Chiro-optical properties of lyotropic ethyl cellulose derivatives

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Abstract

Novel derivatives of partially substituted ethyl cellulose (EC) were prepared and their chiro-optical properties studied as a function of degree of substitution. As had been previously reported for acetyl ethyl cellulose (AEC), the propanoate (PEC) and hexanoate (HEC) esters of EC undergo a degree of substitution dependant reversal of their chiral nematic (N^*) helical twisting sense. The critical degree of substitution (DS^*), above which this reversal of handedness takes place, was found to be considerably lower ($DS^* \cong 0.1$) for these derivatives than that for the reversal of handedness of AEC ($DS^* \cong 0.18$–0.21) lyotropic solutions in chloroform. This reversal of supramolecular twisting sense was not observed for the benzoate ester of EC (BEC), rather these derivatives enter the compensated nematic state at low degrees of substitution ($DS > 1.0$) but no reversal of handedness is observed at higher DS. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the discovery of the liquid crystalline properties of hydroxypropyl cellulose [1], the field of liquid crystalline cellulose derivatives has been of interest to academics and industrialists alike. Many lyotropic and thermotropic cellulose derivatives display chiral nematic (cholesteric) mesophases, which are capable of selective Bragg type reflection. The wavelength of reflection (λ_{max}) is related to the helical pitch by the de Vries equation [2]

$$\lambda_{max} = nP \sin \theta \qquad (1)$$

where n is the refractive index of the mesophase, θ is the incident angle and P is the helical pitch length. Hence mesophases whose helical pitch lengths are of the order of visible light will appear iridescent due to selective reflection of the appropriate wavelengths.

As with other helices the spiral structure developed in the chiral nematic phase can have either right or left handed helical twisting senses. This leads to a maximum possible reflection of 50% of the incident radiation, as a left handed chiral nematic phase will only reflect the right handed component of circularly polarised light and vice versa. In recent years systems which display a reversal of their helical twisting senses by solvent effects [3–6] or chemical modi-

fication [7–9] have been of particular interest. One such system displaying a degree of substitution dependant reversal of helical twisting sense is acetyl ethyl cellulose (AEC). Gray and Guo [10,11] found that upon the acetylation of the unsubstituted hydroxyl moieties of ethyl cellulose (EC) (Degree of substitution (ethyl) = 2.5), a reversal in the supramolecular twisting sense takes place at a critical degree of substitution (DS^*). This critical degree of substitution can be as little as $DS^* = 0.19$ (with respect to acetyl groups) for AEC in m-cresol. In any system in which there is a reversal of helical twisting sense, there will exist a null point were the effect leading to left or right handed helical structures are balanced and where a compensated or quasi-nematic phase is formed. This compensated nematic state can be thought of as a chiral nematic phase were the helices have unwound to infinite pitch.

In this paper we report on the synthesis and chiro-optical properties of a number of different esters of ethyl cellulose and the factors controlling this reversal of helical twisting sense.

2. Experimental

2.1. Materials

Ethyl cellulose was used directly as purchased from Aldrich, ethoxyl content 46% ($DS_{ethyl} = 2.5$), Viscosity (5 wt%, v/v 60:40 ethanol/toluene) = 100 cP.

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Table 1
Reaction conditions for the preparation of the propyl (PEC), hexyl (HEC) and benzyl (BEC) esters of ethyl cellulose

Sample	Reaction time (h)	Reaction temperature (°C)	Degree of substitution (DS)
PEC1	0.5	25	0.05
PEC2	1	25	0.07
PEC3	2	25	0.1
PEC4	18	25 then 70 (1 h)	0.5
HEC1	0.5	25	0.04
HEC2	1	25	0.08
HEC3	2	25	0.1
HEC4	18	25 then 70 (1 h)	0.5
BEC1	1	25	0.03
BEC2	3	25	0.06
BEC3	18	25	0.38
BEC4	24	25 then 70 (1 h)	0.5

The alkyl acid chlorides (propanoyl, hexanoyl and benzoyl chloride) were also used directly as purchased from Aldrich without further purification.

2.2. Preparation of esters of ethyl cellulose

Ethyl cellulose (3 g, 13 mmol repeat units, 6.5 mmol hydroxyls) was dissolved in anhydrous chloroform (40 ml) in a three-necked flask, in the presence of dry pyridine (10 ml) to give a clear, viscous, homogeneous solution at which point the solution was cooled to 0°C in an ice/water bath. A solution of the particular acid chlorides (37 mmol) in dry chloroform (10 ml) was added slowly via a dropping funnel over a period of 5–10 min. The reaction mixtures were then allowed to come up to the desired temperature, for the required amount of time as summarised in Table 1. After the allotted time the chloroform was removed under reduced pressure and the polymer residues were redissolved in tetrahydrofuran (50 ml). Once homogeneous solutions were formed the products were isolated by precipitation into cold, distilled water (500 ml).

The resultant polymers were further purified by reprecipitating four times from tetrahydrofuran (50 ml) into cold, distilled water (500 ml) and finally by continuous Soxhlet

Table 2
Chiro-optical properties of lyotropic chloroform solutions of esters of ethyl cellulose (40 wt%).

Sample	DS_{ester}	Helical twisting sense	λ_{max} (refl.)(nm)	T_{cl} (°C)
PEC1	0.05	Left	670	53
PEC2	0.07	Not found	Not found	47
PEC3	0.10	Not found	Not found	41
PEC4	0.5	Right	630	Above b.p.
HEC1	0.04	Left	370	57
HEC2	0.08	Not found	Not found	44
HEC3	0.10	Not found	Not found	39
HEC4	0.50	Right	550	Above b.p.
BEC1	0.03	Left	440	Above b.p.
BEC2	0.06	Left	470	Above b.p.
BEC3	0.38	Not found	Not found	48
BEC4	0.5	Not found	Not found	45

extraction with distilled water (24 h). The products were dried in a vacuum oven at 80°C for 3 days giving white, fibrous polymers.

2.3. Determination of the degree of substitution (DS)

The DS (with respect to ester groups) for the polymers prepared was determined by FTIR spectroscopy. By comparing the ratios of the relative absorbance values of the OH stretch and carbonyl stretch for a sample of unknown DS and a reference sample taken to be the fully substituted alkyl ester of ethyl cellulose. As the latter showed no discernible OH stretching signal, I^{OH} was taken to be the average value of $I^{baseline}$. The DS can then be calculated using the following equation:

$$(DS)x = 0.5(I^{C=O}/I^{OH})_x (I^{C=O}/I^{OH})_{Fully\ Sub}. \qquad (2)$$

where $I^{C=O}$ and I^{OH} are the maximum intensities of the carbonyl and hydroxyl peaks, respectively and the subscript x indicates the sample under consideration.

2.4. Instrumentation and characterisation

All infra red spectra where recorded on a Perkin Elmer 1720X FT-IR spectrophotometer. Specular reflectivity measurements were taken on a Perkin Elmer Lambda 9 spectrophotometer and CD spectra were measured at room temperature on a Jasco-600 spectropolarimeter. The optical polarising microscope used in this work was an Olympus 'BH2' fitted with a Linkam 'PR 600' hot stage.

3. Results and discussion

In comparing the results obtained for the ethyl cellulose derivatives studied in this work several trends become apparent and are discussed below.

3.1. General behaviour
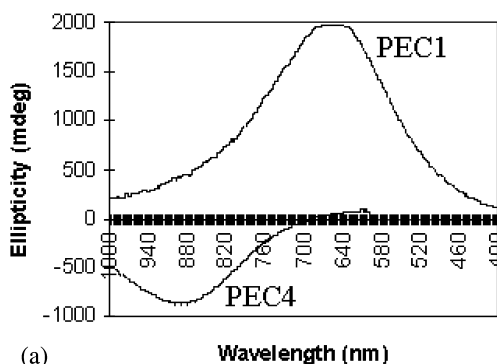
Each of the alkyl ester substituted ethyl cellulose

Table 3
Critical concentration for mesophase formation of EC derivatives (fully sub.) (CHCl$_3$)

Polymer	Critical concentration (wt%) (CHCl$_3$)
PEC4	22.5–25.
HEC4	25–27.5
BEC4	27.5–30

(a)

(b)
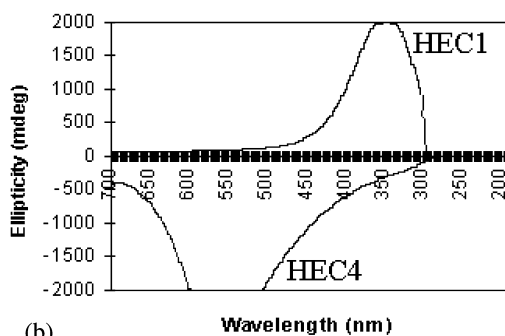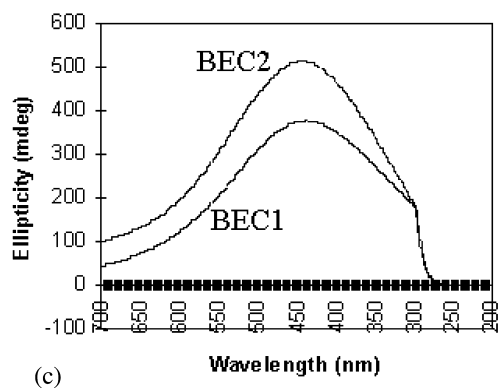
(c)

Fig. 1. CD spectra of lyotropic chloroform solutions of esters of ethyl cellulose.

derivatives studied, exhibited lyotropic liquid crystalline behaviour in chloroform and m-cresol. Solutions of the derivatives (40 wt%) in both solvents, were examined using a polarising microscope and all, with the exception of sample BEC-4 in chloroform, showed typical chiral nematic textures. After shearing and relaxation of the samples the characteristic banded textures were observed. The only exception to this general behaviour was observed for BEC-4 in chloroform which exhibited an optical pattern similar to normal nematic phases suggesting that the sample was in a compensated nematic phase. However, when BEC-4 was dissolved in m-cresol it adopted a chiral nematic phase.

All of these observations were made at ambient temperature, but on heating the samples, the liquid crystalline phases remained stable up to the clearing temperatures. These are listed in Table 2 for chloroform solutions. In a few cases the clearing temperature could not be established as the liquid crystalline phase was stable up to the solvent boiling point.

The critical concentrations, representing the point at which the first signs of self assembly took place, lie in the range 25–30 wt%. Liquid crystallinity is fully developed above 30 wt% in both solvents and solutions of the PEC and HEC samples are relatively easy to handle at these higher concentrations. In the BEC series, the viscosities of the solutions were quite high and this increased up to the critical point but only decreased slightly after this was reached. This made the samples more difficult to handle and molecular organisation was much slower in developing.

Many, but not all, of the solutions exhibited colours that matched the wavelengths of selective reflection as measured by CD. Those that were optically clear and showed no visible light reflections gave a CD response which indicated the selective reflection lay in the infra-red region or were probably in the compensated nematic state, such as the BEC-4 sample. This behaviour is seen more clearly in the CD spectra and the results are summarised in Table 2.

3.2. Critical concentrations

The fully substituted ethyl cellulose derivatives showed critical concentrations in the ranges shown in Table 3. It was observed that, in all ethyl cellulose derivatives studied the critical concentration for mesophase formation (determined by polarising microscopy studies) increases with increasing degree of substitution of the residual hydroxyls. This is most likely due to a combination of two complementary effects. First, as a result of the synthetic method employed in the preparation of the ethyl cellulose starting material (Williamson-etherification) the distribution of substitution is such that residual, unsubstituted hydroxyls are most likely to be found at the C2 or C3 positions. It has been recognised recently that the C3 hydroxyl undergoes primarily intramolecular hydrogen bonding which is maintained in solution, leading to a stiffening of the cellulose chains and thus a
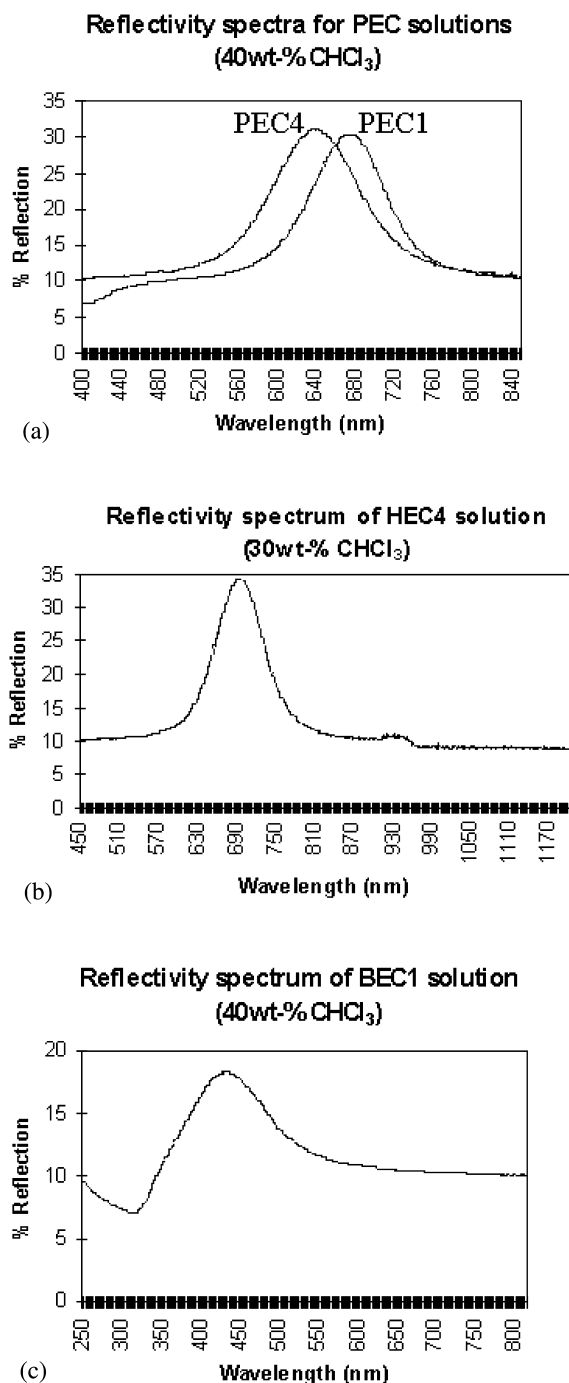
Reflectivity spectra for PEC solutions (40wt-% CHCl₃)

(a)

Reflectivity spectrum of HEC4 solution (30wt-% CHCl₃)

(b)

Reflectivity spectrum of BEC1 solution (40wt-% CHCl₃)

(c)

Fig. 2. Reflectivity spectra of lyotropic chloroform solutions of esters of ethyl cellulose.

In addition to this, any substitution of the ethyl cellulose structure will lead to a broadening of the chain diameter and thus a decrease in the axial ratio; again this leads to an increase in the critical concentration with increasing degree of substitution. The critical concentration also increases with the bulk of the substituent, as larger groups will lead to a greater decrease in the axial ratio than smaller groups. This trend is shown by the data in Table 3, where the critical concentration for fully substituted EC derivatives increases with increasing molar volume of the side group.

3.3. Chiro-optical properties

Examples of the CD spectra and reflectivity spectra obtained for lyotropic chloroform solutions of the polymers studied in this work were measured at room temperature. The results are shown in Figs. 1 and 2, respectively. Note that a positive CD signal corresponds to a left handed chiral nematic structure and vice versa. A full summary of the optical properties is given in Table 2.

As previously reported for AEC [11], lyotropic solutions of PEC and HEC polymers undergo a degree of substitution dependant reversal of helical twisting sense and pitch (see Fig. 1a and b). It was also observed that left handed PEC and HEC lyotropic solutions (PEC1 and HEC1 (40 wt%, CHCl₃)) displayed a negative temperature dependence of helical pitch. This effect could be observed by the change in visible selective reflection colours, to shorter wavelength, upon heating the samples on a hot stage. Conversely, right handed derivatives (PEC4 and HEC4 (40 wt%, CHCl₃)) displayed a positive temperature dependence of pitch. This is similar to the behaviour observed by Guo and Gray [11] for right handed and left handed lyotropic solutions AEC. Unfortunately, this temperature dependence of helical pitch could not be measured due to the lack of variable temperature reflectivity or CD measurement techniques used in this study.

Lyotropic solutions of BEC polymers show an increase in pitch with increasing DS but do not undergo a reversal of the helical twisting sense; rather polymers with high-degrees of substitution exhibit compensated nematic lyotropic mesophases. All BEC polymers prepared in this work formed highly viscous, almost gel like lyotropic solutions. The poor alignment in these solutions is reflected by the inhomogeneous texture observed by polarising microscopy and by the broad reflectivity maxima of the CD spectra and reflectivity spectra exhibited by these polymers (Figs. 1c and 2c). Lyotropic solutions of BEC polymers did not show any discernible temperature dependence of helical pitch length. For these samples heating only resulted in visibly poorer alignment as observed by polarising microscopy.

Due to the narrow range of degrees of substitution of the polymers prepared, DS* could not be determined accurately. However DS* must lie in the region of PEC3 and HEC3 for each polymer series as these polymers exhibited compensated nematic structures in lyotropic solutions and films, as

more extended chain conformation [11]. Any extension of the chain conformation will lead to a more rigid polymer and a higher axial ratio [12]. Subsequent substitution at this position leads to a loss of intramolecular hydrogen bonding, a loss of rigidity and hence a decrease in the axial ratio of the extended polymer chain. As is known from Flory's analysis [13], any decrease in the axial ratio will increase the critical concentration for mesophase formation, thereby explaining the experimentally observed increase.

these showed no discernible CD signal. Therefore the critical degree of substitution for these polymers (PEC and HEC) must be in the region of $DS^* \cong 0.1$. This value of DS^* is considerably lower than that quoted for lyotropic solutions of AEC ($DS^* = 0.18$–0.2, $CHCl_3$) [11]. It may be the case that the reversal of handedness for PEC and HEC lyotropic solutions occurs at lower degrees of substitution, due to the greater steric bulk of the propanoate and hexanoate groups in comparison to the acetyl group.

4. Conclusions

The lyotropic solutions of the propanoate (PEC) and hexanoate (HEC) esters of ethyl cellulose undergo a DS_{ester} dependant reversal of handedness of their helical twisting senses in both chloroform and *m*-cresol. The critical degree of substitution for the reversal of helical twisting sense for these polymers appears to be approximately half that for AEC polymers. By preparing and studying a wider range of polymers with respect to degree of substitution it should prove possible to gain control of the selective reflection behaviour and helical twisting sense over a broad range of the spectrum. These effects are now being examined in greater detail.

BEC polymers do not exhibit such a reversal, rather these polymers form compensated nematic structures at high-degree of substitution with respect to the benzoate groups. Furthermore the liquid crystalline properties of lyotropic solutions of these polymers are ill-defined due to the poor alignment in these samples brought about by their almost gel like viscosity.

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