

Preparation and Chiroptical Properties of a Regioselectively Substituted Cellulose Ether with PEO Side Chains

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ABSTRACT: A novel regioselectively substituted cellulose ether with poly(ethylene oxide) (PEO) side chains, 6-O-trityl-2,3-O-PEOcellulose (TPEOCELL), was synthesized and characterized. The polymer is a thermotropic liquid crystalline material and forms a right-handed chiral nematic phase which reflects visible light at room temperature. The effect of salt on its cholesteric liquid crystallinity was investigated with CD spectroscopy. It has been found that adding small amounts of LiCF_3SO_3 to TPEOCELL ($[\text{Li}]/[\text{O}] < 0.0145$) causes a significant untwisting of the cholesteric structure. The effects of other salts on the cholesteric properties of TPEOCELL were also examined.

Introduction

Cellulose, poly(1,4'-anhydro- β -D-glucopyranose), is one of the most abundant, naturally occurring polymers used commercially. The first report on the cholesteric liquid crystalline behavior of (hydroxypropyl)cellulose (HPC) in aqueous solutions¹ spurred considerable interest in this old material, leading to numerous reports of cellulose derivatives which form chiral nematic phases in concentrated solutions or in bulk.

Cholesteric liquid crystals are well-known for their unique optical properties arising from the helicoidal supramolecular structures characterized by a pitch (P) and handedness. A cholesteric liquid crystal may selectively reflect left- or right-handed circularly polarized light with the handedness determined by its twist sense, and the wavelength of reflection (λ) is related to its pitch (P) by the de Vries equation²

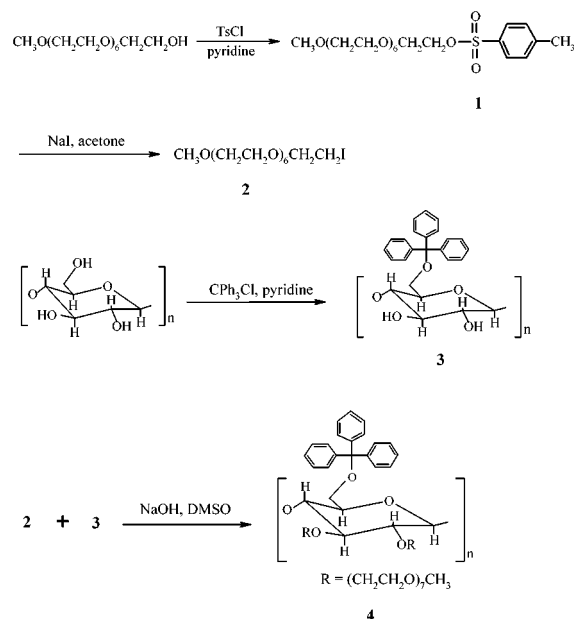
$$\lambda = \bar{n}P \sin \theta$$

where \bar{n} is the average refractive index of the mesophase and θ is the angle between the incident light and the cholesteric plane. This forms a basis for a circular dichroism (CD) spectrum of a chiral nematic liquid crystal, which may give an apparent negative CD band for a right-handed cholesteric mesophase or an apparent positive CD band for a left-handed cholesteric mesophase.

Triphenylmethylcellulose (tritylcellulose) is an important material in the preparations of regioselectively substituted cellulose derivatives. It has been found that the alkylated and benzylated derivatives of tritylcellulose form chiral nematic phases in a variety of organic solvents, with the pitch and handedness depending on the side chain chemistry, e.g., structure and degree of substitution (DS).^{3,4} However, none of them was reported to exhibit thermotropic liquid crystallinity, probably due to the high softening temperatures of those polymers.⁴

In this paper, we report the preparation of a novel tritylcellulose ether having poly(ethylene oxide) (PEO) side chains, TPEOCELL, which is thermotropic and

Scheme 1. Synthesis of TPEOCELL



forms a chiral nematic mesophase at room temperature. More interestingly, the remarkable complexing ability of PEO side chains makes the polymer a good solid solvent for salt and thus provides a good opportunity to examine the influence of salt on the cholesteric properties, which has not been reported in a thermotropic polymer system so far.

Experimental Section

Materials. Cellulose acetate (acetyl content 39.8 wt %, $M_n = 30\,000\text{ g mol}^{-1}$), poly[(ethylene glycol) methyl ether] ($M_n = 350\text{ g mol}^{-1}$) (PEG-350), *p*-toluenesulfonyl chloride (tosyl chloride), triphenylmethyl chloride, sodium iodide, and anhydrous acetonitrile were used as received from Aldrich. Lithium triflate (LiCF_3SO_3), sodium triflate (NaCF_3SO_3), and copper(II) triflate ($(\text{CF}_3\text{SO}_3)_2\text{Cu}$) were supplied from Adrich, and lithium perchlorate (LiClO_4) was supplied from Fluka-Garantie; all the salts were dried at 373 K for 4 h in vacuo prior to use. Dimethyl sulfoxide (DMSO), pyridine, and acetone were dried and distilled using standard procedures.⁵

Synthesis. TPEOCELL was synthesized using a multistep procedure illustrated in Scheme 1. Here the PEG-350 is simply

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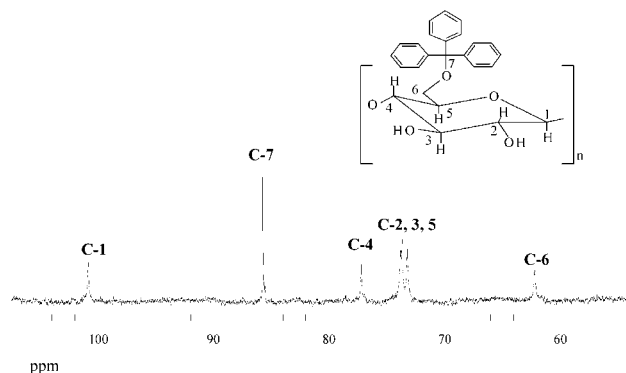


Figure 1. ^{13}C NMR spectrum of the backbone carbon region of tritylcellulose in d_6 -DMSO at 95 $^{\circ}\text{C}$ (12 032 scans were accumulated).

represented as $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_6\text{CH}_2\text{CH}_2\text{OH}$, but its molecular structure is quite polydisperse and so are its derivatives.

Methoxypoly(ethylene oxide) Tosylate (PEO-350 Tosylate) (1). PEG-350 (50 g, 0.14 mol) was added to anhydrous pyridine (20 mL), and the solution was stirred at 273–278 K in an ice bath under nitrogen. Tosyl chloride (41 g, 0.21 mol) was added in several portions; then the slurry was stirred at this temperature for 4 h, after which time it was diluted with dichloromethane (100 mL) and left at room temperature overnight with continual stirring. The mixture was diluted with dichloromethane (300 mL), and the organic phase was washed with water (2×200 mL), diluted HCl aqueous solution (200 mL), and saturated sodium bicarbonate aqueous solution (200 mL) subsequently and then dried over magnesium sulfate. Removal of the solvent yielded a colorless liquid. Yield: 94%. IR: 1595, 1454, 1373, 1176, 1108, 816 cm^{-1} . ^1H NMR (CDCl_3): δ (ppm) 2.30 (s, 3H, Ar-CH₃), 3.18 (s, 3H, -OCH₃), 3.30–3.65 (m, 28H, -CH₂-O-), 7.10–7.70 (2 \times d, 4H, Ar-H).

Methoxypoly(ethylene oxide) Iodide (PEO-350 Iodide) (2). Sodium iodide (80 g, 4 mol equiv) was added to a stirred solution of PEO-350 tosylate (68 g, 0.13 mol) in dry acetone (400 mL), and the mixture was then refluxed for 24 h under nitrogen. The acetone was removed; chloroform (500 mL) and water (300 mL) were added to the solid mixture. The separated organic phase was washed with dilute sodium thiosulfate aqueous solution (300 mL), water (2×300 mL), and saturated NaHCO₃ aqueous solution (300 mL) subsequently and then clarified with silica gel before being dried over magnesium sulfate. Removing the solvent gave a slightly yellow liquid. Yield: 86%. IR: 2870, 1109 cm^{-1} . ^1H NMR (CDCl_3): δ (ppm) 3.05–3.15 (t, 3H, I-CH₂-), 3.18 (s, 3H, -OCH₃), 3.30–3.60 (m, 26H, -O-CH₂-).

6-O-Tritylcellulose (3). To obtain a derivative that can afford a relatively easy alignment of molecules, a low-molecular-weight cellulose was required. Cellulose acetate ($M_n = 30\,000$ g mol⁻¹, 10 g) was stirred in a NaOH (10 g) solution in methanol (500 mL) for 4 h at room temperature, and the mixture was neutralized. The filtered cellulose was washed with methanol and water thoroughly before being dried in vacuo overnight at 353 K. The complete deacetylation was confirmed by the disappearance of the carbonyl peak in the IR spectrum. The preparation of 6-O-tritylcellulose followed a procedure described by Harkness and Gray.³ Elemental analysis (%): C, 75.20; H, 5.94. The regioselectivity of this reaction was confirmed by its ^{13}C NMR spectrum recorded in d_6 -DMSO, and here only the cellulose backbone carbon region is shown in Figure 1, which will be discussed later.

6-O-Trityl-2,3-O-PEOcellulose (TPEOCELL) (4). 6-O-Tritylcellulose (1 g, 0.005 mol [OH]) was dissolved in anhydrous DMSO (50 mL) at room temperature under nitrogen, and powdered sodium hydroxide (2 g, 0.050 mol) was added. The mixture was stirred for 2 h, followed by the addition of PEO-350 iodide (23.6 g, 0.050 mol) in anhydrous DMSO (20 mL) over a period of $\frac{1}{2}$ h, and then was heated to 343 K with the stirring continued for 48 h under nitrogen. Most of the

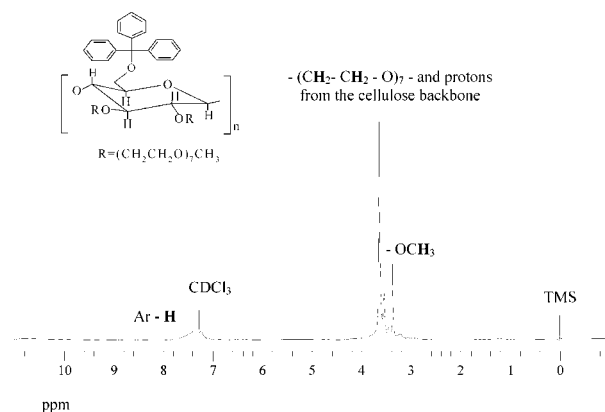


Figure 2. ^1H NMR spectrum of TPEOCELL.

DMSO was removed by vacuum distillation; the viscous solution was precipitated into diethyl ether to yield a sticky mass which was dissolved in chloroform (300 mL). The chloroform phase was washed subsequently with diluted HCl aqueous solution (200 mL), water (2×200 mL), and saturated NaHCO₃ aqueous solution (200 mL), then clarified with silica gel, and dried over magnesium sulfate. The solution was concentrated and precipitated into diethyl ether; the resultant product was purified by dissolution–precipitation three times before being dried to constant weight in vacuo at room temperature. Yield: 2.3 g. IR: 1597, 1489 1449, 1108, 1043, 706 cm^{-1} . ^1H NMR (CDCl_3) is shown in Figure 2.

Preparation of Polymer–Salt Complexes. The polymer–salt complexes were prepared by dissolving appropriate amounts of salt and polymer in anhydrous acetonitrile and slowly evaporating the solvent in a dry nitrogen atmosphere. The complexes were dried under vacuum. The concentration of the salt in the complexes is described as the molar ratio of cations to the oxygens in the polymer chain, $[\text{M}]/[\text{O}]$ (where M is referred to the cations). The oxygens include those in the PEO side chains as well as those in the cellulose backbone, although the latter might play a less important role in the ion coordinations.

Characterization. IR spectra were recorded on a Perkin-Elmer RX FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz and a Bruker DPX 400 MHz spectrometer, respectively. Elemental analysis was performed using an Exeter CE-440 elemental analyzer.

The thermal properties of TPEOCELL were examined using a differential scanning calorimeter (a DSC 2010 TA instrument) at a heating rate of 10 K min⁻¹ in a nitrogen atmosphere. The polarizing microscopy observations were made on an Olympus BH-2 equipped with a Linkam PR600 hot stage. The samples were prepared by placing a small amount of TPEOCELL or complex between a glass slide and a coverslip, which was then heated to ~ 353 K for a few minutes and pressed into a thin film. The photographs were taken after the samples were allowed to equilibrate for 1 month in a desiccator.

The CD spectra were recorded using a Jasco 600 spectropolarimeter at a scanning rate of 50 nm min⁻¹ at room temperature. The samples were prepared in the form of a thin film (~ 50 μm) using the same procedure as used for polarizing microscopy and allowed to equilibrate for 1 week in a desiccator before the spectra were recorded. The average refractive indices, \bar{n} , were measured at room temperature with an Abbé refractometer.

Results and Discussion

Synthesis. The high regioselectivity of tritylation of cellulose has been intensively studied either in a heterogeneous or a homogeneous condition.^{6–8} Heaton et al.⁶ reported that at least 90% of the primary hydroxy groups were tritylated for a sample with a DS of 1.03 prepared via a heterogeneous reaction. This was verified

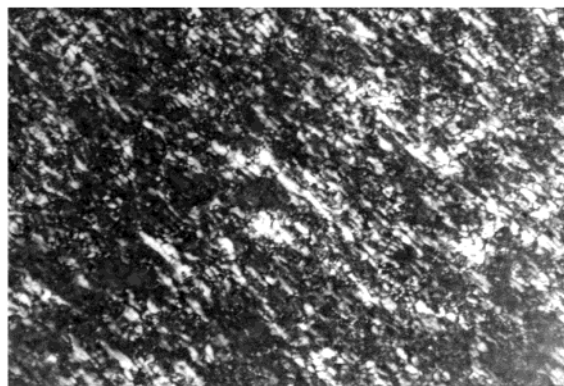


Figure 3. Optical texture of TPEOCELL at room temperature under crossed polars (magnification 100 \times).

later by Harkness and Gray.⁹ However, as summarized by Green,¹⁰ the selectivity of 6-O-tritylation varies with the reaction time and the molar ratio of anhydroglucose units/trityl reagent. The elemental analysis of the tritylcellulose prepared in this work gave a DS value of ~ 1.1 , which is in a good agreement with the result of Harkness and Gray.³ The regioselectivity of this reaction was confirmed by its cellulose backbone carbon spectrum illustrated in Figure 1, where the peaks were assigned by referring to the related work reported by Takahashi et al.¹¹ and Camacho Gómez et al.⁸ As can be seen, the absence of significant splitting of the peaks for the C-1 and C-6 carbons implies that most of the trityl groups are situated at the C-6 positions of the anhydroglucose units comprising the cellulose backbone.¹¹

TPEOCELL was synthesized by treating 6-O-tritylcellulose with PEO-350 iodide using a procedure similar to that used for alkylation of tritylcellulose.⁴ The conversion of PEG-350 to PEO-350 iodide was accomplished by treatments with tosyl chloride and sodium iodide subsequently, which is a well-established route in organic preparations. The degree of PEO substitution (DS_{PEO}) is ~ 1.9 , as determined by its 1H NMR spectrum recorded in $CDCl_3$ (Figure 2), and its ^{13}C NMR spectrum is dominated by the resonances of the PEO and trityl side chains while those of the cellulose backbone are hardly visible.

Liquid Crystalline Properties of TPEOCELL. TPEOCELL is a light brown tacky material, displaying iridescent colors at room temperature which indicates the formation of a chiral nematic phase. This is different from a related, highly substituted cellulose ester containing only PEO side chains where the thermotropic liquid crystallinity is fairly weak,¹² implying that the presence of trityl groups may strengthen the liquid crystallinity in these systems. The DSC thermogram of TPEOCELL, however, revealed only a glass transition at 221 K before the occurrence of degradation. The polymer has a very broad clearing temperature range, and its T_c is ~ 413 K, as determined using a polarizing microscope at a heating rate of 10 K min^{-1} , which means its liquid crystalline (LC) temperature range is fairly wide. The freshly prepared sample displayed a typically marbled texture between crossed polars and relaxed into a planar texture (Figure 3) after standing in a desiccator for 1 month. The cholesteric structure of TPEOCELL was determined with CD spectroscopy, and its room temperature average refractive index (\bar{n}), 1.5240, was used for the calculation of the cholesteric pitch. As shown in Figure 4, it exhibits a strong negative CD band

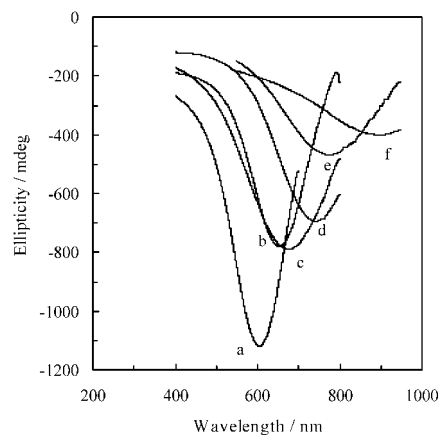


Figure 4. Apparent CD spectra of TPEOCELL and its $LiCF_3SO_3$ complexes at room temperature. CD band a is for TPEOCELL; CD bands b–f are for the complexes with the $[Li]/[O] = 0.0025, 0.0075, 0.0100, 0.0125,$ and 0.0145 , respectively.

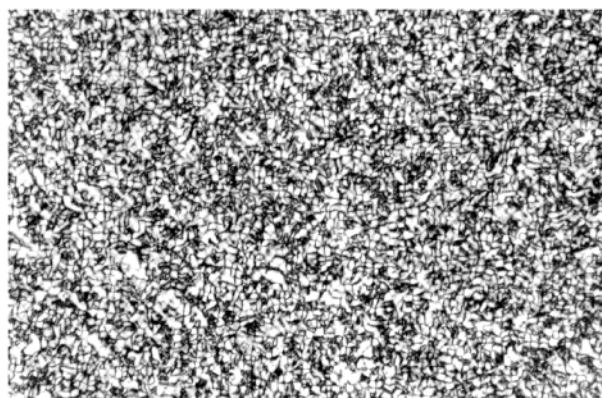


Figure 5. Optical textures of the TPEOCELL– $LiCF_3SO_3$ complex with $[Li]/[O] = 0.0100$ at room temperature (magnification 100 \times).

with the reflective maximum at ~ 605 nm, indicating the chiral nematic phase is right-handed with a pitch length of ~ 400 nm.

Effect of Salt on the Chiroptical Properties of TPEOCELL. Figure 4 also illustrates the CD spectra of the $LiCF_3SO_3$ complexes of the polymer. These complexes have the $[Li]/[O]$ ratios varying from 0 to 0.0145, which corresponds to a $LiCF_3SO_3$ weight percent range of 0–3.6. Typically, marbled or sanded textures were observed between crossed polars for these materials, which reoriented into a kind of texture having some features of focal conic as shown in Figure 5, after standing in a desiccator for 1 month.

As can be seen in Figure 4, the addition of small amounts of $LiCF_3SO_3$ results in red shifts in the wavelength of maximum reflection, which increase with increasing salt concentration. To calculate the cholesteric pitch for these complexes, it is necessary to find out the effect of salt concentration on the average refractive index (\bar{n}). The refractive indices of two $LiCF_3SO_3$ complexes were measured at room temperature; the one with $[Li]/[O] = 0.0100$ is 1.5222, and the other with $[Li]/[O] = 0.0710$ is 1.5085. Both values are smaller than that of the undoped polymer ($\bar{n} = 1.5240$), and the decrease in \bar{n} caused by adding salt is $\sim 0.1\%$ and $\sim 1.0\%$ of the \bar{n} of the polymer for the two complexes, respectively. These are not large, especially the one for the complex with $[Li]/[O] = 0.0100$; therefore, it is presumed

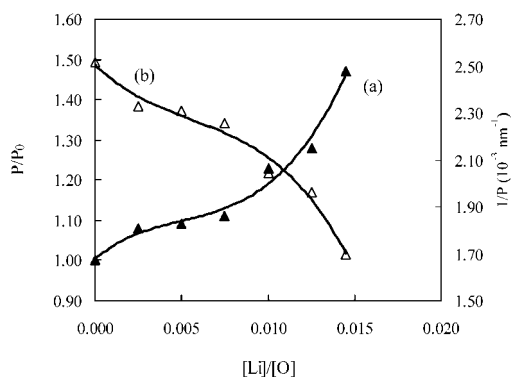


Figure 6. Cholesteric pitch behavior of the TPEOCELL–LiCF₃SO₃ complexes as a function of [Li]/[O] at room temperature: (a) P/P_0 (the ratio of the cholesteric pitch between a complex and TPEOCELL); (b) $1/P$.

that using the \bar{n} of the pure polymer to calculate the cholesteric pitch of these complexes ($[\text{Li}]/[\text{O}] \leq 0.0145$) would not cause significant errors.

Figure 6 illustrates the variation of the cholesteric pitch of these complexes as a function of salt concentration, where P/P_0 is the ratio of the pitch between a complex and the undoped polymer. A lengthening effect of LiCF₃SO₃ on the cholesteric pitch is evident for all the complexes, increasing nonlinearly with salt concentration. The pitch increases slowly at the early stage of increasing salt content and then increases sharply after the [Li]/[O] ratio exceeds 0.0075. Given the small amounts of salt employed (≤ 3.6 wt %), such significant changes cannot be explained simply as an effect of dilution caused by adding salt.

Generally speaking, for neutral molecules, the formation of a cholesteric LC phase can be regarded as a result of two kinds of intermolecular interactions: the anisotropic energetic interaction originating from the chirality of the molecules and the anisotropic steric interaction related to the molecular conformation.¹³ In the cases of cellulose derivatives, the semirigid cellulose backbone affords these polymers mesogenic character, and the chirality of the anhydroglucose units results in small asymmetric forces between the chain segments, producing the macroscopic helicoidal structures of the cholesteric states.¹⁴ TPEOCELL has oxyethylene units in the side chains which are able to coordinate with the cations of the salts, leading to partial ionization of the salts and consequent dissolution.¹⁵ Therefore, the introduction of salt would give rise to the electrostatic interactions not only between cations and anions but also between the side chains and cations. This will in turn affect the chiral interactions and the main-chain conformation, leading to a change in the cholesteric liquid crystalline properties. Clearly, this kind of Coulombic interaction depends on salt concentration and becomes much stronger when salt concentration is increased, producing a pronounced effect on the cholesteric pitch.

The electrostatic interactions in solid polymer electrolytes are very complicated, and this is probably due to the formation of various ion aggregates and the involvement of the polymer chains. The extensive ion association is evident even at a low salt concentration.^{16–18} The molar conductivity studies at low salt concentrations ($\leq 0.1 \text{ mol dm}^{-3}$ corresponding to a [Li]/[O] ratio of 0.005 or less), reported by Bruce et al.,¹⁷ revealed evidence of the presence of various ion aggregates.

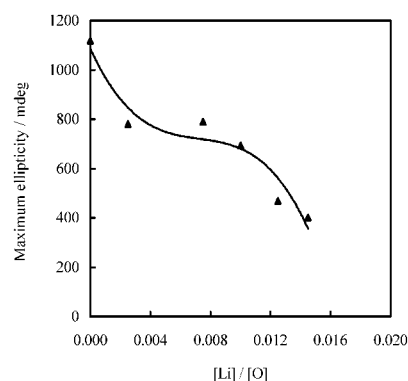


Figure 7. Maximum ellipticity of the apparent reflection bands as a function of salt concentration for the TPEOCELL–LiCF₃SO₃ complexes at room temperature.

Similar work presented by Tomlin et al.¹⁸ was consistent with most salt being present as ion pairs and triplets at salt concentration around 0.01 mol dm^{-3} . The formation of different ion aggregates alters the corresponding Coulombic interactions, which means the sum of the Coulombic interactions in a solid polymer electrolyte is not a simple function of salt concentration. The observed relationship between P/P_0 and the concentration of LiCF₃SO₃ in the TPEOCELL complexes might be associated with the complicated nature of the electrostatic interactions in this medium.

The reciprocal pitch ($1/P$) is proportional to the twist angle between adjacent molecular planes in a cholesteric structure¹⁹ and can be taken as a measure of the helical twisting power (HTP).²⁰ As also shown in Figure 6, the HTP for these complexes decreases with increasing the LiCF₃SO₃ concentration, indicating the chiral interactions become weaker. In other words, the electrostatic interactions interfere with the chiral interactions, leading to an unwinding of the cholesteric twist in these systems.

The effect of LiCF₃SO₃ on the cholesteric structures of these complexes is also reflected in the corresponding change in the shape of the CD reflection bands. As can be seen in Figure 4, with increasing salt concentration the CD bands are broadened, and the apparent reflection ellipticity is decreased, which becomes much more pronounced when the [Li]/[O] ratio exceeds 0.0075. The decrease in the ellipticity at the reflection maxima is more clearly illustrated in Figure 7 as a function of [Li]/[O].

The shape of a CD band generally depends on the degree of order, the texture of the mesophase, and the thickness of the sample. A uniform planar texture generally gives a sharp CD band while a structure composed of a random distribution of chiral nematic polydomains affords a broad CD band. All the samples were prepared in the form of a thin layer between a glass slide and a coverslip, which favored the formation of a planar texture. The thicknesses of these samples were kept nearly constant ($\sim 50 \mu\text{m}$), and all the samples were given the same time for the molecular alignment to take place before the spectra were recorded. Therefore, it may be concluded that the observed changes in the CD reflection bands of these complexes caused by increasing salt concentration indicate a decrease in both the twisting power and the molecular orientation order of the cholesteric structures.

The influence of other salts, LiClO₄, NaCF₃SO₃, and Cu(CF₃SO₃)₂, on the selective reflection of TPEOCELL

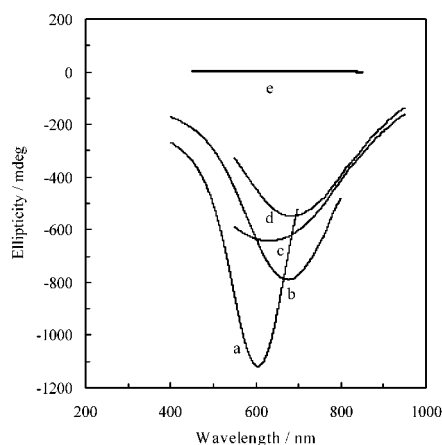


Figure 8. Apparent CD spectra of TPEOCELL complexes with $[M]/[O] = 0.0075$. Here M refers to the cation. CD band a is for TPEOCELL; CD bands b–e are for the complexes with LiCF_3SO_3 , LiClO_4 , NaCF_3SO_3 , and $\text{Cu}(\text{CF}_3\text{SO}_3)_2$, respectively.

was compared with that of LiCF_3SO_3 ; these complexes all have the $[M]/[O] = 0.0075$ (M refers to the cation) and are liquid crystalline in nature at room temperature as confirmed by polarizing microscopy. It can be observed in Figure 8 that, compared with TPEOCELL, these complexes display different red shifts in the reflection maxima with the exception of the $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ complex. This may be ascribed to the different electrostatic interactions caused by the variation of cations or anions. The absence of a CD band of the $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ complex is probably due to the stronger Cu(II) Coulombic interactions which shift the CD reflection beyond the accessible range of CD spectroscopy or untwist the cholesteric structure to form a nematic phase. However, this will require further investigation on the CD reflection of the copper(II) triflate complexes with $[\text{Cu}]/[O] < 0.0075$.

The above results are the first observation of the influence of salt on the cholesteric properties in a thermotropic polymer system. Several authors^{21–23} have carried out similar studies in lyotropic systems. A lengthening of the cholesteric pitch exerted by adding salt was observed in some micellar chiral nematic systems, and further addition of salt initiated a transition from the chiral nematic phase to a lamellar phase.²¹ Dong et al.²² reported a shortening effect of salt on the cholesteric pitch of the anisotropic suspensions of acid-hydrolyzed cellulose. Both effects have been found in the aqueous HPC liquid crystalline solutions, depending on the nature of the salt.²³ All these suggest that the structures of the host and the salt play important roles in governing the salt effect on the cholesteric properties.

Another series of the TPEOCELL– LiCF_3SO_3 complexes have also been investigated. This series has a high $[\text{Li}]/[O]$ range of 0.038–0.167, corresponding to a LiCF_3SO_3 weight percent from 9.0 to 30.0, which were mainly used for the ac conductivity studies. The detailed properties of this series will be presented elsewhere.²⁴ Here they are simply used as a comparison to allow the salt effect on the liquid crystallinity to be examined in a much wider range. Apart from the sample with $[\text{Li}]/[O] = 0.167$ where the salt aggregated severely to cause phase separation after long time standing, all the other complexes are anisotropic fluids at room temperature. The freshly prepared samples typically displayed sanded or marbled textures between crossed polars, which all realigned into sanded textures after standing

in a desiccator for 1 month. No CD reflection bands were observed for these complexes.

Comparing the two series, questions arise as to what happens to the cholesteric supramolecular structures of the TPEOCELL complexes on increasing the $[\text{Li}]/[O]$ ratio from 0.0145 (the upper limit of the first series) onward, and what is the nature of the liquid crystalline phases formed by the second series? It has been demonstrated that the presence of small amounts of LiCF_3SO_3 ($[\text{Li}]/[O] \leq 0.0145$) causes an untwisting of the cholesteric structure accompanied by a decrease in the molecular ordering. This becomes much more significant when the $[\text{Li}]/[O]$ ratios exceed 0.0075, and the corresponding changes in the apparent CD reflection bands with increasing salt concentration are reminiscent of what occurs in a thermotropic cholesteric system when the temperatures approach the isotropization temperature.²⁵ However, in this specific case, the liquid crystalline order does not vanish on further addition of LiCF_3SO_3 , as demonstrated by the presence of strong birefringence in the second series. The salt concentrations in the second series are up to 10 times higher than that of the first series if comparing the two upper limits of salt concentrations. Given the fact that such a pronounced unwinding of the helicoidal twist is caused by adding such small amounts of LiCF_3SO_3 , it is unlikely that the cholesteric helicoidal arrangements could be maintained at higher LiCF_3SO_3 concentrations. Therefore, it may be argued that further increasing the $[\text{Li}]/[O]$ ratio from 0.0145 onward may lead to a transition from a chiral nematic to a nematic phase, and the liquid crystalline phases formed by the second series are likely to be nematic. The concentration of LiCF_3SO_3 corresponding to this phase transition could be roughly determined by extrapolation of curve a in Figure 6 to infinite pitch, which gives a $[\text{Li}]/[O]$ ratio of ~ 0.025 , or by extrapolation of the plot in Figure 7 to zero ellipticity, which gives a $[\text{Li}]/[O]$ ratio of ~ 0.017 . But the validity of the two extrapolations is dubious because of the limited amount of data points. Measurements on the cholesteric pitch of the complexes with the $[\text{Li}]/[O]$ ratio higher than 0.0145 were not possible in the case of CD spectroscopy, as the selective reflection wavelengths, if present, were beyond the experimental limit. It might be worthwhile to try other techniques to look at the variation of pitch in a wider $[\text{Li}]/[O]$ range.

Conclusions

A specifically substituted, multifunctional cellulose ether, 6-O-trityl-2,3-O-PEOcellulose (TPEOCELL), was synthesized. It is thermotropic and forms a right-handed chiral nematic mesophase at room temperature. The effect of adding salt on the cholesteric properties of this polymer has been examined with CD spectroscopy and optical polarizing microscopy, which implied that the presence of small amounts of LiCF_3SO_3 ($[\text{Li}]/[O] \leq 0.0145$) interrupts severely the chiral interactions necessary for the formation of a chiral nematic phase.

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References and Notes

- Werbowsky, R. S.; Gray, D. G. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 97.

- (2) de Vries, A. *Acta Crystallogr.* **1951**, 4, 219.
- (3) Harkness, B. R.; Gray, D. G. *Macromolecules* **1990**, 23, 1452.
- (4) Harkness, B. R.; Gray, D. G. *Can. J. Chem.* **1990**, 68, 1135.
- (5) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Pergamon Press: New York, 1988.
- (6) Hearon, W. N.; Hiatt, G. D.; Fordyce, C. R. *J. Am. Chem. Soc.* **1943**, 65, 2449.
- (7) Honeyman, J. *J. Chem. Soc.* **1947**, 168.
- (8) Camacho Gómez, J. A.; Erler, U. W.; Klemm, D. O. *Macromol. Chem. Phys.* **1996**, 197, 953.
- (9) Harkness, B. R.; Gray, D. G. *Macromolecules* **1991**, 24, 1800.
- (10) Green, J. W. *Methods Carbohydr. Chem.* **1963**, 3, 327.
- (11) Takakashi, S.-I.; Fujimoto, T.; Barua, B. M.; Miyamoto, T.; Inagaki, H. *J. Polym. Sci., Part A: Polym. Chem. Ed.* **1986**, 24, 2981.
- (12) Yue, Z.; Cowie, J. M. G. *Polymer*, in press.
- (13) Fukuda, T.; Takada, A.; Miyamoto, T. In *Cellulosic Polymers, Blend and Composites*; Gilbert, R. D., Ed.; Carl Hanser Verlag: Munich, 1994; Chapter 3.
- (14) Tseng, S.-L.; Valente, A.; Gray, D. G. *Macromolecules* **1981**, 14, 715.
- (15) Gray, F. M. *Solid Polymer Electrolytes Fundamentals and Technological Applications*; VCH Publishers: New York, 1991.
- (16) Gray, F. M. *Solid State Ionics* **1990**, 40/41, 637.
- (17) Bruce, P. G.; Gray, F. M.; Shi, J.; Vincent, C. A. *Philos. Mag. A* **1991**, 64, 1091.
- (18) Tomlin, A. S.; MacCallum, J. R.; Vincent, C. A. *Eur. Polym. J.* **1986**, 22, 787.
- (19) Keating, P. N. *Mol. Cryst. Liq. Cryst.* **1969**, 8, 315.
- (20) Baessler, H.; Labes, M. *J. Chem. Phys.* **1970**, 52, 631.
- (21) Ocak, C.; Acimis, M.; Akpınar, E.; Gök, A. *Phys. Chem. Chem. Phys.* **2000**, 2, 5703.
- (22) Dong, X. M.; Kimura, T.; Revol, J.-F.; Gray, D. G. *Langmuir* **1996**, 12, 2076.
- (23) Nishio, Y.; Kai, T.; Kimura, N.; Oshima, K.; Suzuki, H. *Macromolecules* **1998**, 31, 2384.
- (24) Yue, Z.; McEwen, I. J.; Cowie, J. M. G., submitted for publication.
- (25) Ritcey, A. M.; Gray, D. G. *Macromolecules* **1988**, 21, 1251.

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