

TEXTURES OF ETHYL-ACETYL CELLULOSE MESOPHASE

HUANG Yong (黄 勇) and LI Lisheng (李历生)

(Guangzhou Institute of Chemistry, Academia Sinica, Guangzhou)

ABSTRACT

There was phase separation between the anisotropic and isotropic phases in the ethyl-acetyl cellulose /dichloroacetic acid cholesteric liquid crystalline solutions. The textures of mesophase varied with the concentration. The mesophases could form the disc-like texture, oily streaks texture and texture of domains gathered randomly. In the first two textures the layers of the ordered molecular chain were perpendicular to the slide surface and the axes of the helical structure were parallel to the slide surface.

INTRODUCTION

Many cellulose derivatives can form lyotropic liquid crystals in certain solvents and most of them are cholesteric^[1]. Optic and rheological properties of cellulose derivative liquid crystals have been studied by many investigators. But investigation about the textures of mesophase for the cellulose derivative solutions is rarely reported.

We have reported^[2] that the ethyl-acetyl cellulose ((E-A)C) can form cholesteric liquid crystalline phase in the dichloroacetic acid (DCA) and there is phase separation between the anisotropic and the isotropic phases in the biphasic solutions. The mesophase in the solution shows the special textures. Robinson et al.^[3-5] reported the textures of the cholesteric liquid crystalline solutions of the polypeptides. We have found that there is a similarity of the textures for the (E-A)C mesophase and the polypeptide mesophase. In this article we study the textures of mesophase in the (E-A)C /DCA solution by using polarized microscopy and small angle light scattering (SALS).

EXPERIMENTAL

The (E-A)C was obtained by the esterification of ethyl cellulose in acetic acid^[6]. Degree of substitution for the ethyl is about 1.82 and for the acetyl is about 0.26. The DCA is a CP reagent. The (E-A)C was mixed with the DCA at room temperature and the solutions were sealed up in tubes. The solutions were laid over 6 months after having been heated at 50 °C for 10 hours. Then, the solutions were spread between the microscope slides.

Birefringent textures of the solutions were observed with a polarized microscope (Leitz, ORTHOPLAN-POL).

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SALS patterns of the solutions were obtained by means of a small angle laser light scattering instrument (LS-1; Yingkou measuring and testing instrument factory, Liaoning, China).

RESULTS AND DISCUSSION

Birefringence of the solutions can indicate the textures of mesophase. Fig. 1 is a series of polarized light micrographs of the (E-A)C/DCA mesomorphic solutions at different concentration. The (E-A)C/DCA solution is biphasic at the concentration between 26—35wt. %^[2]. From Fig. 1a, it can be seen that there are clear boundaries between the anisotropic and the isotropic phases in the biphasic solution, that is, there is phase separation in the solution. The anisotropic and the isotropic phases can be mixed under a force. But the phase separation occurs again when the force is removed. The isotropic phase is continuous at lower concentration and the anisotropic phase is continuous at higher concentration. Compatibility of the two phases is poor and the blend of them is unstable. But the mesophase in the solution is steady and does not transform to the other phases with time. Therefore, the anisotropic and the isotropic phases exist steadily and respectively in the biphasic solution although there is the phase separation in it.

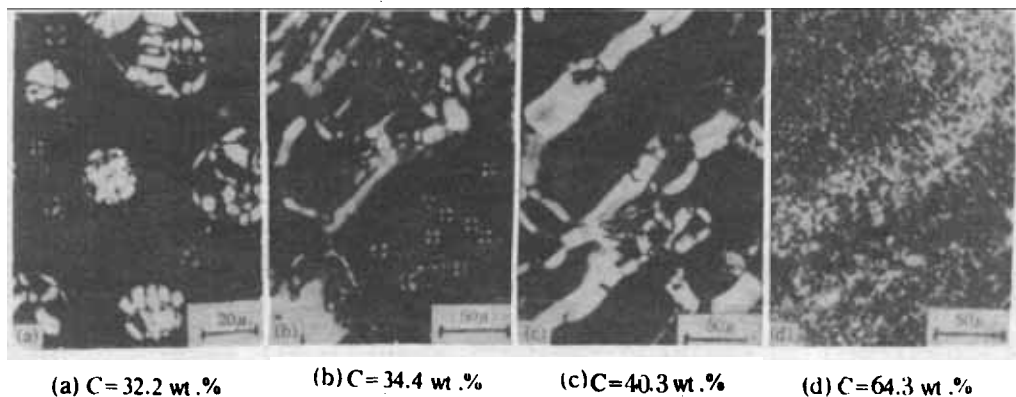


Fig. 1 Polarized light micrographs of the (E-A)C/DCA solutions, 25 °C

Fig. 1 also shows that the birefringent textures are different between biphasic and unitary mesophase solutions. In the biphasic solution, there is a disc-like texture at lower concentration but at higher concentration there is an oily streaks texture. In the unitary mesophase solution there is the oily streaks texture, too. But this texture is destroyed with increasing concentration and domains become more and more but smaller and smaller. Finally, there is only the texture of domains gathered randomly at the certain concentration.

Stein and his colleagues^[7] have confirmed that the SALS H_v pattern of the cholesteric liquid crystals is four-leaf shape. We have also found that the (E-A)C/DCA mesomorphic solutions give the four-leaf H_v pattern of which the diameter increases with the increase of the concentration (Fig. 2). This confirms that the element of scattering in the cholesteric phase or the size of the domains decreases with increasing concentration.

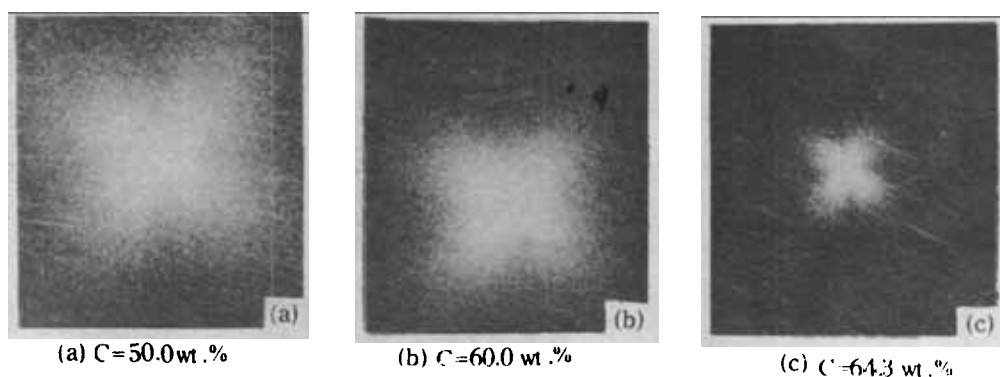


Fig. 2 SALS H_v patterns of the (F-A)C / DCA solutions .

For the oily streaks texture, when the sample is rotated to the oily streaks are parallel to the polar direction of the polarizer or the analyser, it is observed that the oily streaks are divided into many segments of which the length is about $1 - 100 \mu\text{m}$. Moreover, the oily streaks are composed of many equidistant parallel bands. The other parts of the solution look as if they are isotropic. But in fact they are anisotropic lamellar phase and their birefringence is very weak. This is a pseudoisotropic texture^[8] which has been found in lyotropic liquid crystals of many small organic molecules.

In the biphasic solution, we can see the formation of the round aggregate of mesophase (Fig. 3) which can flow with the solution when the slide is tilted slightly. The aggregates can contact with each other and combine to form a bigger one if they are on the same plane (Fig. 3a, b and c) but can not contact if they are on the different planes (Fig. 3d and e). This can be confirmed by focusing the aggregates of mesophase in the polarized microscope. The thickness of the solution layers between two slides, which is measured with a micrometer, is about $10 - 30 \mu\text{m}$. The diameter of the round aggregates of mesophase can be as large as $100 \mu\text{m}$. Therefore, the round aggregates of mesophase in plane are discal instead of spherical in space. The vertical distance between two round aggregates of mesophase, which has been measured by adjusting the focus of them correctly, is about $5 - 20 \mu\text{m}$. Then, the thickness of the round aggregates is not larger than $25 \mu\text{m}$. Nishio and his colleagues^[9] believed that the disc-like structure was a basic structural element in the mesophase after they observed the hydroxypropyl cellulose film casting from mesomorphic solutions by electron microscopy. But the diameter of the disc-like structure they have observed is 1-2 power smaller than that of the disc-like aggregates of mesophase we have observed.

The discal aggregates of mesophase form quickly and can exist steadily for a long time. They can be destroyed by a small force but re-form in several minutes after the force is removed. This mesophase texture has also been observed in poly- γ -benzyl-L-glutamate^[3,10], ethyl cellulose^[11] and hydroxypropyl cellulose^[12] lyotropic liquid crystalline solutions. It is worth to notice that all of these liquid crystals are cholesteric.

The disc-like texture of mesophase has an extinction cross in the polarized microscope under crossed polars. After inserting the compensator (λ plate) into the microscope

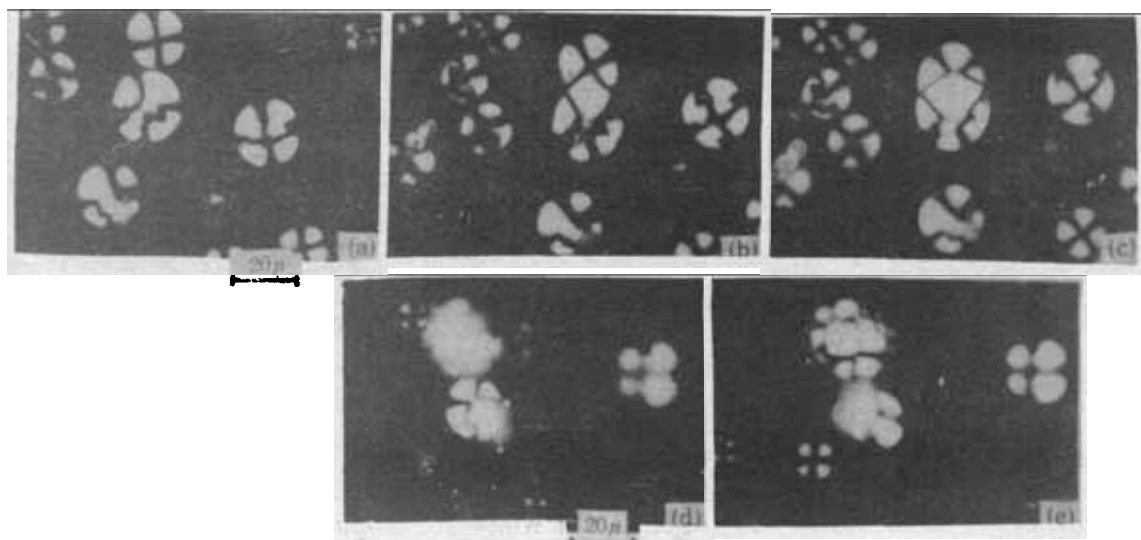


Fig. 3 Polarized light micrographs of the (E-A)C/DCA solution, 25 °C, $C = 34.4$ wt. %.

at 45 ° to the crossed polarizers, the interference color in the first and third diametrically opposed quadrants of the cross is yellow and in the second and fourth ones is blue. This indicates that the disc-like texture is negative in optics. If the solution is sheared, the band-like texture forms and the molecular chains orient along the shear direction^[13]. On insertion of a first-order plate at 45 ° to the crossed polarizers, the bright and dark bands become alternately blue and yellow. If the sample is rotated, with the crossed polarizers fixed, the interference color is yellow at all when the bands cross the first and third diametrically opposed quadrants of the cross and blue at all when the bands cross the second and fourth ones. The bands are perpendicular to the orientation direction of the molecular chains. Then, the orientation direction of molecular chains in the discal aggregate are perpendicular to the radial directions.

Some disc-like textures consist of two parts and form a core-shell structure in which the smaller disc inserts in centre of the larger one (Fig. 4). The birefringence of the shell is stronger than that of the core. In other words, the degree of order for the molecular chains in the shell is higher than that in the core. In a few of disc-like textures, molecular chains disorder wholly in the core, i. e., the core is isotropic and the shell is anisotropic (Fig. 4b).

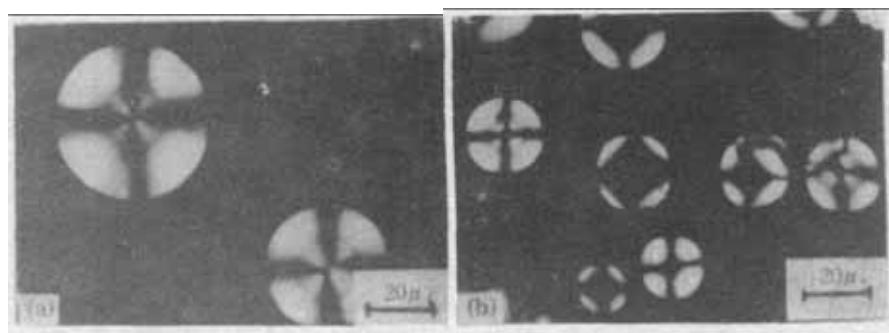


Fig. 4 Polarized light micrographs of the (E-A)C/DCA solution, $C = 32.2$ wt. %, 25 °C.

There are finer structures in the disc-like texture. Fig. 5 shows that the disc-like texture is made up of a series of concentric extinction rings around the centre of each discal aggregate. The distance between two rings is about $0.1 - 1.0 \mu\text{m}$. This ring structure has also been observed in polyethylene spherulites^[14] and this phenomenon is due to a co-ordinated twisting of the crystalline lamellae leading to a situation where periodically the observation direction is down an optic axis.

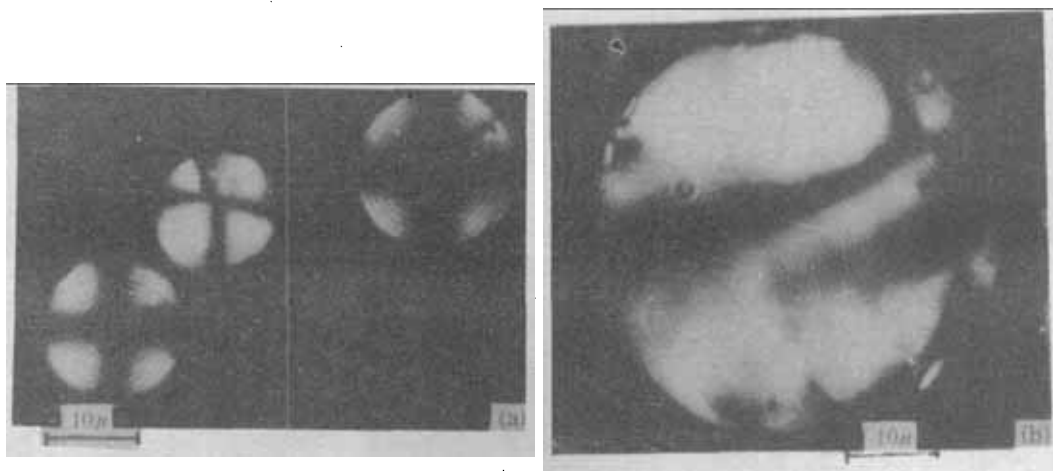


Fig. 5 Polarized light micrographs of the (E-A)C / DCA solution, $C = 33.3 \text{ wt. \%}$, 25°C .

The cholesteric liquid crystal is helical structure (Fig. 6). As mentioned above, the orientation direction of the molecular chains is perpendicular to the radial direction in the disc-like texture.

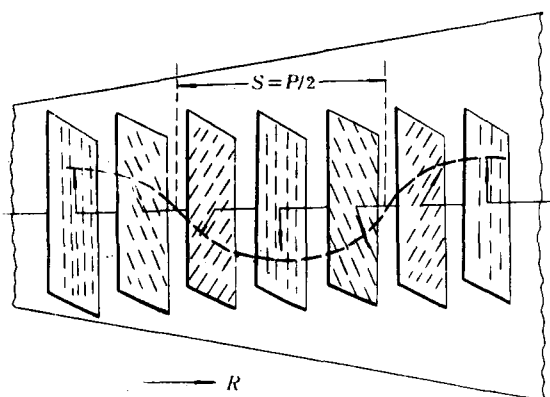


Fig. 6 Scheme of the helical structure in cholesteric phase.

Then, it is believed that the axes of the helical structure are parallel to the radial directions and the layers of the ordered molecular chain are perpendicular to them (Fig. 7). The distance between two rings is equal to half pitch. All disc-like textures of the cholesteric liquid crystal for polymer solutions may be concentric ring structure. But in many cases, the rings can not be distinguished clearly and only the round structures are observed in plane because the pitch is too small or many helical structures are

overlapped. The pitch decreases with increasing the concentration^[2]. The ring structure in the cholesteric phase can be seen at lower concentration where the pitch is larger but cannot be seen at higher concentration where the pitch is smaller.

In some cases, the axial direction of the helicoid in the disc-like texture are not along the radial directions but are nearly parallel each other at the same direction (Fig. 5b). The extinction cross can not be seen in the polarized microscope. But the aggregate is still round in plane and the dark and bright bands of half pitch width are very clear.

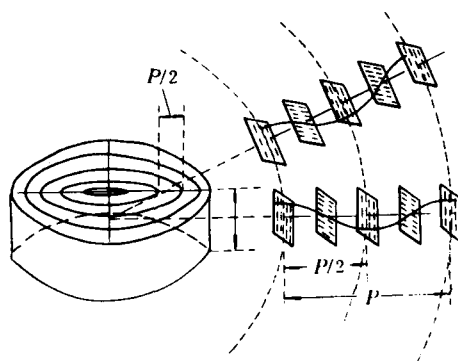


Fig. 7 Scheme of the disc-like aggregate of cholesteric phase.

CONCLUSIONS

The (E-A)C / DCA mesomorphic solutions show different birefringent textures at different concentration. The compatibility of the anisotropic and the isotropic phases is poor in the biphasic solutions. In the cholesteric phase, the layers of the ordered molecular chain can be perpendicular to the slide surface and gather to form the disc-like texture and oily streaks texture. When the concentration is high enough, the aggregates of mesophase are formed of domains gathered randomly.

Keywords :

Ethyl-acetyl cellulose, phase separation, mesophase, texture, helical structure.

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