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Textures of Methyl Cellulose/Dichloroacetic Acid Mesomorphic Solutions

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Textures of methyl cellulose/dichloroacetic acid mesomorphic solution were studied by polarizing microscope and small angle light scattering. It was found that the mesomorphic solution showed the characteristics of cholesteric liquid crystals and the mesophase texture was closely related with the concentration. The mesomorphic solution showed the disk-like texture when mesophase appeared at first. After the mesophase became a continuous phase, however, there were observed the band-like texture and the pseudoisotropic texture in the solution. With the further increasing of concentration, the band-like texture was gradually destroyed and the pseudoisotropic texture changed to focal-conic structure. In the disk-like texture and the band-like texture, the axes of helicoids in cholesteric phase were parallel to the solution plane. In the pseudoisotropic texture they were perpendicular to it. The pitch of cholesteric mesophase decreased with changing from the disk-like texture to the band-like texture.

INTRODUCTION

It has been found that cellulose and many of its derivatives can form liquid crystals in the appropriate condition[1–3] since the observation of the cholesteric liquid crystals in the hydroxypropyl cellulose/water system by Werbowyj and Gray.[4] Moreover, cellulose and its derivative liquid crystals are generally cholesteric.

Many investigations about the phase transition, optica properties and rheological properties of cellulose and its derivative liquid crystals have been reported.[5–10] Chanzy *et al.*[11] have prepared the oriented film and fiber of cellulose from both the isotropic solutions and the liquid crystalline solutions. They found that there is a structural difference between fibers produced from both solutions. Nishio *et al.*[12] have studied the morphology and the structure of the hydroxypropyl cellulose film casted from mesomorphic solutions by electron microscopy and observed that many round particles composed of stacked disks are densely packed in the interior of a quiescently cast film. We reported[13,14] the textures of the ethyl-cyanoethyl cellulose/dichloroacetic acid and the ethyl-acetyl cellulose/dichloroacetic acid mesomorphic solutions and found that there were the disk-like texture, the oily streak texture or the band-like texture, the pseudoisotropic texture and the planar texture at different concentrations.

Methyl cellulose (MC) is a cellulose derivative and can be dissolved in dichloroacetic acid (DCA). In this report, we studied the formation and the textures of the mesomorphic MC/DCA solution by polarizing microscopy and small angle light scattering.

EXPERIMENTAL

The MC was supplied by Shanghai Chemical Reagent Factory. Its degree of polymerization was about 230, which was calculated by the following equation[15]:

$$[\eta] = 0.06(DP)^{0.86}$$

Where DP was the weight average degree of polymerization and $[\eta]$ was measured in 4M HCl solution at 25°C after degradation modification. The degree of substitution for methyl was about 1.16, which was calculated from the carbon content of the MC measured by elementary analysis. The DCA was a chemically pure reagent.

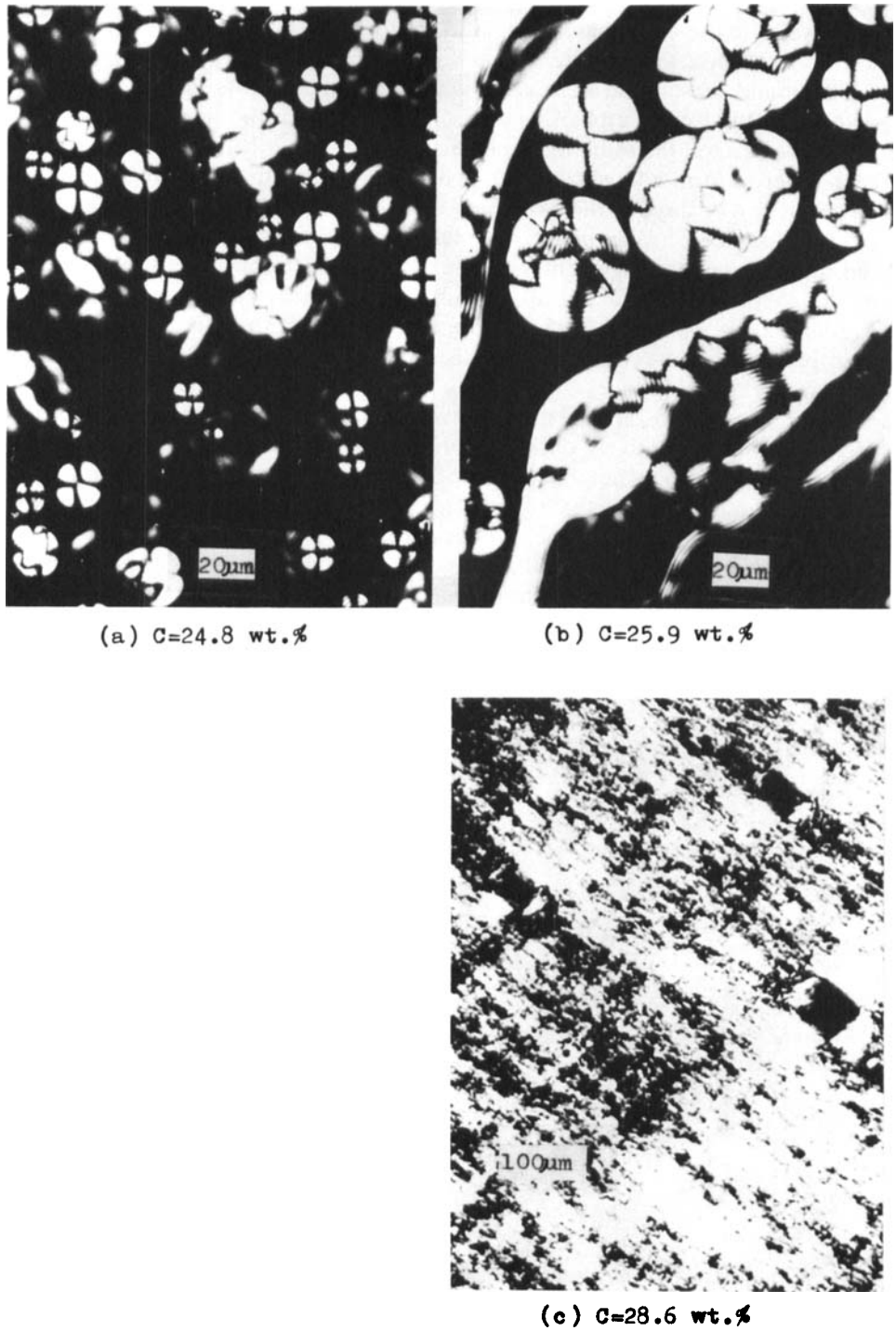
The MC was mixed with the DCA at room temperature and the sample was tightly sealed in the test-tube. After heating at 50°C for 10 hours, the solution was stored at room temperature for 3 months in order to obtain the equilibrium solution until used. The FTIR spectrum showed the absence of dichloroacetate substituents in this solution.

The MC/DCA solution was sandwiched between a microscope slide and a cover glass and formed a solution film which was about 10–30 μm in thickness. Mesophase textures of the solution were observed by a polarizing microscope (Leitz, ORTHOPLAN-POL). A small angle laser light scattering instrument (LS-1, Yingkou Measuring and Testing Instrument Factory, Lianing, China) was employed to observe the small angle light scattering (SALS) patterns of the solution.

RESULTS AND DISCUSSION

The MC/DCA solution is isotropic and shows no birefringence when concentration is less than 24.2 wt%. As the concentration increases, the solution becomes turbid and passes light between crossed polars at the concentration of 24.2 wt%, which means the appearance of the mesophase in the solution.

Figure 1 shows the mesophase texture of the MC/DCA solution at different concentration. It is obvious that the mesophase texture varies with the concentration. When the mesophase appears at first, there coexist both the isotropic and the anisotropic phases called biphasic. Mesophase mostly shows round texture with the clear Maltese extinction cross when it is a noncontinuous phase (Figure 1a). With the increase of concentration, mesophase gradually becomes a continuous phase. The band-like texture and the pseudoisotropic texture appear in the solution (Figure 1b). When the concentration increases further, the band-like texture is



(a) C=24.8 wt.%

(b) C=25.9 wt.%

(c) C=28.6 wt.%

FIGURE 1 Polarized micrographs of the MC/DCA mesomorphic solutions, 30°C.

destroyed and the mesophase changes to the focal-conic structure with the domains which are randomly distributed (Figure 1c).

The round mesophase aggregates with the Maltese cross in the domains can suspend in the isotropic phase and they can flow when the slide is slightly tilted. When they are on the same focus plane and close each other, they can merge with each other to form a larger domain. When they are on the different focus planes, however, two or three of them can be overlapped without touch each other (Figure 2). The distance between their focus planes can be 15–20 μm and the diameter of the round mesophase aggregates can be as large as 50 μm. Because the thickness of the solution film is about 10–30 μm, the thickness of the round mesophase aggregates can be less than 5–10 μm. It is believed, therefore, that the round mesophase aggregates show the disk-like texture instead of the three dimensional spherical texture in space.

From Figure 1 and 2 it can be also observed that the disk-like texture is composed of concentric alternatively dark and bright rings or helices. In this texture, the layers of ordered polymer chains are perpendicular to both the solution film and the radial directions. The axes of helicoids in the cholesteric mesophase are parallel to both them (Figure 3). If the arrangement of the helicoids is almost ordered in radial directions, the concentric alternatively dark and bright rings or helices can be observed in the disk-like texture. The distance between two rings or width of the helix is equal to a half pitch.

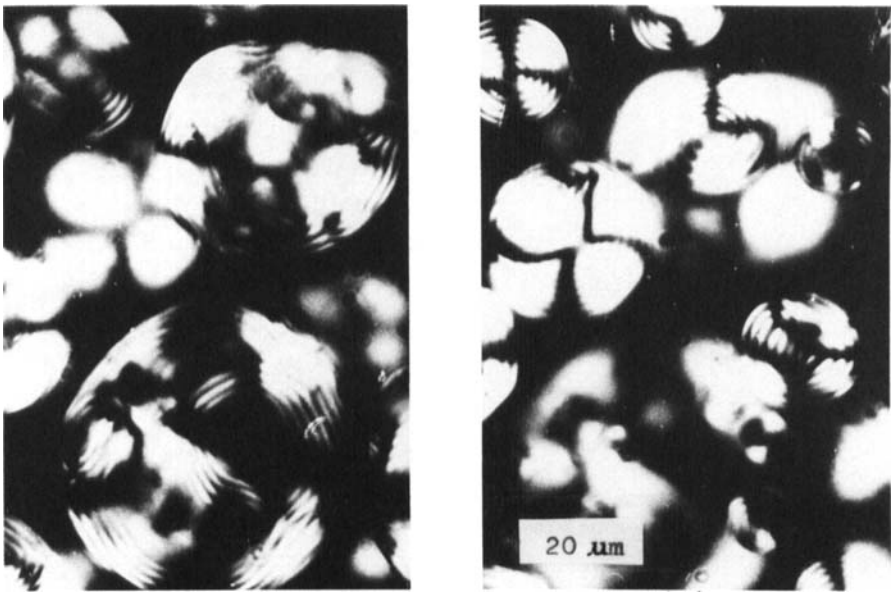


FIGURE 2 Polarized micrographs of the MC/DCA mesomorphic solution, the distance between the focus planes of (a) and (b) is 17 μm.

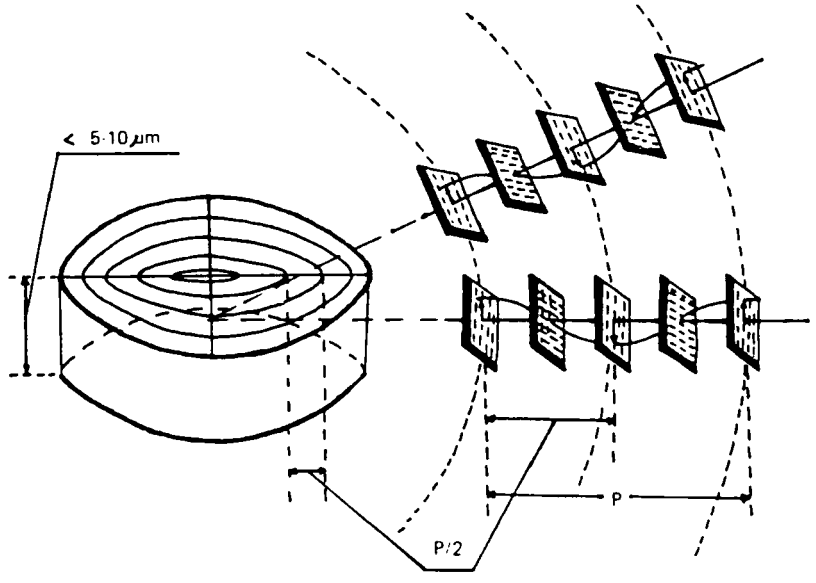


FIGURE 3 Scheme of the arrangement of the layers of ordered polymer chains in the disk-like texture.

In the disk-like texture, the axial direction of helicoids is the same as the radial directions. Furthermore, the arrangement of the helicoids is completely symmetrical in the radial directions if the disk-like texture is composed of concentric rings (Figure 4a). If the disk-like texture is composed of helices, however, the helicoids dislocate each other, which means the layers of ordered polymer chains with the same orientation direction are not on the same circumference (Figure 4b). Thus, the extinction zones are displaced relatively to each other in the radial directions. If the extinction zone moves a half pitch over a turn, the texture is a single helix; if it moves one pitch, the texture is a bihelix; for one and a half pitch, it is a trihelix and so on. The disk-like texture in the cholesteric mesophase has also been observed in the liquid crystalline solutions of poly-r-benzyl-L-glutamate,[16] ethyl-cyanoethyl cellulose[13] and ethyl-acetyl cellulose.[14]

With increasing concentration, mesophase can gradually change from noncontinuous phase to continuous one (Figure 1b). In a continuous phase, mesophase shows two textures: One is the pseudoisotropic texture and the other is the band-like texture. The former texture is actually a lamellar anisotropic phase of which birefringence is very weak. In the lamellar phase, the layers of ordered polymer chains are parallel to the solution film and the axial direction of the helicoids, which are composed of the layers of ordered polymer chains, is perpendicular to the solution film.[17] As shown in Figure 5 it can be observed that the band-like texture is composed of parallel equidistant and alternatively dark and bright strips, which is about 0.5–1.5 μm in width. The layers of ordered polymer chains are perpendicular to the solution film. The axes of the helicoids are parallel to the solution film and perpendicular to the band direction (Figure 6). When the ar-

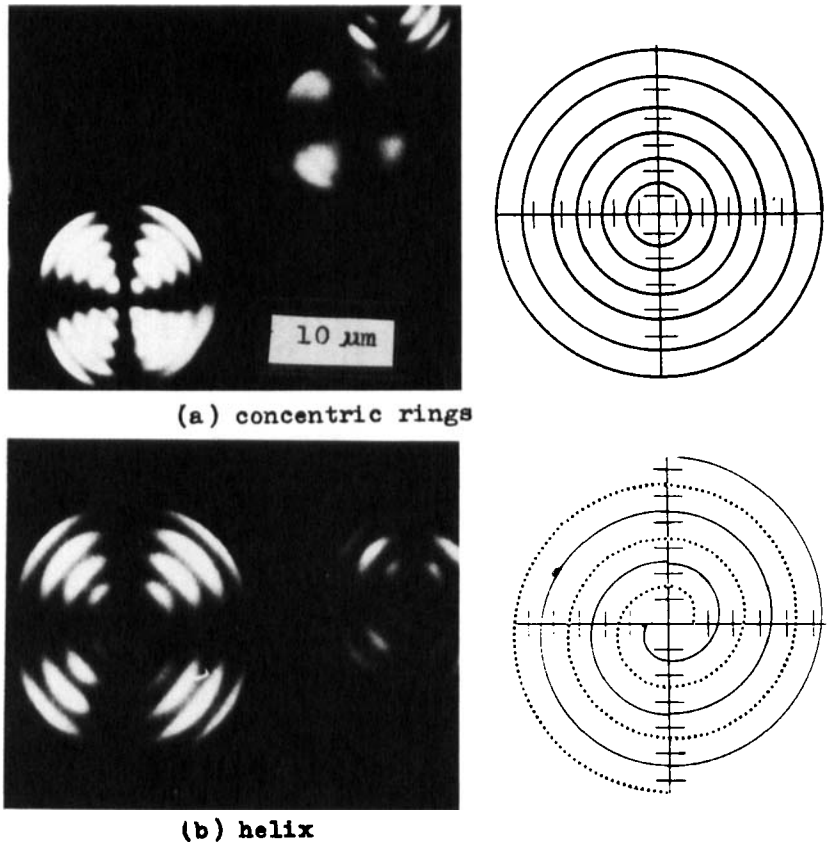


FIGURE 4 The concentric rings and the helices in the disk-like texture and their schemes.

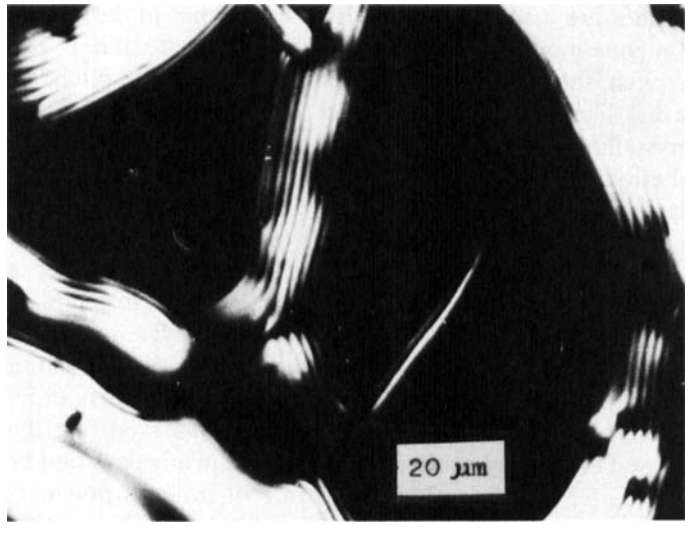


FIGURE 5 The band-like texture in mesophase, C = 25.9 wt%, 30°C.

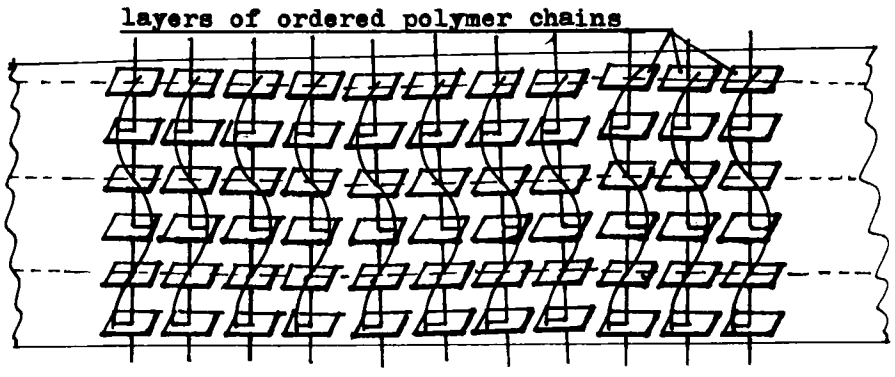


FIGURE 6 Scheme of the arrangement of helicoids in the band-like texture.

rangement of the helicoids is ordered and the layers of ordered polymer chains with the same orientation direction are on the same plane, the equidistant and alternatively dark and bright strips can appear in the band-like texture. The width of the strip is equal to a half pitch.

The width of the strip in the band-like texture is generally less than the distance between two concentric rings or the width of the helix in the disk-like texture (Figure 7), which indicates that the pitch of cholesteric mesophase in the disk-like texture is larger than that in the band-like texture. The result suggests that in the cholesteric mesophase, the layers of ordered polymer chains are packed closer in the band-like texture than in the disk-like texture, which is closely related with the formation of the band-like texture.

After inserting the compensator (λ plate) into the microscope with an angle of 45° to the crossed polarizers, the interference colour in the first and third diametrically opposed quadrants of the cross is yellow and in the second and fourth

FIGURE 7 The disk-like texture and the band-like texture in mesophase C = 25.9 wt%, 30°C.

ones is blue, which indicates that the mesophase is negative in optics. In the band-like texture, when the band is laid across the first and third quadrants of the cross, the interference colour is blue and when it is laid across the second and fourth ones, it is yellow. The vibration direction of the larger of the two refractive indices of the mesophase, which is measured by the polarizing microscope with a tilting compensator, is perpendicular to the radical direction in the disk-like texture but parallel to the band direction in the band-like texture. These results suggest, therefore, that the band-like texture is formed from the disk-like texture with increasing concentration. Figure 8 shows the process of the formation of the band-like texture from the disk-like texture. Mesophase aggregates grow gradually with increasing concentration. The mesophase aggregates with the disk-like texture can merge with each other when they become large enough and combine to form bigger ones. In this process, the concentric rings and helices are pressed each other and the deformation of them can take place. Finally, the band-like texture appears in the mesophase if the ordering arrangement of the helicoids of the cholesteric phase is not destroyed (Figure 8). Because the mesophase aggregates are pressed each other in the process of the formation of the band-like texture, the layers of the ordered polymer chains become closer than before and the pitch in the band-like texture become smaller than that in the disk-like texture. Furthermore, there are several bands with the different directions in some large mesophase region (Figure 9), which again indicates the process of the formation of the band-like texture mentioned above. The concentric rings or the helices can be pressed in different directions when the mesophase aggregates with the disk-like texture merge and combine with each other. The bands, therefore, can be formed in different directions. The band-like texture can be destroyed at the higher concentration and the pseudoisotropic texture can also change to the focal-conic structure with the domains which are randomly distributed (Figure 1c).

The existence of the disk-like texture in the mesophase at the lower concentration can also be confirmed by the SALS experiments. Figure 10 shows the SALS H_v

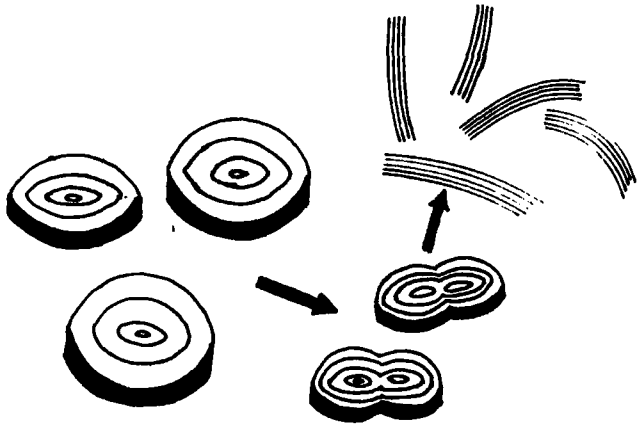


FIGURE 8 Scheme of the formation of the band-like texture.

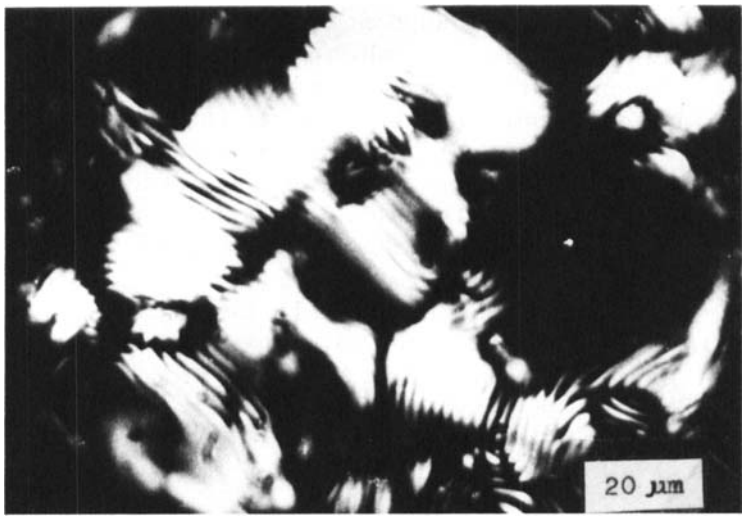


FIGURE 9 The band-like texture with different directions in mesophase, C = 24.2 wt%, 30°C.

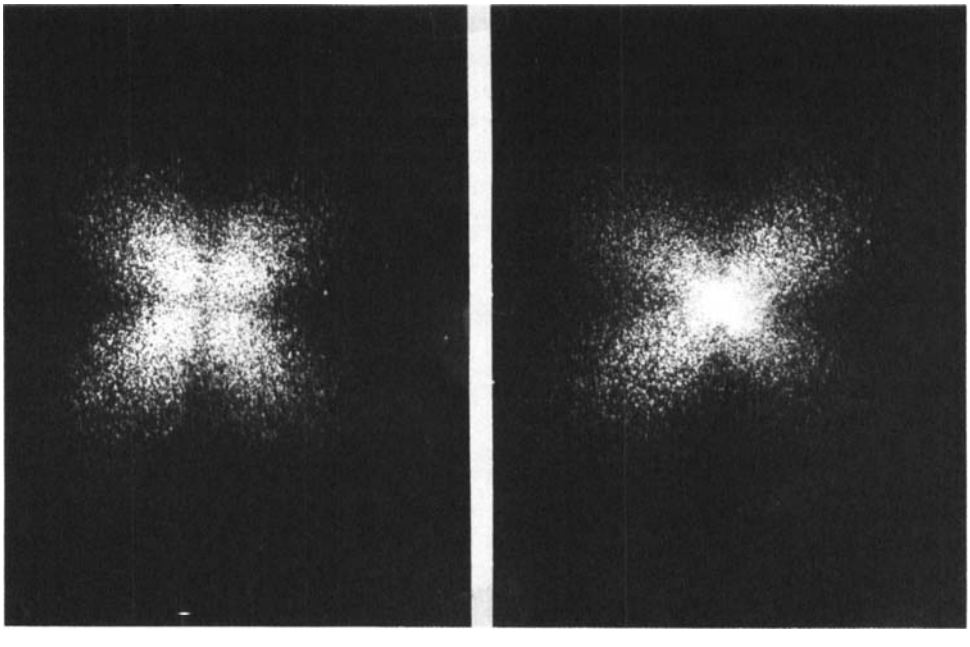


FIGURE 10 SALS H_v patterns of the MC/DCA mesomorphic solutions.

patterns of the MC/DCA mesomorphic solution at the concentrations of 25.4 wt% and 31.0 wt%. At the lower concentration, the SALS H_v pattern of the solution is composed of two four-leaf patterns which are overlapped. One is located in centre, of which the intensity is strong and the size is small. The other is located in outside, of which the intensity is weak and the size is larger than that of former. It is considered that the outer four-leaf pattern is attributed to the domains of the cholesteric mesophase[18] and the central four-leaf pattern is attributed to the mesophase aggregates with the disk-like texture. At the higher concentration, however, there is observed no disk-like texture in the mesophase and the SALS H_v pattern becomes one four-leaf style, of which the size is large and the intensity is weak (Figure 10b), which is obviously attributed to the domains of the cholesteric mesophase. Therefore, the results of the SALS experiments and the observation by the polarizing microscope supported the existence of the disk-like texture in the mesophase at the lower concentration.

CONCLUSIONS

The MC/DCA can form liquid crystalline solution above the concentration of 24.2 wt% and show different mesophase textures at different concentrations. The disk-like texture can be observed when mesophase is noncontinuous, which is composed of concentric alternatively dark and bright rings or helices. After mesophase becomes continuous, there are observed the band-like texture and the pseudoisotropic texture. The former is composed of parallel, equidistant and alternatively dark and bright strips. The latter shows very weak birefringence. When concentration increases further, the band-like texture is destroyed gradually and the pseudoisotropic texture changes to the focal-conic structure with the domains which are randomly distributed. The pitch of the cholesteric mesophase in the disk-like texture is larger than that in the band-like texture.

Acknowledgment

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