

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

The chiroptical properties of a new liquid-crystalline polymer: (trityl)(pentyl)cellulose

B. R. Harkness^a; D. G. Gray^a

^a Paprican and Department of Chemistry, McGill University, Pulp and Paper Research Centre, Montreal, PQ, Canada

To cite this Article Harkness, B. R. and Gray, D. G.(1990) 'The chiroptical properties of a new liquid-crystalline polymer: (trityl)(pentyl)cellulose', *Liquid Crystals*, 8: 2, 237 – 245

To link to this Article: DOI: 10.1080/02678299008047345

URL: <http://dx.doi.org/10.1080/02678299008047345>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The chiroptical properties of a new liquid-crystalline polymer: (trityl)(pentyl)cellulose

by B. R. HARKNESS and D. G. GRAY

Paprican and Department of Chemistry, McGill University,
Pulp and Paper Research Centre, Montreal, PQ, Canada H3A 2A7

(Received 8 November 1989; accepted 5 March 1990)

The chiroptical properties of a new liquid crystalline polymer, trityl pentyl cellulose (TPeC), are discussed. This polymer forms lyotropic liquid-crystalline phases in tetrahydrofuran and chloroform. The cholesteric twist sense is right handed in both solvents. The dilute solution optical activity of the phenyl chromophores, measured by circular dichroism (CD), showed no evidence of the exciton splitting expected for a helical arrangement of chromophores. The sign and magnitude of the CD signals were found to change considerably upon mesophase formation.

1. Introduction

Due to their intrinsic chirality and chain stiffness, cellulose and many of its derivatives form cholesteric liquid-crystalline phases in concentrated solution [1]. The chiroptical properties of these materials has generated some interest. Most of the work to date has involved attempts to elucidate the factors influencing the sign and position of the cholesteric reflection band [2]. Very little work has been done on the effect of mesophase formation on the optical activity due to the electronic transitions intrinsic to the chiral cellulose backbone. The cellulose backbone does not contain suitable chromophores with optically active transitions that can be observed in an easily accessible region of the spectrum. Studies on the optical activity of chromophoric groups attached to the cellulose backbone [3] have been carried out in an attempt to obtain information concerning the conformation of these cellulose derivatives in dilute solution. In one example, Stipanovic and Stevens [4] measured the vacuum ultraviolet circular dichroism spectrum (CD) of cellulose acetates and from their results proposed a 'pseudo helical' conformation for these macromolecules in solution. More recently, Ritcey and Gray [5] studied the CD spectra for Congo red bound to methyl cellulose and cellulose oligomers and obtained evidence for a helical conformation for these systems in aqueous solution. These two groups utilized the exciton chirality theory introduced by Moffit to determine a helical contribution to the observed optical activity [6]. This theory predicts that, for polymers with a helical conformation, the coupling of strong monomer transitions can lead to the splitting of the CD band into two components which are symmetrically disposed at higher and lower frequencies about the monomer transition frequency.

Recently, we have shown by CD that tritylated cellulose derivatives display interesting chiroptical activity in dilute solution [7]. The optical activity results from the preferential absorption of one component of circularly polarized light by the

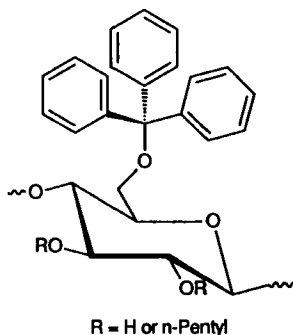
aromatic chromophores attached to the cellulose mainchain. These systems also form liquid-crystalline phases in several organic solvents and exhibit cholesteric reflection bands at specific polymer concentrations. It is therefore possible to study the effect of mesophase formation on the chiroptical properties of the aromatic absorption bands. It has been already been shown for the polybenzyl glutamates (PBLG) [8, 9] that the benzyl chromophores show apparent CD bands which result from the ordering of the chromophores in the cholesteric state. The optical activity is lost at polymer concentrations below the critical concentration for mesophase formation [9]. The absence of dilute solution optical activity from the PBLG phenyl chromophores can be explained on the basis that the chromophores are free to assume many orientations relative to the nearest chiral centre as the result of rotations about the bonds joining the aromatic group to the chiral mainchain. The structural flexibility results in a weakening of the aromatic optical activity to the point where it is no longer measurable [10]. For tritylated cellulose derivatives, the aromatic chromophores on the bulky trityl moiety experience less conformational mobility due to steric interactions with the cellulose backbone and hence show observable optical activity in dilute solution [7].

In this paper, we report the chiroptical properties of a new polymer, 6-*O*-(triphenylmethyl)-2,3-*O*-pentyl cellulose, in which a trityl (triphenylmethyl) moiety has been specifically attached to the hydroxyl group on the six position of the cellulose anhydroglucose units. This polymer shows phenyl group chiroptical properties and also forms a liquid-crystalline phase that exhibits a cholesteric reflection band at specific polymer concentrations.

2. Experimental

2.1. Materials

6-*O*-(Triphenylmethyl)-2,3-*O*-pentyl cellulose (TPeC) was prepared from trityl cellulose according to the procedure of Isogai *et al.* [11]. To a three neck round bottom flask containing 300 ml of dry DMSO was added 10 g of trityl cellulose (degree of substitution (DS) for the trityl group = 1.06) [12]. The trityl cellulose was stirred for several hours to ensure complete dissolution. The solution was degassed for 30 min. prior to the addition of 10 g of powdered sodium hydroxide (prepared with a mortar and pestle). The solution was stirred for 1 hour following which 100 g of iodopentane was added dropwise over a period of 2 hours. The mixture was stirred for approximately 24 hours at 50°C and then quenched in methanol. The precipitated product was filtered and dried. Purification was accomplished by reprecipitating the product from THF into methanol and water. The final product yield was 11.2 g (96 per cent).



2.2. Characterization

The ^1H NMR spectrum for TPeC was measured with a Varian XL 300 spectrometer at a frequency of 300 MHz. The spectrum was recorded in chloroform- d_1 with tetramethyl silane as the internal reference. A DS of 0.87 was obtained for the pentyl group by comparison of the integrated intensities of the pentyl and cellulose proton signals. This gives a total DS of 1.93 for the polymer.

The infrared spectrum for TPeC was recorded with an Analect AQS-18 FTIR spectrometer. The spectrum showed a small hydroxyl stretching band at 3500 cm^{-1} indicating that complete substitution of the cellulose backbone had not occurred and thus supporting the NMR result.

The weight-average molar mass, M_w , of TPeC was measured in THF with a Chromatix KMX 6 low-angle laser light scattering photometer. Measurement of the Rayleigh factor for each solution was made at a scattering angle of $6\text{--}7^\circ$. The value of the specific refractive index increment, dn/dc , for TPeC in THF measured with a Brice-Phoenix differential refractometer was 0.167, giving a value of 190 000 for M_w .

2.2. Solution properties

Liquid-crystalline solutions of TPeC were prepared by adding approximately 0.15 g of the polymer and an excess amount of solvent into small glass vials. The isotropic solutions were partially sealed and the solvent allowed to evaporate slowly until the desired concentration had been reached. This process took approximately 1 week.

CD spectra of liquid-crystalline phases were recorded with a Jasco J-500 spectropolarimeter equipped with a Mettler hotstage; samples were prepared as thin layers ($\sim 0.1\text{ mm}$ thickness) between quartz plates. Reflectivity spectra were recorded with a Pye Unicam SP8-150 UV/Vis spectrophotometer which was also equipped with a Mettler hotstage. The samples for reflectivity measurements were prepared as thin layers between glass plates that had been tightly sealed with epoxy. The temperature dependence measurements were obtained by heating the samples at a rate of $1^\circ\text{C}/\text{min}$ and allowing the samples to equilibrate for several minutes prior to each reading.

The dilute solution measurements were made by dissolving TPeC in spectrograde chloroform or tetrahydrofuran and measuring spectra in 1.0 cm or 0.1 cm quartz cells at ambient temperature.

3. Results and discussion

3.1. Chiroptical effects due to cholesteric reflection band

Concentrated solutions of TPeC dissolved in chloroform were observed as thin layers under a polarizing microscope. This system, above a critical concentration of approximately 29 mass per cent polymer, was observed to display the anisotropy and microscopic textures that are characteristic of a liquid-crystalline phase. Iridescent colours were observed when the polymer concentration was greater than 36 mass per cent in chloroform. TPeC also showed liquid-crystalline textures and iridescent colours when dissolved in THF. Trityl cellulose itself has not been found to produce a lyotropic phase. This polymer has limited solubility and tends to form gels when concentrated in polar solvents. It appears that partial substitution of trityl cellulose at the 2 and 3 positions may disrupt intermolecular hydrogen bonding by the hydroxyl groups, preventing gelation and allowing liquid-crystalline phases to form in several solvents.

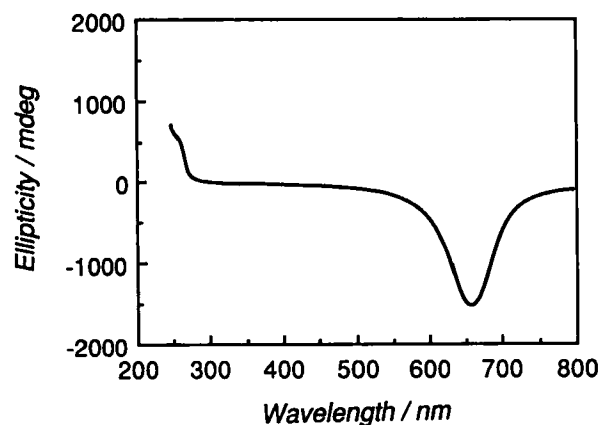


Figure 1. The CD spectrum for TPeC in chloroform at a concentration of 37 mass per cent polymer.

Cholesteric liquid-crystalline solutions may reflect either left or right handed circularly polarized light. This results in an apparent CD peak at the wavelength of the selective reflection. The CD spectrum of TPeC at a concentration of 37 mass per cent polymer in chloroform is shown in figure 1. It is apparent that there are two signals present in this spectrum. A large signal exhibiting negative ellipticity is located at a wavelength of 661 nm. This signal is due to the cholesteric reflection and indicates that the liquid-crystalline solution reflects right handed circularly polarized light and has a right handed twist sense. A second signal with positive ellipticity appears in the ultraviolet region of figure 1. This signal lies below 280 nm and may represent the preferential absorption of left handed circularly polarized light by the phenyl chromophores of the trityl group. The chiroptical properties of the phenyl chromophores will be discussed below.

According to the theory proposed by deVries [13], the pitch, P , of the supramolecular helicoidal structure can be related to the reflection wavelength, λ_0 , by the average refractive index of the mesophase, \bar{n} , according to the relationship,

$$\lambda_0 = \bar{n}P.$$

If the average refractive index of the mesophase is known, it is possible to calculate the pitch of the cholesteric structure if the reflection wavelength is known. For the system TPeC/chloroform, difficulties in accurately measuring \bar{n} were encountered as a result of the volatility of the solvent, and only the values for the reflection wavelength are quoted.

Figure 2 shows the apparent absorption peaks due to the cholesteric reflection for TPeC in chloroform at a concentration of 38 mass per cent polymer at several different temperatures. At 6°C the reflection band is located at 500 nm and moves to longer wavelengths as the temperature is increased. At 30°C the reflection band has moved almost 200 nm towards the red. The change in the reflection wavelength with temperature is almost linear and quite reversible (figure 3).

The reflection wavelength for TPeC in chloroform changes only slightly with concentration. As the polymer concentration was increased from 36 to 47 mass per cent the reflection wavelength decreased by less than 100 nm. In fact, all of the solutions in this concentration range exhibited red iridescence at room temperature.

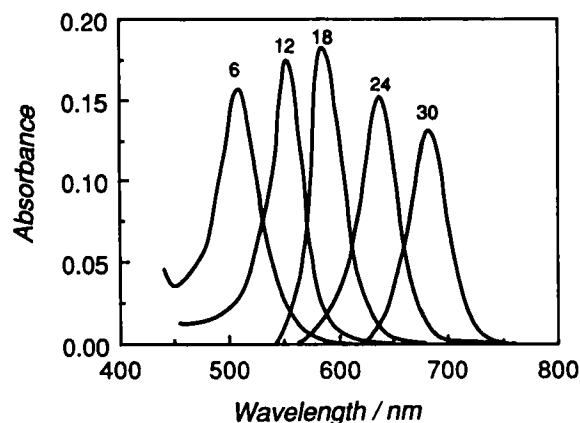


Figure 2. The apparent absorption peak for TPeC in chloroform (38 mass per cent polymer) as a function of temperature (from left to right; 6, 12, 18, 24 and 30°C).

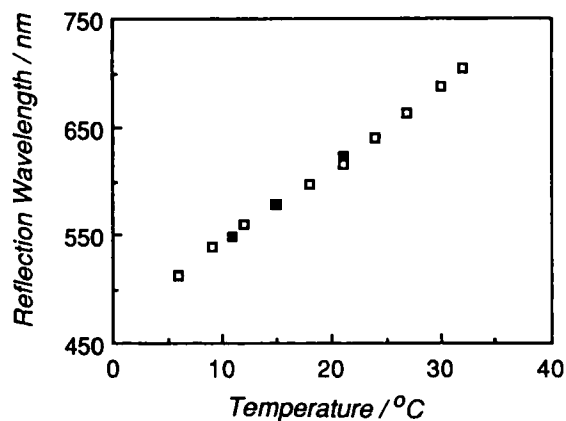


Figure 3. The change in reflection wavelength with temperature for 38 mass per cent TPeC in chloroform (open squares, heating; solid squares, cooling).

3.2. Chiroptical effects due to (triphenylmethyl) chromophores

Tritylated cellulose derivatives show observable optical activity from the phenyl chromophores attached to the cellulose backbone. In order to determine whether any correlation exists between the dilute solution optical activity and the optical properties of the liquid-crystalline phase, dilute solution optical measurements were performed in chloroform and THF.

The absorption spectrum for TPeC in chloroform, at a concentration of 4.1×10^{-4} g/ml, is shown in figure 4. The 1L_b transition for the phenyl chromophore is centred at a wavelength of about 260.4 nm. The vibrational fine structure for this transition is also evident, although poorly resolved. Part of the 1L_a transition, which appears at shorter wavelengths, is also visible. The CD spectrum for TPeC at a concentration of 8.1×10^{-4} g/ml is also shown in figure 4. The 1L_b transition appears centred at 261.7 nm and shows negative ellipticity. The 1L_a transition appears to show positive ellipticity at wavelengths just below the 1L_b transition. The general shape of the 1L_b band observed in the CD spectrum appears to be very similar to that of the

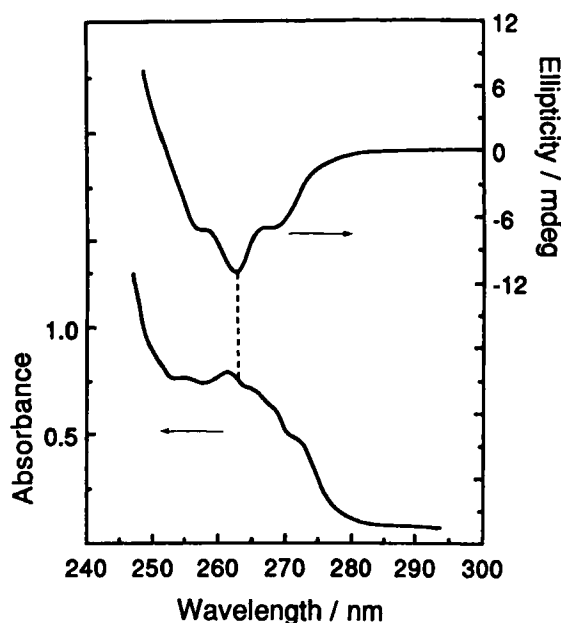


Figure 4. The absorption and CD spectra for dilute solutions of TPcC in chloroform. The sample concentrations were 4.1×10^{-4} and 8.1×10^{-4} g/ml respectively.

absorption band, although the absorption band appears to show more fine structure, and the CD band shows a 1.3 nm red shift.

These CD results resemble those for the polymer trityl-benzyl cellulose (TBzC) [7]. The dilute solution CD spectra for TBzC and TPcC are almost identical in shape, indicating that the benzyl substituents on the 2 and 3 positions of the anhydroglucose units of TBzC have little influence on the observed optical activity. This was confirmed by measuring the CD spectrum of 6-*O*-acetyl-2,3-di-*O*-benzyl cellulose (AcBzC), in which the optical activity from the remaining phenyl substituents was very weak [14].

It is apparent from figure 4 that there is no noticeable splitting of the 1L_b transition in the CD spectrum. The lack of exciton splitting is likely due to the fact that the 1L_b transition is an electronic-dipole-forbidden transition which is too weak to give rise to exciton interactions. Therefore, the observed optical activity is simply the result of the dissymmetry of the phenyl chromophores attached to the chiral cellulose backbone. Figure 5 shows the CD spectrum for TPcC in THF at a concentration of 3.1×10^{-4} g/ml, measured in a 0.1 cm quartz cell. Under these conditions the weak 1L_b transition is no longer visible and the 1L_a transition shows positive ellipticity with a maximum at 228 nm. There is no evidence that this transition is split into an exciton form. Limitations in solvent and polymer solubility prevented measurement of the fully allowed ${}^1B_{a,b}$ transition, that occurs at shorter wavelengths.

The CD spectrum for the dissymmetric model compound (*S,S*)-(-)-3-phenyl-2-phenylsulphonyloxazirine, studied by Forni and co-workers [15], showed exciton splittings for the phenyl 1L_a and ${}^1B_{a,b}$ transitions but no splitting of the 1L_b transition. This indicates that interactions between 1L_a transitions on adjacent phenyl groups can give rise to exciton coupling if the chromophores are in a suitable geometry. If the phenyl chromophores on TPcC are arranged in a dissymmetric helical array along the

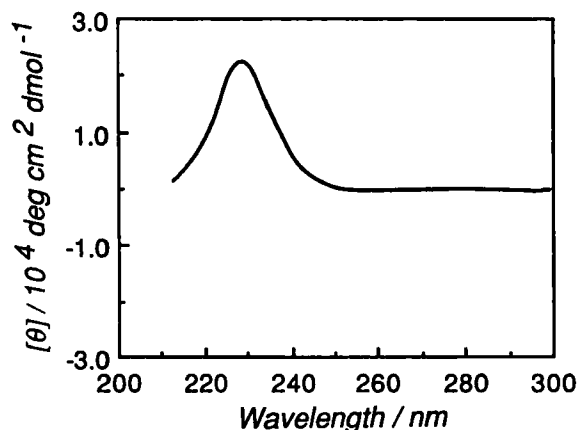


Figure 5. The CD spectra for TPcC in THF at a concentration of 3.1×10^{-4} g/ml in a 0.1 cm quartz cell.

cellulose backbone, splitting of the 1L_a transition may be expected to occur. The absence of such splitting indicates that the polymer may be in a non-helical conformation. Alternatively, the TPcC backbone may be in an extended helical conformation analogous to that proposed for cellulose [16, 17]. In such a conformation, the helix pitch may be too long, or the orientation of the phenyl groups too disordered to allow for exciton coupling.

The forbiddenness of the 1L_b transition does have one distinct advantage, in that it has a very low extinction coefficient which allows the transition to be measurable when the chromophore is in high concentration. Figure 6 shows the CD spectrum for the 1L_b transition for the liquid-crystalline phase of TPcC in chloroform. In this diagram the CD spectrum for both the dilute solution and the mesophase are shown. The apparent CD spectrum obtained from the mesophase now shows the 1L_b transition with positive ellipticity as a shoulder on the more intense 1L_a transition. There

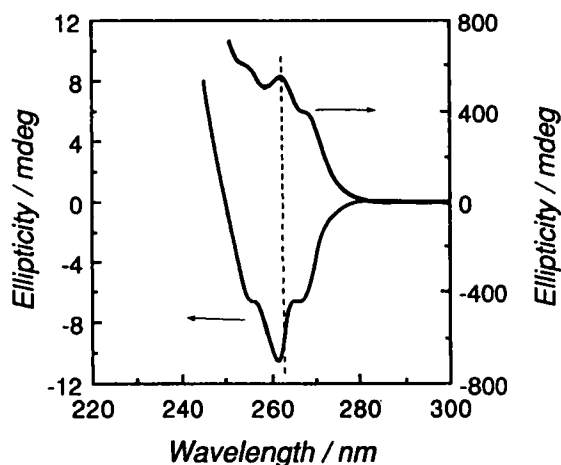


Figure 6. The CD spectra for TPcC in chloroform in the liquid-crystalline state and in dilute solution. The mesophase at 37 mass per cent polymer is shown as the upper curve (scale to the right).

is also a large change in the observed ellipticity for the 1L_b transition upon mesophase formation. In the dilute solution spectrum the ellipticity maximum for the 1L_b transition was very small and negative. However, upon mesophase formation the ellipticity increased dramatically by several hundred millidegrees. The 1L_b transition maximum was shifted slightly to the red by approximately 1.2 nm with respect to the dilute solution spectrum. The changes in sign and magnitude of the CD band may reflect the ordering of the aromatic chromophores into a three dimensional array in the mesophase analogous to the ordering of the phenyl groups in polybenzyl glutamate liquid crystals [8]. Saeva and co-workers have examined the circular dichroism of cholesteric mesophases containing achiral aromatic solutes [18, 19]. These studies have shown that the intensity of the optical activity induced by the cholesteric helicoidal structure depends on its pitch, temperature, cholesteric matrix properties, wavelength and texture. The sign of the induced optical activity was found to depend on the position of the pitchband relative to the absorption band of the solute, the cholesteric twist sense and the cholesteric matrix properties. It should be noted that the unusual changes in the band sign and magnitude may also represent artifacts produced by the coupling of an anisotropic medium with the imperfect optics and electronics inherent in CD spectrometers [20, 21]. These problems are associated with the measurement of circular dichroism in a medium which is also circularly and linearly birefringent and linearly dichroic. Experimentally, it was observed that the rotation of the TPcC/chloroform mesophase by 90° orthogonal to the incident beam in the CD spectrometer had little or no effect on the magnitude, sign or shape of the apparent CD signal. Unfortunately, a simple rotation by 90° does not change the sign of the circular birefringence, which also contributes to the apparent circular dichroism.

The temperature dependence for the apparent ellipticity of the 1L_b transition at a wavelength of 263 nm is shown in figure 7 for TPcC in chloroform at a concentration of 36 mass per cent polymer. As the temperature of the mesophase is increased the ellipticity decreases and the pitch band also moves to longer wavelength. Similar behaviour was observed for the optical activity originating from the phenyl chromophores in polybenzyl glutamate liquid crystal [8] and for pyrene dissolved in a

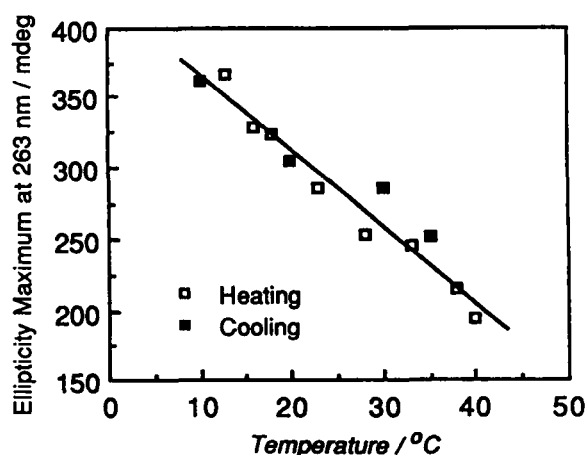


Figure 7. The temperature dependence for the ellipticity maximum at 263 nm for TPcC in chloroform at a concentration of 36 mass per cent polymer. The solid line indicates the trend of the data.

cholesteric mesophase of 70:30 (wt %) cholesteryl nonanoate-cholesteryl chloride [18]. These results can be interpreted on the basis of reduction in the degree of order in the liquid crystalline state as the result of an increase in the temperature of the mesophase [18].

We thank the Natural Sciences and Engineering Research Council of Canada for support. B.R.H. thanks the Pulp and Paper Research Institute of Canada for a postgraduate scholarship.

References

- [1] (a) GRAY, D. G., 1983, *J. appl. Polym. Symp.*, **37**, 179. (b) GILBERT, R. D., and PATTON, P. A., 1983, *Prog. Polym. Sci.*, **9**, 115.
- [2] (a) RITCEY, A. M., HOLME, K. R., and GRAY, D. G., 1988, *Macromolecules*, **21**, 2194. (b) ZUGENMAIER, P., and HAURAND, P., 1987, *Carbohydr. Res.*, **160**, 369. (c) TAMAGISHI, T., FUKUDA, T., MIYAMOTO, T., and WATANABE, J., 1989, *Cellulose Structural and Functional Aspects*, edited by J. F. Kennedy, G. O. Phillips and P. A. Williams (Ellis Horwood), Chichester, p. 391.
- [3] (a) BITTIGER, H., and KEILICH, G., 1959, *Biopolymers*, **7**, 539. (b) MUKHERJEE, S., MARCHESSAULT, R. H., and SARKO, A., 1972, *Biopolymers*, **11**, 291.
- [4] STIPANOVIC, A. J., and STEVENS, E. S., 1983, *J. appl. Polym. Sci. appl. Polym. Symp.*, **37**, 277.
- [5] RITCEY, A. M., and GRAY, D. G., 1988, *Biopolymers*, **27**, 479.
- [6] CHARNEY, E., 1979, *The Molecular Basis of Optical Activity*, 2nd edition (Wiley), Chap. 8.
- [7] HARKNESS, B. R., and GRAY, D. G., 1990, *Macromolecules*, **23**, 1452.
- [8] UEMATSU, I., and UEMATSU, Y., 1984, *Adv. Polym. Sci.*, **59**, 37.
- [9] IIZUKA, E., and YANG, J. T., 1974, *Molec. Crystal liq. Crystals*, **29**, 27.
- [10] BEYCHOK, S., 1966, *Science, N.Y.*, **154**, 1288.
- [11] ISOGAI, A., ISHIZU, I., and NAKANO, J., 1984, *J. appl. Polym. Sci.*, **29**, 3873.
- [12] Trityl cellulose was prepared according to the procedure of: HEARON, W. M., HIATT, G. D., and FORDYCE, C. R., 1943, *J. Am. chem. Soc.*, **65**, 2449.
- [13] DE VRIES, H., 1951, *Acta crystallogr.*, **4**, 219.
- [14] HARKNESS, B. R., and GRAY, D. G. (unpublished results).
- [15] BUCCIARELLI, M., FORNI, A., MORETTI, I., TORRE, G., BRÜCKNER, S., and MALPEZZI, L., 1988, *J. chem. Soc. Perkin Trans. II*, **8**, 1403.
- [16] PIZZI, A., and EATON, N., 1985, *J. Macromolec. Sci. Chem. A*, **22**, 105.
- [17] SIMON, I., SCHERAGA, H., and MANLEY, R. ST. J., 1988, *Macromolecules*, **21**, 983.
- [18] SAEVA, F. D., SHARPE, P. E., and OLIN, G. R., 1973, *J. Am. chem. Soc.*, **95**, 7657.
- [19] SAEVA, F. D., 1979, *Liquid Crystals: The Fourth State of Matter*, edited by F. D. Saeva (Marcel Dekker).
- [20] SHINDO, Y., NAKAGAWA, M., and OHMI, Y., 1985, *Appl. Spectrosc.*, **39**, 860.
- [21] SHINDO, Y., and OHMI, Y., 1985, *J. Am. chem. Soc.*, **107**, 91.