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Influence of polymerization on the cholesteric structure in ethyl-cyanoethyl cellulose/acrylic acid solutions

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Abstract

Ethyl-cyanoethyl cellulose ((E-CE)C) forms cholesteric liquid crystals in acrylic acid (AA) and the cholesteric order in the solutions can be frozen when the AA is quickly polymerized but the cholesteric structure is changed after the polymerization though the property of the selective reflection is reserved. The maximum wavelength of the selective reflection of the cholesteric phase λ_{max} is shifted to the shorter wavelength direction and the selectivity and the intensity of the reflection are decreased after the AA polymerization. It is found that the shift of the reflection wavelength results from the decrease of the cholesteric pitch after the polymerization and the variation of the cholesteric pitch is decreased with increasing the (E-CE)C concentration. The decrease of the pitch after the AA polymerization is due to the volume shrinkage of the solvent monomer during the polymerization and it depends on the polymerization temperature.
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Keywords: Cholesteric structure; Polymerization; Ethyl-cyanoethyl cellulose

1. Introduction

Cellulose and its derivatives are semi-rigid chain polymers and can form lyotropic cholesteric liquid crystals in appropriate solvents [1]. The cholesteric phase of liquid crystals generally shows brilliant colors because of its selective reflection to the visible light [2]. If the solvent is a monomer that can be polymerized, the cholesteric liquid crystalline structure in the solutions can be solidified when the solvent is quickly polymerized. Tsutsui and Tanaka [3] have polymerized the vinyl monomer solvent in the polypeptide/acrylate solutions and prepared chromatic cholesteric composite films. Kozakiewicz and Maginess [4] have reported that the solvents in cellulose diacetate/acrylic acid liquid crystalline solutions and cellulose diacetate/*N*-vinyl-2-pyrrolidinone liquid crystalline solutions are polymerized by free radical polymerization and when the polymerization rate is faster than the phase separation rate, homogeneous composites with one T_g are obtained, which can be used as passive optical devices, such as circular polarizing discs, filter plates and so on.

Ethyl-cyanoethyl cellulose ((E-CE)C) is a cellulose derivative with two kinds of ether groups and can form lyotropic liquid crystals in many solvents when the concentration is higher than the critical one [5]. (E-CE)C can be dissolved in acrylic acid (AA) and form cholesteric liquid crystals [6] and (E-CE)C/polyacrylic acid (PAA) composites can be prepared by polymerizing the AA in the (E-CE)C/AA solutions [7,8]. Because of the incompatibility of (E-CE)C and PAA, phase separation occurs during the polymerization and the cholesteric structure of (E-CE)C/AA liquid crystalline solutions may be partly destroyed. In this work, the influence of the AA polymerization on the cholesteric structure was studied and the relationships between the variation of the cholesteric structure and the (E-CE)C molecular weight (M_w), the volume shrinkage of the monomer during the polymerization and the polymerization conditions were discussed.

2. Experimental

(E-CE)C was prepared by the reaction of ethyl cellulose

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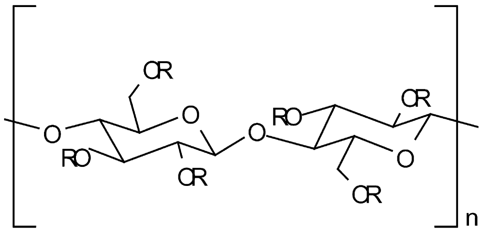
with acrylonitrile [5]. The molecular formula of the (E-CE)C is shown in Fig. 1. (E-CE)C with different molecular weights was prepared from the ethyl cellulose with different molecular weights that was prepared by degradation of it with hydrochloric acid. The molecular weight of (E-CE)C, M_w, was measured by gel permeation chromatography (GPC) (Waters ALC/244/GPC) with the tetrahydrofuran as the solvent and standard polystyrenes for calibration. The degree of substitution (DS) for cyanoethyl was calculated from the content of nitrogen of (E-CE)C that was measured by elementary analysis (Heraeus, CHN-O-RAPID). The AA was refined by vacuum distillation before use. A 250-Watt high-pressure mercury lamp was used as an ultraviolet source to initiate the AA polymerization. The opaque solution was sandwiched between two glass slides and placed in a thermostat that is inserted into the UV chamber. The distance between the samples and the ultraviolet source was about 5 cm. The concentration of benzoin ethyl ether, the initiator, was 2.0 wt% with respective to the solvent AA.

The refractive index of (E-CE)C/AA solutions and (E-CE)C/PAA composites was measured by an Abbe refractometer (Shanghai Optical Instrument Factory, 2WA) with a polarizer [9]. The maximum wavelength of the selective reflection, λ_{max}, of the (E-CE)C/AA liquid crystalline solutions and (E-CE)C/PAA composites was measured by an UV–VIS spectrophotometer (SHIMADZU, UV-2550). The morphology of the (E-CE)C/PAA composites was observed by a transmission electron microscope (TEM) (JEOL, JEOL-100CX/II).

3. Results and discussion

Fig. 2 shows the reflection spectra of the 45.0 wt% (E-CE)C ($M_w = 9.9 \times 10^4$, DS = 0.34)/AA cholesteric liquid crystalline solution (**a**) and the (E-CE)C/PAA composite film (**b**) prepared from the solution. It can be seen from Fig. 2 that the selective reflection to visible light of the system is reserved after the AA polymerization, although microphase separation occurs and the size of the microphase is about 200 nm [10]. This indicates that the cholesteric order in the system is retained. But the reflection intensity and the selectivity of the system are decreased after the polymerization due to a disturbance of the cholesteric phase during the AA polymerization. It can also be seen from Fig. 2 that the maximum wavelength of selective reflection of the cholesteric phase (λ_{max}) is blue shifted.



R=H, CH₂CH₃, CH₂CH₂CN

Fig. 1. The molecular formula of (E-CE)C.

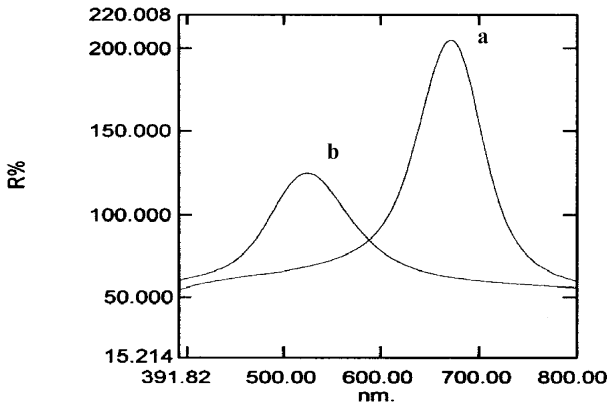


Fig. 2. Reflection spectra of the 45.0 wt% (E-CE)C ($M_w = 9.9 \times 10^4$, DS = 0.34)/AA cholesteric solution (**a**) and the (E-CE)C/PAA composite film (**b**) prepared from the solution.

The cholesteric phase in the (E-CE)C/AA solutions exhibit the planar texture with vivid colors in the certain concentration region [6] because of the selective reflection of the cholesteric phase to visible light. The maximum wavelength of selective reflection λ_{max} is related to the pitch of cholesteric phase P and can be described by following equation [11]:

$$\lambda_{max} = nP \sin \varphi \tag{1}$$

where $n = (n_e + n_o)/2$ (n_e and n_o are extraordinary and ordinary refractive index) is mean refractive index of the system, φ is the angle between the incident light and the ordered molecular layers in the cholesteric phase.

The refractive index of the (E-CE)C/AA solutions and corresponding composite films is shown in Table 1 and it can be found that the refractive index is generally increased after the polymerization. According to Eq. (1), therefore, it is believed that the blue shift of the selective reflection wavelength after the polymerization is not due to the variation of the refractive index but the decrease of the cholesteric pitch (P), or the decrease of the angle between incident light and the ordered molecular layers in the cholesteric phase (φ) or both.

Fig. 3(a) is a schematic diagram of the measurement of reflection spectra. The angle between incident light and the

Table 1
The refractive index of the (E-CE)C/AA solutions and the composites

	C (wt%)					
	40	42.5	45	47.5	50	52.5
n_s	1.4464	1.4480	1.4505	1.4522	1.4530	1.4536
n_p	1.4870	1.4860	1.4875	1.4865	1.4905	1.4890
$n_p/n_s - 1$	0.028	0.026	0.026	0.024	0.026	0.024

n_s is the refractive index of (E-CE)C/AA solution and n_p is the refractive index of (E-CE)C/PAA composite film.

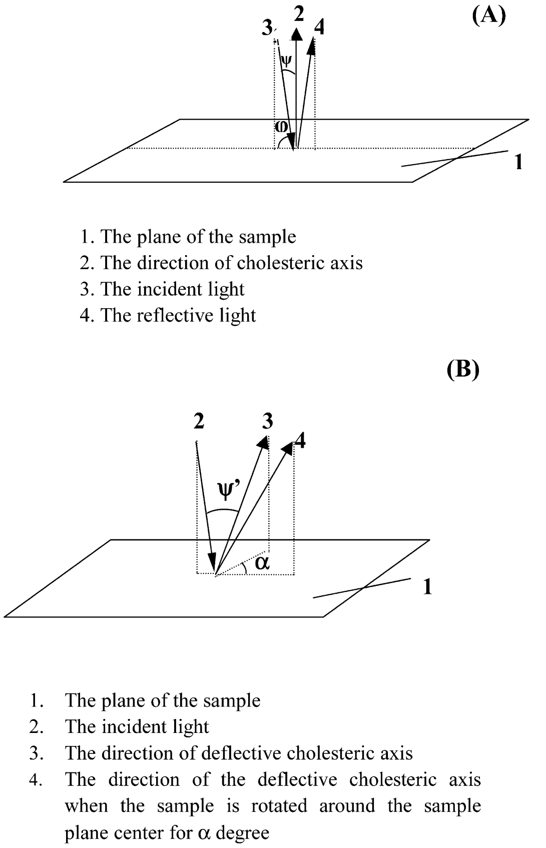


Fig. 3. The schematic diagram of the feflection measurement, before (A) and after (B) the sample is rotated around the sample plane center for α degree.

surface of the solution film with the planar texture is 82°, which means that the angle φ is 82°. Because the cholesteric axis of samples is normal to the slide planes which is fixed during the sample preparation, the angle between incident light and the cholesteric axis ψ is 8°.

If the blue shift of $\lambda_{\max}$ results from the decrease of the angle φ, the cholesteric axis should be deflected after the polymerization and it is no longer normal to the solution film surface. When the film is rotated on the film surface by α degree, at this time, the angle between incident light and the cholesteric axis will be changed from ψ to ψ' (Fig. 3(b)) and the selective reflection wavelength will be changed.

The value of $\lambda_{\max}$ of the (E-CE)C/PAA composite films with different angle α is listed in Table 2. The reflection wavelength of the system before polymerization is 559 nm and its shift to the short wavelength direction is more than 100 nm after the AA polymerization. In Table 2, the maximum and the minimum of the reflection wavelength is 451 and 444 nm, respectively. The variation of $\lambda_{\max}$ with the angle α is very small and the deflective angle ($\Delta\varphi$) of the cholesteric axis can be calculated.

Table 2
The values of λ_m of the (E-CE)C/PAA composite with different α

	α (°)					
	0	30	60	90	120	150
$\lambda_{\max}$ (nm)	451	449	445	448	450	444
α (°)	180	210	240	270	300	330
$\lambda_{\max}$ (nm)	445	450	446	446	449	446

When the selective reflection wavelength is the minimum (λ_1), the angle α is α_1 and the angle between incident light and the molecular layers of the cholesteric phase φ_1 is $82° - \Delta\varphi$. When α_2 is $\alpha_1 + 180°$, the angle between the incident light and the molecular layers of the cholesteric phase φ_2 is $82° + \Delta\varphi$. According to Eq. (1)

$$\lambda_1 = n_p P' \sin(82° - \Delta\varphi) \tag{2}$$

$$\lambda_2 = n_p P' \sin(82° + \Delta\varphi) \tag{3}$$

Dividing Eq. (2) by Eq. (3), Eq. (4) is obtained.

$$\frac{\lambda_1}{\lambda_2} = \frac{\sin(82° - \Delta\varphi)}{\sin(82° + \Delta\varphi)} \tag{4}$$

and

$$tg\Delta\varphi = tg82°\left(\frac{\lambda_2 - \lambda_1}{\lambda_2 + \lambda_1}\right) \tag{5}$$

In Table 2, the minimum selective reflection λ_1 is 444 nm and α_1 is 150°. Then, α_2 is 330° and λ_2 is 446 nm. $\Delta\varphi$ calculated from Eq. (5) is 0.9° and it is clear that $\Delta\varphi$ is very small. Therefore, the measurement of $\lambda_{\max}$ of the (E-CE)C/PAA composite films with the angle α indicates that the cholesteric axis is almost still normal to the film surface after the AA polymerization. It is implied that the blue shift of the reflection wavelength is not resulted from the inclination of the cholesteric axis but the decrease of the cholesteric pitch.

The variation of the cholesteric pitch may be induced by the volume shrinkage of the AA during the AA polymerization. The degree of the volume shrinkage of monomer during polymerization can be expressed by the volume shrinkage ratio x, $x = (V_m - V_p)/V_m$. The volume shrinkage ratio of styrene is 14.5%, of methyl methacrylate is 21.2% and of acrylic acid is 22.0%. The volume shrinkage ratio x is decreased when an extender is added to the system. Table 3 lists the volume shrinkage ratio x of (E-CE)C/AA dilute solutions which are polymerized at 25 °C. The (E-CE)C molecular weight M_w in series A is 9.9×10^4 and in series B is 3.6×10^4. It can be found that the volume shrinkage ratio

Table 3
The volume shrinkage ratio of the AA for the (E-CE)C/AA solutions at 25 °C

	C (wt%)						
	0	1.0	2.0	5.0	10.0	15.0	20.0
x(A) (%)	22.0	14.9	13.0	8.4	–	–	–
x(B) (%)	22.0	18.4	17.2	14.0	12.7	10.5	8.8

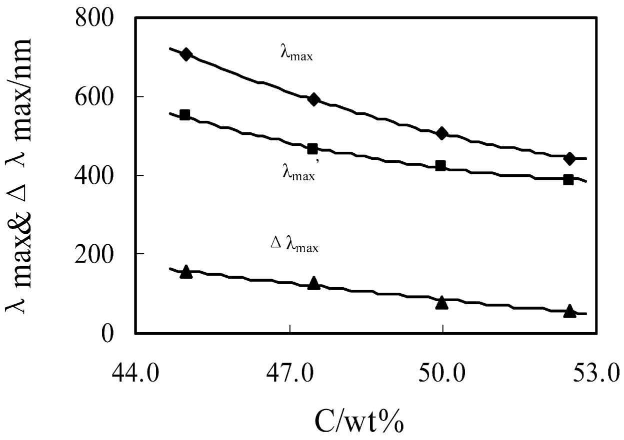


Fig. 4. The curves of the reflection wavelength of the solution λ_{max} and the composite film λ'_{max} and $\Delta\lambda_{max}$ vs. the (E-CE)C concentration.

is decreased with increasing the (E-CE)C concentration and the (E-CE)C molecular weight M_w, which may result from the increase of the viscosity of the system by increasing both (E-CE)C concentration and viscosity.

Fig. 4 shows the concentration dependence of the reflection wavelength of the cholesteric phase before and after the polymerization and the difference of them, $\Delta\lambda_{max}$. It can be found that $\Delta\lambda_{max}$ decreases with increasing the (E-CE)C concentration and therefore, the difference between the cholesteric pitch before and after the polymerization ΔP is decreased with increasing the (E-CE)C concentration (Fig. 5).

Fig. 6 shows the concentration dependence of the variation ratio of the cholesteric pitch ($\Delta P/P$) and it can be found that $\Delta P/P$ is also decreased with increasing the (E-CE)C concentration, which means that the variation of the cholesteric structure due to the polymerization is decreased. The solutions with high (E-CE)C concentration or high viscosity show a small volume shrinkage ratio in the polymerization. The movement of molecules in the solution with high viscosity is more difficult than that with low viscosity and therefore, the variation of the cholesteric order during the AA polymerization is decreased with increasing the viscosity of the solutions, which is indicated by the decrease of ΔP with increasing (E-CE)C concentration (Fig. 5).

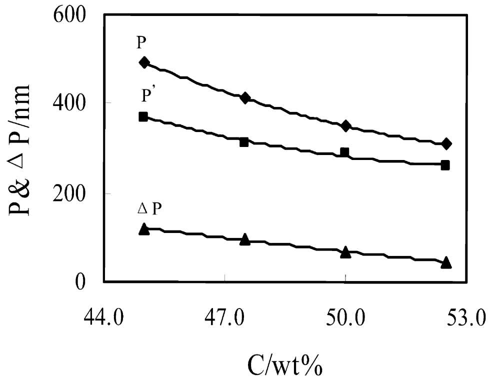


Fig. 5. The curves of the pitch of the solution P and the composite film P' and ΔP vs. the (E-CE)C concentration.

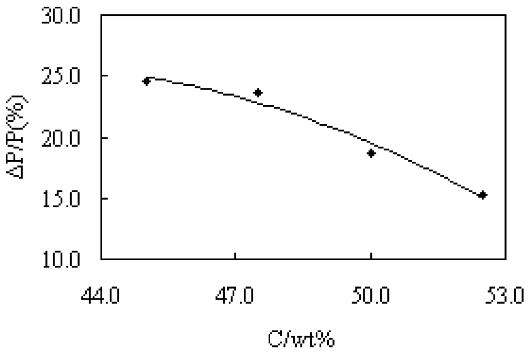


Fig. 6. The variation ratio of the pitch vs. the (E-CE)C concentration after the polymerization.

The decrease of the cholesteric pitch after the polymerization is weakened when the trimethylpropane tri-acrylate (TMPTA) or divinylbenzene (DVB), as the cross-linking reagents for polyacrylic acid, is added into the cholesteric solutions (Figs. 7 and 8). It can also be found, from Figs. 7 and 8, that the volume shrinkage of AA is also decreased with increasing the concentration of the cross-linking reagent. It is confirmed that the decrease of the pitch during the polymerization is closely related with the volume shrinkage of AA. The solidification of the system is accelerated when the cross-linking reaction occurs, which results in the decrease of the volume shrinkage during the AA polymerization and the decrease of the pitch.

Table 4 lists the values of the reflection wavelength λ_{max} and the pitch P of the (E-CE)C/AA cholesteric solution and those of the composite films λ'_{max} and P', the variation of the reflection wavelength $\Delta\lambda_{max}$ and the variation ratio of the pitch $\Delta P/P$ and the volume shrinkage ratio of the AA (X_{AA}), during the polymerization at 0 and 25 °C. It can be seen that the λ_{max} and P are decreased with increasing polymerization temperature and the variation ratio of the pitch at 0 °C is smaller than that at 25 °C, which means that the variation ratio of the cholesteric pitch is decreased with decreasing the polymerization temperature. The volume shrinkage ratio of the AA in the polymerization at 0 °C is 14.8% that is smaller than that of 22.0% at 25 °C and it results in the

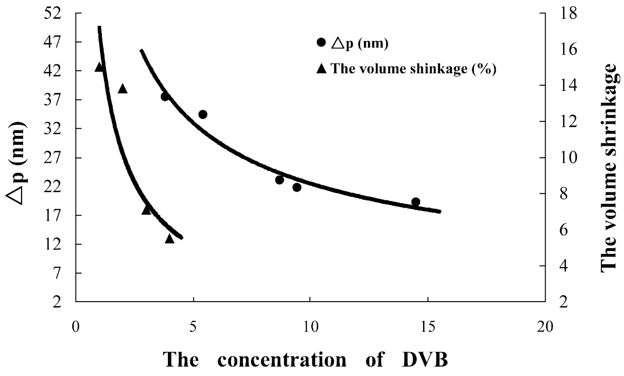


Fig. 7. The plots of ΔP and volume shrinkage vs. the DVB concentration.

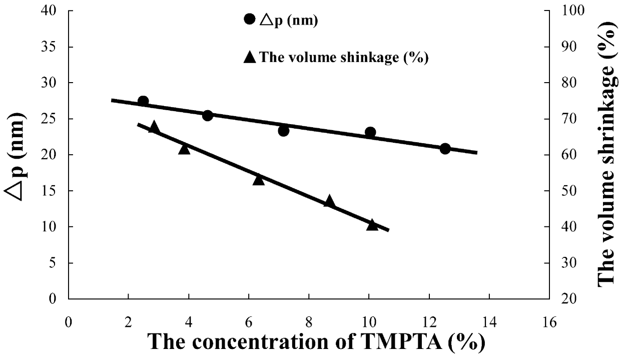


Fig. 8. The plot of ΔP and volume shrinkage vs. the TMPTA concentration.

smaller variation ratio of the pitch at 0 °C. It is suggested again from the data in Table 4 that the variation of the cholesteric structure during the polymerization is weakened by the higher viscosity of the (E-CE)C/AA solutions at 0 °C.

4. Conclusions

(E-CE)C is dissolved in AA and forms cholesteric liquid crystalline solutions. (E-CE)C/PAA composite films with cholesteric order are prepared by polymerizing the AA in the solutions. The cholesteric order in the system is reserved and the selective reflection of the cholesteric phase is retained after the polymerization. The intensity and the selectivity of the reflection, however, are decreased and the maximum wavelength of the selective reflection of the cholesteric phase shifts to short wavelength direction. The decrease of the pitch results from the volume shrinkage of the solvent during the polymerization and it is influenced by the rate of the solidification of the system. The decrease of the $\lambda_{\max}$ and the cholesteric pitch during the polymerization and their variation ratio, $\Delta\lambda_{\max}$ and ΔP, are decreased with increasing the (E-CE)C concentration. The variation of the cholesteric pitch is almost the same as that of the volume shrinkage of AA in the polymerization and the variation of the cholesteric order during the polymerization is weakened by the cross-linking reactions.

Table 4
The values of the $\lambda_{\max}$, P, $\Delta P/P$ before and after polymerization and the volume shrinkage ratio at 0 and 25 °C

	Temperature	
	0 °C	25 °C
$\lambda_{\max}$ (nm)	746	692
$\lambda'_{\max}$ (nm)	589	495
P (nm)	519	481
P' (nm)	399	335
$\Delta\lambda_{\max}$ (nm)	157	198
$\Delta P/P$	0.23	0.30
X_{AA} (%)	11.1	22.0

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