

BAND-LIKE TEXTURE OF ETHYL-CYANOETHYL CELLULOSE MESOPHASE*

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ABSTRACT

In the ethyl-cyanoethylcellulose ((E-CE)C)/dichloroacetic acid (DCA) cholesteric liquid crystalline solution, the band-like texture is formed when the mesophase aggregates with the disk-like texture grow to big enough and merge with each other with increasing concentration. The band-like texture is composed of parallel equidistant bright and dark alternative strips which are about 0.2-2.0 μm in width. In the band-like texture, the layers of ordered polymer chains are perpendicular to the solution film and the axes of helicoids are parallel to it. The width of the strips is different in different zones. Under the effect of an external magnetic field, the strips in the band-like texture first become wider and then narrower gradually. Moreover, the axes of helicoids in the (E-CE)C/DCA mesomorphic solution change from the direction normal to the magnetic field to the agreement with the magnetic field direction.

INTRODUCTION

Many research papers about the investigation of cellulose and its derivative liquid crystals have been published^[1, 2]. They are mainly concentrated on the rheological and optical properties of liquid crystalline systems and the effect of various factors such as molecular weight, substituent, degree of substitution, solvent system and temperature on the formation of mesophase. Recently, some investigations about the textures of cellulose derivative liquid crystals have been reported by the author^[3, 4] but the comprehension about the texture is still very incomplete.

In 1985, Nishio et al.^[5] observed the morphology and structure of the hydroxypropyl cellulose film casting from the liquid crystalline solution by electron microscopy and found the existence of the disk-like structure within the mesophase. We have found^{3, 4} that the ethyl-cyanoethyl cellulose mesophase and the ethyl-acetyl cellulose mesophase can show the disk-like texture and the oily streak texture in the specific concentration ranges. In this report, the band-like texture in the ethyl-cyanoethyl cellulose / dichloroacetic acid mesomorphic solution and the effect of the external magnetic field on it by polarizing microscopy, have been investigated.

EXPERIMENTAL

The ethyl-cyanoethyl cellulose (C-CE)C was obtained by the reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.56 and the molecular weight was about 3.8×10^4 . The dichloroacetic acid(DCA) was a chemically pure reagent. The (E-CE)C was

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mixed with the DCA at room temperature and the solution was tightly sealed in the test-tube. After heating at 50 °C for 10 hours, the solutions were stored at room temperature for more than 15 months in order to obtain the equilibrium solutions until used. The FTIR spectrum showed the absence of dichloroacetate substituents in the solution when it was used.

The (E-CE)C/DCA mesomorphic solution was sandwiched between a microscope slide and a cover glass and formed a solution film which was about 10-30 μm in thickness. The textures of the solution were observed by a polarizing microscope (Leitz, ORTHOPLAN-POL). The specimen was placed in a homogeneous magnetic field, of which the intensity was about 4300 G and the direction was normal to the solution film. The variation of the mesophase texture was followed by the polarizing microscope.

RESULTS AND DISCUSSION

In the (E-CE)C/DCA solution, mesophase begins to form when the concentration is about 23.1 wt.% at room temperature^[6]. When the solution is biphasic and the mesophase noncontinuous, there are many mesophase aggregates with the disk-like texture dispersed in the isotropic phase. After the mesophase becomes continuous, however, the mesophase shows the oily streak texture and the pseudoisotropic texture^[4]. Moreover these three textures can be observed in the same specimen at appropriate concentration. If the concentration is low enough, mesophase aggregates are small and there is only the disk-like texture observed in the solution. When the concentration is above 35 wt.%, i. e. the mesophase becomes continuous, however, only the band-like texture and the pseudoisotropic one can be observed. While, when the mesophase changes from a noncontinuous phase to a continuous one with increasing concentration, the small mesophase aggregates show the disk-like texture and the large ones show both the band like and the pseudoisotropic textures. In many cases, the oily streak texture is composed of parallel equidistant bright and dark alternative strips, which can actually be called a band-like texture. Fig.1 shows the typical band-like texture of the (E-CE)C/DCA mesomorphic solution. In this texture, the layers of ordered polymer chains are perpendicular to the solution film plane and the axes of helicoids of cholesteric phase are parallel to it but normal to the band



Fig.1 The band-like texture of the 26.0 wt. % (E-CE)C/DCA solution, 25 °C

direction. The scheme of the parallel arrangement of helicoids in the band-like texture is given in Fig. 2. When some helicoids arrange side by side along the band direction and the layers of ordered polymer chains with the same orientation direction are on the same plane, the band-like texture with parallel equidistant bright and dark alternative strips can be observed under the crossed polarizing light.

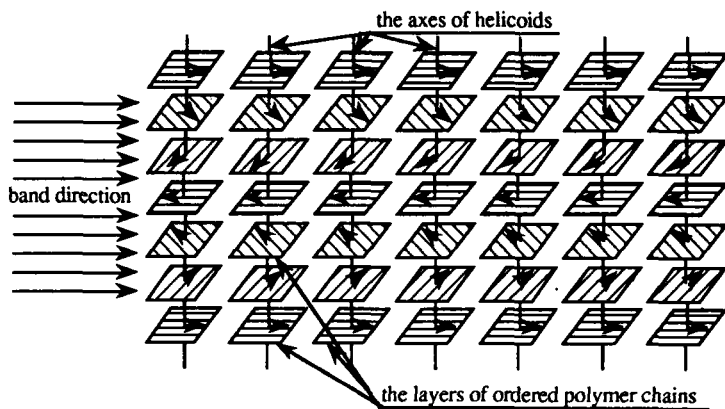


Fig. 2 The scheme of the ordering arrangement of helicoids in the band-like texture

How does the band-like texture form in cholesteric phase? The vibration direction of the larger refractive index of mesophase with the disk-like texture perpendicular to the radial direction and with the band-like texture parallel to the band direction, which are measured by the polarizing microscope with tilting compensator.

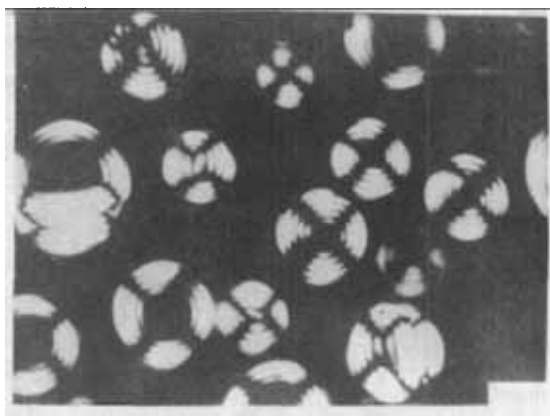


Fig. 3 The disk-like texture of the (E-CEC /DCA mesomorphic solution. 25 °C

At a lower concentration, small mesophase aggregates show the disk-like texture which is composed of concentric rings or helices (Fig. 3). It has been known that with increasing concentration, mesophase aggregates increase gradually in dimension. The mesophase aggregates with the disk-like texture can merge each other when they are big enough and combine to form larger ones. In this process, the

concentric rings or the helices are deformed. They are pressed with each other to become strip-like and finally, the band-like texture appears in mesophase if the ordering arrangement of the helicoids in cholesteric phase is not destroyed. This process is schematically demonstrated in Fig. 4.

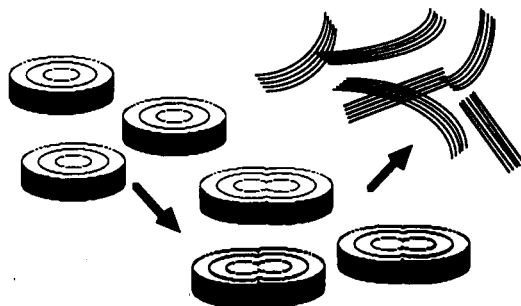


Fig. 4 The scheme of the formation process of the band-like texture.

When many mesophase aggregates with the disk-like texture are merged with each other, a large mesophase zone with the band-like texture can be formed (Fig. 5), in which the band direction is different in various small zones. This further confirms the process of the formation of the band-like texture mentioned above. The concentric rings and helices can be pressed in different directions when the mesophase aggregates with the disk-like texture merge and combine. The bands, therefrom, can be formed in different small zones and are different in the direction.



Fig. 5 The disk-like texture and the band-like texture of the (E-CE)C/DCA mesomorphic solution, 25 °C

This kind of band-like texture in cholesteric liquid crystalline solution can also be observed in the chiral smectic C phase^[7]. In the band-like texture of the chiral smectic C phase, similar to the cholesteric phase, the width of the strips is equidistant and is directly related with its interplanar distance. The reason for the similarity between the cholesteric texture and the smectic texture is that their equilibrium structures have translational periodicity of half of the pitch in the cholesteric phase

and of half of the interplanar distance in the smectic phase. From the observations of the band-like texture, the pitch of helicoids in the cholesteric phase of the (E-CE)C/DCA solution is about $0.1\text{--}1.0\mu\text{m}$, which depends on the concentration and the temperature. The interplanar distance in the smectic phase is almost constant but the pitch in the cholesteric phase is variable. In the (E-CE)C/DCA cholesteric liquid crystalline solution, therefore, the width of the strips in the band-like texture can easily be changed by the influence of external factors.

In the biphasic solution, the band-like texture often appears nearby the interface with the isotropic phase (Fig. 6). Inside the mesophase, however, there is the pseudoisotropic texture besides the band-like texture. The pseudoisotropic phase is a lamellar anisotropic phase and its birefringence is very weak^[8]. The difference of the mesophase texture in different mesophase zones indicates that the interaction of polymer chains or the pattern of the arrangement of the helicoids in cholesteric phase is different between inside the mesophase and nearby the interface with the isotropic phase. Furthermore, the strips in the band-like texture nearby the interface are always arc because the noncontinuous phase is always circular or nearly circular in the biphasic solution. But the strips are mostly straight inside the mesophase.

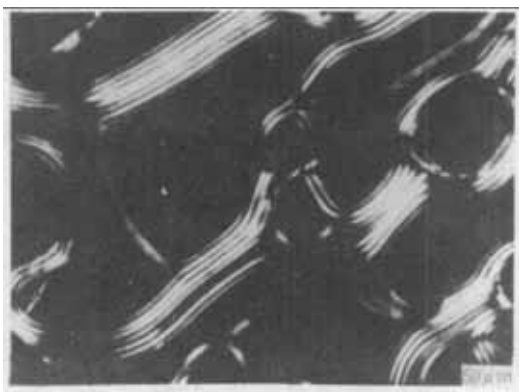


Fig. 6 The band-like texture inside the mesophase and nearby the interface with the isotropic phase, 25°C

The band-like texture with wider strips, which are about $3\mu\text{m}$ in width, can also be observed in some mesophase zones, i. e. in these places the pitch of helicoids is about $1.5\mu\text{m}$. The pitch of cholesteric phase is related with both the concentration and the temperature in the mesomorphic solution. Therefore, the existence of the strips with the different width in different zones demonstrates that the concentration is different in the mesophase. In other words, the distribution of the concentration is heterogeneous in the mesophase.

The band-like texture is influenced by an external magnetic field. Fig. 7 shows the variation of the strips under the effect of the external magnetic field whose direction is normal to the solution film. The strips have not obviously been changed after the specimen is placed in the magnetic field for several hours. But after two days (53hrs) some strips in the bank-like texture have become wider (Fig. 7b). These wider strips generally appear at the intersection of the bands and tend

to forming concentric rings or helices (Fig. 7 C and D). In the cellulose derivative liquid crystalline solution, the pitch of cholesteric phase decreases with increasing concentration⁹. The wider strips appeared in the band-like texture demonstrate that the concentration is different between the intersection of the bands and other mesophase zones. The concentration is smaller in the intersection zone of the bands than in the other zones. It is possible, therefore, that the distribution of the concentration varies due to that the polymer chains in the mesophase reorder and re-arrange under the effect of the external magnetic field.

Furthermore, it can also be seen from Fig. 7, on the one hand, that the width of the strips in the band-like texture decreases with the time of the effect of the magnetic field. Table 1 shows the variation of the width of the strips in the band-like texture with the period when the solution is in the magnetic field. It can be seen that since the specimen is placed in the magnetic field, the strips in the band-like texture become wider at the beginning but then, narrower with the

Table 1 The width of the strip in the band-like texture.
C=33.3 wt. %, 25 °C.

t (hr)	0	7.5	53.5	96	120	216	360
$W1$ (μm)	1.11	1.43	1.25	1.18	1.12	0.91	0.82
$W2$ (μm)	—	—	2.67	—	2.67	—	1.34

t : The period when the solution is placed in the magnetic field.

$w1$: the width of the normal strips.

$w2$: The width of the wider strips.

period when the solution is in the magnetic field. The wider strips in the intersection of the bands also decrease in width with the time of the effect of the magnetic field after they appear. This result indicates that the pitch of cholesteric phase first increases and then decreases gradually under the effect of the magnetic field. The mesophase with the band-like texture, on the other hand, becomes smaller with the period when the solution is in the magnetic field. It changes to the pseudoisotropic texture gradually. In the band-like texture, the axes of helicoids are parallel to the solution film and in the pseudoisotropic texture, however, the layers of ordered polymer chains are parallel to the solution film and the axes of helicoids are perpendicular to it. The direction of the magnetic field is normal to the solution film. It can be considered therefore, the axes of helicoids in the (E-CE)C/DCA mesomorphic solution change from the direction normal to that parallel to the magnetic field under the effect of the magnetic field.

CONCLUSIONS

The (E-CE)C/DCA mesomorphic solution can show the band-like texture which is composed of parallel equidistant bright and dark alternative strips in a certain concentration range. In the band-like texture the helicoids order arrange side by side in the band direction and the axes of the helicoids are parallel to the solution film. The formation of the band-like texture in mesophase is

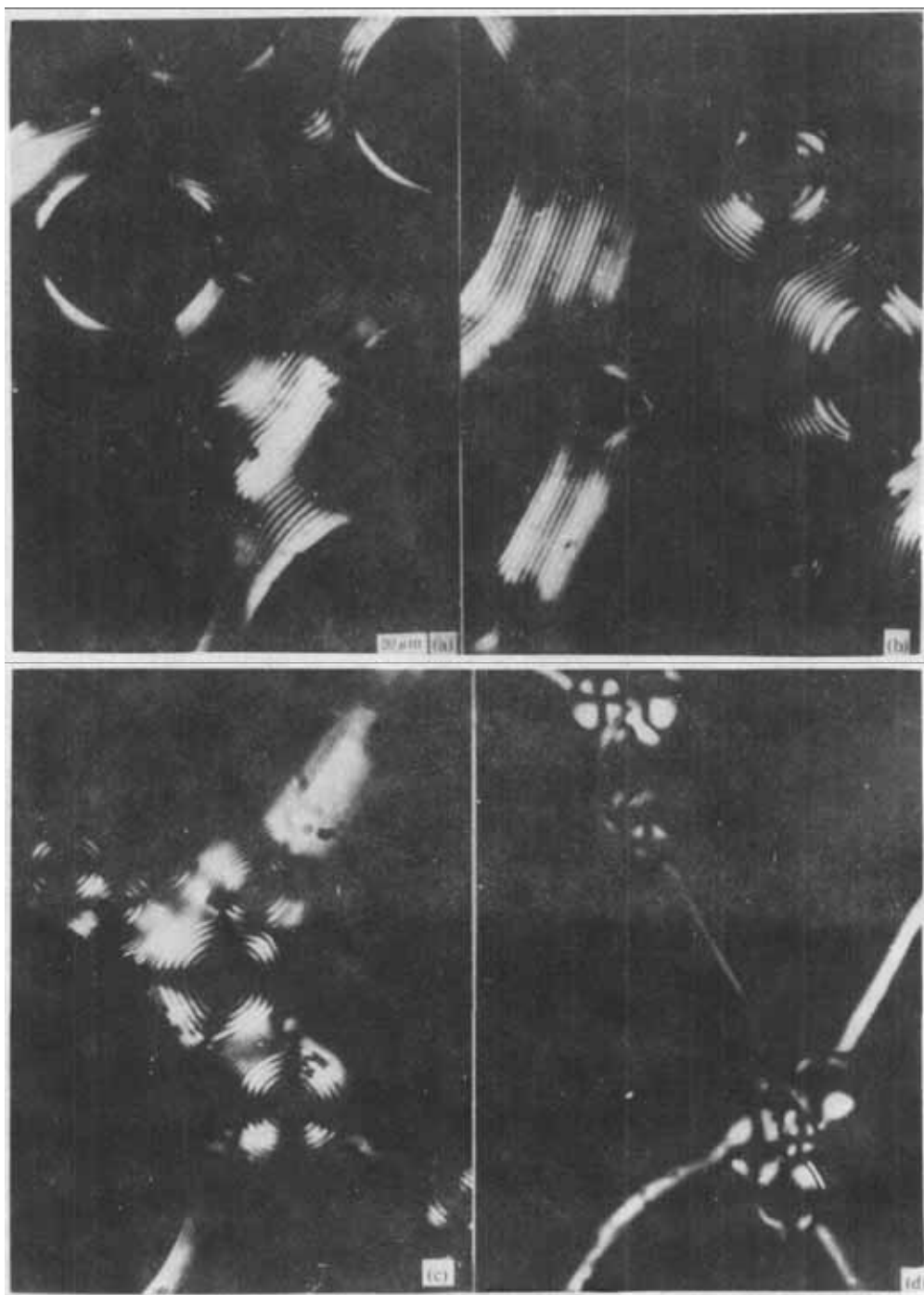


Fig. 7 The band-like texture of the 33.3 wt. % (E-CE)C/DCA solution, which has been in the magnetic field for (a) 7.5 hours, (b) 53.5 hours, (c) 360 hours and (d) 1056 hours, 25 °C

due to that the mesophase aggregates with the disk-like texture which is composed of concentric rings or the helices pressed with each other and the concentric rings and the helices deformed to become strips.

The width of the strips in the band-like texture is different in varied mesophase zones, which suggests that the distribution of the concentration is heterogeneous in the mesophase. Under the effect of the external magnetic field, the width of the strips first increases and then decreases gradually with the period when the solution is in the magnetic field. Moreover, the axes of helicoids in cholesteric phase of the (E-CE)C/DCA solution can change from the direction normal to the magnetic field to parallel to it.

Keywords:

Band-like texture; Ethyl-cyanoethyl cellulose ; Cholesteric mesophase

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