Effect of temperature on the reflective properties of chiral nematic (trityl)(hexyl)-cellulose films

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6-*O*-Trityl-2,3-*O*-hexyl cellulose derivatives form solid films with 'frozen in' chiral nematic order when cast from several organic solvents. Casting from chloroform or tetrahydrofuran can result in films that display iridescent colours due to the chiral nematic reflection band. Films with both left-handed and right-handed chiral nematic structure have been prepared. The chiroptical behaviour of these coloured films has been examined as a function of temperature. The chiroptical activity of the films below the glass transition temperature of the polymer is quite stable, but above this temperature the intensity of the reflection band changes reversibly or irreversibly, depending on the polymer.

(Keywords: cellulose ethers; chiral nematic polymers; chiroptical properties)

INTRODUCTION

(Triphenylmethyl) cellulose (trityl cellulose) serves as a useful starting material for the preparation of specifically substituted cellulose derivatives. The heterogeneous tritylation of cellulose results in a polymer in which the trityl group has preferentially substituted at the primary hydroxyl position of the repeating anhydroglucose units composing the cellulose backbone[1]. Following tritylation, the remaining secondary hydroxyl groups at positions two and three can be selectively substituted with a variety of side-groups. It has been shown that the etherification of these positions can be accomplished by reacting trityl cellulose, dissolved in dimethylsulphoxide, with sodium hydroxide as base and an appropriate alkylating agent. Under these conditions several (trityl)(alkyl)cellulose derivatives with high degrees of alkyl substitution have been prepared[2].

The alkylated derivatives of trityl cellulose form lyotropic chiral nematic liquid crystalline phases when dissolved at high polymer concentrations in a variety of organic solvents[2]. These solutions exhibit chiral nematic reflection bands which in several cases occur at wavelengths in the visible region. Chiral nematic mesophases have the unique property of being able to selectively reflect one component of circularly polarized light with the handedness of the reflected component determined by the twist sense of the chiral nematic helicoidal structure[3]. The (trityl)(alkyl)cellulose polymers form both left- and right-handed chiral nematic structures, depending on the nature of the alkyl side-group substitution[2].

(Trityl)(alkyl)cellulose polymers exhibit dilute solution chiroptical activity that arises from the phenyl chromophores attached to the cellulose backbone[2,4,5]. Circular dichroism (CD) spectroscopy has shown that the signs and magnitudes of the phenyl transitions change markedly as the polymer concentration is increased above the critical concentration for mesophase formation. The twist sense of the chiral nematic structure also influences the sign of the CD signals from the phenyl chromophores[2]. In the mesophase, the signs of the CD bands for the phenyl transitions are positive for a right-handed mesophase but change to negative for a left-handed mesophase. No correlation has been found between the dilute solution chiroptical activity of the phenyl chromophores and the twist sense of the chiral nematic mesophases.

(Trityl)(alkyl)cellulose derivatives have also been found to form solid films with chiral nematic order when cast from chloroform or tetrahydrofuran solutions[2]. Several of these films display iridescent colours in the visible region of the spectrum; 6-*O*-trityl-2,3-*O*-hexyl cellulose (THeC1) with a trityl group degree of substitution (DS) of 1.06 and a hexyl group DS of 1.21 forms a film with a 'frozen in' chiral nematic structure with a right-handed twist sense when cast from chloroform. On the other hand, 6-*O*-trityl-2,3-*O*-hexyl cellulose (THeC2) with a trityl group DS of 1.03 and a hexyl group DS of 1.92 forms a chiral nematic film with a left-handed twist sense when cast from tetrahydrofuran[2].

There have been some prior reports of synthetic polypeptides and cellulose derivatives that form solid films with chiral nematic reflection bands when cast from solution. Cast films of (hydroxypropyl)cellulose (HPC) have been observed to have a chiral nematic structure with a pitch in the range of 100–200 nm, depending on the casting conditions[6]. Heating these films to tempera-

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tures between 130 and 175°C resulted in the reflection band moving irreversibly into the visible region. This indicated that the films were not thermotropic but a metastable phase induced by casting from a liquid crystalline solution. An increase in the thermal motion of the polymer above 120°C, as determined by dynamic mechanical measurements, was assumed to be responsible for the change in the optical properties of this polymer at higher temperatures.

Solid films possessing chiral nematic order have also been prepared from synthetic polypeptides. Tobolski and Samulski have shown that cast films of poly-γ-benzyl-L-glutamate (PBLG) have this ordered structure[7]. Films of PBLG have been observed to display a chiral nematic reflection band in the visible region when cast from a mixed solvent of dimethylformamide and *m*-cresol[8]. Films of poly-γ-methyl-glutamate cast from 1,2-dichloroethane or dichloromethane-dimethylformamide solutions have chiral nematic order and exhibit reflection bands in the visible region[8,9]. The position of the reflection band depends on the initial concentration of the solution and the rate of solvent evaporation. The samples that evaporate more slowly have been found to show reflection bands at longer wavelengths[9]. Poly-γ-methyl-glutamate forms left- and right-handed chiral nematic films depending on the chirality of the monomer units. Poly-γ-methyl-D-glutamate forms a left-handed chiral nematic film whereas poly-γ-methyl-L-glutamate forms a right-handed chiral nematic film. The chiral nematic order of these films is quite stable to temperatures up to 180°C.

This paper describes the preparation of solid films of 6-*O*-trityl-2,3-*O*-hexyl cellulose (THeC1 and THeC2), that possess chiral nematic order. The chiroptical properties of these polymer films are discussed with respect to the twist sense of the frozen-in chiral nematic structure. The thermal behaviour of the chiroptical activity of these films is examined and compared to the dynamic mechanical properties of the bulk polymer.

EXPERIMENTAL

Preparation and characterization of materials

The preparation and characterization of 6-*O*-trityl-2,3-*O*-alkyl cellulose derivatives by the reaction of trityl cellulose in dimethylsulphoxide with sodium hydroxide and an appropriate alkyl iodide have been described previously[2]. Two different samples of 6-*O*-trityl-2,3-*O*-hexyl cellulose (THeC1 and THeC2) were prepared. The samples THeC1 (DS trityl = 1.06, DS hexyl = 1.21, for a total DS of 2.27) and THeC2 (DS trityl = 1.03, DS hexyl = 1.92 for a total DS of 2.95) gave values for M_w of 166 000 and 158 000 g mol^{-1}, respectively[2].

Dynamic mechanical thermal analysis

Dynamic mechanical analyses were performed on samples compression moulded into rectangular blocks at a temperature of approximately 220°C. The sample dimensions were about 12 mm × 36 mm × 2 mm. The measurements were made with a Polymer Laboratories dynamic mechanical thermal analyser in the temperature range of 50–250°C at frequencies of 1, 10 and 30 Hz. The heating rate was 1°C min^{-1} for all of the runs. The glass transition temperature, T_g, was taken as the temperature at which the tan δ peak showed a maximum at a frequency of 1 Hz.

Film preparation

Chiral nematic films were prepared by dissolving the polymer in chloroform or tetrahydrofuran at a concentration of about 15% (a concentration where the sample is isotropic and can easily be poured from a vial) and pouring this solution onto a glass microscope slide. The solution was immediately covered with a second slide to form a sandwich with the polymer solution as a thin layer in the middle. The two slides were gently drawn apart and the solvent allowed to evaporate at room temperature. The films cast from the mesophase were prepared by placing approximately 0.15 g of the polymer into small vials and adding chloroform or tetrahydrofuran to the polymer until an isotropic solution formed. The solvent was allowed to evaporate slowly over several days until a lyotropic mesophase had formed. The vials were then weighed to determine the polymer concentration. The polymer solutions were quickly removed from the vials and placed as a thin layer between glass plates and the films prepared as described above. Films were also prepared by placing a small quantity of the polymer solutions (approximately 4 mm depth) into glass vials (21 mm × 55 mm) and allowing the solvent to evaporate slowly at room temperature. To ensure complete dryness, the films were placed in a vacuum oven for 3 days prior to examination. The films were easily removed from the glass slides or glass vials by immersion in distilled water. Films cast from THeC1 in chloroform and THeC2 in tetrahydrofuran were observed to display iridescent colours due to the chiral nematic reflection band. The colour of the films was not uniform throughout and appeared to depend on the thickness of the sample. A more uniform colour was obtained for the films prepared in the glass vials. The thickness of the films was measured with a micrometer at the position where the chiroptical properties were examined.

Film characterization

Liquid crystalline textures were observed with a Reichert polarizing microscope equipped with a Mettler FP82 hot stage. Circular reflectivity spectra were recorded with a Jasco J-500 spectropolarimeter equipped with a Mettler hot stage.

RESULTS AND DISCUSSION

Lyotropic and isotropic (concentration ~15%) solutions of the 6-*O*-trityl-2,3-*O*-hexyl cellulose derivatives were cast into clear solid films possessing chiral nematic order. (6-*O*-Trityl-2,3-*O*-butyl cellulose and 6-*O*-trityl-2,3-*O*-pentyl cellulose derivatives[2] also formed chiral nematic films.) Several of these films exhibited chiral nematic reflection bands in the visible region when prepared from solutions with chloroform or tetrahydrofuran. Attempts to form thermotropic liquid crystalline phases from these polymers in the bulk phase by heating small samples between glass cover slides to temperatures above 220°C were unsuccessful. The samples failed to show liquid crystalline textures and iridescent colours were never observed. Chiral nematic order in solid films of 6-*O*-trityl-2,3-*O*-alkyl cellulose derivatives, where the alkyl substituents were butyl, pentyl or hexyl, was only observed in films cast from solution.

Figure 1 shows the apparent CD spectra for solid films cast from THeC1 in chloroform. The solid CD curve was obtained from a solid film (thickness 58 μm) derived

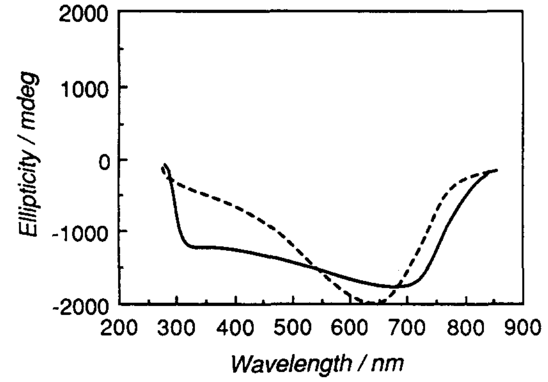

Figure 1 Apparent circular dichroism due to reflection of circularly polarized light from films of THeCl cast from chloroform: ——, film cast from isotropic solution; – – –, film cast from anisotropic solution

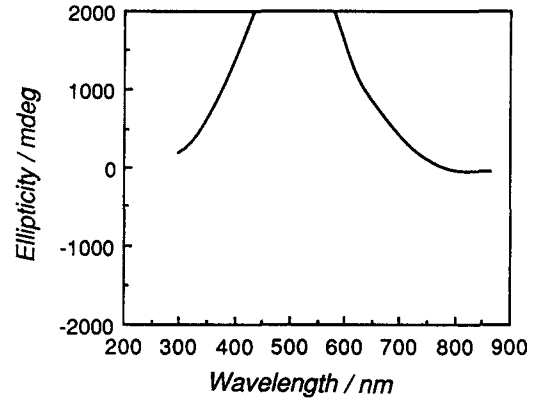

Figure 2 Apparent circular dichroism due to reflection of circularly polarized light from a coloured film of THeC2 cast from tetrahydrofuran

from an isotropic solution of THeCl in chloroform at a concentration of approximately 15 mass% polymer. The film appeared red to the naked eye but exhibited a very broad reflection band ($\lambda_{max} = 679$ mm), showing high ellipticity over a large bandwidth. Examination of this film under a polarizing microscope showed a polydomain liquid crystalline texture. The dashed CD curve in *Figure 1* was obtained from a solid film (thickness 64 μm) cast from an anisotropic solution of THeCl in chloroform at a concentration of approximately 26 mass% polymer. Compared to the film cast from dilute solution, the film prepared from the anisotropic solution showed a much narrower chiral nematic reflection bandwidth with a maximum around 645 nm.

The position, width and intensity of the reflection bands depends on the degree of order and the texture of the mesophase. A highly ordered monodomain (planar) texture gives the sharpest reflection peaks. Very sharp peaks can be achieved with lyotropic[11] and thermotropic[12] cellulose derivatives, but kinetic constraints during casting lead, in general, to polydomain structures with broad reflection peaks at wavelengths that depend on initial concentration, rate of solvent evaporation and sample thickness[6,9].

As shown in *Figure 1*, the sign of the reflection band in the CD spectrum for the coloured THeCl films cast from chloroform is negative, indicating that they have a right-handed chiral nematic structure. The CD spectrum for a coloured film of THeC2 cast from tetrahydrofuran is shown in *Figure 2*. The large intensity of the reflection band results in an off-scale peak. The sign of the reflection band is positive, indicating that this solid film has a left-handed chiral nematic structure.

Films of THeCl cast from tetrahydrofuran did not exhibit a reflection band in the visible region, but films of a low DS pentyl derivative (TPeCl)) were right-handed[2], so the handedness is not solely due to the casting solvent. Films of THeC2 did display reflection colours when cast from chloroform, but the negative reflection bands were very broad, making it difficult to assign peak maxima.

The optical properties of the solid films of THeCl, cast from chloroform, were examined as a function of temperature in order to determine the thermal stability of the chiral nematic structure. *Figure 3* shows the change in the reflection band for a thin film of THeCl (thickness 17 μm) as the temperature is increased at a rate of 1°C min^{-1}. (The room temperature reflection band in this case is at shorter wavelengths than the band shown in *Figure 1* for the thicker sample; this is probably not due to thickness *per se*, but to different initial concentrations and uncontrolled rates of solvent evaporation.) The reflection band decreases in intensity and moves to longer wavelengths as the temperature is increased from 25 to 224°C. As shown in *Figure 4*, there is a slight increase in the reflection wavelength of approximately 0.1 nm $°C^{-1}$ at temperatures below 170°C, after which the reflection wavelength begins to change more rapidly, with a rate of change of approximately 0.9 nm $°C^{-1}$. The change in the reflection maxima with temperature is small, on the order of about 80 nm over a range of 200°C, with most of the change occurring in the temperature interval

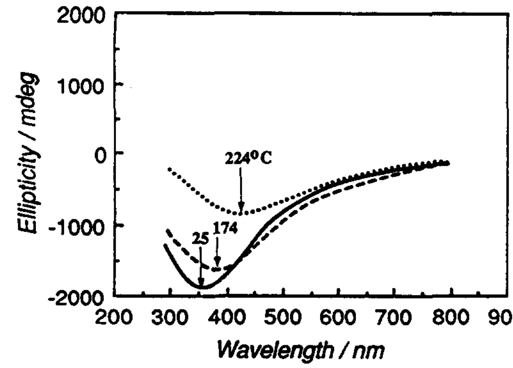

Figure 3 Effect of temperature on the reflection band for a film of THeCl, cast from chloroform, when heated at a rate of 1°C min^{-1}. Spectra were recorded at 25°C (——), 174°C (– – –) and 224°C (· · ·)

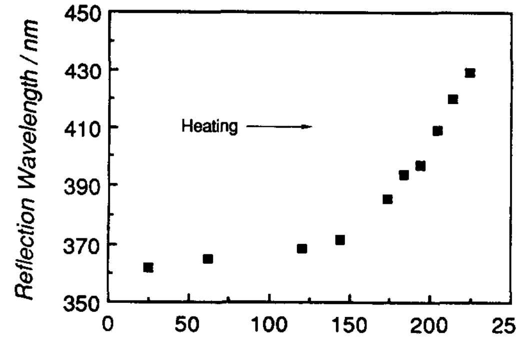

Figure 4 Temperature dependence for the reflection wavelength maximum for a THeCl film heated at a rate of 1°C min^{-1}

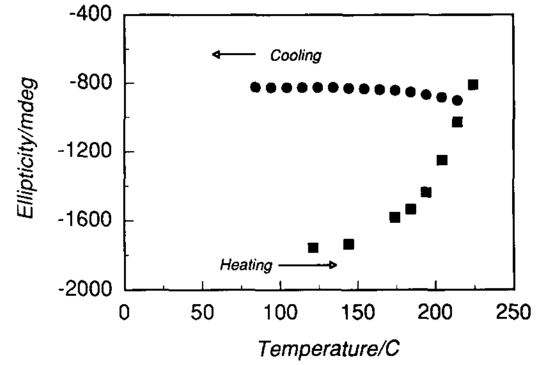

Figure 5 Temperature dependence for the maximum ellipticity of the reflection band for a THeC1 film heated at a rate of 1°C min^{-1} (■) and then cooled from 234°C at a rate of 1°C min^{-1} (●)

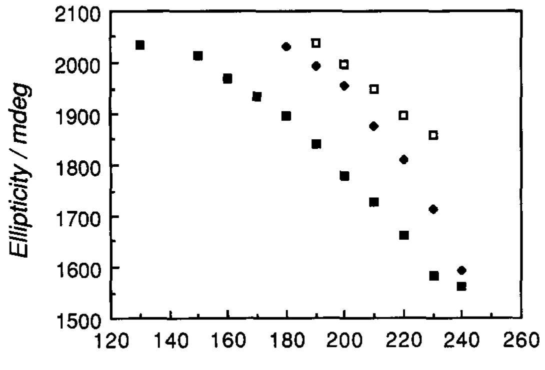

Figure 6 Temperature dependence for the maximum ellipticity of the reflection band for a THeC2 film cooled from 235°C at a rate of 1°C min^{-1} (□), heated to 240°C (◆) and cooled a second time from 240°C (■)

160–230°C. Heating these samples to temperatures above 235°C resulted in yellowing of the film.

The ellipticity of the reflection band for the THeC1 film also changed with temperature (*Figure 5*). A slight decrease in the ellipticity of approximately 1.5 m deg $°\mathrm{C}^{-1}$ was observed up to a temperature of 160°C, after which the ellipicity of the reflection band decreased rapidly at a rate of approximately 15.5 mdeg $°\mathrm{C}^{-1}$. Between the temperatures of 160 and 230°C the ellipticity was observed to decrease by over 50%, but it did not disappear completely, as was observed at the clearing temperature of the thermotropic (2-ethoxypropyl)cellulose[12].

To determine whether these changes in the chiroptical properties were reversible, a thin film of THeC1 was heated to a temperature of 234°C at a rate of 1°C min^{-1} and then allowed to cool at the same rate. On cooling, it was found that the ellipticity continued to decrease until a temperature of approximately 160°C was reached. Below 160°C the ellipticity of the film remained constant. Clearly, the changes in reflection band intensity are irreversible (*Figure 5*). There was only a slight decrease in the reflection wavelength with a decrease in the temperature of the film, indicating that the small change in the reflection wavelength upon heating is also irreversible.

Heating of the left-handed film THeC2 gave slightly different results. An increase in the temperature of the film resulted in only a small change in reflective properties at low temperatures, but at higher temperatures the reflection band began to move to slightly higher wavelengths and the ellipticity maxima of the reflection band decreased. For this polymer, the change in the reflective properties with temperature is partially reversible, whereas the changes in the THeC1 films were not reversible. The reflection intensity as a function of temperature for a THeC2 film cast from tetrahydrofuran is shown in *Figure 6*. On cooling the sample from 230°C, the ellipticity of the reflection band increases. When the temperature of the film is increased the ellipticity decreases and when the sample is cooled for a second time from 240°C the ellipticity again increases. Thus at a given temperature there is only a minor decrease in the intensity of the reflection due to the thermal cycling. No significant change in the peak wavelength was observed upon heating and cooling.

The reflection properties of chiral nematic films of HPC[6] and synthetic polypeptides[8] are sensitive to sample heating. Increasing the temperature of a chiral nematic HPC film results in an increase in the reflection wavelength[6]. Most of this change occurs at temperatures above 120°C, which corresponds to the temperature at which an increase in molecular mobility occurs. The ellipticity of the reflection maximum is also observed to decrease significantly above this temperature. An interesting reversal of the temperature dependence of the reflection band wavelength has been observed in films of PBLG[8]. Heating these films results in an initial increase in the pitch, but at temperatures above 135°C the pitch moves irreversibly to a shorter wavelength.

Dynamic mechanical thermal analysis of the (trityl)-(alkyl)cellulose derivatives was performed in order to determine whether a correlation exists between the temperature dependence of the chiroptical properties of the cast films and molecular mobility in the films. The storage modulus, E', and the loss tangent, $\tan\delta$, for THeC1 measured at a frequency of 1 Hz are shown as a function of temperature in *Figure 7*. The modulus decreases rapidly from a value of about 10^9 Pa at 150°C to 10^6 Pa at 200°C. A further decrease in the modulus occurs at temperatures above 225°C, but this may be due to polymer degradation (the sample became yellow). The large and rapid decrease in the modulus in the temperature interval 150–200°C is indicative of a glass transition[13]. The temperature dependence of $\tan\delta$ at a frequency of 1 Hz for THeC1 shows a single maximum at 175°C. Decomposition or flow of the polymer at higher temperatures leads to a further increase in $\tan\delta$ at

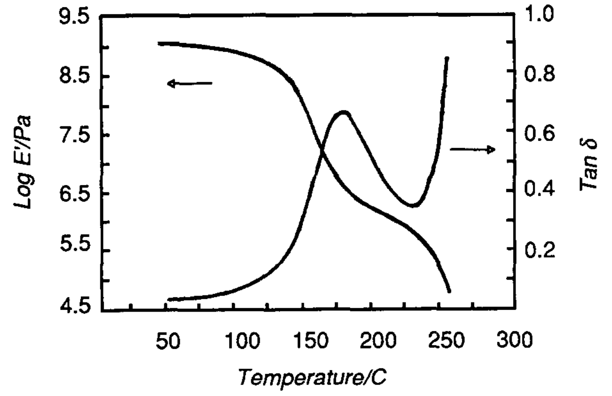

Figure 7 Storage modulus, E', and $\tan\delta$ as a function of temperature for THeC1, measured at a frequency of 1 Hz

temperatures above 225°C. The corresponding peak in tan δ for the more highly substituted THeC2 sample occurred at a rather lower temperature (155°C), indicating a higher degree of internal plasticization by the alkyl side chains.

The glass transition represents the temperature at which there is an onset in the cooperative segmental backbone motion[13]. An increase in the backbone motion of THeC1 and THeC2 above T_g may be related to the change in the chiroptical properties of the polymer films in this temperature region. For example, the shift in the reflection wavelength and the large decrease in ellipticity for the chiral nematic reflection band of the THeC1 film occurred at temperatures of approximately 170 and 180°C, respectively. These transition temperatures are close to the T_g value of 175°C as determined by dynamic mechanical measurements at 1 Hz. On cooling, the more mobile THeC2 sample shows marked changes in ellipticity down to ~150°C (*Figure 6*).

It is clear that these solid films, like those of HPC[6], behave quite differently from true thermotropic mesophases such as (2-ethoxypropyl)cellulose[12]. In the latter case, the reflection band wavelength and intensity change more or less reversibly with temperature in the range 70–150°C. The reflection band of HPC film displays irreversible changes in wavelength and intensity[6]. The THeC2 film shows virtually no changes in wavelength, but some reversibility in intensity is apparent, and the THeC1 film shows a minor irreversible change in wavelength and a marked irreversible change in intensity with temperature. Evidently, chain mobility is not the only factor controlling the supramolecular structure of these films. Above T_g, formation of other crystalline or liquid crystalline phases is possible, but X-ray diffraction showed no evidence of more ordered phases. It may be that steric interference from the very bulky trityl groups prevents attainment of the chiral nematic structure that is the presumed equilibrium state of these materials.

CONCLUSIONS

Several 6-*O*-trityl-2,3-*O*-alkyl cellulose derivatives form solid films with chiral nematic structure when cast from solution in chloroform or tetrahydrofuran. Some films display iridescent colours that result from a chiral nematic reflection band at visible wavelengths. Films of THeC2 cast from tetrahydrofuran are found to have a left-handed chiral nematic structure whereas films of THeC1 cast from chloroform have a right-handed chiral nematic structure. Heating of the THeC1 films to a temperature just below T_g (175°C) has a very small effect on the chiroptical properties of the film. Above this temperature, the reflection band shifts to slightly longer wavelengths and its intensity decreases sharply. This process is irreversible for the THeC1 film but partially reversible for the more highly substituted THeC2 film. Thus, the chiral nematic order in these (trityl)(alkyl)-cellulose films is not an equilibrium state.

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