A more complete report of this work will appear elsewhere.

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Cellulose Crystallites: A Perspective from Solid-State ^{13}C NMR

In a solution, rapid molecular tumbling provides an averaged environment for each chemically distinct nucleus, resulting in an averaged chemical shift. In the solid-state, the molecules are constrained in the matrix and rapid molecular tumbling is no longer possible. Different molecular environments, be they due to inter- or intramolecular inequivalencies within the solid matrix, may give rise to multiple resonance lines for each nucleus. In the case of cellulose, while the solution ^{13}C NMR spectrum shows only six lines for the six carbons of the glucose residue,[1] the solid-state ^{13}C NMR spectra show additional lines. It has become evident that they are of two categories. The origin of each category, however, is a subject of continuous dialogue. The first category, which is apparent on C4 and C6, is manifested in a narrow and a broad component. These were initially assigned to different morphological sites.[2] Later studies[3,4] assigned them respectively to ordered and disordered regions. The most recent study[5] suggests that the narrow component arises from crystalline domains, and the broad component is associated with the surface of crystalline domains as well as with disordered regions. The present study will focus on the origin of the multiplets of the second category—those found on the narrow components of the first category.

In an early ^{13}C NMR study of solid cellulose conducted at 15.0 MHz,[6] doublets were observed for C1 in cellulose I and for C1 and C4 in cellulose II. Since C1 and C4 are the two carbons involved in the glycosidic linkages, these doublets were interpreted as reflecting two distinct glycosidic linkages within the same cellulose chain, i.e., a nonsymmetrical cellobiose-like repeat unit rather than a twofold helical conformation for successive glucose units. Dudley and co-workers[7] have recently come to a different conclusion. On the basis of NMR spectral analysis of a series of cellulose oligomers, they demonstrated that the observed doublets in cellulose II are due to two independent chains in the unit cell. This conclusion agrees well with the previous X-ray crystallographic studies,[8,9] which also show that cellulose II has a two-chain unit cell (see Figure 1) with the center chain staggered differently and of opposite polarity from the corner chains. In addition, the symmetry of the unit cell proposed from X-ray diffraction data is $P2_1$, and this symmetry precludes any equivalence between corner and center chains. Thus the observed doublets probably result from these two different crystallographic sites.

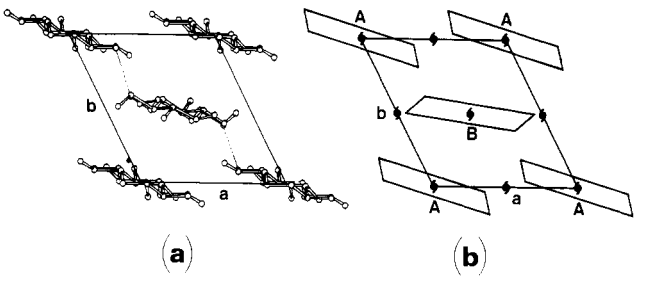

Figure 1. (a) Projection of cellulose II chains perpendicular to the *ab* plane along the fiber axis (courtesy of F. J. Kolpak[8]) and (b) schematic of the two-chain unit cell of cellulose II superimposed on a lattice with $P2_1$ symmetry.

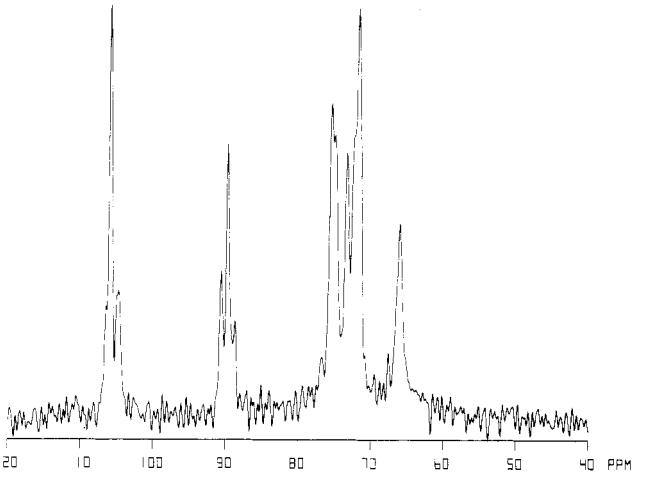

Figure 2. CP/MAS ^{13}C NMR spectrum of cellulose I (*Valonia macrophysa*), resolution enhanced.

In contrast to cellulose II, our 50.3-MHz spectrum of cellulose I (Figure 2) exhibits triplets for both C1 (105.7 ppm) and C4 (89.6 ppm). Earl and VanderHart[2] observed this same phenomenon earlier. In an attempt to reconcile this observation with an earlier study,[6] they suggested a unit cell containing four inequivalent glucose units with two different types of glycosidic linkages. We feel, however, that the origin of the observed triplets for cellulose I of *Valonia* and the doublets for cellulose II have a common basis, i.e., the symmetry and packing of chains in the unit cell. The absence of odd 00*l* reflections in the X-ray data[10,11] of crystalline cellulose indicates that any deviations from twofold screw symmetry must be very small. In addition, conformation analyses[12] favor cellulose chains possessing a conformation with or very close to a twofold screw symmetry. We note also that for most native celluloses, the 0-level (*hk*0) X-ray data can be indexed on a one-chain unit cell.[10,11] This implies that for cellulose I, the chain polarity is parallel and each chain has the same

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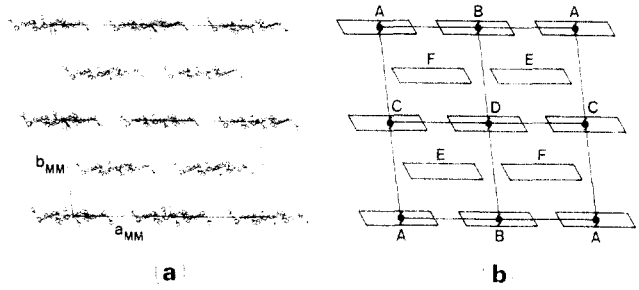

Figure 3. (a) Projection of cellulose I chains perpendicular to the *ab* plane along the fiber axis[11] (courtesy of F. J. Kolpak[16]). (b) Schematic of the eight-chain unit cell of cellulose I superimposed on a lattice with $P2_1$ symmetry. a_{MM} and b_{MM} represent two-chain unit cells proposed by Meyer and Misch.[17]

rotational orientation about the fiber axis. Furthermore, Woodcock and Sarko,[13] in their X-ray diffraction study of native ramie cellulose, attempted to relax the twofold helical symmetry requirement for individual chains. The result of that analysis indicates that there is no preference for any significant departure from twofold symmetry, as the two dihedral angles which define the rotation across the glycosidic linkage each changed by <0.5° from the values which define the twofold helix. Taken together with the observation of triplets in the ^{13}C NMR spectra of cellulose I, the data can no longer be explained simply by the alternation of inequivalent glucose units along the same chain. A further differentiating mechanism is required.

Both electron diffraction[14] and X-ray[10,11,15] studies have suggested the presence of an eight-chain unit cell (figure 3) for cellulose I in *Valonia* algae. Analogous to cellulose II, the unit cell has $P2_1$ symmetry. However, there are now six independent chains, labeled A–F, which occur in the ratio 1:1:1:1:2:2. The use of an eight-chain unit cell model was necessitated by the presence of three weak reflections (out of a total of 41) which could not be indexed for a two-chain unit cell. However, the small number and weak intensity of these reflections suggest that the deviation from the two-chain unit cell is small. For this reason, each quadrant of the eight-chain unit cell shown in Figure 3 (e.g., A–B–D–C) should approximate that of the two-chain Meyer–Misch unit cell.[17] Thus, while A, B, C, and D are crystallographically distinct sites in an eight-chain unit cell, we expect them to exhibit nearly identical chemical shifts. Chains at sites E and F, however, can be staggered or rotated differently from each other and therefore possess different chemical shifts.

The eight-chain unit cell model derived from electron diffraction and X-ray data thus predicts three distinct chemical shifts, corresponding to those chains at sites A–D, E, and F, with a predicted intensity ratio of 4:2:2, or 2:1:1. These predictions correspond well with the observed three-line pattern for both C1 and C4 shown in Figure 2.[18] Parenthetically, we note that this multiplet is derived from three different chemical shifts rather than from scalar coupling. Ideally, we would expect a 1:2:1 intensity ratio; however, due to overlap and differing line widths, the observed peak height ratios are not precisely 1:2:1.

The requirement of an eight-chain unit cell to explain the X-ray data of *Valonia* cellulose derives from the observation of three weak reflections. In ramie cellulose, however, these reflections are not observed, and hence the structure of cellulose I from ramie as determined from X-ray data is completely indexed on the two-chain unit cell.[13] For this reason we would expect to see two lines for one or more of the carbon resonances in the ^{13}C NMR spectrum. However, the spectrum we observe for ramie cellulose does not meet this expectation. After resolution

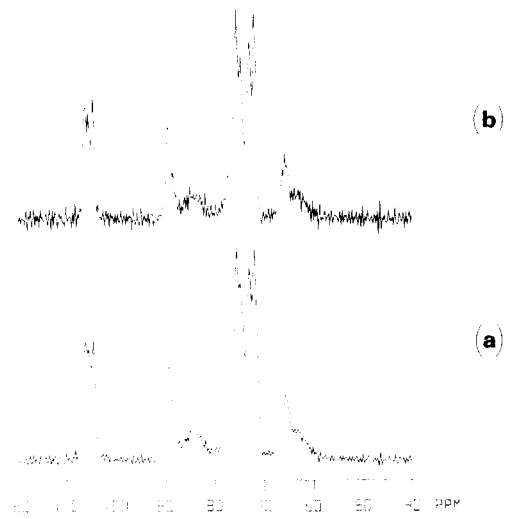

Figure 4. CP/MAS ^{13}C NMR spectrum of cellulose I (ramie) with (a) mild resolution enhancement and (b) more extreme resolution enhancement.

enhancement (Figure 4a), C1 shows a pattern of three overlapping lines, which we interpret as being predominantly a doublet, overlapping with a weaker triplet. The splitting of C4, which is usually smaller than that of C1, does not resolve well at all. Overlap of the center line of a weak triplet with a narrowly split, more intense doublet would result in the observed pattern; more extreme resolution enhancement does suggest the outer lines of the triplet (see Figure 4b).

Thus the NMR evidence suggests the presence of both two-chain and eight-chain unit cells in ramie cellulose, with the former predominating. Spectra of native cellulose from a variety of sources can likewise be interpreted as showing the simultaneous presence of crystallites of these two crystallographic forms. Since the two-chain and eight-chain unit cell structures are closely related, small distortions would be expected to lead to regions of the sample corresponding to one or the other structure.

Atalla and VanderHart,[5] on the basis of observations similar to ours, have come to a somewhat different conclusion. They propose two crystalline forms for cellulose I, which they name I_α and I_β. These model species were not observed directly but were derived from linear combinations of observed spectra. In the critical C1 region, they attribute a singlet to the I_α form and a doublet to the I_β form.

Analogous to their work, we too conclude that the spectra of various native celluloses are linear combinations of two spectra. In contrast to their view, however, we identify the C1 region of these spectra as containing not a singlet and a doublet, but a triplet and a doublet. The triplet, being the manifestation of the eight-chain unit cell region of the cellulose, is observable essentially isolated in the *Valonia* spectrum. We do not observe the isolated doublet resulting from two-chain unit cell regions, but the ramie spectrum seems to exhibit predominantly that form. In the case of the ramie spectrum, the three lines of C1 can be decomposed satisfactorily into a triplet and a doublet—the spacing of the doublet is approximately the same as that between the outer lines of the triplet. In the ramie spectrum (Figure 4) the doublet splitting is 1.6 ppm, while a spacing of 1.7 ppm is seen between the outer lines of the triplet in the *Valonia* spectrum (Figure 2). In the case of C4, the spacing between the outer lines of the triplet in the ramie spectrum (Figure 4b) has an identical value of 1.7 ppm with that in the *Valonia* spectrum (Figure 2).

On the basis of spectral decomposition alone, our explanation and that of Atalla and VanderHart[5] are equally satisfactory. However, our interpretation is based on cellulose models derived from X-ray fiber diffraction studies. As is typical in most cases of X-ray studies of polymer fibers, the observed X-ray data of cellulose fibers are limited and the computed results are underdetermined. Using the "linked-atom" least-squares methods, crystallographers have been able to carry out meaningful structural refinements and in testing the statistical significance of various models.[19] For instance, they were able to establish that in native cellulose, the "parallel chain" model is preferred over the "antiparallel chain" model by a factor of more than 200 to 1.[11] Nevertheless, due to the underdetermined nature of the system, there is still a residual feeling that the cellulose models may not have been definitively derived. That the line splitting patterns in the solid-state ^{13}C NMR spectra of cellulose I and II can now be explained, in a consistent manner, by these X-ray-derived models seems to lend further support to their validity.

Our interpretation of solid-state ^{13}C NMR data gives us the perspective that most native cellulose contain crystallites of varying distribution of two- and eight-chain unit cells. This is in agreement with the view held by Gardner and Blackwell, who, in their X-ray diffraction study,[11] concluded that small, systematic "distortions" in the packing of two-chain unit cells may lead to larger eight-chain unit cells.

Sample Preparations. Emptied *Valonia* vesicles were placed in a British disintegrator for 15 s to help break up the vesicles. They were then boiled in a 1% aqueous sodium hydroxide solution for 3 h. This procedure was repeated once on the same batch of *Valonia* fibers. Subsequently, the fibers were drained and washed with distilled water, followed by a 1-min disintegration. Afterward, a series of solvent exchanges took place: water/acetone (50:50), acetone/methanol (50:50), methanol (100%). This was then filtered in a fritted glass funnel and dried in a vacuum oven.

Delignified ramie was examined in this study without further purification.

Spectroscopic Parameters. Solid-state ^{13}C NMR spectra were obtained on a Varian XL-200 spectrometer operating at 50.3 MHz for ^{13}C. Spectra were obtained with cross-polarization and magic angle spinning, using repetition rates of 2.0 and cross-polarization times of 0.5 ms. The decoupling field strength was 40 kHz, and spin rates ranged from 2.0 to 2.7 kHz. Spectra were referenced externally by assigning the aromatic carbon of hexamethylbenzene to 132.1 ppm. The resolution enhancement composition was carried out by using an increasing exponential weighting with a time constant of 6 ms together with a Gaussian apodization time constant of 18 ms.

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Non-Gaussian Corrections at the Θ Point: Comparison between Theory, Experiment, and Numerical Simulations

The Θ state, as defined by the vanishing of the osmotic second virial coefficient A_2, is frequently identified approximately with an idealized Gaussian state having no polymer–polymer interactions.[1] Experiments on the ratio of the hydrodynamic radius R_H to the radius of gyration R_G at the Θ point, however, exhibit marked deviations[2] from ideal Gaussian chain predictions, perhaps indicating limitations to the naive identification of Gaussian and Θ-point conditions. A number of numerical simulations[3-6] have been performed to estimate the corrections to Gaussian chain predictions arising from residual polymer–polymer interactions as well as from the preaveraging approximation used to calculate R_H. Simulations have been made for the Kirkwood approximation to the hydrodynamic radius[1] R_H(Kirkwood) and substantial deviations are *still* found from Gaussian statistics even for very long chains.[3]

Theoretical calculations, on the other hand, have used a variety of approaches including the three-parameter model[7] with two- and three-body interaction parameters and other models of local chain stiffness[7-11] which employ the Gaussian state as a reference point. Predictions of these calculations are often mutually contradictory[12] and at variance with the results of the lattice chain numerical simulations, leading to the possible interpretation (reinvestigated below) that properties of Θ-state polymers are theoretically nonuniversal, i.e., model dependent.

First, it is clear that large length scale polymer properties, such as A_2, R_H, and R_G, should not be too sensitive to small length scale properties of the true polymer–polymer interactions or those of a model theory, except for a dependence on quantities like the binary and ternary interaction parameters. Hence, it is meaningful to consider these latter properties in a long length scale limit where only a few coarse-grained parameters can possibly appear. It is then sufficient to describe these large-scale observables with models having idealized δ-function type interactions

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