transition. This is a unique system since confinement-induced hysteresis exists during these transitions.

The materials used in our experiment include a polymerizable monomer 4-4'-bis[6-(acryloyloxy) hexyloxy]biphenyl (3.6 wt %), a photoinitiator benzoin methyl ether (0.4 wt %), nematic LC mixtures E48 (92.5 wt %), and a chiral dopant R1011 (3.5 wt %) [11]. The pitch is around 1  $\mu\text{m}$ . To enhance the hysteresis and facilitate the experiment, we dispersed the cholesterics with a polymer network [12,13]. Another functionality of the polymer network is to stabilize the FC state; otherwise, it will relax to a planar state if a rubbed polymer surface is used.

The mixtures were agitated to mix well and then filled into LC cells made using two ITO (indium tin oxide) glass plates whose inner surfaces were coated with rubbed polyimide to promote a planar alignment. We used a planar alignment in order to evaluate the competing effects of a polymer network and a surface anchoring. The cell thickness was 5  $\mu\text{m}$  with a deviation within 5%. The filling process was done in a vacuum chamber. Filled LC cells were uv cured for about 15 min in the  $H$  state in the presence of an ac electric field (1 kHz). Less curing time resulted in unstable polymer networks. The voltage was 30 V (rms) and the intensity of uv radiation was 18  $\text{mW}/\text{cm}^2$ . Scanning electron microscopy and many other measurements indicate that the so-formed polymer network is anisotropic and perpendicular to the cell surface and it is finely distributed down to the nanometer scale [13,14].

The transition voltages  $V_{fh}$  and  $V_{hf}$  were measured by an electro-optical method [15]. They are 16.2 and 13.8 V, respectively, close to those measured under a microscope. The pattern growing and shrinking processes were studied under a polarizing microscope in a transmission mode. The process was videotaped for later analysis. The time resolution of the recording system was 1/30 s. To study

the pattern growing process, a high voltage was first used to align the material to the  $H$  state, then the voltage was quickly reduced to a bias level. Gradually decreasing the voltage also worked and the resulting growing process was similar. To study the pattern shrinking process, the voltage was changed slowly since a sudden change could not give a stable pattern.

The  $H$ -FC transition is continuous in an infinite space [4]. In a confined geometry, however, it becomes first order since the topologies of  $H$  and FC are incompatible and heterogeneous nucleation is involved in the initial stage. Thus, the defects structure can mediate this transition [16]. There were a lot of point defects in our cells due to the polymer network as well as surface irregularity. Figures 1(a)–1(f) show typical FC patterns formed during  $H$ -FC transition. Figure 1(g) summarizes the history of these micrographs. When the bias voltage was reduced below  $V_{hf}$ , FCs nucleated around some point defects. Figure 1(a) was taken about 8 s after the nucleation began when the bias voltage was 13.6 V. It is a random structure, different from those when the voltage was further reduced. Figure 1(b) shows a pattern when the bias voltage was 10 V, which was taken after the pattern had grown for 3.5 s. The FC domains have a round shape. This shape transition was continuous. We did not see any abrupt change as we reduced the voltage.

A detailed observation shows that the nucleation density depends on the bias voltage: When the bias voltage is low, the number of nucleation sites becomes high. If there is no polymer network and the surface favors a homogeneous anchoring, the FCs have an anisotropic shape due to surface anisotropy [17]. Here, the isotropic growth [both Figs. 1(a) and 1(b)] implies that the surface in-plane anisotropy effect is screened by that of the polymer network out-of-plane anisotropy and thus plays a less important role.

If the bias voltage was fixed, the pattern in Fig. 1(b) would keep growing until the whole LC cell was filled by FCs, while the pattern in Fig. 1(a) would not fill the whole cell within our observation time. The later case may reflect the irregularity of the cell due to the variation of the concentration of polymer network. A larger concentration of polymer network results in a larger hysteresis [13]. By adjusting the focal depth, we found that the patterns in Figs. 1(a) and 1(b) fill the cell vertically which rules out the possibility that the pattern in Fig. 1(b) is just a superposition of the pattern in Fig. 1(a).

If the bias voltage was increased but still less than  $V_{hf}$ , the pattern kept growing but at a lower speed. When the voltage was increased close to  $V_{hf}$ , the pattern in Fig. 1(a) appeared again as shown in Fig. 1(c) [The inner part in Fig. 1(c) grew 5 s, less than Fig. 1(b)]. When the voltage

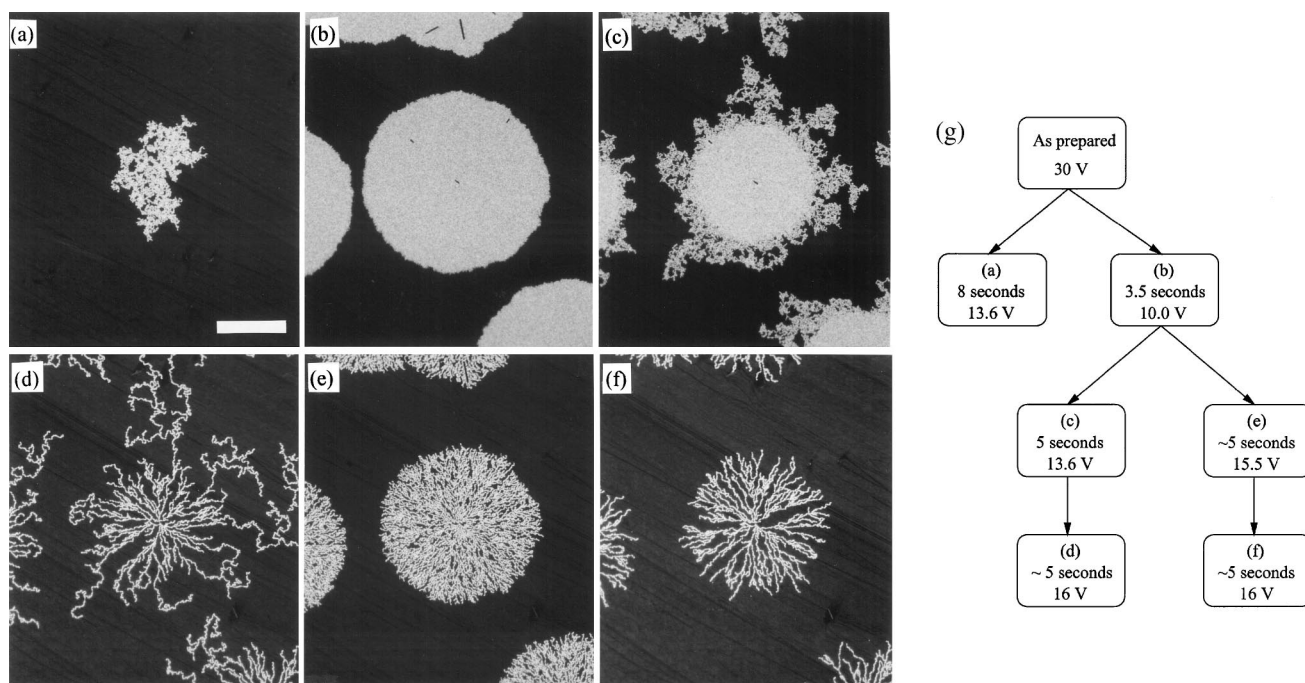


FIG. 1. Optical micrographs of cholesteric liquid crystals taken under a polarizing microscope. The electric field was applied perpendicular to the cell surfaces during the curing and in the observation. The scale bar in (a) corresponds to  $200 \mu\text{m}$ . All pictures have the same scale. (a) A growing pattern when the bias voltage was reduced slightly below  $V_{hf}$ , (b) a round domain after the applied voltage was reduced to 10 V directly from 30 V. The pattern in (b) changed to (c) when the voltage was increased to a value slightly below  $V_{hf}$ , and to (d) when the voltage was changed to 16 V afterwards. If the voltage was changed quickly to above  $V_{hf}$ , the patterns are different from those in (c) and (d). For (e), the voltage was 15.5 V. The voltage was increased to 16 V afterwards and the pattern changed to (f). (g) Summarizes the history of these micrographs.

was further increased, the FC pattern faded to a stable fractal-like structure [18]. Figure 1(d) was such a pattern when the voltage was 16 V. If the voltage was higher than  $V_{fh}$ , the fractal-like pattern disappeared.

From Fig. 1(b), if the voltage was increased rapidly to a value higher than  $V_{hf}$  but less than  $V_{fh}$ , the pattern in Fig. 1(b) would directly fade to the pattern shown in Fig. 1(e), where the bias voltage was 15.5 V. It was stable until the bias voltage was changed again. When the voltage was increased to 16 V, Fig. 1(e) evolved to Fig. 1(f) which was also stable. Figure 1(f) is similar to Fig. 1(d) except the outmost region in the latter. Both Figs. 1(e) and 1(f) are strikingly similar to the diffusion-limited aggregation (DLA) pattern [19].

At a fixed bias voltage, the radius of the round FC domain increased linearly with time as demonstrated by Fig. 2. The straight line fitting works well and the slope gives the growth speed. Also revealed by Fig. 2 is that the growth speed depends on the field strength: the lower the voltage, the higher the growth speed. We measured the growth speeds under various voltages ranging from 6.5 to 13.2 V and the results are shown in Fig. 3. We were unable to measure the growth speed when the voltage was below 6.5 V since both the number of nucleation sites and the growth speed increased rapidly and our recording system had a limited time resolution.

From a free energy analysis, we know that the growth speed  $v \propto \Delta F \propto V_{hf}^2 - V^2$ , where  $\Delta F$  is the free energy difference, and  $V$  is the applied bias voltage. The inset of Fig. 3 is the plot of  $v$  against  $V_{hf}^2 - V^2$ . The data can be well fitted by a straight line which confirms the validity of this simple analysis.

The above evolution process was also observed when we changed the cell thickness, pitch, surface treatment, or some combination. The growing and shrinking process around the cell edge was similar to the process reported above. Here, we briefly discuss the underlying mechanism.

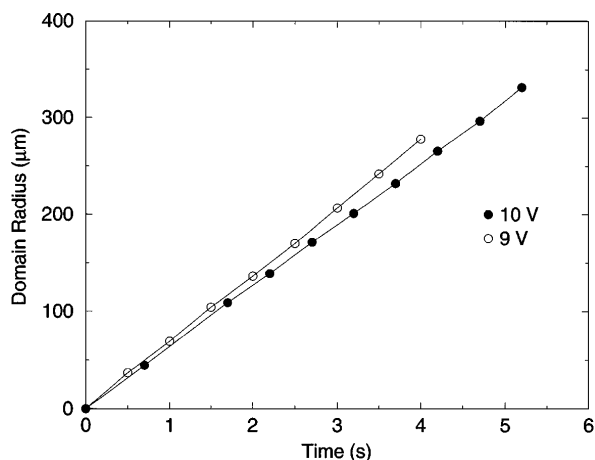


FIG. 2. Linear dependence of pattern radius and growth time when the voltage was changed from 30 V to 9 or 10 V.

The molecular arrangement in these FCs and FC filaments (fingers) have been discussed before [20]. We thus focus on the pattern growing and shrinking process. The system is complicated by the polymer network which was a random medium. In the whole process, defects structure, density, and distribution played an important role. A detailed analysis is not possible at present and we can only phenomenologically discuss the growing and shrinking process.

It is known that in a homogeneous environment the finger grows in a fixed direction. While the tip of this finger is growing, the part behind the tip undergoes an undulation expanding laterally to balance the excessive energy. The undulation process becomes quick when the voltage is far below  $V_{hf}$  [21]. The same process happened in our cell since we observed the same process when no polymer network was present. However, due to the irregularity of the polymer network, the tip of the finger could not keep growing in a fixed direction even there was a rubbed polymer surface. The bulk effect was dominant. Instead, the tip changed growth direction and underwent a tip-splitting process during its growing and undulating process. Tip growing and splitting processes were extensively discussed in systems where negative material and  $H$  surface were used [22]. In our system, the polymer network may play some role as a  $H$  alignment agent. In Fig. 1(a), since the voltage was just slightly below  $V_{hf}$ , the undulation process was weak. But the tip did change its growth direction and split. Since the undulation process was weak, the tip could take a zig-zag path and not grow out. When the applied voltage was far below  $V_{hf}$ , the undulation became strong. So, after the tip grew and split, the left space was immediately filled by the undulating FCs and the tips had to grow out. The dense round shape in Fig. 1(b) can be explained by this. The pattern in Fig. 1(c) is then also understandable.

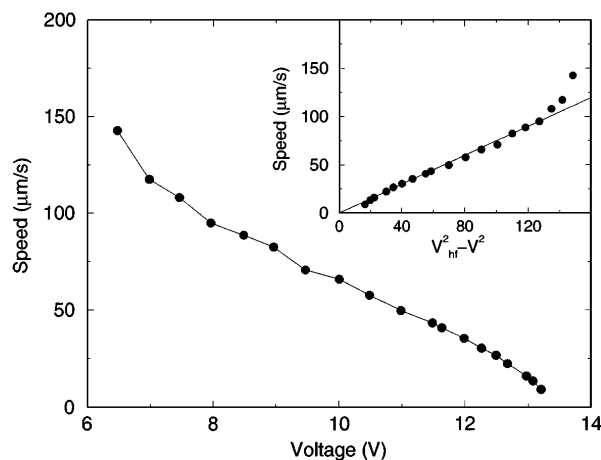


FIG. 3. Relationship between growth speed and applied voltage when the voltage was reduced from 30 V. The inset shows the growth speed as a function of  $V_{hf}^2 - V^2$ , which can be fitted by a straight line.

As for the pattern shrinking process, we need to mention the pattern shrinking behavior of cholesterics in a uniform environment where the pattern retreats non-uniformly as the voltage is increased. The undulated parts shrink first. One can even observe an elongated finger during the retreating period. A similar retreating process was reported in [20]. The same thing happened in our cell. As the voltage was increased, the parts that had expanded to fill the whole space during the growing period shrank first and the path along which the tips split and grew out was left. The patterns in Figs. 1(d)–1(f) can be understood this way.

There is a screen effect during DLA pattern formation: The particles later added to the pattern have a small chance to reach the interior region as the outgrowing branches almost shield that part. This effect causes the ramified structure in the DLA pattern formation. In our system, there also was a screen effect. As we mentioned above, when the voltage was far below  $V_{hf}$  the undulating finger filled the left inner space quickly and the tip had to grow out: This causes the screen effect for the tip growth. When the voltage was increased, the undulated part shrank first and the path of the growing tip was left.

In summary, we have observed an interesting pattern growing and shrinking process of cholesteric liquid crystals in a polymer network environment. The focal conic growing from a homeotropic background can be controlled by the applied voltage, and the growing pattern depends on the field strength. The shrinking pattern can be mediated also by the bias field and these patterns resemble the DLA pattern. We explained the growing and shrinking process phenomenologically, and the origin of the DLA resemblance was explained by the screen effect during the pattern growing process.

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