Macromolecules 1990, 23, 1452-1457

(6) Rand, P. B.; Montoya, O. J. SAND86-0638, Sandia National Labs, Albuquerque, NM 1986.
(7) Coudeville, A.; Eyharts, P.; Perrine, J. P.; Rey, L.; Rouillard, R. *J. Vac. Sci. Technol.* **1981**, *18*, 1227.
(8) Castro, A. J. U.S. Patent 4,247,498, 1981.
(9) Kesting, R. E. *Synthetic Polymeric Membranes—A Structural Perspective*; John Wiley & Sons, Inc.: New York, 1985.
(10) Van Aarsten, J. J. *Eur. Polym. J.* **1970**, *6*, 919.
(11) Cahn, J. W. *J. Chem. Phys.* **1965**, *42*, 93.
(12) Aubert, J. H. *J. Cellular Plastics* **1988**, *24*, 132.
(13) Lifshitz, I. M.; Slyozov, V. V. *J. Phys. Chem. Solids* **1961**, *19*, 35.
(14) de Gennes, P. G. *J. Chem. Phys.* **1980**, *72*, 4756.
(15) Mullins, W. W. *J. Appl. Phys.* **1957**, *28*, 333.
(16) Huse, D. A. *Phys. Rev. B* **1986**, *34*, 7845.
(17) Toral, R.; Chakrabarti, A.; Gunton, J. D. *Phys. Rev. Lett.* **1988**, *60*, 2311.
(18) Roland, C.; Grant, M. *Phys. Rev. Lett.* **1988**, *60*, 2657.
(19) McMaster, L. P. *Aspects of Liquid–Liquid Phase Transition Phenomena in Multicomponent Polymeric Systems*; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1975; p 142.
(20) Tomotika, S. *Proc. R. Soc. London* **1935**, *150*, 322.
(21) Voigt-Martin, I. G.; Leister, K.-H.; Rosenau, R.; Knoingsveld, R. *J. Polym. Sci.: Part B Polym. Phys.* **1986**, *24*, 723.
(22) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.
(23) Chou, Y. C.; Goldburg, W. I. *Phys. Rev. A* **1979**, *20*, 2105.
(24) Wong, N.-C.; Knobler, C. M. *Phys. Rev. A* **1981**, *24*, 3205
(25) Fujita, H.; Teramota, A. In *Polymer Compatibility and Incompatibility*; K. Solc, Ed.; Harwood Academic Publishers: Chur, Switzerland, 1982; pp 125-138.
(26) De Groot, S. R. *Thermodynamics of Irreversible Processes*; Interscience Publishing Inc.: New York, 1952.
(27) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; John Wiley and Sons: New York, 1975.
(28) Shinozaki, K.; Van Tan, T.; Saito, Y.; Nose, T. *Polymer* **1982**, *23*, 728.

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Preparation and Chiroptical Properties of Tritylated Cellulose Derivatives

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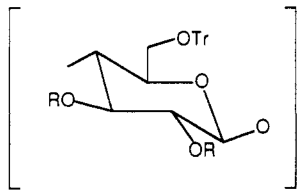
ABSTRACT: Two specifically substituted cellulose derivatives, 6-*O*-trityl-2,3-di-*O*-benzylcellulose (TBzC) and 6-*O*-trityl-2,3-di-*O*-ethylcellulose (TEtC) were found to form lyotropic mesophases in concentrated solution with several organic solvents. The TBzC mesophase in bromoform exhibited cholesteric reflection colors. The cholesteric pitch, measured from the wavelength of apparent circular dichroism of the reflection band, increased with temperature and decreased with increasing polymer concentration. Measurements of the circular dichroism of dilute solutions of TBzC and TEtC showed peaks characteristic of the aromatic substituents, but the sign and magnitude of these peaks changed markedly upon mesophase formation.

Introduction

Cellulose-based liquid crystals have been observed to form both left- and right-handed macroscopic helicoidal structures.[1] In a few rare cases cholesteric inversion or change in the twist sense has been observed to occur as the result of a solvent change,[2,3] chemical modification of the cellulose derivative,[4-6] and change of temperature.[7]

In light of these observations we have begun to study the effects of site-specific cellulose modifications on the optical properties of cellulose mesophases, using (triphenylmethyl)cellulose (tritylcellulose) as a starting material. The heterogeneous preparation of tritylcellulose has been known for many years,[8] and extensive research has shown that the trityl protecting group shows high selectivity for the primary hydroxyl group on the 6-position of the repeating anhydroglucose units composing the cellulose backbone.[9] Following tritylation, selective homogeneous modification of the secondary hydroxyl groups on carbons 2 and 3 of the anhydroglucose units can be achieved. In this work, two selectively modified cellulose ethers have been prepared: 6-*O*-trityl-2,3-di-*O*-ethylcellulose and 6-*O*-trityl-2,3-di-*O*-benzylcellulose,[10] both of which form lyotropic liquid crystals. The incorporation of the trityl groups also provides a useful chromophore for circular dichroism (CD) studies in dilute solution and in the ordered mesophase.



Tr = Triphenyl methyl
R = Benzyl or Ethyl

Circular dichroism has been widely used as a tool in the study of the conformations of biological macromolecules in dilute solution.[11] The CD spectra of polysaccharides is often uninformative because in many cases there are no chromophores with absorption bands above 200 nm, and measurements below 200 nm are more difficult because of restrictions on solvents and instrumentation. Most of the CD work to date has been conducted on polysaccharide derivatives in which chromophore-containing groups have been attached to the carbohydrate backbone. Cellulose for example has been studied

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as its tricarbanilate,[12] and Mukherjee and co-workers have studied the CD spectra of cellulose acetate[13] and other polysaccharide acetates.[14] More recently, Stipanovic and Stevens have measured the vacuum ultraviolet CD of cellulose acetates and have proposed a "pseudohelical" order for these macromolecules in solution.[15]

Although there are many examples of induced optical activity in acetylated carbohydrates,[16-18] there are only a few such examples for carbohydrates substituted with aromatic chromophores.[19,20] Both TEtC and TBzC show optical activity in the spectral region between 200 and 300 nm that can be attributed to the aromatic chromophores on the chain. The chiroptical properties of these polymers are sensitive to temperature, and changes are also observed at high polymer concentrations where the liquid crystalline phase forms.

Experimental Section

Preparation of 6-*O*-Tritylcellulose (TrCell). Into a large Erlenmeyer flask containing 900 mL of a 15% aqueous solution of ammonium hydroxide was added 50 g of cellulose acetate (Eastman, acetyl content 39.5%, ASTM viscosity 45). The mixture was stirred for 19 days at room temperature. Complete deacetylation of the cellulose acetate was verified by the absence of a carbonyl stretching band in the infrared spectrum. The filtered cellulose was added to 300 mL of dry pyridine that was then heated to 80 °C for 3 h and filtered off in order to remove the water. This procedure was repeated three times with anhydrous pyridine. The cellulose was added to 500 mL of anhydrous pyridine and 129 g of triphenylmethyl chloride (2.5 molar equiv) in a 1000-mL round-bottom flask. The flask was equipped with a condenser, stirrer, and drying tube and heated to 95 °C for 26 h. The product was cooled to room temperature and poured into 2000 mL of methanol. The tritylcellulose precipitate was isolated by filtration and washed for 12 h in methanol. After a second washing the precipitate was dried at 100 °C under vacuum. The final yield of the product was 71.5 g or 93%.

Preparation of 6-*O*-Trityl-2,3-di-*O*-benzylcellulose (TBzC). Tritylcellulose (20 g) was allowed to dissolve overnight in 300 mL of dry DMSO. Prior to the alkylation reaction the solution was degassed for 1/2 h with nitrogen. The solution was stirred for 2 h with 49.5 g of powdered sodium hydroxide, and then 75 mL of benzyl chloride was added dropwise over 90 min. The reaction was then heated to 70 °C. Four hours after the initial addition, a further 45 mL of benzyl chloride was added. This was again repeated with 25 mL of benzyl chloride after 16 h of reaction time, following which the reaction was stirred for a further 9 h. The mixture was cooled to room temperature and the product precipitated into 1500 mL of methanol. The product was filtered, washed with water, redissolved in THF, and reprecipitated into water. The product was again dissolved into THF and reprecipitated into methanol and pentane before being dried at 100 °C under vacuum. The final yield of the product was 25.6 g or 89%.

Preparation of 6-*O*-Trityl-2,3-di-*O*-ethylcellulose (TEtC). TEtC was prepared in the same way as TBzC. To a degassed solution of 20 g of tritylcellulose dissolved in DMSO was added 49.5 g of sodium hydroxide. Two hours after the addition, 65 mL of ethyl iodide was added dropwise to the flask at room temperature. Following 3 h of reaction, the solution was heated to 60 °C. Five hours after the first addition of ethyl iodide, a further addition of 20 mL of ethyl iodide was made and the reaction stirred at 50 °C for 19 h. A final addition of 14 mL of ethyl iodide was made and the reaction stirred for 3 h prior to the workup. The product was purified by the same method used for TBzC to give 21 g of TEtC, a yield of 92%.

General Analysis. ^{1}H NMR spectra were measured with a Varian XL200 spectrometer at a frequency of 200 MHz. The spectra for TBzC and TEtC were recorded in chloroform-d_1 with tetramethylsilane as the internal reference. The spectrum for TrCell was recorded in DMSO-d_6 with DMSO used as the internal reference.

Infrared spectra of TBzC and TEtC were recorded on an Analect AQS-18 FTIR spectrometer.

The weight-average molar mass, M_w, of TBzC was measured in dioxane with a Chromatix KMX6 low-angle laser light scattering photometer. Measurement of the Rayleigh factor for each solution was made at a scattering angle of 6–7°. The value of the specific refractive index increment, dn/dc, for TBzC in dioxane measured with a Brice-Phoenix differential refractometer was 0.153, giving a value of 49 500 for M_w.

The density of the TBzC sample was determined with a water and potassium carbonate density gradient, giving a value of 1.21, which is close to the density of benzyl cellulose (1.22).[21] Solution weight fractions were converted to volume fractions from the measured density of TBzC, taking 2.894 as the density of bromoform and assuming no volume change on mixing.

Concentrated Solution Properties. A series of solutions containing 28–88 volume % TBzC in bromoform was prepared by adding approximately 0.3 g of the polymer and appropriate quantities of solvent into small glass vials. The vials were tightly sealed and mixed by repeated inversion in a centrifuge until the contents were uniform. The solutions were allowed to equilibrate for 3 days.

The refractive indices of the TBzC/bromoform solutions were measured with an Abbé refractometer equipped with a thermostated circulating system. Two readings for each concentration were obtained, and each sample was allowed to equilibrate for several minutes prior to each measurement.

CD spectra were recorded with a Jasco J-500 spectropolarimeter equipped with a Mettler FP5 hotstage. The samples for CD measurements were prepared as thin films between glass plates that were tightly sealed with epoxy. The temperature dependence of the reflection wavelength was measured by heating the samples at a constant rate of 0.2 °C/min.

The dilute solution measurements were made by dissolving TBzC and TEtC in either distilled dioxane or spectrograde THF (Aldrich) and measuring the spectra in 1.0- and 0.1-cm quartz solution cells at ambient temperature or in a 1.0-cm quartz liquid cell equipped with an outer jacket through which was passed thermostated water from a Haake-FK circulating system.

Results and Discussion

Cellulose Modification and Characterization. Cellulose, prepared by deacetylation of cellulose acetate, was tritylated with triphenylmethyl chloride in pyridine according to the procedure described by Hearon et al.,[9] and the product, trityl cellulose (TrCell), was isolated and purified. The alkylations at positions 2 and 3 on the anhydroglucose units of tritylcellulose required a suitable solvent. Tritylcellulose was found to dissolve quite readily in DMSO, and thus the alkylating conditions developed by Nakano et al.[22,23] were utilized. Tritylcellulose solutions were degassed, and a 12.5 M excess of powdered sodium hydroxide per mole of hydroxyl groups was added, followed by an equivalent molar quantity of benzyl chloride or ethyl iodide, to give 6-*O*-trityl-2,3-di-*O*-benzylcellulose (TBzC) or 6-*O*-trityl-2,3-di-*O*-ethylcellulose (TEtC), respectively. The products were isolated and purified by precipitation from methanol.

TrCell and TBzC showed very similar ^{1}H NMR spectra with broad signals in the regions 2.6–5.1 and 6.7–7.6 ppm. The signals in the region 2.6–5.1 ppm are assigned to the cellulose backbone protons[24] in addition to the benzylic methylene protons in the case of TBzC. The signals at 6.7–7.6 ppm are assigned to the aromatic trityl protons in addition to the benzyl aromatic protons in the case of TBzC. The ^{1}H NMR spectrum of TEtC also showed the same spectral features as TrCell and TBzC with the exception of a broad signal in the region 0.6–1.4 ppm that can be assigned to the methyl groups on the ethyl side chains. The methylene groups on the ethyl side chains were located in the region 2.5–4.5 ppm.

Comparison of the integrated aromatic proton signal with the backbone proton and side chain proton signals

Table I
Degrees of Substitution for TrCell, TEtC, and TBzC

polymer	6-substituent	DS	2,3-substituent	DS	total DS
TrCell	trityl	0.97			0.97
TBzC	trityl	0.97	benzyl	1.9	2.9
TEC	trityl	0.97	ethyl	1.9	2.9

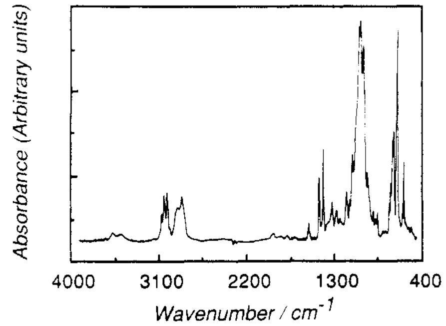

Figure 1. Infrared spectrum of TBzC film (~17 μm thick).

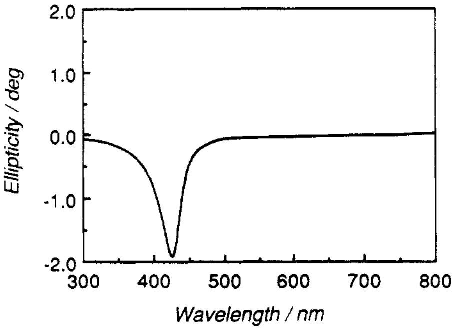

Figure 2. Apparent CD spectra of TBzC in bromoform at a concentration of 29.3 mass % polymer at 35 °C.

enabled the calculation of the trityl and side chain degrees of substitution (DS). Results are shown in Table I. The DS for the trityl group is approximately one, as observed by Hearon et al.[9] The unreacted hydroxyl groups in the trityl cellulose were almost completely substituted by the alkylating reactions, resulting in a total DS of approximately 2.9. These results agree well with the IR spectrum for TBzC and TEtC. Figure 1 shows the IR spectra for TBzC. It is obvious from the magnitude of the hydroxyl absorption band at 3500 cm^{-1} that almost complete substitution of the hydroxyl groups has occurred.

The weight average molecular weight (M_w) for TBzC of 49 500 corresponds to an average degree of polymerization (DP) of 84.

Optical Properties. Highly concentrated solutions of TrCell, TBzC, and TEtC were observed as thin films in a polarizing microscope with crossed polarizers. The TrCell solutions showed no clear optical anisotropy and formed gels rather than liquid crystals in concentrated solution with THF or DMSO. TBzC and TEtC both displayed optical anisotropy and liquid crystalline textures at high concentrations in several organic solvents. TBzC solutions also displayed iridescent colors at certain concentrations, but TEtC solutions did not show any iridescent colors and it is assumed that the cholesteric reflection for this system is outside the visible region of the spectrum.

Cholesteric liquid crystals may reflect left- or right-handed circularly polarized light depending on the handedness of the supramolecular helicoidal structure. This results in an apparent CD peak at the wavelength of the selective reflection. Figure 2 shows the CD spectrum for a thin layer of TBzC dissolved in bromoform at a concentration of 29.3 mass % TBzC. The spectrum was measured at a temperature of 35 °C and clearly shows a strong negative band at 429 nm, indicating that TBzC forms a right-handed cholesteric structure in bromoform. Mesophases of TBzC were also prepared in methylene chloride, chloroform, 1,1,2-trichloroethane, benzene, toluene, chlorobenzene, and THF; in all cases where iridescent colors were observed, the cholesteric structure was found to have a right-handed twist sense. This result is in contrast to the lyotropic polybenzyl glutamate systems where the cholesteric twist sense is strongly dependent on the nature of the solvent.[25]

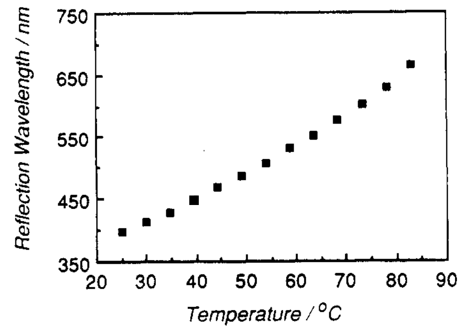

Figure 3. Reflection maxima as a function of temperature for TBzC in bromoform (29.3 mass % polymer).

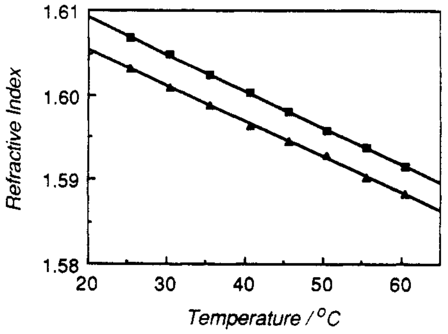

Figure 4. Refractive index as a function of temperature for TBzC in bromoform (29.3 mass % polymer).

The position of the reflection maximum for the cholesteric mesophase TBzC/bromoform moves to longer wavelengths as the temperature is increased. This result has also been observed for other cellulose derivatives exhibiting a right-handed twist sense.[1,26] Figure 3 shows the shift in the wavelength of the reflection maximum as a function of temperature for the TBzC/bromoform mesophase at a concentration of 29.3 mass % TBzC.

According to the theory proposed by deVries,[27] the pitch, P, of the supramolecular helix can be related to the reflection wavelength, λ_0, by the average refractive index of the mesophase, $\bar{n}$, according to the relationship

$$\lambda_0 = \bar{n}P \qquad (1)$$

In order to determine the pitch of the cholesteric mesophase as a function of temperature, it is necessary to determine the average refractive index over the same temperature range. Figure 4 shows the temperature dependence for the refractive indices obtained for a cholesteric mesophase consisting of a 29.3 mass % solution of TBzC in bromoform. At each temperature two boundaries were visible in the Abbé refractometer, each corresponding to a refractive index. The two refractive indices n_x and n_z (across and normal to the refractometer plate, respectively) were easily distinguishable with a polarizing filter.[28] The values for n_x and n_z were measured with the privileged direction of the polarizer parallel and

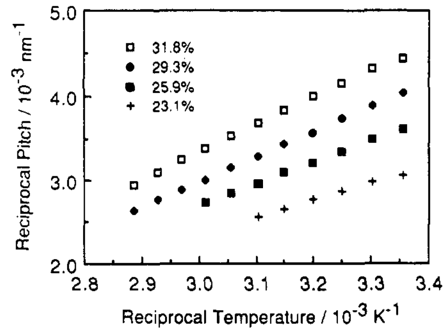

Figure 5. Inverse pitch against inverse temperature for TBzC in bromoform at concentrations of 23.1, 25.9, 29.3, and 31.8 mass % polymer.

perpendicular to the line separating the two fields, respectively. The measured birefringence ($n_x - n_z$) was found to remain relatively constant at 0.0035 ± 0.0002 over the observed temperature range. The average refractive index, $\bar{n}$, for the cholesteric layer is taken as[29]

$$\bar{n} = (2n_x + n_z)/3 \qquad (2)$$

From the values for the average refractive index and reflection wavelength as a function of temperature, the change in the cholesteric pitch was calculated as a function of temperature.

Kimura and co-workers have derived an eq 3 for the dependence of pitch on temperature for a lyotropic cholesteric phase consisting of a system of helical grooved rodlike macromolecules.[30,31] Here, L and D are the length

$$\frac{2\pi}{P} = \frac{24\lambda\Delta}{nLD}cf(c)[(Tn/T) - 1] \qquad (3)$$

and diameter of the rod, λ is a numerical factor, Δ is the height of the ridge of the coil, c is the concentration, $f(c)$ is the concentration function

$$f(c) = [1 - (c/3)]/(1 - c)^2 \qquad (4)$$

and T_N is the nematic temperature where the pitch approaches infinity. According to the theory there should be a linear relationship between the inverse pitch and inverse temperature. Results for the TBzC/bromoform cholesteric mesophase at four different concentrations are shown in Figure 5. In each case, an excellent linear relationship between the inverse pitch and inverse temperature is obtained.

The Kimura theory also predicts the concentration dependence of the pitch. The difficulty in applying this theory to the system TBzC/bromoform is that the value of the nematic temperature, T_N, cannot be determined as a function of concentration since no cholesteric inversion has yet been observed for this system. Several workers[25,32] have found that the cholesteric twisting power is an increasing function of the polymer concentration. At a fixed temperature the relationship between the pitch and the polymer concentration has been empirically described in the form

$$P^{-1} \propto c^n \qquad (5)$$

For the polybenzyl glutamates, the exponent, n, is in the range of 1–2 depending on the temperature of measurement.[25]

To determine the concentration dependence of the pitch, it was necessary to first determine the solution refractive index as a function of the volume fraction of TBzC in bromoform (Table II). A distinct birefringent phase appears at polymer concentrations greater than 58 volume % TBzC. The magnitude of the birefringence was observed to increase with polymer concentration in agreement with results obtained for other cellulose-based mesophases.[28,33,34]

Table II
Refractive Index as a Function of Concentration for TBzC in Bromoform at 30 °C

vol fractn of TBzC in soln	refractive index		birefringence × 10^3
0.282	1.5974		0.0
0.332	1.5983		0.0
0.376	1.5989		0.0
0.428	1.5995		0.0
0.464	1.6002		0.0
0.551	1.6025	1.6003	2.2
0.586	1.6033	1.6008	2.5
0.619	1.6035	1.6007	2.8
0.653	1.6042	1.6011	3.1
0.686	1.6047	1.6012	3.5
0.701	1.6049	1.6009	4.0
0.761	1.6052	1.6013	3.9
0.823	1.6064	1.6022	4.2
0.875	1.6067	1.6017	5.0

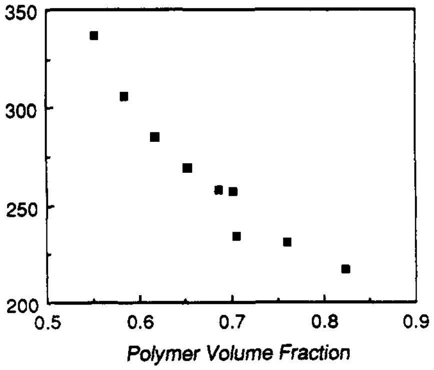

Figure 6. Cholesteric pitch against polymer fraction for TBzC in bromoform at 30 °C.

The concentration dependence of the pitch is shown in Figure 6. The pitch was observed to decrease in a nonlinear fashion as the polymer concentration was increased from 55 to 82 vol % TBzC. Attempts to fit the data to eq 5 were unconvincing. Measurements of the pitch at higher polymer concentrations were not possible because the reflection wavelength drops below 280 nm, where the benzene chromophores on the cellulose backbone begin to absorb the incident radiation. In fact, CD peaks due to benzene ring absorption are detected in the ultraviolet region for dilute TBzC solutions in THF.

Dilute Solution Optical Activity. Achiral chromophores may display chiroptical properties when bound to chiral molecules[11] such as polysaccharides. The magnitude of the observed optical activity of the bound molecules depends on the asymmetry of the site and the conditions under which it is bound. If for example an absorbing chromophore is free to assume many orientations relative to the asymmetric binding site, then the optical activity may become too weak to observe.

Results presented below show that the symmetric triphenylmethyl group displays induced optical activity when attached to the 6-position of the cellulose derivatives TEtC and TBzC.

The absorption spectrum for benzene and benzene derivatives have been thoroughly discussed.[35,36] In general, the near-ultraviolet spectra of alkyl-substituted benzene derivatives consists of three absorption bands. A weak band usually exhibiting fine structure appears in the region 260–280 nm (${}^1L_b$ band) and two stronger bands in the

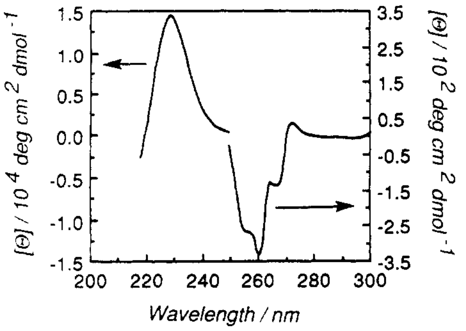

Figure 7. Dilute solution CD spectra for TEtC dissolved in THF.

regions 200–220 and 180–190 nm (^1L_a and ^1B_a bands, respectively).

The ultraviolet spectrum of TEtC in THF showed a band centered at 259 nm that was found to display fine structure consistent with the reported absorption spectrum for triphenylcarbitol.[37] The ^1L_a and ^1B_a bands appear as broad peaks below 247 nm, but the solvent cutoff and band overlap obscured the peak maximum. TBzC showed spectral features similar to TEtC.

The CD spectrum for TEtC dissolved in THF is shown in Figure 7. The ^1L_b band appears as a peak showing fine structure with negative ellipticity centered at 261 nm. A small peak at 272 nm also belongs to the ^1L_b transition. A large positive peak with a maximum at 229 nm may be assigned to the ^1L_a transition.

These results may be compared to the CD spectra recorded for (−)-poly(triphenylmethyl methacrylate).[38] Both spectra are essentially identical, except that the CD spectrum of the methacrylate polymer shows an additional positive peak at 210 nm corresponding to the n,π* transition for the carbonyl group.

The observation of induced optical activity from the trityl group in TEtC is perhaps unexpected because the absorbing chromophores are separated from the nearest asymmetric center by four bonds. The induced optical activity must thus be due to steric interactions between the trityl group and the cellulose backbone and possibly between adjacent trityl groups on the chain, which place limitations on bond rotation. This argument has been used to explain the increase in the Cotton effect observed from the carbanilyl substituents in 6-trityl-2,3-dicarbanilylcellulose[19] and the observation of optical activity from tyrosine residues in some polypeptides. The aromatic side chain residues of poly-L-tyrosine[39] and the aromatic substituent in phenyl alanine[40] give rise to induced optical activity, the magnitude of which is sensitive to temperature. In both of these cases it was found that the aromatic side chains have some degree of motion that decreases with a decrease in temperature. Figure 8 shows a plot of the molar ellipticity against temperature for the 261-nm peak for TEtC in dioxane. It can be seen that as the temperature is decreased from 95 to 10 °C, the ellipticity of the peak at 261 nm increases by 80%. The maximum ellipicity of the 261-nm band for TBzC also increased by 70% as the temperature was lowered from 93 to 10 °C.

The absorption spectra of TEtC was measured as a function of temperature to determine whether the benzene ring absorbance at 261 nm also changed as a function of temperature. It was found that the maximum absorbance of the 261-nm peak did increase 7%, due to the sharpening of the bands[41] as the temperature was lowered from 93 to 11 °C, but this increase is very small compared to the large increase in molar ellipticity. These results suggest that at temperatures as high as 90 °C the benzene groups on the trityl moiety still experience some restriction to rotation.

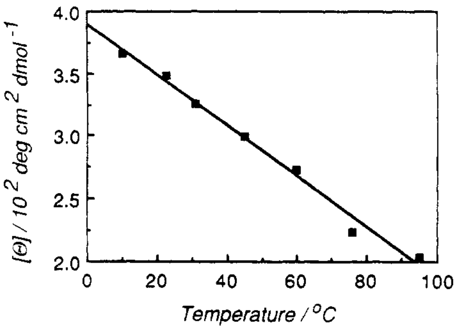

Figure 8. Effect of temperature on the molar ellipticity of TEtC in dioxane.

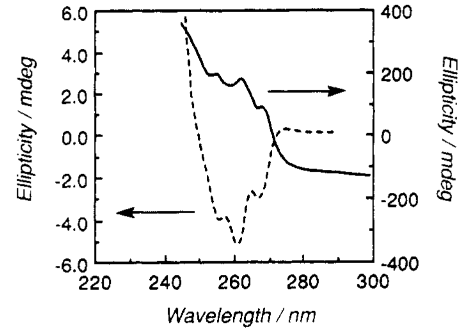

Figure 9. CD spectrum for TBzC in THF at concentrations of 30 (broken line) and 49 (solid line) mass % polymer (0.1-mm layers between quartz plates).

As the concentration of TBzC in THF is increased, the CD spectra also changes. Figure 9 shows the CD spectra for thin layers of TBzC solutions. The spectra were recorded between 240 and 300 nm at polymer concentrations of 30 and 49 mass % TBzC in tetrahydrofuran (THF). The spectrum for 30% polymer shows the same spectral features as the most dilute solution discussed above. At 49% TBzC, the solution forms an anisotropic cholesteric liquid crystalline phase. The CD spectrum for TBzC dissolved in THF at a concentration of 49% is quite different from that recorded at a concentration of 30%. The most noticeable difference is that the ^1L_b band now appears as a shoulder on the ^1L_a band and shows positive ellipticity, in contrast to the dilute solution spectrum in which the ^1L_b band showed negative ellipticity. In addition to the change in sign, the ^1L_b band shows a large change in ellipticity at 263 nm, increasing from −5 to 200 mdeg as the polymer concentration is increased from 30 to 49%. The general shapes of the absorption spectra for the two concentrations are very similar.

The difference in the apparent CD spectra in the isotropic and anisotropic phases may be due to the fact that, in the latter phase, the chromophores are ordered in a macroscopic three-dimensional helicoidal array. In the isotropic phase, this macroscopic chirality is absent, and the aromatic substituents are perturbed by the local chirality associated with the cellulose backbone. The magnitude and sign of the ^1L_b transition is thus different in the two phases. The contribution from the helicoidal array has been observed previously for polybenzyl liquid crystalline solutions[25] (although in this case the CD signal is absent in the dilute solutions).

However, the unusual change in peak magnitude and sign may be due to artifacts produced from the coupling of an anisotropic sample with the imperfect optics and

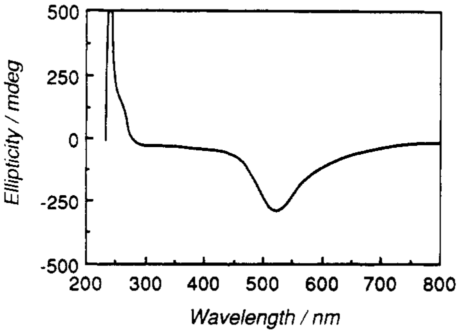

Figure 10. CD spectra for TBzC in THF at a concentration of 45 mass % polymer (0.1-mm layer between quartz plates).

electronics inherent in CD spectrometers. These problems have been addressed by Jensen,[42] Shindo,[43] and Davidson.[44] These workers have illustrated the problems associated with measuring the actual CD spectra of anisotropic systems that are linearly dichroic and linearly and circularly birefringent. It is difficult to assess these contributions to the observed optical activity in cholesteric mesophases. Shindo[43] has discussed the problems associated with the measurement of CD spectra from cholesteric liquid crystalline phases.

Figure 10 shows the entire CD spectrum between 200 and 800 nm, for TBzC dissolved in THF at a concentration of 45 mass percent TBzC. Both the aromatic dichroic band beginning at 284 nm and the cholesteric reflection band at 519 nm are evident.

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References and Notes

(1) Vogt, U.; Zugenmaier, P. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 1217.
(2) Zugenmaier, P.; Haurand, P. *Carbohydr. Res.* **1987**, *160*, 369.
(3) Siekmeyer, M.; Zugenmaier, P. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 511.
(4) Pawlowski, W. P.; Gilbert, R. D.; Fornes, R. E.; Purrington, S. T. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 2293.
(5) Guo, J. X.; Gray, D. G. *Macromolecules* **1989**, *22*, 2086.
(6) Ritcey, A. M.; Holme, K. R.; Gray, D. G. *Macromolecules* **1988**, *21*, 2914.
(7) Yamagishi, T.; Fukuda, T.; Miyamoto, T.; Watanabe, J. *Cellucon 88 Japan Proceedings*; Ellis Horwood: Chichester, in press.
(8) Helferich, B.; Koester, H. *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 587.
(9) Hearon, W. M.; Hiatt, G. D.; Fordyce, C. R. *J. Am. Chem. Soc.* **1943**, *65*, 2449.
(10) 6-*O*-Trityl-2,3-di-*O*-benzylcellulose has been previously prepared by a different method, Bauer, S.; Tihlarik, K. *Carbohydr. Res.* **1970**, *15*, 418.
(11) Beychok, S. *Science* **1966**, *154*, 1288.
(12) Bittiger, H.; Keilich, G. *Biopolymers* **1969**, *7*, 539.
(13) Mukherjee, S.; Marchessault, R. H.; Sarko, A. *Biopolymers* **1972**, *11*, 291.
(14) Mukherjee, S.; Marchessault, R. H.; Sarko, A. *Biopolymers* **1972**, *11*, 303.
(15) Stipanovic, A. J.; Stevens, E. S. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1983**, *37*, 277.
(16) Listowski, I.; Avigad G.; Englard, S. *Carbohydr. Res.* **1968**, *8*, 205.
(17) Beychok, S.; Ashwell G.; Kabat, E. A. *Carbohydr. Res.* **1971**, *17*, 19.
(18) Lewis, D. G.; Johnson, W. C. *Biopolymers* **1978**, *17*, 1439.
(19) Pfannemülle, B.; Berg, A. *Makromol. Chem.* **1979**, *180*, 1201.
(20) Bishop, E. O.; Chittenden, G. J. F.; Guthrie, R. D.; Johnson, A. F.; McCarthy, J. F. *Chem. Commun.* **1965**, *5*, 93.
(21) Kline, G. M., Ed. *Analytical Chemistry of Polymers*; Interscience: New York, 1962; Chapter 1.
(22) Isogai, A.; Ishizu, A.; Nakano, J. *J. Appl. Polym. Sci.* **1984**, *29*, 2097.
(23) Isogai, A.; Ishizu, A.; Nakano, J. *J. Appl. Polym. Sci.* **1986**, *31*, 341.
(24) Ho, F. F.; Klosiewicz, D. W. *Anal. Chem.* **1980**, *52*, 913.
(25) Uematsu, I.; Uematsu, Y. *Adv. Polym. Sci.* **1984**, *59*, 37.
(26) Laivins, G. V.; Gray, D. G. *Polymer* **1985**, *26*, 1435.
(27) deVries, H. *Acta Crystallogr.* **1951**, *4*, 219.
(28) Laivins, G. V.; Gray, D. G. *J. Appl. Polym. Sci.* **1987**, *33*, 137.
(29) LeFèvre, R. I. W. *Adv. Phys. Chem.* **1965**, *3*, 1.
(30) Kimura, H.; Hosino, M.; Nakano, H. *J. Phys.* (*Les Ulis, Fr.*) **1979**, *40*, C3.
(31) Kimura, H.; Hosino, M.; Nakano, H. *J. Phys. Soc. Jpn.* **1982**, *51*, 1584.
(32) Robinson, C.; Ward, J. C.; Beevers, R. B. *Discuss. Faraday Soc.* **1958**, *25*, 29.
(33) Steinmeier, H.; Zugenmeier, P. *Carbohydr.* Res. **1988**, *173*, 75.
(34) Suto, S.; Ise, H.; Karasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1515.
(35) Stevenson, P. E. *J. Chem. Educ.* **1964**, *41*, 234.
(36) Crabbé, P.; Klyne, W. *Tetrahedron* **1967**, *23*, 3449.
(37) Orndorff, W. R.; Gibbs, R. C.; McNulty, S. A.; Shapiro, C. V. *J. Am. Chem. Soc.* **1927**, *49*, 1541.
(38) Kanoh, S.; Kawaguchi, N.; Sumino, T.; Hongoh, Y.; Suda, H. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 1603.
(39) Damle, V. N. *Biopolymers* **1970**, *9*, 937.
(40) Horowitz, J.; Strickland, E. H.; Billups, C. *J. Am. Chem. Soc.* **1969**, *91*, 184.
(41) Sklar, A. L. *J. Chem. Phys.* **1937**, *5*, 669.
(42) Jensen, H. P.; Schellman, J. A.; Troxell, T. *Appl. Spectrosc.* **1978**, *32*, 192.
(43) Shindo, Y.; Nakagawa, M.; Ohmi, Y. *Appl. Spectrosc.* **1985**, *39*, 860.
(44) Davidsson, A.; Norden, B.; Seth, S. *Chem. Phys. Lett.* **1980**, *70*, 313.

Registry No. TBzC, 96956-20-6; TEtC, 124354-87-6; TrCell, 9032-45-5; cellulose, 9004-34-6; triphenylmethyl chloride, 76-83-5; benzyl chloride, 100-44-7; ethyl iodide, 75-03-6.