Solid-State ^{13}C NMR and Raman Studies of Cellulose Triacetate: Oligomers, Polymorphism, and Inferences about Chain Polarity

D. L. VanderHart*

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. A Hyatt

Research Laboratories, Eastman Chemical Company, P.O. Box 511, Kingsport, Tennessee 37662

R. H. Atalla and V. C. Tirumalai

Forest Service−Forest Products Laboratory, U.S. Department of Agriculture, One Gifford Pinchot Drive, Madison, Wisconsin 53705

Received February 14, 1995; Revised Manuscript Received September 8, 1995[⊗]

ABSTRACT: ^{13}C CPMAS NMR and Raman spectra have been taken for oligomers (DP = 2−9) and several preparations of cellulose triacetate (CTA). CTA exhibits polymorphism and the NMR spectra of the CTA-(I) and CTA(II) allomorphs along with the spectrum of noncrystalline CTA have been isolated. Magnetic inequivalence within the unit cell of CTA(II) is greater than for CTA(I), indicating a lower symmetry in the CTA(II) unit cell. An attempt is made to correlate some of the NMR resonances with proposed X-ray crystal structures for each of these allomorphs. From both the Raman and the NMR spectra of the oligomers, in comparison with the different CTA preparations, it is determined that the pentamer and higher oligomers crystallize into the CTA(I) lattice. On the basis of the Raman spectra, it is argued that CTA(I) and CTA(II) are distinguished by backbone conformational differences. In a single attempt to explore the role of the solvent in determining the crystal habit of the oligomers, the pentamer persisted in the CTA(I) lattice even when crystallization took place in dibenzyl ether, the solvent out of which the CTA polymer forms CTA(II) crystallites. Based on these findings, an approach to obtaining a definitive crystal structure of CTA(I) would be to grow and perform a structural determination on a single crystal of an oligomer of DP > 4. Spectra of these oligomers indicated partial crystallinity; hence, care must be taken in growing single crystals. Since it is known that there is a correlation between the allomorphs of CTA formed by heterogeneous acetylation and the allomorphs of the precursor, cellulose, and since there are still points of ambiguity regarding the crystal structures of the allomorphs of cellulose and CTA, the topic of chain polarity (directionality) is addressed herein. As a contribution to the dialogue on the structure of these materials, we present plausibility arguments, i.e., not definitive arguments, that CTA-(I) has parallel and CTA(II) antiparallel chain character.

Introduction

The early work of Sprague et al.[1] has demonstrated the relationship between various preparative schemes for cellulose triacetate (CTA) and its two allomorphs, denoted CTA(I) and CTA(II). They observed that CTA-(I) was only produced by heterogeneous acetylation from cellulose I. On the other hand, the crystalline state produced via homogeneous acetylation and crystallization, or by heterogeneous acetylation of cellulose II, is CTA(II). They also showed that heterogeneously acetylated preparations of both CTA(I) and CTA(II) revert to the corresponding polymorphs of cellulose upon saponification. Thus, it was concluded that the polymorphism of the CTAs is related to the polymorphism of cellulose. This connection has been noted with the crystalline forms of other triesters of cellulose as well.[2] The quest for a rigorous understanding of the crystal structures of the allomorphs of both cellulose and CTA is still in progress, including the topic of chain directionality or chain polarity. Of particular interest is the question whether reversals of chain direction on a nearest-neighbor scale are required in moving from one allomorph to another. Thus, there is a strong interest in elucidating any structural aspect of either of these materials.

More recently, other authors have called into question this strong relationship, proposed by Sprague, between the allomorphs of cellulose and CTA. In particular, CTA(I) has been produced from a solution of CTA in trifluoroacetic acid[3] and from cellulose II via the heterogeneous acetylations of normal rayon and Fortisan, the latter pretreated with glacial acetic acid.[4] The production of CTA(I) by the foregoing methods was not allowed in the scheme proposed by Sprague. The claim by Sprague that saponification of CTA(I) yields cellulose I has also been reexamined.[5] The conclusion of that study was that the dominant saponification product is cellulose IV, not cellulose I. In addition, CTA(I) derived from heterogeneously acetylated cotton is reported[6] to transform to CTA(II) in the presence of formic acid; moreover, in contrast to Sprague's scheme, this CTA-(II) product saponifies to cellulose I. Our study focuses on CTA and its oligomers (exclusively the α-D anomers); from the foregoing, any extrapolations to cellulose structure will be regarded as tentative.

A number of studies of the crystal structures of the CTAs have been reported. For CTA(II), some have studied fiber patterns[7] while others have combined information from fiber patterns with basal plane electron diffraction data from single crystals.[8] Crystal

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

0024-9297/96/2229-0730$12.00/0

structures of CTA(I) have also been proposed[9] based on fiber patterns. In yet another series, CTA(I) and CTA-(II) were examined along with the corresponding polymorphs of other triesters.[2] The crystal structures of the β-D anomers of the CTA dimer and trimer have also been discussed,[10] and it was concluded that the middle and nonreducing residues in the trimer are most likely to mimic the glycosidic torsion angles and the C(6) conformation in both CTA(I) and CTA(II).

Arguments have also been offered[2,8] which link chain polarity in CTA(I) and CTA(II) to the chain polarities in celluloses I and II, respectively. (In this paper, the phrase "chain polarity" refers to chain directionality within a given crystalline unit cell. Cellulose and CTA chains have a directionality arising from the asymmetric monomer structure, and for unit cells containing two chains, one has the choice between "parallel" or "antiparallel" chain polarity. For unit cells involving more than two directionally-variable chains per unit cell, e.g., in the proposed four-chain CTA(II) cell[8] containing two antiparallel pairs, the chain polarity will be said to have "antiparallel character".) At this time, the link between the chain polarities of the celluloses and CTAs is an unproven hypothesis. One group of studies suggests that chains are parallel in cellulose I and antiparallel in cellulose II.[11−14] However, it has also been argued that both forms of cellulose have antiparallel chains.[2] The matter is further complicated by recent evidence pointing to parallel structures for both forms.[15] In addition, two unit cells corresponding to the I_α and I_β allomorphs[16] of cellulose I have been proposed.[17] The unit cell corresponding to I_α is proposed to have only one chain per unit cell, implying parallel chains. From observations of solid-state conversion[18] from I_α to I_β and from the claim[17] that regions of I_α and I_β alternate along the same microfibril, there follows a strong suggestion that both allomorphs of cellulose I would then have parallel chains. Finally, extensive lattice energy calculations have been carried out for CTA[19] but a dominant energy minimum for either the parallel or antiparallel packing arrangement was not found. It is anticipated that progress in understanding the structure of the CTAs may help to clarify certain issues surrounding the structures of cellulose.

Some solid-state ^{13}C NMR spectra of heterogeneously acetylated cellulose I have already been published, in one case[20] as a function of the degree of substitution and in another case[21] as a demonstration that one can take any native cellulose, heterogeneously acetylate it, and return, via saponification, to the form of cellulose I typical of cotton. However, in both these studies, the resonances from the CTA(I) lattice were not so apparent, owing to the lack of a sufficiently vigorous heat treatment. (CTA has a glass transition temperature in the range of 175−189 °C;[22,23] thus, effective annealing must be performed above 200 °C.) Spectra of other CTA samples have also appeared,[24] but a group of narrow resonances that can be clearly associated with a crystalline phase has not been not obvious. One recent ^{13}C survey[25] of several cellulose esters has included both heat-treated CTA(I) and CTA(II) and, while there was no attempt to separate the signals from the crystalline and noncrystalline regions, the major spectral differences between CTA(I) and CTA(II) were identified. As to Raman spectra, we are only aware of one analysis[26] dealing with band assignments for CTA.

It is our purpose in this report to describe and discuss complementary solid-state ^{13}C NMR and Raman spectra of the α-D oligomers of CTA (DP = 2−9) together with spectra of CTA polymer samples containing both CTA crystalline allomorphs. The Raman and ^{13}C spectra are complementary in the sense that each has a sensitivity to different aspects of the structure of the polymeric systems under study. The Raman spectra are primarily sensitive to differences in the conformations between the different forms and much less sensitive to differences in packing in a particular state of aggregation. In contrast, ^{13}C shifts of comparable magnitude can arise from variations of either conformation or packing.[27]

We will demonstrate correspondences between CTA oligomer spectra and CTA(I) spectra. Thereby we hope to encourage someone to solve the CTA(I) crystal structure by choosing an appropriate oligomer, growing a single crystal, and doing the X-ray analysis. In addition, the ^{13}C NMR spectra of the crystalline phases of both CTA(I) and CTA(II) will be isolated. We will also discuss spectra of heterogeneously acetylated cotton and ramie fibers, both with and without prior mercerization and both with and without subsequent heat treatment. Many of our results are consistent with prior X-ray results, especially in emphasizing the need for heat treatment before significant crystallinity is developed.[1] Even though the focus of this study is on the crystalline states of CTA, we will include several spectra of samples with poorly developed crystallinity because (a) there are spectral distinctions between various precursor states which may eventually grant some insight into the transformation to the various crystalline allomorphs and (b) CTA is an active chromatographic substance[19] and the link between structure and chromatographic activity is not at all understood (therefore, it is of potential use to observe the degree to which spectral distinctions can be correlated with order or states which are precursors to ordered states). We will also look for similarities in chemical shifts in the spectrum of the trimer relative to spectra of CTA(I) and CTA(II). Finally, we will consider the degree to which the different assumptions concerning chain polarity provide adequate rationalizations of the spectral observations.

Experimental Section

Materials. α-D-Cellooligosaccharide acetates (dimer through nonamer) were obtained, purified, crystallized from boiling ethanol, and characterized as described previously.[22]

The polymeric samples of CTA will be designated by acronyms which refer to the source materials (RAM = ramie cellulose and COT = cotton cellulose) and to the order of subsequent treatments (HA = heterogeneous acetylation, MER = mercerization, HT = heat treatment, DBE = heating in dibenzyl ether). Thus, for example, the MER-COT-HA-HT sample is a mercerized cotton which has been subsequently heterogeneously acetylated and finally heat treated. One other acronym will be used, NC = noncrystalline, which conveys the meaning that these samples, by choice of preparation, have low crystallinity.

Heterogeneous acetylations for the COT-HA and RAM-HA samples utilized the following procedure: 2.0 g of cotton or ramie cellulose was soaked in 150 mL of 90% acetic acid for 1 h and then in two 150 mL exchanges of 100% acetic acid for 20 min each. The acetic acid-wet fiber was then added to a mixture of 125 mL of toluene, 125 mL of acetic anhydride, and 5 drops of 60% perchloric acid. After standing in this mixture for 20 h at 22 °C, the fiber was removed with a forceps and placed in 500 mL of 95% ethanol. The ethanol-washed fiber was washed with water until the effluent was neutral and then Soxhlet-extracted overnight with methanol. The resulting product was air-dried. Proton NMR analysis gave a degree of

substitution (DS) of 3.03 acetyls/glucose repeat unit for ramie and 3.01 for cotton. Gel permeation chromatography (GPC) indicated weight-average molecular weights, M_w, of 8.5×10^4 for ramie and 1.31×10^5 for cotton and number-average molecular weights, M_n, of 3.3×10^4 for ramie and 4.20×10^4 for cotton (vs polystyrene standards).

Mercerization of cellulose samples, prior to acetylation, was conducted as follows: A 1 g sample of cotton or ramie was placed in a 22 °C solution of 16 wt % NaOH in water. After standing for 10 min, the fiber was removed, washed in a continuous stream of deionized water for 2 h, and air-dried. The resulting mercerized cellulose was acetic acid activated and heterogeneously acetylated as described above. For MER-RAM-HA (and MER-COT-HA), DS = 3.04 (3.05), $M_n = 2.68 \times 10^4$ (2.81×10^4), and $M_w = 6.29 \times 10^4$ (8.94×10^4).

Heat treatments (HT) were performed by inserting for a period of 15 min approximately 0.5 g of material, under nitrogen, in a glass tube into a large metal heating block maintained at 220 °C.

The NC-COT sample was homogeneously acetylated with trifluoroacetic anhydride/acetic acid according to the method of Morooka et al.[28] The resulting cellulose triacetate was dissolved (5 wt %) in 95:5 dichloromethane:methanol and precipitated into methanol. The resulting amorphous polymer was dried in air. The NC-COT-DBE sample was derived from the NC-COT sample by dissolving the latter in nitromethane (5% solution), cooling in liquid nitrogen, and freeze-drying to afford a very low-density, low-crystallinity, foamy polymer. This material (0.6 g) was then crystallized from 150 mL of dibenzyl ether (8 h, 200 °C) according to the method of Chanzy and Roche.[29] The finely powdered product was shown to be cellulose triacetate free of solvent by proton NMR; GPC analysis gave $M_n = 2.39 \times 10^4$ and $M_w = 7.53 \times 10^4$.

NMR. The NMR spectrometer is a noncommercial spectrometer operating at 2.35 T (25.193 MHz). ^{13}C spectra were generated in the usual way[30] by combining the techniques of cross polarization (CP), high-power proton decoupling, and magic angle sample spinning (MAS). The probe utilizes a rotor/stator assembly manufactured by Doty Scientific, Inc.[31] All of these so-called CPMAS spectra were taken with a uniform set of parameters: 1.5 ms of CP time, MAS frequencies of 3−3.2 kHz, and nutation frequencies, corresponding to the radiofrequency field strengths, of 66 and 69 kHz for carbons and protons, respectively. Occasionally we attempted to vary the initial proton spin locking time prior to CP in the hopes that proton rotating frame relaxation, $T_{1\varrho}^H$, in the noncrystalline (NC) regions would be different from relaxation in the crystalline regions so that one might be able to isolate the spectra of the crystalline and NC regions separately by taking linear combinations of such spectra.[32] These attempts were unsuccessful because the lineshape was not a function of the spin locking time, presumably because proton spin diffusion[33] was capable of maintaining internal spin equilibrium over the relatively small lateral dimensions of the CTA morphology. Chemical shifts have been determined, for the most part, using the methine resonance of adamantane as an external reference at 29.50 ppm. Occasionally we would also use an internal standard which consisted of a thin wafer of semicrystalline linear polyethylene positioned in the center of our sample; its "crystalline-phase" peak appears at 33.11 ppm at this frequency.[34]

Raman Spectra. The Raman spectra were acquired using the 5145 Å line of a Spectra Physics argon ion laser for excitation and a Jobin-Yvon (Instruments SA) double monochromator equipped with an RCA photomultiplier detector to record the spectra. Spectrometer conditions were such that the resolution was about 4 cm^{-1}. The spectra as acquired were superposed on a broad fluorescence background which was subtracted prior to generation of the spectra reported here.

Results

Solid-State ^{13}C NMR Spectra. The CPMAS spectra of the CTA oligomers are shown in order in Figure 1 from the dimer (bottom spectrum) to the nonamer (top spectrum); the assignment of resonances to various

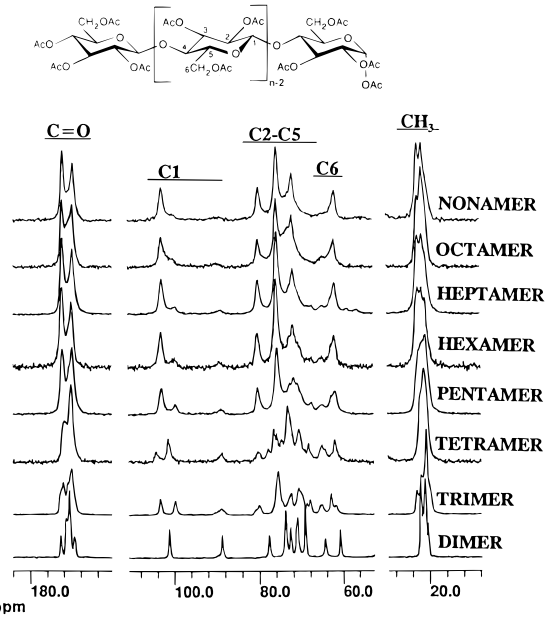

Figure 1. 25.2 MHz ^{13}C CPMAS spectra of the indicated oligomers of cellulose triacetate (CTA). Resonance groupings are indicated and refer to the chemical structure given. These spectra are free of spinning sidebands except for small carbonyl sidebands appearing at about 55 and 59 ppm in the nonamer and heptamer spectra, respectively. Note the consistency of the dominant backbone resonances from the pentamer through the nonamer and the uniqueness of these resonances for the dimer and tetramer. Chemical shift data are collected in Table 1.

carbons is also indicated. Progressing toward the nonamer, the spectra become simpler in the sense that the number of prominent resonances seems to be stabilizing; moreover, the number of resonances in the 60−104 ppm range, i.e., those resonances associated with the carbons of the original glucose repeat units, is converging to five. These five resonances seem quite prominent already in the spectrum of the pentamer. Strong similarities are also seen from the pentamer through the nonamer in the carbonyl region while the methyl region shows a more complex pattern of variation. The C1 region for these oligomers shows a trend in that a resonance at about 102.5 ppm becomes dominant while resonances corresponding in intensity approximately to single C1 sites in the monomer consistently are seen at about 99.5 and 88.5 ppm (the latter is assigned to the reducing-end C1 carbon.[22] The trimer spectrum also shows these three resonances. In fact, the trimer spectrum shares several resonances which are close to those of the nonamer. The latter observation leads some support, albeit weak because of ambiguities in assignments of resonances to residues or carbon sites, to the proposal that the linkage between the two nonreducing residues in the trimer offers a model for the glycosidic linkage in the polymer.[10] (Strictly speaking, however, this claim is made for the β-D anomer and not the α-D anomer whose spectrum we refer to.) Moreover, it has also been proposed[10] that the conformation of O6 and the positioning of the acetate groups in the middle residue also mimic those in CTA-(I). In any case, it seems clear from Figure 1 that, among the oligomers, the dimer and the tetramer seem to have spectra most unlike those of the others. Chemical shifts of identifiable resonances for all oligomers are included in Table 1. The lack of firm assignments in the C2−C5 region, the necessary trend toward greater resonance overlap in the larger oligomers, and the trend

Table 1. Solid-State ^{13}C Chemical Shifts[a] of the Oligomers of CTA and the Two Crystalline Allomorphs of CTA

sample (*n*-mer)	*C*=0	C1	C2−C5		C6	C-Me
2	169.39	88.52	69.07	70.86	60.58	20.16
	170.52	101.04	71.20	72.53	64.24	20.78
	171.32		73.63	77.54		21.38
	172.67					21.85
3	170.00	88.5[c]	67.83	68.65	61.58	19.6[b]
	170.8[b]	99.47	70.6	72.31	62.74	20.45
	172.00	103.05	75.34	79.8	65.10	21.75
	172.7[b]					22.80
4	170.1	88.4	68.2	70.5	61.8	20.9[d]
	171.7	101.2	73.0	74.4	64.0[b]	
		104.1	75.6	76.9	64.9	
			79.9			
5	169.8	88.5[c]	67.5	70.7	61.7[d]	20.5[d]
	172.2	99.4	71.6	72.5	64.8	
		102.7	75.4	80.0		
6	170.0	88.9[c]	71.7[d]	75.4	61.7[d]	20.5[d]
	172.3	99.5	79.8		64.9[c]	21.3[d]
		102.6				22.2[d]
7	169.8	88.6[c]	71.6	75.4	61.6	21.2[d]
	172.2	99.5	79.8		64.8[c]	22.2[d]
		102.6				
8	169.8	89[c]	71.8[d]	75.4	61.7	21.2[d]
	172.2	99.8	79.7		64.7[c]	22.2[d]
		102.6				
9	169.7	89[c]	71.8	75.4	61.3	21.2[d]
	172.2	102.6	79.7			22.2[d]
CTA(I)	169.4	102.2	71.5	75.0	61.6	20.9
	171.9		79.2			22.0
CTA(II)	170.0	100.00	71.1	72.1	63.5	23.4
	172.2		73.3	74.5	66.4	20.8
	173.2		74.9	77.9		
			78.7			

[a] Chemical shifts are referenced externally to the adamantane methine resonance at 29.50 ppm. Uncertainties in the chemical shifts given to two, one, or zero decimal places are estimated at ±0.08, 0.15, or 0.4 ppm, respectively. [b] No well-defined peak, but a distinct shoulder. [c] Broader, isolated, and weaker peak. [d] Peak of an obviously asymmetric resonance; indicates region of strong resonance overlap.

toward lower crystallinity in the larger oligomers must be kept in mind when these data are interpreted.

Consideration is next given to the spectra of various preparations of CTA and to the issue of isolating the CPMAS spectra of CTA(I) and CTA(II). Figure 2 shows CPMAS spectra of nine indicated preparations of CTA; only one of the ramie-related spectra is shown because the others did not differ in any significant way from the spectra of the cotton-related samples subjected to parallel treatments. Samples are identified in the figure. For the arguments presented subsequently, the NC-COT sample is taken to represent the pure NC state of CTA. Only for the COT-HA-HT, NC-COT-DBE, and NC-COT-DBE-HT samples are there significant narrow spectral features which indicate some well-developed crystallinity. At the same time, especially the C1 and C6 resonances take on many different shapes in the spectra of all these different preparations; thus, the absence of well-defined crystallinity does not automatically imply that states of low crystallinity are uniform or homogeneously disordered, a point demonstrated by the various outcomes of heat treatment.

Figure 3 represents spectra resulting from our attempt to isolate the "ordered" phases in eight of the nine samples presented in Figure 2. To accomplish this, the assumption was made that each sample consists of a NC and an ordered phase, the former portion having a lineshape like that of the NC-COT in Figure 2. Hence, the spectra in Figure 3 are generated by subtracting from the corresponding experimental spectrum in Figure 2, a maximum portion of intensity having the lineshape of the NC-COT spectrum. The quantity, f_o, given in this figure, is defined as that fraction of the original spectral intensity associated with these respective "ordered" spectra. Figure 3 serves as a more convenient presentation for highlighting spectral differences, including those associated with the various crystalline phases.

The spectra with the sharpest features, that is, those with the most well-developed crystallinity, provide the basis for the clearest comparison. For the polymer, these spectra correspond to the COT-HA-HT and the NC-COT-DBE-HT samples. It is known from earlier work[1] that the crystalline form represented in the COT-HA-HT spectrum of Figure 3 is the CTA(I) crystal lattice. Similarly, the CTA(II) is the form associated with the DBE treatment.[29] These two spectra are reproduced in Figure 4 along with the spectrum of the nonamer and a synthesized spectrum approximating the crystalline phase of the nonamer. The latter has been generated by subtracting from the experimental nonamer spectrum, the spectrum (not shown) of another NC preparation of the same nonamer sample; implied is a crystallinity of 0.47 in the nonamer. The main point of Figure 4 is to show the close correspondence of resonance positions for the nonamer and the CTA(I) crystalline phase. Chemical shifts corresponding to the CTA(I) and CTA(II) lattices are included in Table 1. It is clear that the nonamer would be an excellent model for the CTA(I) structure. In fact, as noted earlier, any oligomer, from the pentamer through the nonamer, would be a good model for the CTA(I) lattice.

Raman Spectra. The Raman spectra are complementary to the ^{13}C spectra in that similar trends are indicated. In order to provide a basis for discussion of the Raman spectra of specific samples, some general

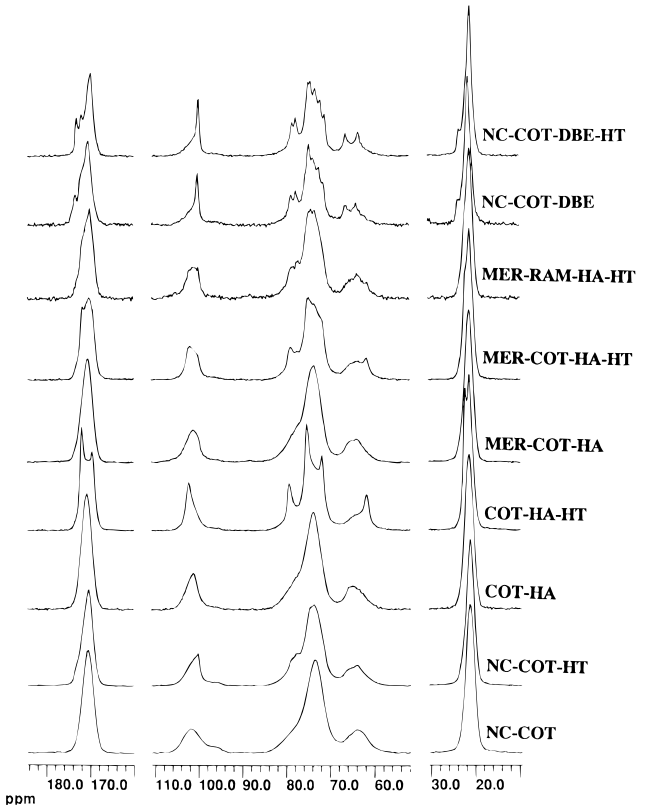

Figure 2. CPMAS spectra of the indicated CTA preparations. Note the weakness or absence of the narrower spectral features in most of these preparations, implying very poor crystalline order. At the same time, note the rich variation in lineshapes evidenced in the C1 and C6 regions. The spectrum of the NC-COT is taken to represent the fully noncrystalline (NC) state.

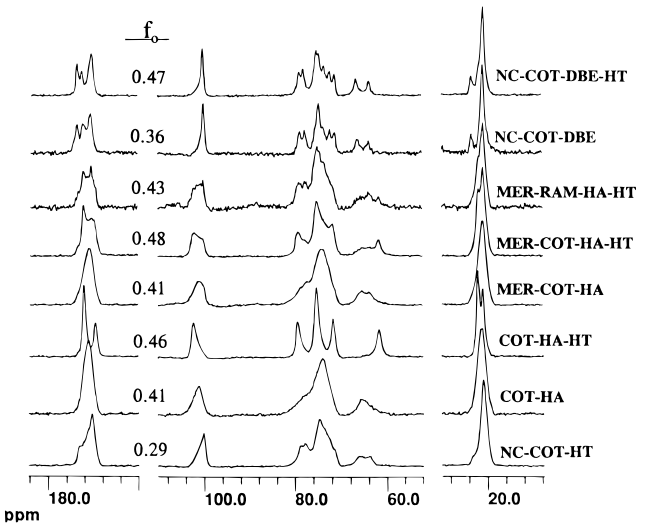

Figure 3. Difference spectra intended to represent the ordered regions in the samples indicated. Spectra were generated by subtracting from the corresponding spectra of Figure 2 a maximum portion of the NC-COT spectrum using the criterion that no negative intensity should be created in these spectra. If the NC-COT spectrum truly represents disordered CTA, then these spectra represent the more ordered regions, and f_o is the fraction of the original spectral intensity in Figure 2 represented by these spectra. The COT-HA-HT and NC-COT-DBE-HT samples represent the CTA(I) and CTA-(II) crystalline forms.

characteristics of the Raman spectra of CTAs will first be considered. Figure 5 shows the full spectrum of the NC-COT sample. The dominant feature is the symmetric methyl stretching vibration at 2934 cm^{-1}, which

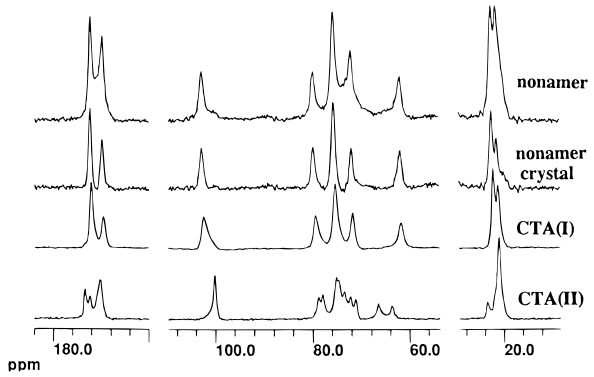

Figure 4. Comparison of the spectra of the crystalline phases of the nonamer and the two CTA allomorphs. The identification of the nonamer crystalline lattice with CTA(I) is unambiguous. In the CTA(I) unit cell, all CTA residues are magnetically equivalent and symmetry, by implication, is high; whereas, in CTA(II), there are two magnetically inequivalent sites. Note the unique chemical shift for one of the six methyl groups at these two sites. The nonamer crystal spectrum has been generated from the nonamer spectrum by subtracting the lineshape corresponding to the NC nonamer. Crystallinity is estimated to be 0.47 for the nonamer. The presence of substantial NC material indicates that considerable care will probably be needed if one wishes to grow a single crystal of an oligomer which relates to the CTA(I) structure.

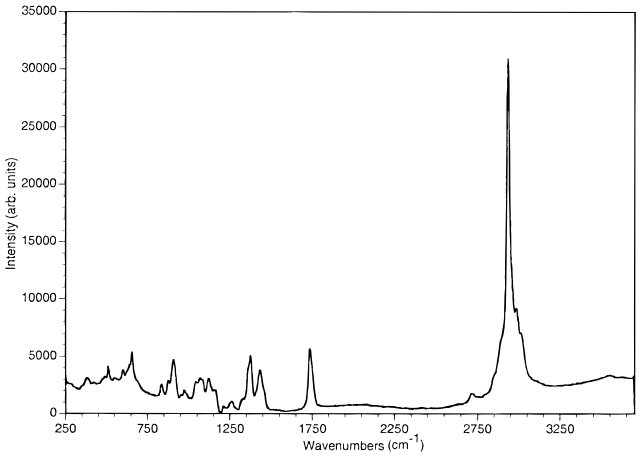

Figure 5. Raman spectrum of the CTA sample called NC-COT. The region near 2900 cm^{-1} is the C−H stretching region.

is approximately 6 times the intensity of the next most prominent band, that of the carbonyls in the acetyl groups at 1736 cm^{-1}. In subsequent discussion, only the region below 2050 cm^{-1} will be considered.

In addition to the samples studied by NMR, samples of NC-COT cellulose acetates with lower degrees of substitution (DS) were investigated in an effort to distinguish the bands which are localized within the acetyl groups. It was found that, with the exception of the changes in the relative intensity of the methyl stretching and carbonyl bands, all bands between 500 and 1500 cm^{-1} in the spectra of the cellulose acetates at a DS of 1.75 and 2.47 were the same as those for NC-COT. The implication of these observations is that the scattering coefficients of the acetyl groups are an order of magnitude higher than those associated with the skeletal structures in this spectral region. Thus, only vibrations that are in one way or another coupled to the acetyl groups result in bands that are strong enough to be observed. On the other hand, it is also clear, from comparisons with spectra of other acetyl-containing compounds, that the entities coupled to the acetyl groups have a significant influence on the band struc-

Table 2. Frequency Ranges of Differemtn Vibrational Motions in the Raman Spectra of Cellulose

freq range, cm^{-1}	dominant[a] internal coordinates
330−550	heavy-atom bending, some heavy-atom stretching
900−1120	HCC and HCO bending at C6, heavy-atom stretching
1150−1330	heavy-atom stretching, HCC and HCO bending
1350−1410	HCC, HCO, and HOC bending
1420−1490	HCH and HOC bending

[a] Heavy-atom bending (CCC, CCO, COC); heavy-atom stretching (C−C, C−O).

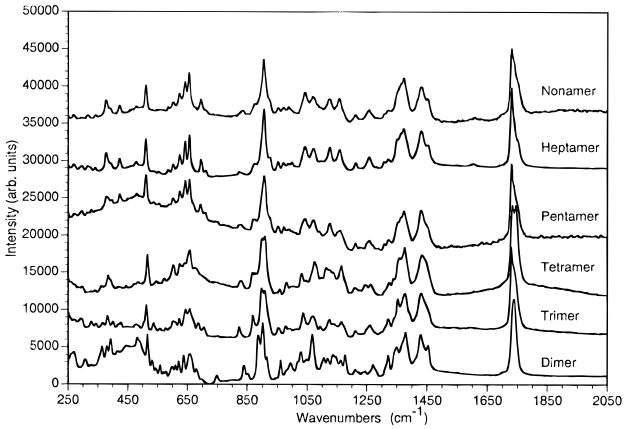

Figure 6. Raman spectra of the indicated oligomers of CTA. Note the strong similarity in the spectra of the pentamer and larger oligomers.

ture. That is, the vibrations of the acetyl groups in the fingerprint region cannot be interpreted as local modes. This is to be expected because the skeletal frequencies of the acetyl groups are in the same range as those of the entities to which they are attached, so that a high degree of coupling between the vibrations is inevitable, this is also the case with the CTAs.

As is the case with cellulose, when each monomer unit has many internal degrees of freedom (120 for CTA), the assignment of individual modes is essentially meaningless. Discussion has to be confined to identifying the classes of skeletal motions that can be expected to contribute to bands in a particular region and the degree to which the couplings between the motions can be sensitive to conformational changes.[35−37] Some information concerning the classes of vibrational motion and the corresponding frequency ranges is summarized in Table 2. These assignments of vibrational motions to specific frequency ranges are based on normal coordinate analyses of model compounds and identification of the internal coordinates which contribute most to the potential energies of vibrations at particular frequencies. The model compounds used include the hexoses,[38] the inositols,[39] and the cellooligodextrins.[40] Considerable conformational sensitivity is exhibited by bands lying in the range from 250 to 600 cm^{-1}. It is anticipated that the distribution and patterns of coupling in the vibrational spectra of CTAs will be quite similar to those for cellulose, particularly with respect to conformational dependence and the couplings with the motions of the acetyl groups.

Figure 6 shows the lower wavenumber portion of the Raman spectra of the oligomers; the hexamer and octamer are not included as they are very similar to the heptamer and nonamer. The same pattern of convergence is revealed as occurs in the CPMAS spectra. For the pentamer and higher oligomers, the spectra show

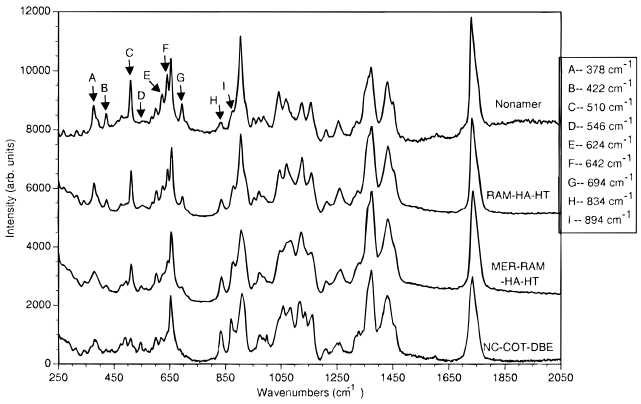

Figure 7. Raman spectra of the indicated CTA materials. Note the similarity of the nonamer and the RAM-HA-HT spectra associated with the CTA(I) allomorph and their contrast in shape with the spectrum of NC-COT-DBE, which contains the CTA(II) allomorph.

only subtle variation. This is especially evident in the spectral ranges centered at 650 and 1100 cm^{-1}. Also, the carbonyl band is split in the spectrum of the tetramer and symmetric in that of the dimer whereas it is asymmetric in the other oligomer spectra. The subtle variations in the bands between 1300 and 1500 cm^{-1} are consistent with variability in the dispositions of the methyl and methylene groups.

The Raman spectra in Figure 7 are those of the nonamer, the RAM-HA-HT, the MER-RAM-HA-HT, and the NC-COT-DBE. The similarity of the nonamer and the RAM-HA-HT sample is evident; the latter sample is among those showing the highest CTA(I) crystallinity. Also evident in Figure 7 is the spectral contrast between the CTA(I) features of the upper two spectra and those of CTA(II) in the NC-COT-DBE sample, the latter being the most crystalline in CTA(II) of those studied by Raman spectroscopy. Of the bands which have been marked in Figure 7, it would appear that A−C and E−G are characteristic of CTA(I) while D, H, and I are dominated by CTA(II). Based on analogy with the differences between the Raman spectra of celluloses I and II,[39] particularly in the low-frequency skeletal angle bending region from 250 to 550 cm^{-1}, we believe that the conformations of CTA(I) and CTA(II) are diffeent from each other. It is also important to note that the spectrum of the MER-RAM-HA-HT sample has a number of the CTA(I) bands persisting at a significant strength, pointing to the coexistence of CTA(I) and CTA-(II); this evidence parallels the pattern revealed in the CPMAS spectra.

Discussion

The CPMAS spectra of CTA(I) and CTA(II) shown in Figure 4 reveal significant differences; notable contrasts appear at C1 where CTA(I) exhibits a resonance at 102.1 ppm and CTA(II) possesses one at 99.9 ppm. Resonances at C6 are also distinctive with a singlet appearing at 61.6 ppm in CTA(I) and a doublet displayed by CTA(II) at 63.6 and 66 ppm. A close look at the C1 and C6 resonance shapes indicates that each of these two crystalline phases is quite free of contamination from the other crystalline form. The number of resonances associated with C2−C5 in the CTA(II) spectrum is also notably larger than in the CTA(I) spectrum, suggesting more magnetic inequivalence in the unit cell of CTA-(II). This can be interpreted in terms of a unit cell of higher symmetry for CTA(I). These observations are

consistent with but not unique to the view adopted in one of the cited structural studies[8] where the twofold screw axis is thought to be coincident with the chain axis in CTA(I) and to lie between the chains in CTA(II). Alternatively, these experimental results can be interpreted in terms of different degrees of departure from the twofold axes of symmetry, as suggested in the second group of structural studies on the cellulose esters.[2] In this latter framework, the departure from twofold symmetry would be sufficiently small in CTA(I) that any splittings of the resonances would not be resolved, whereas the departure would be larger in CTA(II) and sufficient to cause splittings. The presence of the doublet at C6 in CTA(II) is also consistent with the suggestion[8] that in alternating residues down each chain, the C6 acetate groups shows a substantial variation in orientation relative to the pyranose ring, even though the conformation of the C6−O6 bond relative to the C5−O5 and C5−C4 bonds remains nominally gauche−gauche.[8,19] In this connection, it is also possible that the methyl resonance at 23.3 ppm in the CTA(II) spectrum may be associated with the acetate group at one of these C6 sites since this line comprises about one-sixth of the total methyl intensity. Implicit in this suggestion is the assumption that the acetates at the C2 sites are similar to one another in all residues as are those at C3 sites. In the spectra of the oligomers, the trimer exhibits the most downfield methyl resonance at 22.7 ppm; this is still 0.5 ppm upfield of the CTA(II) methyl line under discussion. Thus, it is doubtful that any of the oligomers possesses the geometry of that particular acetyl group in CTA(II); hence, it appears dubious that the crystal structures formed for any of the lower α-D oligomers could be used with confidence as models for the CTA(II) structure.

It is interesting that the three C6 resonances in CTA(I) and CTA(II) span the range from 61.6 to 66 ppm. Horii et al.[41] studied the trend in C6 chemical shifts for glucose, certain disaccharides, and cellulose I and concluded, on the basis of the known structures of these materials, that there was a correlation between the C4−C5−C6−O6 dihedral angle and the C6 chemical shift. However, the bulky nature of the acetyl group and the results of conformational energy calculations[8,19] (which predict a severe restriction on this dihedral angle) make it very unlikely that the C6 chemical shifts in CTA arise from changes in this angle. Thus, we are not inclined to interpret these C6 shifts in terms of specific conformations.

Other points emerge in comparisons of the spectra of Figure 3. First, several of the samples show evidence of some CTA(I) and/or CTA(II) crystallinity. CTA(I) and CTA(II) spectral features can be distinguished quite clearly at the C6 and C1 resonance positions; the doublet at 78.6 and 77.5 ppm in the CTA(II) spectrum is also quite distinctive. By examing these spectral regions in Figure 3, one can recognize CTA(II) features in the NC-COT-HT, NC-COT-DBE, MER-COT-HA-HT, and the MER-RAM-HA-HT samples in addition to the NC-COT-DBE-HT sample just discussed; these are not surprising in light of earlier reports.[1] CTA(I) features can be seen in the COT-HA-HT sample, as discussed, and, perhaps more remarkably, in the MER-COT-HA-HT and MER-RAM-HA-HT samples. The MER-COT-HA-HT and MER-RAM-HA-HT samples thus show the presence of both CTA(I) and CTA(II); they differ in that the CTA(I) component is relatively stronger in the MER-COT-HA-HT sample. Recall that the Raman spectra in Figure 7 also indicated the presence of both CTA(I) and CTA(II). We are not sure why there is this coexistence; we surmise that the mercerization was incomplete. Note that the NC-COT-HT spectrum is characterized by rather poor resolution in spite of the unmistakable correspondences with CTA(II) resonance positions, particularly those at C1, C6 and the 78-ppm doublet. The implication is that crystallites in this sample are rather small and/or imperfectly formed. Nevertheless, the absence of any peak at 61.6 ppm indicates that no CTA(I) crystallites form.

The second point emerging in Figure 3, on the basis of the values of f_o, is the indication that the ordered phase constitutes a sizable fraction of these samples and that heat treatment causes only a nominal increase in the fraction of ordered material. Furthermore, the variations in the shapes of the spectral features in Figure 3, especially those at C1 and C6, offer some possibility that additional information about the intermediate sites of order might be deduced from these spectra. However, we do not yet know the rules for such interpretations. Nevertheless, it is well to keep in mind that the analysis of Figure 3 is predicated on the assumption that the NC-COT sample well represents disordered CTA. In defense of this approximation, it certainly served well for isolating the CTA(I) and CTA(II) spectra.

It is interesting that the COTA-HA and MER-COT-HA samples show little spectral evidence of ordered structures; yet these spectra must not reflect totally random states, given the diverse outcomes of heat treatment. There is a strong implication that, during heterogeneous acetylation, chain mobility is minimal, although considerable lattice distortion and swelling (hence, some chain mobility) must accompany this acetylation. Relative to this partial disorder, the substantial width of the C1 resonance, whose chemical shift might be most logically tied to glycosidic geometry[41] (the C4 resonances cannot be identified unambiguously), may well imply that considerable disorder exists in the glycosidic linkage. (From rotor-synchronized T_2 measurements[42] on the NC-COT sample, the uncertainty broadening in this line is only 0.3 ppm; therefore, the observed linewidths for the C1 carbon are dominated by chemical shift dispersion which, in turn, arises from variations in molecular packing and chain geometry.[27,42]) However, the ambiguity in the origin of chemical shift dispersion means that we cannot equate this shift dispersion, with full confidence, to disorder in the glycosidic linkage rather than to packing disorder.

Late in our study, we added two other experiments in which COT-HA, rather than NC-COT, was immersed for 2 h either in diphenyl ether (DPE) at 200 °C or in dibenzyl ether at 220 °C. Subsequently, these samples were dried and heat-treated in the usual way. We label these samples COT-HA-DPE-HT and COT-HA-DBE-HT. The purpose was to test whether these poor solvents could fully change the partially ordered CTA of COT-HA so that, upon heat treatment, one would obtain CTA(II), just as one did from the NC-COT-DBE-HT sample. Alternatively, these solvents might cause the COT-HA to "slip into" the CTA(I) unit cell considering that simple heat treatment had this effect. Qualitative observations during exposure to these solvents suggested that DPE was the better solvent. At 200 °C the CTA in DPE became a clear, stirrable yellowish liquid (a good indication but not an absolute proof of a true solution) while the CTA in DBE at 220 °C remained

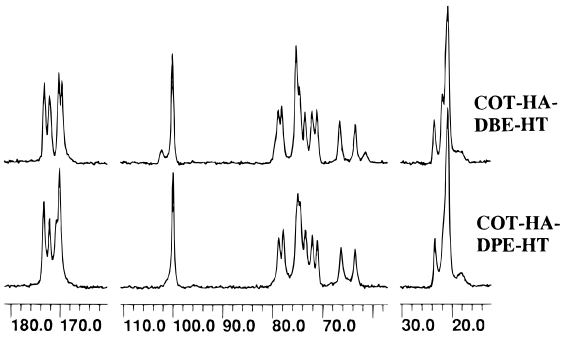

Figure 8. ^{13}C lineshapes associated with the crystalline regions of COT-HA-DBE-HT (top) and COT-HA-DPE-HT samples. Crystalline-component spectra have been isolated as in Figure 3. Crystallinities deduced from the analysis are respectively 0.40 and 0.45. Note the coexistence of both CTA-(I) and CTA(II) in the COT-HA-DBE-HT spectrum.

somewhat cloudy, a definite indication of incomplete solubilization. These CTAs precipitated when the heating mantles were turned off and the mixtures cooled in place. Solvent elimination and heat treatment followed. ^{13}C spectra of the crystalline fractions of these two samples are shown in Figure 8. A product incorporating only the CTA(II) allomorph (crystallinity 0.45) was obtained in the case of exposure to DPE. The mixed-crystal character of the DBE sample is apparent (see Figure 4), especially in the C1 and C6 regions. By integration, about 85−90% of the 0.40 crystalline fraction was CTA(II) and the balance was CTA(I). Also, there is a slight improvement in resolution for both of these samples, relative to the CTA(II) spectrum of Figure 4, thereby implying that these crystallites are somewhat larger or more perfectly formed relative to the crystallites in the NC-COT-DBE-HT sample. The spectrum of the DPE-crystallized sample in Figure 8 differs slightly from the CTA(II) spectrum of Figure 4; the biggest difference is the appearance of the upfield wing (≈8% of the total methyl intensity) in the methyl resonance. We do not know the origin of this, but from the greater breadth of this signal, relative to the sharper features, we are skeptical whether this wing truly originates from the crystalline phase. This wing may be present because the NC-COT spectrum is becoming a less accurate representation of the NC phase of the samples of Figure 8.

With respect to the Raman spectra, the two key observations are the convergence of the oligomer spectra to those of the polymer at the pentamer and the differences in the low-frequency skeletal region between the spectra of CTA(I) and CTA(II). The convergence at the pentamer is similar to the pattern observed for the cellooligodextrins.[40] The differences between CTA(I) and CTA(II) also are distributed in the same frequency regions as those between celluloses I and II and can be interpreted, both by analogy and on the basis of normal coordinate analyses of model compounds, as reflecting differences in conformations. A difference between the celluloses and the CTAs is that the oligomer spectra converge to those of the II form for cellulose[40] but to the I form for CTA.

The exact nature of the differences in conformations of the cellulose skeleton, suggested by the Raman spectra, remain poorly understood. If cellulose I and II both have parallel or both have antiparallel chain polarities, then the observed reversion of CTA(I) to cellulose I (sometimes) and CTA(II) to cellulose II upon saponification probably relates to some memory of conformation which persists. Hayashi first suggested this and spoke of the two different conformations as the "bent" and "bent−twisted" conformations.[43] He also noted that this memory effect is observed with all cellulose esters that can be prepared by heterogeneous esterification reactions.

We now consider the issue of chain polarity in CTA-(I) and CTA(II) by presenting a *plausibility* argument that CTA(I) and CTA(II) have opposite chain polarity, the latter exhibiting antiparallel character. We do not consider this argument definitive; yet, in the context of the extended debate over chain polarity in cellulose and its derivatives, we believe this review of the relevant considerations is a worthy one to undertake.

Since there are no NMR observables which are directly related to chain polarity, arguments must be indirect. The experimental observations we wish to consider in our argument are the following: (a) Most of the samples showed considerable disorder prior to heat treatment; yet, upon heat treatment, a preference for one or the other allomorphs was shown *in spite of the significant disorder of the precursor state.* (b) The NC-COT sample gave rise only to the CTA(II) allomorph even though crystallinity was poorly developed. (c) A separate attempt to crystallize the CTA pentamer from DBE (the solvent from which CTA(II) was obtained for the polymer in this study and the solvent producing CTA(II) for a polymer[8] with a DP of 60) gave the result that the pentamer still crystallized into the CTA(I) lattice. Thus, DBE does not seem to be the crucial factor for determining the crystal habit; furthermore, there must be a crossover between a DP of 5 and 60, where the CTA(II) form becomes the more stable precipitant from DBE. (d) Exposure of COT-HA to DBE resulted in partial dissolution with the formation of a mixed-crystalline sample, dominated by CTA(II) but containing CTA(I) (see Figure 8). The implication is that in hot DBE, the thermodynamic stability of a CTA(I) crystal is comparable to that of a CTA(II) crystal; if it were not, there should be a continuous process of CTA(I) dissolution and CTA(II) precipitation.

This plausibility argument arises from an attempt to present the most reasonable hypothesis for explaining points a and b above. The argument can be presented in the following outline: If the polarity of chains in CTA-(I) and CTA(II) is the *same*, why is only CTA(II) formed from a very disordereed, NC state, whereas either CTA-(I) or a mixture of CTA(I) and CTA(II) is formed from the considerably disordered COT-HA and MER-COT-HA samples? Would not this result be more logically understood as the expected outcome if the polarity of chains were *different* in the two allomorphs, especially if it is true that the thermodynamic stabilities of CTA-(I) and CTA(II) are very close?

Arguments for comparable thermodynamic stability of CTA(I) and CTA(II) include (1) a report[1] that CTA(I) is stable up to 290 °C given that the CTA melting point is 300−310 °C. (There is a report[3] that already at 260 °C, small CTA(I) crystallites, formed from lyotropic solutions, transform to CTA(II) crystallites but this transformation may be explained on the basis of the instability of crystals of small lateral size, the increased stability of larger crystals, and the possible lack of sufficiently numerous nearest neighbors of the same chain polarity as CTA(I)) and (2) points c and d cited two paragraphs above.

A final ingredient in the argument is the recognition that the relatively high T_g for CTA, along with the

existence of extensive disorder in many heterogeneously acetylated samples, is a sign that chain mobility is very sluggish. In addition, Wolf et al.,[19] who did extensive lattice energy calculations for CTA, claimed that they would often see rather rapid changes in lattice energy for small changes in bond angles; hence, they argued that there should be numerous local minima, leading to polymorphism and a stabilization of various kinds of "imperfections". If this were true, one might expect polymorphism in CTA, but the depth of each energy minimum should not be so deep as in cellulose, owing to the absence of strong hydrogen bonding. In fact, this may be an important insight into why the amount of disorder in many CTA preparations is high and why the glass transition temperature is also high. Sluggish chain mobility enters our argument in that the crystallites which form upon heat treatment probably take advantage of *existing* local order among chains; i.e., chain mobility during heat treatment is not likely to be so extensive as to accomplish the sorting of chains of random directionality to produce a unit cell with parallel chains. This argument, combined with the foregoing arguments, points to the likelihood that CTA(II) has antiparallel chain character, assuming that local chain chain orientation in the NC-COT sample is approximately random. If CTA(I) and CTA(II) have comparable energies, as discussed, then the most plausible corollary is that CTA(I) has parallel chains and is unfavored statistically; otherwise, one would expect a mixture of allomorphs from the heat treatment of NC-COT.

We wish to emphasize that we do not regard the foregoing as a proof but rather an indication of the model most readily reconciled with the observations. We view the question of chain polarity in both celluloses and CTAs to be an open one. In distinction from cellulose, CTA is a material which offers more flexibility in examining the question of chain polarity since CTA can be heat treated to alter its crystallinity, whereas chemical degradation results if cellulose is elevated to similar temperatures. The most analogous experiment that we have done in our laboratory on cellulose is to immerse a ball-milled, fully NC cellulose, which was originally a cellulose I sample, in water. The result is that some cellulose I re-forms, a result at least consistent with the foregoing argument regarding chain polarity.

Finally, it should be noted that while some effort to present a case for allomorphs with contrasting chain polarities has been made, most of the results reported in this paper are independent of that question and stand in their own right.

Conclusion

We have taken ^{13}C CPMAS and Raman spectra both of the oligomers (dimer through nonamer) of cellulose triacetate (CTA) and of several preparations of polymeric CTA. We have isolated the ^{13}C spectra associated with the two allomorphs of CTA, CTA(I) and CTA(II). On the basis of both Raman and ^{13}C spectra, the crystalline states of the oligomers from the pentamer through the nonamer, formed by crystallization from dilute ethanol, have also been identified with the CTA(I) lattice. If suitable crystals of any one of these oligomers can be grown, this should aid in refining the CTA(I) crystal structure. Caution, however, is in order, since the higher oligomers were found to be semicrystalline. The growth of single crystals of adequate size will, therefore, require considerable care. As to the differently prepared polymeric CTA samples, much of what had been observed by Sprague in his X-ray work[1] has been verified. Molecular order, in the absence of heat treatment, is generally poor for heterogeneously acetylated samples derived from semicrystalline cellulose; yet, there is partial order, distinct from the fully disordered NC state. Depending on which state of order one has, heat treatment results in the formation of either CTA(I) or a mixture of CTA(I) and CTA(II). We have indicated that the model most readily reconciled with our results, when combined with considerations of limited diffusion and chain statistics, is the one wherein the CTA(I) unit cell has parallel chains and CTA(II) antiparallel chains. Important elements in our analysis are the considerations (1) that the CTA chains have very sluggish mobility in directions normal to the chain axes during crystallization via heat treatment in the solid state and (2) that CTA(I) and CTA(II) are very close in energy. The problem that was posed in this context was how to explain, *if both allomorphs have the same polarity and very similar energies*, the experimental observations that heat treatment of disordered CTA materials produces differing results, i.e., only the CTA(II) allomorph is generated from a fully noncrystalline CTA, whereas CTA(I) or a mixture of CTA(I) and CTA(II) is generated from the partially ordered, but still quite disordered, heterogeneously acetylated cotton or mercerized cotton. In other words, especially for the noncrystalline cotton, should one not expect that heat treatment would generate a mixture of the two allomorphs? These comments on chain polarity are limited and are offered to contribute to a broader perspective; we still consider the question of chain polarity in CTA allomorphs to be an open question.

In the process of isolating the spectra of the CTA(I) and CTA(II) lattices, we were able to make some qualitative observations regarding the assumptions which underlie previous X-ray analyses of these structures. The CTA(I) spectrum shows only one magnetic environment for the four residues (two chains) in the unit cell and is consistent with the assumption that a twofold screw axis coincides with the chain axis. In CTA(II), there are at least two magnetically inequivalent sites in the unit cell, and this is consistent with the proposed X-ray structure[8] which contains four chains, pairwise antiparallel (eight repeat units), and a twofold screw axis lying off the chain axis. Moreover, there was discussion in that X-ray analysis that the acetate groups connected to the C6 carbon may have contrasting geometries in alternating residues down each chain. We have found support, though not absolute proof, for this suggestion in the CTA(II) spectrum.

References and Notes

(1) Sprague, B. S.; Riley, J. L.; Noether, H. D. *Text. Res. J.* **1958**, *28*, 275.
(2) Steinmeier, H.; Zugenmaier, P. *Carbohydr. Res.* **1987**, *164*, 97.
(3) Roche, E. J.; O'Brien, J. P.; Allen, S. R. *Polym. Commun.* **1986**, *27*, 138.
(4) Watanabe, S.; Takai, M.; Hayashi, J. *J. Polym. Sci., Part C* **1968**, *23*, 825.
(5) Venkataraman, A.; Subramanian, D. R.; Soosamma, P. C. *Text. Res. J.* **1982**, *52*, 506.
(6) Creely, J. J.; Conrad, C. M. *Text. Res. J.* **1965**, *35*, 184.
(7) Dulmage, W. J. *J. Polym. Sci.* **1957**, *26*, 277.
(8) Roche, E.; Chanzy, H.; Boudeulle, M.; Marchessault, R. H.; Sundararajan, P. R. *Macromolecules* **1978**, *11*, 86.
(9) Stipanovic, A. J.; Sarko, A. *Polymer* **1978**, *19*, 3.
(10) Pérez, S.; Brisse, F. *Biopolymers* **1978**, *17*, 2083.
(11) Gardner, K. H.; Blackwell, J. *Biopolymers* **1974**, *13*, 1975.

(12) Kolpak, F. J.; Blackwell, J. *Macromolecules* **1976**, *9*, 273.
(13) Sarko, A.; Muggli, R. *Macromolecules* **1974**, *7*, 486.
(14) Stipanovic, A. J.; Sarko, A. *Macromolecules* **1976**, *9*, 851.
(15) Maurer, A.; Fengel, D. *Holz als Roh- und Werkstoff* **1992**, *50*, 493.
(16) VanderHart, D. L.; Atalla, R. H. In *The Structures of Cellulose*; Atalla, R. H., Ed.; ACS Symposium Series 340; American Chemical Society: Washington, DC, 1987; p 88.
(17) Sugiyama, J.; Vuong, R.; Chanzy, H. *Macromolecules* **1991**, *24*, 4168.
(18) Horii, F.; Yamamoto, H.; Kitamaru, R.; Tanahashi, M.; Higuchi, T. *Macromolecules* **1987**, *20*, 2946.
(19) Wolf, R. M.; Francotte, E.; Glasser, L.; Simon, I.; Scheraga, H. A. *Macromolecules* **1992**, *25*, 709.
(20) Doyle, S.; Pethrick, R. A.; Harris, R. K.; Lane, J. M.; Packer, K. J.; Heatley, F. *Polymer* **1986**, *27*, 19.
(21) Hirai, A.; Horii, F.; Kitamaru, R. *Macromolecules* **1987**, *20*, 1440.
(22) Buchanan, C. M.; Hyatt, J. A.; Kelley, S. S.; Little, J. L. *Macromolecules* **1990**, *23*, 3747.
(23) Kamide, K.; Saito, M. *Polym. J.* **1985**, *17*, 919.
(24) Fyfe, C. A.; Dudley, R. L.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. *Rev. Macromol. Chem. Phys.* **1983**, *C23* (2), 187.
(25) Hoshino, M.; Takai, M.; Fukuda, K.; Imura, K.; Hayashi, J. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2083.
(26) Firsov, S. P.; Zhbankov, R. G. *Zh. Prikl. Spektrosk.* **1982**, *37*, 276.
(27) VanderHart, D. L. *J. Magn. Reson.* **1981**, *44*, 117.
(28) Morooka, T.; Norimoto, M.; Yamada, T.; Shiraishi, N. *J. Appl. Polym. Sci.* **1984**, *29*, 3981.
(29) Chanzy, H. D.; Roche, E. J. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1117.
(30) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1975**, *8*, 291.
(31) Certain commercial companies are named in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.
(32) Pérez, E.; VanderHart, D. L. *Macromolecules* **1986**, *19*, 1902.
(33) Abragam, A. *Principles of Nuclear Magnetism*; Oxford University Press: London, 1961; Chapter V.
(34) VanderHart, D. L. *J. Chem. Phys.* **1986**, *84*, 1196.
(35) Atalla, R. H. *J. Appl. Polym. Sci. Symp.* **1976**, *28*, 659.
(36) Wiley, J. H.; Atalla, R. H. *Carbohydr. Res.* **1987**, *160*, 113.
(37) Wiley, J. H.; Atalla, R. H. In *The Structures of Cellulose*; Atalla, R. H., Ed.; ACS Symposium Series 340; American Chemical Society: Washington, DC, 1987; p 151.
(38) Wells, H.; Atalla, R. H. *J. Mol. Struct.* **1990**, *224*, 385.
(39) Williams, R. M.; Atalla, R. H. *J. Phys. Chem.* **1984**, *88*, 508.
(40) Carlson, K. P. Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, WI, 1979.
(41) Horii, F.; Hirai, A.; Kitamaru, R. *Polym. Bull.* **1982**, *8*, 163.
(42) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361.
(43) Hayashi, J.; Hiroshi, K.; Takai, M.; Hatano, M.; Nozawa, T. In *The Structures of Cellulose*; Atalla, R. H., Ed.; ACS Symposium Series 340; American Chemical Society: Washington, DC, 1987 p 135.

MA9501860