Cellulose Derivative-based Cholesteric Networks

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ABSTRACT: Ethyl-cyanoethyl cellulose [(E-CE)C]/acrylic acid (AA) solution could form cholesteric networks when the AA was quickly photopolymerized. The cholesteric structure in the solution was changed during the polymerization but the variation of the cholesteric order could be depressed by crosslinking of the system. The dependence of λ_{max} for the cholesteric phase on both the crosslinker concentration and the polymerization temperature was studied by UV-Vis spectrometry. It was found that the cholesteric pitch variation is decreased with increasing the concentration of the crosslinking reagent and the water sensitivity of the cholesteric network is effectively suppressed and dependent on the types of crosslinker. The pitch of cholesteric network was decreased sharply with increasing the polymerization temperature, due to the increase of the volume shrinkage of the solvent during the polymerization. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1648–1653, 2005

Key words: cholesteric liquid crystal; composites; networks; ethyl-cyanoethyl cellulose; swelling

INTRODUCTION

The cholesteric phase of liquid crystals shows outstanding optical properties. It selectively reflects (Bragg reflection) visible light and exhibits brilliant colors if the pitch of the cholesteric helix coincides with the wavelength of visible light.[1]

Networks based on semirigid polymers are considered to be rather interesting systems because of their peculiar behavior. Recently, highly crosslinked cholesteric pigments have been reported as the dye pigments for cars or as "copy safe" colors for documents or money.[2] These cholesteric pigments have been prepared so far from cholesteric monomers or oligomers by a photo-*cross*-linking process.[3–5] Helical biopolymers offer the same potential ability and both thermotropic and lyotropic phases that exhibit selective reflection have been reported for polypeptides[6] and cellulose derivatives.[7] Maxein et al.[8,9] and others[10] have reported a system of lyotropic cholesteric mesophase based on chiral polyisocyanates and aryl urethanes of cellulose in mono- or bifunctional derivatives of acrylic and methacrylic acids. The cholesteric structure can be frozen by polymerizing the solvent and the semiinterpenetrating network of cholesteric structure is fabricated.

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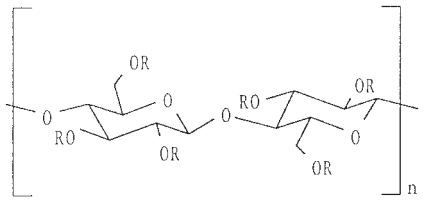
Cellulose and its derivatives are semirigid chain polymers and can form lyotropic cholesteric liquid crystals in appropriate solvents.[11] If the solvent is a monomer that can be polymerized, the cholesteric structure in the solutions can be solidified when the solvent is quickly polymerized. Tsutsui and Tanaka[12] have polymerized the vinyl monomer in polypeptide/acrylate solutions and prepared chromatic cholesteric composite films. Kozakiewicz and Maginess[13] 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 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, etc. It has also been found that the cholesteric structure is changed due to the volume shrinkage of the solvent monomer during the polymerization,[14] although the selective reflection was reserved and a cholesteric network was obtained. The maximum wavelength of the selective reflection of the cholesteric phase (λ_{max}) is blue shifted and the selectivity as well as the intensity of the reflection is decreased after the polymerization of the solvent.

In this work, the cholesteric network composed of ethyl-cyanoethyl cellulose [(E-CE)C]/crosslinked polyacrylic acid (PAA) was prepared by polymerization of the AA in the (E-CE)C/acrylic acid (AA) cholesteric liquid crystalline solutions. Furthermore, with changing (E-CE)C concentration, different dependence of



R=H, CH_2CH_3, CH_2CH_2CN

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

the selective reflection with the crosslinking reagents and polymerization temperature was discussed.

EXPERIMENTAL

Materials

(E-CE)C was prepared by the reaction of ethyl cellulose with acrylonitrile.[15] The molecular formula of the (E-CE)C is shown in Figure 1. The molecular weight of (E-CE)C, M_w, was measured by gel permeation chromatography (GPC) (Waters ALC/244/GPC) with tetrahydrofuran as the solvent and standard polystyrenes for calibration. The degree of substitution (DS) for cyanoethyl was calculated from the nitrogen content of (E-CE)C measured by elementary analysis (Heraeus, CHN-O-RAPID). The AA was refined by vacuum distillation before use. A 250-W high-pressure mercury lamp was used as an ultraviolet source to initiate the AA polymerization. The three types of crosslinking reagents used in this work were divinylbenzene (DVB), trimethylpropane triacrylate (TMPTA), and dipentaerythritol hexaacrylate (DPHA), which were supplied by U.C.B Chemical Company. Their molecular formulas are shown in Figure 2.

Preparation of (E-CE)C/crosslinked PAA cholesteric network

The LC solution was prepared by mixing the (E-CE)C, AA, photopolymerizing initiator [2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocure 1173, supplied by the Ciba Company), 4 wt %, with respect to AA], and crosslinking reagents (0–20 wt %, respect to AA) together at room temperature. The solution then was stored in the dark at room temperature for about 2 weeks to achieve an equilibrium state.

The opaque solution was sandwiched between two glasses slides and sealed with wax. The sample then was placed in the water bath with setting temperature and inserted into the UV chamber. The distance between the sample and the ultraviolet source was about 5 cm.

Measurement

The refractive index of (E-CE)C/AA/crosslinker solutions and (E-CE)C/PAA cholesteric network was measured by an Abbe refractometer (Shanghai Optical Instrument Factory, 2WA). The selective reflection of the solutions, λ_{max}, and (E-CE)C/PAA cholesteric networks, λ_{max}', was measured by an UV-VIS spectrophotometer (SHIMADZU, UV-2550). The volume shrinkage during the polymerization was measured by the capillary method.

All samples for the water-swelling test were prepared as a thin film with a size of 1×1 cm^2 and treated in the oven at 80°C for about 4 h until the weight of the every slice was constant. The films then were placed into the distilled water for swelling. The values of the swelling ratio were determined at 25°C.

RESULTS AND DISCUSSION

Figure 3 shows the reflection spectra of the (E-CE)C/AA cholesteric liquid crystalline solution and (E-CE)C/PAA cholesteric network (dashed lines) prepared from the solution. It can be seen from Figure 3 that the selective reflection of the system is reserved after the AA polymerization, which indicates that the cholesteric order in the network is retained. But the maximum wavelength of the selective reflection λ_{max} has a blue shift, which means that the cholesteric pitch of the system is decreased according to the equation:

$$\lambda_{max} = nP\sin\varphi \quad (1)$$

where n is mean refractive index of the system and φ is the angle between the direction of incident light and the molecular layer surface. Moreover, the reflection intensity and the selectivity of the system are de-

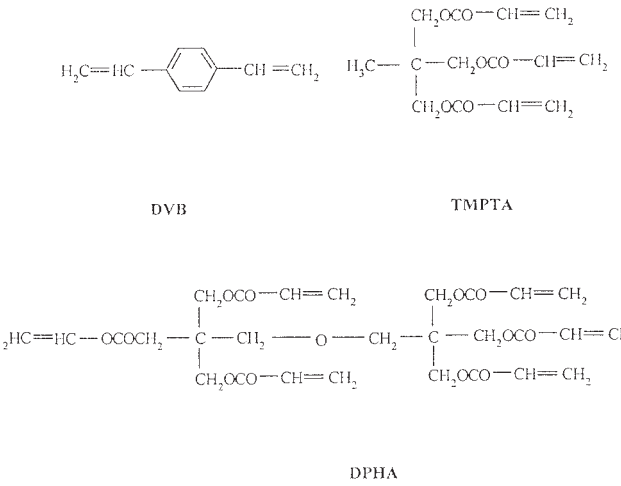


Figure 2 The molecular formula of DVB, TMPTA, and DPHA.

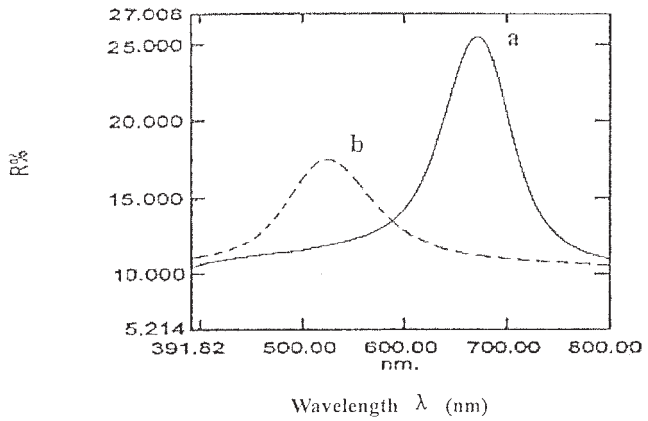


Figure 3 The reflection spectra of the (E-CE)C/AA choleteric solution and the (E-CE)C/PAA cholesteric network. (a) (E-CE)C/AA choleteric solution. (b) (E-CE)C/PAA cholesteric network (dashed lines).

creased after the polymerization due to a disturbance of the cholesteric order during the AA polymerization. Broer and Heynderickx[16] and Zhang et al.[14] indicated that the volume shrinkage in the polymerization results in the decrease of the cholesteric pitch in the liquid crystal/vinyl monomers system. It is also found that the difference of the pitch between the solution and the cholesteric network prepared from the solution, ΔP, is decreased with increasing (E-CE)C content. So, it is suggested that the volume shrinkage can be depressed by increasing the (E-CE)C concentration.

Figure 4 shows that the pitch of the cholesteric network with the 52.5 wt % (E-CE)C is varied with the DVB concentration. It can be found that the pitch of the cholesteric network is blue shifted with increasing the DVB content. Meanwhile, both the difference of the pitch between the cholesteric solution and the cholesteric network, ΔP, and the volume shrinkage are decreased with increasing the DVB content (Fig. 5),

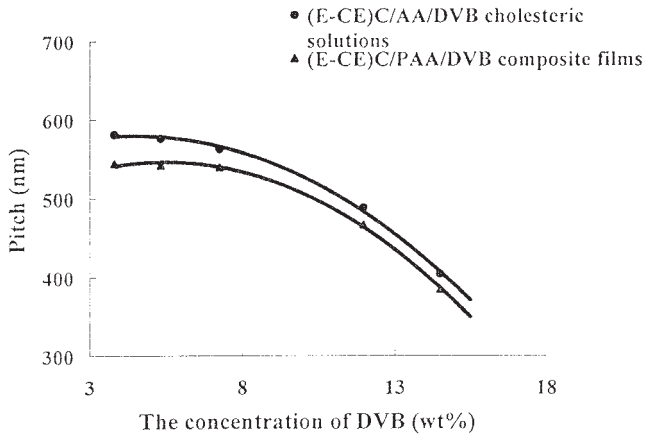


Figure 4 Plots of the pitch of the (E-CE)C/AA/DVB solution and its cholesteric network versus the DVB content.

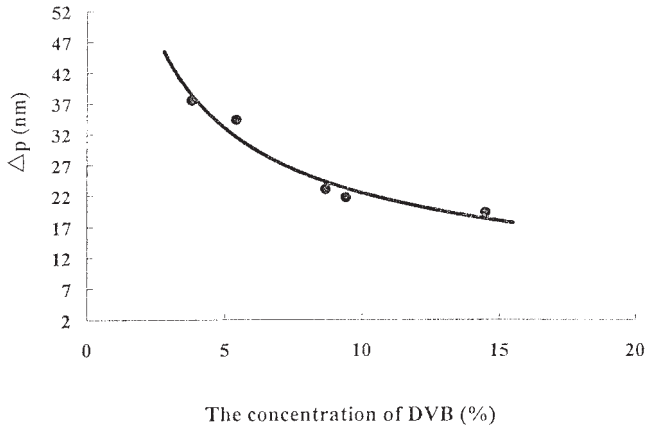


Figure 5 Plots of ΔP versus the DVB content.

which confirms again that the volume shrinkage is suppressed by adding the crosslinker in the systems.

The variation of the pitch with the content of the crosslinker in the cholesteric network with TMPTA or DPHA is also dependent on the crosslinker concentration (Fig. 6). The pitch of both systems decreases with increasing the crosslinker concentration. But the pitch difference, ΔP, between the cholesteric and the cholesteric network with the TMPTA is lower than that with the DPHA at the same crosslinker content (Fig. 7). It is suggested, according to the coagulation theory,[17,18] that the cholesteric network with DPHA has the lower crosslinking degree than that with TMPTA, because the DPHA has the higher functionality than the TMPTA, and the value of ΔP in the cholesteric network with DPHA, thus, is higher than that in the cholesteric network with TMPTA.

The volume shrinkage ratio of the AA in the dilution solution is influenced by adding the crosslinking reagents and it has been measured by the capillary method during the polymerization at 0°C. Table I gives the values of the volume shrinkage ratio in these solutions. It can be seen from Table I that the ratio of the volume shrinkage, x%, is decreased with increasing the concentration of the crosslinking reagent, which means that the addition of the crosslinkers can effectively suppress the volume shrinkage of AA during the polymerization. It can also be found from Table I that the solution with the crosslinker of high functionality shows a lower value of volume shrinkage, such as the solution with the DPHA, but that with the low functionality has a higher value of volume shrinkage. It is implied that the suppression of the crosslinker on the volume shrinkage is more effective for the crosslinker with higher functionality than that with lower functionality.

The results mentioned above indicate that the variation of the pitch in the fabrication of the cholesteric network is influenced by the volume shrinkage during the polymerization and it is well known that the vol-

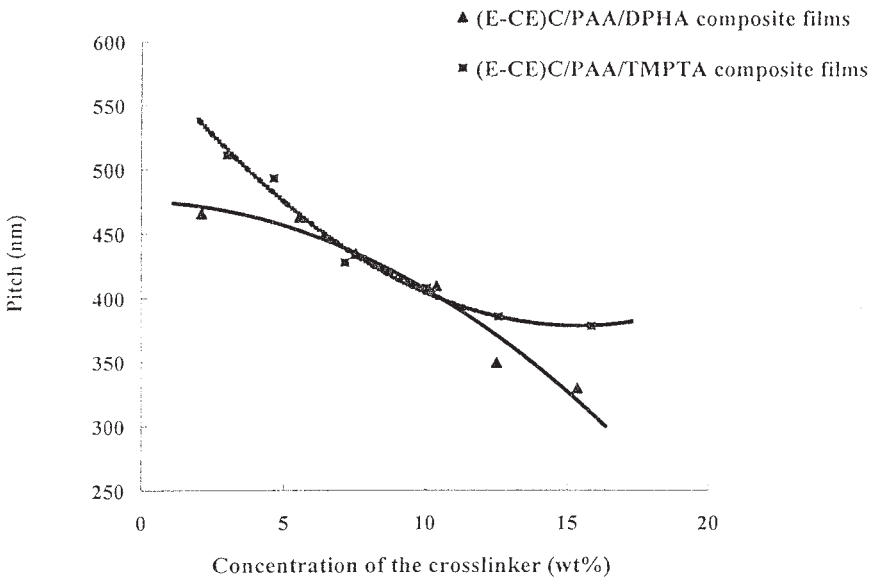


Figure 6 Plots of the pitch of the (E-CE)C/PAA/TMPTA and (E-CE)C/PAA/DPHA cholesteric networks versus the crosslinker content.

ume contraction for vinyl monomer during the polymerization is remarkable dependent on the polymerization temperature. Therefore, it is implied that the variation of the cholesteric pitch in the fabrication of the cholesteric network is influenced by polymerization temperature. However, the variation of the pitch, ΔP, is also influenced by many factors. Table II lists the maximum wavelength of the selective reflection of the cholesteric network with DPHA when the polymerization temperature is 0, 10, 20, and 40°C. It can be seen from the Table II that the maximum wavelength of the selective reflection of the cholesteric network is decreased sharply with the increase of the polymerization temperature. Moreover, the variation of the maximum wavelength of the selective reflection, $\Delta\lambda$, during the fabrication of the cholesteric network is also decreased with increasing both the (E-CE)C concentration and the DPHA content at the same temperature, because of higher viscosity, lower AA concentration, and less volume contraction. The same results have also been found in other lyotropic cholesteric systems.[19–21]

The (E-CE)C/PAA cholesteric networks without crosslinkage show poor resistance to water because the PAA chains can absorb the water in the swelling process. Figure 8 shows curves of the swelling ratio, $S\%$ (g/g), versus the swelling time of the cholesteric networks in distilled water. It can be seen from Figure

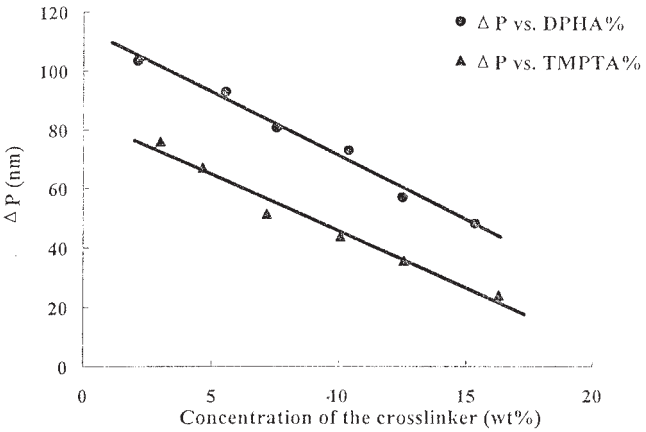


Figure 7 Plots of ΔP versus the TMPTA and DPHA content.

TABLE I
Volume Shrinkage Ratio (x%) of the Dilute Solutions of AA/DVB, TMPTA, and DPHA UV-Polymerizing under 0°C for 10 min

Sample	Concentration of the sample (wt %)	x%
DVB	4.0	37.5
	5.4	34.4
	7.8	23.0
	9.4	21.8
	14.5	19.3
TMPTA	2.9	27.4
	4.0	25.4
	6.3	23.3
	8.7	23.1
	10.1	20.8
DPHA	2.5	27.67
	4.3	21.23
	7.2	20.65
	9.9	16.83
	13.1	15.06
	14.5	14.81

TABLE II
The Value of Δ after the Polymerization of the AA at Different Temperatures

Samples	Δλ (nm) at Different Polymerization Temperatures			
	0 °C	10 °C	20 °C	40 °C
(E-CE)C 43.1 wt %	77	82	198	404
(E-CE)C 47.5 wt %	28	44	139	400
(E-CE)C 47.5 wt % + 5.5 wt % DPHA	31	64	102	198
(E-CE)C 47.5 wt % + 7.5 wt % DPHA	16	60	80	113
(E-CE)C 47.5 wt % + 10.0 wt % DPHA	14	27	60	—[a]

[a] The maximum wavelength of the selective reflection of the composite film that is cured at 40°C, λ_{max} is beyond the region of the reflection spectra measurement.

8 that the swelling ratio is increased with swelling time but it is unchanged after 8 h of swelling. The value of the equilibrium swelling ratio is decreased with increasing the content of the crosslinking reagent and it is clear that the cholesteric network without any crosslinker has the maximum equilibrium swelling ratio. The equilibrium swelling ratio is also dependent on the types of crosslinker. The system with DVB shows a lower equilibrium swelling ratio than that with TMPTA when the content of the crosslinker is the same. So, it is concluded that the swelling behavior of the cholesteric network is also influenced by crosslinker properties.

Figure 9 shows the variation of the λ_{max} of the cholesteric network with the DVB content, before swelling and after reaching to the equilibrium swelling. It is shown that λ_{max} is red shifted after swelling in distilled water, but the degree of the red shift is decreased with increasing the concentration of the crosslinker. It can also be found from Figure 9 that the variation of λ_{max} after the swelling, $\Delta\lambda_{max}$, is also decreased with increasing the crosslinker content, which suggests that the swelling behavior of the cholesteric network is suppressed by adding the crosslinker in the systems and the suppression with increasing the crosslinker content.

CONCLUSIONS

The (E-CE)C/PAA cholesteric network is fabricated by rapid polymerization of the monomer solvent AA in the (E-CE)C/AA cholesteric liquid crystalline solution with crosslinker. The addition of the crosslinker in the systems can suppress the volume shrinkage during the AA polymerization and the water sensitivity of the cholesteric networks is decreased with increasing the crosslinker concentration. The pitch of the cholesteric networks is decreased sharply with increasing the polymerization temperature. However, the variation of the pitch after swelling is depressed by the crosslinkage of the system and is also influenced by the properties of the crosslinker.

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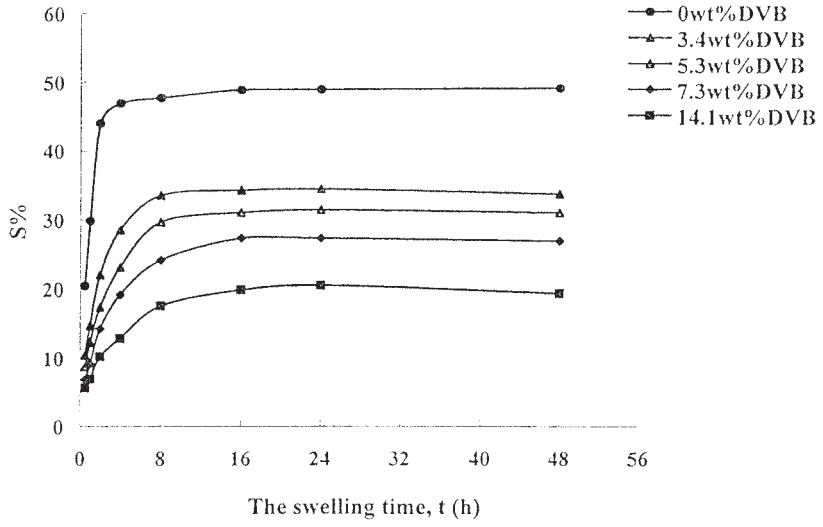

Figure 8 Plots of *S*% versus the swelling time of the cholesteric networks in distilled water.

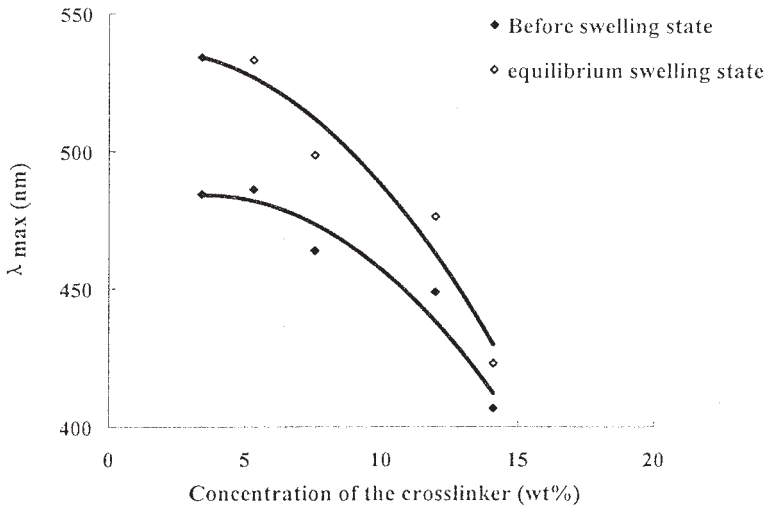

Figure 9 Plots of λ_{max} of the cholesteric networks of (E-CE)C/PAA/DVB versus the concentration of DVB before swelling and equilibrium swelling state.

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