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Effects of concentration and boundary conditions on (E-CE)-C cholesteric phase

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Abstract

Effects of concentration and boundary conditions on the cholesteric liquid crystalline condensed state structure and optical property of ethyl-cyanoethyl cellulose were investigated. When cholesteric phase and isotropy phase were coexistent, the solution showed the multi-texture behavior with variation of concentration. With homeotropic anchoring boundary condition, molecules of cholesteric phase inclined to aggregate with focal-conics arrangement. With homogeneous anchoring boundary condition, molecules of cholesteric phase inclined to aggregate with planar arrangement. In addition, the effect of boundary anchoring on the cholesteric condensed state structure could be restrained by the surface tension of the interphase.

Introduction

Cellulose and many of its derivatives can form cholesteric liquid crystals in the appropriate solvents[1]. Ethyl-cyanoethyl cellulose [(E-CE)C], which is a cellulose derivative with two different ether groups, can form cholesteric liquid crystals in many organic solvents[2], such as dichloroacetic acid (DCA) and acrylic acid (AA). Observing by an optical polarizing microscope, (E-CE)C cholesteric liquid crystalline solutions can show multi-texture behavior with variation of concentration [3]. When concentration is above 35 wt%, there is an uniform cholesteric phase in the (E-CE)C/DCA solution, and the mesophase generally shows planar texture or oily-streaks texture which are characterized by the optical reflective properties. When concentration is in the region of 25-35 wt%, there are both cholesteric and isotropic phases in the (E-CE)C/DCA cholesteric solutions. The mesophase generally shows the disk-like texture, the fingerprint texture and the mosaic texture with concentration increase. Besides the influence of the concentration, the texture of (E-CE)C cholesteric phase can be influenced by temperature and external fields. After being sheared, the mesophase could form the banded texture[4]. And the direction of helix axis of the (E-CE)C cholesteric phase could varied from normal to parallel to the direction of an external magnetic field[5]. In addition, the mesophase texture may be influenced by different boundary conditions, because of small elastic constants of liquid crystal. Generally, with the slides imposing a homeotropic anchoring condition, the

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cholesteric phase tends to form fingerprint texture in which molecules aggregate with focal-conics arrangement[6-8]. The homogeneous anchoring on the slides is beneficial to the planar arrangement of liquid crystalline phase[9, 10].

In our study, the variation of the (E-CE)C/DCA mesophase texture with different boundary conditions was investigated and the effects of concentration and the boundary conditions on the cholesteric liquid crystalline condensed state structure were also discussed.

Experimental

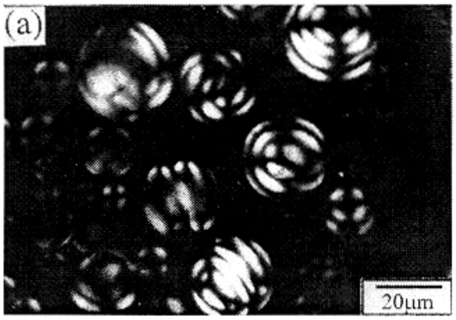
Materials. The (E-CE)C was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.33, determined by an Elemental Analysis (CHN-O-RAPID, Heraeus, Germany). The molecular weight of (E-CE)C, M_n, measured by a gel permeation chromatograph (GPC) (Waters-ALC-244-GPC) and calibrated by standard polystyrene, was 7×10^4. DCA was chemically pure reagents.

Sample Preparation. The (E-CE)C was mixed with DCA at room temperature and the solution was sealed in a test-tube. The solution was laid aside at room temperature for over 20 days to achieve an equilibrium solution, after heated at 50°C for about 10 hours. Two glass microscope slides were filled with a lecithin/ethylether solution in order to achieve homeotropic anchoring condition. And the glass slides surface was treated with a polyvinyl alcohol aqueous solution to achieve homogeneous anchoring condition. The solvents were evaporated before the liquid crystalline solution was sandwiched between the slides. Then, the specimens were sealed with solid wax, and observed by an Optical Polarizing Microscope (ORTHOPLAN-POL, Leitz, Germany) after three days. The level dimensions of cell were 15 mm x 15 mm, and the film thickness was about 10 µm.

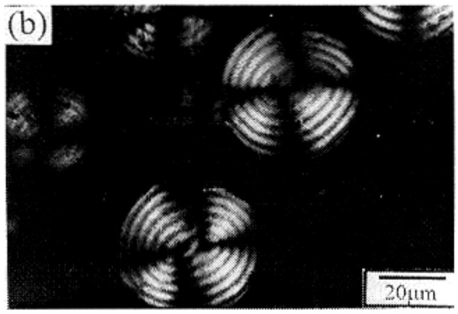
Results and Discussion

Effect of different boundary conditions on the disk-like texture

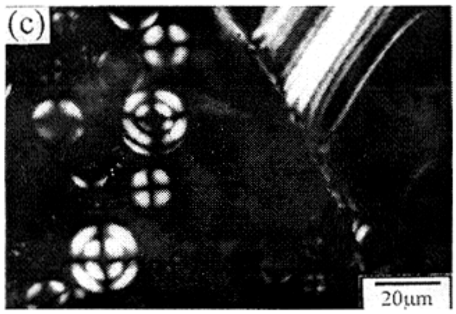
When concentration was 26 wt%, cholesteric phase dispersed in isotropic phase and generally showed a disk-like texture in the (E-CE)C/DCA liquid crystalline solution. Due to the surface tension of interphase, the cholesteric phase generally form "disk" shape for minimizing the free energy. And this disk-like (or spherulite) texture have been observed in many polymer cholesteric liquid crystalline solutions[11-13], such as DNA fragment[12], polypeptide[13]. The diameter of "disk" was about 20-30 µm and some periodical concentric extinction rings (Fig. 1a) were observed in the mesophase, in which the distance between neighbor concentric rings was about 3.9 µm. With the slides imposing homeotropic anchoring condition, the distance between neighbor concentric rings decreased to 3.2 µm, and the average diameter of the "disk" increased (Fig.1b). With the slides imposing homogeneous anchoring condition, the distance between neighbor concentric rings increased to 5.2 µm, and the average diameter of the "disk" decreased (Fig.1c).



(1a) no anchoring, the distance between neighbor rings was about 3.9 μm



(1b) with homeotropic anchoring, the distance was decreased to 3.2 μm



(1c) with homogeneous anchoring, the distance was increased to 5.2 μm

Figure 1. Effect of different boundary conditions on the disk-like texture of (E-CE)C/DCA solution, observed by a crossed polarizing light.

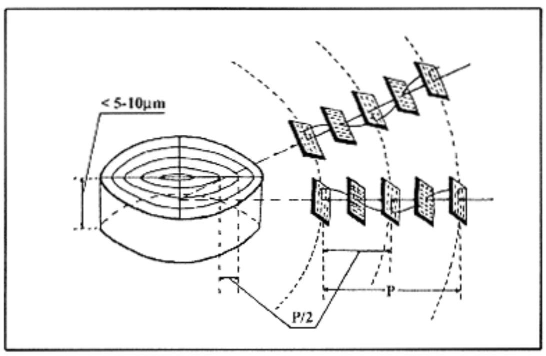
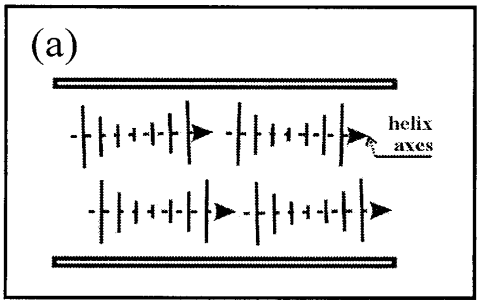


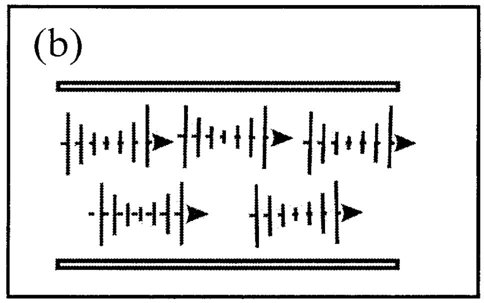
Figure 2. Model of molecule aggregation of the disk-like texture mesophase.

Because of the lower concentration, the disk-like mesophase was dispersed exceedingly in the solution, so the aggregation of the liquid crystal molecules in each domain would not influence other domain. The model of molecule aggregation in the disk-like texture mesophase is shows in Fig.2[3].

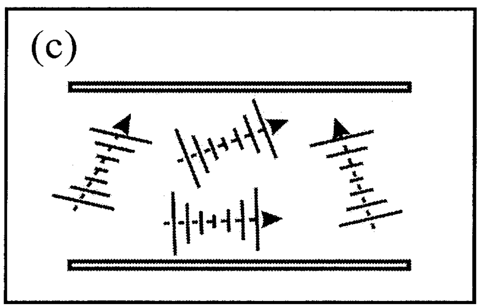
In each domain, molecules spontaneously twisted and aggregated with focal-conics arrangement in which the helix axis aligned along the radial direction and paralleled to the slide surface (Fig.3a). The concentric rings were resulted from changes in the total phase difference between ordinary and extraordinary waves (Fig. 4), the scheme of the periodical extinction structure. The coordinate system was chosen such that the sample lay in the **X-Z** plane, with **Z**-axis indicating the direction of the helix axis. The **Y**-axis is along the light path. To cholesteric molecule, another coordinate system was chosen such that the *c*-axis is invariant along the helix axis (parallel to **Z**). The molecular layer lay in the ***a-b*** plane, ***a***-axis is perpendicular the long-axis of molecule, ***b***-axis is along to the long-axis of molecule, and ***a-b*** plane would twist along the helix axis. When light transmit perpendicular to the helix axis, light separate into ordinary and extraordinary waves. The Optic Path Difference (δ) between ordinary and extraordinary waves is periodical varied with the molecule twist along the helix axis (Fig.4). And it results in the concentric extinction rings. The distance of neighbor concentric rings is equal to one-half of the helical pitch.



（3a） no anchoring



(3b) with homeotropic anchoring



(3c) with homogeneous anchoring

Figure 3. Scheme of the effect of boundary conditions on molecular focal-conics arrangement.

With the slides imposing homeotropic anchoring condition, molecules would be induced to align perpendicular to the slide surface. And the twisting power of cholesteric phase competed with the anchoring power of the boundary. The combination of both twisting and anchoring power resulted in the decease of the cholesteric pitch (Fig. 3b) and then, the effect of the homeotropic anchoring condition on the slide surface was decreased. With the slides imposing homogeneous anchoring condition, molecules would be induced to align parallel to the slide surface. But the effect of anchoring power was restrained due to the surface tension of interphase was strong. Most of molecules were still aggregated with focal-conics arrangement and some of theirs helix axis oblique aligned to the slides. The homogeneous anchoring resulted in the loosen arrangement in polymer chains packing. Because part of molecules were aligned parallel to the slide surface, which resulted the increase of cholesteric pitch. Part of mesophase was changed to the domains with planar arrangement, in which helix axis aligned perpendicular to the slides, and the diameter of the domain with dike-like texture decreased (Fig.3c).

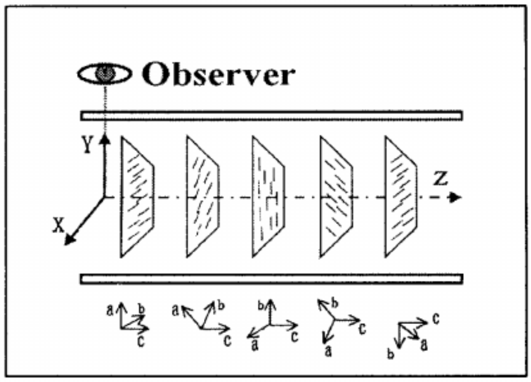


Figure 4. The scheme of the periodical extinction structure.

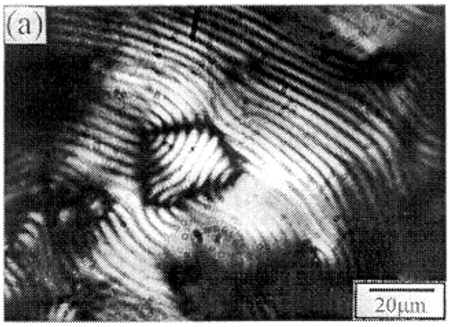
Effect of different boundary conditions on the fingerprint texture

When the concentration was 29 wt%, the cholesteric phase became continued and generally showed the fingerprint texture in the (E-CE)C/DCA liquid crystalline solution. Some parallel equidistant dark and bright alternative striations were observed in the mesophase, and the orientation of the striations was different in each domain. The width of the striations in the mesophase was about 2.6 μm (Fig. 5a). With the slides imposing homeotropic anchoring condition, the average width of the domains with the striations was increased, and the width of the striations was decreased to 1.8 μm (Fig. 5b). With the slides imposing homogeneous anchoring condition, the average width of the domains with the striations was decreased, and the striations almost disappeared. It was only observed some narrow strips in the solution, and the phase showed the mesophase with pseudoisotropic texture and oily-streaks texture (Fig 5c).

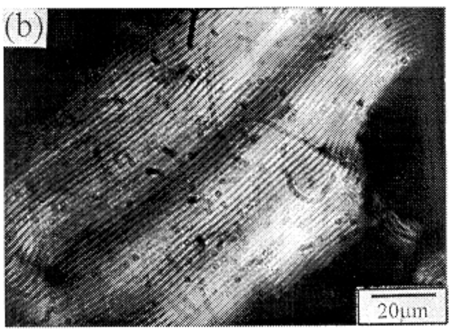
Similar to the disk-like texture, the helix axis aligned parallel to the slides in the fingerprint texture, molecules aggregated with focal-conics arrangement. The parallel striations were also resulted from the changes in the total phase difference between ordinary and extraordinary waves; the width of the striations was equal to one-half of the helical pitch. The variation of the mesophase coincided with the boundary conditions. With the slides imposing homeotropic anchoring condition, molecules aggregated with a tight focal-conics arrangement in the fingerprint texture and the pitch was decreased (Fig.3b) because of the combination of the twisting and the anchoring power. With the slides imposing homogeneous anchoring condition, molecules were induced to align parallel to the slide surface in which the helix axis aligned perpendicular to the slide surface. And molecules formed planar arrangement (Fig.3c), so the phase showed planar texture and oily-streaks texture.

Effect of different boundary conditions on the mosaic texture

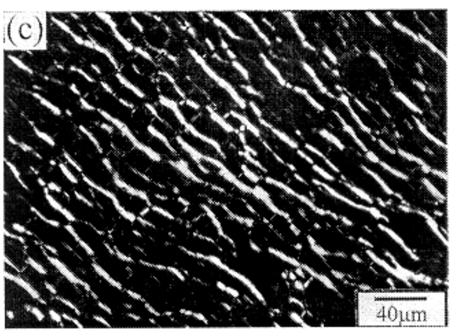
When the concentration was 32 wt%, the cholesteric phase became the continuous phase and the isotropic phase was dispersed in the cholesteric phase. The mesophase generally showed the mosaic texture in the (E-CE)C/DCA cholesteric liquid crystalline solution. Observed by polarizing microscope, the size of the isotropic phase areas was very small, and the most part was cholesteric phase in the observing scope. In the mosaic texture, some extinction schlierens were observed in the boundary of the domains, and them generally showed hyperbolic shapes (Fig.6a). With the slides



(5a) no anchoring, the width of the striations in the mesophase was about 2.6 µm

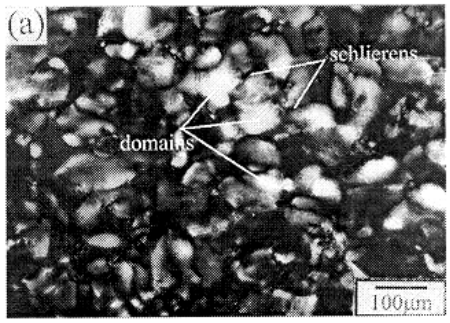


(5b) with homeotropic anchoring, the width was decreased to 1.8 µm

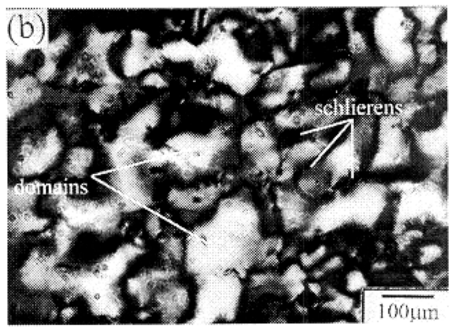


(5c) with homogeneous anchoring, the striations almost disappeared, the mesophase showed oily-streaks texture

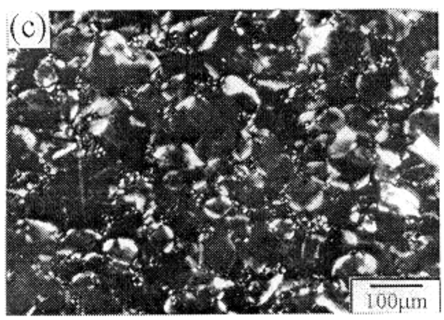
Figure 5. Effect of different boundary conditions on the fingerprint texture, observed by a crossed polarizing light.



(6a) no anchoring, some hyperbolic schlierens were observed in the boundary of the domains



(6b) with homeotropic anchoring, the domains were increased



(6c) with homogeneous anchoring, the domains were decreased.

Figure 6. Effect of different boundary conditions on the mosaic texture, observed by a crossed polarizing light.

imposing homeotropic anchoring condition, the area of each cholesteric domain and the length of the schlierens increased (Fig.6b). With the slides imposing homogeneous anchoring condition, the area of each cholesteric domain decreased, the intensity of birefringence and the length of the schlierens were also decreased (Fig. 6c).

In the mosaic texture, the helix axis formed a certain inclination angle with the slide surface, and it was very similar to the fan texture of smectic phase. In each domain, the helix axis aligned along with same direction, molecules also aggregated with focal-conics arrangement[14,15]. Other neighbor domains would restrain the growth and aggregation of each domain, and in the area of neighbor domain contacting, the direction of the helix axis was discontinued. The disclination lines generally showed hyperbolic shapes because the growth and aggregation of each domain were different. Because of the strong twisting power, the anchoring power was restrained. With the slides imposing homeotropic anchoring condition, the combination of the twisting and the anchoring power induced the increase of each domains. The length of disclination lines was also increased. With the slides imposing homogeneous anchoring condition, the anchoring power restrained the aggregation of the mosaic texture mesophase, which resulted in the decrease of the domain in size and the length of disclination lines was also decreased. Part of the mesophase was changed to the domains with the planar texture in which the helix axis aligned perpendicular to the slide.

Due to the intensity of twisting power enhance with the increasing of concentration of cholesteric phase, the effect of boundary conditions on the mosaic texture was small than that on the fingerprint texture.

Conclusion

When both cholesteric and isotropic phases exist in the (E-CE)C/DCA solutions. The helix axis generally aligned along the slides and the disk-like texture, the fingerprint texture and the mosaic texture continual was formed in the solution with the concentration increasing. When the pitch is large enough, due to liquid crystal molecules periodical twist along with the helix axis, the periodical changes in the total phase difference between ordinary and extraordinary waves resulted in periodical extinction phenomena, observed by a polarizing microscope. And the morphology of (E-CE)C/DCA cholesteric mesophase can be influenced by different boundary conditions. In sum, with the slides imposing homeotropic anchoring condition, molecules of cholesteric phase inclined to aggregate with focal-conics arrangement in which the helix axis aligned parallel to the slides. With homogeneous anchoring boundary condition, molecules inclined to aggregate with planar arrangement in which the helix axis aligned perpendicular to the slides, and the focal-conics arrangement would be restrained. In addition, the surface tension of interphase could restrain the effect of anchoring power. For instance, the morphology of disk-like texture remained with the homogeneous anchoring. The helical twisting power would compete with the anchoring power, when the concentration increased, the twisting power enhanced and it reduced the effect of boundary conditions on the cholesteric phase.

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