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Cholesteric Properties of Cellulose Acetate and Triacetate in Trifluoroacetic Acid

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ABSTRACT: The optical properties of cellulose acetate and cellulose triacetate cholesteric liquid crystals in trifluoroacetic acid are investigated by circular reflectivity measurements. The reflection properties of the cellulose acetate mesophase are extremely time dependent. The observed changes are attributed to trifluoroacetylation of the unsubstituted hydroxyl groups of the polymer. Analysis of the polymer recovered from trifluoroacetic acid solution, by NMR and FT-IR spectroscopy, confirms this chemical modification. No significant decrease in molecular weight occurs on the time scale of the change in optical properties. The presence of trifluoroacetate groups on the cellulose chains causes a reversal of the handedness of the cholesteric supramolecular helicoidal structure and also influences the magnitude of the concentration dependence of the pitch.

Introduction

Both cellulose acetate (degree of substitution ~2.4) and cellulose triacetate have been reported to form lyotropic liquid crystalline phases in trifluoroacetic acid.[1] Patel and Gilbert[2] observed that the cellulose triacetate mesophase exhibits the shimmering colors, as well as the microscopic fingerprint texture and high optical rotation, characteristic of cholesteric liquid crystals. The cholesteric nature of the liquid crystalline solutions of both the partially substituted[3] and the fully acetylated derivative[4] has been confirmed by circular dichroism studies, giving positive reflection bands in both cases. The phase diagram of cellulose acetate in trifluoroacetic acid has been investigated by differential scanning calorimetry[5] and in a number of other solvents by polarizing light microscopy.[6,7] The critical concentration for mesophase formation has also been evaluated from the concentration dependence of rheological properties.[8]

The unique optical properties of cholesteric liquid crystals are the result of the selective reflection of light by the helicoidal arrangement of molecules found within these ordered phases. de Vries[9] formulated the theory for these optical properties, modeling the cholesteric phase as a series of twisted birefringent layers. His theory predicts the reflection of circularly polarized light at wavelengths corresponding to the pitch of the supramolecular helicoidal structure. In addition to being selective with respect to wavelength, this reflection is selective with respect to handedness: right-handed cholesteric liquid crystals reflect only right-circularly polarized light and, similarly, left-handed cholesterics reflect only left-circularly polarized light. At wavelengths within the reflection band, the intensity of light transmitted by a cholesteric mesophase will therefore be different for incident light of the two circular polarizations and the reflection properties can be monitored as apparent circular dichroism or "circular reflectivity".

Circular reflectivity studies of the cholesteric liquid crystals formed by cellulose acetate and cellulose triacetate in trifluoroacetic acid reveal significant differences in behavior between these two polymers in this solvent. This difference arises from reaction between the polymer and trifluoroacetic acid in the case of the partially acetylated derivative. The presence of trifluoroacetate substituents is found to have a remarkable effect on the cholesteric properties of the resulting liquid crystalline phases.

Experimental Section

Materials. Cellulose acetate (4644 lot no. A6A, ASTM viscosity 3, acetyl content 39.8%) and cellulose triacetate (no. 2314) were obtained from Eastman Kodak. Trifluoroacetic acid (Matheson, Coleman & Bell) was used as supplied.

Sample Preparation. Liquid crystalline solutions of both cellulose acetate and cellulose triacetate in trifluoroacetic acid were prepared by adding the required amount of solvent to polymer samples of known weight. Mesophase samples which were to be studied as soon as possible after dissolution were stirred with a glass rod and centrifuged to remove bubbles.

Polymer samples were recovered from liquid crystalline solution by precipitation in absolute ethanol. A trifluoroacetic acid liquid crystalline solution containing ~1 g of polymer was diluted with dioxane (10 mL) and added dropwise to absolute ethanol (~75 mL) with rapid stirring. Care is necessary to avoid moisture, which hydrolyses the trifluoroacetate substituents and thus masks the derivatization. The white precipitate was collected by filtration, washed with absolute ethanol, dried in vacuo, and stored in a desiccator. The polymer was recovered from the cellulose acetate mesophase after being in solution for 3 days.

Mesophase Optical Properties. Cholesteric liquid crystals were studied as thin samples pressed between two glass slides. Circular reflectivity spectra were recorded with a Jasco J-500C spectropolarimeter and liquid crystalline textures were observed with a Reichert polarizing microscope.

Light Scattering. The mass-average molar mass was determined by low-angle laser light scattering with a Chromatix KMX-6 LALLS photometer. The scattered intensity was measured at 3–6° to the incident beam. Solutions in dioxane were passed through a 0.2-μm Millipore filter (type FGLP) to remove any foreign particles before entering the light scattering cell. The refractive index increment, dn/dc, was determined at 546 nm with a Brice-Phoenix differential refractometer.

NMR Spectroscopy. All NMR spectra were recorded on a Varian XL300 spectrometer, operating at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C. ^{1}H NMR spectra for cellulose acetate samples dissolved in DMSO-d_6 were recorded at 90 °C and referenced to DMSO at δ 2.49. ^{13}C NMR spectra were acquired for solutions of ~10% w/w cellulose acetate in acetone-d_6, at 40 °C, and were referenced to the acetone methyl signal at δ 29.8.

FT-IR Spectroscopy. Fourier transform infrared spectra were recorded with a Mattson Instruments Cygnus 25 spectrometer equipped with a standard globar source and a TGS detector. Samples were prepared as thin free-standing films cast from dioxane solution and dried under vacuum.

Results and Discussion

Mesophase Optical Properties. The optical properties of the lyotropic mesophase formed by cellulose acetate in trifluoroacetic acid are extremely dependent on the age of the solution. The circular reflectivity spectra of such a sample (27% polymer by weight) recorded as a function of time are shown in Figure 1. The first spectrum, recorded ~1 h after the solvent was added to the polymer, has a wavelength of maximum reflection of 560 nm. The reflection band moves to longer wavelengths with time,

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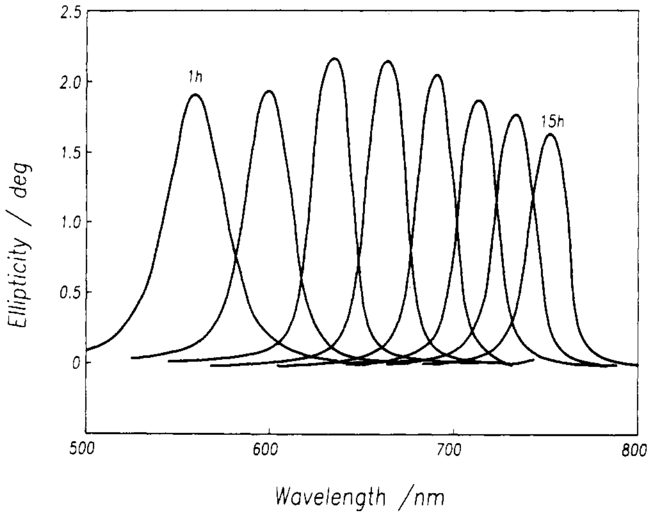

Figure 1. Circular reflectivity spectra of cellulose acetate in trifluoroacetic acid (27% polymer by weight) recorded as a function of time. The first spectrum was recorded ~1 h after sample preparation and spectra were acquired at 2-h intervals thereafter.

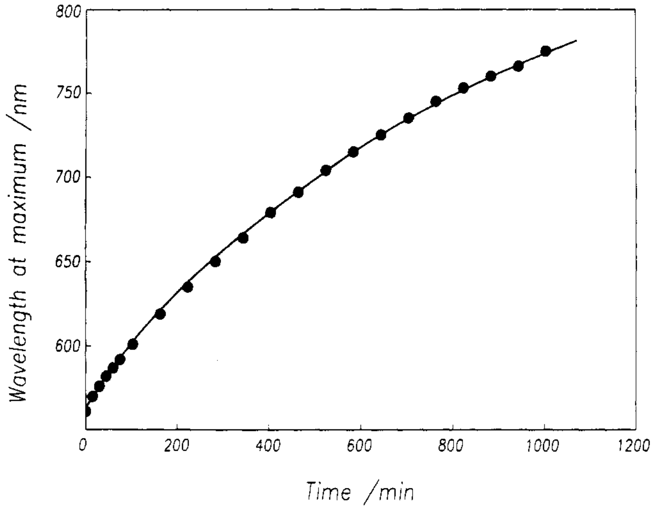

Figure 2. Time dependence of the wavelength of maximum reflection for a cellulose acetate mesophase (27% polymer by weight) in trifluoroacetic acid.

reaching a position of 785 nm 15 h after sample preparation. The wavelength of maximum reflection is plotted as a function of time in Figure 2. After 15 h, the pitch can no longer be determined by CR spectroscopy but continues to increase as indicated by the appearance of the fingerprint lines typical of long pitch samples. Four days after solution preparation, line spacings corresponding to a value of $P/2 = 6$ μm are observed.

Samples of cellulose acetate in trifluoroacetic acid, prepared in the concentration range 39–42% polymer by weight, exhibit cholesteric reflection bands in the visible region. These colors appear 3–7 days after sample preparation and are reasonably stable with time. Surprisingly, circular reflectivity measurements indicate that the cholesteric liquid crystalline phases are right-handed, as illustrated by the negative CR band in Figure 3. The reflection spectrum of a cellulose triacetate mesophase in the same solvent is also shown and the positive reflection band indicates that the cholesteric liquid crystal formed by the fully acetylated polymer is left-handed. The pitch of the cellulose triacetate mesophase does not show the rapid increase with time that was observed for the partially acetylated derivative.

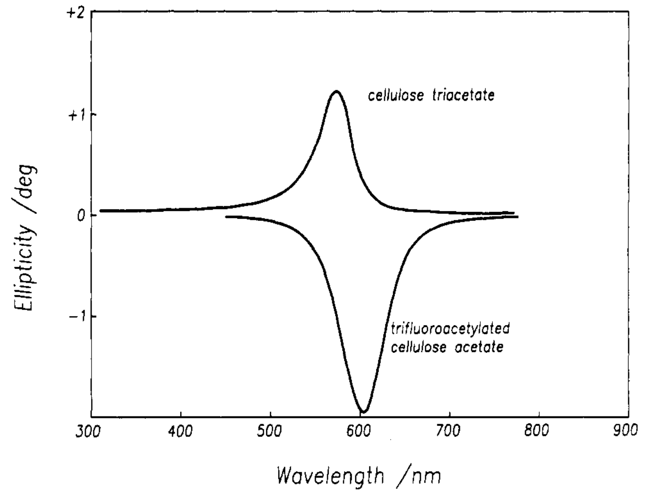

Figure 3. Circular reflectivity spectra of mesophase solutions prepared from cellulose triacetate (26% polymer by weight) and cellulose acetate (40% polymer by weight) in trifluoroacetic acid. Spectra were recorded 5 days after sample preparation.

Table I
Handedness of Cholesteric Liquid Crystalline Solutions of Cellulose Acetate and Triacetate in Trifluoroacetic Acid

init polym	init polym concn	soln age	handedness
cellulose triacetate	26%	1 day	left
(DS $\sim$3.0)	26%	5 days	left[a]
cellulose acetate	27%	1 h	left[b]
(DS $\sim$2.4)	27%	4 days	unknown ($p/2 = 6$ μm)
	40%	5 days	right

[a] Pitch and trifluoroacetyl content increasing slowly with time.
[b] Pitch and trifluoroacetyl content increasing rapidly with time.

Patel and Gilbert[2,10] observed that the cholesteric pitch of cellulose triacetate liquid crystalline solutions in mixed solvents of trifluoroacetic acid and methylene chloride or 1,2-dichloroethane changed with time. For long pitch samples, they found an exponential increase in fingerprint spacings over 2–10 days, with samples eventually becoming isotropic. They attributed this behavior to polymer degradation in the strongly acidic medium.

Lematre et al.[3] reported a shift in the wavelength of maximum reflection in trifluoroacetic acid but since the pitch seemed to reach a steady-state value after 1 h, this time dependence was considered to be due to relaxation of the internal strains induced by sample preparation.

The initial rapid increase in the pitch is observed only for cellulose acetate and not for the fully acetylated polymer. This suggests that the changes are due, not to polymer degradation or stress relaxation, but to chemical change. A significant change in the chemical structure of the polymer with time is also implied by the initial formation of a left-handed cholesteric mesophase by cellulose acetate, while the steady-state mesophase formed at longer times is right-handed.

Three possible mechanisms for chemical alteration of the cellulose acetate/trifluoroacetic system can be envisioned: (1) hydrolysis of glycosidic linkages (depolymerization), (2) hydrolysis of ester linkages, and (3) trifluoroacetylation of free hydroxyl groups. NMR and FT-IR spectroscopic analysis of the recovered polymer confirm that trifluoroacetylation does occur in trifluoroacetic acid solution. There appears to be little or no reaction through routes 1 or 2. The data confirming these observations will be discussed in the section on polymer characterization below.

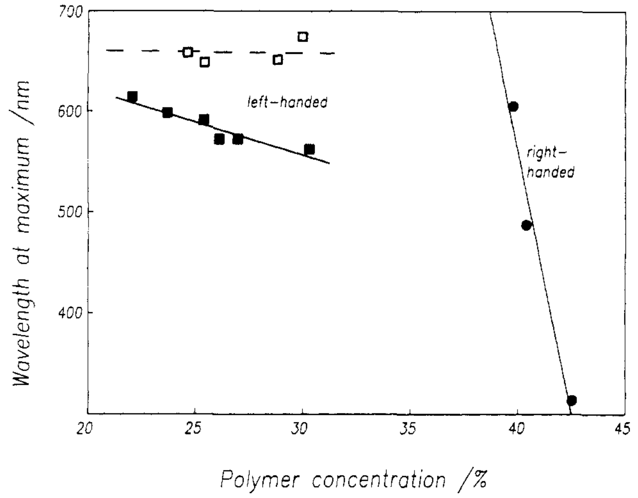

Figure 4. Concentration dependence of the wavelength of maximum reflection for mesophase solutions prepared from cellulose triacetate (filled squares) and cellulose acetate (filled circles) in trifluoroacetic acid, recorded 1 and 5 days after sample preparation, respectively. The open squares represent the reflection wavelength observed for cellulose triacetate samples after 7–9 days.

To summarize (see Table I), cellulose triacetate and cellulose acetate both form left-handed cholesteric liquid crystals in trifluoroacetic acid, giving visible reflection colors at similar polymer concentrations. The polymer which contains free hydroxyl groups, however, undergoes trifluoroacetylation to give a mixed ester which exhibits cholesteric behavior that is quite different from that of the parent polymer. The most striking difference is a reversal in handedness of the supramolecular helicoidal structure. Mesophase solutions formed by the trifluoroacetylated derivative are also of much longer pitch than those formed at the same polymer concentration by cellulose acetate before chemical reaction.

The presence of trifluoroacetate groups has a marked effect on the concentration dependence of the pitch, as illustrated by the plots in Figure 4. The cholesteric pitch of mesophase solutions formed by the mixed ester derivative crosses the visible region of the spectrum upon very small changes in polymer concentration (filled circles). This is in sharp contrast to the behavior of cellulose triacetate mesophases where little variation in the pitch is observed over the entire concentration range within which liquid crystalline samples can be prepared (filled squares).

Meeten and Navard[4] observed a similar concentration dependence for a different cellulose triacetate sample, although their reported values for the pitch are consistently higher than those observed here. The pitch of cellulose triacetate samples does in fact increase slowly with time and the value observed 7–9 days after sample preparation is plotted in Figure 4 (open squares). The FT-IR spectrum of the polymer recovered from mesophase solution 25 days after sample preparation exhibits a carbonyl peak at the frequency characteristic of the trifluoroacetate group,[11] indicating that an ester exchange reaction has taken place through shifts in the equilibrium for the formation of the two types of esters. This reaction is, however, much slower than the trifluoroacetylation observed for the partially acetylated cellulose derivative. The observed increase in pitch with time for the fully acetylated polymer is therefore consistent with the increase in pitch associated with a presence of trifluoroacetate substituents.

The large differences between mesophases formed by cellulose triacetate and those formed by the mixed acetate–trifluoroacetate derivative indicate that the development of the cholesteric twist is the result of some molecular property that is extremely sensitive to this relatively minor chemical change. Obviously, these cellulose derivatives cannot be treated with the same general approach that seems valid for highly substituted cellulosics where the polymer can be considered as a chiral backbone surrounded by isotropic side groups.[12,13]

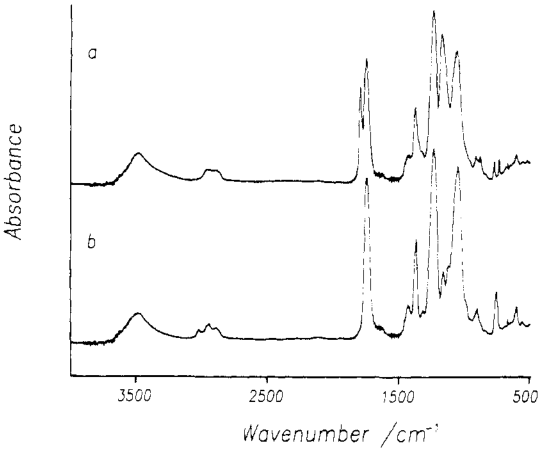

Figure 5. FT-IR spectrum of the polymer precipitated from a cellulose mesophase in trifluoroacetic acid (a) and that of the original cellulose acetate sample (b).

Polymer Characterization. The FT-IR spectrum of the polymer precipitated from a cellulose acetate mesophase is shown in Figure 5 along with that of the original cellulose acetate sample. The chemical change resulting from treatment with trifluoroacetic acid is reflected by the significant differences between the two spectra. The spectrum of the treated polymer contains two peaks (1745 and 1790 cm^{-1}) in the carbonyl region. The second peak, appearing at a higher frequency than that of the acetate carbonyl of the parent polymer, is consistent with the assignment of a trifluoroacetate carbonyl.[11] A new absorption also appears at 1170 cm^{-1} and is characteristic of a carbon–fluorine stretch.[14] Minor changes are evident in the 2800–3000-cm^{-1} region and are probably the result of shifts in methylene vibrations accompanying the conversion of free hydroxyl groups at C-6 to trifluoroacetate esters.

Cellulose triacetate precipitated from trifluoroacetic acid after 25 days gave a very similar FT-IR spectrum, thus indicating that not only are free hydroxyl groups esterified but a slower process involving deacetylation followed by trifluoroacetylation is also possible.

The ^{1}H and ^{13}C NMR spectra of both the parent cellulose acetate and the sample recovered from trifluoroacetic solution were recorded in order to further identify structural changes to the polymer. The most significant difference in the ^{13}C NMR spectra shown in Figure 6 is the occurrence of a peak at δ 67.2 for the recovered sample. The chemical shift of this peak is consistent with that expected for C-6 of a 6-O-trifluoroacetylated residue.[15] Resonances corresponding to C-6 of both the 6-*O*-acetyl and 6-OH residues are seen in both spectra (δ 63.3 and 60.8, respectively), although the latter has a reduced intensity in the trifluoroacetic acid sample. The primary C-6 hydroxyl is likely to be the most important group in terms of reactivity; signal overlap in the δ 70–85 region obscures evidence of 2-O and 3-O trifluoroacetylation. Another difference between the ^{13}C NMR spectra is the appearance of signals at δ 155–160, corresponding to the carbonyl carbon of the trifluoroacetate groups. The CF$_3$ carbons of the trifluoroacetate substituents are visible as overlapping quartets at δ 116. The multiplicity of both the tri-

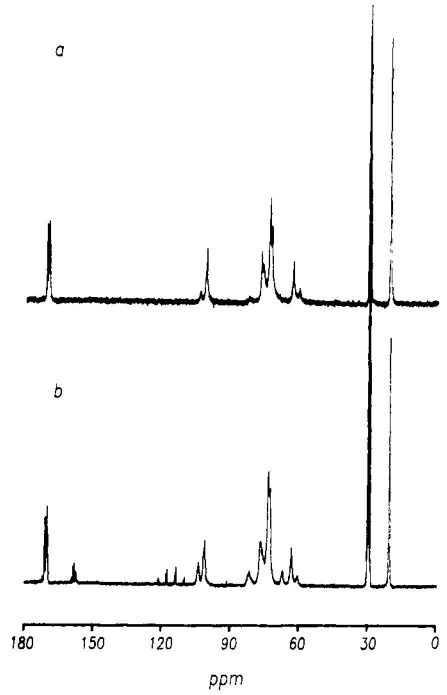

Figure 6. ^{13}C NMR spectrum of the parent cellulose acetate (a) and the sample recovered from trifluoroacetic acid solution (b).

fluoroacetate carbonyl and CF_3 resonances suggests that these substituents are located not only at C-6 but at other positions on the backbone as well. The relative intensities of the three main acetate carbonyl signals (δ 169–172), and acetate methyl peaks (δ 20–21), are altered in the spectrum of the recovered material. The latter observations probably result from exchange of ester groups, rather than from esterification.

Although the ^{1}H NMR spectrum of the original cellulose acetate and the sample recovered from trifluoroacetic acid are very similar, changes in the intensity of the acetate methyl signals (δ 1.75–2.25) were detected. In particular, the methyl resonance furthest downfield (δ 2.13) shows a marked reduction in intensity. Again, this indicates that ester exchange is taking place, probably at the primary C-6 position. Integration of the ring proton (δ 3.0–5.5) and methyl proton (δ 1.75–2.25) regions provides a measure of the degree of substitution (DS), which for the original cellulose acetate was 2.4 and for the recovered sample, 2.2. Loss of acetate through hydrolysis is therefore indicated. (Integration of the whole methyl region of the parent cellulose acetate gave a DS of ~2.6, in agreement with the reported acetyl content of 39.8%. However, a very narrow resonance in the methyl region, which was obviously not part of the polymer, contributed to the integral. Subtraction of this contribution gave the DS of 2.4 reported above.)

Low-angle laser light scattering measurements indicate that a very minor decrease in the degree of polymerization occurs in the 2–3-day period where rapid changes in liquid crystalline behavior are observed. The average molecular weights are 90 000 and 75 000 for cellulose acetate and the trifluoroacetylated polymer, respectively.

Finally, cellulose acetate was treated with trifluoroacetic anhydride to provide an authentic synthetic sample of a trifluoroacetylated cellulose acetate. The main features of the FT-IR and ^{1}H and ^{13}C NMR spectra of the material recovered from liquid crystalline solution matched those of the synthetic sample. In total, the data summarized here indicate that structural changes to the cellulose acetate are occurring due to esterification with trifluoroacetic acid. There is little or no apparent contribution from glycoside hydrolysis and little deacetylation when anhydrous trifluoroacetic acid is used as a solvent.

Conclusions

Cellulose acetate undergoes fairly rapid esterification in trifluoroacetic acid to produce the mixed acetate–trifluoroacetate derivative. The replacement of acetate groups with trifluoroacetate is also possible through a shift in the ester equilibrium. Trifluoroacetic acid is thus a rather reactive "solvent" for functionalized polymers.

The introduction of trifluoroacetate groups strongly affects the behavior of the cholesteric liquid crystals formed by these polymers in trifluoroacetic acid. The presence of trifluoroacetate groups also changes the sign of the cholesteric twist from left-handed to right-handed and strongly influences the concentration dependence of the pitch. The observations indicate that the development of a helicoidal supramolecular structure in concentrated solutions of these polymers is not just the result of the intrinsic chirality of the cellulosic backbone but must also involve specific orientations or interactions of substituent groups.

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Registry No. Cellulose acetate, 9004-35-7; cellulose triacetate, 9012-09-3; trifluoroacetic acid, 76-05-1.

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