

Optical Properties of Ethyl-Cyanoethyl Cellulose/Poly(acrylic acid) Cholesteric Liquid Crystalline Composite Films

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ABSTRACT: Ethyl-cyanoethyl cellulose [(E-CE)C]/poly(acrylic acid) (PAA) composite films were prepared by photopolymerizing acrylic acid (AA) in (E-CE)C/AA cholesteric liquid crystalline solutions. With the selection of suitable concentrations, (E-CE)C/PAA composite films showed vivid colors due to the selective reflection property of the cholesteric phase. It was found that the wavelength of reflection was a function of the concentration of (E-CE)C, and

the reflectivity was increased with increasing thickness of the film. The selective reflection of the composite holds well upon heating at temperatures below 160°C. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 213–217, 2004

Key words: optics; liquid-crystalline polymers; photopolymerization; composites

INTRODUCTION

One of the great features of the cholesteric liquid crystalline (LC) phase is its selective reflection optical property. When normal incident light illuminates the material from the direction parallel to the helical axis, light of the same handedness as the cholesteric structure is reflected over a narrow wavelength band while light of the other handedness, along with light of all other wavelengths, is transmitted. The maximum wavelength of the reflected light (λ_{\max}) depends on the pitch (P) and can be described by the following equation:¹

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

where n is the average refractive index of the mesophase.

The optical property of selective reflection of the cholesteric LC phase shows some potential commercial applications. It could serve as a polarized light source,^{2,3} or for "photocopy-safe" materials.⁴ In order to use cholesteric LC phases for these applications, lyotropic cholesteric LC solution is usually formed as a solid film to retain the cholesteric structure. The LC film can be prepared by several methods, such as

casting,^{5,6} crosslinking,^{7–9} quenching¹⁰ and polymerizing the solvent of LC polymer solutions.^{11–15}

Cellulose and its derivatives are semirigid chain polymers and can form liquid crystals in appropriate solvents,¹⁶ most of which are in the cholesteric phase. Ethyl-cyanoethyl cellulose [(E-CE)C], which is a cellulose derivative with two different ether groups, ethyl and cyanoethyl, can form cholesteric LC solutions in many organic solvents, such as dichloroacetic acid (DCA)¹⁷ and acrylic acid (AA).¹⁸ In our previous studies, we found that the cholesteric structure of the (E-CE)C/AA solution can be frozen in (E-CE)C/poly(acrylic acid) (PAA) composite by photopolymerization of the solvent AA.¹² As a potential material for application, however, the details of the optical properties of (E-CE)C/PAA cholesteric LC composites are not very clear.

In this article, based on previous studies, advanced research on the selective reflection of (E-CE)C/AA cholesteric systems was reported. The dependence of the selective reflection property on concentration, film thickness and temperature was investigated in detail by using UV-VIS spectroscopy and DSC.

EXPERIMENTAL

Materials

(E-CE)C was prepared by the reaction of ethyl cellulose and acrylonitrile.¹⁹ The degree of substitution of ethyl groups was about 2.1, and for cyanoethyl groups

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it was about 0.33. The molecular weight of (E-CE)C, M_w , was 19×10^4 .

Preparation of (E-CE)C/AA Solutions and (E-CE)C/PAA Composites

The (E-CE)C was mixed with AA and 2 wt % initiator, benzoin ethyl ether (with respect to the solvent AA), at room temperature (about 20°C). AA was distilled in vacuum at 50°C before use, and all of the reagents were chemically pure. The mixture was allowed to sit for about 2 weeks, and the resulting homogeneous solutions were then stored in the dark until used. The concentration of the (E-CE)C/AA cholesteric LC solutions was controlled in the region of 42–56 wt %. The solutions were sandwiched between two glass slides, sealed with solid wax and stored in the dark for several hours. The thickness of the solution films was controlled between 80 μm and 0.66 mm by different Teflon spacers. Then, the solution films were inserted into an ultraviolet chamber equipped with a 250 W high-intensity mercury arc lamp for 2 min. The (E-CE)C/PAA composites were prepared after the polymerization of AA. The distance between the lamp and the sample was 5 cm, and the polymerization temperature was 0°C. The photopolymerization of AA was generally completed, and the conversion of acrylic acid was larger than 99.5% within 1 min because the composite film was very thin.

Measurements

The selective reflection spectra of the (E-CE)C/AA cholesteric LC solutions and the (E-CE)C/PAA cholesteric composite films were measured by UV-VIS spectrophotometry (UV-2550, SHIMADZU, Japan). The texture and morphology of the mesophases were observed with a polarized optical microscope (POM) (ORTHOPLAN-POL, Leitz). The effect of temperature on the selective reflection was studied by using a hot stage and a temperature controller (STC200c, INSTEC, USA), with a heating program that involved heating from 20 to 270°C, with a heating rate of 5°C/min, with a 5 min isothermal period in each 10°C step during heating. A differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2C) was used to measure the thermal behavior of the (E-CE)C/PAA composites, with a heating rate of 10°C/min, in a nitrogen atmosphere.

RESULTS AND DISCUSSION

When the (E-CE)C concentration is above 33.8 wt %, the cholesteric phase begins to appear in the (E-CE)C/AA solution and the (E-CE)C/AA LC solution is a uniform anisotropic phase when the (E-CE)C concentration is above 42 wt %. The mesophase gen-

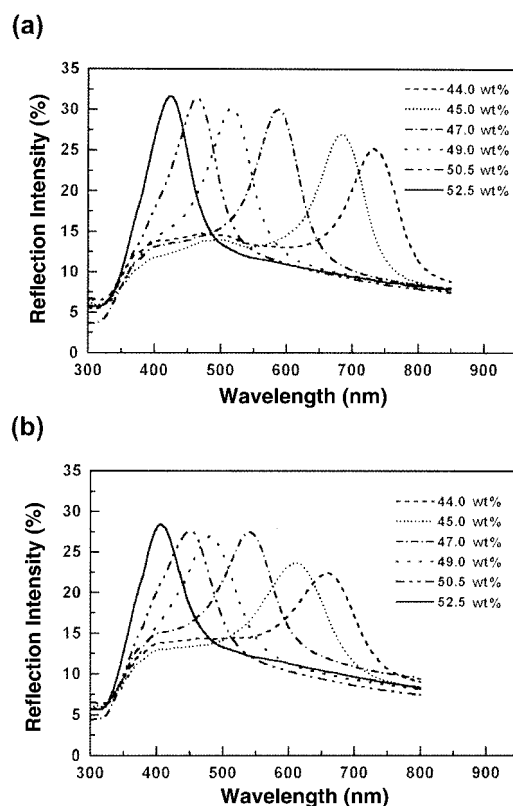


Figure 1 Selective reflection spectra of (a) (E-CE)C/AA cholesteric LC solutions and (b) (E-CE)C/PAA composites versus (E-CE)C concentration. Thickness of the films was 0.45 mm.

erally shows the planar texture in which the helical axes align perpendicular to the substance film surface. The pitch of the solutions approaches the visible light wavelength, and the solutions exhibit vivid colors due to the selective reflection of visible light. The maximum wavelength of the reflection of the cholesteric phase, λ_{max} , decreases with increasing (E-CE)C concentration [Fig. 1(a)]. This relationship is a typical phenomenon in cholesteric LC phase.^{20–23}

After the photopolymerization of AA, the cholesteric order of (E-CE)C/AA solutions can be retained in the (E-CE)C/PAA composites.¹² From Figure 1(b), it can be seen that the (E-CE)C/PAA composite also shows the selective reflection property. The relationship between λ_{max} and the concentration in the composite is the same trend as that in the solution; that is, the λ_{max} of the composites decreases with increasing (E-CE)C concentration. But all reflection peaks in the spectra of the composites shift to the short wavelength direction (blue shift) compared to those of the solutions, and the selectivity and reflectivity are decreased after the solidification of the cholesteric phase [Fig. 1(b)]. It has been shown that the relationship between the pitch (P) and the concentration of the cholesteric phase can be described by the following equation.^{20,21}

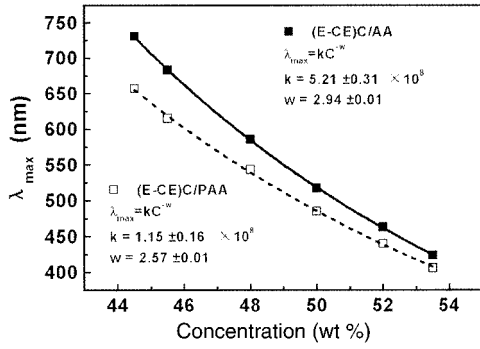


Figure 2 Variation of λ_{\max} before and after photopolymerization versus (E-CE)C concentration.

$$P = k_1 C^{-w} \quad (2)$$

where C is the concentration, k_1 is a constant, and w is an exponent that relates to the cholesteric structure. The exponent w has different values in different cholesteric phases, such as 2 for poly- γ -benzyl-L-glutamate (PBLG)/dioxane cholesteric solution²⁰ and 3 for hydroxypropylcellulose (HPC)/water solution.²¹ According to eq. (1), λ_{\max} is directly proportional to the pitch (P). The relationship between λ_{\max} and the concentration of the cholesteric phase can be derived from eqs. (1) and (2):

$$\lambda_{\max} = kC^{-w} \quad (3)$$

where k , a constant, is equal to $k_1 n$. From the variation of λ_{\max} with concentration, shown in Figure 1(a), the constant k and the exponent w for the (E-CE)C/AA solution can be calculated; they are 5.21×10^8 and 2.94, respectively (Fig. 2). The exponent w of the (E-CE)C/AA cholesteric solution approaches that of the HPC solution, maybe because both (E-CE)C and HPC are cellulose derivatives and have similar cholesteric structures in solution. From the variation of λ_{\max} with concentration shown in Figure 1(b), the constant k and the exponent w for the (E-CE)C/PAA composite can be calculated to be 1.15×10^8 and 2.57, respectively (Fig. 2). Thus, the reflection wavelength and the color of the composite film can be controlled by the concentration. The decrease of k indicates that the magnitude of the relationship between λ_{\max} and concentration is decreased, and the decrease of w indicates that the variance ratio between λ_{\max} and concentration is increased, which means that λ_{\max} is more sensitive to change in concentration. This result may be due to the volume shrinkage of the solvent monomer (contraction ratio of pure PAA is 14.8%), which results in the decrease of the distance between neighboring molecular layers and the pitch. Thus, the blue shift occurs according to eq. (1). The decrease of the selectivity and

the reflectivity may be caused by the disordering of the arrangement of the cholesteric structure during polymerization. Moreover, with increasing (E-CE)C concentration, the concentration of AA naturally decreases, resulting in less volume contraction after polymerization; therefore, the variation of λ_{\max} during AA polymerization, $\Delta\lambda_{\max}$, decreases with increasing (E-CE)C concentration (Fig. 2).

According to de Vries' theoretical prediction,¹ the reflectivity of the cholesteric phase increases with increasing sample thickness initially, reaching a plateau at 50% of incident light when the thickness is more than 50 μm . Figure 3 shows that the reflectivity of the (E-CE)C/PAA composites is proportional to the film thickness, but it is much smaller than that predicted by de Vries' theory. It is believed that the discrepancy between the actual and the theoretical values results from the fact that the cholesteric structure is not as uniform in terms of the arrangement of cholesteric helical axes as it is assumed to be in the theoretical calculation.²³

Besides concentration and film thickness, temperature is another important factor that can affect reflection. The reflection wavelength shifts to the longer direction with increasing temperature. The temperature dependence of the reflection wavelength of (E-CE)C/PAA cholesteric composite film is shown in Figure 4. When the temperature is lower than 160°C, the reflection peak shifts to slightly longer wavelengths with elevating temperature (only changed by about 25 nm), and the selectivity and the reflectivity gradually decrease. When the temperature is above 160°C, however, the reflectivity decreases quickly and the reflection peak completely disappears at 270°C. Observed by POM, the color of the (E-CE)C/PAA composite film changed to black and the birefringence disappeared. There is a mesophase-isotropic phase transition at about 160°C at which the (E-CE)C/PAA cholesteric phase begins to transform into the isotropic phase. When the temperature is below 160°C, the ar-

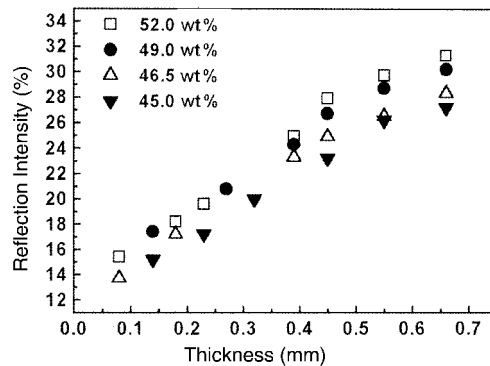


Figure 3 Variation of reflectivity of (E-CE)C/PAA composites versus film thickness.

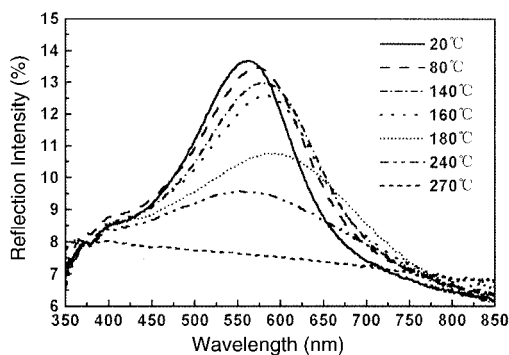


Figure 4 Selective reflection spectra of 49 wt % (E-CE)C/PAA cholesteric composite at different temperatures. Thickness of film was 80 μm .

rangement of chains in the cholesteric structure is gradually disordered by heating, but the cholesteric order is not destroyed at this time. The selectivity and reflectivity decrease slightly with increasing temperature. Above 160°C, the cholesteric structure of the (E-CE)C/PAA composite is destroyed very quickly, and selective reflection begins to disappear. Finally, when the temperature increases to about 270°C, the cholesteric structure is destroyed completely, and the reflective property totally disappears. The mesophase-isotropic phase transition was also confirmed by DSC experiments. Figure 5 shows the thermogram of the (E-CE)C/PAA cholesteric composite films; the endothermic peak at about 160°C is attributed to the mesophase-isotropic phase transition, and the endothermic peaks above 270°C are attributed to the degradation of the composite. It was also found that the mesophase-isotropic phase transition in the (E-CE)C/PAA films is irreversible because the cholesteric structure of the solid film is destroyed. Figure 6 shows that the phase transition has occurred after the first heating run from 60 to 180°C. After cooling to room temperature, the film cannot return to its original color, and the endothermic peak never appears in the second heating run. This is different from the other thermo-

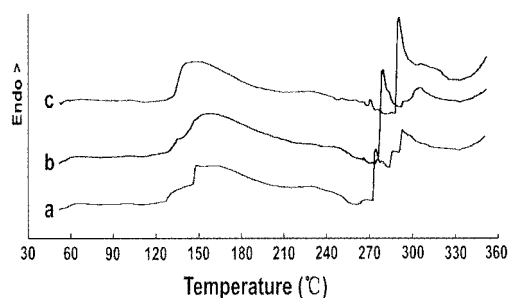


Figure 5 DSC curves (first heating run) for (a) 46.5 wt %, (b) 49 wt % and (c) 52 wt % (E-CE)C/PAA cholesteric composite films.

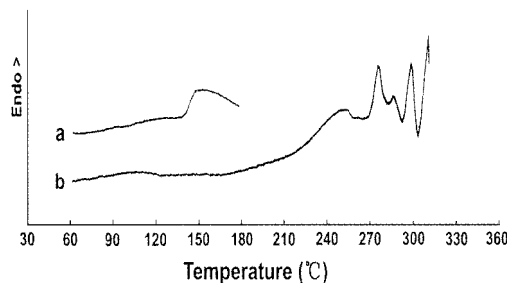


Figure 6 DSC curves for 49 wt % (E-CE)C/PAA cholesteric composite film for (a) the first heating run (60–180°C) and (b) the second heating run (60–320°C).

tropic cellulose cholesteric LC solutions,^{7,24–27} in which the shift in color caused by the mesophase-isotropic phase transition was reproducible after cooling. From these results, it is suggested that the selective reflection of (E-CE)C/PAA cholesteric composite films is stable upon heating when the temperature is lower than 160°C, and that the thermostability of the composites is better than that of PBLG cholesteric film but worse than that of the crosslinked HPC cholesteric film, for which the transition temperatures are about 135°C⁶ and 208°C,⁷ respectively.

CONCLUSIONS

After the photopolymerization of AA, the selective reflection property of the (E-CE)C/AA solutions is retained in the (E-CE)C/PAA composite films. The wavelength of the reflection of the composite decreases with increasing (E-CE)C concentration and can be controlled precisely. The reflectivity is proportional to the thickness of the composite films. The selective reflection property of the (E-CE)C/PAA composites is stable on heating, and the reflection peak shifts only in the long wavelength direction with increasing temperature below 160°C. When the temperature is higher than 160°C, however, the cholesteric structure is quickly destroyed and the selective reflection property disappears.

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References

1. de Vries, H. *Acta Crystallogr* 1951, 4, 219.
2. Schadt, M.; Funfchilling, J. *J Appl Phys* 1990, 29, 1974.
3. Broer, D. J.; Mol, G. N.; van Haaren, J. A. M. M.; Lub, J. *Adv Mater* 1999, 11, 573.
4. Revol, J. -F.; Godbou, L.; Gray, D. G. *J Pulp Paper Sci* 1998, 24, 146.
5. Samuels, R. J. *J Polym Sci, Part A-2* 1969, 7, 1197.
6. Uematsu, I.; Uematsu, Y. *Adv Polym Sci* 1984, 59, 37.
7. Bhadani, S. N.; Gray, D. G. *Mol Cryst Liq Cryst* 1984, 102, 255.

8. Suto, S.; Inoue, M. *Polymer* 1999, 40, 2455.
9. Tsutsui, T.; Tanaka, R. *J Polym Sci, Polym Lett Ed* 1980, 18, 17.
10. Watanabe, J.; Goto, M.; Nagase, T. *Macromolecules* 1987, 20, 298.
11. Kozakiewicz, J. J.; Maginess, J. E.; *J Appl Polym Sci* 1987, 34, 1109.
12. Jiang, S. H.; Huang, Y. *J Appl Polym Sci* 1993, 49, 125.
13. Hikmet, R. A. M.; Zwerver, B. H. *Liq Cryst* 1993, 65, 1989.
14. Zhao, C. -T.; Cai, B. -L. *Macromol Rapid Commun* 1995, 16, 323.
15. Muller, M.; Zentel, R.; Keller, H. *Adv Mater* 1997, 9, 159.
16. Gray, D. G. *Appl Polym Symp* 1883, 37, 179.
17. Huang, Y. *J Macromol Sci Polym Phys Ed* 1989, B28, 131.
18. Jiang, S. H.; Huang, Y. *J Appl Polym Sci* 1993, 50, 607.
19. Wang, L.; Huang, Y. *Macromolecules* 2002, 35, 3111.
20. Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss Faraday Soc* 1958, 25, 29.
21. Onagi Y, White J.; Feller, J. *Polymer Sci Polym Phys Ed* 1980, 18, 663.
22. Shimamoto, S.; Gray, D. G. *Chem Mater* 1998, 10, 1720.
23. Shimamoto, S.; Uraki, Y.; Sano, Y. *Cellulose* 2000, 7, 347.
24. Tseng, S. -L.; Valente, A.; Gray, D. G. *Macromolecules* 1981, 14, 715.
25. Tseng, S. -L.; Laivins, G. V.; Gray, D. G. *Macromolecules* 1982, 15, 1262.
26. Siekmeyer, M.; Zugenmaier, P. *Makromol Chem* 1990, 191, 1177.
27. Muller, M.; Zentel, R. *Macro Chem Phys* 2000, 201, 2055.