polymer papers

Optical properties of (acetoxypropyl)cellulose mesophases: factors influencing the cholesteric pitch

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(*Received 19 November 1984*)

(Acetoxypropyl)cellulose (APC) forms a thermotropic cholesteric liquid crystalline phase, and with dibutyl phthalate (DBP) it also forms a lyotropic cholesteric phase. The reflection bands for the mesophases occur in the visible region, at wavelengths which depend on concentration and temperatures. The pitch of the cholesteric helicoidal structure is derived from measurements of the mean refractive indices and of the reflection band wavelengths for mesophase samples containing from 0 to 30% diluent at temperatures from ambient to 170°C. The pitch of the thermotropic mesophase increases with increasing temperature and with decreasing molar mass. The pitch of the lyotropic mesophase increases with increasing temperature and diluent content. Pitch values approach infinity at temperatures close to the clearing temperature of the mesophase, and no reversal in the sense of the pitch with temperature or diluent content was detected. The experimentally observed changes in pitch with composition and temperature are in reasonable agreement with the predictions of a recent theory for cholesteric mesophases composed of helical rod-like species. The average distance between chains in the mesophase is estimated from X-ray diffraction measurements, and hence the average angle of twist between neighbouring APC molecules may be found. The angle decreased from 2.2° for pure APC to 0.9° for a volume fraction of 0.73 APC in DBP.

(Keywords: (acetoxypropyl)cellulose; cholesteric liquid crystal; cholesteric reflection bond; dibutyl phthalate; helicoidal pitch)

INTRODUCTION

The characterization and liquid crystalline phase formation from (acetoxypropyl)cellulose (APC) in dialkyl phthalate diluents has been reported recently[1]. Without diluent, this cellulose derivative forms a thermotropic cholesteric. With high boiling diluents, such as dibutyl phthalate (DBP), the properties of the resultant lyotropic cholesteric mesophase may be studied over a wide range of temperatures and polymer concentrations. In this paper, the pitch of the supermolecular helicoidal arrangement of the polymer chains is investigated for the APC/DBP system. The results extend previous work on cholesteric mesophases of (hydroxypropyl)cellulose[2,3]. The optical measurements are supplemented by wide-angle X-ray diffraction experiments in an attempt to identify the contributions of interchain separation and interchain angle to the overall twist of the helicoidal structure.

Most experimental studies of the optical properties of cholesteric polymeric mesophases have been on polypeptide systems. The temperature dependence of the cholesteric pitch of poly(alkyl) glutamate solutions was found to be expressed adequately[4] by the empirical equation:

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

The parameter b is a constant for a given polymer–solvent concentration. However, b, for a given polymer–solvent combination, is known to increase as the polymer concentration increases[5]. The compensation temperature, T_N, is defined as the temperature at which the cholesteric pitch is infinite. At this temperature the molecular arrangement resembles that in a nematic mesophase. The equation satisfactorily rationalized the thermally induced reversals of the cholesteric helicoidal twist observed for polypeptide lyomesophases[6,7]. This equation also predicts the temperature dependence of the thermotropic cholesteric mesophases of copoly(n-alkyl glutamates), although a reversal in the helicoidal twist has not been reported[5].

The temperature dependence of the pitch for cholesteric lyomesophases involving cellulosic derivatives has yet to be quantitatively determined although some studies over a limited temperature range suggest a linear relationship[8,9]. Most of the optical studies with lyotropic cellulosic systems have focused on the factors affecting the pitch[2,3,8–20]. An increase in the pitch with a decrease in the polymer concentration is exhibited by these cellulosic systems with the exception of cellulose tricarbanilate in methyl ethyl ketone, which forms the only reported left handed helicoidal cholesteric superstructure[21]. A number of cellulosic derivatives which form thermotropic cholesteric mesophases have recently been reported[9,12,14,15,22]. The temperature dependence of the pitch follows equation (1).

EXPERIMENTAL

Temperature dependence of the pitch for APC

The APC was prepared and characterized as described previously[1]. The molar masses of the fractions, ranging from 2.2×10^4 to 6.5×10^5 g mol^{-1}, were measured by low-angle laser light scattering, and are thus weight average values. Thin samples of APC between microscope slide and coverglass showed reflection colours character-

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istic of planar structures over a range of temperatures.

The change in the reflection wavelength, λ_0, with temperature was monitored with a Pye-Unicam SP8-150 UV/VIS spectrophotometer. The maximum in the reflection peak, λ_0, corresponds to the cross-over wavelength in the optical rotatory dispersion spectrum of the sample. The pitch, P, was related to the reflection wavelength, λ_0, by the average refractive index of the mesophase, $\bar{n}$, according to de Vries' equation[23,24]:

$$\lambda_0 = \bar{n}P \tag{2}$$

Equation (2) presumes that the incident light is normal to the surface of a monodomain planar cholesteric. The refractive index value of 1.450[25] was assumed to be independent of molar mass, temperature and wavelength.

The reflection spectra were extremely sensitive to the thermal history of the sample. Several treatments were attempted and rejected as the reflection wavelength changed in an erratic or unpredictable manner. To overcome these problems, a new sample of the unfractionated polymer was prepared for each temperature. The procedure was to melt or mould a piece of the (acetoxypropyl)cellulose sample onto a microscope slide, which was heated to the desired temperature on a Mettler FP-52 microscope hot stage. Once the material had softened, a coverglass was pressed onto the sample. Following a 24–48 h equilibration period at the desired temperature, the hot stage with the microscope slide was placed in a upright position normal to the beam, inside the cavity of the spectrophotometer. The reflection curves tended to be broad, and decreased slowly on the short wavelength side of the peak. A peak width of less than 100 nm at half peak height was arbitrarily chosen as a minimum standard for the acceptance of a reflection curve.

Lyotropic (acetoxypropyl)cellulose–dibutyl phthalate samples

To investigate the temperature dependence of the lyotropic samples, a small quantity of the sample was sandwiched between a microscope slide and coverglass. The sample was heated, at the desired temperature, in an oven regulated to ±0.1°C for an equilibration period ranging from 24 to 48 h. To verify that the thermal treatment of the samples had not changed the concentration of the samples, due to solvent evaporation or polymer degradation, the spectra of all the samples were obtained at room temperature after the completion of the heating experiment. The 'before and after' spectra of the samples at ambient temperatures did not indicate a significant change in the reflection peak maximum. The quality of the spectra with respect to curve broadness and peak flatness was variable. Those reflection peaks which occurred at 600 nm were the sharpest. The curves became broader and showed less tendency to return to the baseline for compositions and temperatures which had reflection peak maxima above and below 600 nm. No special criteria were used for the rejection of the spectra.

The samples were removed from the oven and placed in the Mettler FP-52 hot stage, which was positioned vertically in the spectrophotometer and was set at the same temperature as the oven. The spectrum was obtained within five minutes following the introduction into the hot stage to minimize shearing of the sample under gravity.

The mean refractive indices of the samples were calculated from an appropriate average of the anisotropic refractive indices measured with an Abbé refractometer, as described in detail elsewhere[25].

X-ray diffraction

Thin-walled quartz capillaries, diameter 0.5 mm, were filled with (acetoxypropyl)cellulose–dibutyl phthalate solutions whose polymer weight fractions ranged from 0.5 to 0.9. The filling process entailed gentle suction of the solution until the capillary was two-thirds full. The process required 1–2 h depending on the viscosity of the solution. The capillaries were then flame sealed and dipped into molten wax to fill any pin holes. The samples were allowed to equilibrate for several days in order to remove any shear orientation. Solutions whose (acetoxypropyl)cellulose weight fraction exceeded 90% did not flow and thin films of these samples were prepared. The Warhus flat film camera chamber containing the sample and camera film was evacuated to remove air, which causes background scattering. X-ray scattering experiments were performed with a Philips PW 1730 nickel filtered CuKα ($\lambda = 0.154$ nm) X-ray generator. The voltage and current settings were 40 kV and 20 mA, respectively. The X-rays passed through a collimator, inner diameter 0.02 mm, through the sample and onto a 'no-screen' film, Kodak NS-57, located 17.4 cm from the sample. The exposure time ranged from 30 min for the thin samples to over 16 h for the 0.50 (acetoxypropyl)-cellulose weight fraction sample. The diameter of the X-ray halo was measured with a double beam recording microdensitometer (Joyce, Loebl and Co. Ltd.). A duplicate X-ray experiment was performed at each concentration with a new sample. The reproducibility of the diameter value for samples of the same concentration was good.

RESULTS AND DISCUSSION

Temperature dependence of the pitch of undiluted APC fractions

The breadth of the reflection spectra for the thermotropic (acetoxypropyl)cellulose fractions indicated a pronounced dependence on the chain length. The lower molar mass fractions exhibited sharp and intense reflection peaks, while the spectra of high molar mass fractions were diffuse. A comparison of the intensities of the reflection curves was impossible since the thickness of the samples was unknown. However, the breadth of the curves measured at half peak height increased with molar mass. The breadth of the reflection spectra can be related to the disorder exhibited by an imperfectly oriented planar texture (polydomain cholesteric) sample[3,26]. The degree of orientation attained by the fractions of a low molar mass is greater than for those with a high molar mass. As the chain length increases, the development of a planar texture may be hindered. Kinetic factors appear to be significant. For a high molar mass fraction, the reflection peak becomes sharper as the temperature increases. However, at high temperatures, the development of a planar texture is hindered by thermal motion, thus increasing the breadth of the reflection curve.

The temperature dependence of the pitch for undiluted (acetoxypropyl)cellulose and its fractions plotted according to equation (1) is shown in *Figure 1*.

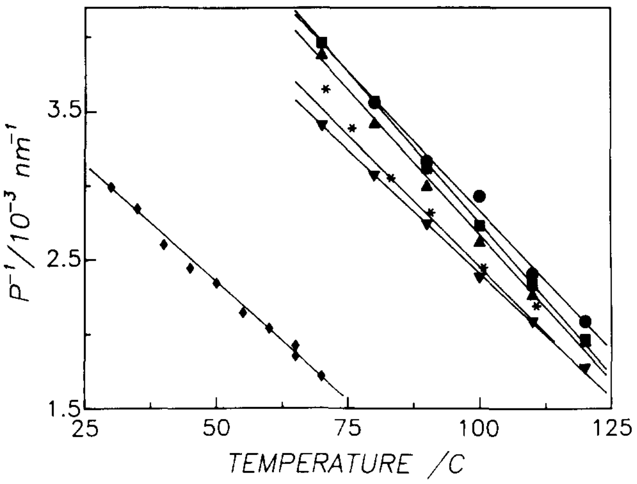

Figure 1 The variation of the reciprocal pitch with temperature for the undiluted (acetoxypropyl)cellulose polymer and fractions. The diamonds, inverted triangles, triangles, squares and circles represent the data for the fractions of molar mass 2.18, 7.65, 13.3, 19.4 and 28.0×10^4 g mol^{-1}, respectively. The stars are for unfractionated polymer (molar mass 21.4×10^4 g mol^{-1})

Table 1 The temperature dependence of the pitch and compensation temperature of (acetoxypropyl)cellulose as a function of molar mass

Molar mass (10^5 g mol^{-1})	Slope* (10^{-5} nm^{-1} K^{-1})	T_N (K)	Clearing temperature† (K)
2.80	−3.76	449	458
1.94	−4.08	441	455
1.33	−3.92	442	453
0.765	−3.33	446	454
0.218	−3.18	397	433
2.14‡	−3.56	442	455

*Slope of plot $1/P$ against T

†The clearing temperature is defined as the temperature at which the birefringence of the sample disappeared

‡Unfractionated (acetoxypropyl)cellulose

The pitch of an (acetoxypropyl)cellulose sample at a given temperature appears to be dependent on the molar mass. At any temperature the fractions with a higher molar mass exhibited a lower pitch value than the short chain fractions. The dependence of the pitch on the molar mass is particularly pronounced for the lowest fraction. A relatively slow decrease in the pitch as the chain length increases is indicated for the other fractions. The only exception is the unfractionated (acetoxypropyl)cellulose polymer, whose pitch is larger than that of some fractions with a lower molar mass. This discrepancy presumably results from the large number of short chains which strongly affects the pitch of the unfractionated samples. An inverse relationship between the pitch of a sample and the chain length has been observed with lyotropic solutions of poly(benzyl-L-glutamate) fractions[27]. A pitch independent of the molar mass had previously been reported for solutions with polydisperse fractions of poly(benzyl-L-glutamate)[28]. Recently, however, an increase in the pitch with an increase in the molar mass has been reported for lyotropic solutions of cellulose acetate in trifluoroacetic acid[29]. A satisfactory theoretical prediction for the dependence of the pitch upon the chain length for semiflexible chains has yet to be formulated. For helically grooved rod-like molecules an increase in the pitch with chain length has been predicted[30].

It is difficult to see why the molar mass should affect the pitch values for long semiflexible chains. The pitch is presumably due to chiral segment–segment interactions between neighbouring chains[31–33,35], as some optically active centre is required for a cholesteric structure to form[36–38]. One possibility is that the density of low molar mass polymers is lower than that of high molar mass fractions, so that the segment density and hence the chiral forces will be somewhat diluted. The pitch therefore increases for low molar mass samples. A general decrease in density with decreasing molar mass is of course observed for many polymers[39]. More direct evidence for a molar mass dependent density for APC is supplied by X-ray measurements. APC samples with molar masses of 2.14×10^5 and 2.18×10^4 g mol^{-1} gave mean intermolecular distances of 1.22 nm and 1.25 nm, respectively. Thus, there is some justification for associating the increase in pitch for the low molar mass fraction with the increase in segment separation. (The segment separation can of course also be increased by adding diluent, with a corresponding increase in pitch, as discussed later. The addition of a diluent may, however, do more than simply increase the intermolecular spacing[40].)

At the compensation temperature, T_N, the pitch becomes infinite and $1/P$ goes to zero. At temperatures above T_N, but below the mesophase to isotropic transition temperature (the clearing temperature), the senses of the cholesteric helix should reverse. The slope, b/T_N, and the compensation temperature, T_N, of the plot of the reciprocal pitch against the temperature equation (1) as a function of the molar mass of the fractions are compiled in *Table 1*.

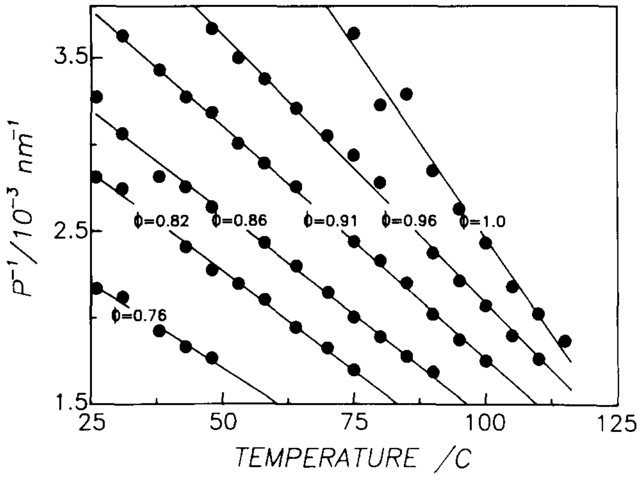

Figure 2 The variation of the reciprocal pitch with temperature for unfractionated (acetoxypropyl)cellulose in dibutyl phthalate. The polymer volume fraction of each solution is shown

Table 2 The temperature dependence of the pitch and compensation temperature for (acetoxypropyl)cellulose predicted by the concentration functions

Concentration function	Compensation temperature T_N (K)	Slope* (10^{-5} nm^{-1} K^{-1})
ϕ^{-2}	432	−4.06
ϕ^{-3}	446	−3.41
ϕ^{-4}	460	−2.93

*Slope of plot of $1/P$ against T

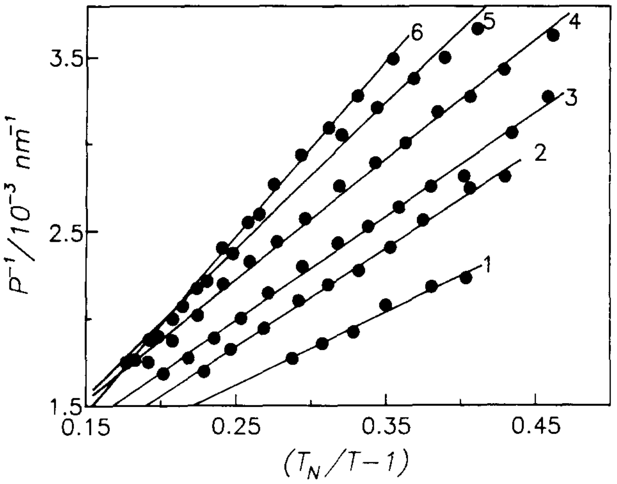

Figure 3 The variation of the reciprocal pitch with temperature for several lyotropic (acetoxypropyl)cellulose–dibutyl phthalate samples, plotted according to Kimura *et al.* (equation (3)). The polymer volume fractions are 0.78 for curve 1, 0.82 (2), 0.87 (3), 0.91 (4), 0.96 (5) and 0.98 (6)

Despite the high correlation coefficients attained for the linear plots, the uncertainty associated with the compensation temperature is large, as a consequence of the long extrapolation to a reciprocal pitch value of zero. In spite of the uncertainty, it is interesting to note the similarity of the compensation temperature and the observed clearing temperature for the mesophase to isotropic transition (*Table 1*). For every fraction, the compensation temperature is 10° to 15° lower than the clearing temperature. The reversal of the sense of the twist from a right handed to a left handed helicoidal structure above the compensation temperature is thus possible. However, the pitch at a temperature just above the compensation temperature would be extremely large and change rapidly with a small thermal alteration, rendering measurement of the effect difficult. For (acetoxypropyl)cellulose fractions, reversal of the sense of the twist was not observed, probably due to the close proximity of the compensation temperatures with the transition temperatures.

The temperature dependence of the pitch of the (acetoxypropyl)cellulose fractions in *Table 1* does not exhibit any pronounced dependence on the chain length of the molecule. The slopes are constant. If the pitch is density dependent, then the temperature dependence of the pitch should be related to the thermal expansion of the material. The molar mass independence of the slopes implies a constant thermal expansivity. This seems reasonable; polystyrene fractions of various densities have similar thermal expansion coefficients[39].

(Acetoxypropyl)cellulose–dibutyl phthalate lyotropic samples

Mixtures of dibutyl phthalate and (acetoxypropyl)cellulose at polymer weight fractions exceeding 0.75 form lyotropic mesophases which exhibit cholesteric reflection colours at room temperature. The reflection colours were measured spectrophotometrically, and the pitch was calculated from the de Vries equation. The reflection colours progressed from violet through green to red as the volume fraction of dibutyl phthalate in the system was slowly increased. Due to the low volatility of dibutyl phthalate, it was possible to investigate the changes in pitch of the lyotropic samples at elevated temperatures without altering the concentration of the sample.

Concentration dependence of the pitch

Due to the relatively narrow range of concentrations in which the samples exhibit reflection colours, plots of the pitch against the concentration raised to a number of different exponents (ϕ_p^a, $a=1, -1, 1/3, -2, -3, -4, -5$) all appear linear. The correlation coefficients for all the functional relationships are extremely high at each temperature. Thus, it is difficult to choose the functional relationship from the correlation coefficients.

An alternative way to test the concentration dependence of the pitch was tried. For each concentration function, the pitch of the pure thermotropic (acetoxypropyl)cellulose was estimated by extrapolating the linear plot of the pitch against the concentration function to a polymer volume fraction of one, thus obtaining the pitch of the undiluted polymer. The pitch of the undiluted (acetoxypropyl)cellulose was calculated at each temperature for each concentration function. The slope and the temperature intercept for each of the plots of the reciprocal pitch of the undiluted polymer against the temperature are compiled in *Table 2*, for several of the concentration functions. A comparison of the parameters shown in *Table 2*, with those for the unfractionated polymer in *Table 1*, indicates that the concentration function which best predicted the temperature dependence of the pitch for the pure polymer is the inverse cubic. Therefore the concentration dependence of the pitch is assumed to be inverse cubic for the APC–DBP lyotropic system. The power dependence relating the pitch of cholesteric lyomesophases to their polymer concentration appears to be a property of the polymer. The value of a is 1.1 for double and triple stranded poly(ribonucleotides)[41], 2 for poly(benzyl-L-glutamate)[42], and three or greater for the cellulosics[3,10–12].

Temperature dependence of the pitch for the lyotropic samples

The temperature dependence of the pitch for lyotropic (acetoxypropyl)cellulose–dibutyl phthalate solutions of varying polymer volume fractions is shown in *Figure 2*.

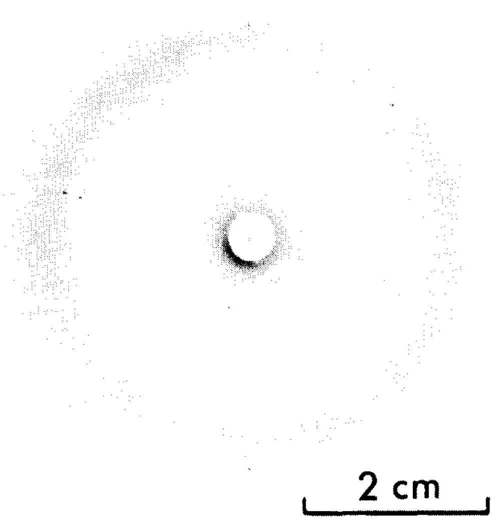

Figure 4 X-ray diffraction halo for unfractionated (acetoxypropyl)cellulose. The film to sample distance is 17.4 cm

Table 3 The compensation and clearing temperatures as a function of the (acetoxypropyl)cellulose volume fraction in dibutyl phthalate

Polymer volume ϕ_{APC}	Compensation temperature (°C)	Clearing temperature (°C)
1.000	169	182
0.977	163	175
0.973	170	172
0.958	167	172
0.942	165	172
0.931	167	165
0.914	165	162
0.893	166	158
0.870	160	152
0.850	158	148
0.841	153	142
0.825	148	138
0.803	151	133
0.784	151	128
0.7685	136	123
0.743	141	115

The data qualitatively indicate that the chiral forces between polymer molecules which are responsible for the helicoidal twist angle are attenuated due to the addition of a solvent. The attenuation is illustrated by the decreasing slope in the plots of the reciprocal pitch against the temperature as the diluent concentration decreases. In other words, the change in the pitch of the cholesteric helix due to a change in the temperature becomes less pronounced as the amount of solvent increases. A similar attenuation in the slope of the plot of the reciprocal pitch against temperature with increasing solvent concentration has been reported for cholesteric lyomesophases of poly(benzyl-D-glutamate)[4,5].

A comparison between the compensation temperature, the intercept of the plot of the reciprocal pitch against temperature, and the mesophase to isotropic clearing temperature as a function of polymer volume fraction is presented in *Table 3*. The clearing temperature was determined by optical microscopy as reported in a previous paper[1]. The fairly large scatter in the compensation temperatures can be attributed to the long extrapolation to obtain the temperature intercept of the plot of the reciprocal pitch against temperature. An uncertainty of 5% in the slope produces an uncertainty of 5°–6°C in the compensation temperature. Furthermore, a displacement of the wavelength of the maximum reflection to a shorter wavelength was found to occur for the broad spectra due to the non-Gaussian shape. Since the reflection curves broadened at low and high concentrations, the reciprocal pitch value quoted at both extremities is too large. For samples whose reflection wavelength is large at ambient temperatures, the slope of the plot is too flat and the compensation temperature too high. These samples have a large diluent concentration. A steeper slope occurs for the samples which have small pitch values at room temperature. As a consequence, the compensation temperature of these samples, which have a high polymer concentration, is too low. It is thus probable that the true compensation and transition temperatures are close together, and hence any reversal in the sense of the cholesteric helix for the lyotropic samples is difficult to observe. A solvent- or temperature-induced reversal of the helicoidal twist has yet to be reported for any lyotropic or thermotropic cellulosic system.

Estimating the chiral chain dimensions from the model proposed by Kimura et al.

Kimura *et al.*[30,43] have developed a statistical theory for the ordering of an assembly of helical rodlike molecules in a solvent. The pitch, P, of the cholesteric helicoidal structure formed as a function of the temperature, T, and polymer volume fraction, ϕ_P, is given by:

$$\frac{1}{P}=\frac{12\tilde{\lambda}\Delta}{\pi^2 Ld}\phi_P f(\phi_P)\left(\frac{T_N}{T}-1\right) \tag{3}$$

where

$$f(\phi_P)=(1-\phi_P/3)/(1-\phi_P)^2 \tag{4}$$

The quantities L and d represent the length and diameter of the helical rod, while $\tilde{\lambda}$ and Δ are parameters dependent on the details of the molecular shape. The height of a ridge which runs along and around the rod in a helical pattern is Δ.

The theory thus predicts that a reversal in the sense of the cholesteric twist is not related to a change in the handedness of the helical grooves in the rod, as predicted by several earlier theories[44,45]. The reversal of the sense of the cholesteric twist should occur at T_N. The variation in pitch with concentration is more complex than the empirical power law.

The temperature dependence of the pitch for each lyotropic solution of (acetoxypropyl)cellulose dissolved in dibutyl phthalate plotted according to this theory is shown in *Figure 3*. The value of the compensation temperature used in the calculations was assumed to equal the transition temperature for the sample. The data indicate a good agreement with the theory, as a linear plot is obtained at each concentration.

According to the theory, the slope of the plot equals $12\Delta\tilde{\lambda}\phi_P f(\phi_P)/(\pi^2 Ld)$ and thus increases as the polymer volume fraction increases. A constant concentration independent term, $A=12\Delta\tilde{\lambda}/(\pi^2 Ld)$ should be obtained by dividing the slope of the plot of the reciprocal pitch against $(T_N/T)-1$ by the concentration term, $\phi_P f(\phi_P)$. The parameters ($\tilde{\lambda}$, Δ, L, d) are assumed to be concentration

Table 4 The variation of A_{APC} and A_{cell} with the (acetoxypropyl)-cellulose and cellulose volume fraction

Slope* (10^{-3} nm^{-1})	$\phi_{APC}f(\phi_{APC})$	A_{APC}† (10^{-4} nm^{-1})	$\phi_{cell}f(\phi_{cell})$	A_{cell}‡ (10^{-2} nm^{-1})
4.16	8.49	4.90	0.318	1.31
4.39	12.40	3.54	0.343	1.28
4.89	15.09	3.24	0.357	1.37
5.86	19.60	2.99	0.371	1.58
5.76	23.90	2.41	0.384	1.50
5.83	27.12	2.15	0.389	1.50
6.15	36.39	1.69	0.405	1.52
6.48	54.45	1.19	0.421	1.54
7.07	86.1	0.82	0.436	1.62
8.02	134	0.60	0.450	1.78
7.95	194	0.41	0.462	1.72
8.57	373	0.23	0.473	1.81
9.27	927	0.10	0.485	1.91
10.27	1300	0.08	0.489	2.10

* Slope of the plot of $1/P$ against $(T_N/T)-1$. See text

† A_{APC} = column 1/column 2

‡ A_{cell} = column 1/column 4

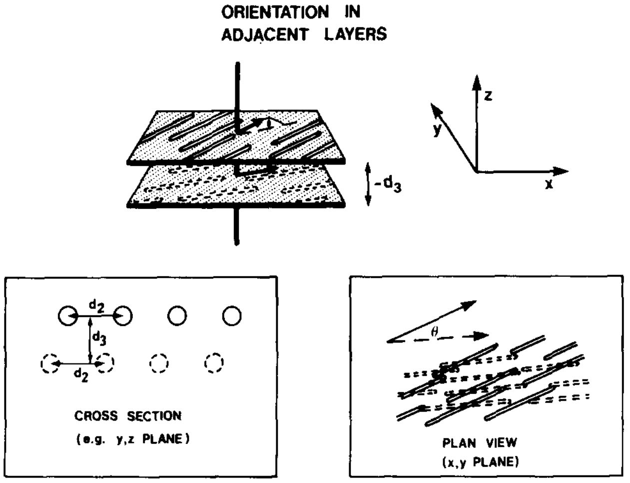

Figure 5 A simple model for the cholesteric mesophase. The average angular twist between molecules in successive 'layers' of the structure is θ

independent. Experimentally, the trend of an increasing slope with an increase in (acetoxypropyl)cellulose volume fraction is exhibited. However, when the slope is divided by the concentration term, the result is not constant, but decreases markedly with increasing (acetoxypropyl)cellulose concentration, as shown by the values of A_{APC} in *Table 4*.

The theory assumes an interaction between optically active chiral rods. The side chains of the (acetoxypropyl)cellulose molecule are flexible, and may not form a part of the optically active rod, but rather behave as diluent. As a limiting case, the cellulosic core may be taken as the chiral rod. The volume fraction of cellulose, ϕ_{cell}, may be calculated from the weight fraction of (acetoxypropyl)cellulose, ω_{APC}, using the equation:

$$\frac{1}{\phi_{cell}}=\frac{M_{APC}}{M_{cell}}\rho_{cell}\left[\frac{1}{\rho_{APC}}+\frac{1}{\rho_{DBP}}\left(\frac{1}{\omega_{APC}}-1\right)\right] \qquad (5)$$

where M_{APC} and M_{cell} are the molar masses of 435^{25} and $162\,g\,mol^{-1}$ for the (acetoxypropyl)cellulose and cellulose anhydroglucose units, respectively. The densities of the polymer, ρ_{APC}, dibutyl phthalate, ρ_{DBP}, and for cellulose, ρ_{cell}, are 1.17^{12}, 1.043^{46}, and 1.50^{47} g ml^{-1}, respectively. However, when A is calculated in terms of the volume fraction of cellulose, it increases with an increase in the cellulose volume fraction, as shown in *Table 4* by the values of A_{cell}. Nevertheless, the change in the relative magnitude of A_{cell} is much smaller than that for A_{APC}.

To estimate the dimensions of the model chiral rod it is necessary to correlate the change of the slopes (*Table 4*) with the change in magnitude of the function $\phi_p f(\phi_p)$ within a certain concentration range so that a concentration independent A_p term is attained. The concentration term $\phi_{APC}f(\phi_{APC})$ increases too rapidly to match the change in the slopes of the plots of Kimura's equation, *Figure 3*, for the experimental pitch data. However, when the volume fraction of the cellulose molecule is used the function, $\phi_{cell}f(\phi_{cell})$, increases too slowly to match the change in the slopes. As a consequence, neither a constant A_{APC} nor A_{cell} is obtained for the lyomesophases studied. If the Kimura theory is valid for the lyotropic solutions of (acetoxypropyl)cellulose and dibutyl phthalate, then the theoretical optically active rod has dimensions greater than those of the cellulose molecule, but less than those of the (acetoxypropyl)cellulose molecule. Examination of the change in magnitude exhibited by the slopes of the plots of the reciprocal pitch, $1/P$, against $(T_N/T)-1$ indicate that they match the change in magnitude of the function $\phi_P f(\phi_P)$ with ϕ_P in the region of $\phi_P=0.45$ to 0.60. (For comparison, the corresponding values for ϕ_{APC} in these solutions ranged from 0.74 to 0.98, and for ϕ_{cell} from 0.21 to 0.28.) Therefore, the optical rod required to fulfill the concentration expression for the temperature dependence of the pitch of lyotropic samples predicted by the Kimura theory would include the cellulose molecule and some part of the acetoxypropyl side chains. This seems physically reasonable. The side chains in APC are achiral and flexible and only influenced by the cellulosic chirality close to the main chain.

X-ray diffraction from mesophases

All the (acetoxypropyl)cellulose–dibutyl phthalate lyomesophases exhibited diffuse halos (*Figure 4*). The diameter of the halo decreases and the halo becomes progressively more diffuse as the (acetoxypropyl)cellulose concentration decreases.

The $\bar{d}$-spacing was calculated from the radius of the halo, r, using Bragg's scattering equation:

$$\lambda=2\bar{d}\sin\psi \qquad (6)$$

where λ is the wavelength of the X-ray beam, and $\bar{d}$ is the distance between scattering elements. The diffraction angle, ψ, is defined by

$$\tan(2\psi)=r/l \qquad (7)$$

where l is the distance of the sample from the film. Values for $\bar{d}$ as a function of the polymer volume fraction are compiled in *Table 5*.

Due to the narrow ranges of the polymer volume fraction and the $\bar{d}$-spacing values, it is difficult to unambiguously determine the functional relationship between the mean intermolecular distance and the volume fraction from the experimental data. A simplified model for the cholesteric array[11] is shown in *Figure 5*. Consider

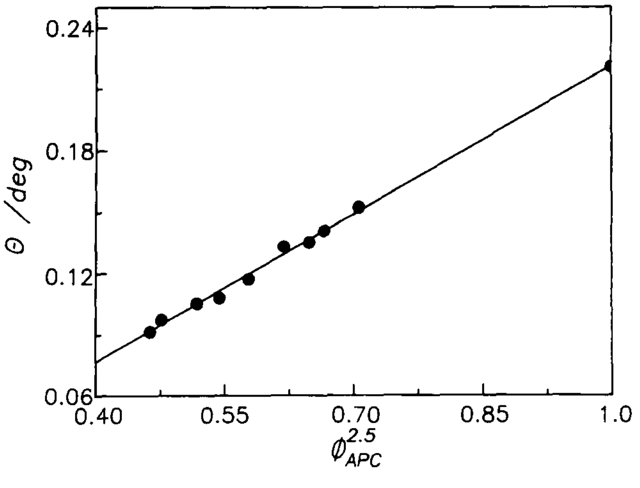

Figure 6 The relationship between the twist angle, θ, between APC chains and the APC volume fraction (equation (13))

Table 5 Variation of $\bar{d}$ with polymer volume fraction for (acetoxypropyl)cellulose in dibutyl phthalate at ambient temperatures

ϕ_{APC}	Molar mass of APC (10^5 g mol^{-1})	$\bar{d}$ (Å)
0.520*	2.14	14.90 ± 0.02
0.719	2.14	13.77 ± 0.09
0.784	2.14	13.40 ± 0.07
0.893	2.14	12.68 ± 0.05
0.942	2.14	12.55 ± 0.03
1.000	0.218	12.50 ± 0.06
1.000	2.14	12.20 ± 0.05
1.000	7.66	12.18 ± 0.05

* Isotropic sample

the addition of a diluent to the cholesteric array of infinitely long polymer molecules. The volume fraction of a polymer, ϕ_P, in such a two dimensional array is:

$$\phi_P = c/C \tag{8}$$

where c is the cross-sectional area of the polymer molecule, and C is the cross-sectional area of the volume element containing the molecule:

$$C = d_2 d_3 \quad \text{for a two dimensional array} \tag{9}$$

and

$$\phi_P = c\bar{d}^{-2} \quad \text{or} \quad \bar{d} = c^{1/2}\phi_P^{-1/2} \tag{10}$$

where $\bar{d}$ represents the intermolecular distance obtained from the X-ray scattering experiment. A linear relationship with a correlation coefficient of 0.990 is obtained for the plot of the intermolecular distance against the inverse square root of the polymer volume fraction. However, the slope of the line which corresponds to the intermolecular distance for pure (acetoxypropyl)cellulose is 7 Å. The average intermolecular distance obtained from X-ray scattering for the pure polymer is 12.2 Å assuming cubic packing or 10.2 Å for hexagonal packing. Evidently, this model is oversimplified.

As discussed above, the empirical relationship between the pitch, P, and the (acetoxypropyl)cellulose volume fraction in dibutyl phthalate is approximately inverse cubic.

$$P = P_0\phi_P^{-3} \tag{11}$$

If the interlayer twist angle, θ, were constant, then from equations (10) and (12) the pitch should be proportional to $\phi_P^{-1/2}$ rather than ϕ_P^{-3} (equation (11)). The inverse cubic power dependence of the pitch on the polymer volume fraction for (acetoxypropyl)cellulose lyotropic samples implies that a change in the twist angle occurs as solvent is added.

The pitch of the cholesteric helix, P, can be related to the twist angle, θ, between the layers by the equation:

$$P = (2\pi/\theta)d_3 \tag{12}$$

The twist angle, θ, of the lyotropic solutions of (acetoxypropyl)cellulose dissolved in dibutyl phthalate, which exhibited a reflection colour at ambient temperatures, was calculated using this equation. The calculated twist angle as a function of polymer volume fraction is shown in *Table 6*.

The average twist angle between the axes of chains in the z direction decreases from 2.2° for the pure (acetoxypropyl)cellulose to only 0.92° for a lyotropic sample whose polymer volume fraction is 0.735. The introduction of a solvent into the polymer matrix attenuates the intermolecular forces. The average twist angle increases 2.4 fold, while the pitch of the cholesteric helix decreases 2.7 fold over the same concentration interval. Meanwhile, the average distance between layers decreases 1.1 fold over a polymer volume fraction interval from 0.735 to 1.0. It is impossible to decide whether the large change in the twist angle is a direct consequence of the small change in the distance between layers or the changing dielectric medium between the chains. However, the importance of the twist angle between layers in describing the behaviour of the pitch must be considered. A similar trend of a decreasing twist angle with the addition of a solvent has been measured for cellulosics[11] and in the pioneering work on polypeptides[28].

The twist angle, θ, can be expressed in terms of the volume fraction of (acetoxypropyl)cellulose, ϕ_{APC}, by combining the last three equations to obtain:

$$\theta = K'\phi_{APC}^{5/2} \tag{13}$$

where K' is the constant $2\pi c^{1/2}P_0^{-1}$. This plot is shown in *Figure 6*.

ACKNOWLEDGEMENTS

G.V.L. thanks the Pulp and Paper Research Institute of Canada for a graduate scholarship. The support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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Table 6 Calculated angular twist between successive layers of the cholesteric structure for (acetoxypropyl)cellulose lyomesophases in dibutyl phthalate at 26°C

Volume fraction ϕ_{APC}	Pitch (nm)	Average $\bar{d}$ spacing (nm)	θ (degrees)
0.735	538.8	1.37	0.925
0.743	504.8	1.36	0.97
0.768	461.0	1.35	1.05
0.784	447.6	1.34	1.08
0.803	407.0	1.32	1.17
0.825	355.5	1.315	1.33
0.841	347.8	1.31	1.35
0.850	332.6	1.30	1.41
0.870	305.4	1.29	1.52
1.000	201.1	1.23	2.21

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