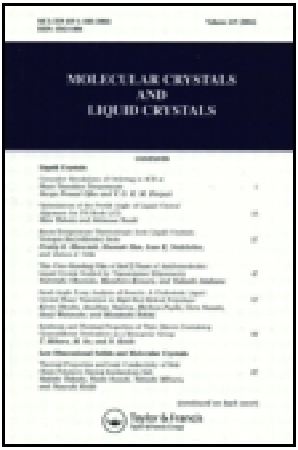

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The Planar Texture of Ethyl-acetyl Cellulose Mesophase

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The Planar Texture of Ethyl-acetyl Cellulose Mesophase

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Ethyl-acetyl cellulose ((E-A)C)/dichloroacetic acid (DCA) cholesteric liquid crystalline solution could form a homogeneous planar texture which exhibits a vivid colour. In the planar texture, there were two kinds of domains which had a homogeneous structure and a periodically changed structure, respectively. The increase of both concentration and temperature could cause a change of the wavelength of selective reflection arising from the cholesteric phase to shorter wavelength. The cholesteric phase had different colours when the incident angle and the reflecting angle were changed. The colour of the (E-A)C/DCA cholesteric phase had a higher thermal stability than that of small organic molecule cholesteric phase.

INTRODUCTION

Cholesteric liquid crystals exhibit unique optical properties arising from the selective reflection of light by the helicoidal arrangement of molecules. If cholesteric liquid crystals with the planar texture are viewed under the polarizing microscope, the field of view is one colour threaded by lines (disinclination lines) which separate the field into domains. Microscopic observation of the cholesteric phase with the planar texture exhibits a vivid colour if illuminated with white light under conditions in which the pitch of the helix corresponds to the wavelength region for visible light. The planar texture of cholesteric liquid crystals can appear either spontaneously or in the converting process from the focal-conic texture to the planar texture by mechanical disturbance of the cholesteric liquid crystal film.[1] The planar texture is stable if once formed. If an orienting influence is not present which causes a conversion to the focal-conic texture, the planar texture will persist. However, as Dixon and Scala[2] have found, dust and fiber particles can provide such a reorientation influence and for this reason cleanness in the fabrication of long life cholesteric liquid crystal film is essential.

Cellulose and many of its derivatives can form liquid crystals in the appropriate conditions because of their semirigid backbone[3–5] and moreover, most of cellulose derivative liquid crystals are cholesteric.

Ethyl-acetyl cellulose ((E-A)C) is a cellulose derivative with both ester and ether groups. It can be dissolved in the organic acid solvents such as trifluoroacetic acid (TFA), dichloroacetic acid (DCA) and acetic acid and form cholesteric liquid crystals when the concentration is high enough.[6] At room temperature, the texture of the (E-A)C/DCA mesomorphic solution varies with the concentration.[7] Mesophase can show disk-like texture, oily streak texture, pseudoisotropic texture and homogeneous planar texture. In the present paper, we study the features and the optical properties of the planar texture in the (E-A)C/DCA cholesteric liquid crystalline solution and examine the dependence of the selective reflection on the concentration and the temperature of the solution.

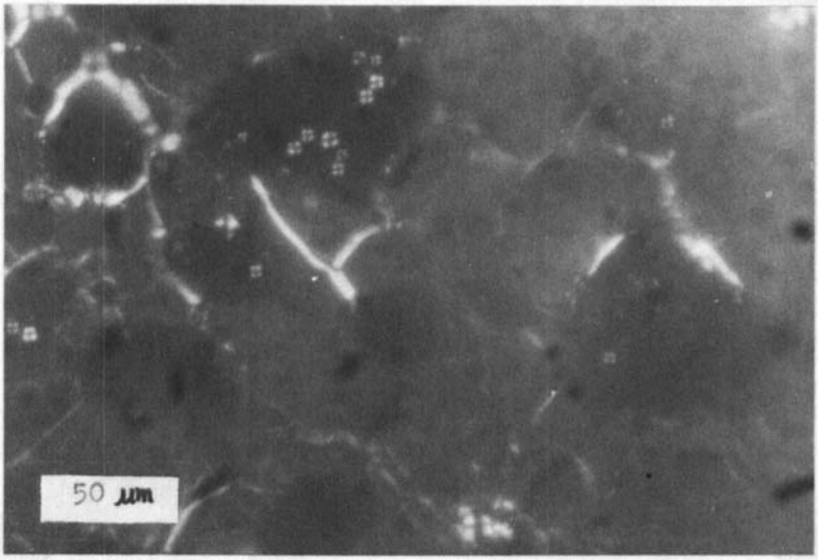
EXPERIMENTAL

The (E-A)C was obtained by the ester reaction of ethyl cellulose and acetic acid. The degree of substitution for ethyl was about 1.82 and for acetyl was about 0.26, which were calculated from the carbon and the oxygen contents of the (E-A)C measured by elementary analysis. The DCA was a chemically pure reagent. The (E-A)C was 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 solution was stored at room temperature more than 6 months in order to obtain the equilibrium solution until used. The IR spectrum showed the absence of dichloroacetate substituents in the solution.

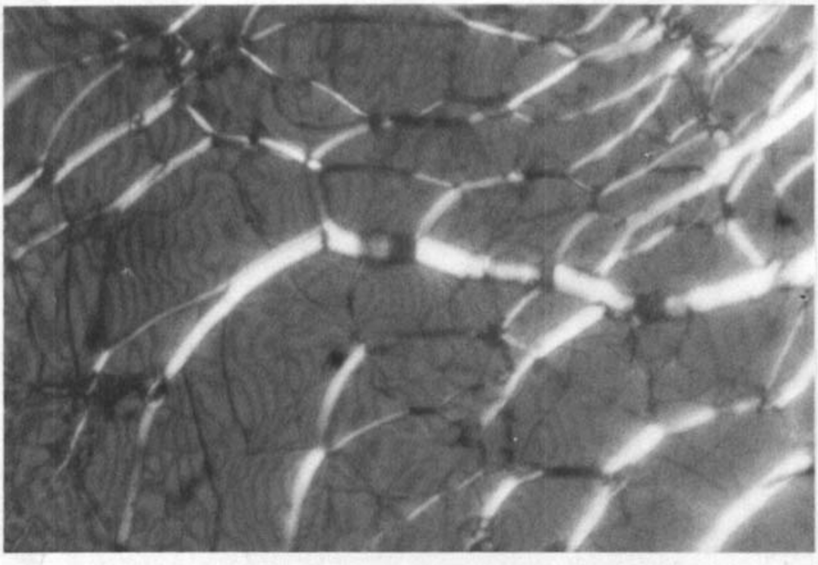
The solution was sandwiched between a microscope slide and a cover glass and formed a solution film which was about 10–30 μm in thickness. The texture of the mesomorphic solution was observed by a polarizing microscope (Leitz, ORTHO-PLAN-POL). The visible spectra of the solution were recorded with an UV-VIS spectrophotometer and the change of the colours of the mesomorphic solution was observed by the naked eye at different temperatures.

RESULTS AND DISCUSSION

The texture of the (E-A)C/DCA cholesteric liquid crystalline solution varies with the concentration. At the incipience of the formation of mesophase, the disk-like texture appears at first in the solution. With increasing concentration, mesophase can also show the oily streak texture and pseudoisotropic texture. The homogeneous planar texture, which shows a vivid colour, is formed in the solution at a higher concentration.[6,7] Figure 1 shows the variation of the planar texture of the solution with the concentration. Firstly, with the variation of the concentration the planar texture of cholesteric phase exhibits different colours under polarizing microscope. The planar texture is red when the concentration is about 36.5 wt% and blue when it is about 53.5 wt%, which means that the colour of the mesomorphic solution changes to the shorter wavelength with increasing concentration. Secondly, it can be seen from Figure 1 that there are a few of bright strips, which are oily streaks. In turn, there coexist both the planar texture and the oily streak texture in the

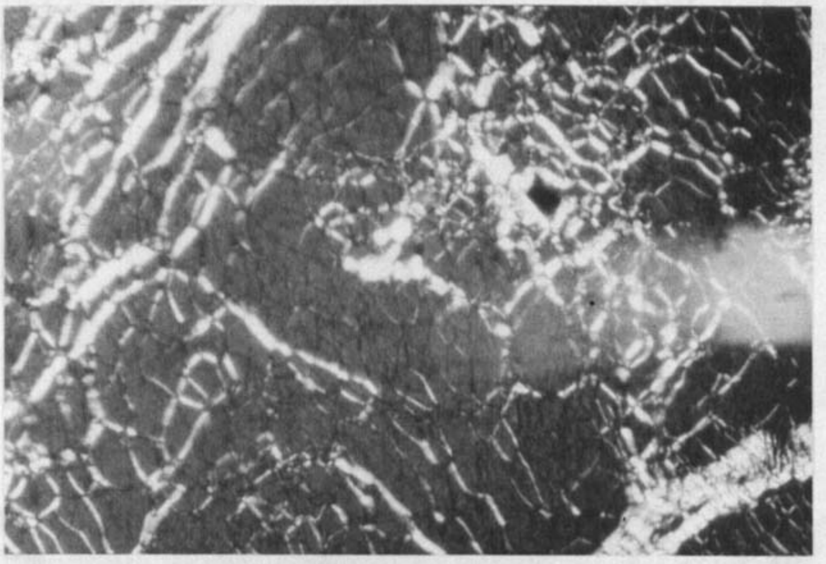


(a) C=36.5 wt.%

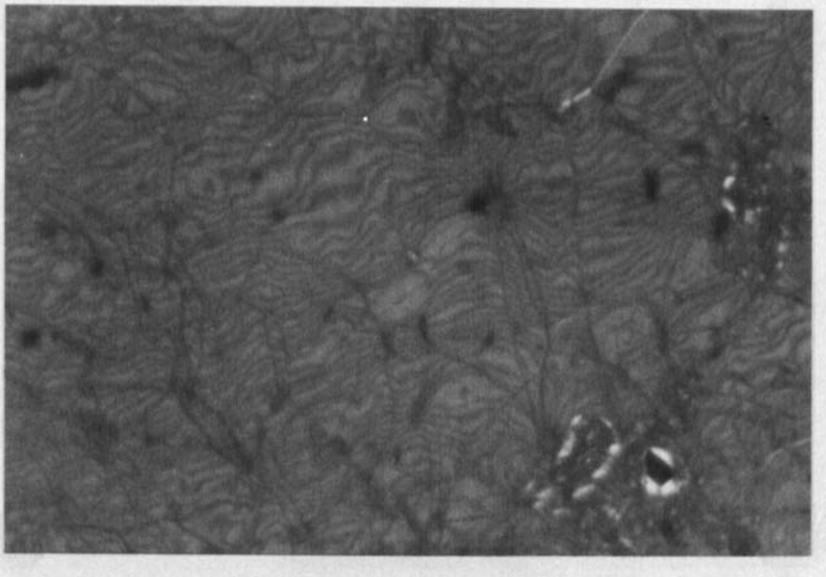


(b) C=48.7 wt.%

FIGURE 1 Planar textures of the (E-A)C/DCA mesomorphic solutions. See Color Plate III.



(c) C=51.2 wt.%



(d) C=53.5 wt.%

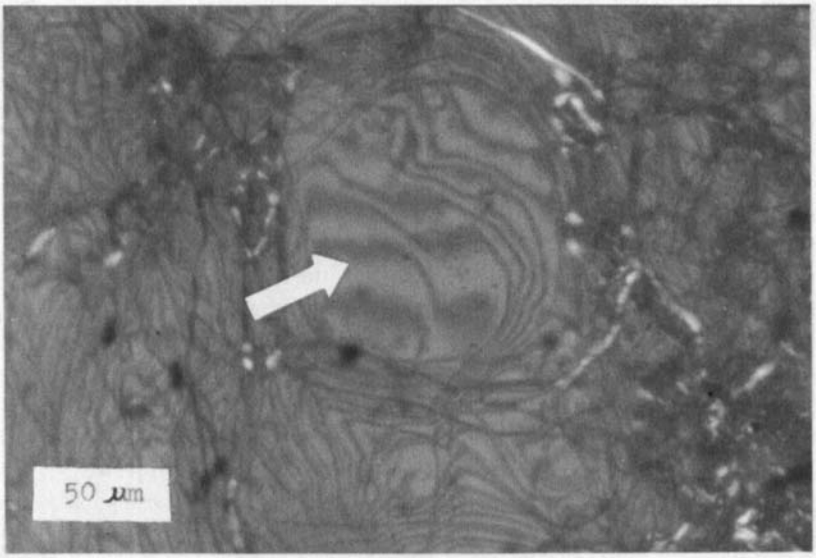
FIGURE 1 Continued. See Color Plate IV.

mesophase. In the former texture, the layers of ordered polymer chains are parallel to the solution film and the axes of the helicoids of cholesteric phase are perpendicular to it. But in the latter texture, the layers of ordered polymer chains are perpendicular to the solution film and the axes of the helicoids of cholesteric phase are parallel to it. Under the crossed polarizing light, therefore, the optical effect and feature of these two textures are different.

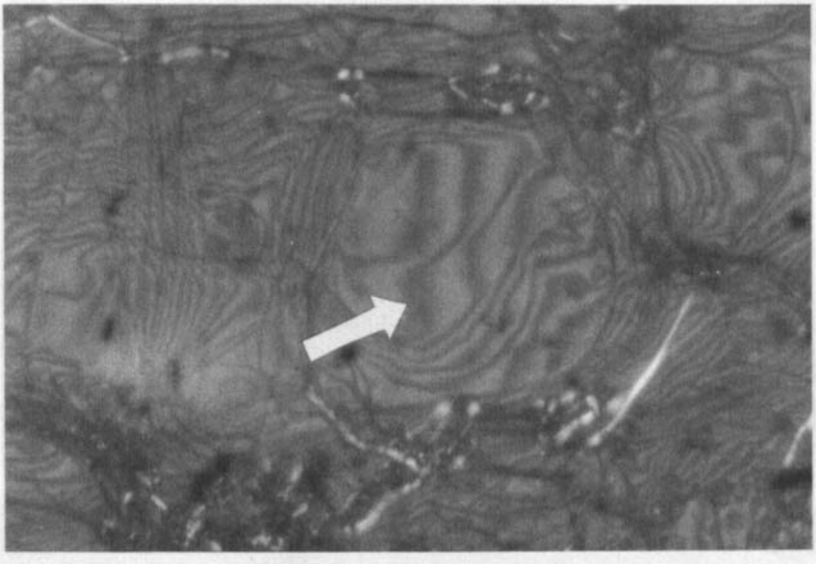
Furthermore, a few of dark strips can be observed in the mesophase except the bright strips. Some of them are wide and dark strips and the other are narrow ones which have the colour deeper than the background (Figure 2). These two kinds of strips are obviously different from those in the oily streak texture mentioned above. Under the crossed polarizing light the wide and dark strips can move with the rotation of the sample. The translational periodicity can appear after the sample is rotated from 0° to 180°. The narrow strips with the deep colour, however, cannot be changed with the rotation of the sample. These phenomena may suggest that the reasons of the appearance of these two kinds of strips are different. The narrow strips with the deep colour divide the mesophase into small areas, in which the optical behaviour and appearance are uniform. It is believed that these small areas are domains existing in the mesophase. Within the domains, the layers of ordered polymer chains with the same orientation direction are on the same plane, and therefore, the domains show the uniform optical behaviour and appearance. Between two neighbouring domains, however, the layers of ordered polymer chains with the same orientation direction are on the different planes, i.e. in the interface between the domains. In other words, the layers of ordered polymer chains with the same orientation direction are dislocated. As a consequence, the pitch of the cholesteric phase can actually become smaller at the interface between the domains, which causes the change of the selective reflection of cholesteric phase towards the short wavelength and even out of the visible light region. It is believed, therefore, that the narrow strips with the deep colour in the planar texture are boundary of the domains in the mesophase.

Especially in the large domains, there are several wide and dark strips which vary periodically with the rotation of the sample (the bold arrows indicated in Figure 2), which reflects the existence of the periodically changed structure in the domains. In these domains, the axes of the helicoids of cholesteric phase are perhaps inclined to each other and normal to the glass surface so that the optical behaviour and appearance are heterogeneous. In the planar texture of the (E-A)C/DCA cholesteric liquid crystalline solution, therefore, there are two kinds of structures: one is a homogeneous structure and the other is a periodically changed structure.

Because the planar texture of the cholesteric phase can reflect light selectively in a certain wavelength, a vivid colour of the mesomorphic solution can be easily observed when the wavelength of the selective reflection is in the visible light region and the transmission light is absorbed by the blackbody. The colour of the mesomorphic solution varies with the concentration. The wavelength where the apparent absorbane is maximum caused by the selective reflection of the cholesteric liquid crystalline solution decreases gradually with increasing concentration (Figure 3), which means that the selective reflection changes to the shorter wavelength



(a)



(b)

FIGURE 2 Planar textures of the 50.0 wt% (E-A)C/DCA solution, (b) is at an angle of 90° with (a). See Color Plate V.

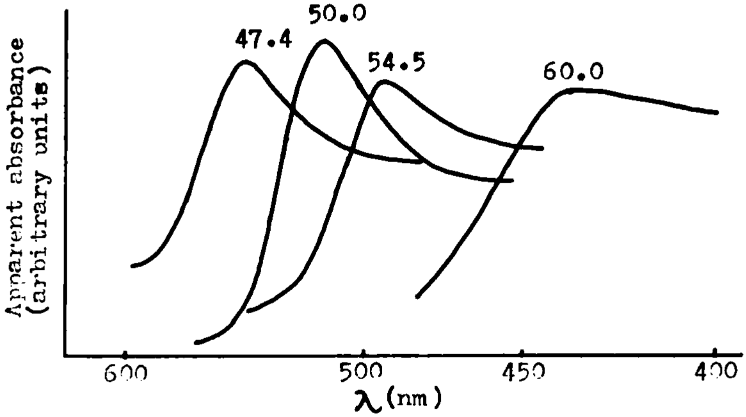


FIGURE 3 Reflection spectra of the (E-A)C/DCA mesomorphic solution as a function of the concentration, 25°C.

gradually with increasing concentration. The colour of the mesomorphic solution is red at a lower concentration and blue at a higher one.

The colour of the (E-A)C/DCA cholesteric liquid crystalline solution can also vary with the incident angle and reflecting angle. The colour of the solution changes from red to violet during the increase of the reflecting angle, i.e. the wavelength of the selective reflection changes towards the shorter wavelength. Similarly, when the incident angle increases, the wavelength of the selective reflection changes to the shorter wavelength (Figure 4) and the colour of the mesomorphic solution varies gradually from red to violet. Moreover, the changing rate of the wavelength due to the selective reflection of the cholesteric liquid crystalline solution increases when the incident angle increases.

The optical behaviour of the selective reflection for the cholesteric liquid crystals arises from the helical structure of the cholesteric phase. The axes of the helicoids are perpendicular to the solution film. The selective reflection of the cholesteric

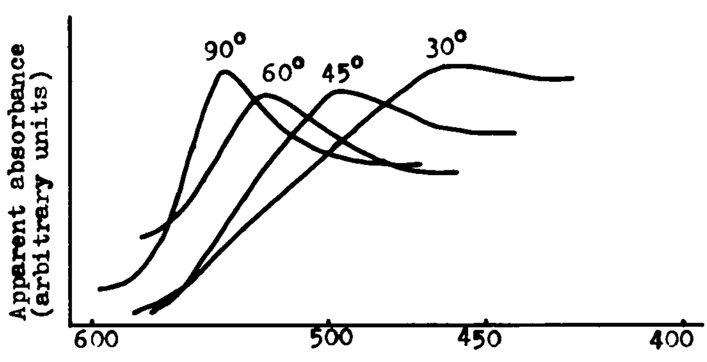


FIGURE 4 Reflection spectra of the (E-A)C/DCA mesomorphic solution as a function of the incident angle, 25°C.

mesophase is closely related with the pitch of the cholesteric phase and varies with both the incident angle and the reflecting angle. The cholesteric mesophase, therefore, shows different colours when the incident angle and the reflecting angle are changed. The variation of the wavelength of the selective reflection with the concentration also demonstrates that the pitch of the (E-A)C/DCA cholesteric liquid crystalline solution decreases with increasing concentration according to the de Vries' equation,[8] $\lambda_o = np$, where n is the average refractive index of the mesomorphic solution, measured with an Abbé refractometer and λ_o corresponds to the wavelength of the maximum reflection peak shown in Figure 3. A plot of pitch against the concentration is presented in Figure 5.

Temperature can also influence the colour of the (E-A)C/DCA cholesteric phase. It can be seen from Table I that when temperature decreases, the colour of the cholesteric phase changes to the longer wavelength, i.e. the cholesteric phase reflects the light with the shorter wavelength at a higher temperature and with the longer wavelength at a lower temperature. This result indicates that the pitch of the cholesteric mesophase decreases with increasing temperature.

Both concentration and temperature exhibit the opposite aspects for the formation and the stabilization of mesophase. The increase of the concentration is beneficial to the formation and the stabilization of lyotropic liquid crystals but the increase of the temperature can lead to the instability of the mesophase. However, the increase of both concentration and temperature can cause the decrease of the pitch of the cholesteric mesophase. When the wavelength of the selective reflection is in the infrared region, the cholesteric mesophase shows no colour. The increase

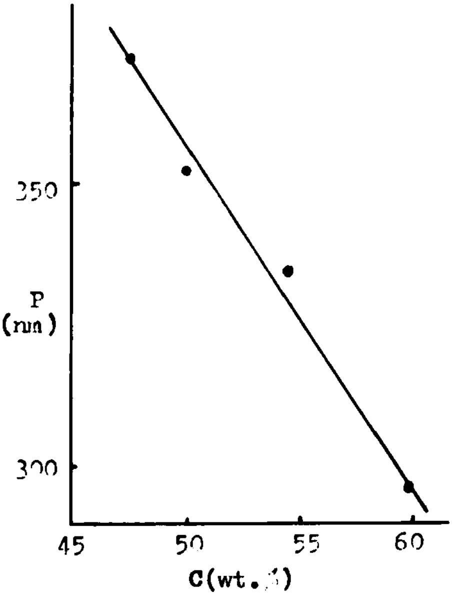


FIGURE 5 The pitch of the (E-A)C/DCA cholesteric liquid crystalline solution as a function of the concentration, 25°C.

TABLE I

Colours of the (E-A)C/DCA mesomorphic solutions at different temperatures

temp. (°C) / concn. (wt.%)	30	12	−2	−20	−40
47.4	yellow	yellow + red	red	red	red
50.0	green	green + yellow	green + yellow	yellow	yellow + red
54.6	dark green	green	green + yellow	yellow	yellow
60.0	blue	blue	dark green	dark green	green

of temperature of the solution may lead to change of the wavelength of the reflection towards the visible light region. In addition to this, it also causes the transformation from the anisotropic phase to the isotropic one and the decrease of the optical effect of the mesomorphic solution. In this case, therefore, the solution cannot show any vivid colour with increase of temperature. The increase of concentration, however, can not only decrease the pitch of the cholesteric mesophase resulting in the change of reflection wavelength from the infrared region to the visible light region, but also be beneficial to the stable existence of the mesophase and to the increase of the optical effect of the liquid crystalline solution. As a consequence, increasing concentration is more beneficial than increasing temperature to obtain a cholesteric liquid crystalline system with a vivid colour.

The colour for the cholesteric liquid crystals of small organic molecules is also varied from red to violet with increasing temperature.[9] However, the range of temperature for colour change in the cholesteric liquid crystals of small organic molecules is very small. The cholesteric mesophase can change colors from red to violet only within the temperature range of twenty degrees. For the (E-A)C/DCA cholesteric mesophase, however, changing only one color to the other, i.e. from red to yellow, or from yellow to green, or from green to dark green and so on, needs the temperature range of twenty or thirty degrees or even more. From these observations, it may be concluded that the color of the (E-A)C/DCA cholesteric liquid crystalline solution is more thermally stable than that of the cholesteric liquid crystals of small organic molecules.

CONCLUSIONS

The (E-A)C/DCA cholesteric liquid crystalline solution shows the homogeneous planar texture in a certain concentration range. In the planar texture, there are two kinds of domain structures: One is a homogeneous structure exhibiting a uniform optical behaviour and appearance. The other is a periodically changed structure.

The increase of both concentration and temperature can lead to a variation of the wavelength of the reflection towards the shorter wavelength, i.e. the decrease of the pitch of the cholesteric mesophase. The wavelength of the reflection can also change to the shorter wavelength with the decrease of the incident angle and the reflecting angle which results in the color change of the mesomorphic solution from red to violet. The color of the (E-A)C/DCA cholesteric liquid crystalline solution is more thermally stable than that of small organic molecular cholesteric phase.

Acknowledgment

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