

Textures of Ethyl Cellulose–Dichloroacetic Acid Mesomorphic Solution

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SYNOPSIS

Textures of the ethyl cellulose (EC)–dichloroacetic acid (DCA) mesomorphic solution were studied systematically by polarizing microscopy and small-angle light scattering. It was found that with increasing polymer concentration, the mesophase could show a disklike texture, an oily streak texture, a pseudoisotropic texture, and an iridescent planar texture. Within the mesophase the ordering degree is different in different zones. The phase transition between anisotropic and isotropic phases could also be accomplished by changing temperature. With increasing temperature the mesophase with the lower degree of order could first transform to the isotropic phase and the phase transition from an anisotropic phase with a higher degree of order to the isotropic one could take place only at the higher temperature. A disklike texture was also observed during the phase transition between the anisotropic and isotropic phases when the solution was heated and it was probably a basic texture in polymer cholesteric liquid crystals.

INTRODUCTION

Cellulose and many of its derivatives can form liquid crystals in many solvent systems because of their semirigid backbone.^{1–3} Panar and Willcox¹ have reported that ethyl cellulose (EC) can form liquid crystals in acetic acid, tetrachloromethane, and trifluoroacetic acid. Bheda et al.⁴ have found that EC can form a mesophase in dichloroacetic acid (DCA). Suto⁵ has studied the rheological properties of the EC–chloroform mesomorphic solution. Nishio et al.⁶ have studied the morphology and structure of EC films cast from the liquid crystalline solution. Until now many studies about the EC mesophase have been reported, but the texture of the EC mesophase and its variations with both concentration and temperature have still not been systematically reported.

Separation or permeation of gases through EC films and sorption of gases in EC films have been reported^{7–10} by a few of researchers. Therefore, it is possible for EC to be used as a gas or liquid separation film material. It is very important to understand the solution structure in casting films because

the film morphology and structure and its properties can be changed to some extent with the structure of the mesomorphic solution. The mesophase texture is one of the key factors to influence the film structure and its properties because EC can form a mesophase in many solvent systems at the concentration over the critical value.

We have reported^{11,12} that the mesophase of the ethyl-cyanoethyl cellulose and ethyl-acetyl cellulose in dichloroacetic acid can show a disklike texture, oily streak texture, pseudoisotropic texture, and homogeneous planar texture at different concentrations. The mesophase texture is also greatly influenced by the solution temperature. In this report the textures of the EC–DCA solution and the influence of both concentration and temperature on the mesophase texture are studied by polarizing microscopy and small-angle light scattering. The selective reflection of the planar texture in the mesomorphic solution is also discussed.

EXPERIMENTAL

The EC sample used in this study was of commercial reagent grade (Guangzhou Chemical Reagent Factory) of which the degree of polymerization was

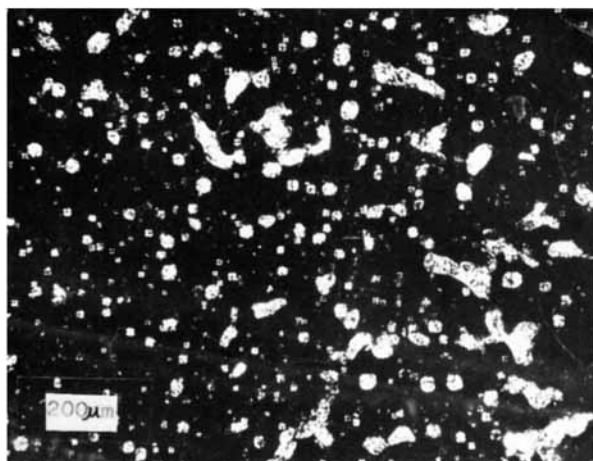
about 160 and the degree of substitution with ethyl groups was about 2.1. The DCA was a chemically pure reagent. The EC was mixed with the DCA at room temperature and the solution tightly sealed in the test tube. The sample was heated at 50°C for 10 h and then stored at room temperature for about 12 months in order to obtain an equilibrium solution until it was used. The FT IR spectrum showed the absence of esterification of the EC polymer by the solvent although it is a strong acid when the solution was used.

The EC-DCA liquid crystalline solution was sandwiched between microscope slides and formed a solution film about 10–30 μm thick. Mesophase textures were observed by a polarizing microscope (Leitz, ORTHOPLAN-POL). The sample was

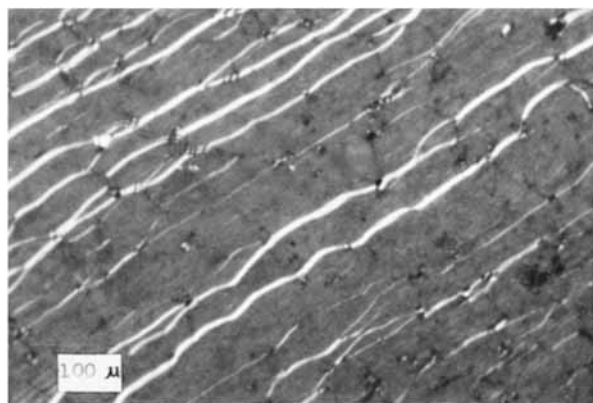
heated by a hot stage (Leitz, Microscope Heating Stage 350) and the heating rate was less than 1°C/min. A small-angle laser light scattering instrument (LS-1, China) was employed to observe the small-angle light scattering (SALS) patterns of the solution. The visible spectrum of the mesomorphic solution was recorded with an UV-VIS spectrophotometer (Carl Zeiss Jena, SPECORD UV-VIS) at room temperature.

RESULTS AND DISCUSSION

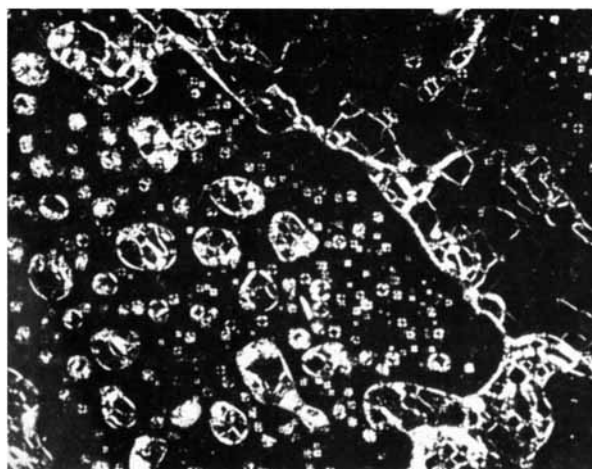
The EC-DCA solution begins to form a mesophase at concentrations of about 25.9 wt % [Fig. 1(a)]. At this time, however, the mesophase is noncontinuous and liquid crystalline aggregates are dispersed in the isotropic phase. The proportion of the mesophase increases with increasing polymer concentration, and the mesophase gradually changes to a



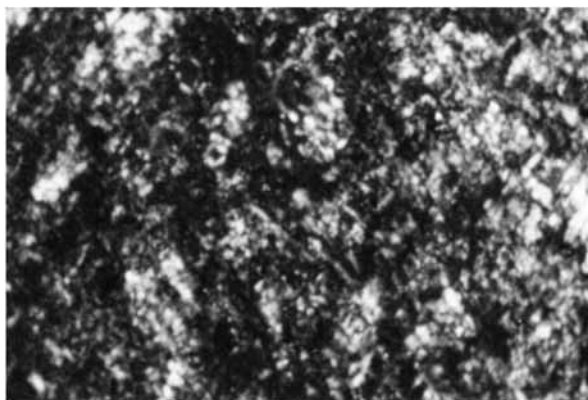
(a) $C=25.9$ wt. %



(c) $C=31.0$ wt. %



(b) $C=28.6$ wt. %



(d) $C=39.4$ wt. %

Figure 1 Polarized light micrographs of the EC-DCA mesomorphic solutions at different concentrations of EC, 25°C. (a) $C = 25.9$ wt %; (b) $C = 28.6$ wt %; (c) $C = 31.0$ wt %; (d) $C = 39.4$ wt %.

continuous phase [Fig. 1(b)]. When mesophase is noncontinuous, there are many circular mesophase aggregates with the Maltese extinction cross under crossed polarizing light [Fig. 2(a)]. They can be destroyed when the cover glass is slightly pressed. A few minutes later, however, they can appear again in the solution. These circular mesophase aggregates, which can be 20–50 μm in diameter, can move with the flow of the solution, i.e., they are suspended in the solution. They can touch and merge with each other to form bigger ones when they are on the same focus plane. When they are on the different planes, however, they will be overlapped in the direction normal to the solution film and do not touch each other (Fig. 2). This can be confirmed by focusing on the mesophase aggregates in the polarizing microscope. The thickness of the solution film, which is measured with a micrometer, is about 10–30 μm , and the distance between the mesophase aggregates in the direction perpendicular to the solution film can be 10–15 μm . On the other hand, the diameter of the circular mesophase aggregates can be as large as 50 μm , which is much larger than their thickness. It is considered, therefore, that the circular mesophase aggregates with the Maltese extinction cross show a disklike texture instead of the three-dimensional spherical texture in space. After inserting the

compensator (λ plate) into the microscope with an angle of 45° to the crossed polarizers, the interference color in the first and third diametrically opposed quadrants of the cross is yellow and the second and fourth one is blue. This indicates that the disklike texture is negative in optics. The vibration direction of the larger of two refractive indices of the mesophase, which is measured by the polarizing microscope with a tilting compensator, is perpendicular to the radial direction in the disklike texture. This reflects that the axes of the helix lie in the radial direction. Figure 3 schematically shows the arrangement of the helix in the disklike texture. The layers of ordered polymer chains are normal to both the solution film and the radial direction; and the axes of the helix are parallel to both of them. The disklike mesophase texture has also been observed in the other polymer cholesteric liquid crystals.^{11–13}

When the mesophase just becomes a continuous phase with increasing EC concentration, there are two kinds of textures in the mesophase. One is the oily streak texture and the other is the pseudoisotropic texture, which is usually called the lamellar anisotropic phase and has very weak birefringence. In the former texture the layers of ordered polymer chains are normal to the solution film, which is similar to the proposed structure of the disklike texture,

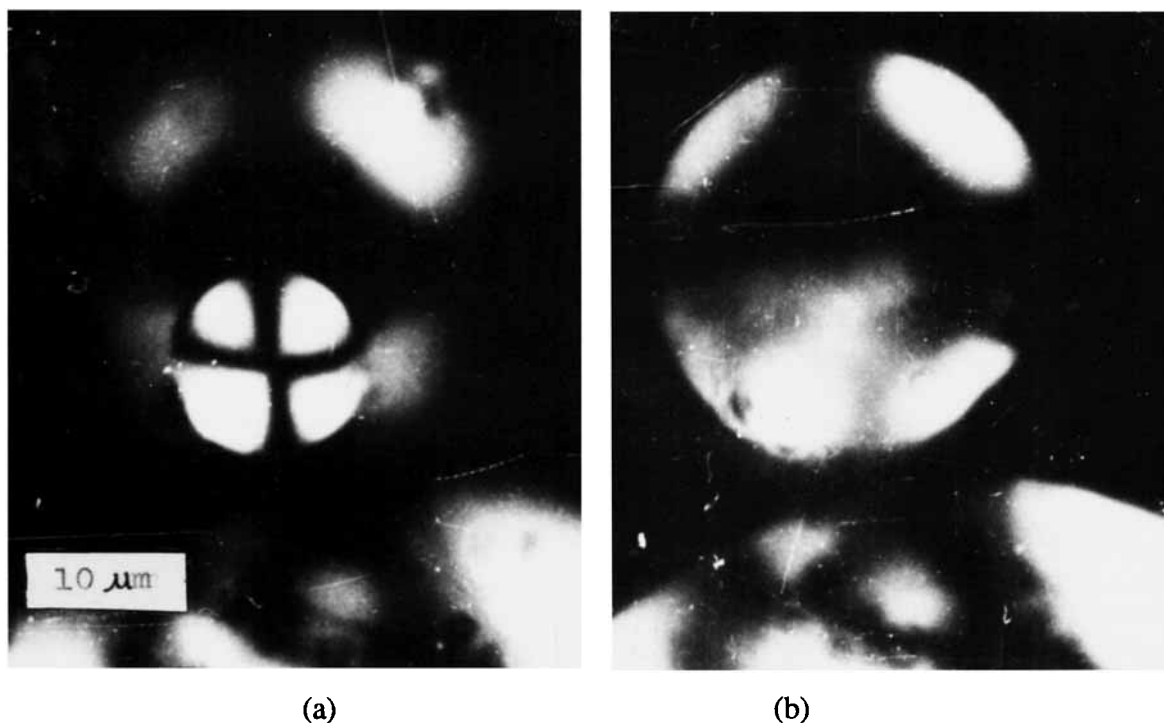


Figure 2 Polarized light micrographs of the 28.6 wt % EC–DCA solution; the distance of the focus planes between (a) and (b) is 13.5 μm , 25°C.

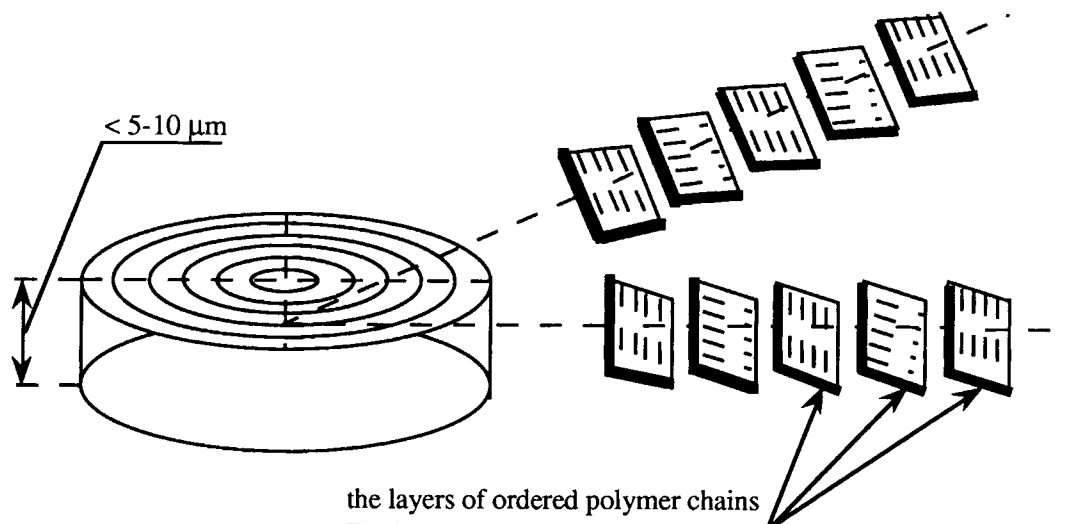


Figure 3 Proposed structure of the disklike texture in the EC-DCA mesomorphic solution.

and the helical axes are parallel to it. In the latter texture, however, the layers of ordered polymer chains are parallel to the solution film and the axes of helicoids are perpendicular to it. These two textures can steadily coexist in the continuous mesophase. The vibration direction of the larger of two refractive indices of the mesophase is parallel to the streak direction in the oily streak texture. This suggests that the axes of helices are normal to the streak direction in the oily streak texture.

When the EC concentration is larger than 31 wt %, the mesophase shows a homogeneous planar texture that exhibits a vivid color [Fig. 1 (c) and (d)]. In the planar texture, like the pseudoisotropic texture, the axes of helices of the cholesteric phase are normal to the solution film,¹⁴ and the wavelength of selective reflection of the cholesteric phase is in the visible light region. At this time, however, the oily streak texture is also coexisting with the planar texture in the mesophase. The color of the planar texture gradually changes from green to blue with increasing polymer concentration. The oily streak texture is also gradually changed into a mosaic pattern of region of local birefringence of the order of a few microns, which is called the pseudo-focal-conic structure.

Generally speaking, the disklike texture, the oily streak texture, the pseudoisotropic texture, and the planar texture can exist in the mesomorphic solution in different concentration regions. When the concentration is high enough, there is a pseudo-focal-conic structure in the mesomorphic solution. The axes of helices are parallel to the glass plane in the disklike and the oily streak textures and perpendic-

ular to the glass plane in the pseudoisotropic and the planar textures, which is shown in Figure 4. Therefore, the appearance of these textures in the solution suggests that the layers of ordered polymer chains in the mesophase prefer to lie normal or parallel to the glass plane if the space is large enough for development of the domains. But with increasing EC concentration, the proportion of mesophase in the solution increases, and the space occupied by each domain becomes smaller and smaller. When the concentration is high enough, the layers of ordered polymer chains are at an angle from 0° to 90° with the glass plane because of the interactions between domains and the steric obstruction. Therefore, the textures in which the axes of helices are parallel and normal to the glass plane—i.e., the disklike texture, the oily streak texture, the pseudoisotropic texture, and the planar texture—disappear and the pseudo-focal-conic structure appears in the solution.

Because the planar texture of the cholesteric phase can selectively reflect light at a certain wavelength, a vivid color 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 wavelength where the apparent absorbance is maximum caused by the selective reflection of the planar texture, decreases gradually with increasing concentration (Fig. 5), which means that the selective reflection gradually changes to shorter wavelength with increasing EC concentration.

The color of the cholesteric liquid crystalline solution can also vary with the incident angle and the reflecting angle. The wavelength of the selective re-

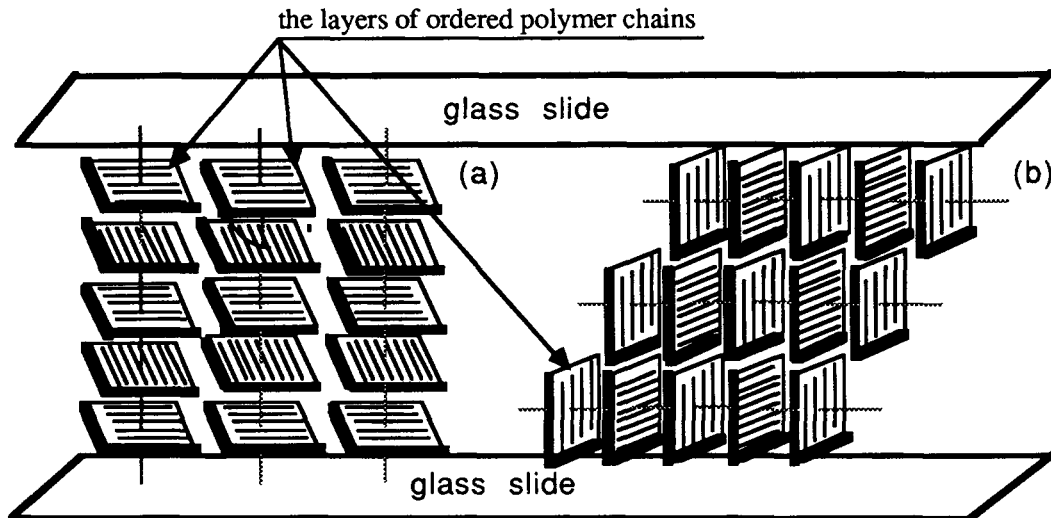


Figure 4 The scheme proposed for the arrangement of the helices in (a) the pseudoisotropic and the planar textures and (b) the oily streak texture.

flection changes to shorter wavelength when the incident angle decreases (Fig. 6). It is well known from small molecule liquid crystal systems that the selective reflection of the cholesteric liquid crystalline solution is closely related with the pitch of the cholesteric phase and varies with both incident and reflecting angles.¹⁵ The cholesteric mesophase, therefore, can show different colors when the incident angle and the reflecting angle are changed. The

variation of the wavelength of the selective reflection with concentration reflects that the pitch of the EC-DCA cholesteric liquid crystalline solution decreases with increasing EC concentration as expected.

Temperature can also greatly affect the mesophase texture. Figure 7 shows polarized light micrographs of the 28.6 wt % EC-DCA mesomorphic solution at different temperatures. When the solution is heated from 26–35°C, both the birefringence and

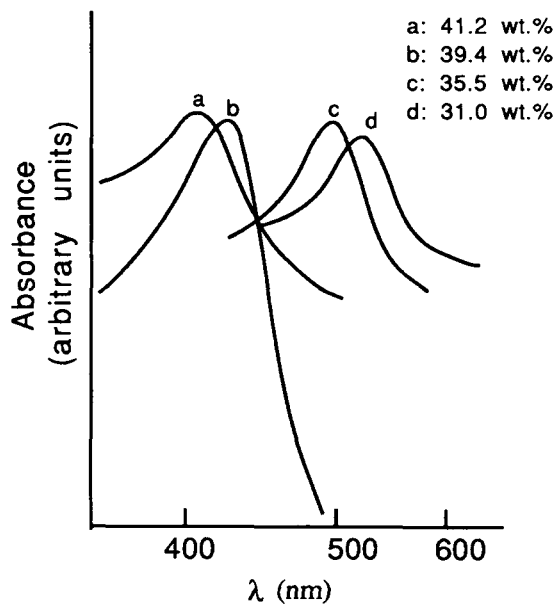


Figure 5 Reflection spectra of the EC-DCA mesomorphic solutions as a function of the concentration, 25°C.

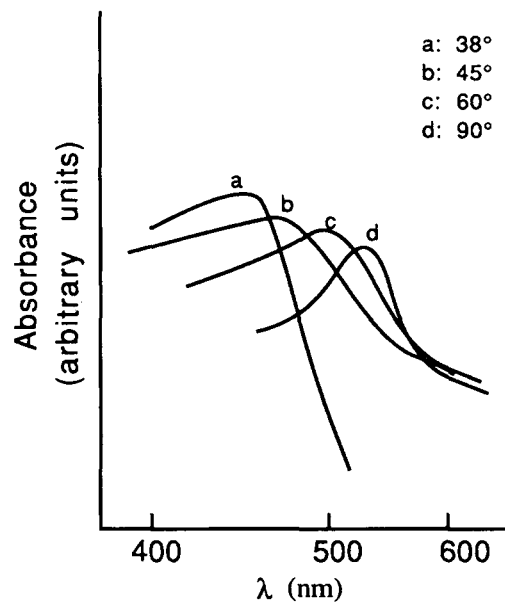
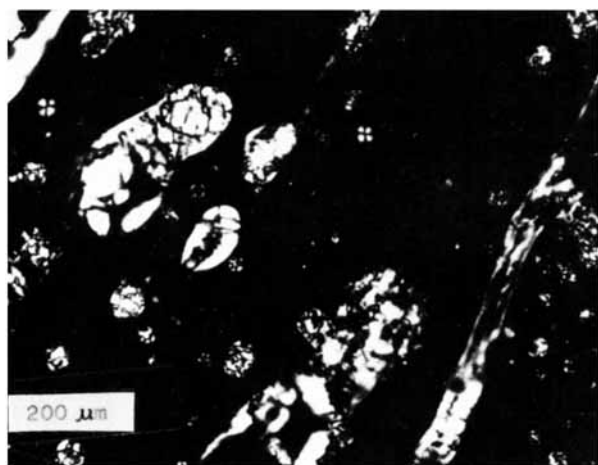
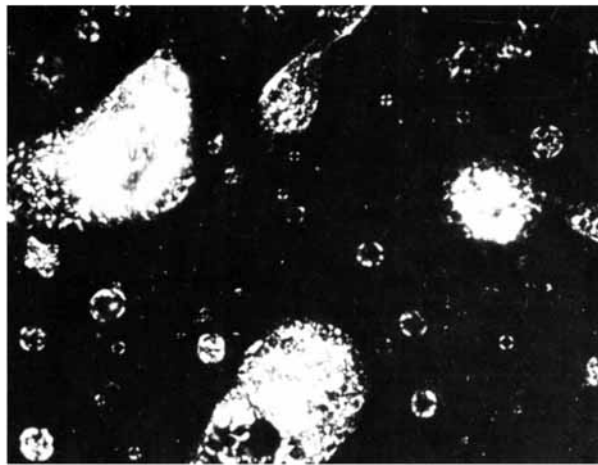


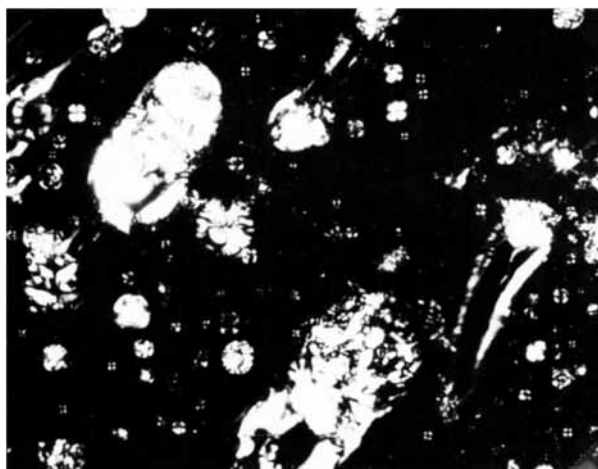
Figure 6 Reflection spectra of the EC-DCA mesomorphic solution as a function of the incident angle, C = 31.0 wt %, 25°C.



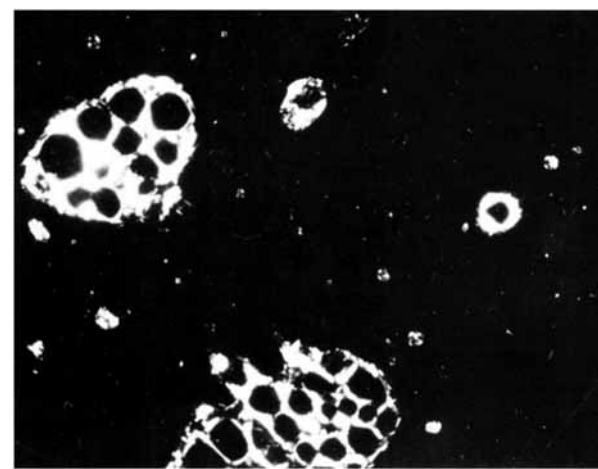
(a) 26°C



(c) 55°C



(b) 35°C



(d) 75°C

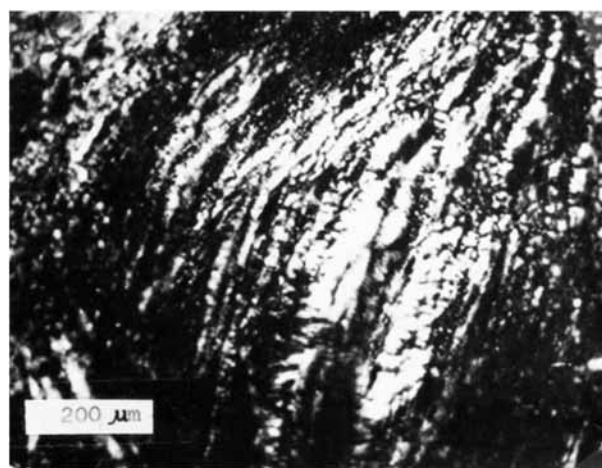
Figure 7 Polarized light micrographs of the 28.6 wt % EC-DCA solution at different temperature; the heating rate is less than 1°C/min. (a) 26°C, (b) 35°C, (c) 55°C, (d) 75°C.

the dimension of the mesophase aggregates seem to increase, but the interface between anisotropic and isotropic phases becomes obscure. This implies that the polymer chains in the mesophase can reorder and rearrange and the degree of order in the mesophase can increase when the temperature of the solution increases in a limited range because the movement of the polymer chains is easier at the higher temperature. At the same time, however, the shape of the mesophase aggregates is changed due to the reordering and rearrangement of the polymer chains within the mesophase. When the temperature increases to 55°C, the phase transition from the mesophase to the isotropic phase begins. The isotropic phase forms inside the mesophase aggregates

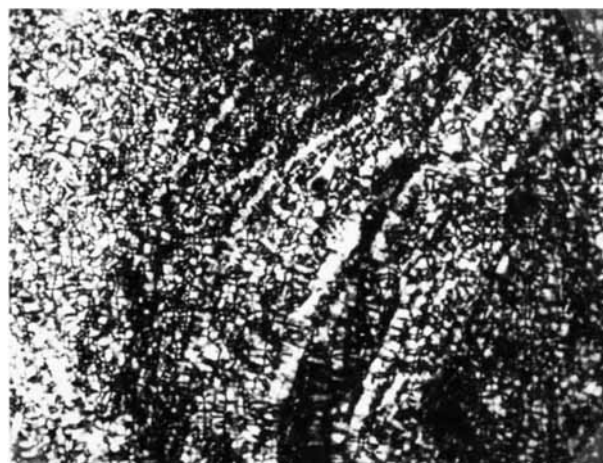
and then increases gradually [Fig. 7(c) and (d)]. In the mesophase, therefore, the degree of order of polymer chains is different in different zones. When the solution is heated, the mesophase with the lower degree of order can first transform to the isotropic phase. The mesophase with the higher ordering degree can transform to the isotropic phase only at the higher temperature. In other cellulose derivative liquid crystals, it has also been found that within the mesophase the degree of order is different in different zones.^{11,16}

When the mesophase is continuous, no disklike texture can be seen in the solution. When the solution is heated, however, many disklike texture mesophase aggregates can appear in the solution

within a certain temperature range, which depends on the concentration [Fig. 8(a) and (b)]. They are overlapped with each other, but their Maltese extinction cross can be seen very clearly under crossed polarizing light. When the temperature is further increased, the isotropic phase appears. The proportion of mesophase decreases gradually with increasing temperature, and the mesophase changes from the continuous phase to the noncontinuous one. Finally, the mesophase disappears completely at a certain temperature, which increases with increasing EC concentration, and the solution becomes an isotropic system. The variation of the mesophase texture with temperature demonstrates that the disklike texture is easily formed and stable within a cer-



(a) 36.5°C

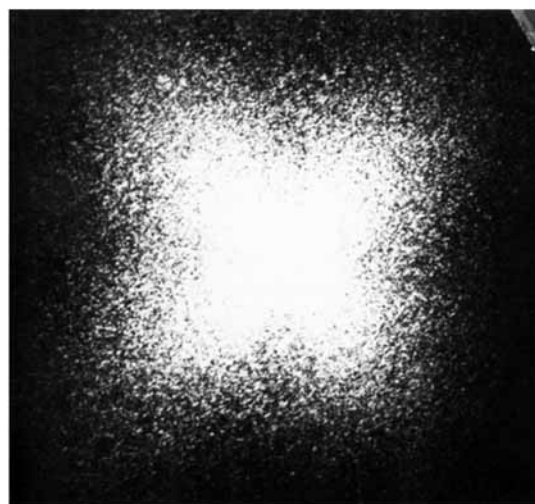


(b) 70°C

Figure 8 Polarized light micrographs of the 33.3 wt % EC-DCA solution at different temperature; the heating rate is less than 1°C/min. (a) 36.5°C, (b) 70°C.



(a) 60°C



(b) 70°C

Figure 9 SALS H_v patterns of the 33.3 wt % EC-DCA solution at different temperatures; the heating rate is less than 1°C/min. (a) 60°C, (b) 70°C.

tain temperature range in the mesomorphic solution. Nishio et al.¹⁷ have found the disklike structure in hydroxypropyl cellulose films cast from the cholesteric liquid crystalline solution. The disklike texture, therefore, is probably a basic texture in polymer cholesteric liquid crystals.

The formation of the disklike texture can also be confirmed by the results of SALS experiments. Figure 9 shows the SALS H_v patterns of the 33.3 wt % EC-DCA solution at 60 and 70°C, respectively. At the low temperature, there is no disklike texture in the mesophase and the SALS H_v pattern, which is only attributed to the domains of the cholesteric

phase, is four-leaf. It is large in dimension and is relatively weak in intensity [Fig. 9(a)]. When the mesomorphic solution is heated to 70°C, however, the H_v pattern becomes two parts, an outer four-leaf and a central one, which is overlapping [Fig. 9(b)]. It is considered that the central four-leaf pattern, of which the intensity is strong and the dimension is small, is attributed to the disklike mesophase aggregates and the outer one, of which the intensity is weak and the dimension is large, is attributed to the domains of the cholesteric phase.¹⁸ Therefore, the results of the SALS experiment indicate the existence of the disklike texture in the mesophase at the higher temperature. Furthermore, the dimension of the outer four-leaf pattern decreases with increasing temperature, which reflects that the size of the domains increases with temperature.

CONCLUSIONS

The disk-like texture can be first formed in the EC-DCA mesomorphic solution with increasing EC concentration, and the disklike mesophase aggregates can merge to form bigger mesophase aggregates or overlap without contacting each other. When the concentration of EC further increases, the oily streak texture and the pseudoisotropic texture can appear in mesophase. The latter texture can change to the planar texture with a vivid color, which changes with the concentration of EC and both the incident and reflecting angles. The planar and the oily streak textures can gradually change to a mosaic pattern with regions of local birefringence of the order of a few microns at the higher concentration.

The degree of order of polymer chains is heterogeneous in the mesophase. The mesophase with the lower degree of order can first transform to the isotropic phase when the solution is heated, and the phase transition from the mesophase with the higher degree of order to the isotropic phase can take place only at higher temperatures. The disklike texture can be observed during the phase transition from

the anisotropic phase to the isotropic one. It is suggested, therefore, that the disklike texture is probably a basic texture in polymer cholesteric liquid crystals.

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