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INFLUENCE OF THE SOLVENT SWELLING ON MACROMOLECULAR CHOLESTERIC LIQUID CRYSTALLINE STRUCTURE*

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Abstract Ethyl-cyanoethyl cellulose [(E-CE)C]/cross-linked polyacrylic acid [PAA] molecular composites with cholesteric order were prepared. It was found that the macromolecular cholesteric structure was changed with the swelling of PAA in the composites. The selective reflection of the cholesteric phase shifted to the longer wavelength and the X-ray diffraction angle shifted to the high angle direction during swelling, which suggested that the cholesteric pitch and the number of the layers of ordered (E-CE)C chains in the cholesteric phase were increased.

Key words Cholesteric liquid crystal, Molecular composite, Ethyl-cyanoethyl cellulose, *in situ* Polymerization, Structure

INTRODUCTION

Macromolecular cholesteric liquid crystalline phase shows a periodical lamellar morphology^[1-3]. The periodicity of the lamellae is equal to a half pitch of the cholesteric phase, which reflects the periodical variation of the orientation direction of macromolecular chains in the cholesteric phase^[4].

Cellulose and its derivatives can form lyotropic cholesteric liquid crystals because of their semi-rigid backbone^[5, 6]. The mesophase textures of cellulose derivative cholesteric liquid crystalline solutions have been observed by light microscopy^[7]. Ethyl-cyanoethyl cellulose [(E-EC)C] can be dissolved in acrylic acid (AA) and forms cholesteric liquid crystalline solution^[8], and [(E-EC)C]/polyacrylic acid (PAA) composites with cholesteric order can be prepared by photopolymerizing AA in the cholesteric phase^[9]. [(E-EC)C]/crosslinked PAA molecular composite can be prepared by adding cross-linking reagents into the solutions before polymerization. In this paper, the variation of macromolecular cholesteric structure during the swelling of composites in water was discussed.

EXPERIMENTAL

The (E-CE)C was obtained by the reaction of ethyl cellulose with acrylonitrile under the catalytic

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action of an alkali^[10]. The degrees of substitution for the ethyl group and the cyanoethyl group in (E-CE)C are about 2.1 and 0.26, respectively. The M_n of the (E-EC)C, measured by gel permeation chromatograph (GPC) (HPLC, Waters Mode-209) with tetrahydrofuran as the solvent and calibrated by the standard polystyrene, is 70,000. The acrylic acid (AA) was a chemically pure reagent and was distilled before use.

The (E-EC)C/AA solutions for polymerization were prepared by mixing the (E-EC)C, AA, photo-initiator (benzoin ethyl ether) and cross-linking reagent (divinylbenzene) in glass vials to form a homogeneous solution. The liquid crystalline solution was sandwiched between two glass slides with a thickness of about 0.2~0.3 mm. The samples were placed in a chamber and were irradiated with a 250W high intensity mercury arc lamp until the polymerization was completed with the formation of (E-CE)C/cross-linked PAA composites.

The composite was swelled in distilled water and the swelling ratio was calculated by the ratio of $(W-W_0)/W_0$, where W and W_0 are the weight after and before swelling. The transmission spectra of (E-CE)C/PAA composites were recorded on an UV-VIS spectrophotometer (Specord UV-Vis, Ziess, Germany). The textures of (E-CE)C/cross-linked PAA composites were observed with a polarizing microscope (Orthoplan-pol, Leitz, Germany). The mean refractive index was measured by an Abbe refractometer (2AW, Shanghai Optical Instrument Factory, Shanghai, China) and X-ray diffraction measurements was carried out on an X-ray diffractometer (D/max-1200, Rigaku, Japan).

RESULTS AND DISCUSSION

The macromolecular cholesteric phase in (E-CE)C/cross-linked PAA composites with 44~54 wt% of (E-CE)C exhibits a planar texture and shows vivid colors because of the selective reflection of the cholesteric phase. The wavelength of the light can be described by the De Vries equation^[11]:

$$\lambda_{\max} = n p \sin \varphi$$

where $\lambda_{\max}$ is the wavelength of visible light selectively reflected by the cholesteric phase, n is the average refractive index of the birefringent cholesteric liquid crystals, and φ is the angle between the direction of incident light and the parallel macromolecular layers. The cross-linked PAA in the composites, which acts as the solvent in the cholesteric phase, can be swelled when the composites are put in water. The wavelength of selective reflection of the macromolecular cholesteric phase in the (E-CE)C/PAA composites shifts to the longer wavelength direction after the cross-linked PAA in the composites is swelled in water. This reflects that the structure of the cholesteric phase is changed by absorbing water of the solvent molecules.

The shift in the wavelength of the selective reflection by the cholesteric phase is increased with the swelling ratio (Fig. 1). However, the mesophase texture of the cholesteric phase, observed by a polarizing microscope, is not changed with the swelling ratio, which suggests that the cholesteric order in the composites is not destroyed when the cross-linked PAA was swelled. After the water was removed from the composite film, the wavelength of the selective reflection of the cholesteric phase is shifted back to the short wavelength direction. The color of the composites is changed from blue to red and finally to colorlessness in the water-absorbing process but it is changed back from colorlessness to red and then to blue in the water-removing process. So the swelling process of (E-EC)C/cross-linked PAA molecular composites in water is a reversible one.

According to the De Vries equation, when $\lambda_{\max}$ is varied, n or p or φ should be varied. From Table 1, it can be seen that the value of the mean refractive index is almost unchanged with the swelling of the composites. If the angle φ is varied with swelling, that is the layers of oriented polymer chains become inclined, $\lambda_{\max}$ should shift to a shorter wavelength. The shift of $\lambda_{\max}$ to the longer wavelength direction, therefore, indicates that the pitch in the cholesteric phase increases with the swelling of the composites. Such an experimental fact has also been observed by electron

microscope^[4].

Figure 2 shows the variation in the position of the X-ray diffraction peak of the cholesteric phase with the swelling of the composites. The X-ray diffraction peak of the cholesteric phase shifts to the high diffraction angle as the water-absorption ratio increases, which indicates that the distance between the two layers of oriented macromolecular chains is decreased.

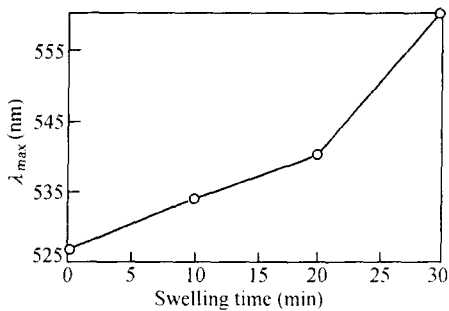


Fig. 1 The variation of the maximum reflection wavelength of (E-CE)C/cross-linked PAA composites with swelling time

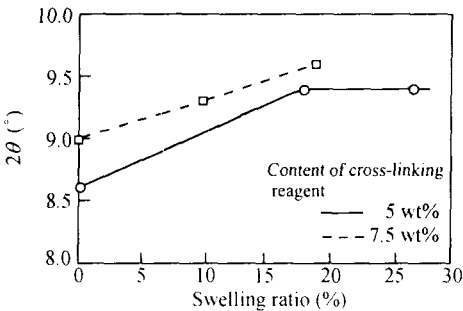


Fig. 2 The shift of X-ray diffraction angle of the cholesteric phase with the swelling ratio of (E-CE)C/cross-linked PAA composites with 48 wt% (E-CE)C

Table 1. Mean refractive index of the composites with different swelling ratio	
Swelling ratio (%)	Mean refractive index
0.0	1.6376
7.1	1.6371
12.0	1.6368
19.4	1.6380

The cross-linked PAA in the composites can absorb water during swelling of the composites while the (E-CE)C can not. The PAA molecules in the composites are dispersed between the (E-CE)C chains and between the layers of oriented polymer chains in the cholesteric phase. The water-absorption of the PAA, therefore, may result in the variation of the arrangement and ordering of (E-CE)C chains in the cholesteric phase. The increase of the pitch and the decrease of the distance between the layers of oriented polymer chains with swelling suggest that the number of the layers of oriented polymer chains in the cholesteric phase is increased.

In the macromolecular cholesteric phase, the layers are formed through the alignment and orientation of the (E-CE)C chains and the PAA existed between and within the layers in the cholesteric phase. The (E-CE)C chains are packed more tightly along the helicoidal axis than in the direction parallel to the layers of oriented polymer chains^[4], which means that there are more PAA molecules within the layers than in the space between the layers. The swelling ratio of the cholesteric phase is different in the two directions. Because the swelling ratio along the helicoidal axis is smaller than in the direction parallel to the layers of oriented polymer chains, the stress between the (E-CE)C polymer chains within the layers is larger than that in the direction along helicoidal axis during swelling. The (E-CE)C chains could protrude out from the original layers of oriented polymer chains and form a new molecular layer in the cholesteric phase. Thus, the number of the layers of ordered (E-CE)C chains in the cholesteric phase increases during swelling, which results in the decrease of the distance between the layers and the increase of the cholesteric pitch.

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