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Effects of Magnetic Field on Ethyl−Cyanoethyl Cellulose Cholesteric Order

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ABSTRACT: Effects of a high magnetic field (with an intensity of 9.4 T) on the cholesteric liquid crystalline structure of ethyl−cyanoethyl cellulose [(E−CE)C] were investigated. The direction of the cholesteric helix axis aligned parallel to the direction of the magnetic field after the (E−CE)C/DCA cholesteric solution was treated in a magnetic field, which indicated that the diamagnetic anisotropy of ethyl−cyanoethyl cellulose molecule is negative. And the correlation between the diamagnetic anisotropy and the molecular structure was discussed. The influence of the magnetic field on the cholesteric order of the (E−CE)C/AA solutions was much smaller than that on the (E−CE)C/DCA solutions, because the pitch in the former system was much smaller than that in the latter one.

Introduction

Liquid crystals are always composed of anisotropic constituents. In the presence of an electric or magnetic field, the arrangement of liquid crystalline molecules may be varied according to its different dielectric or diamagnetic anisotropy along different body axes. From the elastic theory of liquid crystals, a liquid crystal phase will align if the free energy cost to reorient the liquid crystal is less than the energy reduction for alignment in the magnetic field, $F_{\mathrm{mag}} = -{}^{1}/_{2}\chi_{\alpha}(\mathbf{n}\cdot\mathbf{H})^2$, where **n** is the symmetry axis for molecular orientation, **H** is the magnetic field, and $\chi_{\alpha} = \chi_{\parallel} - \chi_{\perp}$ is the diamagnetic anisotropy of the molecule (|| and ⊥ are parallel and perpendicular to **n**, respectively).

If the diamagnetic anisotropy (χ_{α}) is positive, application of a magnetic field would tend to orient molecules with their long axes parallel to the field direction. At a certain critical strength, the cholesteric phase can transform to the nematic phase.[1,2] On the other hand, if $\chi_{\alpha} < 0$, the molecular director, **n**, would tend to be perpendicular to the applied magnetic field. The cholesteric helix axis in the situation will adjust to parallelism with **H** but no distortion results.

In particular, many studies about magnetic field effects on cellolusic materials have been reported. Loeb and Welo[3] measured the diamagnetic anisotropy of a group of cellulosic fibrous materials, and all the fibrous materials had negative diamagnetic anisotropy. Their results show that for materials of given crystalline modification (cellulose I or II) the observed anisotropy was primarily a function of molecular orientation. Sugiyama and co-workers[4] provided evidence that the cellulose microcrystals were oriented by the strong magnetic fields (7 T), because of its negative diamagnetic anisotropy. Liepins and co-workers[5] studied the magnetic field effect on mechanical properties of hydroxypropyl cellulose (HPC). But maybe the intensity of the magnetic field was low (only 1.2 T), and the improvement in the properties was little. But only a few studies of the magnetic field effects on the cholesteric liquid crystalline phase of cellulosic materials have been reported. Recently, Revol and co-workers[6] reported that the cholesteric phase of cellulose crystallites becomes oriented in a magnetic field with its helix axis parallel to the applied field, because of its negative diamagnetic anisotropy. And it is interesting that studies of the magnetic field effects on the cholesteric phase of DNA, which is another biopolymer in living beings, have been reported also to have negative diamagnetic anisotropy by Van Winkle and co-workers.[7,8]

In our study, 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, such as dichloroacetic acid (DCA)[9] and acrylic acid (AA).[10] The goal of our work is to investigate the variations of the cholesteric structure in different solutions by the magnetic field effects.

The cholesteric phases of (E−CE)C/DCA and (E−CE)C/AA solutions have been studied very well. (E−CE)C cholesteric liquid crystalline solutions can show multitexture behavior with variation of concentration.[11] When the concentration is in the region of 25−35 wt %, there are both anisotropic and isotropic phases in the (E−CE)C/DCA cholesteric solutions. The mesophase generally shows disklike texture and fingerprint texture in the cholesteric phase,[11] observed by an optical polarizing microscope. When the concentration is above 35 wt %, there is a uniform anisotropic phase in the (E−CE)C/DCA solution, and the mesophase generally shows the planar texture. The (E−CE)C/AA cholesteric liquid crystalline solutions also show multitexture behavior with variation of concentration.[10] When the concentration is above 35 wt %, the cholesteric phase begins to appear in the solutions. When the concentration is above 43 wt %, the (E−CE)C/AA cholesteric solution is a uniform anisotropic phase, and it shows planar texture in which the helix axis aligns perpendicular to the slide surface.[10] The pitch of (E−CE)C/AA cholesteric solutions ranges from 100 to 300 nm, which is too small to be determined by optical polarizing microscopy. But the cholesteric order in the (E−CE)C/AA liquid crystalline solutions can be solidi-

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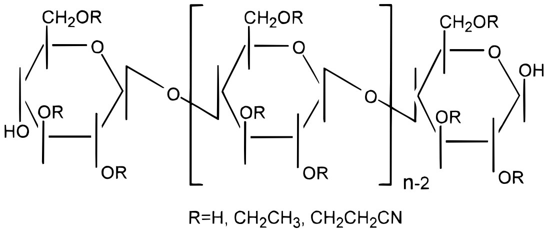

Figure 1. Molecular formula of (E−CE)C.

fied by polymerizing the solvent AA,[12,13] and the pitch and the helical structure can be determined by electron microscopy[14−16] and WAXD.[13]

Experimental Section

Materials. The (E−CE)C was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile, 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, determined by 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 and AA were chemically pure reagents, and AA was distilled in a vacuum at 50 °C before used.

(E−CE)C/DCA Solutions and Magnetic Field Processing. 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, after being heated at 50 °C for about 10 h. The solution film was then sandwiched between a microscope slide and a cover glass and was sealed with solid wax. The level dimensions of cell were 15 mm × 8 mm, and the film thickness was about 10 μm. After being stored at room temperature for 3 days, the specimen was treated in a magnetic field with an intensity of 9.4 T obtained from a Superconducting-Magnet NMR spectrometer (DRX-400 MHz, Bruker, Germany and Switzerland). Then, the specimen was observed by an optical polarizing microscope (ORTHOPLAN-POL, Leitz, Germany).

(E−CE)C/AA Solutions and Magnetic Field Processing. The (E−CE)C was mixed with AA and 2 wt % initiator (with respect to the solvent AA), benzoin ethyl ether, at room temperature. The mixture was allowed to sit for one or more weeks, and the resulting homogeneous solution was then stored in the dark until used. The solution film was sandwiched between two glass slides. The level dimensions of cell were 15 mm × 8 mm, and the film thickness was controlled by inserting Teflon spacers between glass slides, which was 0.8 mm in thickness. Then the specimen was sealed with solid wax and stored in the dark for 3 days. After being treated in the magnetic field (9.4 T), the specimen was inserted into an ultraviolet chamber equipped with a 250 W high-intensity mercury arc lamp for 2−5 min until complete polymerization of the AA. The distance between the lamp and the sample was 5 cm. The variation of the structure and morphology of the cholesteric phase was studied by a X-ray diffractometer (D/MAX-1200, Rigaku, Japan) and a transmission electron microscope (TEM) (JEOL-100CX/II, Japan) after the sample was cut with an ultra microtome (LKB-208B, BROMMA, Switzerland).

Results and Discussion

Magnetic Field Effect on (E−CE)C/DCA Solutions. When the concentration was 29 wt %, the mesophase generally showed fingerprint texture. Some parallel equidistant dark and bright alternative striations were observed in the mesophase. The direction of the helix axis aligned perpendicular to the striations and was variable in the fingerprint texture, in the absence of a magnetic field (see Figure 2a), and the width of the striations was equal to one-half of the helical pitch. After treated in the magnetic field for more than 50 h, the striations formed a zigzag pattern and the helix axis aligned parallel to the direction of the magnetic field (see Figure 2b,c). It indicated that the diamagnetic anisotropy of (E−CE)C is negative. The width of the striations in the mesophase was increased from 2.2 μm before being treated in the magnetic (Figure 2a) to 3.3 μm after have been treated in the magnetic field (Figure 2b).

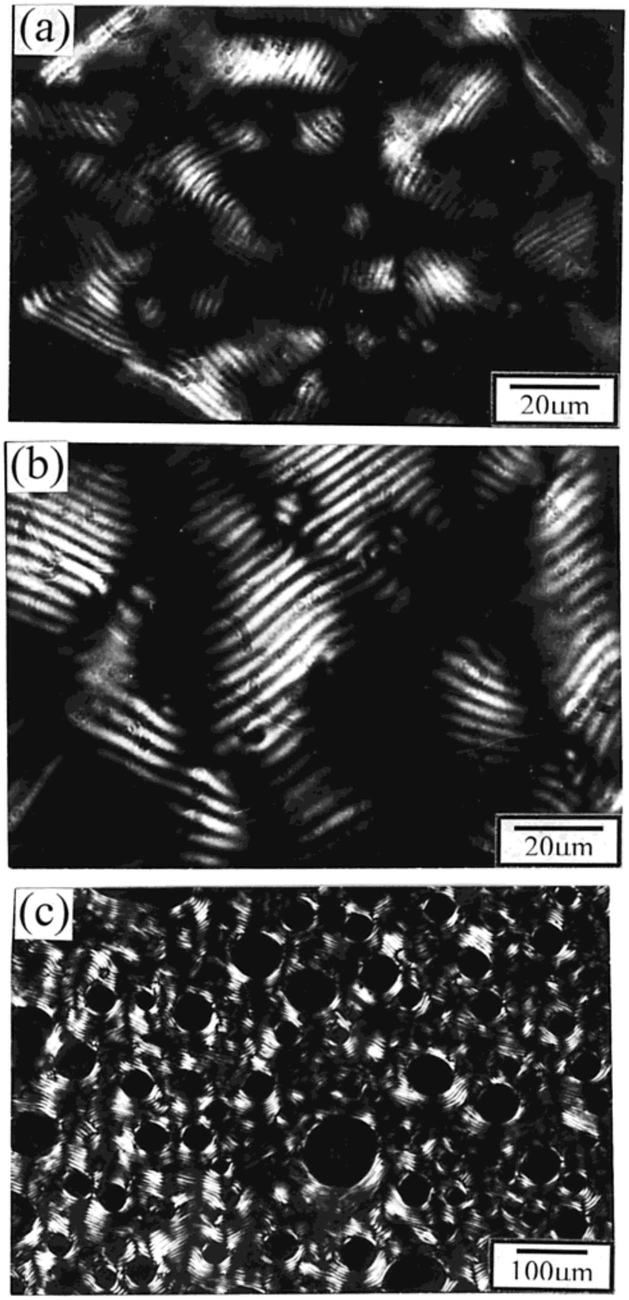

Figure 2. Polarized light micrographs of the 29 wt % (E−CE)C/DCA liquid crystalline solution: (a) in the absence of a magnetic field; (b, c) with treating in the magnetic field. The magnetic field direction was perpendicular to the average orientation of the striations.

To liquid crystalline molecule, the diamagnetic anisotropy is correlated to the molecular structure and strongly influenced by the delocalized π electrons in the benzene rings and the cyano group.[17−19] The diamagnetism of the induced currents in the planes of the benzene rings would orient the long axis of the molecule

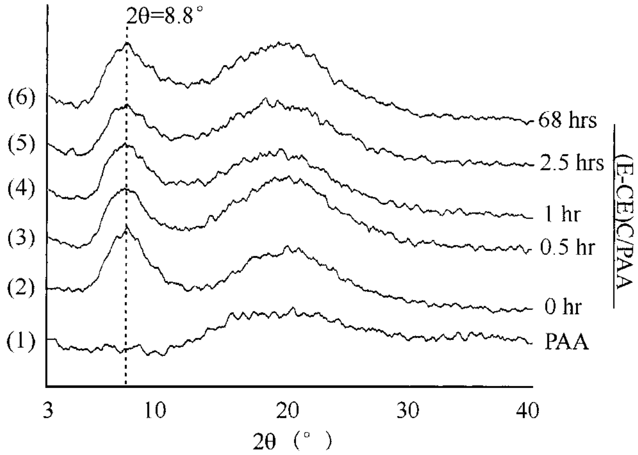

Figure 3. X-ray diffraction spectra of (1) PAA and the 56 wt % (E−CE)C/PAA cholesteric phase which was solidified by polymerizing the AA after the solution was treated in the magnetic field for (2) 0, (3) 0.5, (4) 1, (5) 2.5, and (6) 68 h.

nearly parallel to the magnetic field, and that leads to $\chi_\alpha > 0$. Replacing benzene rings with the cyclohexane rings leads to a decrease of the absolute value of $\chi_\perp$ (for all most organic molecules have negative diamagnetic susceptibility χ); the molecule reveals negative χ_α values, since $|\chi_\parallel|$ is larger than $|\chi_\perp|$ because of the elongated structure of the molecule. Because the cyano groups have a strong dipole moment, the molecule would be oriented parallel to the magnetic field if the molecule has terminal cyano substituents in the main chains. On the other hand, the molecule would be oriented perpendicular to the magnetic field, if it has terminal cyano groups in the side chains. But compared with the six-member rings, the influence of the cyano groups is slight compared to the diamagnetic anisotropy.[18,19]

From conformational energy calculations[20−22] and electron and X-ray diffraction,[23,24] all the stable conformations found of cellulose and its derivatives were rodlike extended helices. In the structure of (E−CE)C (see Figure 1), its backbone consists of 1−4-linked β-D-glucose and no benzene rings; the cyano groups are attached to the side ether groups of the backbone. Both the backbone and the cyano groups would cause the molecule to orient perpendicular to the magnetic field and leads the molecule to reveal negative χ_α.

Magnetic Field Effect on (E−CE)C/AA Solutions. From the magnetic field effect on (E−CE)C/DCA cholesteric phase, we have already known that the diamagnetic anisotropy of (E−CE)C was negative, and it is almost insensitive to solvent.[25,26] So in order to investigate the variation of (E−CE)C/AA cholesteric structure, we chose the 56 wt % (E−CE)C/AA solution because the mesophase shows a tight planar texture, and the specimen was placed to make the magnetic field perpendicular to the helix axis. Thus, the magnetic field oriented the helix axis to align parallel to it. The variation of the (E−CE)C/AA cholesteric order in the liquid crystalline solutions could be revealed by shifting of the X-ray diffraction peak at about $2\theta = 8.8°$ which is attributed to the (E−CE)C cholesteric structure.[13] Figure 3 shows the X-ray diffraction spectra of the 56 wt % (E−CE)C/PAA cholesteric phase which was prepared by polymerizing the solvent AA in the (E−CE)C/AA cholesteric liquid crystalline solution after it was treated in the magnetic field from 0 to 68 h. The diffraction spectrum of PAA in Figure 3 had no diffraction peak at $2\theta = 8.8°$. From Figure 3, it can be observed that the X-ray diffraction peak of the cholesteric phase was not shifted with time treated in the field, which suggested that the structure of the (E−CE)C/AA cholesteric phase was nearly unchanged after the solution was treated in the magnetic field. And Liepins[5] also used this WAXD method to identify the effect of magnetic field.

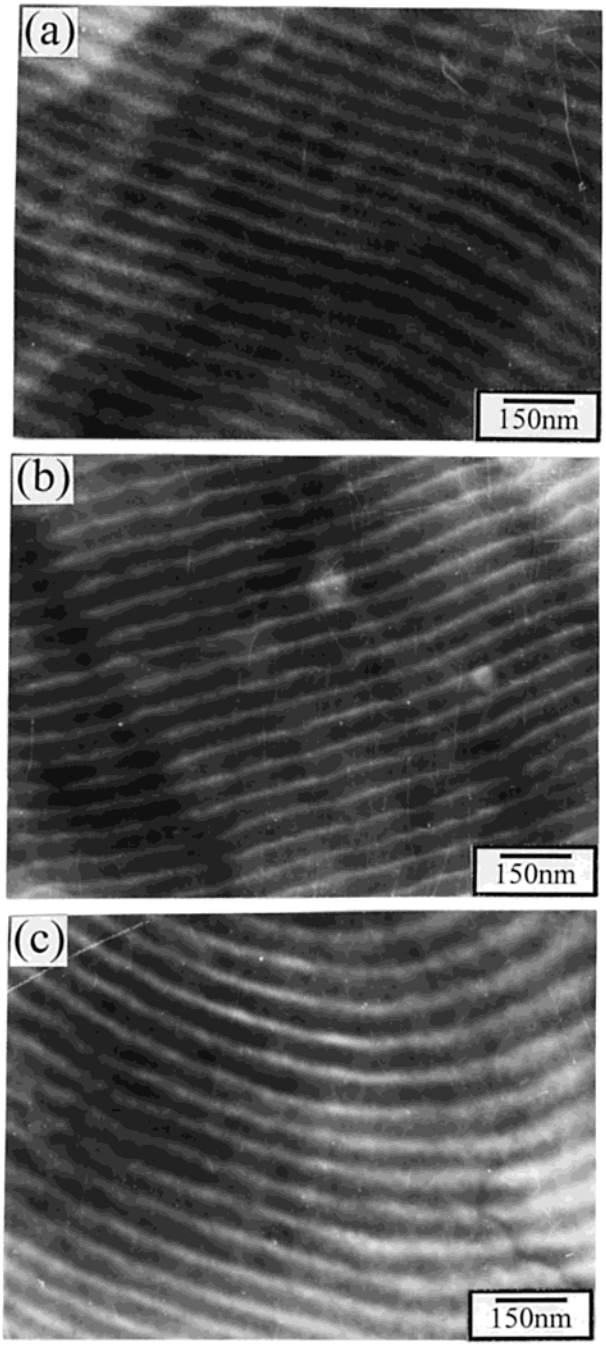

Figure 4. TEM micrographs of the 56 wt % (E−CE)C/PAA cholesteric phase which was solidified by polymerizing the AA after the solution was treated in the magnetic field for (a) 0, (b) 2.5, and (c) 68 h. The magnetic field direction was perpendicular to the surface of the picture.

The results of the transmission electron microscopy (TEM) observations also confirmed that the structure of the (E−CE)C/AA cholesteric phase was not influenced by the magnetic field. Observed by TEM, before being treated in the field, the mesophase of (E−CE)C/PAA composites showed periodical lamellar structure[14] (see Figure 4a), which is a typical morphology of the mac-

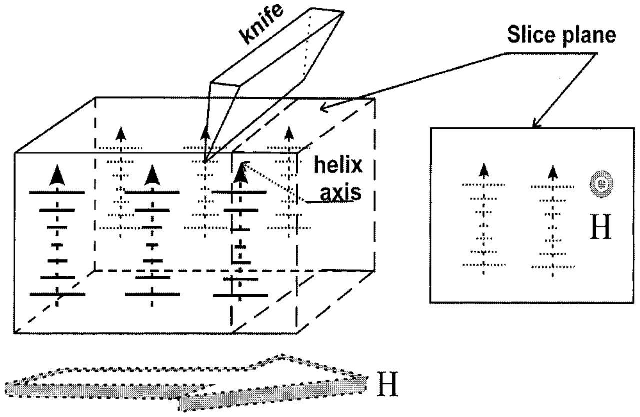

Figure 5. Scheme of the (E−CE)C/PAA slice manufacturing.

romolecular cholesteric phase and reflects the periodical variation of the molecular orientation in the cholesteric phase,[15,16] in which the periodicity coincides with the half pitch (*p*/2).[16] The slices were cut from the plane that the magnetic field penetrated through it (see Figure 5), because if the helix axis had been tended to align parallel to the magnetic field, the periodical lamellar structure would vanished in the plane. But the TEM micrographs (see Figure 4b,c) showed that the periodical lamellar structure still in the plane and not changed after the specimen had treated in the field. It can indicated that the cholesteric order in the (E−CE)C/AA liquid crystalline solution was not changed distinctly after being treated in the magnetic field.

Try to interpret this phenomenon, we used the equation that described the variation of the pitch with the strength of the magnetic field, which derived from de Gennes's theory:[1,27]

$$H_C = (\pi^2/2)(k_{22}/\chi_\alpha)^{1/2}(1/P_0) \qquad (1)$$

where P_0 is the pitch in the absence of the magnetic field and k_{22} is the twist elastic constant.

According to eq 1, the value of H_C depends on the k_{22}/χ_α and P_0. The P_0 of the (E−CE)C/AA cholesteric liquid crystalline solution is 100−300 nm, which is about 20−30 times small than that of the (E−CE)C/DCA cholesteric liquid crystalline solution. H_C is proportional to the $1/P_0$ in eq 1, and if the value of k_{22}/χ_α of the (E−CE)C/AA solution is similar to that of the (E−CE)C/DCA solution, the value of H_C for the (E−CE)C/AA solution is 20−30 times larger than that of the (E−CE)C/DCA solution. Therefore, the effect of the magnetic field with the same intensity on the cholesteric order of the (E−CE)C/AA liquid crystalline solution is much smaller than that on the (E−CE)C/DCA liquid crystalline solution.

From another aspect, the twisting power of (E−CE)/AA enhanced with the concentration increasing, and the effect of the magnetic field may be restrained by the twisting power of high concentration.

It can be concluded that the effect of the magnetic field on the macromolecular cholesteric order will distinctly influenced by the solvent in the cholesteric liquid crystalline solutions.

Conclusions

The (E−CE)C/DCA cholesteric order was oriented in the magnetic field (9.4 T) with its helix axis aligned parallel to the applied field. It indicated the negative diamagnetic anisotropy of (E−CE)C, which cause by the conformation of the *β*-D-glucose backbone and the side cyanoethyl. However, the cholesteric order of the (E−CE)C/AA liquid crystalline solution was nearly unchanged when in the magnetic field, because the pitch of the (E−CE)C/AA cholesteric phase was too small which results in a high value of H_C. The solvent in the cholesteric liquid crystalline solutions may influences the action of the magnetic field on the cholesteric order because the solvents can influences the morphology and the pitch of the cholesteric phase.

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