Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Concentration dependence of magnetic field effects on the ethyl-cyanoethyl cellulose/dichoroacetic acid cholesteric phase

Linge Wang[a]; Yong Huang[b]
[a] Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China, [b] Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China; Institute of Chemistry, Chinese Academy of Sciences, Beijing 10080, PR China,

Online publication date: 06 August 2010

To cite this Article Wang, Linge and Huang, Yong(2001) 'Concentration dependence of magnetic field effects on the ethyl-cyanoethyl cellulose/dichoroacetic acid cholesteric phase', Liquid Crystals, 28: 11, 1673 — 1677

To link to this Article: DOI: 10.1080/02678290110073842

URL: http://dx.doi.org/10.1080/02678290110073842

LIQUID CRYSTALS, 2001, VOL. 28, NO. 11, 1673–1677

Concentration dependence of magnetic field effects on the ethyl-cyanoethyl cellulose/dichoroacetic acid cholesteric phase

LINGE WANG† and YONG HUANG*†‡

†Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China

‡Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

(*Received 23 February 2001; accepted 18 May 2001*)

The effects of an external magnetic field with intensity 9.4 T on the cholesteric phase in ethyl-cyanoethyl cellulose [(E-CE)C]/dichloroacetic acid liquid crystalline solutions were investigated for different concentrations. It was found that the diamagnetic anisotropy of (E-CE)C is negative and the effect of the magnetic field on the orientation of the cholesteric phase is influenced by the concentration of the solution, because the liquid crystalline properties of the solutions vary with the concentration.

1. Introduction

The polymer cholesteric liquid crystalline phase can be changed through the effects of a magnetic field, because most liquid crystalline molecules or polymer moieties have a diamagnetic anisotropy (χ_a). In the presence of a magnetic field, the direction of liquid crystalline molecules can be aligned parallel to the magnetic field direction if the diamagnetic anisotropy is positive. The pitch may increase with increasing strength of the magnetic field and the cholesteric phase can transform to a nematic phase at the critical intensity of the field [1, 2]. If $\chi_a < 0$, molecules may be aligned perpendicular to the applied magnetic field. The cholesteric helix axes in this case will adjust to parallelism with the field, but the cholesteric structure will not be destroyed. Cholesteric solutions of DNA [3, 4] and suspensions of cellulose micro-crystals [5] have been found to have negative diamagnetic anisotropy.

Ethyl-cyanoethyl cellulose [(E-CE)C] is a cellulose derivative with two different ether groups, ethyl and cyanoethyl, and can form cholesteric liquid crystalline solutions in many organic solvents, such as dichloroacetic acid (DCA) [6] and acrylic acid (AA) [7]. (E-CE)C cholesteric liquid crystalline solutions exhibit a multi-textural behaviour with variation of the concentration [7, 8]. An earlier study has shown that the effect of an external magnetic field on the cholesteric phases of (E-CE)C/DCA is much different from that for (E-CE)C/AA solutions [9]. After the fingerprint texture of the (E-CE)C/DCA cholesteric solution has been exposed to the magnetic field, the direction of the cholestric helix axes are aligned parallel to the direction of the magnetic field. However, the cholesteric order of (E-CE)C/AA liquid crystalline solutions is almost unchanged when they are treated in the same magnetic field, because the pitch of the (E-CE)C/AA cholesteric phase is much smaller than that of the (E-CE)C/DCA solutions. The (E-CE)C/DCA cholesteric liquid crystalline solutions can exhibit a disk-like texture, fingerprint texture and oily streak texture in sequence with increasing concentration [8], and the pitch varies inversely with the concentration. In this work, the effects of a magnetic field on the (E-CE)C/DCA cholesteric structure for different concentrations were studied; the concentration (or pitch) dependence of the magnetic field effect on the ethyl-cyanoethyl cellulose cholesteric structure is discussed.

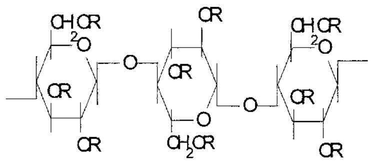
2. Experimental

2.1. *Materials*

The (E-CE)C was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, China) and acrylonitrile [6]. The degree of substitution with ethyl was about 2.1 and with cyanoethyl was about 0.33, determined by an elemental analysis (CHN-O-RAPID, Heraeus, Germany). The molecular mass of (E-CE)C, M_n, measured by gel permeation chromatography (GPC) (Waters-ALC-244-GPC) and calibrated by standard polystyrene, was 7×10^4. The molecular structure of (E-CE)C is shown in figure 1. The DCA was a chemically pure reagent.

*Author for correspondence, e-mail: yhuang@cashq.ac.cn

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110073842



R=H, CH_2CH_3, CH_2CH_2CN

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

2.2. *(E-CE)C/DCA solutions and magnetic field processing*

The (E-CE)C was dissolved in DCA at room temperature and the solutions were sealed in a test tube. The solutions were laid aside at room temperature for over 20 days, after which they were heated at 50°C for about 10 h. A film of the solution was then sandwiched between a microscope slide and a cover glass and sealed with solid wax. The area of a cell was about $15 \times 8\,\mathrm{mm}^2$, and the film thickness was about 10 μm. The specimen was placed in a magnetic field of intensity 9.4 T for about 60 h, after which it was stored at room temperature for 3 days. The variation of the mesophase texture was observed by polarizing optical microscopy (POM) (ORTHOPLAN-POL, Leitz, Germany). The directions of the magnetic field and of observation are shown in figure 2.

3. Results and discussion

3.1. *Effect of the magnetic field on the fingerprint texture*

When the concentration is 29 wt %, there are both anisotropic and isotropic phases present in the (E-CE)C/DCA cholesteric solutions and the mesophase generally shows the fingerprint texture. Some parallel, equidistance alternating dark and bright striations are observed in the mesophase and the width of the striations is equal to a half pitch. The direction of the helical axes is aligned perpendicular to the striations and parallel to the slide surface. Moreover, the direction of the helical axes in different domains of the fingerprint texture is different, see figure 3 (*a*). The helical pitch of the cholesteric phase before treatment in the magnetic field is about 4.5 μm. The striations, however, form a zig-zag pattern and the helices are aligned almost parallel to the direction of the magnetic field after the solutions are treated in the magnetic field, see figures 3 (*b*) and 3 (*c*). This indicates that the direction of the molecular orientation is almost normal to the direction of the field and that the diamagnetic anisotropy (χ_α) of (E-CE)C is negative. As we know, the diamagnetic anisotropy of molecules is related to their molecular structure, and the negative χ_α of (E-CE)C is attributed to the conformation of its β-D-glucose backbone and the side cyanoethyl groups [9].

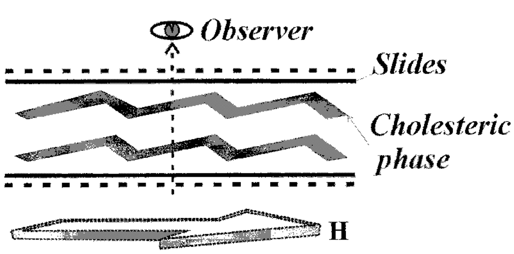


Figure 2. Scheme showing the magnetic field effect on the (E-CE)C/DCA specimen.

3.2. *Effect of the magnetic field on the oily streak texture*

The pitch of the (E-CE)C/DCA cholesteric phase can decrease with increasing concentration. When the concentration is about 40 wt %, there is a uniform cholesteric phase in the (E-CE)C/DCA solutions and the mesophase generally shows the planar texture and oily streak texture, see figures 4 (*a*) and 4 (*b*). In the mesophase, the helical axes are mostly aligned perpendicular to the slide surface for the planar texture, but are aligned parallel or oblique to the slide surface in the oily streak texture. No periodic birefringent striations can be observed by POM in the mesophase, because the pitch is very small ($P < 1$ μm). From figures 4 (*c*) and 4 (*d*), it can be seen that the mesophase texture is nearly unchanged after the solution is exposed to the magnetic field. If the magnetic field can affect the planar texture and the oily streak texture, in the case of $\chi_a < 0$, the helical axes will be realigned from perpendicular to the magnetic field to parallel to it, and the mesophase will be changed to the fingerprint texture. The results indicate that a magnetic field of intensity 9.4 T cannot influence the cholesteric structure of the planar and the oily streak 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 [1, 10]:

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

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

According to equation (1), the value of H_C depends on k_{22}/χ_α and P_0. H_C is proportional to $1/P_0$ and the parameter k_{22}/χ_α for the oily streak texture is equal to that of the fingerprint texture in the (E-CE)C/DCA liquid crystalline solutions. P_0 for the fingerprint texture is 4.5 μm, which is about four times larger than that of the oily streak texture. Therefore, the H_C of the oily

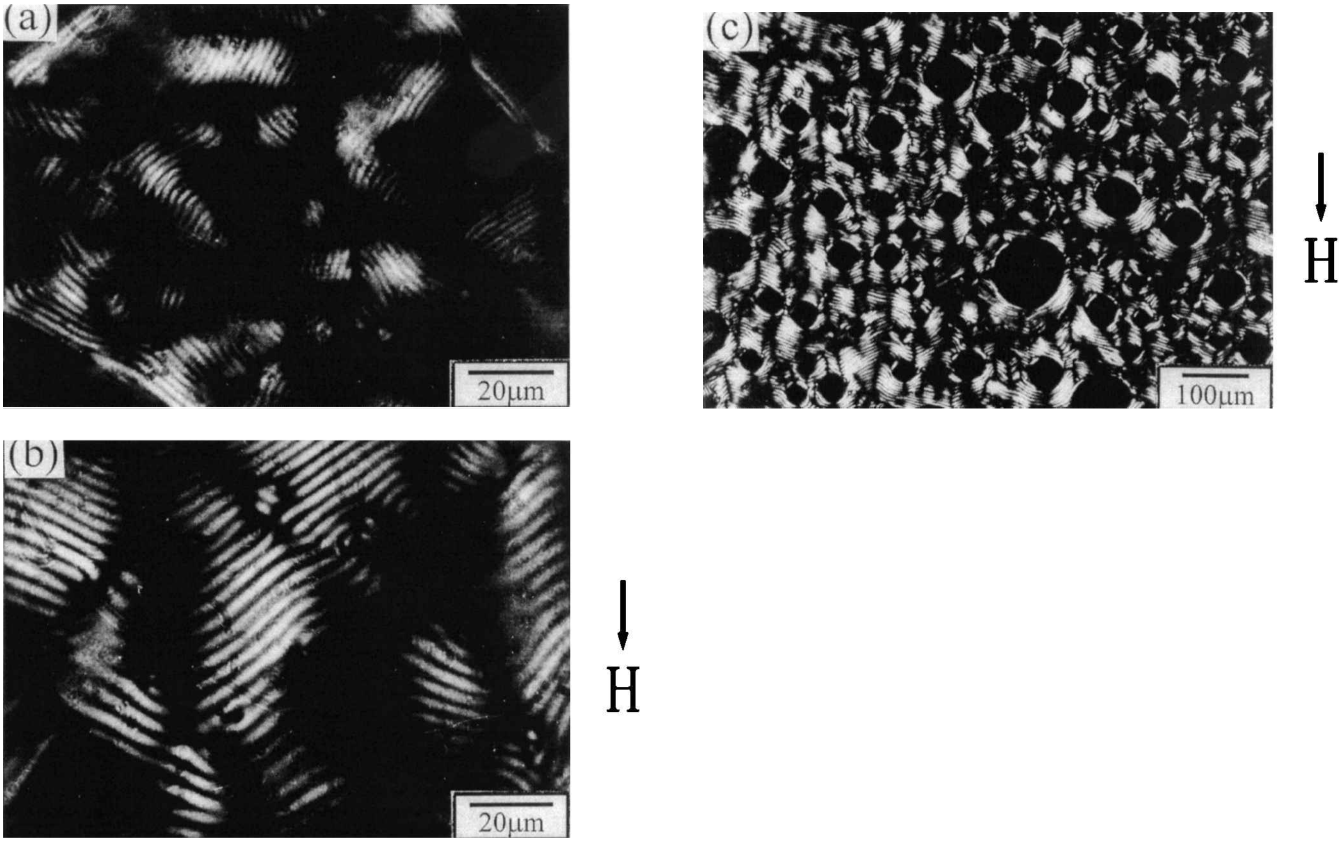


Figure 3. Effect of the magnetic field on the fingerprint texture: (*a*) no applied magnetic field; (*b*) and (*c*) after applying the magnetic field. The magnetic field direction was perpendicular to the average orientation of the striations; the direction of the magnetic field is in the plane of the page and from up to down.

streak texture must be four times larger than that of the fingerprint texture if the influence of the magnetic field on the planar texture and the oily streak texture is the same as that on the fingerprint texture. In a magnetic field with the same intensity, the effect on the fingerprint texture will be larger than on the planar and the oily streak textures. This result is different from that for the magnetic field effect on cholesteric liquid crystalline DNA systems [4]. The diamagnetic anisotropy of the DNA molecules is negative and the helical axes in the planar texture were aligned from perpendicular to parallel to the direction of the magnetic field, and the pitch was about 2.2 μm. We believe the orientation is caused by the fact that the pitch of the cholesteric DNA helix is bigger than that of (E-CE)C/DCA. The decrease of the pitch in the cholesteric phase reflects the increase in the twisting power. The pitch is also decreased with increasing concentration. It is suggested, then, that the twisting power increases with increasing concentration, and the effect of the magnetic field on the cholesteric phase is restrained at a high concentration because of the competition between the cholesteric twisting power and the orientation power induced by the magnetic field.

3.3. *Effect of the 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 a disk-like texture for the (E-CE)C/DCA liquid crystalline solutions. Due to the surface tension of the interface between mesophase and isotropic phase, the cholesteric phase generally forms 'round' shapes to minimize the surface and the free energy. The disk-like texture has also been observed in many macromolecular cholesteric phases [11–13], for such as DNA fragments [12] and polypeptides [13]. The diameter of a 'disk' generally ranges between 20 and 30 μm and some periodic concentric extinction rings are observed in the (E-CE)C/DCA disk-like texture, see figure 5 (*a*). When the concentration is increased, the 'disks' will aggregate and merge into bigger disks of the fingerprint texture [14]. The distance between neighbouring concentric rings in the disk-like texture is equal to a half pitch, which is about 4–6 μm and approaches that of the fingerprint texture. The helices are aligned along the radial directions of the 'disk' and parallel to the slide surface. Figure 5 shows that the effect of the field on the 'disk' seems to be dependent on its diameter. When

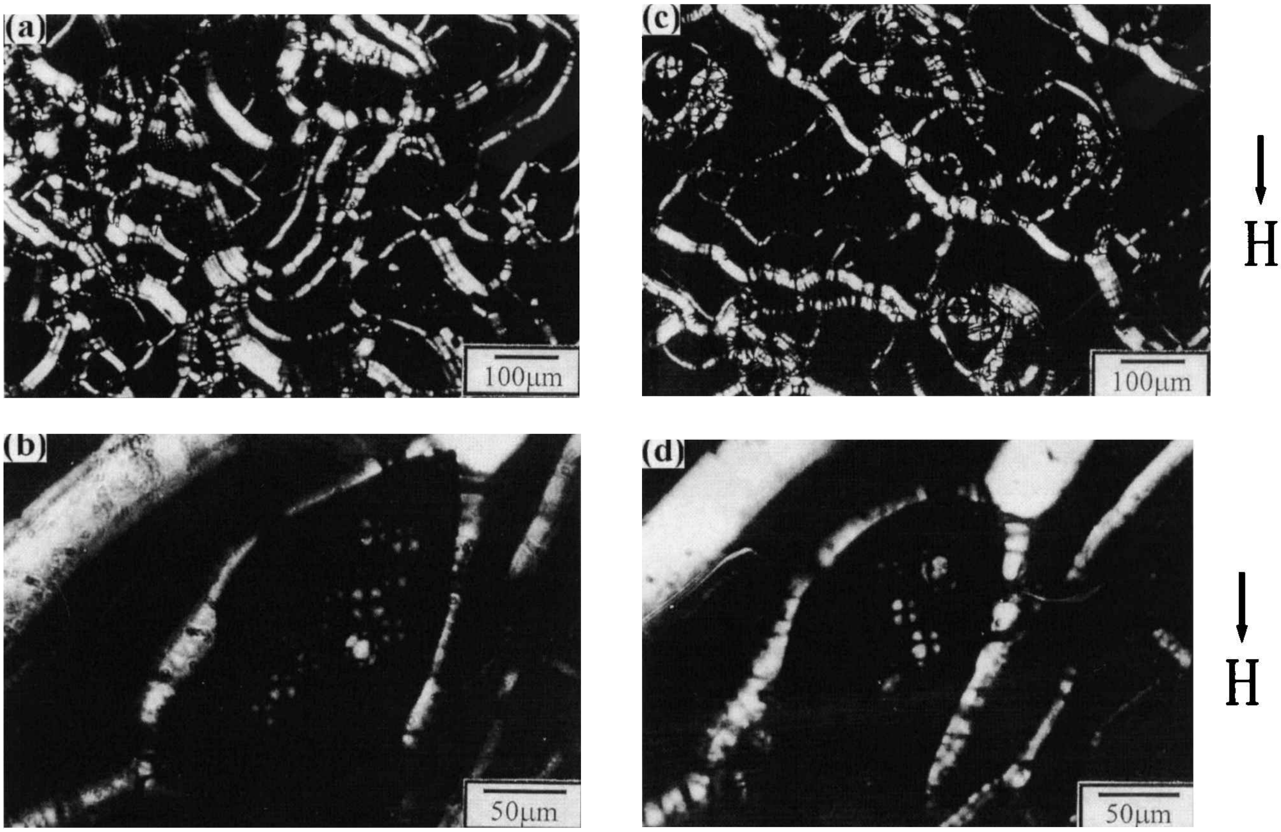


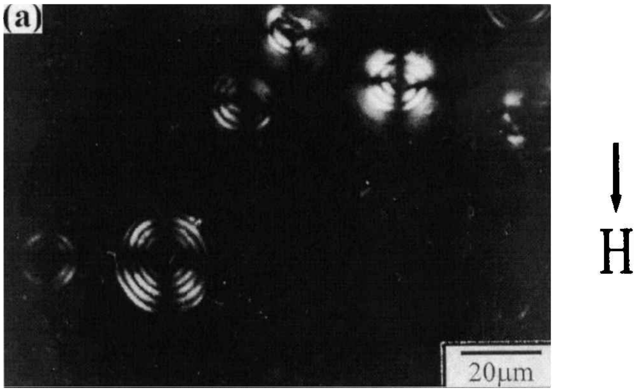
Figure 4. Effect of the magnetic field on the oily streak texture: (*a*) and (*b*) no applied magnetic field; (*c*) and (*d*) after applying the magnetic field, the morphology of the texture remained. Pictures (*b*) and (*d*) are for the same area; the direction of the magnetic field is in the plane of the picture and from up to down.

the diameter is about 28 μm, the shape and morphology are nearly unchanged and the concentric rings still display the round shape after the solution is exposed to the magnetic field, see figure 5 (*a*). It is interesting that when the diameter increases to 42 μm, the shape of the 'disk' is changed to an oval form and the helical axes tend to be aligned parallel to the direction of the magnetic field, see figure 5 (*b*). Candau and co-workers [11] have reported that the critical intensity of the magnetic field varies inversely with the diameter of the spherulites. A magnetic field of intensity 12 T has been used to effect orientation of the cholesteric phase in a spherulitic texture with diameter 122 μm. It is clear that the effect of the magnetic field on a disk-like texture with large diameter is large, but small on one with small diameter. The same phenomenon has been found for the effect of the magnetic field on PBLG cholesteric solutions [13], for which the diameter of the 'spherulites' lies in the range 600–1000 μm and the pitch is 42.6 μm.

These results indicate that the effect of a magnetic field on a cholesteric phase with a fingerprint texture is greater than on that with a disk-like texture. The pitch of a mesophase with the fingerprint texture and a disk-like texture is almost the same, but the surface tension of the cholesteric phase in the fingerprint texture is different from that in the other. It seems that there is a high surface tension in the disk-like texture and that there is a competition between the effect of surface tension and the magnetic field when the solution is exposed to the field. The surface tension of the mesophase with the disk-like texture increases with decreasing diameter of the 'disk'. Therefore, the effect of a magnetic field may be restrained by the effect of the surface tension when the diameter of the 'disk' is small, see figure 5 (*a*). When the diameter is increased sufficiently, the effect of the magnetic field will be larger than the effect of the surface tension and the helical axes tend to be aligned parallel to the magnetic field, see figure 5 (*b*).

An example showing the contrasting magnetic field effects on the fingerprint texture and the spherulite texture is shown in figure 6. The striations in the fingerprint texture are aligned perpendicular to the magnetic field, but the 'disk' retains its original morphology after the solution is exposed to the magnetic field.

It is suggested that the condensed state structure of cholesteric liquid crystals depends on the elastic forces and the twisting power, the external field effects and the surface tension of the cholesteric phase. The effect of



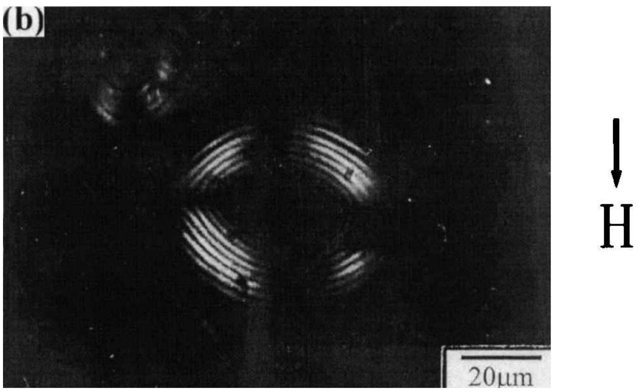


Figure 5. Effect of the magnetic field on the (E-CE)C/DCA spherulite texture: (*a*) unchanged spherulite, diameter $\approx 28\,\mu$m; (*b*) changed spherulite, diameter $\approx 42\,\mu$m. The direction of the magnetic field is in the plane of the picture and from up to down.

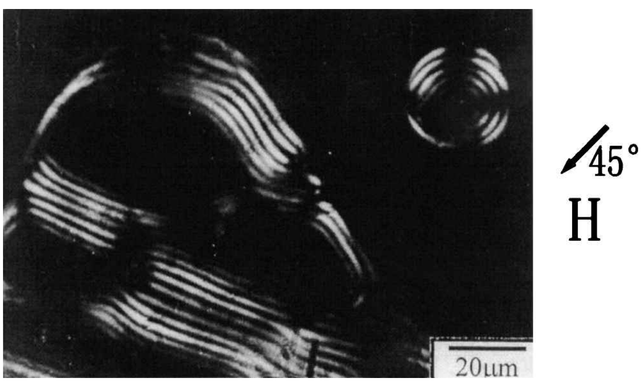


Figure 6. Example showing the contrasting magnetic field effect on the fingerprint and spherulite textures. The striations in the fingerprint texture aligned perpendicular to the magnetic field, but the spherulite retained its morphology. The direction of the magnetic field is at 45° to the horizontal line in the picture.

the magnetic field oriented the helical axes parallel to the field, after the fingerprint texture of the (E-CE)C/DCA cholesteric solution was exposed to the field. It can be seen in figure 3 (*c*) that the round shaped extinction areas are the isotropic phase; the arrangement of the striations in the cholesteric phase around the isotropic phase is influenced by the surface tension of the interface between the mesophase and the isotropic phase, and the zig-zag pattern is formed. The cholesteric order will be influenced by the twisting power and the surface tension of the cholesteric phase is effective in the small diameter disk-like texture. The liquid crystalline molecules may orient along the direction of the external field, electric or magnetic, but the external field effect on the cholesteric order may be restrained by the surface tension of the cholesteric phase [11, 13].

4. Conclusion

The effect of a magnetic field on the (E-CE)C/DCA cholesteric phase is influenced by the concentration. The striations of the fingerprint texture are oriented in a magnetic field of intensity 9.4 T and the helical axes tend to be aligned parallel to the direction of the applied field, indicating that the diamagnetic anisotropy of (E-CE)C is negative. However, the magnetic field effect on the cholesteric structure is influenced by the concentration of the solution and the surface tension of the cholesteric phase. The twisting power increases with increasing concentration, and the effect of the magnetic field on the cholesteric phase is restrained by the twisting power at high concentration and by the surface tension of the cholesteric phase at low concentration.

Financial support by the National Natural Science Foundation of China and National Basic Research Project—Macromolecular Condensed State is greatly appreciated.

References

[1] De Gennes, P. G., 1968, *Solid State Commun.*, **6,** 163.
[2] Meyer, R. B., 1968, *Appl. Phys. Lett.*, **12,** 281.
[3] Van Winkle, D. H., Davidson, M. W., Chen, W. X., and Rill, R. L., 1990, *Macromolecules*, **23,** 4140.
[4] Van Winkle, D. H., Chatterjee, A., Link, R., and Rill, R. L., 1997, *Phys. Rev. E.*, **55,** 4354.
[5] Revol, J.-F., Godbout, L., Dong, X.-M., Gray, D. G., Chanzy, H., and Maret, G., 1994, *Liq. Cryst.*, **16,** 127.
[6] Huang, Y., Chen, M. C., and Li, L. S., 1988, *Acta Chimica Sinica (Chin.)*, **46,** 367.
[7] Jiang, S. H., and Huang, Y., 1993, *J. appl. polym. Sci.*, **50,** 607.
[8] Huang, Y., 1989, *J. macro. Sci. Phys.*, **B28,** 131.
[9] Wang, L.-G., and Huang, Y., 2000, *Macromolecules*, **33,** 7062.
[10] De Gennes, P. G., 1969, *Mol. Cryst. liq. Cryst.*, **7,** 325.
[11] Candau, S., Le Roy, P., and Debeauvais, F., 1973, *Mol. Cryst. liq. Cryst.*, **23,** 283.
[12] Van Winkle, D. H., Davidson, M. W., Chen, W. X., and Rill, R. L., 1990, *Macromolecules*, **23,** 4140.
[13] Patel, D. L., and Duprè, D. B., 1980, *J. polym. Sci.: polym. Phys. Ed.*, **18,** 1599.
[14] Huang, Y., 1991, *Chin. J. polym. Sci.*, **9,** 86.