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Anna M. Ritcey^a; Derek G. Gray^a

^a Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, Montreal, QC, Canada

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Optical rotatory dispersion from liquid crystalline solutions and films of hydroxypropylcellulose

by ANNA M. RITCEY and DEREK G. GRAY

Pulp and Paper Research Institute of Canada and Department of Chemistry, McGill University, 3420, University Street, Montreal, QC, Canada H3A 2A7

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The chiroptical properties of (hydroxypropyl)cellulose (HPC) in methanol are measured by optical rotatory dispersion (ORD), both in isotropic solution and in the cholesteric liquid crystalline phase. The ORD spectra of HPC films cast from lyotropic solution are also examined. Isotropic solutions of HPC in methanol provide no ORD evidence for the presence of a helical conformation, or for concentration-induced changes in conformation. The ORD curve of HPC in methanol, when expressed as specific rotation, is independent of polymer concentration for isotropic solutions containing between 1 and 43 per cent polymer by weight. From the slope of Drude plots, the Cotton effect responsible for the observed ORD curve occurs at 175–180 nm. However a 45 per cent liquid crystalline solution exhibits plain positive dispersion, and the magnitude of the specific rotation is also much greater than that found for solutions containing less than 43 per cent polymer. Results for more concentrated solutions confirm that ORD spectra of lyotropic liquid crystals of HPC in methanol contain a significant positive component that is not accounted for by the de Vries equation for cholesteric reflection. ORD measurements in other solvents and on dry films show that this contribution to the optical activity vanishes when the solvent is removed or when hydrogen bonding is disrupted. The effect is tentatively ascribed to a hydrogen bonded structure that contributes strongly to the optical rotation.

1. Introduction

Since the initial report [1] 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 [2, 3]. HPC, however, continues to be the cellulosic most frequently studied in the liquid crystalline state, probably because of its commercial availability and solubility in both water and numerous organic solvents.

Based on prior observations [4] some chiroptical properties of HPC are reexamined, both in isotropic solution and in the cholesteric liquid crystalline phase. Since HPC contains no accessible chromophores, these properties must be examined as optical rotatory dispersion (ORD) spectra. In the absence of a helical conformation the isotropic ORD spectrum should be described by the Drude equation [5]

$$\alpha = \frac{A}{\lambda^2 - \lambda_0^2}, \quad (1)$$

where α is the observed optical rotation at a wavelength λ , A is a constant and λ_0 is the wavelength of the absorption maximum of the band responsible for the signal. This equation can be rearranged to

$$\alpha\lambda^2 = A + \alpha\lambda_0^2, \quad (2)$$

so that a plot of $\alpha\lambda^2$ against α should be linear and the crossover wavelength λ_0 can be evaluated from the slope.

If the solution forms a planar cholesteric liquid crystal above the critical concentration, the ORD spectrum should follow the de Vries [6] equation:

$$\alpha = \frac{\pi\Delta n^2 b P}{4\lambda^2 [1 - (\lambda/\lambda_0)^2]}, \quad (3)$$

where P is the cholesteric pitch, b is the sample thickness, λ_0 is the wavelength of maximum reflection and Δn is the layer birefringence. This equation implies that a plot of α against $\{\lambda^2[1 - (\lambda/\lambda_0)^2]\}^{-1}$ should be linear and the layer birefringence can be evaluated from the slope.

Such plots for the HPC/water mesophase outside the immediate reflection band wavelengths were reasonably linear [4]. However, the apparent layer birefringence was rather high, and a re-examination of a number of ORD curves for HPC/water mesophases showed systematic deviations from equation [3]. In addition to unreasonably high birefringences, the plots showed non-zero intercepts at $\lambda = \lambda_0$, and the slope of the plots increased with decreasing wavelength, suggesting that some factor in addition to cholesteric reflection might be contributing to the observed positive rotation. These effects were more easily observed for samples with reflection bands at long wavelengths. The excess positive contribution to the rotation observed for liquid crystalline samples was not due to the intrinsic rotation of the optically-active polymer chains, because isotropic aqueous HPC solutions showed plain negative Drude curves [4]. It seemed worthwhile to re-examine these chiroptical properties, to see if they provide evidence for the development of a helical conformation that may precede or accompany the isotropic to liquid crystal phase transition. (HPC is known to have a helical molecular conformation in the crystalline state [7], but there is as yet no evidence for a helical conformation in dilute solution or in the mesophase.) Methanol was chosen as a convenient solvent; HPC dissolves readily without aggregation, it forms a lyotropic mesophase in methanol at a critical concentration of 43 per cent polymer by weight [4] and HPC mesophases in methanol are found to relax rapidly to give narrow cholesteric reflection bands.

Recently, it has been reported [8] that HPC films cast from lyotropic solution retain their cholesteric order, and show thermotropic behaviour when heated. The ORD spectra of these films are also examined.

2. Experimental

2.1. Materials

HPC (Aldrich, nominal molecular weight 100 000) was dried under vacuum overnight and then stored in a desiccator until solutions were prepared in methanol (Caledon Laboratories, ACS spectro grade).

2.2. Sample preparation

Solutions were prepared gravimetrically. Mixing was aided by stirring for dilute solutions of low viscosity and by the repeated inversion of the sample vials in the case of mesophase samples. Mesophase samples required 1–2 weeks to reach uniformity. Samples were also prepared at concentrations (~ 43.5 per cent by weight) where the liquid crystalline phase exists in equilibrium with isotropic solution. These solutions

were centrifuged until the cloudy anisotropic phase was observed to separate from the clear isotropic solution.

Cholesteric films were prepared on quartz from aqueous liquid crystalline solutions. A small aliquot of mesophase was pressed between a quartz slide and a glass slide covered with a thin polyethylene sheet. The sample was allowed to relax until a uniform cholesteric reflection colour was observed (typically several days) and then the glass slide was removed, leaving the thin sample pressed between quartz and the polyethylene film. After slow drying, the polyethylene was easily removed to yield a cholesteric HPC film on the quartz surface.

Mesophase samples of extremely high polymer concentration were prepared by exposing dry cholesteric films to a methanol atmosphere. The cholesteric films were placed in a small desiccator, which was then evacuated. Solvent vapour was introduced from a reservoir of methanol connected to the desiccator inlet. On exposure to methanol vapour, the free surface of HPC films cast on quartz rapidly lost the initial high degree of order. Cholesteric films were therefore cast between two rigid compression-molded sheets of poly(4-methyl-1-pentene) (ICI TPX RT-20). After it had been verified that this polymer did not contribute to the ORD signal, mesophase samples were pressed between the poly(4-methyl-1-pentene) slides and allowed to dry. The permeability of this polymer to methanol permitted the uniform addition of solvent to the HPC film without loss of order due to free surfaces.

ORD spectra were recorded with a Jasco model ORD/UV5 spectropolarimeter. Cylindrical quartz cells (Hellma) of pathlength 1.0 or 0.1 cm were used for dilute solutions. Concentrated solutions were examined in a cell made from two quartz plates, one etched to give a sample thickness of either 0.1 or 0.01 mm. Mesophase samples were sealed with paraffin wax and allowed to relax overnight before spectra were recorded.

3. Results and discussion

3.1. HPC solutions in methanol

A typical ORD curve for an isotropic solution of HPC in methanol is shown in figure 1. This polymer contains no chromophores with electronic absorptions in the U.V.-visible region of the spectrum and the observed ORD signal therefore consists only of the long wavelength tail of Cotton effects located below 190 nm. This curve shape is known as 'plain negative dispersion' and the data give a good straight line when plotted in the linear form of the Drude equation (equation [2]).

The ORD curve of HPC in methanol, when expressed as specific rotation, is independent of polymer concentration for solutions containing between 1 and 43 per cent polymer by weight. From the slope of the linear Drude plots, the crossover wavelength of the Cotton effect responsible for the observed ORD curve occurs at 175–180 nm. This value is constant within the concentration range specified above and agrees well with the reported position of the electronic absorption corresponding to the $n \rightarrow \sigma^*$ transition for the lone pair electrons of the ring and linkage oxygen atoms [9]. Since there are no non-bonding orbitals associated with C–C or C–H bonds, the lowest energy transitions for the rest of the polymer are $\sigma \rightarrow \sigma^*$ transitions and will occur at much shorter wavelengths. Vacuum UV-CD spectra of cellulose acetates [10] show a decrease in the acetate carbonyl peak with decreasing degree of acetylation, but no new peaks appear above 140 nm corresponding to the hydroxyl groups of polymers which are not fully acetylated. This implies that the

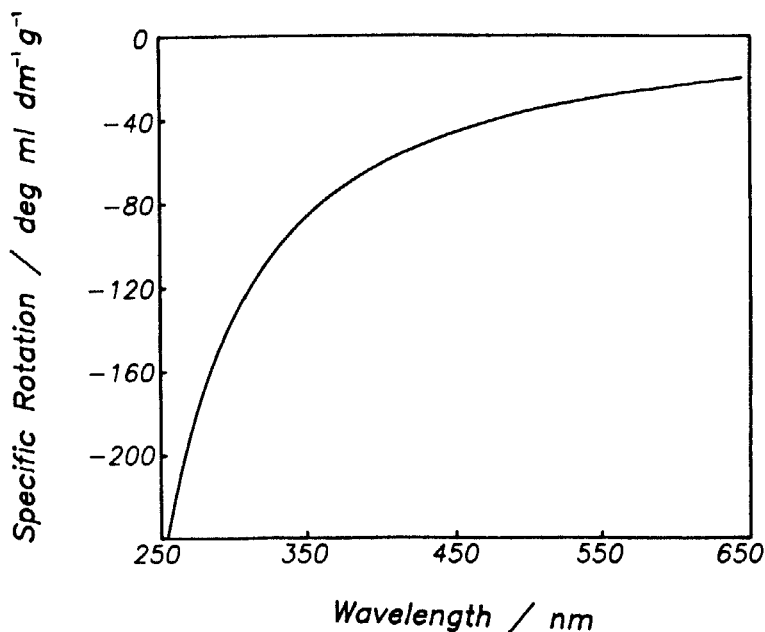


Figure 1. ORD spectrum of an isotropic solution of HPC in methanol recorded in a 1 cm cell.

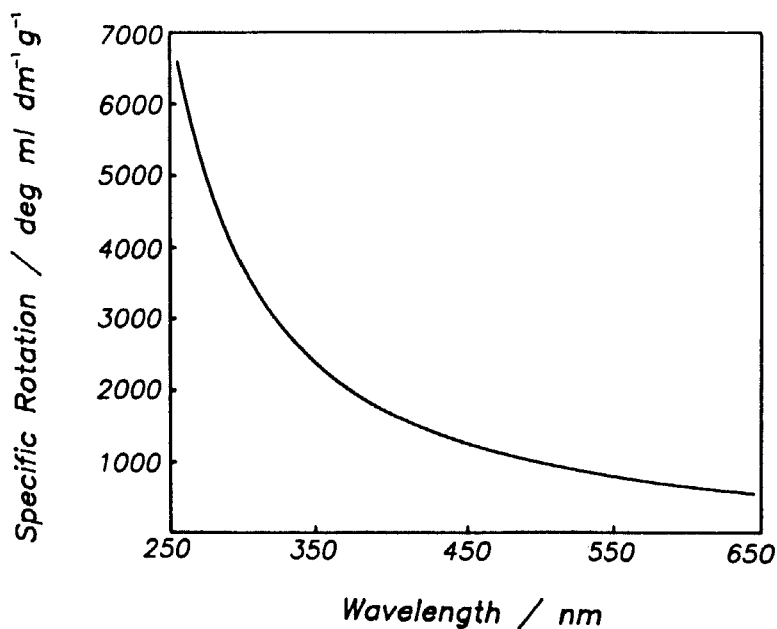


Figure 2. ORD spectrum of a liquid crystalline solution of HPC in methanol (45 per cent polymer by weight) recorded in a 0.01 mm quartz cell. For comparison with figure 1, the measured optical rotation has been converted to the concentration independent specific rotation by dividing the measured value by the polymer concentration (g/mL) and the pathlength (dm).

hydroxyl groups are free to adopt random orientations relative to the chiral anhydroglucose ring and therefore do not contribute to the optical activity of cellulose derivatives.

The ORD spectrum of isotropic solutions of HPC in methanol can be accounted for by the intrinsic optical activity of the polymer and thus provides no evidence for the presence of a helical conformation. Furthermore, no concentration-induced changes in conformation are indicated.

Although the ORD spectrum of HPC in methanol is independent of concentration below 43 per cent polymer by weight, the spectra of solutions exceeding this concentration are very different. This is illustrated by the ORD curve in figure 2, recorded for a 45 per cent solution of HPC in methanol. This solution exhibits plain positive dispersion, indicating a change in sign from that observed for less concentrated solutions. The magnitude of the specific rotation is also much greater than that found for solutions containing less than 43 per cent polymer. The specific rotation at 300 nm is plotted in figure 3 as a function of polymer concentration. The dramatic change at the critical concentration is evident.

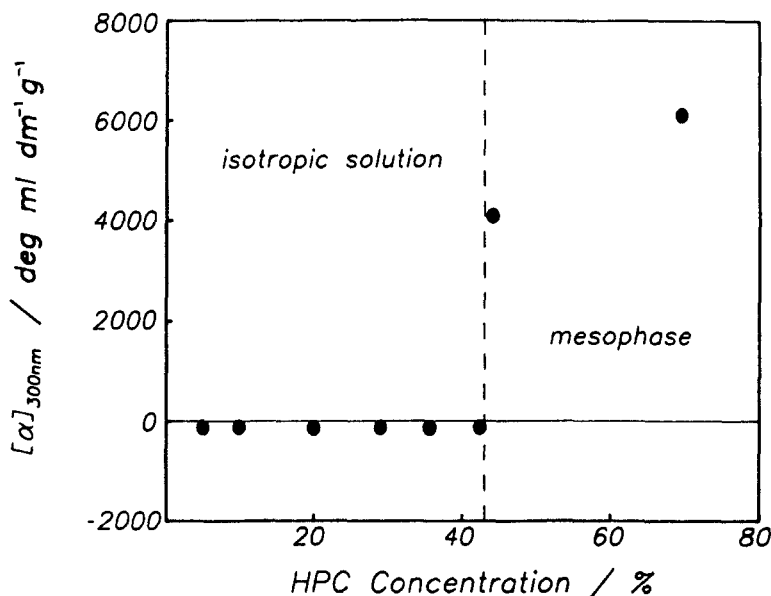


Figure 3. Specific rotation at 300 nm for solutions of HPC in methanol as a function of polymer concentration (wt %).

Large increases in optical rotation have been reported to accompany, and in fact, precede, the formation of the cholesteric liquid crystalline phase of poly(γ -benzylglutamate) [11, 12]. The enhancement of optical activity in the 'pretransition regime' was attributed to short-range chiral ordering of macromolecules in the isotropic state. The isotropic solution of HPC in methanol obtained from the separation of a biphasic sample by centrifugation has an ORD spectrum typical of dilute solutions and therefore no pretransitional ordering is indicated.

Since the liquid crystalline phase formed by HPC is known to be cholesteric, any analysis of the optical rotation of the ordered solutions must include the predicted behaviour of this chiral phase. These properties are described by the de Vries equation. Figure 4 shows an experimental ORD curve for a HPC mesophase in

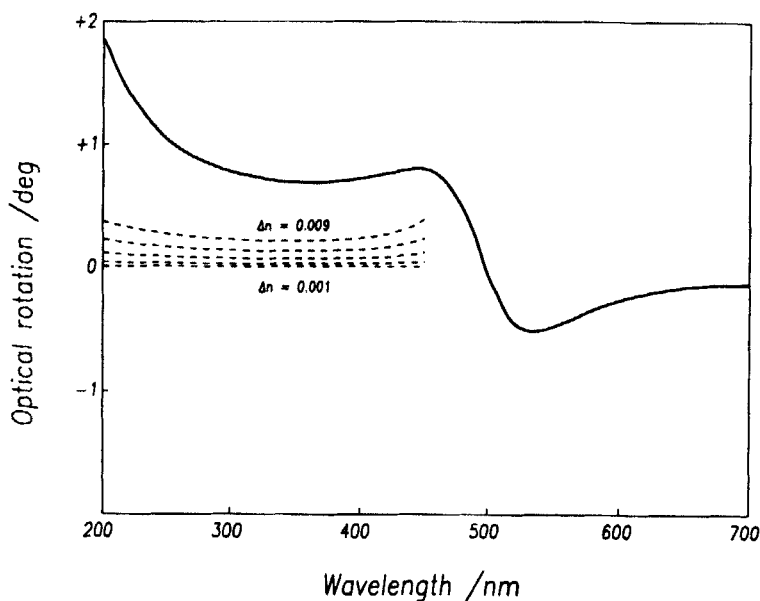


Figure 4. ORD spectrum of a mesophase solution of HPC in methanol (72 per cent by weight). The dashed lines are curves generated from the de Vries equation with $\Delta n = 0.001, 0.003, 0.005, 0.007, 0.009$; sample thickness = $10 \mu\text{m}$ and mean refractive index = 1.43 .

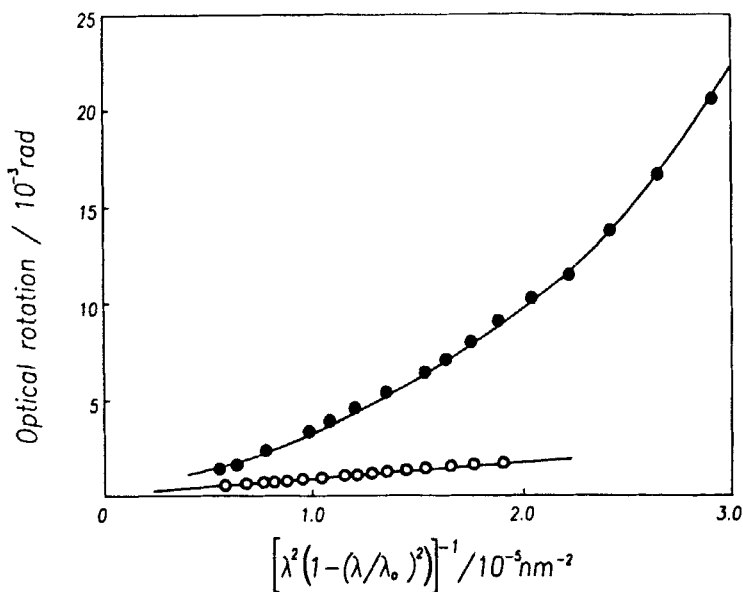


Figure 5. Plots of the linear form of the de Vries equation for HPC cholesteric mesophases in methanol (filled circles) and DMSO (open circles). (Points corresponding to low wavelengths appear at the right of this plot.)

methanol at a solution concentration where the pitch is in the visible region of the spectrum. The wavelength of maximum reflection corresponds to the crossover point of the Cotton effect at 490 nm . When plotted in the linear form of the de Vries equation (figure 5), the data show a marked deviation from linearity. The value for

the apparent layer birefringence obtained from the slope of the quasi-linear portion of this plot at longer wavelengths is unreasonably large (0.023), when compared to the reported value of 0.055 for the birefringence of cellulose chains in highly oriented crystalline samples [13]. The birefringence of HPC mesophase samples in methanol, measured with an Abbé refractometer, varies from 0.002 to 0.006 over concentrations from 44 to 70 per cent HPC by weight [4]. Similar results have been reported for this polymer in a variety of other solvents [14]. Theoretical curves generated with values of the layer birefringence in this range are also shown in figure 4. A large deviation from the predicted curve is evident at low wavelengths. Poor agreement between the de Vries equation and the observed optical rotation at low wavelengths has also been observed for the cholesteric liquid crystalline phase formed by the polysaccharide schizophyllan [15]. This polymer is known to have a helical conformation in solution.

Contributions from electronic absorptions are not considered in the derivation of the de Vries equation. It is obvious from the ORD curve of figure 1 that HPC possesses electronic absorption bands that have a non-zero contribution to the ORD spectrum at accessible wavelengths. This contribution, however, if it is to account for the observed behaviour in mesophase samples, has changed both in sign and in magnitude from the dilute solution plain negative dispersion of figure 1. One possible explanation for these changes is the formation of a helical conformation by the polymer chains in the liquid crystalline phase. This conformation change could be induced by the chain ordering which takes place on liquid crystal formation. A second possibility is that these changes in the optical activity arise from the influence of the cholesteric matrix on the chromophores responsible for the absorption contributions to the ORD spectrum. Induced optical activity has been observed for dye molecules dissolved in cholesteric phases [16].

3.2. HPC films

The ORD curve of a dry cholesteric HPC film cast from mesophase solution is shown in figure 6, curve (a). The pitch of HPC liquid crystals moves to shorter wavelengths with increasing polymer concentration and the pitch of the dry film is therefore located below 200 nm. The large plain positive dispersion component that was observed for the lyotropic mesophase is absent. On heating the cholesteric film above its melting point for 30 minutes and then quenching to room temperature, the observed ORD signal decreases as the contribution from the cholesteric reflection is lost. (The circular reflectivity spectra for melt-formed films shows no cholesteric reflection band [8].) The plain negative dispersion that remains for the isotropic film is of the same order of magnitude as the inherent optical activity of this polymer estimated from the dilute solution measurements. The fact that the cholesteric film does not show the positive rotation shown by HPC mesophases in water and methanol, but is in fact more negative than would be expected from the intrinsic optical activity of the HPC chain, suggests that the positive rotation is not due to a cholesteric ordering in the polymer. It must be admitted, however, that a positive contribution might be masked by the negative long-wavelength tail of the reflection band centered below 200 nm.

3.3. Solvent addition to cholesteric films

The plain positive dispersion that is absent from spectra recorded for dry cholesteric films is observed for lyotropic liquid crystalline solutions of HPC in

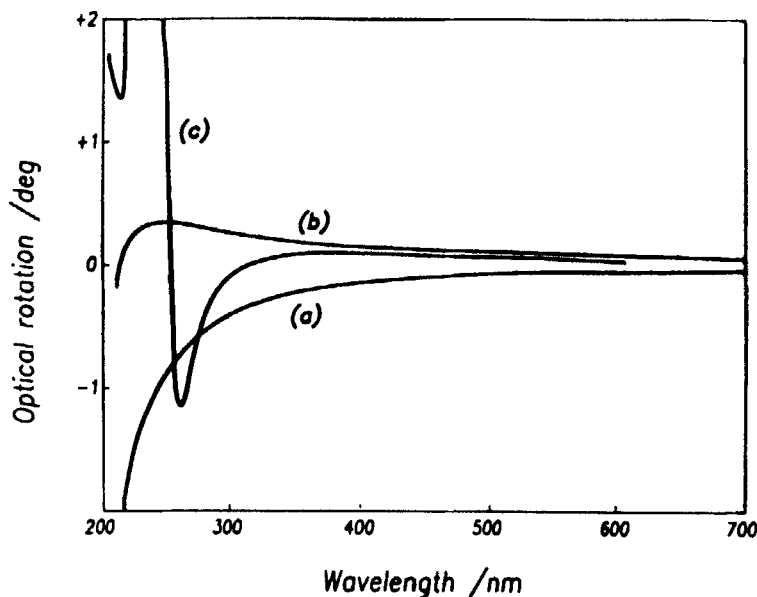


Figure 6. ORD spectrum of a cholesteric HPC film cast between two rigid films of poly(4-methyl-1-pentene) before (a) and after (b), (c) exposure to methanol vapour.

methanol and therefore must appear upon the addition of solvent to the dry films. The ORD spectrum of such a film after exposure to methanol vapour is shown in figure 6, curve (b). The presence of the plain positive component is evident as the optical rotation increases with decreasing wavelength from 500 nm to 230 nm. Near 230 nm the signal changes sign as the contribution from the reflection Cotton effect becomes dominant. Although the exact amount of methanol added to the film is unknown, the polymer concentration can be estimated as > 92 per cent from the extremely short pitch (< 200 nm).

The further addition of methanol moves the reflection band into the accessible region of the spectrum, as shown in figure 6, curve (c). The large difference observed between the intensities of the positive and negative components of the reflection Cotton effect indicates the presence of the additional positive signal.

3.4. Lyotropic solutions in methanol: dimethyl sulphoxide mixtures

The observation that dry cholesteric HPC films do not show the unexplained positive contribution to the low wavelength optical rotation that is found in the presence of solvent implies that this signal arises from a solvent-specific structure or conformation. The polymer is rich in hydroxyl groups and thus one obvious possibility is the formation of hydrogen bonds. Dimethyl sulphoxide (DMSO) is a dipolar aprotic solvent. Although it is polar, this solvent is incapable of donating a hydrogen atom to a hydrogen bond. The addition of DMSO could therefore be expected to disrupt any hydrogen bonded structure. The ORD curves observed for HPC lyotropic mesophases in methanol, DMSO and a 50:50 mixture (by volume) of these two solvents are shown in figure 7. The positive dispersion at low wavelengths is greatly reduced by the presence of the aprotic solvent, supporting the conclusion that this signal is related to a hydrogen bonded structure. In fact, the ORD spectrum of the lyotropic HPC mesophase in DMSO is well described by the de Vries equation, as

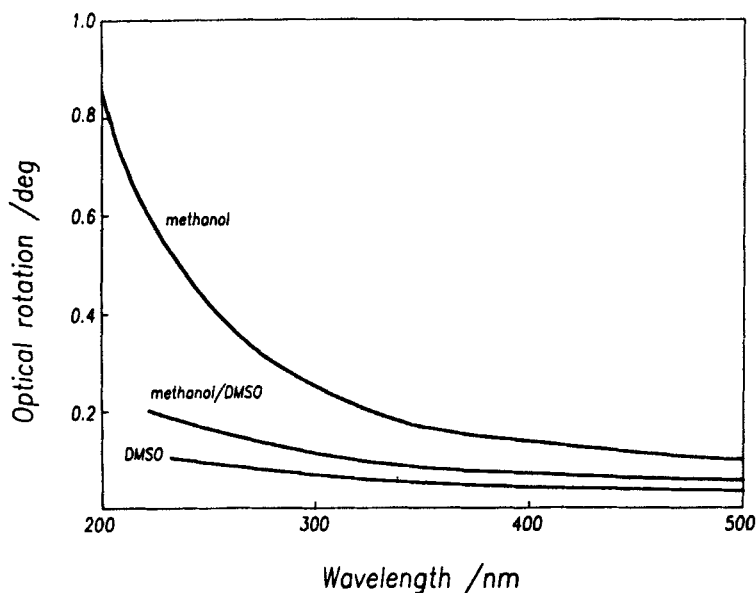


Figure 7. ORD spectra of lyotropic mesophases of HPC in methanol, dimethyl sulphoxide and a 50:50 mixture of the two solvents. The polymer volume fraction equals 0.55 in all cases. Spectra were recorded with a 0.01 mm quartz cell.

illustrated by the linear plot in figure 5. The slope of this plot gives a reasonable value of 0.0004 for the layer birefringence. The difference between the success of the de Vries equation in describing the ORD spectra of HPC mesophases in methanol and in DMSO is clear from the plots in figure 5.

3.5. Addition of urea

The helical conformation of polypeptides is stabilized by hydrogen bonding and the addition of urea, a strong hydrogen bond acceptor, is known to disrupt this secondary structure. Urea was therefore added to mesophase samples of HPC in methanol to determine if a similar interference with the hydrogen bonded structure indicated by the ORD spectra could be detected. Liquid crystalline samples of HPC in methanol containing from 0.5 to 10 per cent urea by weight give essentially the same ORD curves as samples in methanol alone. Anomalously high values of the layer birefringence are obtained from the slopes of the corresponding de Vries plots, which show deviations from linearity at low wavelengths similar to those found for methanol solutions in the absence of urea. This indicates that urea does not disrupt the structure responsible for the plain positive dispersion observed in the ORD curves of HPC mesophases in methanol.

4. Conclusions

The ORD spectra of isotropic solutions of HPC in methanol are well described by the Drude equation and provide no evidence for the presence of a helical conformation. The invariance of the spectra with concentration below 43 per cent polymer by weight also indicates that no concentration-induced changes in conformation occur.

ORD spectra of lyotropic liquid crystals of HPC in methanol (and water) contain a significant positive component that is not accounted for by the de Vries equation. This contribution to the optical activity vanishes when the solvent is removed or when hydrogen bonding is disrupted. It appears that this signal originates from a hydrogen bonded structure, possibly a solvent supported helical conformation, that contributes strongly to the optical rotation of these samples. The optical activity of HPC might also be enhanced by the formation of a solvate (not necessarily helical) involving hydrogen bonding with the chain hydroxyls, thus fixing the orientation of the hydroxyls relative to the chiral backbone and increasing the contribution from the electronic absorptions of the hydroxyl groups to the optical rotation. The proposed solvate structure collapses on drying, and the positive dispersion is not observed for dry films.

The nature of the solvent-generated structure will require further investigation. However, the formation of a cholesteric HPC mesophase in DMSO illustrates that this structure is not required for liquid crystal formation.

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