

# A Method To Preserve the Chiral Nematic Order of Lyotropic Ethylcellulose and (Acetyl)(ethyl)cellulose Mesophases in Solid Films

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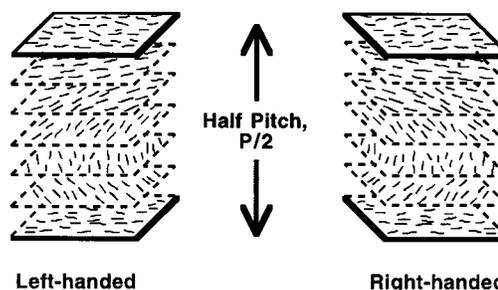
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Solid films that reflect visible light due to chiral nematic order can be prepared from lyotropic ethylcellulose (EC) and (acetyl)(ethyl)cellulose (AEC) mesophases by a three-step casting method. A thin uniform film of desired thickness is cast from dilute solution onto a substrate. The film and substrate are then equilibrated with a mesophase of the same polymer in an appropriate solvent. The mesophase is a convenient source of solvent vapor at an appropriate composition and vapor pressure for the equilibration process. After equilibration, the solvent is allowed to evaporate, leaving a film that reflects visible light. The reflection wavelength of the EC film depends on the activity of the equilibrating vapor and the degree of polymerization. Reflection intensity is governed by the degree of polymerization and the length of the equilibration period. The EC films showed good selectivity in reflection of left-circularly polarized light. Acetylation of EC gives AEC, which forms mesophases that reflect right-circularly polarized light. The three-step casting process was used to produce right-circularly polarizing films of AEC. The effects of degree of polymerization, equilibration concentrations, and temperature on the wavelength and intensity of the AEC reflection peak were measured by apparent circular dichroism and UV–visible spectrometry.

## Introduction

Many cellulose derivatives form liquid crystalline phases in solutions or in melts.<sup>1–3</sup> As a result of the chirality of the cellulose backbone, most cellulosic liquid crystalline phases form chiral nematic structures.<sup>4</sup> Chiral nematic structures may be represented by the right- and left-handed helicoidal arrangements of small rodlike species shown in Figure 1, where the rods represent the orientation of segments of the cellulose backbone. This type of supermolecular arrangement results in remarkable optical properties such as strong rotatory power and selective reflection of circularly polarized light in a narrow region of wavelengths. The selective reflection of light is oriented along the chiral nematic axis, according to de Vries' theoretical prediction, and the wavelength of the selective reflection is given by  $\lambda_0 = nP$  where  $\lambda_0$  is the wavelength of reflection maxima,  $n$  is the average refractive index, and  $P$  is the chiral nematic pitch.<sup>5</sup> Proposed applications of selective



**Figure 1.** Right- and left-handed chiral nematic structures. The lines represent the orientation of segments of the polymer chains, and  $P$  is the helicoidal pitch.

reflection from chiral nematics include polarizers in laser systems<sup>6</sup> and liquid crystalline displays.<sup>7</sup>

Efforts have been made to make solid films that maintain the chiral nematic order and optical properties of polymeric liquid crystalline phases. Such films would have advantages in moldability, handling, and stability compared to fluid mesophases. For example, Tsutsui and Tanaka reported that solid cholesteric films can be prepared from the poly( $\gamma$ -butyl-L-glutamate)/triethylene glycol dimethacrylate system by polymerization of the triethylene glycol dimethacrylate component.<sup>8</sup> Bhadani

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(1) Chemical Characteristics of Cellulosic Liquid Crystals. Gray, D. G. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 257–264.

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(3) Thermotropic Cellulose Derivatives. Fukuda, T.; Takada, A.; Miyamoto, T. In *Cellulosic Polymers, Blends and Composites*. Gilbert, R. D., Ed.; Hanser: New York, 1994; pp 47–70.

(4) Chiral Nematic Ordering of Polysaccharides. Gray, D. G. *Carbohydr. Polym.* **1994**, *25*, 227–284.

(5) Rotatory Power and Other Optical Properties of Certain Liquid Crystals. de Vries, Hl. *Acta Crystallogr.* **1951**, *4*, 219–226.

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(8) Solid Cholesteric Films for Optical Applications. Tsutsui, T.; Tanaka, R. *Polymer* **1980**, *21*, 1351–1352.

and Gray described preparation of cholesteric films from a thermotropic acrylic ester of (hydroxypropyl)cellulose by cross-linking.<sup>9</sup> Suto and Suzuki prepared cross-linked (hydroxypropyl)cellulose from (hydroxypropyl)cellulose/methanol/cross-linker systems.<sup>10</sup> Jiang and Huang prepared chiral nematic solids from (ethyl)-(cyanoethyl)cellulose by photopolymerizing the acrylic acid solvent.<sup>11</sup>

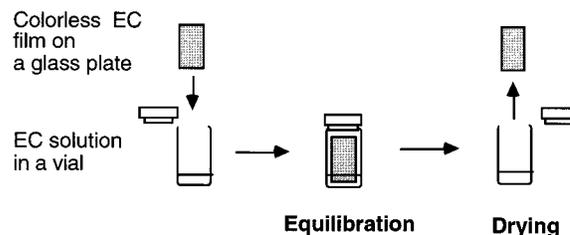
Simple casting of polymer/solvent systems can also give solid chiral nematic films as demonstrated by Watanabe and co-workers<sup>12</sup> and Charlet and Gray.<sup>13</sup> However, the chiral nematic pitch of such films is often outside the desired range that gives reflection of visible light, or the order is disrupted during the casting process. So, factors governing the preservation of chiral nematic ordering in casting methods are of great interest.

Uniform thin films are easily cast from dilute solutions of film-forming cellulosic polymers. In many cases, such solutions must pass through concentrations at which lyotropic mesophases form on their way to dryness, but the drying process may not allow sufficient time for the polymer chains to form a well-oriented mesophase. Conversely, it is hard to prepare films directly from concentrated mesophases, as the shear forces involved in spreading the viscous solutions distort the orientation in the mesophases. The essence of the proposed method is a three-step process in which (i) a film of the desired dimensions is cast from dilute solution, (ii) the film is equilibrated with solvent vapor at a concentration and temperature to optimize liquid crystal properties, and then (iii) the film is dried under conditions that optimize the chiral nematic orientation of the resultant film.

In this study, we report the preparation of films with chiral nematic order from lyotropic ethylcellulose (EC) and (acetyl)(ethyl)cellulose (AEC) mesophases by a casting method. Some factors affecting the reflection properties will also be discussed.

## Experimental Section

Five EC samples with degree of substitution (DS) of 2.5 were purchased from Aldrich, Sigma, and Tokyo Kasei. (This degree of substitution indicates that, on average, 2.5 of the 3 available hydroxyl groups on each glucose unit have been replaced by ethoxy groups.) The viscosity specifications provided by the manufacturers for 5% solutions in toluene/ethanol (8/2) as a measure of degree of polymerization (DP) were 22, 45, 50, 100, and 300 cP. The samples were used without further purification. Chloroform and dichloromethane were reagent grade. AEC samples were prepared from three ECs (50, 100, and 300 cP) by the procedure reported previously.<sup>14</sup> IR spectra of the



**Figure 2.** Procedure for making films with visible reflection.

AEC samples were recorded with a Bruker ISF48 spectrometer. The degree of acetyl group substitution (acetyl DS) was determined by absorption of the carbonyl group at  $1750\text{ cm}^{-1}$ . The molecular weights of the AEC samples were evaluated by means of size-exclusion chromatography, with a Waters 510 HPLC pump, a Hewlett-Packard HP 1047A refractive index detector, and a column set of six Waters Styragel (HMW 6E, HR 5E, HR 4, HR 3, HR 1, and HR 0.5) columns, with dioxane solvent flowing at  $1\text{ mL/min}$ . The columns were calibrated with polystyrene standards. The molecular weight values ( $M_w$ ) reported for the cellulose derivatives are those for an equivalently sized polystyrene molecule.

Liquid crystalline solutions for spectroscopic measurements were prepared by placing polymer and solvent in rectangular glass capillaries ( $0.4 \times 4 \times 50\text{ mm}$ , Vitro Dynamics, Inc.). The capillaries were cooled in dry ice and then sealed by flame. The contents were well mixed by centrifuging back and forth to give uniform solutions. The resulting uniform solutions were allowed to stand for 1 week before spectra were measured. AEC films for apparent CD measurement were prepared by dissolving  $0.13\text{ g}$  of polymer in  $10\text{ mL}$  of chloroform to give an isotropic solution. It was poured into a  $9\text{ cm}$  dia. glass dish, and the solvent was allowed to evaporate in ambient conditions to give  $20\text{ }\mu\text{m}$  thick films.

To obtain ethylcellulose films that reflect visible light, solid colorless ethylcellulose films were first prepared from dilute solutions in chloroform/methanol (8/2, v/v) by casting on glass plates. The plates were placed in vials containing a lyotropic mesophase of the same polymer. The films were allowed to equilibrate with the solvent vapor in the vials for 3 days to obtain thin mesophase films on the glass plates. The glass plates were then removed from the vials and allowed to dry under normal laboratory conditions. The procedure is illustrated in Figure 2. In our preliminary experiments, it took about 12 h for the films on the glass plates to show the same colors displayed by the mesophase solutions in the vials; an equilibration period of 2 or 3 days was used routinely to allow the polymer on the glass plate to reach the same concentration as the solution in the vial. Film thicknesses were adjusted to  $10\text{ }\mu\text{m}$  for the apparent circular dichroism measurements and  $40$  or  $60\text{ }\mu\text{m}$  for the UV-visible reflection measurements.

Microscopic observations were made with a Nikon Microphot-FXA microscope. UV-visible reflection spectra were recorded with a Perkin-Elmer Lambda 14 UV/Vis spectrometer. When required, the unpolarized incident light was converted into circularly polarized light by a combination of a linear polarizer and a quarter-wave plate, oriented at a  $45^\circ$  angle to each other and inserted in that order between the light source and the sample.<sup>15</sup> Apparent circular dichroism spectra were recorded with a Jasco J-500C spectropolarimeter.

## Results and Discussion

**I. Ethylcellulose. Chiral Nematic Phase Formation.** EC with a DS of 2.5 is known to form lyotropic chiral nematic phases with dichloromethane and chlo-

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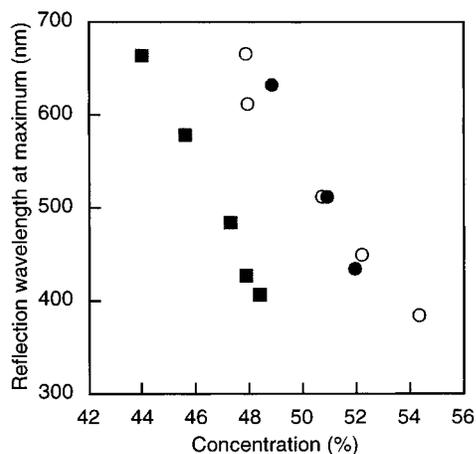
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(12) Cholesteric Twisted Structure in Solid Films of Poly( $\gamma$ -methyl-D-glutamate). Watanabe, J.; Sasaki, S.; Uematsu, I. *Polym. J.* **1977**, *9*(3), 337–340.

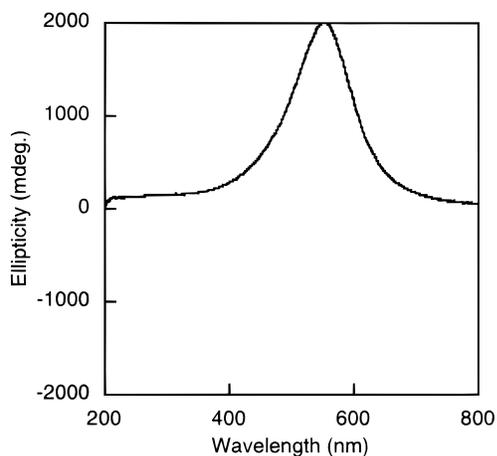
(13) Solid Cholesteric Films Cast from Aqueous (Hydroxypropyl)cellulose. Charlet, G.; Gray, D. G. *Macromolecules* **1987**, *20*, 33–38.

(14) Preparation and Liquid Crystalline Properties of (Acetyl)-(ethyl)cellulose. Guo, J.-X.; Gray, D. G. *Macromolecules* **1989**, *22*, 2082–2086.

(15) Chiroptical Filters from Aqueous (Hydroxypropyl)cellulose Liquid Crystals. Charlet, G.; Gray, D. G. *J. Appl. Polym. Sci.* **1989**, *37*, 2517–2527.



**Figure 3.** Wavelength of reflection peak maximum against ethylcellulose concentration for mesophases made from EC (100 cP)/dichloromethane (●), EC (100 cP)/chloroform (■), and EC (22 cP)/dichloromethane (○).



**Figure 4.** Apparent CD spectrum of film prepared from the EC (45 cP)/chloroform system. The film thickness is 10  $\mu\text{m}$ .

reform.<sup>16,17</sup> The peak reflection wavelengths of EC chiral nematic phases in dichloromethane and chloroform are shown as a function of concentration in Figure 3. The concentration dependence of the reflection wavelength was negative in all systems. The results are consistent with those of Budgell.<sup>16</sup> In terms of the relationship between reflection wavelength and concentration, there was no significant difference between EC with high DP and EC with low DP.

**EC Film Preparation.** We found that solid films with visible reflection and essentially no macroscopic linear birefringence can be obtained from lyotropic chiral nematic phases of EC in chloroform and dichloromethane by the procedure illustrated in Figure 2. The apparent circular dichroism spectrum of a green film prepared from an EC/chloroform system is shown in Figure 4. The rotation of the film about the normal to the film surface did not change the profile of the spectrum. Therefore, the film did not display a macroscopic linear birefringence which would affect the magnitude and sign of the

apparent circular dichroism.<sup>18</sup> The wavelength at the reflection maximum, 550 nm, is qualitatively consistent with the observed green color. The positive sign of the spectrum is the same as that observed for EC mesophases.<sup>16,17</sup> This spectrum indicates that light transmitted by the film is depleted in one hand of circularly polarized light. This component, which peaks at 550 nm, is reflected by the sample. From these results, it was concluded that the reflection of the film is due to preservation of the left-handed chiral nematic order of the mesophase in the solid state.

To obtain solid films that reflect visible light, the concentrations of the mesophases used in the equilibration stage of film preparation had to be lower than those which give visible reflections in the solution state. In other words, the mesophases used for the film equilibration had to have chiral nematic pitches larger than the wavelength of visible light. This means that the chiral nematic pitch of the films decreases during the drying process.

On the basis of extrapolation of the observed negative concentration dependence of the equilibration chiral nematic reflection wavelength shown in Figure 3, it would be expected that the reflection wavelength of solid films or highly concentrated solutions should be smaller than that of visible light. The fact that chiral nematic pitch can be fixed at the order of visible wavelength in the solid state strongly suggests that the change in chiral nematic pitch is too slow to keep up with the change in concentration in the preparation during the drying step.

Charlet and Gray prepared UV-visible-reflecting films from the (hydroxypropyl)cellulose/water system by removing the solvent from a dilute solution or from a thin mesophase which was kept under its own vapor pressure.<sup>15</sup> These methods were not successful for the EC/dichloromethane and chloroform systems, probably because these solvents are too volatile to allow a uniform chiral nematic structure to form before they evaporate.

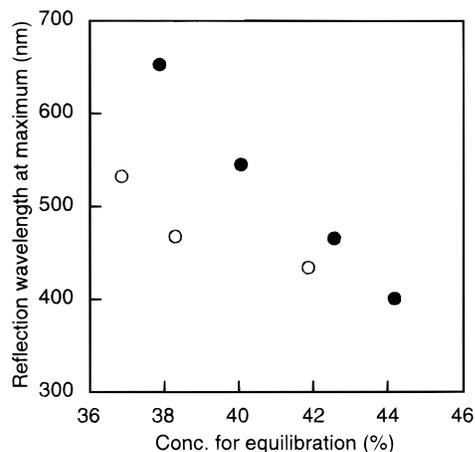
**EC Reflection Wavelength.** UV-visible reflection spectra of films prepared from EC/chloroform and EC/dichloromethane showed a decrease in reflection wavelength with increases in the EC concentration in the mesophase used for equilibration. This is probably due to the negative concentration dependence of the reflection wavelength for the mesophase. When equilibrated at the same mesophase concentration, EC with a low DP gave films with shorter reflection wavelengths than EC with a high DP (Figure 5), although the chiral nematic pitches of the mesophases were comparable at the same concentration. This means that the change in chiral nematic pitch in the course of the drying is greater for EC with low DS, presumably because the more mobile low-DP molecules can form a more tightly twisted chiral nematic structure.

**EC Reflection Intensity.** The EC mesophases made from low-DP polymer showed more intense reflection colors than those made from the high-DP sample. Surprisingly, the films made from these mesophases showed the opposite trend; the low-DP films showed less intense reflection than those made from the high-DP

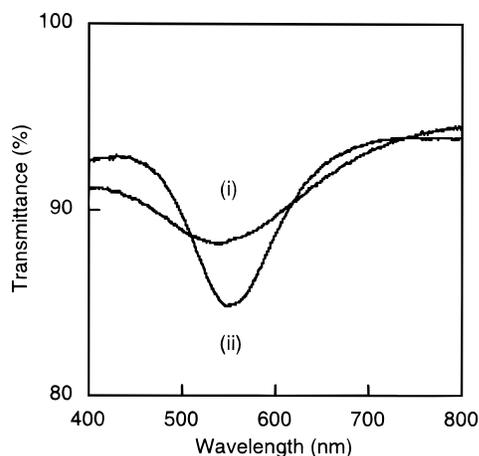
(16) Budgell, D. R. *Liquid Crystalline Properties of Ethyl Cellulose*. Ph.D. Thesis, McGill University, Montreal, 1989.

(17) Chiroptical Behavior of (Acetyl)(ethyl)cellulose Liquid Crystalline Solutions in Chloroform. Guo, J.-X.; Gray, D. G. *Macromolecules* **1989**, *22*, 2086–2090.

(18) Effect of Residual Linear Orientation on the Optical Properties of Cholesteric Films. Ritcey, A. M.; Charlet, G.; Gray, D. G. *Can. J. Chem.* **1988**, *66*, 2229–2233.



**Figure 5.** Plot of reflection wavelength of EC film versus concentration for equilibration for EC (100 cP)/dichloromethane (●) and EC (22 cP)/dichloromethane (○). Film thickness is 40  $\mu\text{m}$ .



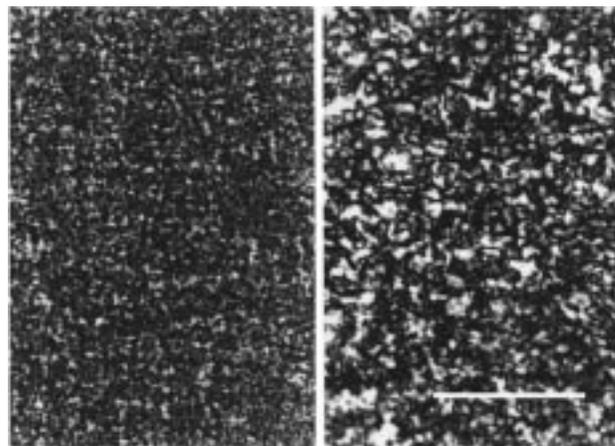
**Figure 6.** UV-visible reflection spectra of films prepared from the EC (100 cP)/chloroform system after a 3-day (i) and a 19-day equilibration (ii). Film thickness is 40  $\mu\text{m}$ .

polymer. This suggests that the uniformity in chiral nematic ordering of EC with low DP is more perturbed in the course of solidification. This is probably due to the greater change in chiral nematic pitch during solidification.

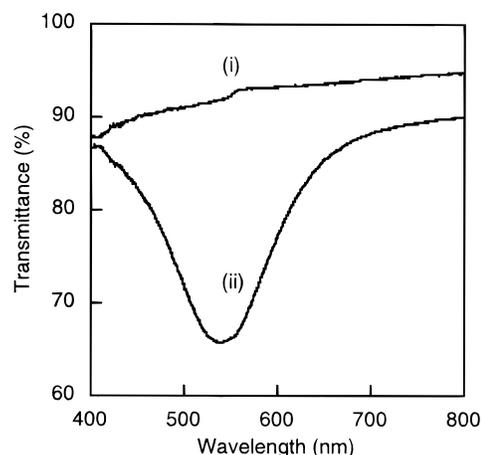
In our procedure for the film preparation, reflection intensity was improved by prolonging the equilibration period as shown in Figure 6. Microscopic observations on these films revealed that the film prepared by the longer equilibration possessed a larger texture as shown in Figure 7. From these results, it was concluded that the longer equilibration resulted in larger chiral nematic domains, thus improving reflection intensity.

**Selectivity in Reflection.** Because the spectropolarimeter used in this work is far too sensitive for highly reflective films, they were investigated by use of a UV-visible spectrometer equipped with a circular polarizer. Typical results are shown in Figure 8. As expected from the apparent circular dichroism measurement mentioned above, highly reflective films selectively reflected left-circularly polarized light. The reflection band appears as an absorption peak in the transmission spectra.

**II. (Acetyl)(ethyl)cellulose.** The ethylcellulose mesophases and films described above all reflect left-circularly polarized light. Guo and Gray found that



**Figure 7.** Polarized photomicrographs showing texture of films prepared from the EC (100 cP)/chloroform system after equilibration for 3 (left) and 19 days (right) with a mesophase solution. Scale bar, 100  $\mu\text{m}$ .

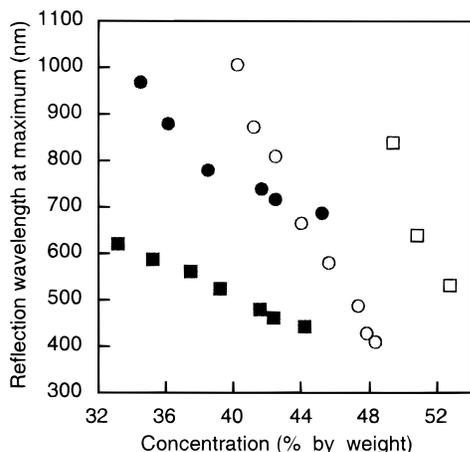


**Figure 8.** UV-visible transmission spectra of film prepared from the EC (100 cP)/chloroform system after a 19-day equilibration. Illumination: right-circularly polarized light (i) and left-circularly polarized light (ii). Film thickness is 40  $\mu\text{m}$ .

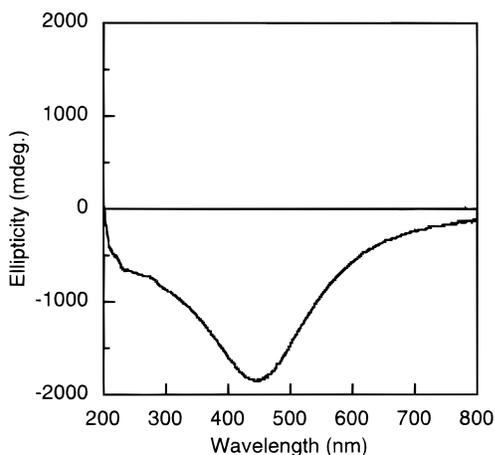
acetylation of ethylcellulose reversed this handedness; cholesteric liquid crystalline solutions of AEC prepared from EC with a DS of 2.5 changed from a left-handed to a right-handed helicoidal structure with increasing acetyl content.<sup>17</sup> The change occurred at a critical acetyl DS of around 0.18–0.20; the cholesteric pitch increased with increases in acetyl DS below the critical acetyl DS but decreased with increases in acetyl DS above the critical acetyl DS. Typical results for the reflection wavelength and handedness of the current AEC samples are shown in Figure 9. The dependence of handedness and reflection wavelength on acetyl DS are consistent with the results reported previously.<sup>17,19</sup> In Figure 9, it should be noted that the concentration dependence of the reflection wavelength for left-handed chiral nematic mesophases is about 3 times larger than that for right-handed ones.

**Casting of Solid AEC Films from Isotropic Solution.** Solid films were prepared from the AEC samples, with acetyl DS values of 0.18, 0.43 and 0.50, by evaporation of chloroform under ambient conditions from dilute

(19) Effect of Degree of Acetylation and Solvent on the Chiroptical Properties of Lyotropic (Acetyl)(Ethyl)Cellulose Solutions. Guo, J.-X.; Gray, D. G. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 2529–2537.

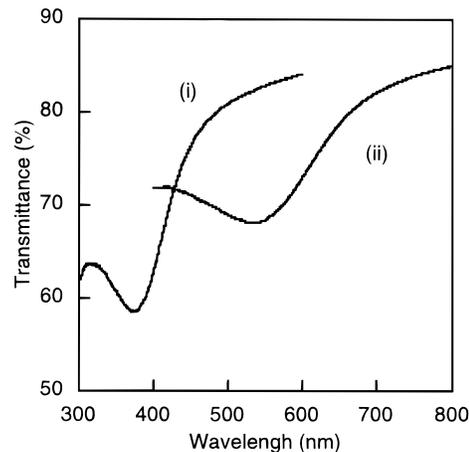


**Figure 9.** Plot of reflection wavelength versus concentration of ethylcellulose (EC) and (acetyl)(ethyl)cellulose (AEC) in chloroform for EC with a viscosity of 100 cP (○) and AEC with acetyl DS of 0.18 (□), 0.43 (●), and 0.50 (■). The AECs were prepared from the EC sample. The unfilled and filled symbols are for left- and right-handed chiral nematic phases, respectively.



**Figure 10.** Apparent CD spectrum of film prepared from a dilute solution of AEC in chloroform. The AEC (acetyl DS, 0.43;  $M_n$ , 300 000) was prepared from EC with a viscosity of 100 cP. Film thickness is 20  $\mu\text{m}$ .

isotropic solutions (0.13 g of polymer in 10 mL of chloroform). The polymers that form left-handed mesophases in chloroform (EC and AEC with acetyl DS of 0.18) showed no colors observable by eye, either in the final films or during solvent evaporation. On the other hand, the AEC sample with acetyl DS of 0.43 resulted in a film that had a faint blue color. The apparent CD spectrum of the film is shown in Figure 10. The negative sign of the spectrum indicates that the film reflects right-handed circularly polarized light. The reflection wavelength at the peak maximum (450 nm) is qualitatively consistent with the observed blue color. The color in the film is due to a preservation of right-handed chiral nematic ordering which is formed in concentrated solutions of the AEC. AEC with acetyl DS of 0.50 gave a colorless film, but the solution showed red, green, and blue colors successively in the course of drying. The difference between left- and right-handed systems in the preservation of chiral nematic structure in the film may be due to the difference in the concentration dependence of chiral nematic pitch. Because of their rapid change of pitch with concentration, it seems



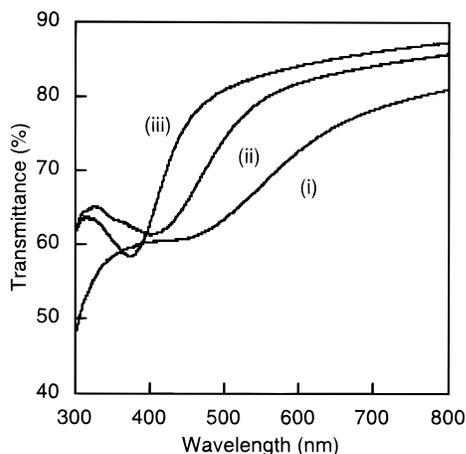
**Figure 11.** UV-visible reflection spectra of films prepared from the AEC ( $M_n$ , 340 000)/chloroform system by equilibration with 37 wt % mesophase. (i) AEC with acetyl DS of 0.43. (ii) AEC with acetyl DS of 0.37. Film thickness is 60  $\mu\text{m}$ .

to be difficult for the left-handed EC and AEC systems to maintain a uniform chiral nematic structure in the course of solvent evaporation.

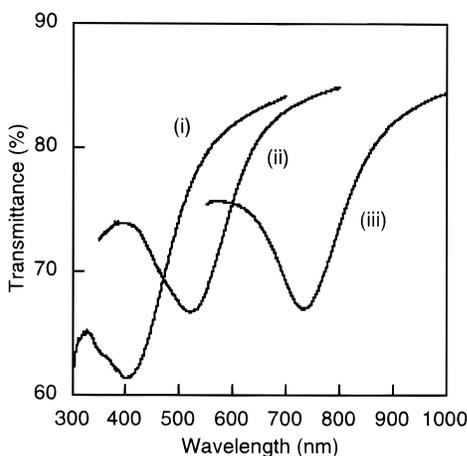
*Casting of Solid Films from Liquid Crystalline AEC Solution. (1) Effect of Acetyl DS and Molecular Weight.* The preservation of chiral nematic ordering of right-handed lyotropic AEC solutions in chloroform was further studied by the three-step film preparation procedure, described above. Small differences in acetyl DS affected the reflection wavelength of the resulting film, as shown in Figure 11. When viewed through a circular polarizer made from a linear polarizer and a quarter-wave plate, the films selectively reflected right-circularly polarized light. The films thus possess right-handed chiral nematic ordering. The effect of acetyl DS on the reflection wavelengths of the resulting films is qualitatively consistent with that of the right-handed liquid crystalline AEC phases mentioned above.<sup>17</sup> The reflection wavelengths of the AEC liquid crystalline mesophases corresponding to the films shown in Figure 11 were 740 and 1040 nm at 37 wt % for samples with acetyl DS values of 0.43 and 0.37, respectively. Not surprisingly, the chiral nematic pitch decreases in the course of drying to give reflection wavelengths for the corresponding films of 380 and 530 nm. Thus, a decrease in acetyl content results in an increase in chiral nematic pitch for right-handed AEC liquid crystalline phases and solid films.

UV-visible reflection spectra of films prepared from AECs with various molecular weights are shown in Figure 12. The reflection bandwidth broadens with decreases in chain length. On the other hand, no significant difference in reflection spectra is observed for the corresponding liquid crystalline AEC mesophases. The differences must therefore arise during the drying process, suggesting that the perturbation of chiral nematic ordering during drying is greater for low molecular weight samples, as observed above for reflective films made from left-handed lyotropic mesophases of EC.

*(2) Effect of Casting Conditions.* In the three-step method, the solvent equilibration step and the film drying step may be carried out at different temperatures. AEC films were prepared by drying at room



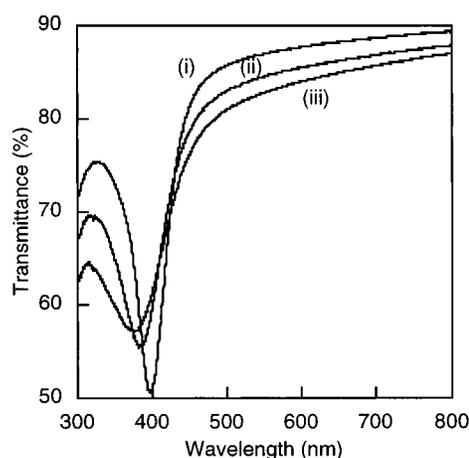
**Figure 12.** UV-visible reflection spectra of films prepared from the AEC (acetyl DS, 0.43)/chloroform system by equilibration with 37 wt % mesophase, for AEC with  $M_r$  of 220 000 (i), 300 000 (ii), and 340 000 (iii). Film thickness is 60  $\mu\text{m}$ .



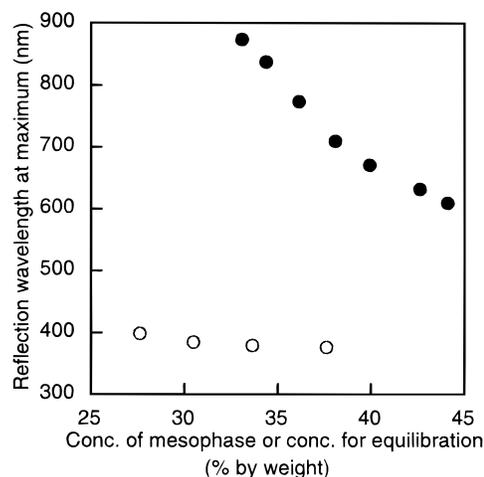
**Figure 13.** UV-visible reflection spectra of films prepared from the AEC (acetyl DS, 0.43;  $M_r$ , 300 000)/chloroform system by equilibration with 37 wt % mesophase. Temperatures for equilibration were 23 (i), 40 (ii), and 55 °C (iii). Film thickness is 60  $\mu\text{m}$ .

temperature immediately after equilibrating with solvent vapor at the desired temperatures. The effect of equilibration temperature on reflection spectra of the resulting films is shown in Figure 13. The reflection wavelength increased with increasing equilibration temperature. (A higher equilibration temperature, of course, also generates a higher solvent vapor pressure.) It has been shown that the chiral nematic pitch of right-handed liquid crystalline solutions of AEC has a positive temperature dependence.<sup>17,19</sup> The effect of equilibration temperature on the reflection wavelength of the film is probably due to the temperature dependence of the chiral nematic pitch.

Figure 14 shows the effect of changing the concentration of mesophase in equilibration with the film (in effect, changing the solvent vapor pressure in equilibration with the film at constant temperature). The major effect here is on the shape of the reflection peak. A sharp peak indicates a uniform well-oriented chiral nematic structure. The reflection bandwidth decreased with decreasing polymer concentration (i.e., with increasing solvent vapor pressure). By equilibrating at 28 wt % polymer, the resulting film showed a high reflectivity close to the theoretical maximum of 50%.<sup>5</sup>



**Figure 14.** UV-visible reflection spectra of films prepared from the AEC (acetyl DS, 0.43;  $M_r$ , 340 000)/chloroform system. Concentrations of mesophase for equilibration were 28% (i), 31% (ii), and 34% (iii) by weight. Film thickness is 60  $\mu\text{m}$ .



**Figure 15.** Plot of reflection wavelength of AEC mesophase in chloroform (●) and of film prepared from AEC versus concentration for equilibration (○). AEC acetyl DS, 0.43;  $M_r$ , 340 000. Film thickness is 60  $\mu\text{m}$ .

However, further lowering the concentration of equilibration mesophase below 28% produced broad and less intense reflections. Unfortunately, attempts to make films with the high reflectivity shown in Figure 14 were not successful at wavelengths higher than 400 nm. An increase in chiral nematic pitch must reduce the total number of chiral nematic pitch lengths that can be accommodated along the thickness direction at a given thickness, and this may contribute to the lower intensity of reflection at longer wavelengths.

Changing the equilibration concentration had a strong effect on mesophase reflection but surprisingly did not have a significant effect on the reflection wavelength of the resulting AEC films, as shown in Figure 15. In contrast, the reflection wavelengths of films prepared from EC were found to depend strongly on the equilibration concentration (Figure 5). A possible explanation is that in the course of drying the AEC samples, the change in chiral nematic pitch could initially keep up with the change in concentration, but that at some fixed concentration the pitch stopped changing despite further solvent evaporation, and the reflection band was thus frozen at a specific wavelength, irrespective of the initial concentrations. On the other hand, the EC mesophases

seem unable to follow even the initial change in equilibrium chiral nematic pitch with concentration and become frozen at a range of wavelengths, depending on the initial mesophase concentrations. The difference in reflection properties may thus depend on differences in mobility or viscosity of EC and AEC. (The right-handed AEC mesophases have a much smaller empirical flow time than the original EC.<sup>17</sup>)

### **Conclusions**

Films of ethylcellulose and (acetyl)(ethyl)cellulose that reflect circularly polarized visible light may be prepared in a three-step process, where an initially formed

nonreflective film is equilibrated with an EC- or AEC/solvent mesophase system. Several equilibrium and kinetic factors influence the wavelength and intensity of solvent-cast chiral nematic films. The results for EC and AEC show clearly that the colors displayed by these chiral nematic films are not simply related to equilibrium chiral nematic structures but also depend intimately on kinetic factors involved in the response of such structures to the removal of solvent.

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