Effects of External Fields on Macromolecular Cholesteric Phase

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Summary: Effects of external fields such as magnetic field and boundary conditions on supramolecular structure, molecular arrangement and the texture of the ethyl-cyanoethyl cellulose cholesteric liquid crystalline solutions were investigated. It was found that the molecules of (E-CE)C are oriented to perpendicular to the magnetic field and the diamagnetic anisotropy of (E-CE)C is negative. With homeotropic anchoring boundary condition, the molecules are aggregated with focal-conics arrangement the molecules are aggregated with planar arrangement with homogeneous anchoring boundary condition. The effects of the external field on the orientation of the cholesteric phase were influenced by the concentration of the solution because the twist power of the cholesteric was varied with the concentration. And the effects are also restrains 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 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. When concentration is above 35 wt%, there is an uniform cholesteric phase in the (E-CE)C/DCA solution, and the mesophase generally shows the oily-streaks texture and the planar texture which are characterized by the optical reflective

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properties.

Liquid crystals are always composed of anisotropic constituents. In the presence of a magnetic field, the arrangement of liquid crystalline molecules may be varied according to its different diamagnetic anisotropy along different body axis. And liquid crystalline molecules may be influenced by different boundary conditions, because of the small molecular elastic constants. Generally, with the slides imposing a homeotropic anchoring condition, the cholesteric phase tends to form fingerprint texture in which molecules aggregate with focal-conics arrangement[4-6]. The homogeneous anchoring on the slides is beneficial to the planar arrangement of liquid crystalline phase[7,8]. In the paper, the variations of the (E-CE)C/DCA mesophase textures under external fields, a magnetic field and different boundary conditions, were investigated. And the effects the external fields on the cholesteric LC supramolecular structure were also discussed.

Experimental

Materials and Sample Preparation

The (E-CE)C was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile[2] and its molecular structure is shown in Figure 1. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.33, calculated from the content of nitrogen of (E-CE)C that was determined by elementary analysis (Heraeus, 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. 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. Then, the solution was sandwiched between two glass slides to form the solution film with the thickness of about 20 μm and sealed with solid wax. The mesophase texture of the solution was observed by a polarizing optical microscope (POM) (ORTHOPLAN-POL, Leitz, Germany).

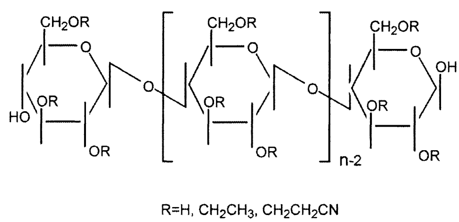

Figure 1. Molecular formula of (E-CE)C.

Magnetic Field Processing

The specimen was treated in a magnetic field with an intensity of 9.4 T that got from a Superconducting-Magnet NMR Spectrometer (DRX-400 MHz, BRUKER, Germany and Switzerland). Then, the specimen was observed by POM.

Boundary Conditions

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.

Results and Discussion

Effects of Magnetic Field on the Fingerprint Texture

When the concentration is 29 wt%, there are both anisotropic and isotropic phases in the (E-CE)C/DCA cholesteric solutions and the mesophase generally shows the fingerprint texture. Some parallel equidistant dark and bright alternative striations are observed in the mesophase and the width of the striations is equal to a half pitch. The direction of the helix axis is aligned perpendicular to the striations and parallel to the slide surface. Without effect of the magnetic field, the direction of the helix axis of the fingerprint texture is random in different domains (Figure 2a). The striations, however, are formed a zigzag pattern and the helix axis are aligned almost parallel to the direction of the magnetic field after the solutions is treated in the magnetic field (Figure 2b). It is indicated that the direction of the molecular orientation is almost normal to the direction of the field and the diamagnetic anisotropy (χ_α) of (E-CE)C

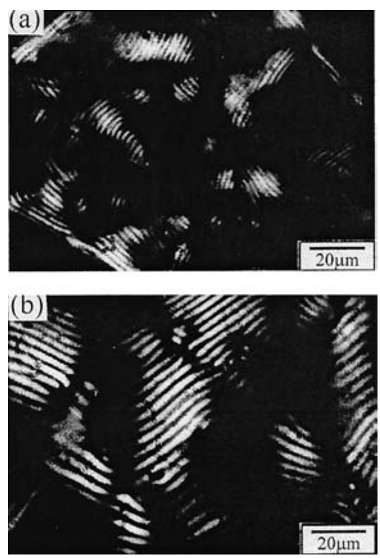

Figure 2. Effect of magnetic field on the fingerprint texture: (a) absence of the magnetic field; (b) after treated in the magnetic field.

is negative[9]. As we know, the diamagnetic anisotropy of molecules is correlated to the molecular structure, and the negative χ_α of the (E-CE)C is attributed to its conformation of the β-D-glucose backbone and the side cyanoethyl groups[9].

Effects of Magnetic Field on the Oily-Streaks Texture

The pitch of the (E-CE)C/DCA cholesteric phase decreases with increasing the concentration. When the concentration is about 40 wt%, there is an uniform cholesteric phase in the (E-CE)C/DCA solutions and the mesophase generally shows the planar texture and the oily-streaks texture (Figure 3a). In the mesophase, the helix axis is mostly aligned perpendicular to the slide surface for the planar texture but aligned parallel or oblique to the slide surface in the oily-streaks texture. No periodical birefringent striations can be observed by POM in the mesophase, because the pitch is very small ($P <$ 1μm). From Figure 3b, it can be observed that the mesophase texture is nearly unchanged after the solution is treated in the magnetic field. If the magnetic field can effect on the planar texture and the oily-streaks texture, in the case of $\chi_\alpha<0$, the helix axis will be aligned from perpendicular to the magnetic field to parallel to it and the mesophase will be changed to the fingerprint texture. The results indicate that the magnetic field with the intensity of 9.4 T cannot influence the cholesteric structure of the planar and the oily-steaks textures. The variation of the pitch with the critical intensity of the magnetic field, in which the cholesteric order is changed, can be described by the equation derived from the de Gennes's theory[10]:

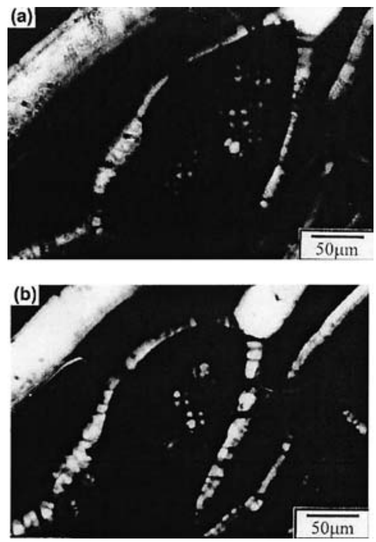

Figure 3. Effect of magnetic field on the oily-streaks texture: (a) in absence of the magnetic field; (b) after treated in the magnetic field; the morphology of the texture was remained.

$$H_C = (\pi^2/2)(k_{22}/\chi_\alpha)^{1/2}(1/p_0) \quad (1)$$

Where H_C is the critical intensity of the magnetic field, P_0 is the pitch in the absence of the magnetic field, k_{22} is the twist elastic constant. According to the equation (1), the value of H_C depends on the k_{22}/χ_α and P_0. H_C is proportional to the $1/P_0$, because the parameter of k_{22}/χ_α of the oily-steaks texture is equal to that of the fingerprint texture in the (E-CE)C/DCA liquid crystalline solutions. The P_0 of the fingerprint texture is about 4-6 μm, which is about 4 times larger than that of the oily-streak texture. Therefore, the H_C of the oily-streak texture must be 4 times larger than that of the fingerprint texture if the influence of the magnetic field on the planar texture and the oily-streaks texture is the same as on the fingerprint texture. In the magnetic field with the same intensity, the effect on the fingerprint texture will be larger than on the planar and the oily-streaks textures. This result is different from that of the magnetic field effect on cholesteric liquid crystalline DNA systems[11]. The diamagnetic anisotropy of the DNA molecules is negative and the helix axis in the planar texture were aligned from perpendicular to parallel to the direction of the magnetic field, and the pitch of about 2.2 μm. We believe the orientation is cause by the pitch of the cholesteric DNA is bigger than that of (E-CE)C/DCA.

Effects of Magnetic Field on the Disk-Like Texture

At a low concentration, 26 wt%, the cholesteric phase is dispersed in the isotropic phase and the mesophase generally shows the disk-like texture in the (E-CE)C/DCA liquid crystalline solutions. Due to the surface tension of interphase between the mesophase and the isotropic phase, the cholesteric phase generally forms "round" shape for minimizing the surface and the free energy. The disk-like texture has also been observed in many macromolecular cholesteric phases[12-14], such as DNA fragment[13] and polypeptide[14]. The diameter of "disk" general is ranged between 20-50 μm and some periodical concentric extinction rings are observed in the (E-CE)C/DCA disk-like texture (Figure 4a). When the concentration is increased, the "dike" will be aggregated and merged to fingerprint texture. The distance between the neighboring concentric rings in the disk-like texture is equal to the half pitch, which is about 4-6 μm and is approached to that in the fingerprint texture. The helix axis is aligned along the radial directions of the "disk" and parallel to the slide surface. Figure 4 shows that the effect of the field on the "disk" seems to be dependent on its diameter. When the diameter of the "dike" is about 28μm, the shape and the morphology are nearly unchanged and the concentric rings are still shown the round shape (see Figure 4a) after the solution is treated in the magnetic field. It is interesting that when the diameter increased to 42μm, the shape of the "disk" is changed to the oval form and the helix axis tends to be aligned to parallel to the direction of the magnetic field (Figure 4b). Candau and co-workers[12] have reported that the critical intensity of the magnetic field is inversely varied with the diameter of the spherulites. The magnetic field with the intensity of 12 T has been used to effect the orientation of the cholesteric phase in the spherulite texture with the diameter of 122 μm. It is clear that the effect of the magnetic field on the disk-like texture with large diameter is large but on one with small diameter is small. The same phenomenon has also been found in the effect of the magnetic field on PBLG cholesteric solutions[14], in which the diameter of the "spherulites" is ranged between 600-1000μm and the pitch is 42.6μm.

The results mentioned above indicate that the effect of the magnetic field on the cholesteric phase with the fingerprint texture is more effective than that with the disk-like texture. The pitch of the mesophase with the fingerprint texture and the disk-like texture is almost the same and the surface tension of the cholesteric phase in the fingerprint texture is different from that in the in the disk-like texture. It seems that there is high surface tension in the disk-like texture and there exists a competition between the effect of the surface tension and the magnetic field when the solution is treated in the field. The surface tension of the mesophase with the disk-like texture increases with decreasing the diameter of the "disk". So, the effect of magnetic field may be restrained by the effect of the surface tension when the diameter of the "disk" is small (Figure 4a). When the diameter is increased to big enough, the effect of the magnetic field will be larger than the effect of the surface tension and the helix axis are tended to be aligned parallel to the magnetic field (Figure 4b).

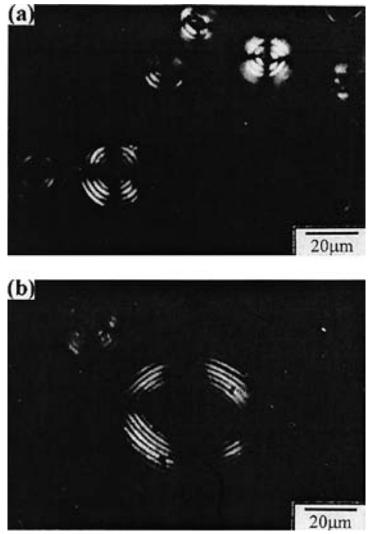

Figure 4. Effect of the magnetic field on the (E-CE)C/DCA disk-like texture: (a) unchanged disk, diameter ≈ 28μm; (b) changed disk, diameter≈42μm.

Effects of Different Boundary Conditions on the Fingerprint Texture

Without any effects of anchoring power, the width of the striations in the (E-CE)C/DCA fingerprint texture is about 2.6 μm (Figure 5a). With the slides imposing homeotropic anchoring condition, the width of the striations decreases to 1.8 μm (Figure 5b). With the slides imposing homogeneous anchoring condition, the striations almost disappeared, in which only some narrow strips can be observed in the solution and the mesophase shows the planar texture and oily-streaks texture (Figure 5c). In each domain, molecules are spontaneously twisted and aggregated with focal-conics arrangement in which the helix axis aligned along the radial direction and paralleled to the slide surface (Figure 6a). With the slides imposing homeotropic anchoring condition, molecules may be induced to align perpendicular to the slide surface and the twisting power of cholesteric phase competes with

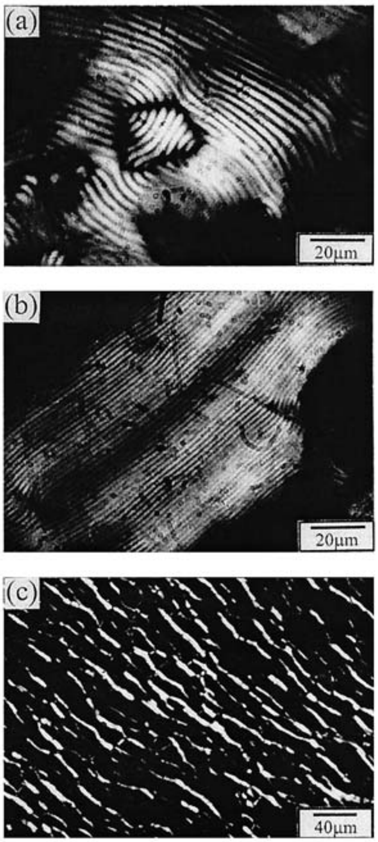

Figure 5. Effect of different boundary conditions on the fingerprint texture: (a) no anchoring; (b) with homeotropic anchoring; (c) with homogeneous anchoring.

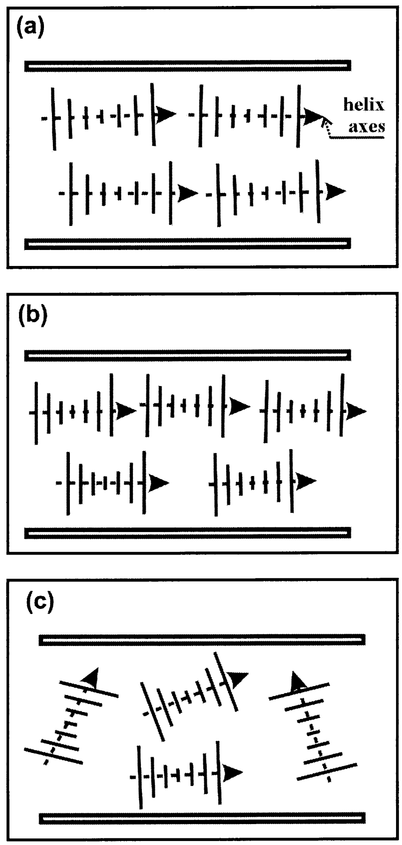

Figure 6. Scheme of the effect of boundary conditions on molecular focal-conics arrangement: (a) no anchoring; (b) with homeotropic anchoring; (c) with homogeneous anchoring.

the anchoring power of the boundary. The combination of both twisting and anchoring power results in the molecule orientation perpendicular to the slide surface but the cholesteric supramolecular structure is retained and the cholesteric pitch decreases (Figure 6b). With the slides imposing homogeneous anchoring condition, molecules may be induced to align parallel to the slide surface in which the helix axis is aligned perpendicular to the slide surface. And molecules are ordered according to the planar texture arrangement (Figure 6c), and the mesophase shows the planar texture and the oily-streaks texture.

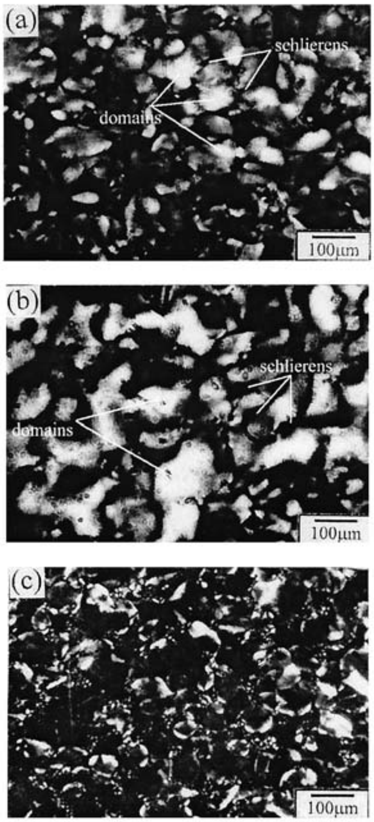

Figure 7. Effect of different boundary conditions on the mosaic texture: (a) no anchoring; (b) with homeotropic anchoring; (c) with homogeneous anchoring.

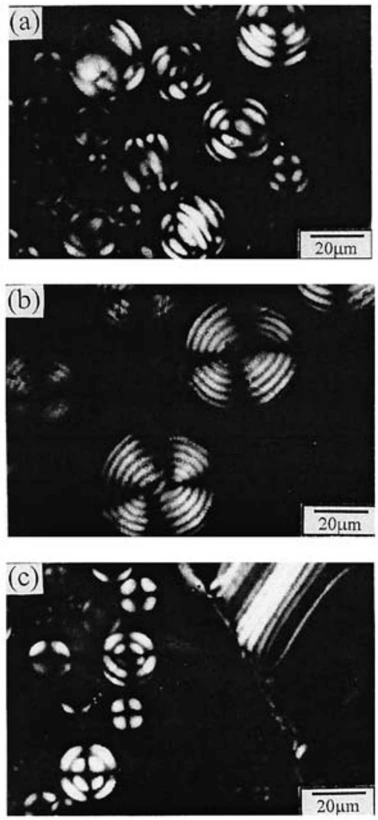

Figure 8. Effect of different boundary conditions on the disk-like texture of (E-CE)C/DCA solution: (a) no anchoring; (b) with homeotropic anchoring; (c) with homogeneous anchoring.

Effects of Different Boundary Conditions on the Mosaic Texture

When the concentration is 32 wt%, the cholesteric phase becomes the continuous phase and the isotropic phase is dispersed in the cholesteric phase. The mesophase generally shows the mosaic texture in the (E-CE)C/DCA cholesteric liquid crystalline solution. In the mosaic texture, some extinction schlierens are observed in the boundary of the domains and they generally show hyperbolic shapes (Figure 7a). With the slides imposing homeotropic anchoring condition, the area of each cholesteric domain and the length of the schlierens increases (Figure 7b). With the slides imposing homogeneous anchoring condition, the area of each cholesteric domain decreases the intensity of birefringence and the length of the schlierens are also decreased (Figure 7c).

In the mosaic texture, the helix axes are located in a certain inclination angle with the slide surface and it is very similar to the fan texture of smectic phase. In each domain, the helix axis aligns along with same direction molecules are also aggregated with focal-conics arrangement. The growth and aggregation of each domain are restrained by other domains and the direction of the helix axis is discontinued in the boundary of the domains. The disclination lines generally show hyperbolic shapes because the growth and aggregation of each domain are different. The anchoring power is restrained by the strong twisting power. With the slides imposing homeotropic anchoring condition, the combination of the twisting and the anchoring power induces the increase of each domains. The length of disclination lines is also increased. With the slides imposing homogeneous anchoring condition, the aggregation of the mosaic texture mesophase is restrained by the anchoring power, which results in the decrease of both the domain in size and the length of disclination lines. Parts of the domains are changed to the planar texture in which the helix axis aligns 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 is smaller than that on the fingerprint texture.

Effect of Different Boundary Conditions on the Disk-Like Texture

Without any effects of anchoring power, the distance between neighboring concentric rings is about 3.9 μm (Figure 8a). With the slides imposing homeotropic anchoring condition, the distance between neighboring concentric rings decreases to 3.2 μm, see Figure 8b. With the slides imposing homogeneous anchoring condition, the distance between neighboring concentric rings increases to 5.2 μm (Figure 8c).

With the slides imposing homeotropic anchoring condition, molecules may be induced to align perpendicular to the slide surface, the pitch of the disk-like texture is decreased. With the slides imposing homogeneous anchoring condition, molecules may be induced to align parallel to the slide surface, but the mesophase retains the disk-like texture. The effect of anchoring power is restrained due to the surface tension of interphase is strong. Most of molecules are still aggregated with focal-conics arrangement and some of theirs helix axes are oblique aligned to the slides. The homogeneous anchoring results in the loosen arrangement in polymer chains packing and the increase of cholesteric pitch, because part of molecules are aligned parallel to the slide surface.

Conclusion

The supramolecular structure of (E-CE)C/DCA cholesteric LC solutions depends on the twisting power, the external field effects and the surface tension of interphase. The twisting power increases with increasing the concentration and results in the pitch decreasing. Without the external field, the cholesteric texture is changed with the variation of the concentration. Under the effects of the external fields such as the magnetic field and different boundary conditions, the molecules are aligned to the field and the structure will be influenced by the competition between the cholesteric twisting power and the orientation power. The effect of the external field on the cholesteric order is restrained when the concentration is high, because the twist power is increased with increasing the concentration. Moreover, the surface tension of interphase is powerful in the low concentration and restrains the effect of the external fields on the cholesteric order.

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