Chiroptical Properties of 6-*O*-α-(1-Naphthylmethyl)-2,3-di-*O*-pentylcellulose

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ABSTRACT: A novel specifically substituted polymer, 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose ((MeNp)(Pe)C), has been synthesized and characterized. This cellulose derivative forms a chiral nematic thermotropic liquid crystalline phase that exhibits a reflection band in the visible region of the spectrum. The naphthyl chromophores attached to the cellulose backbone exhibit chiroptical activity in both dilute solution and the liquid crystalline phase. The sign and magnitude of the observed circular dichroism were found to differ in the isotropic and chiral nematic phases. Dilute-solution circular dichroism studies indicate that the naphthyl chromophores may be arranged in a helical arrangement along the cellulose backbone.

Introduction

(Triphenylmethyl)cellulose (tritylcellulose) serves as a useful starting material for the preparation of specifically substituted cellulose derivatives. The heterogeneous tritylation of cellulose results in a cellulose 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 2 and 3 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 tritylcellulose, dissolved in dimethyl sulfoxide, with sodium hydroxide as base and an appropriate alkylating agent. Under these conditions several tritylalkylcellulose derivatives with high degrees of alkyl substitution have been prepared.[2]

The alkylated derivatives of tritylcellulose form lyotropic chiral nematic liquid crystalline phases when dissolved at high polymer concentrations in a variety of organic solvents.[2] The high softening temperatures for these polymers (where the alkyl side groups vary from ethyl to hexyl) did not permit the formation of a thermotropic liquid crystalline phase. Polymer decomposition was observed to occur at temperatures just above the softening temperature.

The lyotropic mesophases derived from these tritylalkylcellulose polymers exhibit chiral nematic reflection bands that 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 tritylalkylcellulose polymers have been observed to form both left- and right-handed chiral nematic structures, depending on the nature of the alkyl side-group substitution. Several of these polymers have also been found to form films with "frozen-in" chiral nematic order that display visible reflection colors when the films are cast from chloroform or tetrahydrofuran.[2]

An interesting property of the tritylalkylcellulose polymers is that they exhibit dilute-solution chiroptical activity which 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 considerably 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 were positive for a right-handed mesophase but change to negative for a left-handed mesophase. No correlation was found to exist between the dilute-solution chiroptical activity of the phenyl chromophores and the twist sense of the chiral nematic mesophases.

In a continuation of our study of the chiroptical properties of specifically substituted cellulose derivatives, we have prepared a new cellulose derivative in which a naphthalene moiety is preferentially substituted onto position 6 of the anhydroglucose units. To accomplish this modification tritylpentylcellulose dissolved in dry chloroform was exposed to a stream of hydrogen chloride, resulting in the complete removal of the trityl groups to produce 2,3-di-*O*-pentylcellulose. This polymer was found to dissolve quite readily in dimethylacetamide and was subsequently reacted with potassium *tert*-butoxide and 1-(chloromethyl)naphthalene to yield 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose, in which the naphthalene substituent is preferentially attached to the hydroxyl group at position 6. This new derivative was found to form a thermotropic chiral nematic liquid crystalline phase, and this presented the opportunity to examine the chiroptical activity of the naphthalene chromophores both in the liquid crystalline phase and in dilute solution.

The regular arrangement of the naphthalene chromophores along the cellulose chain may allow the observation of a helical contribution to the optical activity by the exciton chirality method.[6] In the case of polymers with a helical conformation in solution, the coupling of strong monomer transitions can lead to the splitting of CD bands into two components that are symmetrically disposed at higher and lower frequencies about the monomer transition frequency. The tritylalkylcellulose polymers failed to show any evidence for exciton splitting of the ^1L_a and ^1L_b transitions between adjacent phenyl chromophores,[4] and spectrometer and solvent limitations did not permit the measurement of the allowed ^1B transition that occurs at shorter wavelengths. Substitution of a naphthalene chromophore for the triphenylmethyl group allows the direct observation of the allowed ^1B_b transition for this polymer when dissolved in cyclohex-

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ane. An analysis of naphthylpentylcellulose in dilute solution by circular dichroism indicates that there is a weak exciton contribution to the optical activity of this chromophore when attached to the cellulose backbone in a regular array.

Experimental Section

Materials. 6-*O*-Trityl-2,3-di-*O*-pentylcellulose (TPeC2) was prepared according to a procedure described previously.[2] The degree of substitution (DS) for the trityl group was approximately 1.03 and the DS for the pentyl group was approximately 1.82 for a total DS of 2.85. The mass-average molar mass, M_w, of this polymer was 144 000. TPeC2 was detritylated according to the following procedure:

TPeC2 (4.0 g) was dissolved in approximately 200 mL of anhydrous chloroform. Dry hydrogen chloride was bubbled through this solution for 4 min while continuous stirring was maintained. The polymer solution was poured into approximately 600 mL of acetone, and the precipitated product was isolated by centrifugation followed by filtration. The product was washed with acetone, filtered, and dried under vacuum at 65 °C for 16 h to yield 2.03 g of 2,3-di-*O*-pentylcellulose ((Pe)C).

2,3-Di-*O*-pentylcellulose (0.40 g) was dissolved in 20 mL of dimethylacetamide. The solution was degassed for 20 min by bubbling dry nitrogen gas through the solution. To the stirring solution was added 0.4 g of potassium *tert*-butoxide. The solution was stirred for 45 min, after which 0.7 g of 1-(chloromethyl)naphthalene was added dropwise. The solution was heated to 50 °C and stirred for 2 h. A further 0.3 g of potassium *tert*-butoxide followed by 0.5 g of 1-(chloromethyl)naphthalene was added, and the solution was stirred at 50 °C for 8 h. The solution was poured into 100 mL of methanol, and the precipitate was removed by decantation. The sticky polymer was washed several times with methanol and dried under vacuum to yield 0.52 g of 6-*O*-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose ((MeNp)(Pe)C). NMR studies indicate that the degree of naphthyl substitution for (MeNp)(Pe)C was approximately 1.0, for a total side-group degree of substitution of 2.82.

General Analysis. ^{1}H NMR spectra were recorded with Varian XL300 and XL200 NMR spectrometers at frequencies of 300 and 200 MHz, respectively. The proton-decoupled ^{13}C solution-state NMR spectrum was recorded with a Varian XL200 spectrometer operating at 50.3 MHz at a temperature of 70 °C. The ^{13}C and ^{1}H NMR spectra of (Pe)C were recorded in pyridine-d_5 with pyridine as the internal reference. The ^{1}H NMR spectrum of (MeNp)(Pe)C was recorded in chloroform-*d* with chloroform as the internal reference.

The ^{13}C CP/MAS NMR spectra were obtained with a Chemagnetics M100 NMR spectrometer operating at a frequency of 25.2 MHz. The contact time was 2.0 ms with a pulse delay of 3.0 s.

A gel permeation chromatogram for (MeNp)(Pe)C in chloroform was obtained with a Waters ALC/GPC 244 system with a RI detector and 10^5, 10^4, 10^3, 500, and 100 Å μ-Styragel columns in series. The elution volume for the polymer was equivalent to that of a polystyrene standard with a number-average molar mass, M_n, of 15 000.

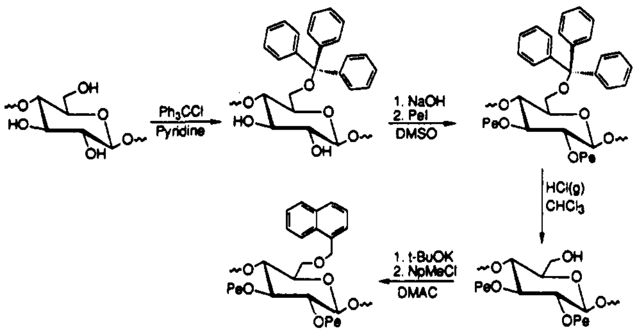
Chiroptical Properties. Thermotropic liquid crystalline films of (MeNp)(Pe)C were prepared by placing a small quantity of the polymer between glass or quartz plates. The plates were then heated to 150 °C for several minutes, which allowed the soft polymer to be pressed into thin films.

The liquid crystalline textures were observed with a Reichert polarizing microscope equipped with a Mettler FP82 hot stage. The clearing temperature for the thermotropic (MeNp)(Pe)C film was determined by heating the sample at a rate of 0.5 °C/min and monitoring the intensity of light transmitted through cross polars with a Mettler 18100 photocell.

Dilute-solution CD measurements were performed on solutions of (MeNp)(Pe)C dissolved in spectrograde cyclohexane and measured in 1.0- and 0.1-cm quartz solution cells at ambient temperature.

Circular reflectivity and circular dichroism spectra were recorded with a Jasco J-500 spectropolarimeter. The magnitude of the circular dichroism is expressed as the ellipticity, θ, which is proportional to the difference in the extinction coefficients for left and right circularly polarized light. Circular reflectivities of thin mesophase samples are given directly as values of θ; dilute-solution values are expressed in conventional concentration-independent units. To measure the circular reflectivity as a function of temperature, the Jasco spectrometer was equipped with a Mettler hot stage operating at a rate of 1 °C/min.

Scheme I



According to de Vries,[3] the pitch, P, of a chiral nematic structure can be related to the reflection wavelength, λ_0, by the mean refractive index of the mesophase, n, according to the relationship

$$\lambda_0 = nP \qquad (1)$$

The mean refractive index, n, for a thin film of (MeNp)(Pe)C was 1.5385 as measured at 60 °C with an Abbé refractometer. This value was used to calculate the pitch at 80 °C.

Fluorescence spectra were recorded for (MeNp)(Pe)C at a concentration of 1.1×10^{-5} M (moles of monomer repeat units) and for 1-methylnaphthalene at concentration of 7.4×10^{-5} M with a SPEX fluorescence spectrophotometer.

Results and Discussion

Synthesis and Characterization. The preparation of 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose ((MeNp)(Pe)C) is shown in Scheme I. In the first step, the primary hydroxyl groups at position 6 of the anhydroglucose units are preferentially substituted with triphenylmethyl groups to give 6-*O*-tritylcellulose. Hearon and co-workers have studied the reaction conditions required to prepare cellulose trityl ethers.[1] They found that the tritylation of the primary groups occurs at a much faster rate than the reaction with the more hindered secondary hydroxyl groups; tritylcellulose, when prepared under moderate conditions with a DS of 1.03 was approximately 90% substituted at the primary hydroxyl groups, with a small number substituted at the secondary hydroxyl positions.

Isogai and co-workers have reported that tri-*O*-alkylcellulose derivatives can be prepared by reacting cellulose, dissolved in the solvent SO$_2$–diethylamine–dimethyl sulfoxide, with powdered sodium hydroxide and the desired alkyl iodide.[7] Since tritylcellulose dissolves quite readily in dimethyl sulfoxide, these alkylating conditions were successfully applied to this polymer in order to etherify selectively the free secondary hydroxyl groups at positions 2 and 3.

Figure 1 shows the ^{13}C CP/MAS NMR spectrum for 6-*O*-trityl-2,3-di-*O*-pentylcellulose. The signals appearing in the region 14.0–30.0 ppm can be assigned to the pentyl carbons with the exception of the pentyl carbon atoms that are α to the ether linkage. The signals for these carbons are located at 74 ppm. The carbon atom at position 6 appears at 61.3 ppm, carbon atoms 2, 3, and 5 appear as a broad signal around 74 ppm, and carbon atom 4 appears at 83.5 ppm. The signal at 86.6 ppm can be assigned to the quaternary methyl carbon of the trityl group[8] and the signal at 101.3 ppm to carbon 1. The

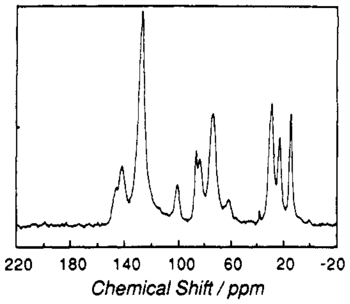


Figure 1. 25-MHz ^{13}C CP/MAS NMR spectrum of 6-*O*-trityl-2,3-di-*O*-pentylcellulose.

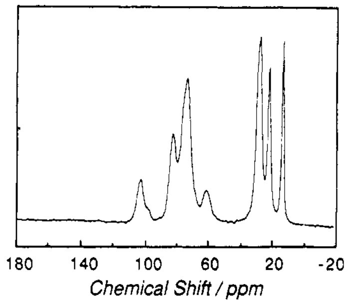


Figure 2. 25-MHz ^{13}C CP/MAS NMR spectrum of 2,3-di-*O*-pentylcellulose.

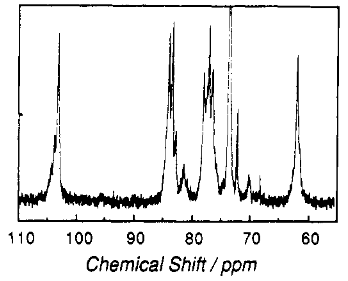


Figure 3. 50-MHz ^{13}C NMR spectrum of 2,3-di-*O*-pentylcellulose in pyridine-d_5 for the spectral region between 55.0 and 110.0 ppm.

aromatic trityl carbon atoms appear as broad signals around 128 and 143 ppm.

There are several methods in the literature for the removal of trityl groups from carbohydrates.[9] Tritylcellulose has been detritylated by suspending the polymer in a solution of methanol and hydrochloric acid[10] but this method failed to remove all of the trityl groups from the trityl–alkyl polymers. The ineffectiveness of this reaction may stem from the inability of the acid to penetrate the glassy polymer. Horton and Just have reported a mild, homogeneous, nondepolymerizing detritylation procedure that was successful in removing the triphenylmethyl groups from the partially trifluoroacetylated polymer (1→4)-2-amino-2-deoxy-6-*O*-trityl-α-D-glucopyranan.[11] This detritylation procedure was applied to 6-*O*-trityl-2,3-di-*O*-pentylcellulose with excellent results. The product, 2,3-di-*O*-pentylcellulose was isolated in high yield by precipitation in acetone. The ^{13}C CP/MAS NMR spectrum for this polymer is shown in Figure 2. It is apparent from the absence of signals in the region of 120–150 ppm that the trityl groups have been completely removed. The absence of triphenylmethyl protons in the ^1H NMR spectrum also supports this conclusion.

The ^{13}C solution-state NMR spectrum for 2,3-di-*O*-pentylcellulose in the spectral region of 55.0–110.0 ppm is shown in Figure 3. The signal for carbon 6 appears at 61.8 ppm. Reuben has reported that carbon 6 in methyl β-2,3-di-*O*-ethyl-(D-glucoside) appears at 62.5 ppm.[12] Substitution of the hydroxyl group at the position 6 with an ethyl substituent has been reported[12,13] to shift the C-6 carbon signal downfield by 7.9–8.7 ppm. Isogai and coworkers have reported that the C-6 signal in tri-*O*-butylcellulose in chloroform-*d* appears at 69 ppm.[14] Partial substitution of the C-6 hydroxyl groups of 2,3-di-*O*-pentylcellulose would therefore be expected to change the chemical shift of the C-6 carbon to the spectral region around 69 ppm. A small broad signal does appear in this region at 69.9 ppm. This signal may represent a small degree of C-6 substitution, since the trityl blocking group protects most but not all of the hydroxyl groups at this position. Miyamoto and co-workers have shown that the integral ratios of the ^{13}C backbone carbon signals can be used to determine the degree of substitution at specific hydroxyl functionalities.[15] Integral ratios of the C-6 signals of (Pe)C indicate that 89% of the primary hydroxyl groups at position 6 are unsubstituted. This result agrees quite well with the results of Hearon et al.,[1] who determined by chemical methods that 90% of the primary hydroxyl groups are substituted for tritylcellulose with a DS of 1.03. The ^{13}C signal for the pentyl carbon atoms α to the ether linkages appears as a sharp band at 73.6 ppm. A smaller, sharp transition located at 72.1 ppm may be due to a small number of pentyl groups substituted at position 6. It has been observed that the side-group carbon α to the ether linkage at position 6 is shifted to a slightly higher field compared to the carbon atoms α to positions 2 and 3.[12] The signal at 103.4 ppm can be assigned to C-1.

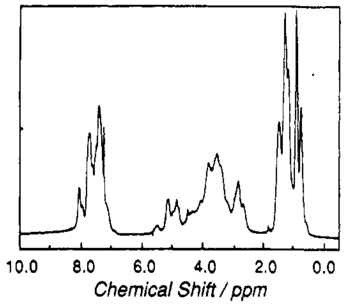


Figure 4. 200-MHz ^1H NMR spectrum of 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose in chloroform-*d*.

The free hydroxyl groups at position 6 of 2,3-di-*O*-pentylcellulose can be substituted with a variety of side groups. Naphthalene groups are good chromophores for the determination of a helical secondary structure in polypeptides by the exciton chirality method.[16,17] Isogai and coworkers[7] have reported the preparation of tri-*O*-α-(naphthylmethyl)cellulose by reacting cellulose, dissolved in a SO_2–DEA–DMSO mixture, with sodium hydroxide and 1-(chloromethyl)naphthalene. Unfortunately, (Pe)C was insoluble in DMSO; however, the etherification of the free hydroxyl groups of 2,3-di-*O*-pentylcellulose was achieved by dissolving the polymer in dimethylacetamide and adding an excess of potassium *tert*-butoxide and 1-(chloromethyl)naphthalene to the solution. These conditions resulted in the clean preparation of 6-*O*-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose with a high degree of substitution of the naphthylmethyl group. Figure 4 shows the ^1H NMR spectrum of 6-*O*-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose in which the naphthyl DS is approximately 1.0 and the total DS is approximately 2.82. The alkyl group proton signals appear in the spectral region 0.5–2.0 ppm, with the signals for the protons on the aromatic naphthalene group appearing in the spectral region 7.0–8.5 ppm.

Liquid Crystalline Properties. 6-*O*-Trityl-2,3-di-*O*-alkylcellulose derivatives form lyotropic liquid crystalline

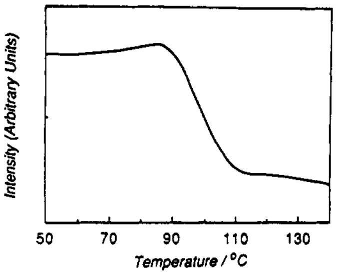


Figure 5. Light intensity passing through a birefringent (MeNp)(Pe)C film between crossed polarizers as the temperature is increased from 50 °C at a rate of 0.5 °C/min.

phases that can exhibit chiral nematic reflection bands in the visible region.[2,4] It is of interest to examine the effect of removing the trityl group on these properties. 6-*O*-Trityl-2,3-di-*O*-pentylcellulose was detritylated according to the procedure described above. The new polymer 2,3-di-*O*-pentylcellulose ((Pe)C) was soluble in a limited number of polar solvents. Complete dissolution was achieved in pyridine and dimethylacetamide but attempts to dissolve the polymer in tetrahydrofuran, chloroform, and dimethyl sulfoxide resulted in gelation of the polymer. The fact that the polymer dissolves in solvents such as pyridine and dimethylacetamide suggests that interchain hydrogen bonding may play a role in preventing dissolution in the other solvents. Concentrated solutions of (Pe)C in pyridine or dimethylacetamide did not show the anisotropy expected for liquid crystal formation when observed as thin layers in a polarizing microscope with crossed polars. The inability of these systems to form lyotropic mesophases may reflect interchain hydrogen bonding that prevents the molecules from assuming an ordered arrangement.

The naphthyl derivative, (MeNp)(Pe)C, had a low softening temperature. This suggested that it might form a thermotropic liquid crystalline phase. A small quantity of pure (MeNp)(Pe)C was placed between two glass slides and heated to 150 °C. At this temperature the polymer became very soft and could be pressed into a thin film quite easily. Upon cooling at a rate of 3 °C/min from an initial temperature of 150 °C, a birefringent phase exhibiting a focal conic texture began to appear at approximately 100–105 °C. Figure 5 shows the light intensity passing through the birefringent (MeNp)(Pe)C film between crossed polars as the temperature was increased from 50 °C at a rate of 0.5 °C/min. It is clear that a birefringent anisotropic phase exists below 110 °C, and above this temperature the film is isotropic and nonbirefringent. Iridescent colors characteristic of a chiral nematic structure were also observed at temperatures below 100 °C. The formation of a thermotropic liquid crystalline phase by (MeNp)(Pe)C was in contrast to the inability of tritylalkylcellulose derivatives to form such a phase. It has been shown that several cellulose derivatives with conformationally flexible side groups, including the ethers[18] and esters[19,20] of (hydroxypropyl)cellulose, form thermotropic liquid crystalline phases. The flexible side groups attached to these polymers give the chains sufficient mobility to form a chiral nematic arrangement even in the absence of solvent. Evidently, the naphthyl group interferes with this mobility much less than the bulky triphenylmethyl groups.

Chiral nematic liquid crystals may reflect either left- or right-handed circularly polarized light, depending on the twist sense of the supramolecular helicoidal structure. This results in an apparent signal in the circular dichroism spectrum at the wavelength of the selective reflection.

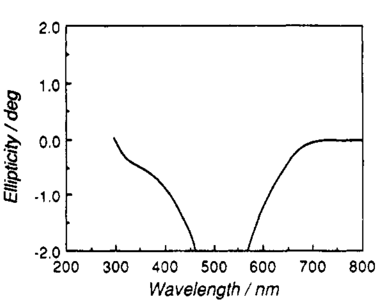


Figure 6. Apparent circular dichroism of a thin film of (MeNp)(Pe)C between glass plates as measured at 80 °C.

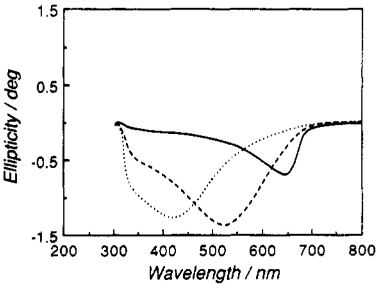


Figure 7. Apparent circular dichroism of a thermotropic (MeNp)(Pe)C film at 50 (dotted line), 80 (dashed line), and 102 °C (solid line).

Typically, the reflection bands for the thermotropic (MeNp)(Pe)C mesophases were quite broad. The band shapes were similar to those reported by Ritcey et al.[18] for the thermotropic phase of (2-ethoxypropyl)cellulose when cooled from the isotropic state. This band shape is indicative of a chiral nematic structure which consists of a random distribution of chiral nematic domains. The absence of a planar texture of (MeNp)(Pe)C when cooled from the isotropic state supports this conclusion. A simple shear of the polymer sample results in the reorientation of the polymer into a planar texture.

Figure 6 shows the circular reflectivity (CR) spectrum for a thin film of (MeNp)(Pe)C between glass plates at 80 °C. In order to obtain this spectrum, the sample was heated to 95 °C, sheared slightly, and quickly cooled to 80 °C. Following equilibration the CR spectrum was recorded. The reflection maximum occurs at approximately 520 nm for a pitch of approximately 340 nm. The right circularly polarized component of the incident light is selectively reflected, indicating that the chiral nematic structure has a right-handed twist sense.

The temperature dependence for the reflection wavelength was found to be completely reversible, moving to longer wavelengths as the sample was heated. This behavior is similar to that observed for the lyotropic mesophases of tritylalkylcellulose derivatives.[2] Figure 7 shows the CD spectra for a (MeNp)(Pe)C film that has been heated to 105 °C, sheared slightly, and cooled slowly at a rate of 0.2 °C/min. Spectra were recorded at temperatures of 102, 80, and 50 °C. The broadening of the reflection bands is quite apparent in these spectra.

Chiroptical Activity of the Naphthalene Chromophore. Achiral molecules may display chiroptical activity when bound to chiral polymers such as polysaccharides. If the chromophores along the polymer chain are arranged in a helical conformation, the CD band for a specific transition may be split into two components of opposite sign.[6] For this splitting to occur, the chromophores must be arranged in a regular fashion along the polymer backbone. This often involves restricting the conformational mobility of the chromophores along the chain.

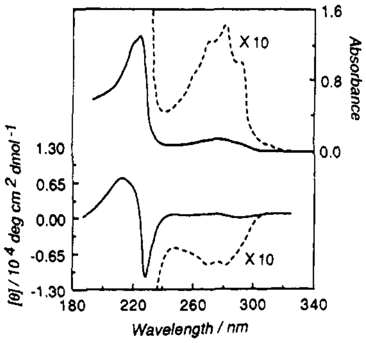


Figure 8. CD and absorbance spectra for dilute solutions of (MeNp)(Pe)C in cyclohexane.

For example, in poly(γ-1-naphthylmethyl L-glutamate), the naphthalene chromophores are separated from the polymer backbone by six bonds through which molecular rotations may occur. As a result of this conformational flexibility, the CD peaks are weak and do not show evidence for exciton coupling.[21] Poly(L-1-naphthylalanine), on the other hand, contains a naphthalene chromophore which is much more conformationally restricted. This polymer shows strong CD peaks for the ^1L_a and ^1B_b transitions, and the allowed ^1B_b transition shows the anomalous peak shape characteristic of exciton splitting.[16]

In addition to conformational rigidity, the distance between adjacent chromophores is also important in determining the extent of exciton splitting. The importance of these geometrical considerations has been demonstrated for a series of α-helical polypeptides that contain naphthyl chromophores with various orientations and distances along the chain.[17] The effect of chromophore orientation and interchromophore distances on exciton coupling has also been investigated in a series of cholesteryl dibenzoates.[22]

There have been reports of cellulose derivatives that give rise to CD bands exhibiting exciton splitting. Cellulose acetate[23] and achiral dyes attached to cellulose derivatives[24] show exciton interactions, but there appear to be no reported examples of exciton coupling in specifically substituted cellulose derivatives.

Figure 8 shows the dilute-solution absorption and CD spectra for 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose in cyclohexane. The absorption spectrum shows the ^1L_a transition centered around 281 nm. The allowed ^1B_b band appears as a strong transition around 225 nm. The CD spectrum shows a weak negative ellipticity band for the ^1L_a transition around 281 nm. There is no evidence for exciton splitting of this transition, in agreement with the lack of splitting of the ^1L_a transition of tritylalkylcellulose derivatives in dilute solution.[4] The ^1B_b transition does appear to show exciton splitting although the intensities of the bands are quite small. The molar ellipticity reaches a maximum of -1.3×10^4 deg cm^2 dmol^{-1} at 228 nm and 0.8×10^4 deg cm^2 dmol^{-1} at 211 nm. The peak shape is similar to that reported for the polypeptide poly(L-1-naphthylalanine) although the molar ellipticities of the transitions for the (MeNp)(Pe)C sample are much smaller.[16] These results provide evidence for a helical arrangement of chromophores along the (MeNp)(Pe)C chain and suggest that this polymer may adopt a helical secondary structure in solution. The apparent weakness of the CD signal from (MeNp)(Pe)C may be due to two factors. The naphthyl chromophore is separated from the cellulose backbone by four bonds through which molecular rotations can occur. This may result in a reduction in the helical order of chromophores along the cellulose backbone. It is also possible that the chromophores on adjacent monomer units are distant from each other, resulting in a weakening of the exciton interaction.

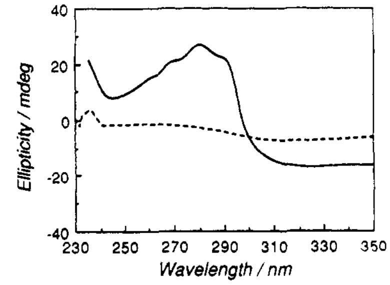


Figure 9. CD spectra in the aromatic region for (MeNp)(Pe)C at temperatures of 25 (solid line) and 120 °C (dashed line).

The arrangement of (MeNp)(Pe)C in a tertiary structure such as a chiral nematic liquid crystal also influences the observed optical activity of the naphthalene chromophores. As discussed previously, (MeNp)(Pe)C forms a thermotropic liquid crystalline phase which arranges the naphthalene chromophores into a macroscopic helicoidal arrangement. It has been shown previously that the observed chiroptical activity of the phenyl chromophores of the tritylalkylcellulose derivatives changes dramatically upon formation of a lyotropic mesophase. This change is due to the organization of the polymer molecules into a chiral nematic arrangement, although it is not know whether the circular dichroism actually changes as has been suggested for polypeptides[25] or that the CD is an artifact resulting from the molecular arrangement.[26,27]

The CD spectrum for a thermotropic film of (MeNp)(Pe)C is shown in Figure 9. Comparing the dilute-solution CD spectrum in Figure 8 with that in Figure 9, it is evident that several changes have occurred. The ^1L_a transition around 281 nm shows positive ellipticity when observed in the thermotropic liquid crystalline state in contrast to the dilute-solution spectrum where this transition showed negative ellipticity. The ^1B_b transition appears to show positive ellipticity at shorter wavelengths when observed in the liquid crystalline state. The negative base line in Figure 9 is due to the broad chiral nematic reflection band. The maximum molar ellipticity of the ^1L_a transition is much greater in the liquid crystalline phase than in the dilute-solution phase.

It has been shown that for right-handed chiral nematic liquid crystalline phases of tritylalkylcellulose derivatives, the signs of the aromatic CD bands were opposite to the pitch band.[2] For example, the CD bands for the aromatic transitions of a right-handed chiral nematic structure exhibited positive ellipticity. This result has been confirmed for the thermotropic (MeNp)(Pe)C polymer, where the right-handed chiral nematic mesophase shows positive CD signals for the aromatic chromophores. Heating of the thermotropic (MeNp)(Pe)C mesophase to a temperature of 120 °C results in the destruction of the chiral nematic structure and the formation of an isotropic film. This transition is reflected in the CD spectrum of Figure 9, where the CD signals from the naphthyl chromophores are greatly reduced (dashed line) at 120 °C.

In comparing the ellipticity maxima for the aromatic transitions of tritylalkylcellulose lyotropic mesophases against that for the (MeNp)(Pe)C polymer films, the maximum molar ellipticities appear to be much lower for the (MeNp)(Pe)C sample.[2,4,5] As stated above, the (MeNp)(Pe)C thermotropic films tend to form a focal conic texture. This results in a broadening of the chiral nematic reflection band and a distortion of the macroscopic

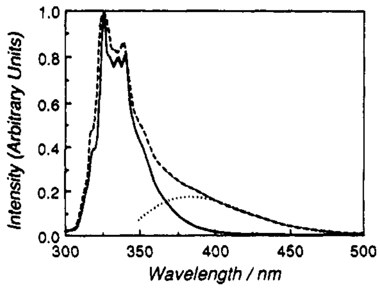


Figure 10. Normalized fluorescence spectra of 1-methylnaphthalene (solid line) and 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose ((MeNp)(Pe)C) (dashed line) in cyclohexane. The dotted line is the difference of the two spectra.

helical arrangement of the chromophores and polymer chains characteristic of the planar texture. It may also be that the thermotropic melts are significantly less ordered than the lyotropic solutions examined previously, and this reduces the chiroptical activity of the naphthalene chromophores.

It has been reported that the fluorescence spectrum for the polypeptide poly(L-1-naphthylalanine) consists essentially of the monomer emission with a very weak excimer emission.[16] The lack of an excimer emission has been explained on the basis that the naphthyl groups along the polypeptide backbone are too conformationally restricted to allow for the chromophores to attain a suitable geometry for excimer formation. An increase in the conformationally flexibility of the chromophores allows these groups to attain the geometry for excimer formation and in this case an eximer emission may be observed. Poly(γ-1-naphthylmethyl L-glutamate)[21] and poly(γ-1-naphthylmethyl L-aspartate)[28] have naphthalene chromophores that are separated from the polypeptide backbone by a flexible spacer. In both of these cases the naphthalene chromophores show strong excimer emissions in their fluorescence spectra and do not show exciton splitting in the CD spectra. The absence of exciton splitting of the CD bands is likely the result of the conformational irregularity of the chromophores along the polymer backbone of these polypeptides.

The normalized fluorescence spectra for (MeNp)(Pe)C and 1-methylnaphthalene in cyclohexane are shown in Figure 10. The (MeNp)(Pe)C spectrum appears to exhibit two bands. The monomer emission appears as a strong band centered around 335 nm with a weak tailing of the spectrum (as evident in the difference spectrum indicated by the dotted line in Figure 10) that can be attributed to excimer formation between the naphthalene chromophores along the cellulose chain. The apparent weakness of the excimer emission and domination of the monomer emission indicate that the chromophores along the chain are not in a suitable geometry to form excimers or that the chromophores may be too distant from each other to interact strongly.

Conclusions

Alkyl ether derivatives of tritylcellulose have been prepared by the reaction of tritylcellulose, dissolved in DMSO, with an excess of sodium hydroxide and an alkyl iodide. The NMR and IR spectra of these polymers show that high degrees of alkylation can be achieved by this method.

The complete removal of the trityl groups from 6-*O*-trityl-2,3-di-*O*-alkylcellulose derivatives can be accomplished by treating the polymer in chloroform with a stream of hydrogen chloride. The ^{13}C NMR spectrum of the product, 2,3-di-*O*-pentylcellulose, indicates that most of the pentyl substituents are located at positions 2 and 3 of the cellulose anhydroglucose units.

6-*O*-α-(1-Naphthylmethyl)-2,3-di-*O*-pentylcellulose was successfully prepared by reacting 2,3-di-*O*-pentylcellulose in dimethylacetamide with an excess of potassium *tert*-butoxide and 1-(chloromethyl)naphthalene.

The cellulose derivative 6-*O*-α-(1-naphthylmethyl)-2,3-di-*O*-pentylcellulose ((MeNp)(Pe)C) forms a chiral nematic thermotropic liquid crystalline phase that exhibits a reflection band in the visible region of the spectrum. The naphthyl chromophores attached to the cellulose backbone exhibit chiroptical activity in both dilute solution and the liquid crystalline phase. The sign and magnitude of the observed optical activity were found to depend on the phase in which it was measured. Dilute-solution circular dichroism studies indicate that the naphthyl chromophores may be arranged in a helical arrangement along the cellulose backbone as indicated by the splitting of the ^1B_b transition. This suggests that this polymer may have a helical secondary structure in solution, although it is not known if or how such a structure can influence the twist sense of the (MeNp)(Pe)C chiral nematic mesophase.

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