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Effect of Magnetic Field on the Texture of (E-A)C/DCA Mesomorphic Solution†

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The ethyl-acetyl cellulose/dichloroacetic acid anisotropic solution film could form pseudoisotropic and oily streak textures in nature and the layers of ordered polymer chains tend to being parallel to the glass slide in the former texture and perpendicular to it in the latter one. Under the effect of the magnetic field, of which the intensity was smaller than the critical value, the changes of mesophase texture were obvious when the direction of the magnetic field ($\vec{B}$) was parallel to the plane on which the helicoids lay but small when the $\vec{B}$ was normal to that. In the former case, the axial direction of helicoids ($\vec{n}$) was more agreement with each other and the degree of anisotropy was higher than that without the effect of the magnetic field. But when the magnetic field was removed, the degree of anisotropy decreased gradually. The arrangement of the helicoids which were composed of the layers of ordered polymer chains played a very important role in the changes of mesophase texture.

Keywords: ethyl-acetyl cellulose, mesophase texture, effect of magnetic field, helical structure

INTRODUCTION

The investigation of cellulose and its derivative liquid crystals has been carried out for more than one decade and is quickly developing. Cellulose and its derivatives can form mesophase in the appropriate conditions because of their semi-rigid chains.[1–3] Moreover, cellulose and its derivative liquid crystals are generally cholesteric. Ethyl-acetyl cellulose ((E-A)C) is a cellulose derivative with both ester and ether groups and can form cholesteric liquid crystals in such solvents as dichloroacetic acid (DCA) and trifluoroacetic acid (TFA).[5] In the (E-A)C/DCA mesomorphic solution, there are different mesophase textures when the concentration is different.[6] The layers of ordered polymer chains can be parallel to the glass slide or normal to it in the different textures.

The ordering and arrangement of polymer chains can vary with the effect of magnetic field. When the intensity of the magnetic field is larger than the critical value, polymer chains can orient along the direction of the magnetic field. Patel and Gilbert[4] have reported that cellulose triacetate mesomorphic solution can be changed from cholesteric to nematic phases with the effect of magnetic field, of

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which the intensity is larger than the critical value. In this case, polymer chains orient along the direction of the magnetic field. The magnetic field with the intensity smaller than the critical value, however, may influence the mesophase texture although it can not lead to any transformation from one phase to another one because the orientation of polymer chains is not changed. The mesophase texture reflects the arrangement of helicoids in cholesteric phase.[6-7] In the magnetic field of which the intensity is smaller than the critical one, therefore, the variation of the arrangement of helicoids in cholesteric phase may play a specific role in the mesophase development. However, almost no work about this subject has been reported because the change of the mesophase texture is very small and is easy to be overlooked. In this report, the variation of mesophase textures in the (E-A)C/DCA solution with the effect of a magnetic field has been studied by polarizing microscopy.

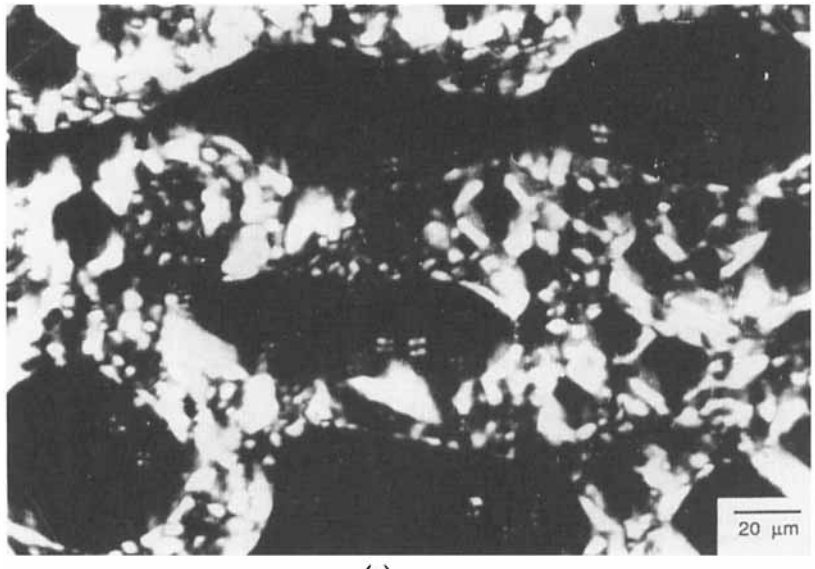
EXPERIMENTAL

The (E-A)C was obtained by ester reaction of ethyl cellulose and acetic acid. The degree of substituent, which was calculated from the carbon and oxygen contents of the (E-A)C measured by elementary analysis, for ethyl was about 1.9 and for acetyl was about 0.26. The DCA was a chemically pure reagent. The (E-A)C was mixed with the DCA at room temperature and the solution was sealed up in a test-tube. The sample was laid in at room temperature for more than 6 months after having been heated at 50°C for 10 hours. The FTIR spectrum showed the absence of dichloroacetate substituents in the solution when it was used although the DCA was a relatively strong acid. The concentration of the solution was 38.5 wt.%.

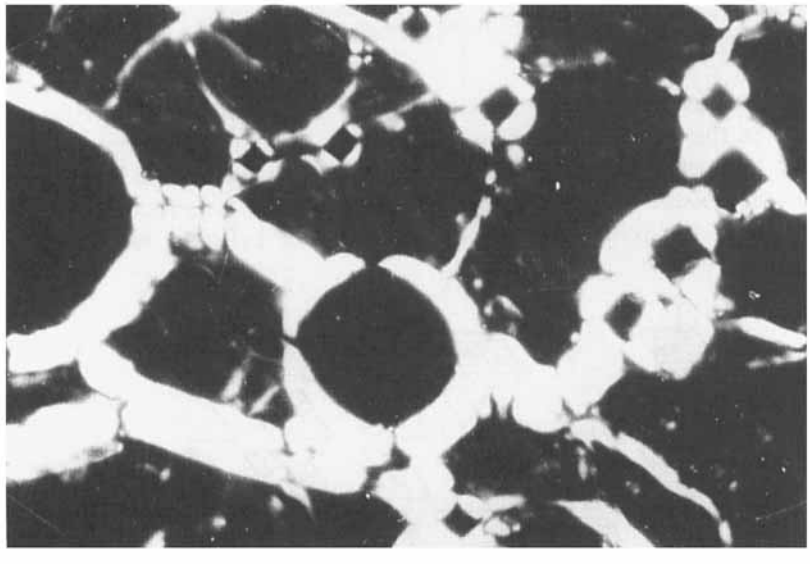
The (E-A)C/DCA mesomorphic solution was sandwiched between two slides and formed a film, of which the thickness was about 10–50 μm. The sample was sealed up by the solid perefine wax and placed in a magnetic field (the intensity was 4,300 G), of which the direction ($\vec{B}$) was parallel and perpendicular to the slides respectively. The mesophase texture of the solution film was observed by a polarizing microscope (Leitz, ORTHOPLAN-POL).

RESULTS AND DISCUSSION

When the concentration is about 38.5 wt.%, the mesophase shows the pseudoisotropic and oily streak texture in the (E-A)C/DCA mesomorphic solution.[6] Figure 1 shows the variation of mesophase texture with time when the solution film has just been formed and is out of the magnetic field. It can be seen that the mesophase is a continuous zone and there is no oily streak texture when the solution film has been formed for 5 minutes (Figure 1a). But about 20 hours later, the mesophase becomes two parts: Pseudoisotropic texture and oily streak texture (Figure 1b). In the former texture, the layers of ordered polymer chains are parallel to the slide and the axis direction of helicoids ($\vec{n}$) in cholesteric phase is perpendicular to it. In the latter texture, however, the layers of ordered chains are normal to the slide



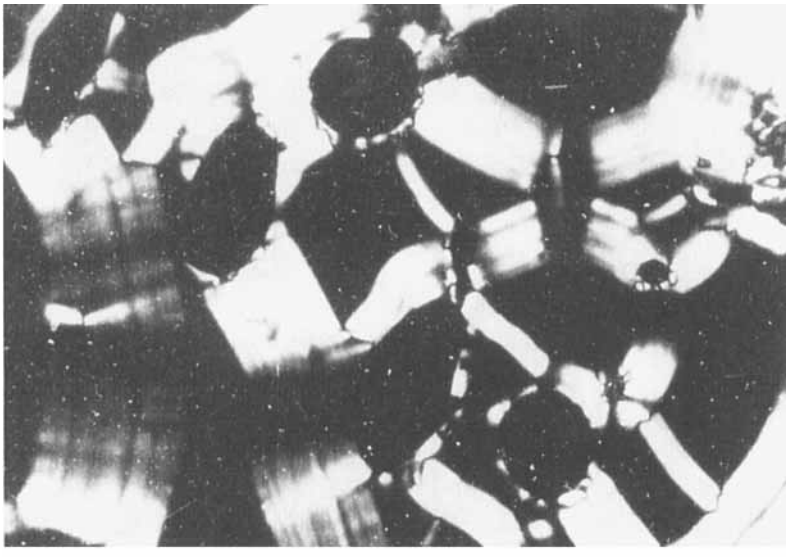
(a)



(b)

FIGURE 1 Polarized micrographs of the (E-A)C/DCA mesomorphic solution film between two glass slides for (a) 5 min, (b) 22.5 hours and (c) 16 days.

and the $\vec{n}$ is parallel to it.[6–8] But at this time, the oily streaks in the oily streak texture are narrow and short, i.e. they are small but the quantity of them is large. About fifteen days later, the streaks become wide and form the wide band (Figure 1c). These bands are composed of many narrow strips, of which the width is about 3–4 μm.



(c)

FIGURE 1 (continued)

It can be measured that the light speed is largest along the streak direction ($\vec{b}$) by means of the polarizing microscope with a tilting compensator. In cholesteric phase the light of which the vibration direction is normal to the layers of ordered chains moves fastest.[9] In the streak, therefore, the $\vec{n}$ is perpendicular to the $\vec{b}$. Figure 2 gives the scheme of the arrangement of helicoids in the streak. The

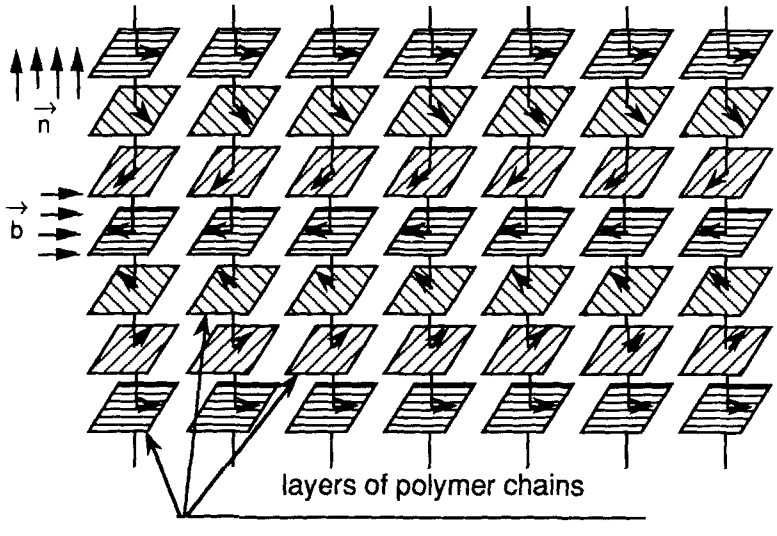
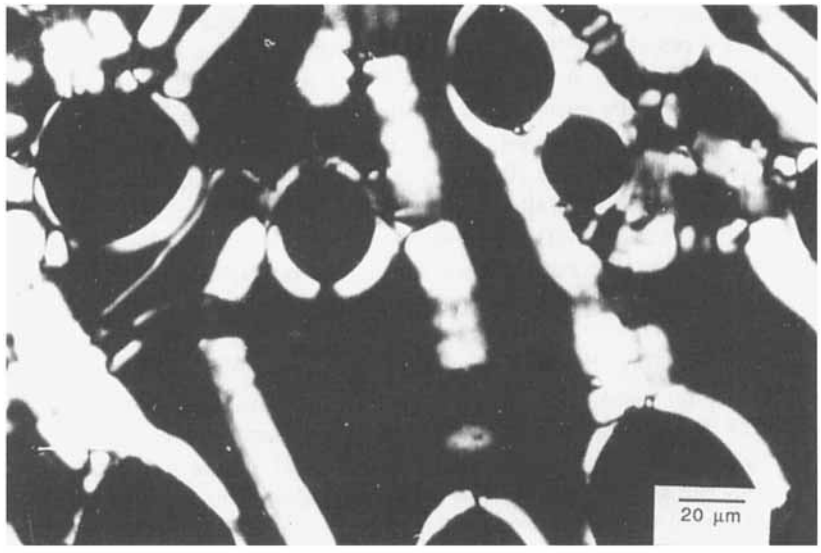


FIGURE 2 Scheme of the arrangement of helicoids in the oily streak texture.

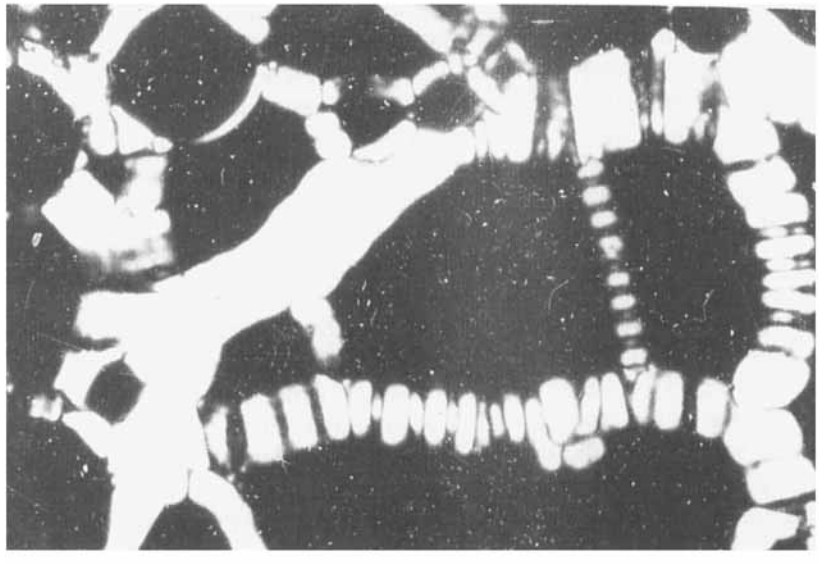
appearance of the oily streak texture in cholesteric phase under the crossed polarizing light is a result that the helicoid orders and arranges side by side along the $\vec{b}$ on the horizontal plane. It can also be found that there are some extinction zone on some streaks and they move along the streak with rotation of the sample, which indicates that the helicoids are not completely parallel with each other but change gradually and continuously in direction. Generally speaking, when the solution forms the film between two slides, the layers of ordered chains can be a state between parallel and normal to the glass plane because of the reaction of the external force. But in the equilibrium state, the axes of helicoids tend to being parallel (in the oily streak texture) or perpendicular (in the pseudoisotropic texture) to the glass plane.

The oily streak texture, however, is changed by the magnetic field whose direction $\vec{B}$ is parallel to the glass slide. There are still the pseudoisotropic and the oily streak textures in mesophase after the solution is placed in the magnetic field for about 20 hours (Figure 3a), which indicates that this magnetic field is not strong enough so that the polymer chains do not orient along the $\vec{B}$. But in comparison with the situation in which the sample is out of the magnetic field (Figure 1b), the streak is wider and longer now. Similarly to the case in Figure 1 at this time, there are extinction zones in some streaks and they move along the streak when the sample is rotated. Therefore, the axes of helicoids are still not completely parallel with each other. After having been placed in the magnetic field for about half month, the streak is divided into a few of segments, which are about 2–8 μm long, under the crossed polarizing light when the $\vec{b}$ is parallel or normal to the polar directions of the polarizers ($\vec{P}$ and $\vec{A}$). When the sample is rotated, no extinction zone moves along the streak. These results indicate that the degree of anisotropy in the streak has been increased. The $\vec{n}$ is completely agreement in each segment from one side of the streak to another one, but slightly different from the neighbouring segment and the layers of ordered chains are also not parallel between two neighbouring segments, which is schematically shown in Figure 4.

After having been in the magnetic field for about fifteen days, the sample is removed from it and laid at room temperature. More than another fifteen days later, the structure of the streak has been changed (Figure 5). When the $\vec{b}$ is nearly parallel or normal to the polar direction of the polarizer, the streak is divided into a few of small segments in the direction not only parallel to the $\vec{b}$, but also normal to the b. The segment is about 2–8 μm along the $\vec{b}$ and 3–4 μm in the direction normal to the $\vec{b}$. The latter dimension is approximately the same as that of the strip in Figure 1c. Furthermore, the longer the sample is laid outside the magnetic field, the more this kind of texture appears in solution film. The results mentioned above indicate that there is a relaxation process for the oriented state after the magnetic field is removed. The difference of $\vec{n}$ between the segment in the streak causes that the streak is divided into a few of pieces along the $\vec{b}$ under the crossed polarizing light. Similarly, because the streak is wide, several helicoids arrange in the head-to-end state on the same across section. The streak can also be divided into several segments in the direction vertical to the $\vec{b}$ under the crossed polarizing light when the $\vec{n}$ is not completely agreement on the same across section. If the $\vec{n}$ is parallel with each other along the $\vec{b}$, it can be seen that the streak is composed



(a)



(b)

FIGURE 3 Polarized micrographs of the (E-A)C/DCA mesomorphic solution film in magnetic field for (a) 22.5 hours and (b) 16 days, the direction of the magnetic field is parallel to the film plane.

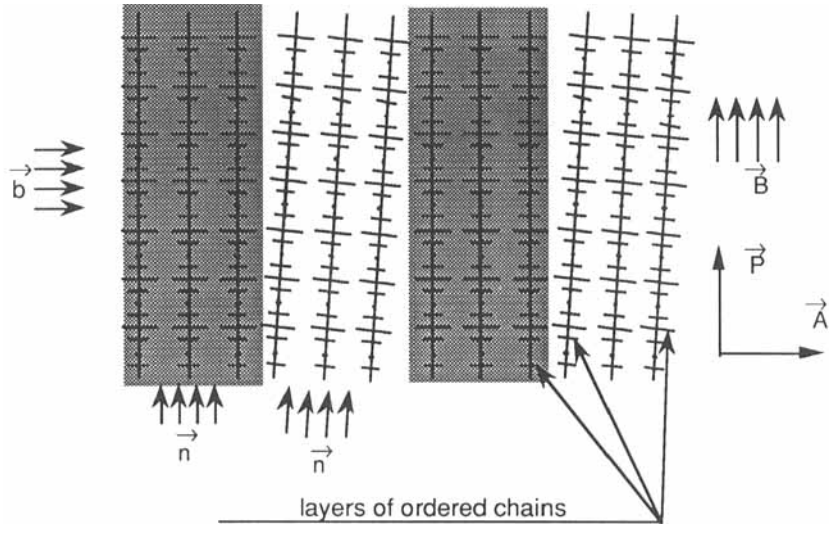
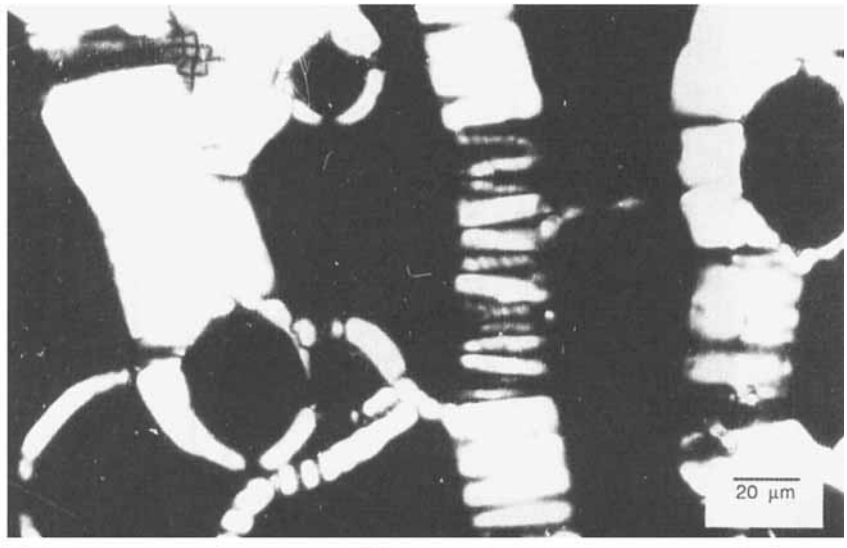


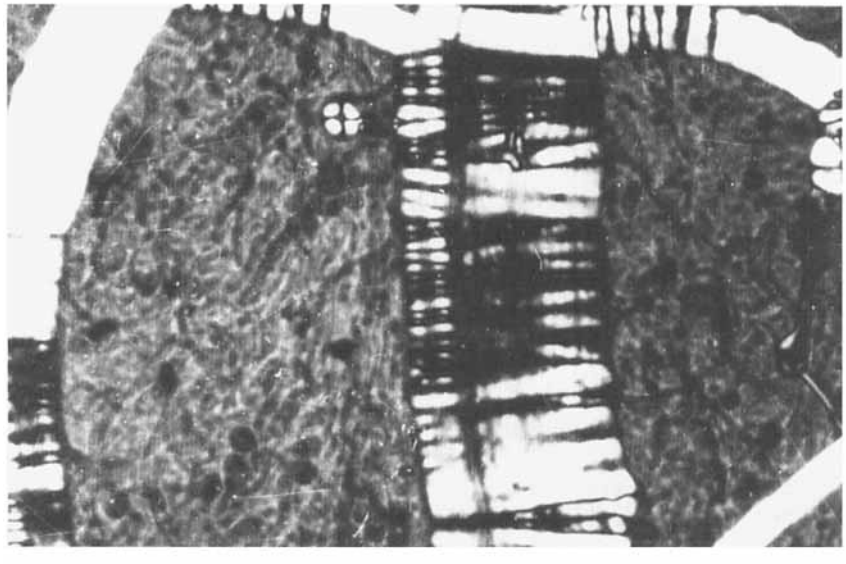
FIGURE 4 Scheme of the arrangement of helicoids in the oily streak texture in the magnetic field.

of a few of narrow strips like those in Figure 1c. Under the effect of the magnetic field the helicoids align in some across sections as shown in Figure 4, and the narrow strips disappear in the streak. But after the magnetic field is removed, the helicoids in the same across section become out of alignment because of their orientation relaxation. They alternatively deviate from the original direction (normal to the $\vec{b}$) left and right and form a sawtooth arrangement, which is similar to the texture of the oriented polymer mesomorphic solution after it is sheared.[10] The zones in which the $\vec{n}$ is parallel or perpendicular to the polar direction of the polarizers will be dark. Figure 6 demonstrates the arrangement of helicoids in these streaks. These results suggest that the degree of anisotropy decreases gradually after the magnetic field is removed.

When the $\vec{B}$ is perpendicular to the mesomorphic solution film no big streak and band can be observed under the crossed polarizing light (Figure 7). The mesophase texture is mainly pseudoisotropic. But there is strong birefringence in the mesophase near the interface between isotropic and anisotropic phases, which indicates that the $\vec{n}$ near the interface is different from that in other mesophase zones. In the pseudoisotropic phase the $\vec{n}$ is normal to the glass plane. By means of the polarizing microscope with a tilting compensator, it can be measured that the $\vec{n}$ in these strong birefringence areas is perpendicular to the interface. Near the interface, therefore, the arrangement of helicoids is similar to that in the streak. It can also be seen from Figure 7 that although the sample has been in the magnetic field for more than half and one month, the mesophase texture does not change obviously. Perhaps the arrangement of helicoids in the pseudoisotropic texture is also slightly changed with the influence of the magnetic field and only can not be observed in the polarizing microscope. It is believed, however, that the effect of



(a)



(b)

FIGURE 5 Polarized micrographs of the (E-A)C/DCA mesomorphic solution film, which has been removed from the magnetic field for (a) 17 days and (b) 45 days after in that for 16 days.

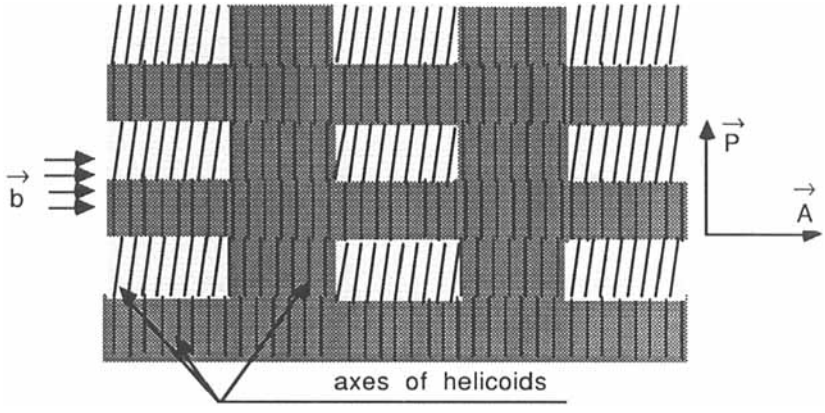
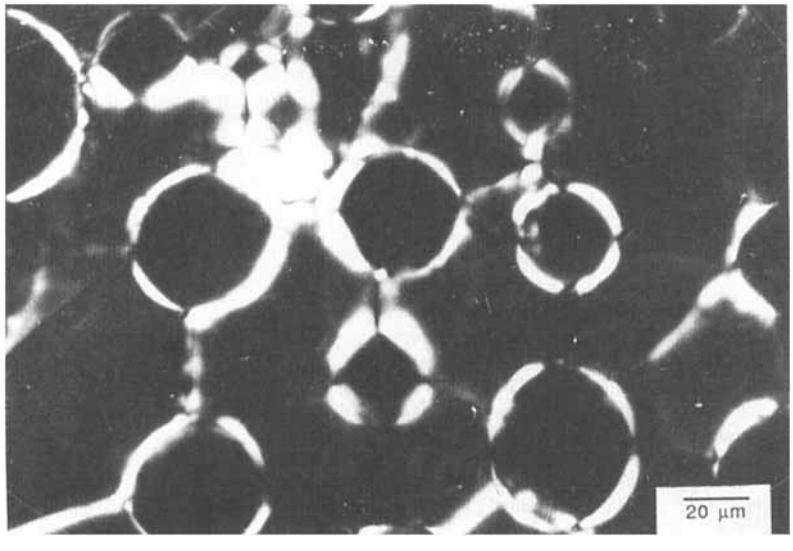


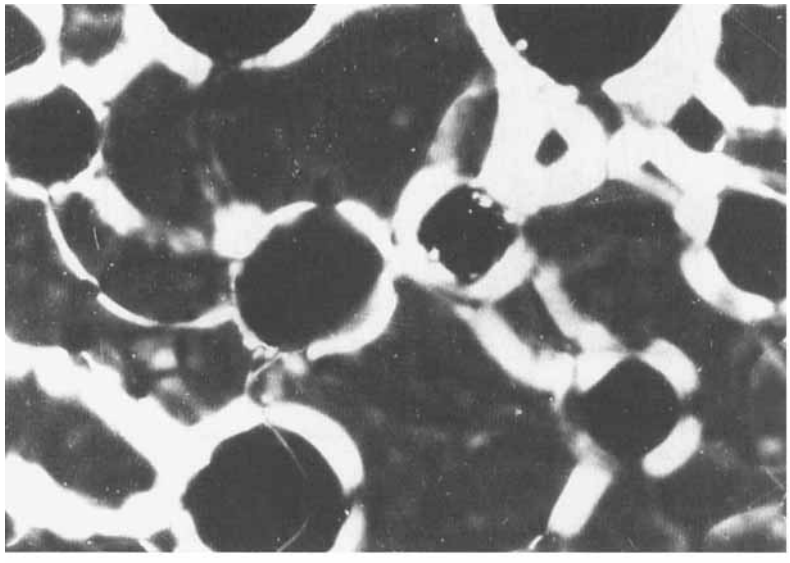
FIGURE 6 Scheme of the arrangement of helicoids in the oily streak texture after the solution film is removed from the magnetic field.

the magnetic field on the arrangement of helicoids is limited when the $\vec{B}$ is perpendicular to the plane on which the helicoids lie. The magnetic field can not cause the orientation of polymer chains along the $\vec{B}$ when its intensity is smaller than the critical one. But it can affect the arrangement of helicoids in cholesteric phase, which is responsible for the mesophase texture, when the B is parallel to the planes on which the helicoid arranges. If the $\vec{B}$ is normal to these planes, however, the influence of the magnetic field is very small on the arrangement of helicoids and the mesophase texture can not be changed obviously.



(a)

FIGURE 7 Polarized micrographs of the (E-A)C/DCA mesomorphic solution film in the magnetic field for (a) 10 days and (b) 45 days, the direction of the magnetic field is normal to the film plane.



(b)

FIGURE 7 (*continued*)

The results mentioned above also suggest that although the layers of ordered polymer chains are the most basic element of the orientation in cholesteric phase, the arrangement of helicoids has more influence on the mesophase texture. Various textures of cholesteric phase reflect the different arrangements of helicoids. The reason of the effect of the magnetic field with the intensity smaller than the critical value on mesophase texture is that the magnetic field can influence the arrangement of helicoids in cholesteric phase. It is believed, therefore, that the helicoid is a basic element in founding the mesophase architecture. In other words, the mesophase texture mainly depends on the arrangement of helicoids.

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