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Phase separation of the liquid crystal in the cholesterin phase

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Abstract

In the ethyl-cyanoethyl cellulose [(E-CE)C]/acrylic acid [AA]/4-cyano-4'-n-heptyl biphenyl (TCB) solutions, 7CB acted as a diluting reagent when it was added into the (E-CE)C/AA cholesteric liquid crystalline solutions. The dispersed phase with 250-300nm in size appeared after the AA in the isotropic (E-CE)C/AA/7CB solutions with the 7CB concentration (C_{7CB}) between 27.4 - 41.2wt% was polymerized at 24°C. There was the dispersed phase rich with 7CB in the (E-CE)C/AA/7CB cholesteric liquid crystalline solutions when C_{7CB} was 43.0wt% at 24°C. The temperature at which the anisotropic phase in the dispersed phase transformed to the isotropic phase in the solutions was increased after the polymerization of the AA, but the transition temperature of the dispersed phase in both the solutions and the films was lower than that of the pure 7CB.

Key words Phase separation, cholesteric phase, ethyl-cyanoethyl cellulose and 4-cyano-4'-n-heptyl-biphenyl.

Introduction

Cellulose and its derivatives can form cholesteric liquid crystalline solutions and are good model polymers for studying the macromolecular cholesteric order because of their semi-rigid backbone[1,2]. Ethyl-cyanoethyl cellulose [(E-CE)C] can be dissolved in many organic solvents and form cholesteric liquid crystalline solutions[3]. In the (E-CE)C solutions with both the cholesteric liquid crystalline phase and the isotropic phase, the phase separation between two phases occurs when the cholesteric phase begins to be formed and the mesophase texture depends on the variation of the concentration[4]. The structure of the solutions is also influenced by adding small molecular liquid crystals in the systems. In the polymer dispersed liquid crystal systems, for example, the phase equilibrium temperature and the phase separation mechanism depend on the thermodynamics of the systems and many theoretical research works in this field are the focus of condensed physics[5-10].

In this paper, the phase separation between the small molecular liquid crystals and the polymer matrix in either cholesteric liquid crystalline state or isotropic one was studied. The structure variation of the cholesteric phase with the composition was also discussed.

Experimental

The ethyl-cyanoethyl cellulose [(E-CE)C] was obtained by reaction of ethyl cellulose and acrylonitrile with the catalysis of base[3]. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.26. The molecular weight of the (E-CE)C M_n, measured by gel permeation chromatograph (GPC) (HPLC, Waters Mode-209) with tetrahydrofuran as a solvent and calibrated by standard polystyrene, was 70,000. The AA was a chemically pure reagent and was distilled before used. The 4-cyano-4'-n-heptyl biphenyl (7CB), which could form nematic phase, was provided by the Tsinghua University.

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(E-CE)C/AA/7CB solutions were prepared in glass vials by weighing the desired amount of (E-CE)C, AA, 7CB and 2 wt% photo-initiator, ethyl ether benzoin (with respect to AA). In order to obtain an equilibrium solution, the solutions were held at room temperature for about one to eight weeks. The solution was sandwiched between two glass slides with the thickness of about 0.2-0.3 mm and sealed with wax. The sample was then, placed in 24°C water bath and inserted into a chamber with a 250 W high intensity mercury arc lamp until complete polymerization of the AA occurred to form a solid film.

The samples were heated by using a hot stage with automatic temperature controller and the variation of the morphologies of the systems was observed by a polarizing microscope (Leitz, ORTHOPLANPOL). The visible light spectra of the systems with cholesteric liquid crystalline phase were recorded by an UV-VIS spectrophotometer (Specord UV-Vis, Ziess, Germany). The phase transition of the liquid crystalline phase was recorded by a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2C) with the heating rate of 10 K/min. The morphology of the films was observed by a scanning electron microscope (SEM) (Hitach-S430) after the sample was ultramicrotomed.

Results and discussion

When the (E-CE)C concentration is above 26 wt%, the (E-CE)C/AA solutions show cholesteric liquid crystalline behavior at room temperature [11]. In the (E-CE)C/AA/7CB ternary solutions, the mass ratio of the [(E-CE)C] to the AA is 46:54 and the structure of the solutions is varied with the variation of the 7CB concentration (C_{7CB}).

When C_{7CB} is below 12 wt%, which means that the total concentration of the (E-CE)C is above 40wt% in the ternary solutions, the solutions exhibit the cholesteric order. Fig.1 is a crossed light polarizing micrograph of the (E-CE)C/AA/ 7CB ternary solutions. The mesophase shows the planar texture with oil-streaks, which is a typical texture of the cholesteric phase.

Fig.2 shows the variation of the selective reflection wavelength with C_{7CB} for the (E-CE)C/AA/7CB cholesteric liquid crystalline solution. It can be observed that the reflection

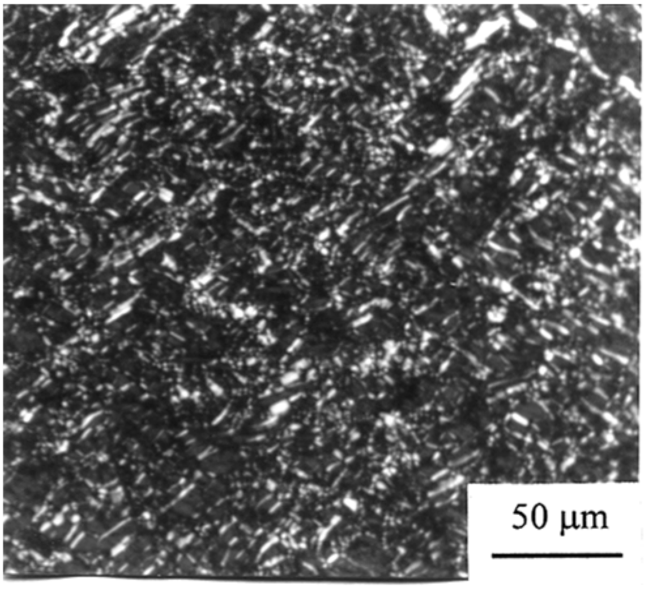

Fig.1 The texture of the lyotropic cholesteric liquid crystal solution with 5.1wt% 7CB observed by polar microscope

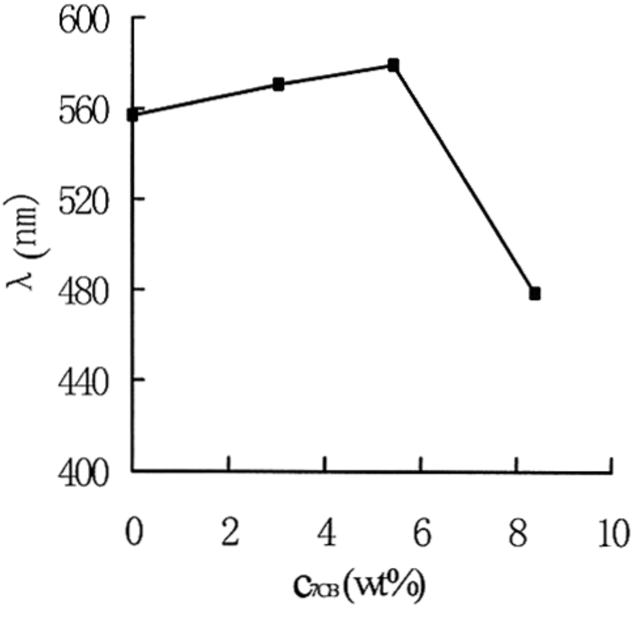

Fig.2 The reflection wavelength variations of the (E-CE)C/AA/7CB cholesteric solutions with increasing C_{7CB} at 24°C

wavelength is firstly shifted to the long wavelength direction and then to the short wavelength direction with increasing C_{7CB}. Since 7CB can be completely dissolved in the AA, 7CB acts as a diluted reagent when C_{7CB} is lower than 5.5 wt%, which results in the decrease of the (E-CE)C concentration. Therefore, the cholesteric pitch is increased with increasing C_{7CB} and the reflection wavelength of the cholesteric phase shifts to the long wavelength direction. When C_{7CB} is above 5.5 wt%, however, the reflection wavelength of the (E-CE)C/AA/7CB cholesteric phase is shifted to the short wavelength direction with increasing C_{7CB}, which suggests that the addition of 7CB into the (E-CE)C/AA solutions may influence the cholesteric liquid crystalline behavior. As a nematic liquid crystal, the 7CB may align orderly in the (E-CE)C/AA/7CB ternary solutions, which may results in the decrease of the distance between ordered layers of (E-CE)C chains in the cholesteric phase and so, the pitch of the cholesteric phase decreases and the reflection wavelength of the cholesteric phase shifts to the short wavelength direction.

With further increasing C_{7CB}, the ternary solution is transformed from the cholesteric order to the biphasic states in which the isotropic phase coexists with the cholesteric phase. The ratio of the cholesteric phase in the solution is decreased with increasing C_{7CB} or decreasing the (E-CE)C concentration. When C_{7CB} is in the range of 13.9-21.3wt%, in which the concentration of the (E-CE)C is 36.2-39.4wt%, there exists the disk-like texture with extinction cross when observed by polarizing microscopy (Fig.3). The cholesteric domains with the disk-like texture are not in the same plane and the diameter of them is about 8-12 μm. After inserting one class red gypsum plank into the light path, the first and third quadrants become blue and the second and fourth ones become red, which suggests that the optical property of the cholesteric phase in the solution is negative, as is the case with the (E-CE)C lyotropic cholesteric phase[11]. The results mentioned above indicate that the 7CB in the solutions acts as the diluted reagent, which results in decreasing the (E-CE)C concentration, and the structure of the solutions is changed from the cholesteric order to the isotropic state.

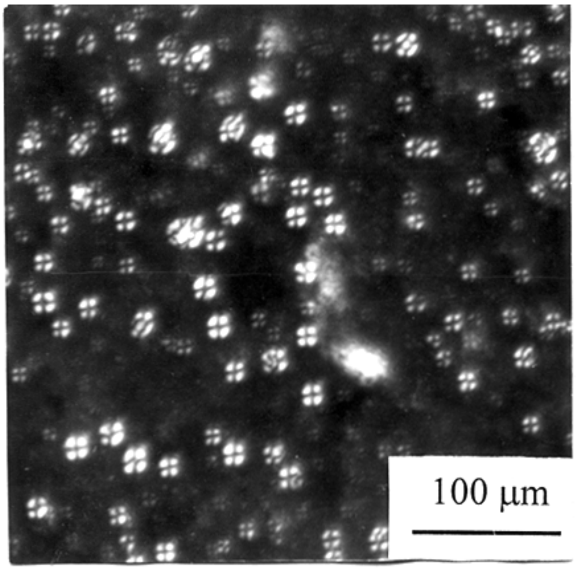

Fig.3 The texture of the (E-CE)C/AA/7CB cholesteric liquid crystal solution with the C_{7CB} of 17.8wt%

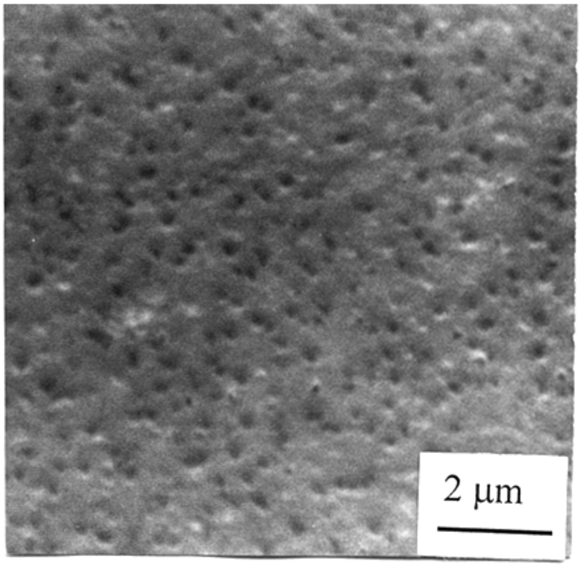

Fig.4 The SEM macrograph of the (E-CE)C/PAA/7CB system prepared from the isotropic solution with C_{7Cb} of 39.3wt%.

With further increasing C_{7CB}, the solution is transformed to an isotropic system and the cholesteric phase completely disappears, which confirms again the diluting effect of the 7CB in the solutions. In the (E-CE)C/AA/7CB isotropic solutions, no phase separation can be observed and the solutions are homogeneous. The phase separation in the systems, however, occurs during the solidification of the systems, in which the AA is polymerized and the dispersed phase is rich in the 7CB because it shows anisotropic behavior and can transform to the isotropic state with increasing temperature. But the continuous phase is still isotropic.

The dispersed phase in the E-CE)C/PAA/7CB films can be directly observed by SEM (Fig. 4) after the polymerization of the AA. The dispersed phase is homogeneously distributed in the isotropic matrix and the size of dispersed phase is about 250-300nm. There are two endothermic peaks in the DSC curves, which are attributed to the melting process and the transition from the liquid crystalline state to the isotropic one (clear point) of the dispersed phase in the systems. In comparison with the transition temperature of the pure 7CB, the melting temperature and the clear point of the 7CB in the dispersed phase of the films are decreased about 3 K and 4 K respectively, which suggested that there is not only pure 7CB in the dispersed phase.

The phase transition temperatures of the dispersed phase in the (E-CE)C/PAA/7CB films are listed in Table 1. The melting temperature (T_m) of the dispersed phase is about 301.7K and the clear point (T_c) is in the range of 310-312K. Both T_m and T_c for the dispersed phase are lower than those for the pure 7CB. The relative transition enthalpy from the anisotropic phase to the isotropic one (H_{rTc}) and that of melting (H_{rTm}), which are defined as the transition enthalpy (H_{Tc} or H_{Tm}) divided by C_{7CB} in the system, are far below the values of the pure 7CB. It is suggested that only part of the 7CB be separated from the ternary system to form the dispersed phase during the polymerization of the AA. This may be because the photo-polymerization is fast and the phase separation of 7CB from the continuous phase can not completely occur. It can be concluded that the 7CB exists in both the dispersed and continuous phases in the (E-CE)C/PAA/7CB films but it is rich in the dispersed phase.

Table 1 Transition temperatures and heat content of (E-CE)C/PAA/7CB Films with different C_{7CB}

C_{7CB}/wt%	T_m/K	T_c/K	H_{Tm}/cal·g^{-1}	*H_{rTm}/cal·g^{-1}	H_{Tc}/cal·g^{-1}	**H_{rTc}/cal·g^{-1}
100	304.97	315.72	23.01	23.01	0.61	0.61
27.4	301.71	-	0.09	0.328	-	-
32.7	301.92	310.44	0.08	0.292	0.13	0.397
39.3	301.56	311.57	0.05	0.119	0.06	0.153

*H_{rTm}= H_{Tm}/C_{7CB}, ** H_{rTc}= H_{Tc}/C_{7CB}

When C_{7CB} is about 43wt%, the 7CB molecules are separated from the (E-CE)C/AA/7CB solutions to form the dispersed phase at room temperature and (E-CE)C/AA forms the continuous phase (Fig. 5A). Both the continuous and dispersed phases in the solutions show the birefringence but in the dispersed phase the birefringence is very strong. The texture with the polygonal shape in the dispersed phase at 0°C is changed to the round shape with dark extinction cross at about 20°C. The first and third quadrants are red and the second and fourth ones are blue after inserting one class red gypsum plank into the light path, which suggests that the optical property of the liquid crystal in the dispersed phase is positive. Therefore, the liquid crystalline structure in the dispersed phase is nematic, which is different from the continuous phase. The continuous phase is transformed to the cholesteric phase with the negative optical property during the phase separation, because the (E-CE)C concentration is increased when C_{7CB} is decreased in the continuous phase. The nematic order in the dispersed phase can be transformed to the isotropic state at 24°C (Fig.5B).

In comparison with the phase transition temperature of the pure 7CB, T_m and T_c of the dispersed phase in the (E-CE)C/AA/7CB two-phase solutions are decreased by12.5K and 19.3K, respectively. The nematic temperature range becomes narrower, from 10K to about 3K. This difference of the transition temperatures between the pure 7CB and the dispersed phase in the solutions may be resulted from the diffusion of the AA and the (E-CE)C) molecules into the dispersed phase.

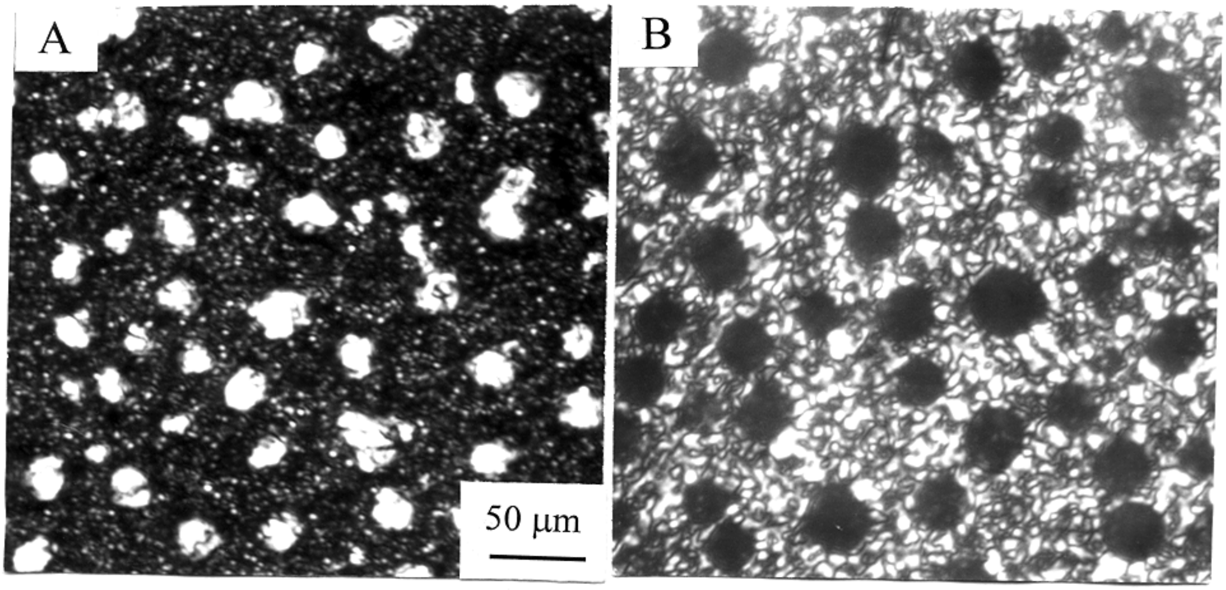

Fig.5 The texture of the (E-CE)C/AA/7CB two-phase solution with 43.05wt% 7CB at the temperature of (A) T=0°C (B) T=24°C.

The structure of the (E-CE)C/AA/7CB two-phase solutions can be solidified by UV-initiated polymerization of the AA to form (E-CE)C/PAA/7CB films at 24°C, at which the dispersed phase is isotropic. The size of the dispersed phase is almost unchanged during the polymerization of the AA (Fig.6). But it is interesting that the dispersed phase is transformed from the isotropic state before polymerization to the anisotropic state after polymerization at 24°C (Fig. 6A). The AA molecules in the solutions can be migrated from the dispersed phase to the continuous phase during the polymerization, in which the AA concentration is decreased in the dispersed phase with decreasing the AA concentration in the continuous phase. This results in the increase of the phase transition temperatures of the dispersed phase. The mesophase texture of the continuous phase is almost unchanged (Fig. 6A and B), which meant that the cholesteric structure in the continuous phase is reserved after the polymerization of the AA.

In addition, the dark extinction cross texture is not observed in the dispersed phase during the increase of the temperature. This indicates that the dispersed phase in the cholesteric matrix is not a single domain. Similarly, the temperature, at which the anisotropic state of the dispersed phase in the films is transformed to the isotropic state, is lower than that of the pure 7CB, which means that there are not only the 7CB molecules in the dispersed phase, but also some AA molecules and/or (E-CE)C chains.

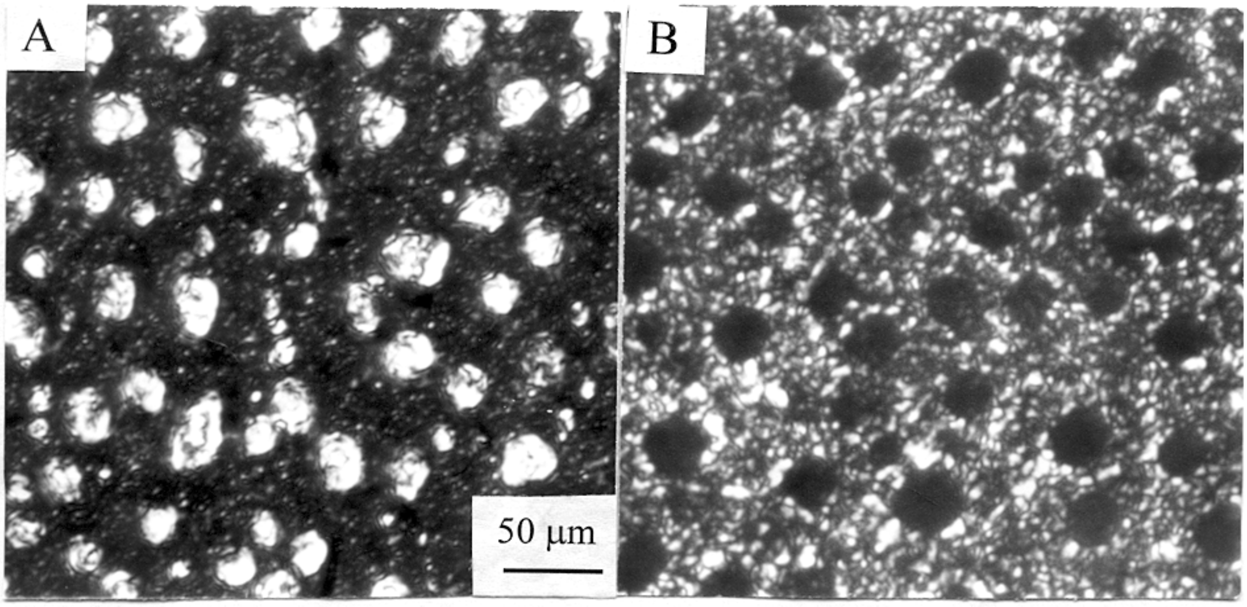

Fig.6 The texture of (E-CE)C/PAA/7CB film prepared from the two-phase solution with 43.05wt% 7CB, the temperature is (A) T=24°C and (B) T=39°C.

Conclusions

The concentration of the 7CB greatly influences the structure of (E-CE)C/AA/7CB ternary solutions. The 7CB in the solutions acts as a diluted reagent when the mass ratio of (E-CE)C and AA is fixed. When the C_{7CB} is in the range of 27-41wt% (the mass ratio of (E-CE)C and AA is 46:54), the solution is isotropic and homogeneous. After the AA in the solution is polymerized, the phase separation between the 7CB and the (E-CE)C/PAA matrix with the isotropic order occurs. When the C_{7CB} is above 42wt%, the phase separation in the ternary solution appears at room temperature and the continuous phase transforms from the isotropic phase to the cholesteric order again. There are some AA and/or (E-CE)C molecules besides the 7CB molecules in the dispersed phase, which results in being lower the phase transition temperature of the dispersed phase than that of the 7CB. The transition temperature of the dispersed phase is increased after the polymerization of the AA in the (E-CE)C/AA/7CB two-phase solutions.

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