Formation and Textures of Ethyl–cyanoethyl Cellulose/ Acrylic Acid Mesophase

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SYNOPSIS

The formation, textures, and optic characteristics of the ethyl–cyanoethyl cellulose [(E–CE)C]/acrylic acid (AA) mesophase were studied using polarizing microscopy, spectrophotometry, and small-angle light scattering (SALS). The disklike, oily streak, planar, pseudoisotropic, polygonal textures and the texture of domains gathered randomly were observed in the mesophase. The polygonal texture in unitary mesomorphic solutions can be regarded as the texture from the combination of deformed mesophase aggregates with the disclike texture. The mesomorphic solution exhibits vivid colors when the concentration is about 42–52 wt % because of its selective reflection to visible light. The wavelength of the light that is selectively reflected shifts to the shorter wavelength, with increasing concentration. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It has been found that cellulose and many of its derivatives can form liquid crystals in the appropriate conditions,[1-3] since the cholesteric liquid crystals were observed in the hydroxypropyl cellulose/water system by Werbowyj and Gray.[4] The cellulose derivative/random-coiled polymer composite with cholesteric structure has been obtained by polymerization of vinyl monomer in the cellulose derivative/vinyl monomer solution.[5,6] This unique blend method recently became more attractive because composites with potential advantages such as high intensity, high toughness, and excellent processability could be achieved.

Ethyl–cyanoethyl cellulose [(E–CE)C], which is a cellulose derivative with two different ether groups, can form cholesteric liquid crystals in many organic solvents.[7] Acrylic acid (AA) is one of the vinyl monomers often used industrially and can be polymerized easily by free-radical initiation. (E–CE)C can be well dissolved in AA and form the mesophase when the concentration is above the critical one. In this report, the formation and characteristics of (E–CE)C/AA liquid crystalline solutions are studied.

EXPERIMENTAL

The (E–CE)C was obtained by the reaction of ethyl cellulose and acrylonitrile. The degree of substitution for ethyl was about 2.1, and for cyanoethyl, about 0.43. The molecular weight, $\bar{M}_n$, of (E–CE)C, measured by a gel permeation chromatograph (GPC) (HPLC, Waters-209), was 7×10^4. The AA was a chemically pure reagent and was distilled in vacuum before using.

The (E–EC)C/AA solution was prepared in vials by weighting the desired amount of (E–CE)C and AA into a vial and mechanically mixing with a spatula for several minutes. The mixtures were laid aside for more than 7 days at about 0–5°C to form homogeneous solutions.

The mean refractive index of (E–CE)C/AA solutions was measured by an Abbe refractometer. The texture of mesomorphic solutions was observed by a polarizing microscope (Orthoplan-Pol, Leitz). The small-angle light-scattering (SALS) pattern of mesomorphic solutions was obtained by a small-angle laser light-scattering instrument (LS-1, Yongkou

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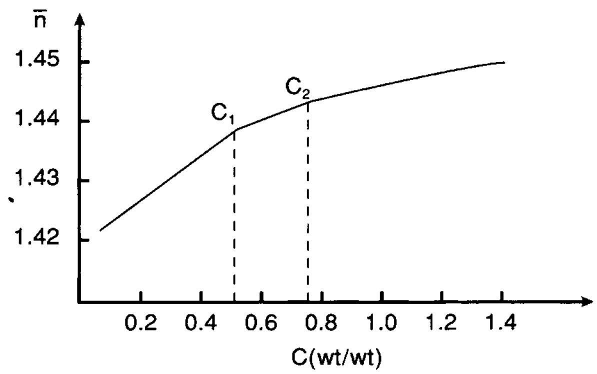


Figure 1 The curve of the mean refractive index vs. concentration of the (E–CE)C/AA solution at 25°C.

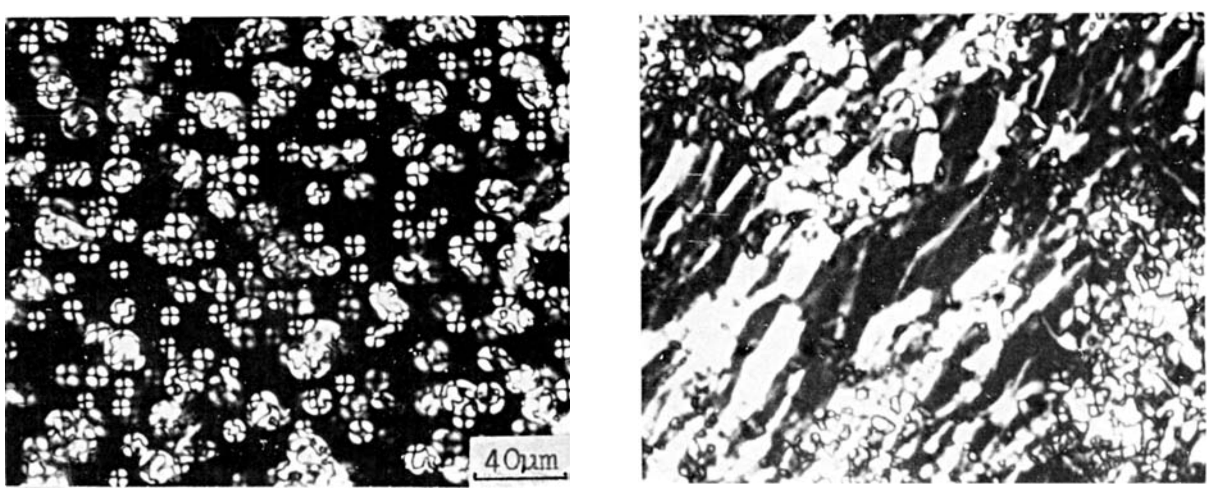
Measuring & Testing Instrument Factory, Liaoning, People's Republic of China). The visible spectrum of solutions was recorded with a UV-vis spectrophotometer (Specord UV-vis, Ziess, Germany).

RESULTS AND DISCUSSION

The (E–CE)C/AA liquid crystalline solution can be formed when the concentration is high enough. The variation of the mean refractive index with concentration can reflect the phase transformation of solutions.[8] Figure 1 shows the relationship between the mean refractive index and the concentration of the (E–CE)C/AA solution. The curve is composed of three straight lines with two turning points. This means that the solution changes with increasing concentration from the isotropic state to an anisotropic one through a biphasic region. The two turning points indicate that the critical concentration, C_1, at which the mesophase begins to appear, is about 33.8 wt %, and C_2, at which the isotropic phase completely disappears, is about 43.1 wt %.

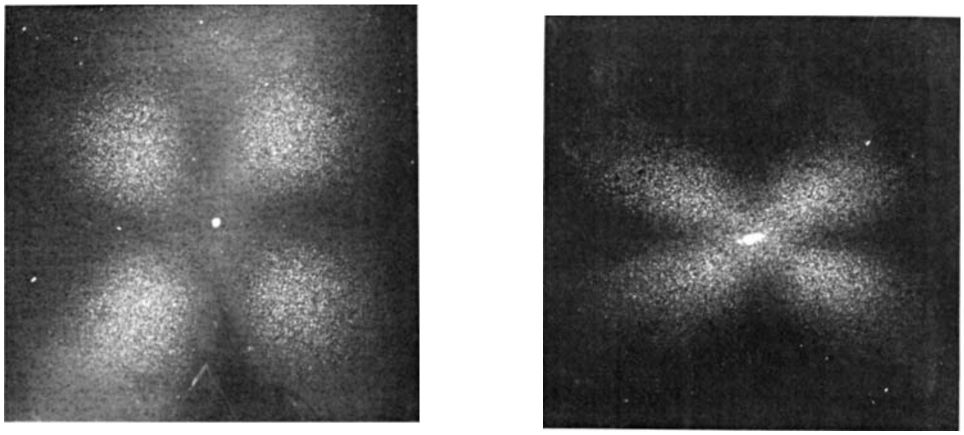
With a polarizing microscope, it was observed that the (E–CE)C/AA solution is isotropic at room temperature when the concentration is below 33.8 wt %. But when the concentration is over that, the anisotropic phase begins to appear in the solution. Figure 2 shows the birefringent textures of the biphasic solutions at different concentrations. It is obvious that the mesophase texture varies with concentration. At the lower concentration, the mesophase is noncontinuous and shows mostly the round texture with the clear Maltese extinction cross [Fig. 2(a)]. While the mesophase gradually becomes continuous with increasing concentration, an oily streak (or bandlike) texture appears [Fig. 2(b)]. Figure 2 shows that there are clear boundaries between the anisotropic and isotropic phases, which indicates the existence of phase separation between the mesophase and isotropic phases and poor compatibility of the two phases.

The diameter of the round texture is about 5 μm. It is so small that it is difficult to determine whether the round texture is two or three-dimensional using



(a) (b)

Figure 2 Polarized micrographs of (E–CE)C/AA solutions at room temperature: (a) C = 34.0 wt %; (b) C = 36.0 wt %.



(a) (b)

Figure 3 SALS H_v patterns of the (E–CE)C/AA solution with round texture, $C = 34.0$ wt %. The incident light is (a) normal to the film plane and (b) at an angle of 30° to the film plane.

only polarizing microscopy. Therefore, the SALS method was used here.

The biphasic solution with the round texture gives an X-type four-leaf SALS H_v pattern that exhibits a maximum with respect to the scattering angle. When the incident light is normal to the solution film plane, there is little difference in the H_v pattern between the two- and three-dimensional spherulites. But when the incident angle is changed, the H_v pattern of the two-dimensional spherulites will obviously change and that of the three-dimensional spherulites will not. In the (E–CE)C/AA system, the four-leaf pattern of the biphasic solution with the round texture is elongated along the declining direction when the specimen is tilted along the polarizing direction of the incident light (Fig. 3). The more declined the specimen is, the longer the four-leaf pattern is elongated. Then, it is believed that the round texture is two-dimensional (disklike texture) but not three-dimensional.

There is an extinction cross in the disklike texture when observed in the polarizing microscope under crossed polars. After inserting the compensator (λ plate) into the microscope at 45° to the crossed polarizers, the interference color in the first and third diametrically opposed quadrants of the cross is yellow, and in the second and fourth ones, blue. This indicates that the mesophase in (E–CE)C/AA solutions is negative in optics. The disklike texture has been observed in many other cholesteric liquid crystalline solutions of cellulose derivatives. In some cases, the disklike texture has concentric extinction rings or helix fine structures that are related to the cholesteric pitch.[9,10] Figure 4 gives the arrangement of the cholesteric helicoids in the disklike texture.[9] The axes of the helicoids are parallel to both the solution film plane and the radial directions, and the layers of ordered polymer chains are perpendicular to them.

In the concentration between 42 and 52 wt % at room temperature, the planar texture of the cholesteric phase appears in the solutions. The vivid colors of mesomorphic solutions can be easily observed because the mesophase selectively reflects light in a certain wavelength. The wavelength, where the ap-

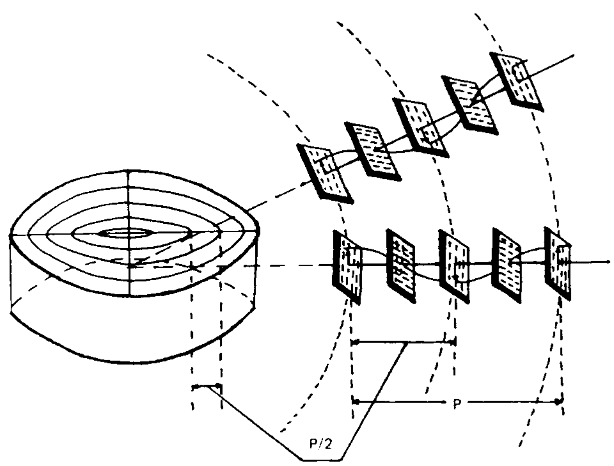


Figure 4 Scheme of the arrangement of the layers of ordered polymer chains in the disklike texture.

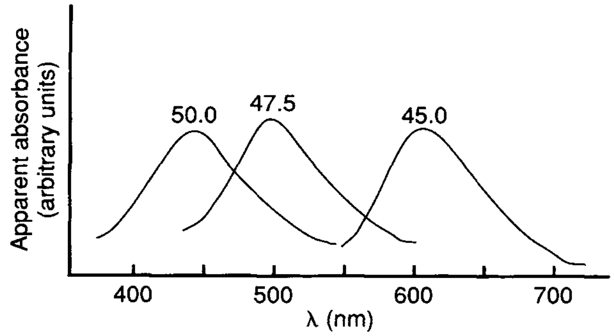


Figure 5 Reflection spectra of (E–CE)C/AA mesomorphic solutions at 25°C.

parent absorbance is maximum caused by the selective reflection of the mesophase, decreased gradually with increasing concentration (Fig. 5), i.e., the reflected light changes to the shorter wavelength direction. The color of (E–CE)C/AA mesomorphic solutions is red at the concentration of about 42 wt % and blue at about 52 wt %.

According to De Vries equation[11]

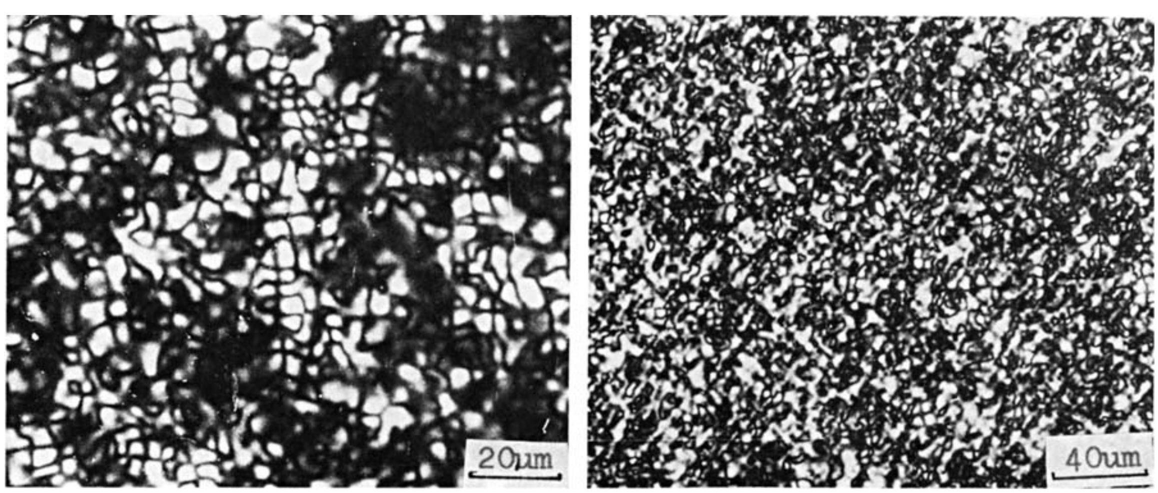
$$\lambda = \bar{n}P$$

where λ is the wavelength of the light reflected; $\bar{n}$, the mean refractive index; and P, the cholesteric pitch. P is directly proportional to λ. Therefore, it can be easily deduced from the relationship between λ and concentration shown in Figure 5 that the cholesteric pitch of the (E–CE)C/AA mesophase decreases with increasing concentration.

At concentrations below 42 wt % or above 52 wt %, (E–CE)C/AA mesomorphic solutions can show a pseudoisotropic texture in some parts of the mesophase. This texture, similar to the planar texture, is actually a lamellar anisotropic phase. It appears isotropic because its birefringence is very weak. In the lamellar phase, the layers of ordered polymer chains are parallel to the solution film plane, and the axes of helicoids, which are composed of the layers of ordered polymer chains, are perpendicular to it. The lamellar cholesteric phase selectively reflects light within a certain wavelength. The wavelength of the light reflected is situated in the visible region in the concentration region between 42 and 52 wt %, so the mesophase shows the colorful planar texture. The wavelength of the light reflected is located outside the visible region when the concentration is too low or too high, and the mesophase shows the pseudoisotropic texture.

In unitary mesomorphic solutions, i.e., when the concentration is higher than 43.1 wt %, the polygonal texture and the texture of domains gathered randomly can be observed in the solution beside the planar or pseudoisotropic texture (Fig. 6). In the polygonal texture, the axes of helicoids are parallel to the solution film plane, but they are distributed randomly in the texture of domains gathered randomly.

The mesophase aggregates with the disklike texture in biphasic solutions are suspended in the iso-



(a) (b)

Figure 6 Polarized micrographs of (E–CE)C/AA mesomorphic solution, C = 45 wt %: (a) polygonal texture; (b) texture of domains gathered randomly.

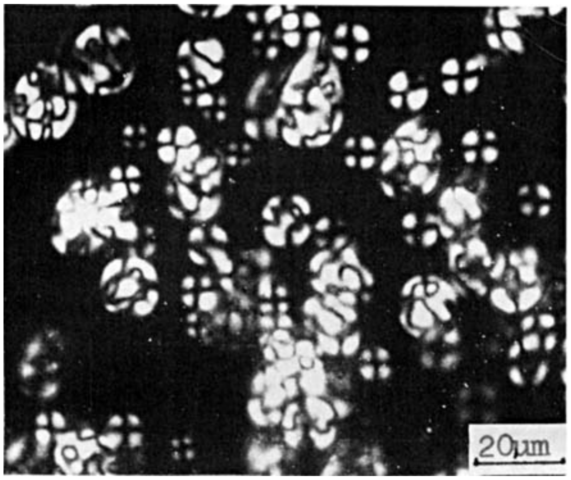


Figure 7 The combination of mesophase aggregates with the disklike texture in the (E–CE)C/AA solution; C = 34.5 wt %.

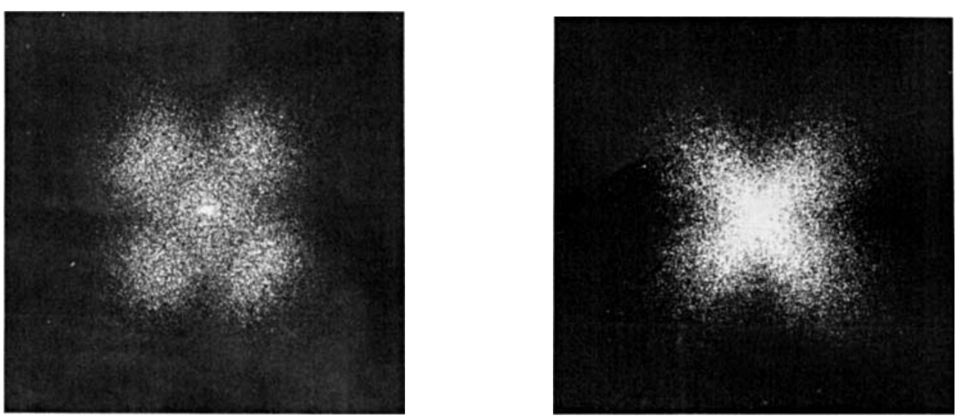
tropic phase and can flow with the solution when the slide is slightly tilted. They combine with each other to form larger aggregates in some areas (Fig. 7). The texture of this kind of larger mesophase aggregates is very similar to the polygonal texture in unitary mesomorphic solutions. The polygonal texture is composed of white areas with some dark lines. When the specimen is rotated, these dark lines are of two types: One does not vary with the rotation of the specimen and it is believed that these dark lines are the boundaries of domains. The other dark lines move with the rotation of the specimen, which implies that the axial direction of cholesteric helicoids in a domain is not along the same direction but changes continuously. It is possible, therefore, that the polygonal texture in unitary mesomorphic solutions can be regarded as the texture from the combination of deformed mesophase aggregates with the disklike texture.

Figure 8 shows the SALS H_v patterns of the (E–CE)C/AA mesophase with the polygonal texture and the texture of domains gathered randomly in Figure 6. The planar texture gives no SALS H_v pattern and the texture of domains gathered randomly gives the rodlike H_v pattern. But for the polygonal texture, a complex H_v pattern appears. It is composed of two parts: One is the X-type of the four-leaf pattern, which exhibits a maximum with respect to scattering angle similar to the H_v pattern of the disklike texture in biphasic solutions. The other is round spot pattern at a low angle.

Supposing that the four-leaf pattern originated from the scattering of mesophase aggregates with the disklike texture, the mean size of scattering units can be calculated from the following equation[12]:

$$R = 3.92\lambda_0/(2\pi \sin \theta_m)$$

where θ_m is the scattering angle at which the scattering is strongest, $\lambda_0 = 0.6328$ μm is the wavelength of the laser light, and R is the radius of the scattering unit. θ_m = 4.8° is given by Figure 8(a). Then, R = 4.7 μm can be calculated. Figure 6 shows that the dimension of the white areas in the polygonal texture



(a) (b)

Figure 8 SALS H_v patterns of the solution with (a) the polygonal texture and (b) the texture of domains gathered randomly; C = 45 wt %.

is about 2–8 μm, which coincides with the mean radium of the scattering units calculated in SALS experiments. The SALS results, therefore, confirmed that the polygonal texture is formed by deformed mesophase aggregates with the disklike texture. One of the white areas in the polygonal texture is one-quarter of a mesophase aggregate with the disklike texture because mesophase aggregates with the disklike texture are divided into four parts by the Maltese extinction cross when observed under crossed polarizing light.

By rubbing the slide with cotton and alcohol along a certain direction and then scouring the alcohol off the slide along the same direction with dry cotton,

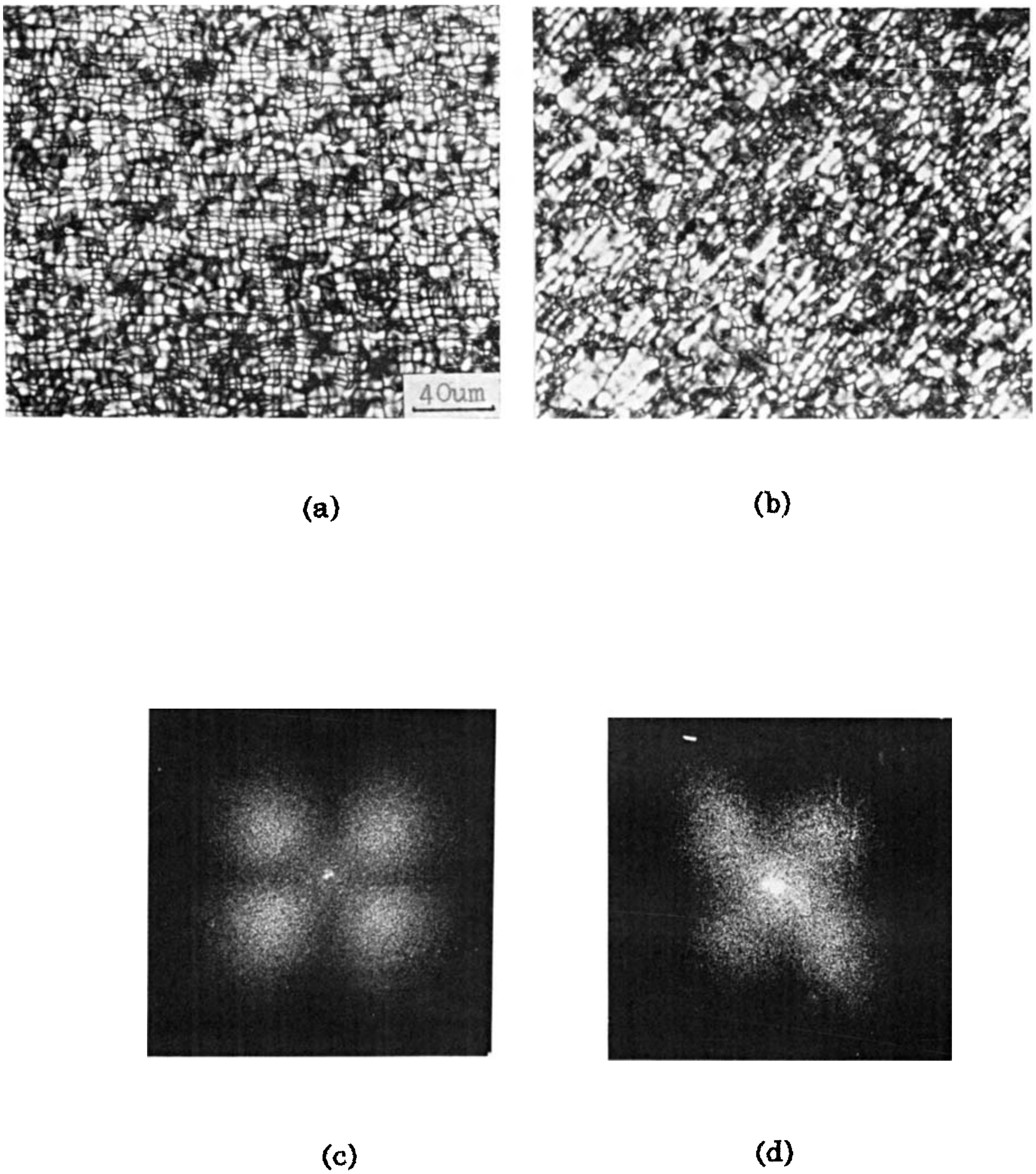


Figure 9 Polarized micrographs (a, b) and SALS H_v patterns (c, d) of (E–CE)C/AA unitary mesomorphic solutions between rubbed slides; the rubbing direction is parallel in (a) and (c) and is at 45° in (b) and (d) to the polarizing direction.

the domains of mesophase in the unitary mesomorphic solution film can arrange in order along the rubbing direction. The regular polygonal texture can be observed when the rubbing direction is parallel to the polarizing direction of the polarizers [Fig. 9(a)]. The round spot pattern in the SALS almost disappears at this position and the whole pattern seems to be that of the disklike texture in biphasic solutions [Fig. 9(c)]. The round spot pattern can appear with the rotation of the specimen. The intensity of the round spot in the SALS pattern becomes the strongest when the specimen is rotated to 45°, and for the four-leaf pattern, the two leaves that are perpendicular to the rubbing direction are elongated to the higher angle, but the other two leaves that are parallel to the rubbing direction are not [Fig. 9(b) and (d)]. From the variation of the H_v pattern with the position of the specimen, it is suggested that the round spot pattern in the SALS is perhaps attributed to the orientation correlation scattering of the domains in the mesophase.

CONCLUSIONS

(E-CE)C can be dissolved in AA and form cholesteric liquid crystalline solutions when the concentration is high enough. The mesophase begins to appear at about 33.8 wt % and the isotropic phase completely disappears at about 43.1 wt %.

The (E-CE)C/AA mesophase texture varies with concentration and the solution shows the disklike, oily streak, planar, pseudoisotropic, polygonal textures and the texture of domains gathered randomly. The polygonal texture in unitary mesomorphic solutions can be regarded as the texture from mesophase aggregates combined with deformed mesophase aggregates with the disklike texture.

(E-CE)C/AA liquid crystalline solutions exhibit vivid colors in the concentration region of 42–52 wt % because of selectively reflecting visible light. The wavelength of the light reflected by mesomorphic solutions shifts to the shorter wavelength with increasing concentration.

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REFERENCES

1. M. Panar and O. B. Willcox, Ger. Offen., 27, 05, 382 (1977).
2. R. D. Gilbert and P. A. Patton, *Prog. Polym. Sci.*, **9**, 115 (1983).
3. D. G. Gray, *Appl. Polym. Symp.*, **37**, 179 (1983).
4. R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst.*, **34**, 97 (1976).
5. Y. Nishio, T. Yamana, and S. Takahashi, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 1043 (1985).
6. J. J. Kozakirwicz, *J. Appl. Polym. Sci.*, **34**, 1109 (1987).
7. Y. Huang, M. C. Chen, and L. S. Li, *Acta Chim. Sin. (China)*, **46**, 367 (1988).
8. Y. Huang and B. T. Li, *Acta Polym. Sin. (China)*, **1**, 51 (1987).
9. Y. Huang, *J. Macromol. Sci. Phys. B*, **28**, 131 (1989).
10. Y. Huang, B. K. Wu, and S. H. Jiang, *Mol. Cryst. Liq. Cryst.*, **188**, 177 (1990).
11. A. De Vries, *Acta Crystallogr.*, **4**, 219 (1951).
12. S. Clough, J. J. Aarsten, and R. S. Stein, *J. Appl. Polym. Sci.*, **36**, 3072 (1965).

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