

The variation of cholesteric order during polymerization of the solvent in liquid crystalline solutions

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Summary

Ethyl-cyanoethyl cellulose [(E-CE)C]/acrylic acid (AA) formed a cholesteric liquid crystalline solution with vivid colors when the concentration is 42–52 wt%. (E-CE)C/polyacrylic acid (PAA) composites with cholesteric structure were prepared by polymerization of the AA in the (E-CE)C/AA liquid crystalline solutions. The layers of ordered polymer chains in the cholesteric phase were inclined during polymerization and the degree of the inclination depended on the polymerization temperature and the concentration of the solution before polymerization.

Key words: Cholesteric structure, polymerization, and selective reflection.

Introduction

Cellulose and its derivatives are semirigid chain polymers and can form lyotropic liquid crystals in appropriate solvents^[1]. Some of cellulose derivatives can form both lyotropic liquid crystals and thermotropic liquid crystals. Most of liquid crystals formed from cellulose and its derivatives are cholesteric. Cholesteric liquid crystals can selectively reflect visible light and exhibit brilliant colors when the cholesteric helical pitch is comparable with the wavelength of visible light^[2]. The temperature-sensitive effects associated with selective reflection have been used in a variety of applications, such as thermal indicators and radiation sensors. In some cases, it is desirable that the wavelength of selective reflection be insensitive to temperature. For this purpose, many color films in which the cholesteric structure is frozen have been prepared^[3,4]. The films are applicable to passive optical devices, such as circular polarizer, bandpass filters notch filters and reflective displays.

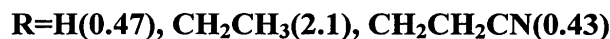
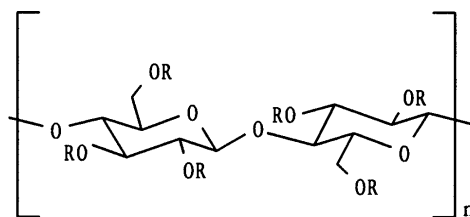
This kind of films can be prepared by many ways. One of them is to dissolve a liquid crystalline polymer in a vinyl monomer solvent to form a lyotropic cholesteric liquid crystalline solution. Upon polymerization of the solvent, the cholesteric order is frozen. Thus, composite films with cholesteric structure can be prepared^[4,5].

We have reported that ethyl cyanoethyl cellulose [(E-CE)C] can be dissolved in acrylic acid (AA) to form a cholesteric liquid crystalline phase, which exhibits brilliant colors when the concentration is in a certain range^[6]. Furthermore, the (E-CE)C/AA cholesteric liquid crystalline solutions can be easily immobilized via photo-polymerizing with the vinyl monomer AA[5]. In this study, the variation of the cholesteric structure in the system during the polymerization of the solvent AA is studied. The influence of the structure of (E-CE)C polymer chains and the cross-linkage of the polyacrylic acid (PAA) on the properties of the (E-CE)C/PAA composite films are also discussed.

Experimental

The preparation of ethyl-cyanoethyl cellulose [(E-CE)C] was achieved by the reaction of ethyl cellulose, of which the degree of substitution for ethyl was about 2.1, with

acrylonitrile. The molecular formula of the (E-CE)C is as shown in following:



The molecular weight of (E-CE)C, measured by gel permeation chromatography (GPC) (HPLC, Waters, Mode-209) with tetrahydrofuran as a solvent and calibrated by standard polystyrene, was 21.3×10^4 . The degree of substitution for cyanoethyl, calculated from the nitrogen content of the (E-CE)C, which was measured by elementary analysis (Heraeus, CHN Rapid Element Analysis Instrument, Germany), was 0.36. The AA was chemically pure and distilled in vacuum before use.

(E-CE)C/AA liquid crystalline solutions were prepared in glass vials. The desired amount of (E-CE)C, AA and the initiator, benzoin ethyl ether, were mixed by a spatula for several minutes in a vial and the mixture was allowed to sit for one week. Finally, a homogeneous solution was formed, which was stored in the dark until being used. (E-CE)C/AA cholesteric liquid crystalline solutions with 2 wt% benzoin ethyl ether (respect to AA) were used in photopolymerization. The solution was sandwiched between two glass slides with the thickness of about 0.3 mm and sealed with wax. The samples were inserted into a chamber with a 250 W high-intensity mercury arc lamp until complete polymerization occurred to form (E-CE)C/polyacrylic acid (PAA) composite films with the thickness of about 0.3 mm. Two different polymerization temperatures, 25°C and 0°C (ice bath), were used. Cross-linked (E-CE)C/PAA composites were prepared by adding cross-linked reagent, glycol diacrylate (GDA), into the solution before polymerization.

The visible spectra of (E-CE)C/AA liquid crystalline solutions and (E-CE)C/PAA composites were recorded by an UV-VIS spectrophotometer (Specord UV-Vis, Ziess, Germany). The textures of (E-CE)C/PAA composites at different temperatures were observed by a polarizing microscope (Orthoplan-pol, Leitz, Germany) with a hot stage. The mean refractive index of the solutions and the composites was measured by an Abbe' refractometer (2AW, Shanghai Optical Instrument Factory, Shanghai, China). T_{gs} of the composites were determined by a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2C). X-ray diffraction of the composites was carried out by a X-ray diffractometer (D/max-1200, Rigaku, Japan).

Results and Discussion

(E-CE)C was dissolved in AA to form cholesteric liquid crystalline solutions at the concentration above 33.8 wt%^[6]. Within the concentration of 42-52 wt%, (E-CE)C/AA liquid crystalline phase in the solutions exhibits a planar texture with brilliant colors because of the selective reflection of visible light of certain wavelength and the wavelength of the maximum reflection of the solutions decreases with increasing concentration. Fig.1 gives the reflection spectra of the 45 wt% (E-CE)C/AA liquid

crystalline solution and the (E-CE)C/PAA composite prepared from the solution. The peaks in spectra reveal that the selective reflection due to the cholesteric order occurs in the visible wavelength. The selective reflection shifts to a shorter wavelength direction after the polymerization of the AA. When the composite is observed by a polarizing microscope, it can be found that the composite shows the strongest birefringence at a certain angle to the normal to the film surface. In other words, there is a local orientation for (E-CE)C polymer chains in the composite.

The selective reflection from cholesteric liquid crystals with the planar texture is attributed to the Bragg-like diffraction of visible light caused by the periodic layers of ordered molecules. The wavelength of the strongest reflection can be expressed by the formula^[7]:

$$\lambda_{\max} = P \cdot n \cdot \sin\phi$$

Where λ_{\max} is the wavelength of the strongest reflection, P is the pitch of the cholesteric mesophase, n is the mean refractive index and the angle ϕ is the angle between the direction of the incident light and the layers of ordered polymer chains. Before polymerization, the liquid crystalline solution shows the planar texture when the concentration is higher than 42 wt% and the layers of ordered polymer chains are parallel to the solution film surface. Thus, the incident light is perpendicular to the layers of ordered polymer chains when it is normal to the solution film surface. Therefore, $\phi = 90^\circ$ before polymerization and according to the formula mentioned above, at this time, $\lambda_{\max} = P \cdot n$. From the pitch of the cholesteric liquid crystalline phase in the (E-CE)C/AA solutions and the periodicity of the lamellar structure in the (E-CE)C/PAA composites with cholesteric order observed by TEM (Table 1)^[5], it is known that the pitch of the cholesteric structure is almost unchanged during the polymerization of the AA in the solution. The mean refractive index of the composites is about 13% larger than that of the corresponding solutions and the ratio of the mean refractive index of the solution and of the composite n_s/n_p is 0.885-0.89 (Table 2). According the formula $\lambda_{\max} = P \cdot n \cdot \sin\phi$, the variation of the mean refractive index should result in the shift of λ_{\max} to the longer wavelength direction but the λ_{\max} actually shifts towards the shorter wavelength direction. Consequently, the variation of the wavelength of the reflection indicates that the ϕ is

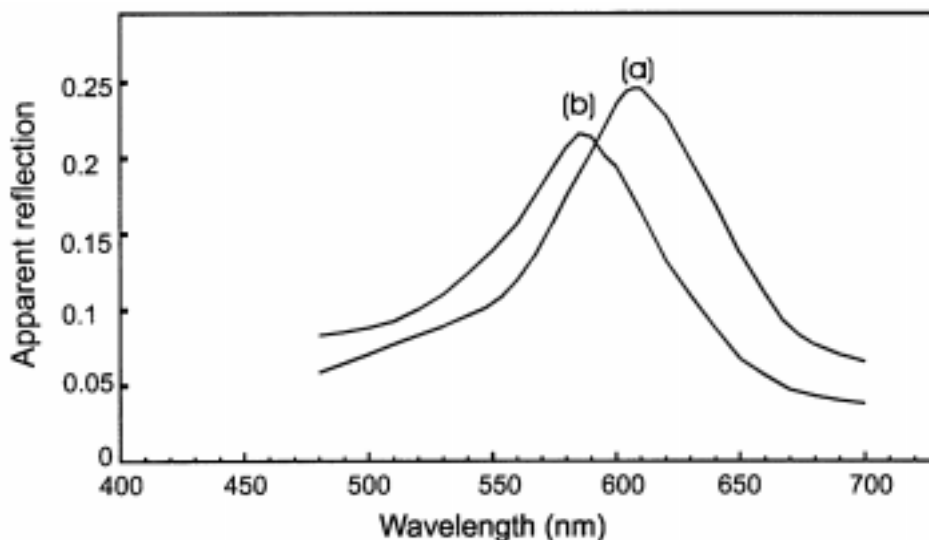


Fig.1. Reflection spectra of the 45 wt%(E-CE)C/AA cholesteric liquid crystalline solution and the (E-CE)C/PAA composite prepared from the solution.

varied and becomes smaller than 90° after the polymerization. Before polymerization, no orientation of the (E-CE)C polymer chains can be observed by polarizing microscopy in the cholesteric phase with the planar texture. But the existence of the orientation for (E-CE)C polymer chains in composites, after polymerization, can be observed by the polarizing microscope, which suggests that the layers of ordered polymer chains are not completely parallel to the solution film surface and the layers of ordered polymer chains are inclined.

The results of X-ray diffraction confirm the inclination of the layers of ordered polymer chains in the cholesteric phase. Fig.3 shows the X-ray diffraction spectra of the 50 wt% (E-CE)C/PAA composite. The diffraction peak at about $2\theta=9^\circ$ is attributed to the layer structure of the cholesteric phase^[8]. Fig.3a is an X-ray diffraction spectrum of the composite when the X-ray diffraction is perpendicular to the composite film surface in measuring and there is a weak diffraction peak at $2\theta=9^\circ$. If the layers of ordered polymer chains in cholesteric phase are totally parallel to the composite film surface, the X-ray diffraction peak at about $2\theta=9^\circ$ should not exist in the spectrum when the X-ray diffraction is parallel to the composite film surface. The existence of the diffraction when

Table 1. Half pitch of (E-CE)C/AA cholesteric solutions P/2 and periodicity of the lamellation for corresponding composites

| (E-CE)C Content (wt%) | 44 | 50 |
|-----------------------|-----|-----|
| P/2 (nm) | 232 | 157 |
| P.S.* (nm) | 240 | 150 |

*P.S. is the abbreviated form of the periodicity of the lamellation in composites.

surface in measuring. There is a very strong

Table 2. Refractive indices of (E-CE)C/AA solutions n_s and (E-CE)C/PAA composites n_p at 31.5°C .

| (E-CE)C Content (wt%) | 38.0 | 50.0 |
|-----------------------|-------|-------|
| n_s | 1.445 | 1.450 |
| n_p | 1.640 | 1.637 |
| n_s/n_p | 0.887 | 0.886 |

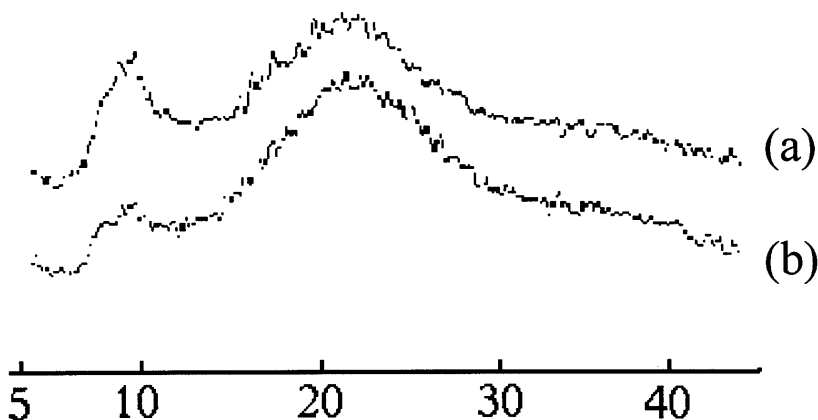


Fig.2. X-ray diffraction spectra of the 50 wt% (E-CE)C/PAA composite with cholesteric order, X-ray beam is (a) perpendicular and (b) parallel to the composite plate surface.

the X-ray diffraction is parallel to the composite film surface, however, indicates that the layers of ordered polymer chains in the cholesteric phase are not totally parallel to the composite plate surface.

Since the incident light is perpendicular to the composite film surface, the angle φ is smaller than 90° . The wavelength of the reflection shifts towards the shorter wavelength direction with decreasing the angle φ , according to the formula mentioned above. The inclination of the layers of ordered polymer chains in cholesteric phase during the polymerization is schematically demonstrated in Fig.4. The angle φ can be calculated from the value of n_s/n_p and λ_{\max} of the solution and the corresponding composite when the incident light is normal to the solution film surface and composite plane surface. The inclination angle of the layers of ordered polymer chains is $90^\circ - \varphi$. The inclination angles of the layers of ordered polymer chains, $90^\circ - \varphi$, in the various composites which are prepared at different temperatures and have different (E-CE)C contents are listed in Table 3. The inclination angle in Table 3 is $36-46^\circ$ and this result is coincided with the results in small angle light scattering (SALS) experiments in which the SALS H_v pattern changes from X type four-leaf to + type one after the polymerization^[5].

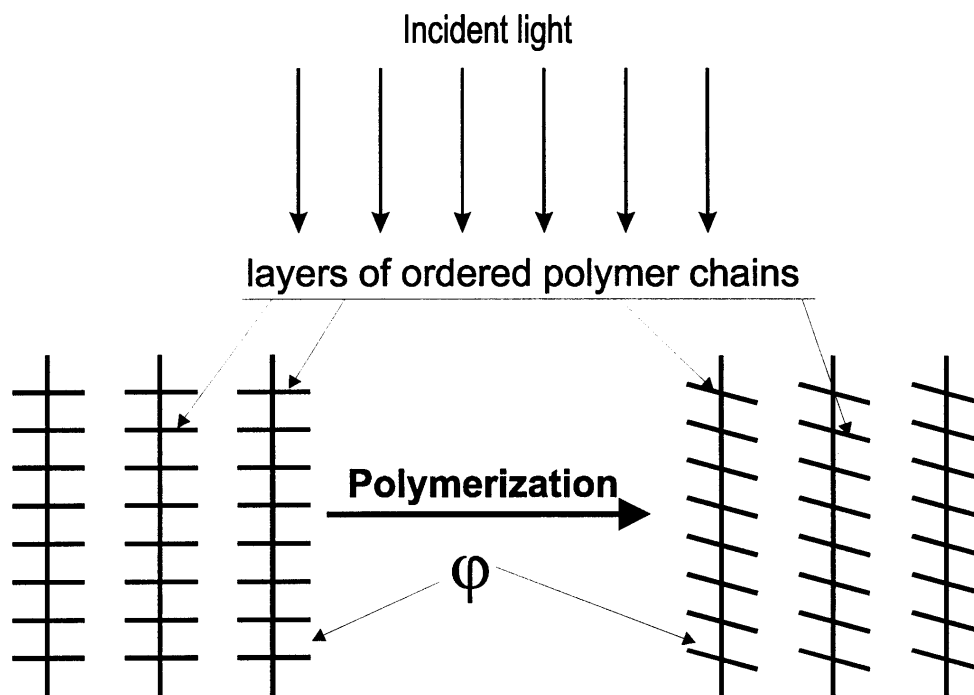


Figure 3. Scheme of inclination of successive layers of polymer chains during polymerization, arrows present the projection of the directions of polymer chains.

The data in Table 3 indicate that the inclination of the layers of ordered polymer chains during the polymerization be influenced by (E-CE)C content and the polymerization temperature. Two polymerization temperatures are employed during the polymerization. One is 0°C , in which the sample is placed in ice water bath during the polymerization, and the other is room temperature. The inclination angle of molecular layers in the cholesteric phase when the polymerization of the solvent is induced at 0°C is smaller than that when the polymerization is induced at room temperature. The inclination angle is also decreased with increasing concentration of the solution before

polymerization. As we know, the viscosity of the solution increases with increasing concentration and decreasing temperature. The motion of polymer chains depends on the viscosity of the system. It is suggested that the inclination of the layers of ordered polymer

Table 3. The inclination angles of the layers of the ordered polymer chains in the cholesteric phase during photo-polymerization.

| Polymerization temperature | 0°C | | | 25°C | |
|----------------------------|------|------|------|------|------|
| C (wt %) | 45 | 47 | 42 | 45 | 47 |
| 90-φ (°) | 35.9 | 34.1 | 45.6 | 44.9 | 43.4 |

chains in the cholesteric phase depend on the viscosity of the solution before polymerization. So, in order to decrease the inclination of the layers of ordered polymer chains during the polymerization and retain the colors of the system after polymerization, the solution concentration should be high and a low polymerization temperature should be used in the polymerization.

Conclusions

The (E-CE)C/PAA composites with cholesteric order can be prepared from cholesteric liquid crystalline solutions by polymerization of the solvent and the maximum reflection wavelength of the composites is shorter than that of the solutions before polymerization. The layers of ordered polymer chains in the cholesteric phase are inclined during polymerization and the degree of the inclination is controlled by the polymerization temperature and the concentration of the solution before polymerization. The inclination angle is small, if the solution with high concentration and the low polymerization temperature are used in polymerization, and the color of the composites may be the same as that of the solution before polymerization.

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