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Circular Reflectivity from the Cholesteric Liquid Crystalline Phase of (2-Ethoxypropyl)cellulose

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ABSTRACT: A new cellulose ether, (2-ethoxypropyl)cellulose, was prepared from (hydroxypropyl)cellulose. The polymer forms highly ordered lyotropic and thermotropic cholesteric liquid crystalline phases characterized by sharp reflection bands. The reflection wavelengths were measured as a function of temperature from the apparent circular dichroism of thin layers of the mesophase. The cholesteric pitch, P, of the thermotropic mesophase increases with temperature, approaching a limiting value of 370 nm at the clearing temperature. A plot of $1/P$ against reciprocal temperature is linear. Thermotropic samples, formed on cooling from the isotropic state, have unusual circular reflectivity spectra that indicate the presence of a random distribution of tilted cholesteric domains. A planar texture and sharp reflection bands can be recovered with gentle shear.

Introduction

Cholesteric liquid crystals possess unique optical properties arising from the selective reflection of light by the helicoidal arrangement of molecules found within these ordered phases. DeVries[1] formulated the theory for these optical properties, modeling the cholesteric phase as a series of twisted birefringent layers. His theory predicts the reflection of circularly polarized light at wavelengths corresponding to the pitch of the supramolecular helicoidal structure. In addition to being selective with respect to wavelength, this reflection is selective with respect to handedness: right-handed cholesteric liquid crystals reflect only right-circularly polarized light and, similarly, left-handed cholesterics reflect only left-circularly polarized light. At wavelengths within the reflection band, the intensity of light transmitted by a cholesteric mesophase will therefore be different for incident light of the two circular polarizations and the reflection properties can be monitored as apparent circular dichroism or "circular reflectivity". This paper illustrates the value of this technique in characterizing the liquid crystalline properties of a new cellulose derivative.

Since the initial report[2] of the formation of a cholesteric liquid crystalline phase in concentrated aqueous solutions of (hydroxypropyl)cellulose (HPC) many other cellulose derivatives have been found to form similar ordered phases.[3,4] Although mesophase formation in cellulose-based polymers is attributed to the rigidity of the anhydroglucose backbone,[5,6] the critical concentration for lyotropic mesophase separation and the temperatures at which thermotropic phases exist do depend heavily on the nature and degree of substitution. Flexible side chains appear to facilitate the orientation of the main chain by increasing its mobility and restricting crystallization.

Although the lyotropic liquid crystalline properties of HPC have been studied in many solvents, the presence of a thermotropic phase has been difficult to ascertain. Rheological studies of the melt suggest that molecular orientation can be induced by shear,[7] but spontaneous cholesteric ordering upon cooling from the melt or upon heating the polymer in its semicrystalline powder form has not been observed. Recently thermotropic behavior has been reported for HPC films cast from lyotropic solution.[8] On heating, such films show a cholesteric reflection band which, as is the case for lyotropic HPC mesophases, moves to longer wavelengths with increasing temperature. However, in the case of pure HPC films this change is totally irreversible. The lack of a true equilibrium cholesteric liquid crystalline phase for HPC is surprising in view of the propensity of this polymer to lyotropic formation and the accessibility of melt temperatures. Interchain hydrogen bonds in HPC may restrict mobility even at temperatures substantially above the glass transition.

A number of ester derivatives of HPC have been prepared and found to form thermotropic cholesteric phases.[9,10] However, in spite of complete substitution of the hydroxyl groups present in HPC, the reflection spectrum of the thermotropic mesophase formed by (acetoxypropyl)cellulose[10] is extremely sensitive to the thermal history of the sample. This implies that flexible side chains alone do not ensure sufficient polymer mobility for good thermotropic properties in cellulose derivatives and that in addition the side chains should be chosen so as to minimize intermolecular interactions. This paper reports the preparation and liquid crystalline properties of the ethyl ether of HPC, (2-ethoxypropyl)cellulose. As shown below, the response of the pitch of the thermotropic mesophase formed by this cellulose derivative to changes in temperature is well-defined and reversible.

Kimura et al.[11] have developed a statistical theory for the cholesteric ordering of polypeptide solutions which predicts that the pitch, P, will show a dependence on temperature, T, of the general form

$$1/P = C(T_N/T - 1) \qquad (1)$$

C is a constant which is a function of the solution concentration and the geometry of the molecular helix. T_N is the compensation temperature, defined as the temperature at which the pitch of the cholesteric structure is infinite.

The temperature dependence of the pitch of lyotropic solutions of poly(alkyl)glutamates has been found to be well described by the empirical relationship[12]

$$1/P = b(1 - T/T_N) \qquad (2)$$

which is equivalent to eq 1 for $T - T_N \gg T_N$. This relationship was also found to hold for the thermotropic liquid crystals formed by five different esters of HPC.[9,10] In addition, the compensation temperature was found to coincide with the clearing temperature of these cellulosic thermotropic mesophases.

Experimental Section

Material. (Ethoxypropyl)cellulose was prepared from HPC (Hercules Klucel E) and iodoethane by the following procedure:[13] HPC (2 g) was dissolved in a mixture of Me_2SO (70 mL) and 1,1,3,3-tetramethylurea (30 mL) by stirring overnight. After filtration and the introduction of a N_2 atmosphere, a solution of potassium *tert*-butoxide (5.6 g) in *tert*-butyl alcohol (28 mL) was added from a syringe. This mixture was cooled to 0 °C and vigorously stirred as iodoethane (8 mL) was introduced in small

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increments. Stirring was continued at room temperature for 10–15 h before the product was precipitated by pouring the reaction mixture into a pH 7 buffer. (Ethoxypropyl)cellulose was washed repeatedly with petroleum ethers, aqueous sodium thiosulfate, and water before a final filtration in acetone solution.

Light Scattering. The mass average molar mass of the polymer was determined by low-angle laser light scattering with a Chromatix KMX-6 LALLS photometer. The scattered intensity was measured at 3–6° to the incident beam. Solutions in tetrahydrofuran were passed through a 0.2-μm Millipore filter (type FGLP) to remove any foreign particles before entering the light scattering cell. The refractive index increment, dn/dc, was determined at 546 nm with a Brice-Phoenix differential refractometer.

Sample Preparation. EPC samples for polarizing light microscopy were prepared from water-swollen polymer. In this state the polymer is soft and samples were easily pressed to a thin film between a micrscope slide and cover slip. The slides were then stored in a desiccator over $Mg(ClO_4)_2$ until dry.

Samples to be studied as thermotropic liquid crystals were prepared between two quartz slides from a 20% solution of EPC in acetone. The solvent was allowed to evaporate under normal laboratory conditions before thorough drying under vacuum. The samples were then heated to 60 °C under a weight (~100 g) for several hours and again allowed to relax overnight in a desiccator before spectra were recorded. Samples prepared in this way had a thickness of ~20–30 μm.

The circular reflectivity spectra of thermotropic samples that have been heated above the clearing temperature show very unusual peak shapes (see discussion below). To recover the planar texture, such samples were heated to ~100 °C on a hot bench for 30 s and then sheared slightly by moving the two slides relative to one another over a distance of 2–3 mm.

Lyotropic samples were prepared by weighing the polymer and solvent into small glass vials. All samples were allowed to mix until a uniform cholesteric color was observed. Samples of EPC in methanol were studied in a quartz cell consisting of two plates, one of which is etched to give a sample thickness of 0.01 mm. Since no precautions were taken to seal the cell the polymer concentration increased with time as the solvent evaporated. Spectra were recorded at various stages of drying over a 3-week period, but the concentration at the time of a specific spectrum is unknown.

Polarizing Light Microscopy. Liquid crystalline textures were observed with a Reichert polarizing microscope equipped with a Mettler FP82 hot stage. The clearing temperature of the thermotropic mesophase was determined by monitoring the intensity of light transmitted through crossed polars as the sample was heated at a rate of 0.2 °C/min. Transmitted light was detected by replacing an ocular with a Mettler 18100 photocell.

Reflectivity Spectra. Circular reflectivity spectra were recorded with a Jasco J-500C spectropolarimeter. Temperature control was achieved by placing samples in a microscope hot stage (Mettler FP52) mounted in the spectrometer beam. All heating and cooling experiments were performed at a rate of 0.2 °C/min. UV–visible spectra were recorded with a Pye Unicam SP8-150 spectrophotometer and Mettler hot stage.

The pitch, P, of liquid crystalline samples was calculated from the wavelength of maximum reflection, λ_0, and the deVries relationship,[1]

$$\lambda_0 = \bar{n}P \tag{3}$$

The mean refractive index, $\bar{n}$, of the polymer was measured at room temperature with an Abbé refractometer as 1.4829. This value was used to calculate the pitch at all temperatures.

Results and Discussion

Laser Light Scattering. The molar mass of the polymer was determined by low-angle laser light scattering from dilute solutions in tetrahydrofuran. A mass average molar mass of 100 000 and second virial coefficient of 2.6 × 10^{-3} mL mol g^{-2} were calculated from the results. Since the (ethoxypropyl)cellulose sample was prepared from HPC of nominal molecular weight 60 000[14] (Klucel E), a molar mass of 100 000 for the ethyl ether indicates that no decrease in the degree of polymerization occurred during the etherification.

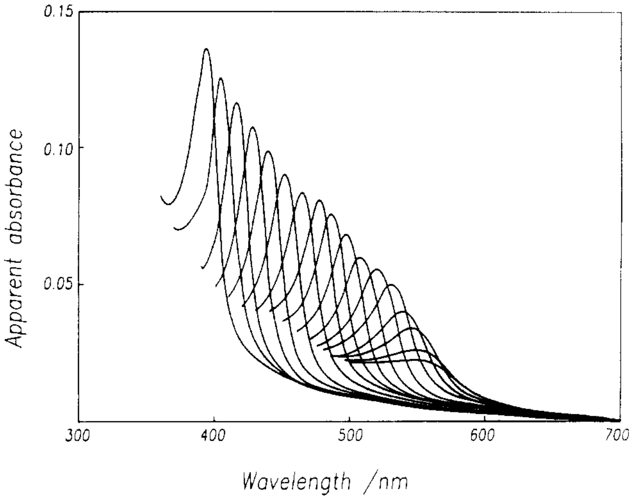

Figure 1. Reflection spectrum of a thermotropic (ethoxypropyl)cellulose mesophase as a function of temperature. Spectra were recorded as apparent absorbance at 2 °C intervals on heating from 130 to 160 °C.

Polarization Light Microscopy. Thin layers of (ethoxypropyl)cellulose, prepared by allowing water swollen samples of the polymer to dry slowly between two glass slides, exhibit birefringent areas separated by distinct dark lines when examined by polarizing light microscopy. The pattern resembles the parabolic focal conic texture typical of HPC lyotropic mesophases.[15] The presence of such a texture in a sample that has been neither heated nor cast from a lyotropic liquid crystalline solution indicates that the polymer exists as a cholesteric liquid crystal at room temperature.

On heating little change is observed in the microscopic appearance of the sample until the clearing temperature is approached. Above 150 °C the bright areas begin to fade, and by 160 °C the field is dark. When the temperature is again lowered, a birefringent texture reappears, but with a much finer grain.

Reflection Properties. Although polarizing light microscopy indicates that liquid crystalline order exists at room temperature, the reflection wavelength corresponding to the cholesteric pitch at 25 °C is too short to be observed spectrophotometrically. The reflection band moves to longer wavelengths upon heating and can be recorded in the UV–visible region of the spectrum from 130 to 160 °C, as illustrated by the series of spectra in Figure 1.

In this temperature range, the reflection properties of the liquid crystal can also be recorded as circular reflectivity (CR) and optical rotatory dispersion (ORD) spectra. Typical spectra are shown in Figure 2. The curves are negative, indicating that this thermotropic cholesteric liquid crystal reflects right-handed circularly polarized light and is therefore also right-handed.

Lyotropic liquid crystalline phases were found to form in acetonitrile, dioxane, and methanol. The CR peaks were negative in all solvents and moved to shorter wavelengths with increasing polymer concentration.

Both the thermotropic and the lyotropic mesophases formed by (ethoxypropyl)cellulose show exceptionally sharp reflection bands. The peaks in methanol all have a width at half height of less than 20 nm. Sharp reflection bands indicate a high degree of order, not only in the sence of there being very little variation in pitch throughout the sample but also in the alignment of the cholesteric axis perpendicular to the surface of the slide.

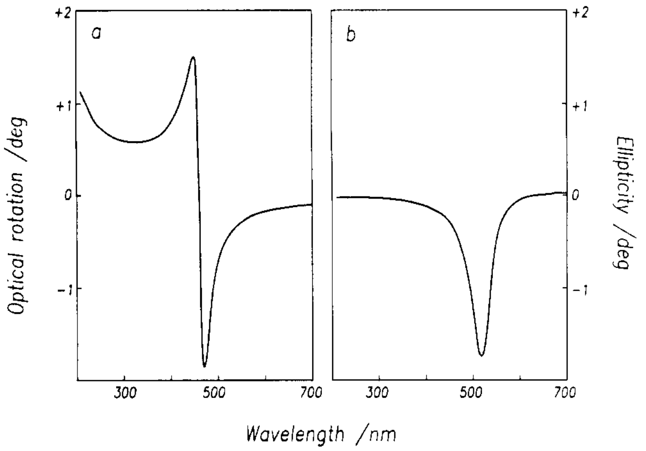

Figure 2. Optical rotatory dispersion (a) and circular reflectivity (b) spectra of a thermotropic (ethoxypropyl)cellulose mesophase recorded at 140 and 152 °C, respectively.

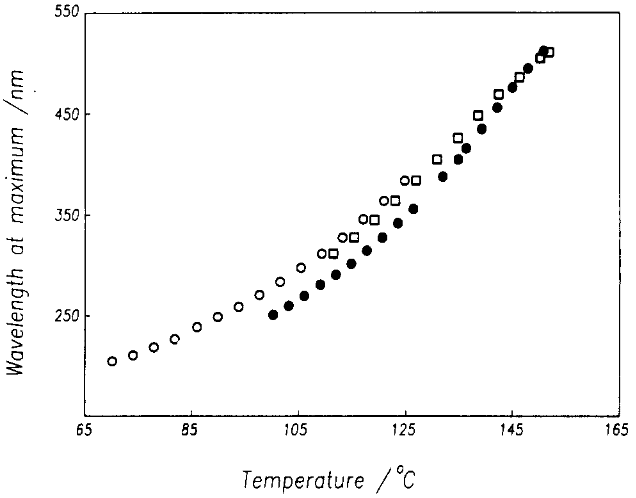

Figure 3. Temperature dependence of the wavelength of maximum reflection, determined from circular reflectivity spectra, for a thermotropic (ethoxypropyl)cellulose mesophase. Peak positions observed on initial heating (filled circles), cooling (open squares), and a second heating (open circles) are shown.

Temperature Dependence of the Pitch. The response of the cholesteric pitch to changes in temperature is reversible, exhibiting little hysteresis. Figure 3 shows the wavelength of maximum reflection, measured by CR, as a function of temperature on both heating and cooling. This behavior is in sharp contrast to that of the parent molecule (hydroxypropyl)cellulose. Thermotropic films of HPC show an irreversible change in pitch with temperature.[8]

A plot of the inverse pitch against reciprocal temperature (Figure 4) is linear as predicted by the theory of Kimura et al.[11] The extrapolation of this curve to infinite pitch, however, does not yield a temperature that corresponds to the clearing temperature where the birefringence disappears. When viewed between crossed polars, the last traces of birefringence disappear and the field becomes dark at 160 °C. T_N, as evaluated from the extrapolation of the plot in Figure 4 to infinite pitch, is 210 °C, but the validity of the extrapolation is dubious because some curvature is evident at the highest temperatures.

The behavior of both the CR and the UV–visible spectra as the clearing temperature is approached also indicates that the pitch does not become infinite. Both types of reflectivity spectra show a sharp decrease in intensity as the temperature characterizing the liquid crystal to isotropic phase transition is approached. The CR spectra recorded from 150 to 160 °C are shown in Figure 5. As the intensity falls to zero, the peak maximum ceases to move to longer wavelengths but approaches a limiting value of 540 nm. Both CR and UV–visible spectra extrapolate to zero intensity near the clearing temperature of 160 °C. Figure 6 shows the intensity of the reflection

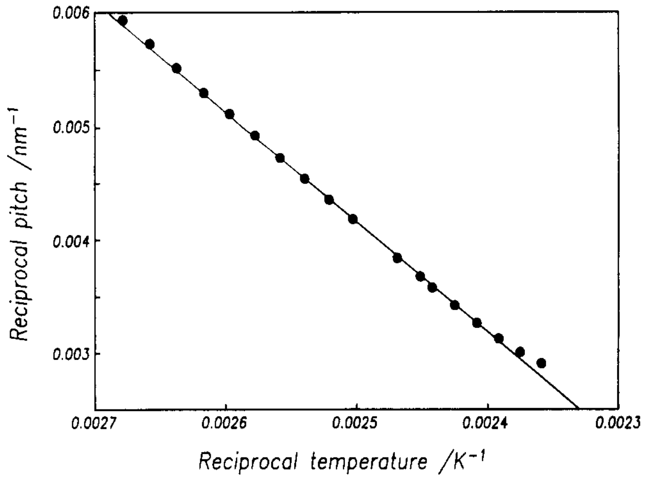

Figure 4. Plot of reciprocal pitch against reciprocal temperature for thermotropic (ethoxypropyl)cellulose.

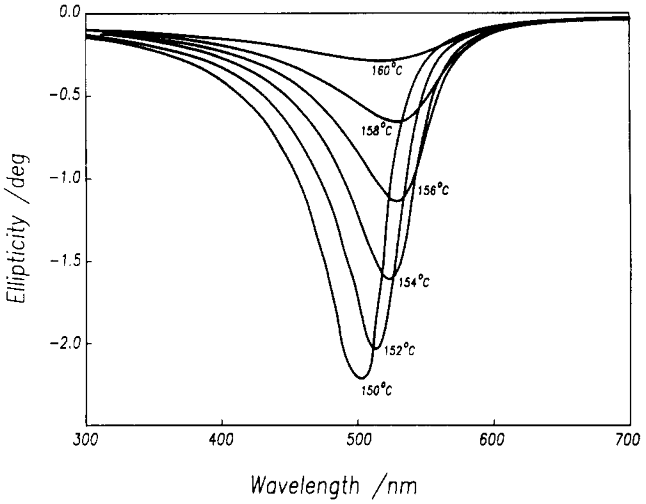

Figure 5. Disappearance of the circular reflectivity band of thermotropic (ethoxypropyl)cellulose as the clearing temperature is approached. The spectra shown were recorded at 2 °C intervals on heating from 150 to 160 °C.

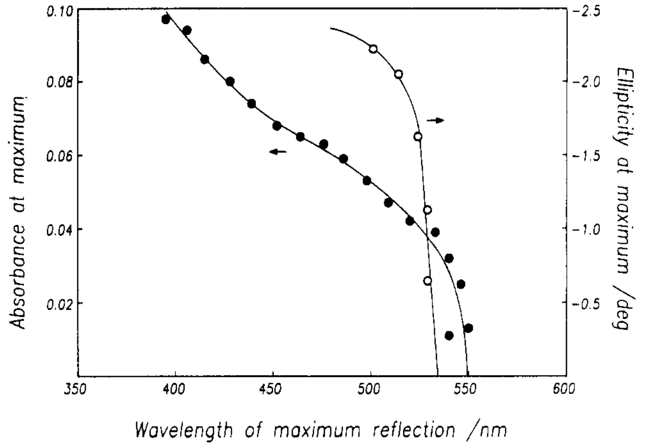

Figure 6. Reflection band intensity, measured both as apparent absorbance (filled circles) and apparent ellipticity (open circles) as a function of wavelength of maximum reflection for thermotropic (ethoxypropyl)cellulose.

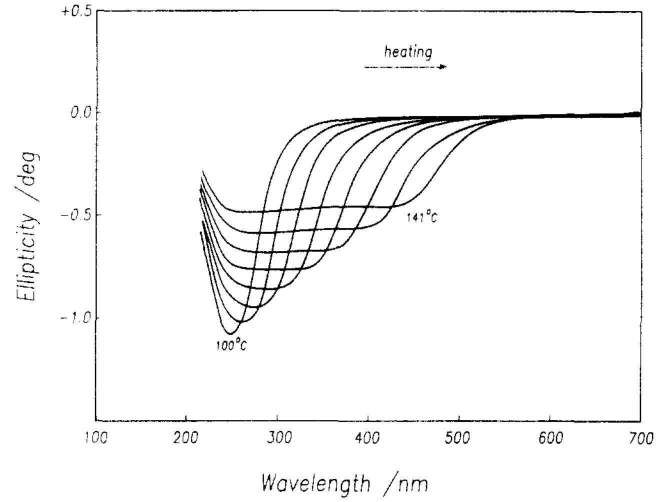

Figure 7. Circular reflectivity spectra recorded on heating a thermotropic (ethoxypropyl)cellulose mesophase sample previously heated to the isotropic state. Spectra were recorded at 15-min intervals while heating at 0.2 °C/min.

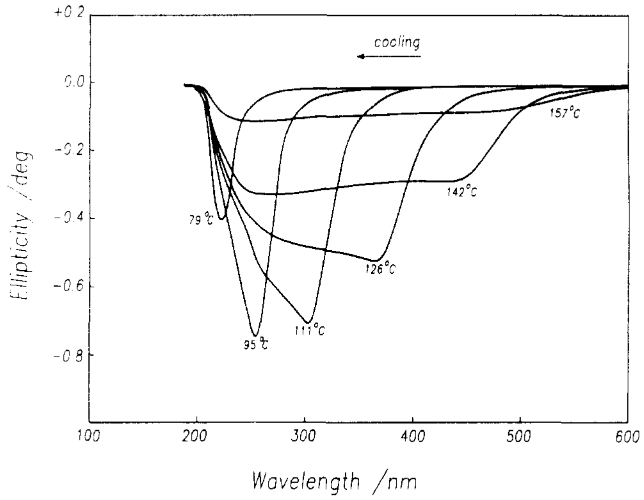

Figure 8. Circular reflectivity spectra at various temperatures for a thermotropic (ethoxypropyl)cellulose mesophase sample obtained on cooling from the isotropic state.

spectra as a function of wavelength. Extrapolation of these curves to zero intensity gives a value of 540–550 nm for the wavelength of maximum reflection at the clearing temperature. This reflection wavelength corresonds to a pitch of 370 nm.

For the esters of HPC, the pitch was found to approach infinity at the limit of the clearing temperature.[9,10] Evidently, this behavior is not general.

Reflection from Nonplanar Samples. The selective reflection of light from the thermotropic mesophase formed by (ethoxypropyl)cellulose is characterized by a sharp reflection band, the position of which shifts reversibly with changes in temperature. This, however, is true only for samples that have never been heated to the isotropic state. Samples heated above the clearing temperature (160 °C) exhibit very unusual circular reflectivity spectra when cooled to temperatures within the thermotropic range. Figure 7 shows the spectra recorded during the heating of a sample that had been previously heated to 165 °C and then cooled to 100 °C. The position of the long wavelength extreme of each of these broad rectangular peaks coincides with the equilibrium wavelength of maximum reflection expected for the corresponding temperature. The observed peak shape indicates that in addition to reflecting circularly polarized light at the expected wavelength, such samples also reflect wavelengths below this value equally well.

Asada[16] has calculated the reflection spectrum expected for a polydomain liquid crystalline sample when the cholesteric axes of the domains are tilted with respect to the incident radiation. When the axis of a domain is tilted at angle θ with respect to the incident beam, the wavelength of maximum reflection, λ_θ, shifts to shorter wavelengths according to

$$\lambda_\theta = \lambda_0 \cos\theta \qquad (4)$$

where λ_0 is the refection maximum at normal incidence. If the domains are assumed to be distributed such that all orientations relative to the normal are equally likely, the probability of the existence of an element with cholesteric axis tilted at an angle between θ and $d\theta$ is given by

$$P(\theta) = (\sin\theta/2\pi)\,d\theta \qquad (5)$$

The reflection intensity as a function of wavelength, $I(\lambda)$, expected for such a distribution of domains can be calculated as the sum of the reflection bands arising from each domain over all tilt angles between 0 and $\pi/2$, weighted by the probability $P(\theta)$. If each reflection band is assumed to be Gaussian with width w, the reflection intensity is given by

$$I(\lambda) = \int_{\theta=0}^{\pi/2} P(\theta) \exp\{-(\lambda - \lambda_0 \cos\theta)^2/w^2\} \qquad (6)$$

Such a summation of peaks yields a flat reflection band with a high wavelength limit corresponding to the reflection wavelength for normal incidence and without limit at low wavelengths. The reflection spectra of Figure 7 agree well with this predicted shape, but a low wavelength limit is observed at 220 nm.

Circular dichroism spectra always have a low wavelength cutoff arising from the difficulty of measuring the difference between the transmitted intensity for left and right circularly polarized light in regions of high absorption. In such cases the spectropolarimeter signal falls to zero and this effect could thus cause the apparent lack of reflection below 220 nm. This is not the case, however, as illustrated in Figure 8 by the presence of the reflection peak recorded at 79 °C. This peak is situated at lower wavelengths than the cutoff value observed for the other spectra, and this cutoff is therefore not an artifact resulting from instrumental limitations.

It should be emphasized that this simple treatment of the reflection of light from tilted domains considers only the effect of oblique incidence on the wavelength of maximum reflection. Reflection spectra recorded with circularly polarized light, such as the CR spectra in Figure 7, will also be sensitive to changes in the polarization of the reflected light. Theoretical considerations[17,18] and experimental observations[19] indicate a loss of polarization selectivity for the reflection from cholesteric liquid crystals at oblique incidence. In fact, Belyakov and Dmitrienko[17] predict a wavelength region, which increases in width with increasing angle of incidence, where light is reflected irrespective of its polarization. Such a reflection could not be detected by circular reflectivity measurements. Outside this region of total reflection, the authors predict a fairly complex dependence of the polarization of the reflected light on the angle of incidence.

Reflection spectra for a monodomain small molecule cholesteric liquid crystal recorded at various angles of incidence[18] confirm the presence of a narrow region of total reflection in the center of the reflection band. Even at wavelengths outside this region, the reflection was observed to become less specific for one handedness of circularly

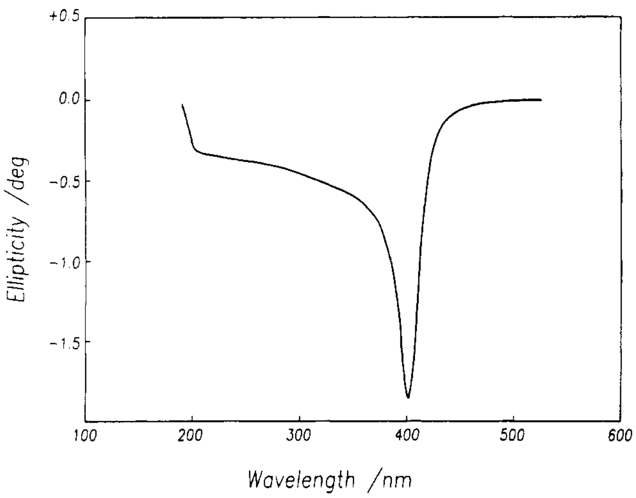

Figure 9. Circular reflectivity spectrum of a thermotropic (ethoxypropyl)cellulose mesophase observed on cooling to 130 °C after being held at 154 °C for 95 min.

polarized light as the angle of incidence was increased.

Therefore, in general, CR spectra should show a decrease in intensity at wavelengths where the reflection originates from domains at high tilt angles. However, the exact nature of the dependence of the polarization selectivity on the angle of incidence is not known, especially in the case of the polydomain sample of relatively low reflectance studied here. It is possible, but somewhat unlikely, that this dependence has a form which results in a sudden loss of CR at some critical angle of incidence.

An alternative explanation for the observed low wavelength limit for the reflection spectra shown in Figure 7 is the existence of a restriction on the range of possible tilt angles, perhaps imposed by the domain size and the sample thickness.

Although all features of the rectangular reflection bands are not completely understood, it is clear that on cooling from the isotropic state (ethoxypropyl)cellulose forms a liquid crystal that does not spontaneously adopt a planar texture. In fact, all orientations of the cholesteric elements appear with equal probability. This indicates that the quartz slide surfaces have no influence on the orientation of the molecules, in spite of the fact that these samples are relatively thin.

A well-ordered planar texture, characterized by sharp reflection peaks, can be recovered in samples that have been heated above clearing by gentle shear.

Some unexpected phenomena were observed close to the clearing temperature. On standing at 154 °C for 95 min, the CR spectrum of a thermotropic sample showed significant loss in reflection intensity but little change in peak shape or position. This indicates that part of the sample has become isotropic at this temperature. The real clearing temperature is therefore lower than 160 °C, but the transition from the anisotropic to the isotropic phase is too slow for equilibrium to be attained at the heating rate of 0.2 °C/min. Since this heating rate was sufficiently slow to maintain an equilibrium pitch, the kinetics of the response of the pitch to changes in temperature must be faster than those for the phase transition from the liquid crystalline to the isotropic state.

When cooled, this sample has a very unusual CR spectrum (Figure 9). The peak consists of a very sharp component, presumably arising from the portion of the sample that remained anisotropic at 154 °C, situated at the extreme right of a very broad peak. This broad peak represents the random distribution of tilted domains found within the portion of the sample that had become isotropic.

The observation that a significant proportion of the liquid crystalline sample can become isotropic while the remaining part maintains the high degree of order indicated by the extremely sharp reflection band of Figure 9 is perhaps surprising. It is, however, in agreement with a recent theory for phase separation in lyotropic systems of rodlike molecules with flexible side chains[20] that predicts a relatively high order parameter (≥ 0.8) for the anisotropic phase in equilibrium with isotropic solution.

Conclusions

(Ethoxypropyl)cellulose forms both thermotropic and lyotropic cholesteric liquid crystals that exhibit very sharp reflection spectra, indicating a high degree of order. The inverse pitch of the thermotropic mesophase varies linearly with reciprocal temperature, and this change in pitch with temperature is completely reversible. This is in sharp contrast to the thermotropic behavior of HPC and indicates the importance of hydrogen bonding in limiting polymer mobility.

The wavelength of maximum reflection for the thermotropic mesophase formed by (ethoxypropyl)cellulose approaches a value of 540–550 nm at the clearing temperature.

The liquid crystalline phase formed on cooling from the isotropic state consists of cholesteric elements that adopt a random distribution of orientations relative to the surface of the slide. This distribution results in a broad flat reflection band. A well-ordered planar texture can be recovered in such samples with gentle shear. The apparent circular dichroism due to polarized reflection from thin mesophase samples is a useful indication of the orientation distribution of the cholesteric axes.[21]

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