Disklike Texture of Ethyl−Cyanoethyl Cellulose Cholesteric Phase

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ABSTRACT: A disklike texture of ethyl−cyanoethyl cellulose/dichloroacetic acid cholesteric solution was investigated using polarizing optical microscopy. This texture was formed by confined cholesteric spherulites in the cholesteric solution between two glass slides and possessed three basic forms: bispirals, concentric circles, and pseudo-concentric circles. Effects of boundary anchoring on the cholesteric condensed structure could lead to an extinction area at the center of the cholesteric disks. Furthermore, effects of a magnetic field on the disklike texture were also investigated.

Introduction

Cellulose and many of its derivatives form cholesteric liquid crystals in appropriate solvents.[1] In particular, ethyl−cyanoethyl cellulose [(E−CE)C], which is a cellulose derivative with two different ether groups of ethyl and cyanoethyl, forms cholesteric liquid crystals in many organic solvents such as dichloroacetic acid (DCA)[2] and acrylic acid (AA).[3] In polarized optical microscopic observations, (E−CE)C/DCA cholesteric liquid crystalline (LC) solution shows multitexture behavior with variation of the polymer concentration.[2,4] When this concentration is in a range of 25−35 wt %, both cholesteric LC and isotropic phases in the (E−CE)C/DCA solution are found. The LC phase generally shows a disklike texture. With increasing the concentration, a fingerprint texture gradually appears. When polymer concentration is above 35 wt %, there is a uniform cholesteric LC phase in the solution, and this phase generally shows a planar texture with vivid colors and oily streaks.

Some results about the disklike texture have been reported in our pervious reports.[2,4] In this study, the disklike texture in (E−CE)C/DCA cholesteric LC solution is studied in detail; different patterns of the texture are classified, and their formation mechanisms are analyzed. In the past, the effect of magnetic field on the fingerprint texture has been investigated;[5] in this report, we would also like to extend this study to the effect of magnetic field on the variation of the disklike texture.

Experimental Section

Materials. (E−CE)C was prepared by reaction of ethyl cellulose (EC) (from Luzhou Chemical Plant, China) and acrylonitrile by the following procedure. 20 g of EC was dissolved in 500 mL of acrylonitrile, and subsequently, 20 mL of 5% NaOH aqueous solution was added. The reaction mixture was kept at 50 °C with continuous stirring for 4 h, and then 50 mL of 5% acetic acid was added to the mixture. The suspension mixture was then poured into distilled water at 96 °C with vigorous stirring to distill excess acrylonitrile. The product was filtered and washed with distilled water for several times. The final product was dried under vacuum at 65 °C. The yield product, (E−CE)C with degree of substitution for ethyl of about 2.1 and for cyanoethyl of about 0.33, was determined by an elemental analysis (CHN-O-RAPID, Heraeus, Germany). The molecular weight of (E−CE)C, M_n, measured by a gel permeation chromatograph (GPC) (Waters-ALC-244-GPC) and calibrated by standard polystyrene, was 9.7×10^4. DCA was a chemically pure reagent.

(E−CE)C/DCA Solution. (E−CE)C/DCA LC solution was formed by mixing (E−CE)C with DCA at room temperature, and then it was sealed in a test tube. To form the disklike texture, the polymer concentration of 26 wt % was used, and to form the fingerprint texture, the polymer concentration of 29 wt % was used. The solution was set aside at room temperature for over 20 days after being heated at 50 °C for about 10 h. The solution was then sandwiched between a microscope slide and a cover glass and was sealed with solid wax. The thickness of the solution film was about 20 μm. After being stored at room temperature for 3 days, the specimen was observed by a polarized optical microscopy (POM) (ORTHOPLAN-POL, Leitz, Germany).

Magnetic Field Processing. The solution film was exposed in a magnetic field with an intensity of 9.4 T. It was then observed in POM.

Results and Discussion

Difference between the Disklike and the Spherical Textures. When the (E−CE)C polymer concentration in DCA is 26 wt %, the LC aggregates of the cholesteric phase disperse in the isotropic phase and show a disklike texture. Because of the surface tension of the interphase between the cholesteric phase and the isotropic state, the LC aggregates generally form a "disklike" shape in minimizing the free energy. The diameter of "disks" is commonly about 30−50 μm, and some of them are as large as 100 μm. In the LC phase, some periodic extinction circles or bispirals (see Figure 1) can be observed, and the distance of neighboring circles or bispirals is equal to one-half of the helical pitch length. This disklike texture is very similar to the spherical texture, which has been observed in many polymer cholesteric LC solutions, such as DNA fragment or polypeptide (poly-γ-benzyl-L-glutamate, PBLG).[6] However, the texture in the (E−CE)C/DCA cholesteric LC solution is different from those in the DNA or polypeptide systems. First, the diameter of the "disk" (50 μm) (see Figure 1) is much larger than the thickness of the specimen (20 μm), and the structure is not spherical but

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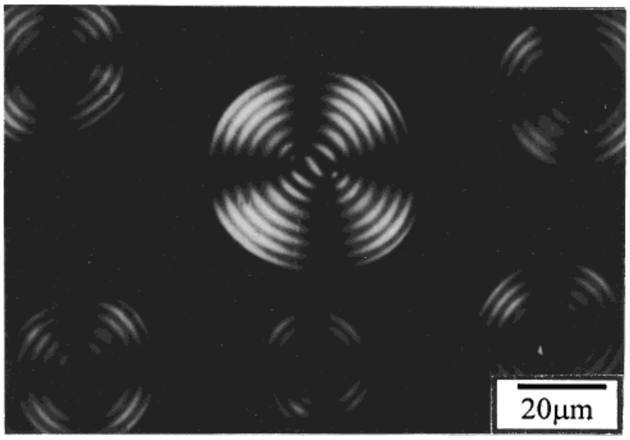

Figure 1. Disklike texture of the 26 wt % (E−CE)C/DCA cholesteric liquid crystalline solution. The disk (50 μm) in the center has bispirals without any disclination line.

oblate. Second, it is found that the "disks" are in different focal planes (see Figure 2) when the solution is observed from the same viewport by POM. Some "disks" are clear and others are blurry due to their different distances from the object lens. Therefore, the thickness of the "disks" must be smaller than that of the solution film. If the LC phase texture is spherical texture, the diameter of the aggregates must be equal to or larger than the thickness of the solution film, and thus, they must contact the top and bottom glass slides. The neighboring aggregates also have to merge with each other. However, this case has not been observed. For example, two "disks" in the center of Figure 2 are located in different focal planes and are not in contact with each other; even they are overlapped when observed along the direction of the substrate normal (see Figure 3). Therefore, it is believed that the LC aggregates in the (E−CE)C/DCA cholesteric LC solution show disklike texture, and the thickness of the "disks" is substantially smaller than the sample thickness.

Patterns of Disklike Texture. For the spherical texture of the cholesteric LC phase, it can be described by the Frank−Pryce model[6,7] (see Figure 4). In this model, the cholesteric spherulite consists of a series of concentric spheres of successive radius, each sphere having a singular point *P* lying on the same common radius *OP*. Consider a family of circles on one of these spheres, all tangential to a line *PQ*, itself tangential to the sphere at *P*; the molecules on the sphere are everywhere arranged parallel to the direction of these circles (see Figure 4c). A similar family of circles may be constructed on the neighboring sphere of the spherulite (see Figure 4d), but the point *P* moves out along the radius to *OP* and the line *PQ′* is inclined so as to make an angle α with the line *PQ*. The molecules on each concentric sphere are arranged parallel to the directions of the appropriate family of circles. Then every molecule is nearly parallel to its neighbors on the same sphere (except near the singular radius *OP*, which corresponds to the disclination line) and will be inclined at an angle α to those on the same radius in neighboring spheres (the direction of cholesteric helix axis). In the POM, concentric circles and the $S = 2$ disclination line can be observed from the viewing direction perpendicular to disclination line, *XZ* projection (see Figure 4a). From the viewing direction parallel to disclination line, *XY* projection, bispirals can be observed (see Figure 4b). Two patterns have been observed in the spherical texture of the PBLG cholesteric solution: "concentric circles" with a disclination line and "bispirals".[6] However, for the disklike texture in the (E−CE)C/DCA cholesteric LC solution, additional patterns are observed. Two patterns are identical to those of spherical texture: the "concentric circles" with a disclination line (see Figure 5) and the "bispirals" (see Figure 1). It is interesting that the shape of the disks is different form that of the spherulites, but they can form the same texture patterns. It seems in forming the disks or the spherulites are dependent on the thickness of samples. In the bulk, both (E−CE)C and PBLG cholesteric LC solutions form spherulites that can be described by the

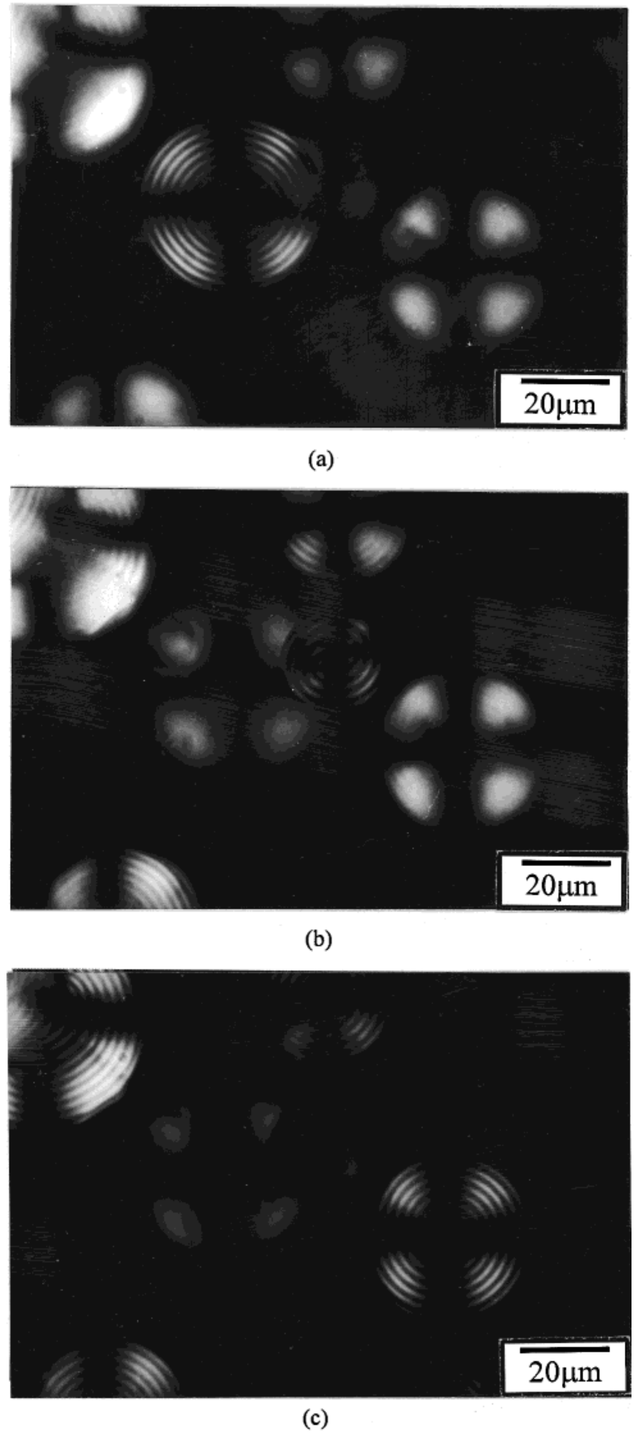

Figure 2. Microphotographs of disks, observed from the same viewport. (a), (b), and (c) are in different focal planes. The two "disk" in the center have not any obvious contact.

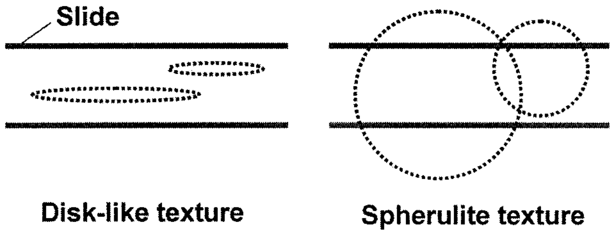

Figure 3. Scheme of the disklike texture. It is in proportion to the two disks in the center of Figure 2b. Left, disklike texture. Right, if it formed spherical texture, the two spherulites would overlap.

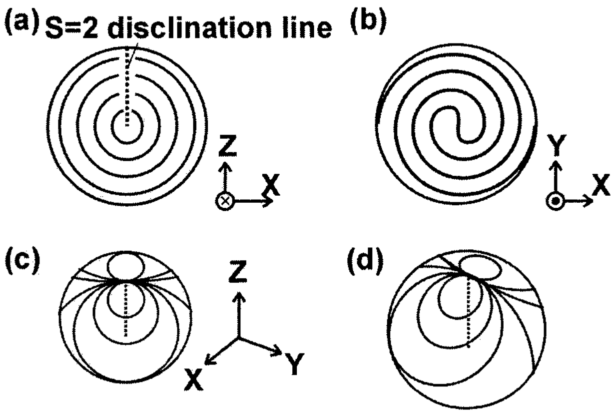

Figure 4. Scheme of the Frank−Pryce model. (a) Concentric circles, disclination line perpendicular to the viewing direction, *XZ* projection. (b) bispirals, disclination line parallel to the viewing direction, *XY* projection. (c) and (d) the director fields on different spheres, the spheres of (d) have an rotating angle with that of (c).

Frank−Pryce model. In the PBLG LC solution films, the thickness of the films was 0.5[7] or 1 mm,[6] which was much thicker than the diameter of the spherulites (about 100 μm), and therefore, the LC phase shows the spherical texture. In the (E−CE)C LC solution films, however, the thickness of the films is about 20 μm, the spherulites are squeezed, the thickness is smaller than the diameter of the spherulites, and thus they form the disks (see Figure 3). Moreover, the bispirals pattern of the (E−CE)C cholesteric phase is mostly counterclockwise, which is different from the clockwise bispirals pattern of the PBLG systems.[6,7] This difference may result from their different molecular conformations. PBLG possesses an α-helical conformation, which is the preferred orientation of the molecules,[6,7] and forms the clockwise bispirals patterns. From conformational energy calculations[8−10] and electron and X-ray diffractions,[11,12] the stable conformations of cellulose and its derivatives are rodlike extended helices. This conformation may lead to the formation of this counterclockwise bispirals pattern of (E−CE)C cholesteric phases.

Besides the patterns of the “concentric circles” and the “bispirals”, another pattern in the disklike texture, “pseudo-concentric circles” can also be observed (see Figure 6). This pattern is similar to that of the “concentric circles” and has an $S = 2$ disclination line, but the “circles” are asymmetric. There is always a redundant half-circle on one side, and it is a single spiral in the disklike texture.

From those patterns observed in the disklike texture, it can be concluded that the disklike texture forms due to confinements of the spherulites in (E−CE)C/DCA LC solution. If the disclination line aligns parallel to the glass slide substrate normal, there is the “bispirals” pattern when the spherulites are confined. The “concentric circles” pattern can be formed if the disclination line aligns perpendicular to the glass slide substrate normal. If the disclination line in the spherulites aligns oblique to the glass slide substrate normal, after being confined, the thickness of the disks is very thin, and the disclination line is almost parallel to the slides and the line can be observed. The single spiral optical pattern is also formed, and this is recognized as the “pseudo-concentric circles” pattern. Since the patterns of the disklike texture depend on the spherulites in the unconfined bulk, the patterns of the disklike texture will change with the arrangement of LC molecules in the spherulites. Figure 7 shows a disklike texture with a bispirals pattern at the center area and a concentric circles pattern in the outside area. The original spherulite that forms these two different patterns must thus have different LC molecular arrangements at the center and in the outside area. The center part is the Frank−Pryce structure having a disclination line that is parallel to the substrate normal, and thus, it forms a bispirals pattern. The disclination line changes its direction, and it is perpendicular to the substrate normal in the outside area. The concentric circles pattern is thus formed. This confirms that the cholesteric LC phase has a very strong twisting power. It can repair distortion of cholesteric

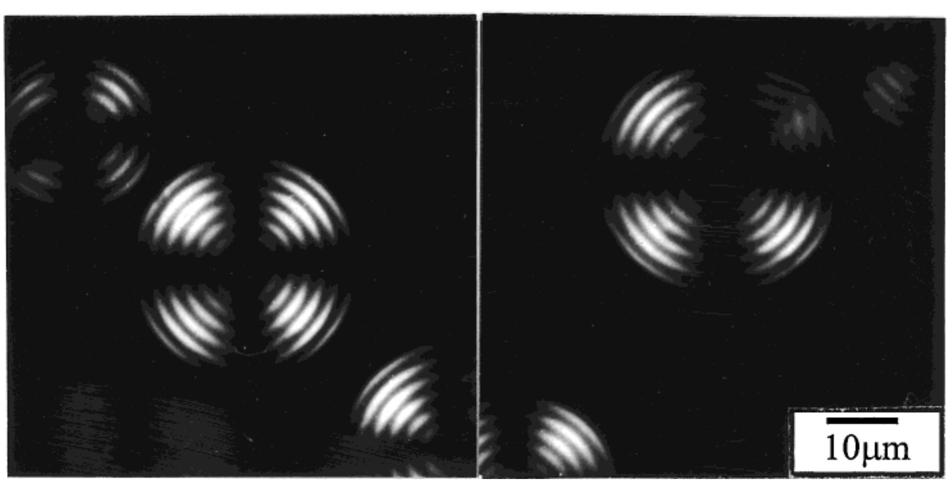

Figure 5. Pattern of concentric circles, with an $S = 2$ disclination line extending along a single radius perpendicular to the direction of observation. Left, the disk with an $S = 2$ disclination line along the polarizer and downward. Right, the disk with a disclination line has a 45° angle with the analyzer.

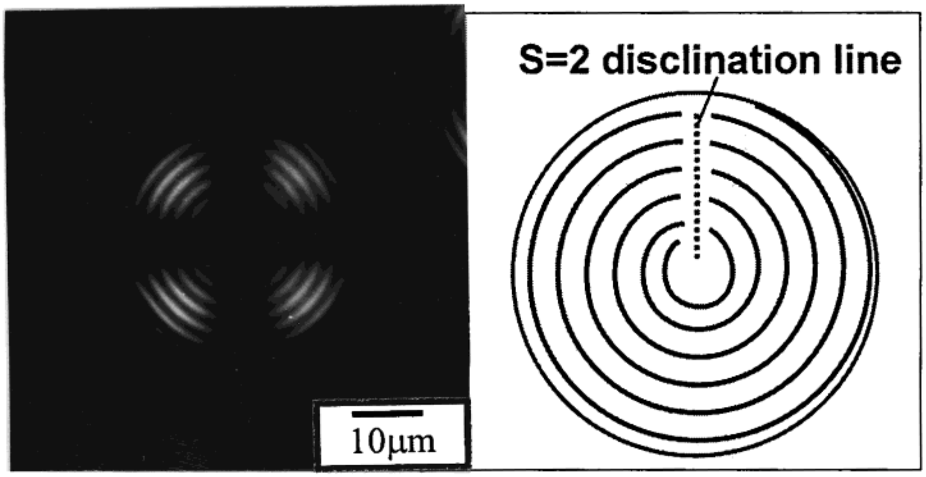

Figure 6. Pattern of pseudo-concentric circles. Left is observed by the POM; right is its structure scheme. It has an $S = 2$ disclination line and single spiral.

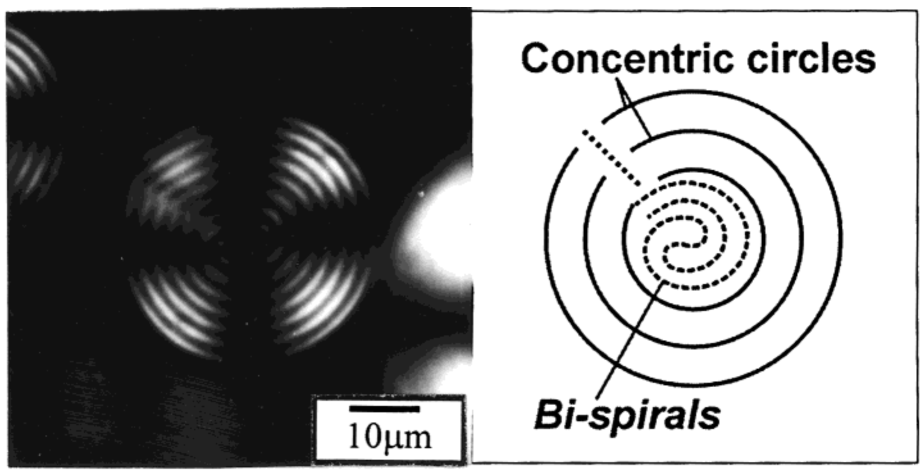

Figure 7. Disk with molecular conformation change. Left is observed by the POM; right is its structure scheme. The center is bispirals pattern; the outside is concentric circles pattern.

structure and makes the structure continued develops. Effects of the twisting power are observed commonly, in one experiment, the thickness of the sample is suddenly decreased, and the disklike texture becomes distorted and the concentric circles and bispirals disappear. These textures can be restored, however, after 1 day if the "disks" are not broken and split. Kitzerbow et al.[13] have reported that if the cholesteric droplet has not been completely reorientated, the volume of the drop can be restored by the twist power when the electric field was turn off.

It is well-known that glass slides have homogeneous anchoring power, and it influences the orientation of liquid crystal molecules, which are nearby the surfaces and lead to an orientation of the molecules parallel to the surface. Homogeneous anchoring power can also influence the nearby disks in the (E−CE)C/DCA cholesteric LC solution. In the oblate disks, molecules on the elliptic polar surface are more close to the slides than those on the equatorial zone, and therefore, a stronger influence is achieved by the anchoring power. These results in the orientation of the molecules align parallel to the slides. Therefore, molecules at the center of disks are aligning with planar arrangement, in which the helix axis is perpendicular to the slides. To those molecules at the outside of the equatorial zone, the influence of the anchoring power is relatively weak, and the molecules can persist the cholesteric orientation direction by the twisting power. The concentric circle patterns in the outside area of the disks are thus preserved. Planar arrangement of the molecules results in an extinction area at the center of the disks.

These three basic patterns of the disklike texture are formed due to the confinement of the glass slides using the influence of homogeneous anchoring power. Figure 8 shows a bispirals disk with center extinction. The bispirals are asymmetry at the center, and the connect point of spirals is out of the center. It is similar to the concentric circles pattern without a disclination line. The disk at the center of Figure 2a shows a concentric circles pattern with center extinction; in comparison with the concentric circles, there is center extinction. Figure 9 shows two forms of the disklike texture with center extinction. The center disk shows a pseudo-concentric circles pattern with center extinction, and both of the left and right ones show the bispirals with center extinction. The effect of homogeneous anchoring power is similar to that of the electric field on polymer dispersed cholesteric droplets with negative dielectric anisotropy, which the center extinction in the cholesteric spherulites, and the radius of the central region increased with increasing voltage.[13,14] It is speculated that the distance between the disks and the surface of glass slides may influence the radius of center extinction in the disklike texture of (E−CE)C/DCA cholesteric solution. If the distance decreases, the influence of the

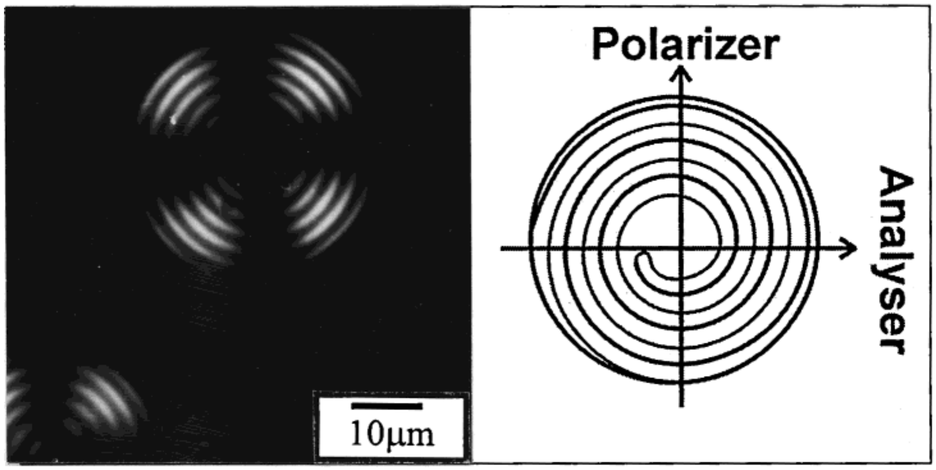

Figure 8. Pattern of bispirals with center extinction. Left is observed by the POM; right is its structure scheme.

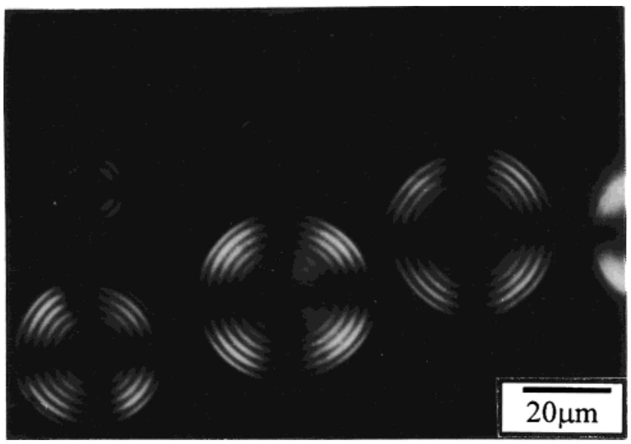

Figure 9. Patterns of pseudo-concentric circles and bispirals with center extinction. Center disk is pseudo-concentric circles; left and right ones are bispirals.

anchoring power should increase and the center extinction in the disks should enlarge.

Effect of Magnetic Field on Disklike Texture. When the fingerprint texture is exposed in the magnetic field having an intensity of 9.4 T, the helix axis is aligned parallel to the direction of the applied field, indicating that the diamagnetic anisotropy of (E−CE)C is negative.[5] The disklike texture is also exposed in the same magnetic field, and Figure 10 shows that the effect of the magnetic field on the disks seems to be dependent on their diameters. When the diameter of the disk is small, about 28 μm, the shape and the morphology are nearly unchanged and the concentric circles pattern still shows a round shape (see Figure 10a) after the solution is exposed in the magnetic field. When the diameter increase to 42 μm, the shape of the disk changes to an oval form, and the helix axis tends to align parallel to the direction of the magnetic field (see Figure 10b). Candau and co-workers[15] reported the same phenomenon that the critical intensity of the magnetic field was inversely varied with the diameter of the cholesteric spherulites. It can thus be concluded that the effect of the magnetic field on the disklike texture with large diameter is more effective than on the small ones.

The effect of the magnetic field on the cholesteric phase with the fingerprint texture is more effective than that with the disklike texture. The pitch of the fingerprint texture and the disklike texture are almost equal, but the interfacial tension of the cholesteric phase in the disklike texture is higher than that in the fingerprint texture. A competition between the effect of the interfacial tension and the magnetic field thus exists when the disklike texture is exposed in the field. The interfacial tension of the disklike texture increases with decreasing the diameter of the disk. The effect of the magnetic field may thus be restrained by the effect of the interfacial tension when the diameter of the disk is small (see Figure 10a). If the diameter is large enough, the effect of the magnetic field becomes dominant, and

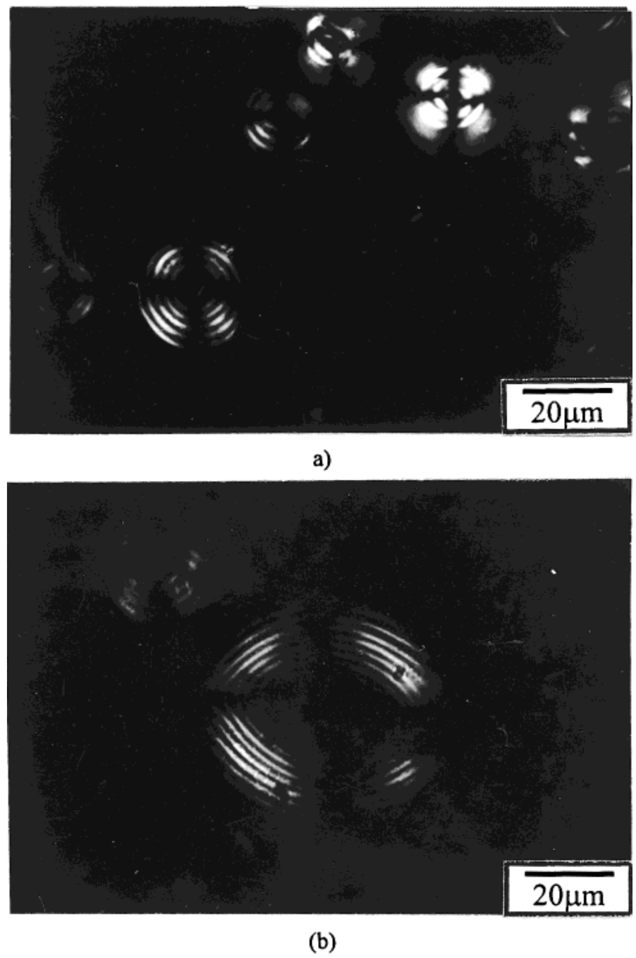

Figure 10. Effect of the magnetic field on disklike texture: (a) unchanged disk, diameter $D \approx 28$ μm; (b) changed disk, diameter $D \approx 42$ μm. The direction of the magnetic field was in the plan of the picture and from up to down.

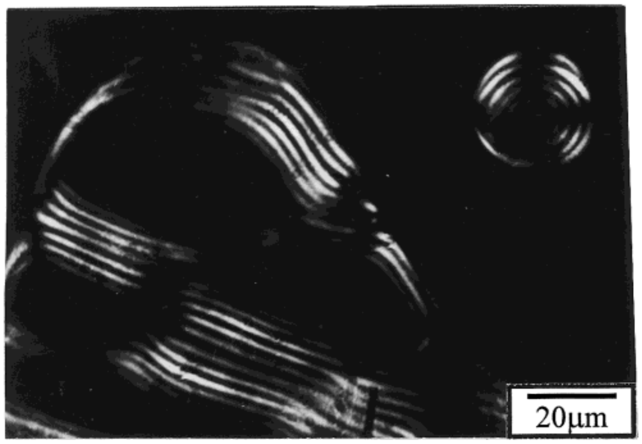

Figure 11. Contrastive example of the magnetic field effect on fingerprint and disklike texture in the 29 wt % (E−CE)C/DCA cholesteric liquid crystalline solution. The direction of the magnetic field is at an angle of 45° with horizontal line in the picture.

the helix axis tends to be aligned parallel to the magnetic field (see Figure 10b).

A contrastive example of magnetic field effect on the fingerprint texture and the disklike texture is shown in Figure 11. The helix axis of the fingerprint texture tends to align parallel to the magnetic field, but the disk retains its original morphology.

Conclusions

The pattern of the disklike texture in the (E−CE)C/DCA cholesteric LC solution is complicated and impressible by sample preparation, cholesteric twisting power, and external boundary condition, which provides homogeneous anchoring power of the slides. In the bulk, the anchoring power can be neglected and the twisting power results in the spherulitic Frank−Pryce structure in the solution. After the sample is confined in the film, three basic patterns of the disklike texture, bispirals, concentric circles, and pseudo-concentric circles can be observed. When some disks are near the slide surface, the anchoring power become strong enough to force the molecules at the center of the disks align in the planar arrangement (the helix axis aligns perpendicular to the slides) which results in the center extinction in the disks. In the magnetic field, the morphological change of the disklike texture depends on the competition between the interfacial tension of the cholesteric phase and the strength of the magnetic field.

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