

ORIENTED TEXTURE OF MESOMORPHIC SOLUTIONS OF CYANOETHYL CELLULOSE/DIMETHYL ACETAMIDE*

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ABSTRACT

Textures of the oriented mesomorphic solutions of cyanoethyl cellulose/dimethyl acetamide were studied by polarized light microscopy, small angle light scattering and depolarized light transmission. If the mesomorphic solutions were sheared, they could form the band-like texture. Molecular chains in the solutions highly oriented almost along the shear direction. But the orientation directions of the molecular chains in the bands neighbouring each other were slightly different.

INTRODUCTION

Molecular chains could orient along the shear direction in polymer process. Therefore, some scientists are interested in studying the oriented textures of the polymer liquid crystals^[1-5]. Above the critical concentration C_1^* , cyanoethyl cellulose (CEC)/dimethyl acetamide (DMA) can form cholesteric liquid crystalline solutions^[6] and show the band-like texture after having been sheared^[7]. We report here some more details about the oriented textures of the mesomorphic solutions studied by polarized light microscopy, small angle light scattering (SALS) and depolarized light transmission.

EXPERIMENTAL

Cyanoethyl cellulose ($\overline{DP} = 300$, $DS = 2.5-3.0$) was mixed with the dimethyl acetamide at room temperature. The samples were sealed up in tubes and laid over 12 hours at room temperature after having been heated at 50°C for 10 hours. The solutions were isotropic when the concentration was under 33wt.% and became anisotropic when it was over 33wt.%. The solutions were spread between two glass slides. Thickness of the solution film is about 20–40 μ m. The glass slides were slipped by shearing and the mesomorphic solution oriented. Birefringent textures could be observed with a polarized microscope (Leitz, ORTHOPLAN-POL). SALS patterns of the solution were obtained with a small angle laser light scattering instrument (LS-1, Yingkou measuring and testing instrument factory, Liaoning, China). The scattering intensity is denoted by V_V when the polarizers have their transmission axes parallel and by H_V when these axes are crossed. Intensity of depolarized light transmissions was measured by the light-measuring system of the automatic microscope camera (Leitz, VARIO ORTHOMAT2).

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RESULTS AND DISCUSSION

When there is not any force acting on the CEC / DMA mesomorphic solutions, the birefringent texture consists of many bright and dark small areas with disordered shapes and distributions (Fig. 1). The darkness and brightness of them changes alternatively under crossed polarized light when the sample is rotated. These confirm that the molecular chains in the small areas have order but the orientation directions of the molecular chains between the small areas are different. These small areas are generally called domains.

The mesomorphic solutions show the birefringence of the band-like texture when they have been sheared (Fig. 2). Many polymer liquid crystals show this texture under certain conditions^[8-10]. Intensity of depolarized light transmission is the strongest when the shear direction is at an angle of 45° to the polar direction of the polarizer and the weakest when it is at angles of 0° and 90° (Fig. 3). According to the depolarizing effect of the crossed polarizers, it is believed that the molecular chains in the mesomorphic solution are oriented along the shear direction after the solution has been sheared. On inserting a first-order plate at 45° to the crossed polarizers, areas between the black bands become blue and yellow. When the sample is rotated, with the crossed polarizers unchanged, the bands are no longer equidistant. They move closer and closer, two by two and then merge at a certain rotation angle. The interference color is yellow at all when the bands lying on the first and third diametrically opposed quadrants of the cross and blue at all when the bands lying on the second and fourth ones.

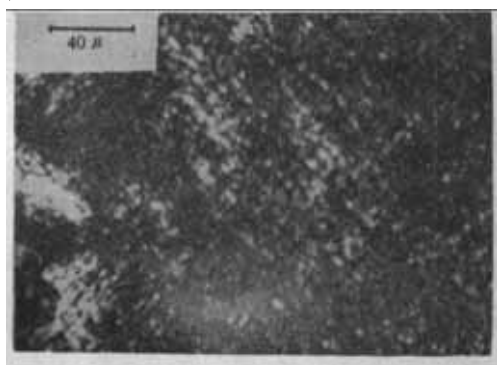


Fig. 1 Polarized light micrograph of the 39.4wt.% CEC/DMA mesomorphic solution.

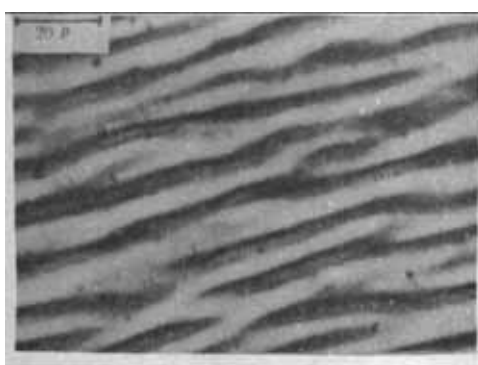


Fig. 2 Polarized light micrograph of the 39.4wt.% CEC/DMA oriented mesomorphic solution.

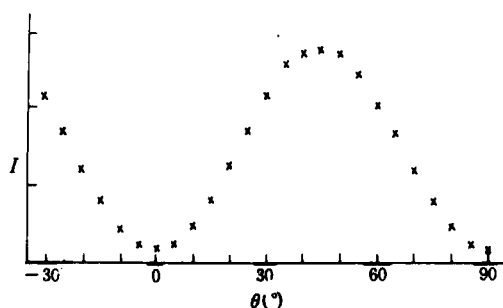


Fig. 3 Dependence of depolarized light transmission on angle between the shear direction and polar direction of polarizer.

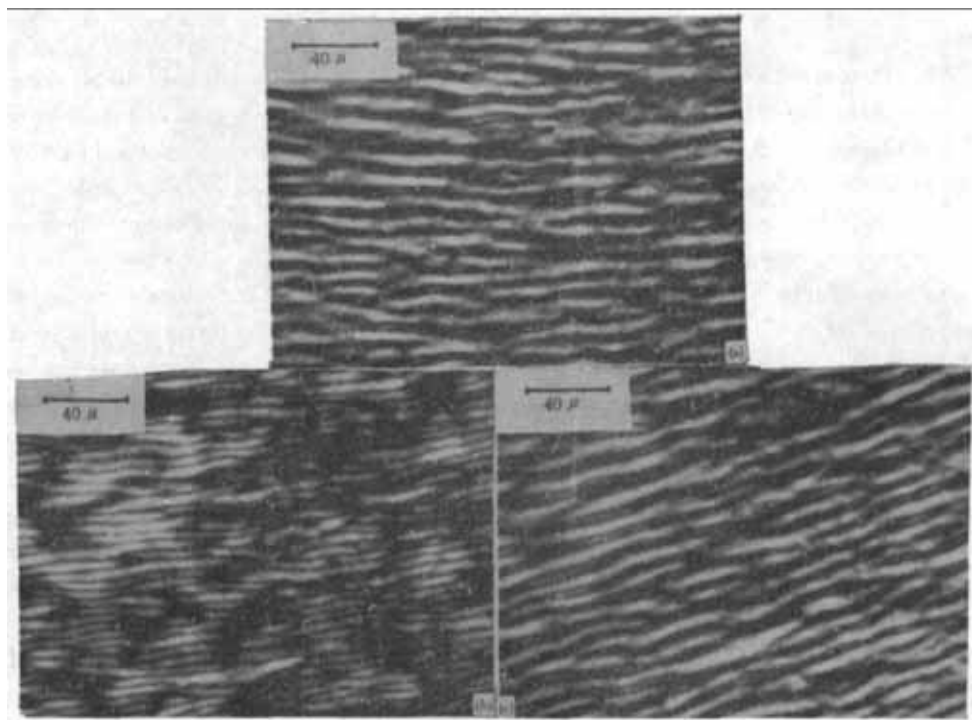
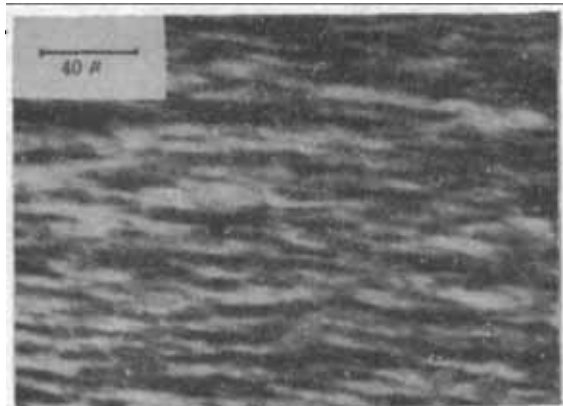


Fig.4 Band-like textures of the 41.2wt.% CEC/DMA oriented mesomorphic solution, θ is (a) 0° , (b) 10° and (c) 20° .

The brightness and darkness of the bands varies with the angle θ between the shear direction and the polar direction of the polarizer. Fig. 4 shows a series of birefringent textures of the oriented mesomorphic solution at different θ . When the θ is zero, between the bright bands there are very narrow dark bands whose widths are about one tenth of the bright bands. But some bright bands become dark as the sample is rotated. When the θ is 20° , the birefringent texture becomes bright and dark bands alternatively with the same widths. The direction of the molecular chain order in the dark bands is parallel to the polar direction of the polarizer but in the bright bands it is at an angle to



$C = 41.2\text{wt.}\%$

Fig. 5 Band-like texture of the CEC/DMA mesomorphic solution which has been sheared at lower shear rate, 20°C .

the polar direction of the polarizer. Therefore, in the oriented mesomorphic solution, the directions of the molecular chain order make a small angle with the shear direction.

The formation of the band-like texture varies with the shear rate. Fig. 5 shows the birefringent texture of the mesomorphic solution which is sheared at lower shear rate. It is clear that the band-like texture in the solution which is sheared at lower shear rate is not so perfect as that at higher shear rate. If the shear rate is low enough the band-like texture cannot be obtained. From Fig. 4 and 5, it is also seen that the orientation of the molecular chains is not uniform. There are dark parts in some bright bands and the dark parts move along the band if the sample is rotated. Then, in a band the orientation directions of the molecular chains may be different slightly on the different segments and change continuously. The orientation directions of the molecular chains are not uniform in large areas of the sample. In the same sample the orientation direction of the molecular chains is at an angle of 15° with the shear direction in some areas but of 20° in other areas. This result is also confirmed by observing the SALS patterns.

The band-like texture of the oriented mesomorphic solution varies with time (Fig. 6), which reflects the relaxation process of the oriented molecular chains after the shear is removed. Molecular chains in the solution move easily and after the shear force is removed the band-like texture begins to be destroyed in several minutes because of the relaxation of the molecular chains. After some time the bands begin to lose their parallelism and form a wavy band texture (Fig. 6b) and in ninety minutes, the band-like texture in some areas has been destroyed completely. This shows that the relaxation process of the oriented molecular chains in the solution is very fast.

Hu and his colleague^[11] proposed to characterize the band-like texture by means of the grating

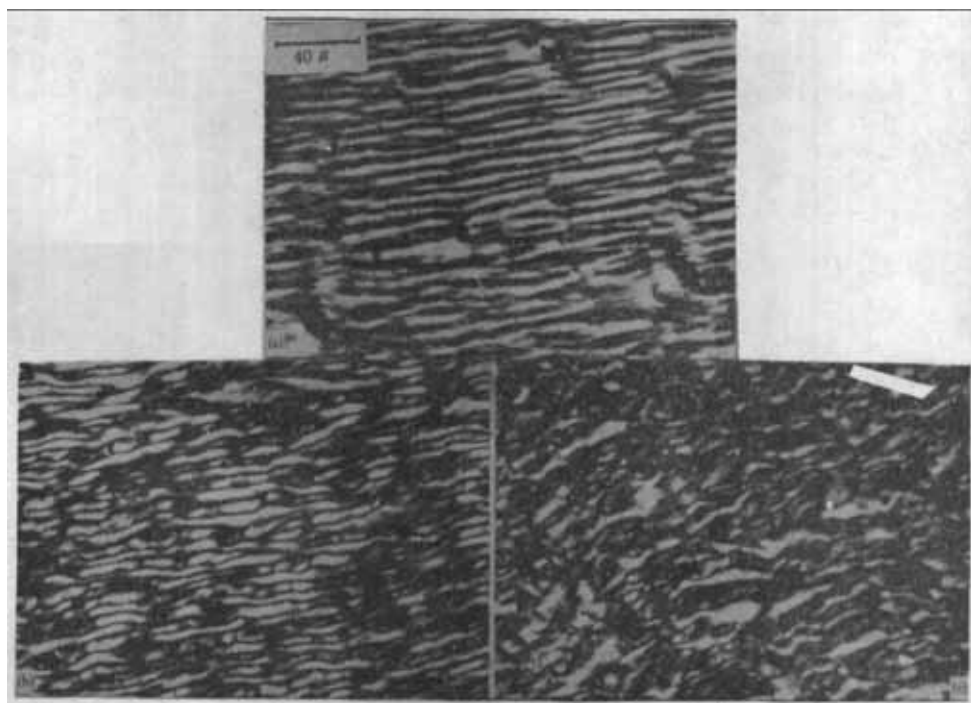


Fig. 6 Birefringent textures of the oriented mesomorphic solution after it was sheared (a) 10 min., (b) 35 min. and (c) 85 min

diffraction theory. We have obtained the grating diffraction points of the oriented mesomorphic solution which shows the band-like texture (Fig. 7). Moreover, in the centre there is a four-leaf pattern which is elongated. It may be contributed by the band-like texture destroyed partly by the disordering relaxation of the molecular chains.

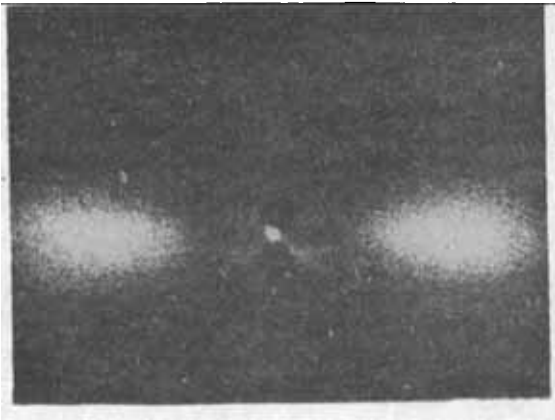


Fig.7 Grating diffraction (H_V-90°) of the oriented mesomorphic solution, $C = 41.2\text{wt.}\%$

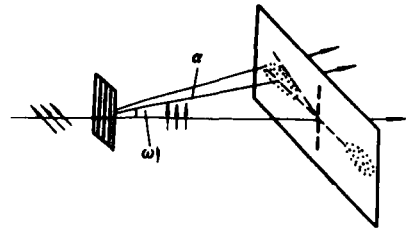


Fig.8 Scheme of the grating diffraction effect

- 1. light source,
- 2. polarizer, 3 band-like texture,
- 4 analyser, 5 film

According to the Bragg's law, the width and the distributions of the bands as well as the distributions of the band orientation can be calculated from the distribution of $I(\omega)$ and $I(\alpha)$ (Fig. 8). A grating with the period of P_n shows the first order diffraction points at $\omega = \sin^{-1}(\lambda/P_n)$ and $\alpha = 0$. Fig. 9 is a distribution curve of $I(P)$ for the sample in Fig. 7. It is considered that $I(P)$ is proportional to the quantity of the parts with the period of P_n , the equation

$$\overline{P_n} = \left[\int P_n I(P) dP \right] / \left[\int I(P) dP \right]$$

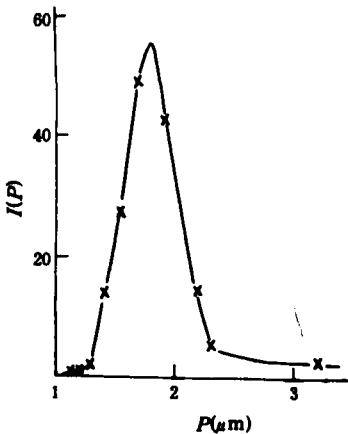


Fig.9 Distribution curve of $I(P)$ for the 41.2wt.% CEC/DMA oriented mesomorphic solution

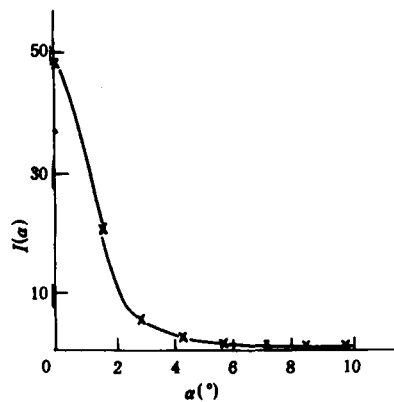


Fig.10 Distribution curve of $I(\alpha)$ for the 41.2wt.% CEC/DMA oriented mesomorphic solution

can be used to calculate the mean value of the period ($\overline{P_n}$). From the distribution curve in Fig. 9 $\overline{P_n} = 1.9 \mu\text{m}$.

For one sample there are different values of $\overline{P_n}$ in different areas. Furthermore, in some areas, the diffraction point rotates with moving the sample along or perpendicular to the shear direction. These results indicate that the width of the bands in the band-like texture is not uniform. In some bands the orientation directions of the molecular chains are not the same but deflect continuously. Meanwhile, some bands are not perpendicular to the shear direction. Therefore, the band-like texture of the oriented mesomorphic solution is not uniform and perfect.

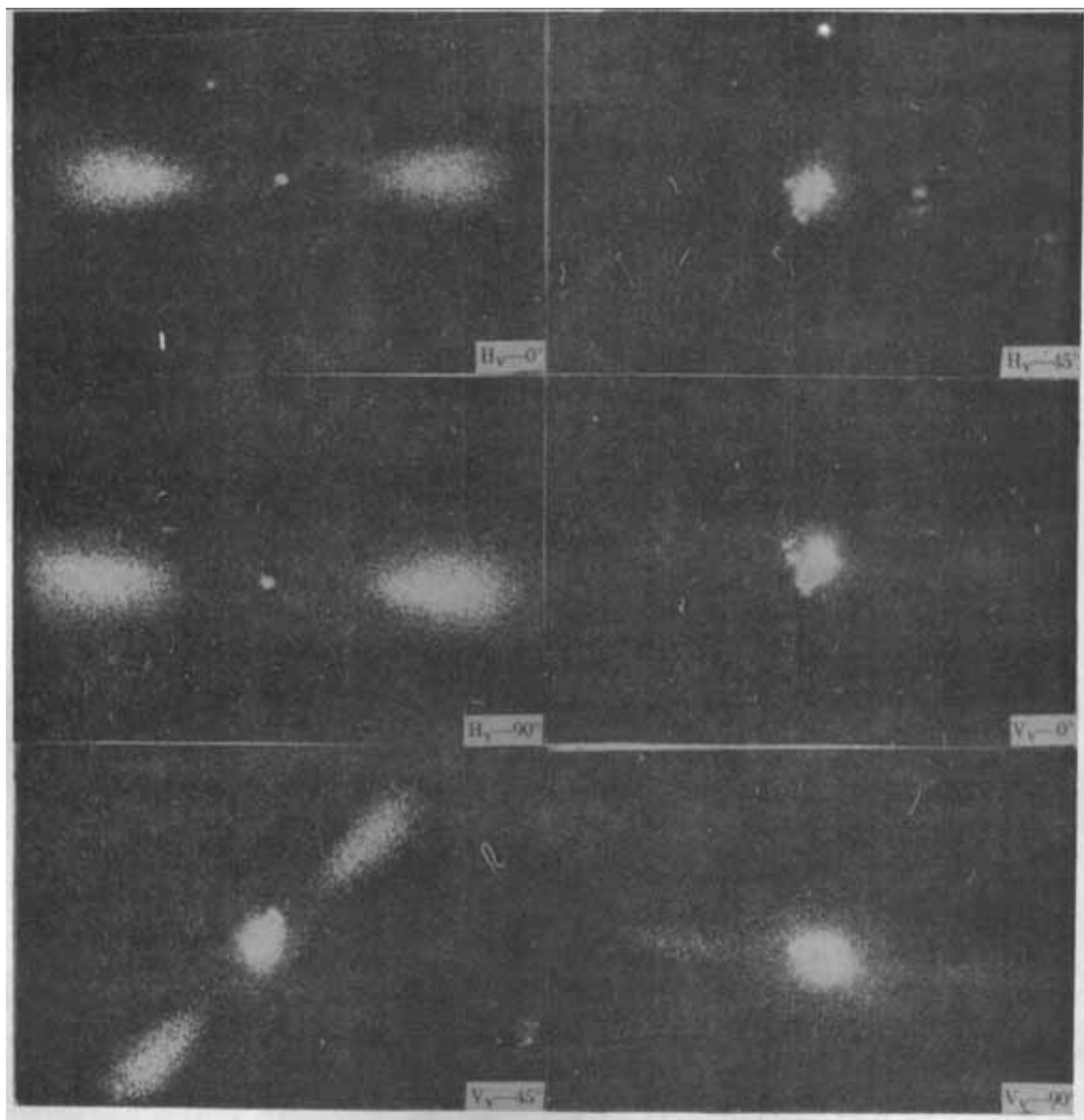


Fig.11 Dependence of the grating diffraction effect on the angle (θ) between the shear direction and the polar direction of the analyser for the oriented mesomorphic solution

The information about the band orientation can be obtained from the distribution of $I(\alpha)$ at the strongest intensity of $I(P)$. Degree of the band orientation can be shown by the mean square cosine of the orientation angle α

$$\overline{\cos^2\alpha} = \left[\int \cos^2\alpha I(\alpha) d\alpha \right] / \left[\int I(\alpha) d\alpha \right]$$

or the orientation factor

$$f = (3 \overline{\cos^2\alpha} - 1) / 2$$

Fig. 10 shows the distribution curve of $I(\alpha)$ for the sample in Fig. 7. From this curve, $\overline{\cos^2\alpha} = 0.9985$, $\alpha = 2.22^\circ$ and $f = 0.998$. Then, the degree of the band orientation in the band-like texture is very high.

When the shear direction is at angles of 0° , 45° and 90° to the polar direction of the analyser, the grating diffraction effect is very strong at H_V-0° , H_V-90° and V_V-45° , but is very weak at H_V-45° , V_V-0° and V_V-90° (Fig. 11). In polarized light system, waves which transmit from neighbouring band must be different in the phase angle and (or) amplitudes in order to obtain the grating diffraction points. The larger the difference in the phase angle and (or) amplitudes, the more obvious the grating diffraction effect is. The difference of the phase angle and (or) amplitudes may be caused by the difference of orientation direction of the molecular chains between neighbouring bands ($d\theta$) and (or) the orientation degree of the molecular chains in the bands ($d\delta$). The angular (angle between the shear direction and the polar direction of the analyser) dependence of the grating diffraction effect is different according to the difference of the orientation direction of the molecular chains between neighbouring bands and (or) the orientation degree of the molecular chains in the bands^[11]. Table 1 shows the comparison of theoretic and experimental results. It indicates that the difference of the orientation direction of the molecular chains between neighbouring bands exists and plays an important role in the grating diffraction effect. At the same time, the difference of the orientation degree of the molecular chains in the bands is small and plays a minor role in the grating diffraction effect.

Table 1 Dependence of the grating diffraction effect on θ

		grating diffraction effect		
		0°	45°	90°
H_V	Contribution of $d\theta$	Strong	Nil	Strong
	Contribution of $d\delta$	Some	Strong	Some
	Experimental result	Strong	Weak	Strong
V_V	Contribution of $d\theta$	Nil	Strong	Nil
	Contribution of $d\delta$	Nil	Strong	Strong
	Experimental result	Weak	Strong	Some

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