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Communications to the Editor

^{13}C NMR and Order in Cellulose

Previous reports of ^{13}C NMR studies of cellulose by the cross polarization/magic-angle spinning (CP/MAS) technique[1] have shown considerable promise.[2–4] The previous work not only yielded fine structure that demonstrates chemical nonequivalences within the resonance bands of the carbons involved in the glycosidic linkages (C-1 and C-4) but also addressed questions of crystal structure and morphology in relationship to sharp and broad components in the C-4 and C-6 resonance regions. Earl and VanderHart[4] have made a case, based on a study of celluloses taken from different biological sources, that the narrow-line components of the C-4 and C-6 bands are due to the internal regions of cellulose fibrils, whereas the broad-line components result from resonances due to regions on the exterior of fibrils. According to this view, the distribution between broad and sharp components depends primarily on the morphology of the cellulose sample rather than simply on the distribution of internal crystalline and amorphous regions. In the present communication we present evidence that supports this conclusion but avoids uncertainties associated with comparing samples from different plant sources. In the present work the morphology of cellulose from a single source was modified mechanically.

Four cellulose samples were prepared from cotton linters (SR210 obtained from Buckeye Cellulose Corp.) by ball milling for different lengths of time ranging from 0 to 80 h. The "apparent crystallinities" of the resulting samples were characterized by X-ray diffraction according to the method of Segal.[5] The crystallinities measured according to this criterion are 66%, 40%, 18%, and 0% for these samples. The quantitative use of Segal's X-ray method for determining cellulose "crystallinity" can be criticized; however, in this case we are interested mainly in a relative ranking, for which this method should be adequate. ^{13}C CP/MAS spectra of these samples were obtained at 37.735 MHz with a modified NT-150 spectrometer. A cross polarization time of 1 ms and a ^{1}H irradiation field of 10 G were employed. Each spectrum represents 5000 1-s repetitions, with 1K data points and zero filling to a total of 8K points. Chemical shifts are given relative to external Me_4Si (determined by substitution). The spectra are shown in Figure 1, together with a spectrum of a Whatman CC31 cellulose sample, for which the same X-ray method indicates a crystallinity of 74%.

The spectra of Figure 1, especially spectra a and b, are reminiscent of previously published cellulose spectra.[2–4] The peak at 105 ppm is assigned to the C-1 (anomeric) carbon and the band in the 70–80-ppm region is assigned to the C-2, C-3, and C-5 carbons of cellulose. The sharper resonance at 89 ppm and the broader resonance at 84 ppm are assignable to C-4; the narrower peak at 66 ppm and the broader peak at 63 ppm are due to C-6 resonances. Comparing spectra b–e, one sees that as the apparent crystallinity decreases, the relative intensities of the broader peaks at 85 and 63 ppm increase, while those of the narrower peaks at 89 and 66 ppm decrease. Also, with decreasing "crystallinity", the relative intensity within the 70–80-ppm band shifts from higher shielding to lower shielding, this band becomes increasingly featureless, and a shoulder appears on the higher shielding side of the C-1 peak at 105 ppm. Overall the resonance lines appear broader in the samples with lower apparent crystallinities.

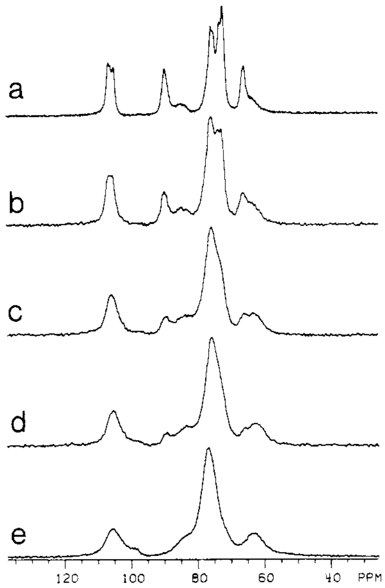

Figure 1. ^{13}C CP/MAS spectra of cellulose samples of different apparent crystallinities: (a) Whatman CC31, 74% crystallinity; (b) cotton linters, 66%; (c) cotton linters, 40%; (d) cotton linters, 18%; (e) cotton linters, 0% (amorphous).

The observed trends clearly identify the narrower peaks at 89 and 66 ppm with cellulose monomers in a more highly ordered environment and the broader peaks at 84 and 63 ppm with less ordered environments. A priori, these less ordered environments could occur in amorphous regions in the interior of fibrils or at the surfaces of highly crystalline fibrils, the extent of the latter being largely determined by sample morphology. We assume that morphology is more likely than internal fibril crystallinity to be affected dramatically by ball milling. Hence, we attribute the ^{13}C NMR spectral changes in Figure 1b–e largely to a change in the degree of monomer order, or regularity, associated with changes in morphology. It is entirely reasonable that the pattern of hydrogen bonding would be different between cellulose monomers in the surface and interior regions and that the surface regions of fibrils would present a much more diverse distribution of structural arrangements, i.e., a lower degree of order. The small peak at about 98 ppm that is most prominent in the spectrum of the amorphous sample (Figure 1e) is likely associated with C-1 carbons of end monomer units, which increase in number as prolonged milling fractures an increased number of cellulose chains. This suggestion is consistent with the 5.9-ppm chemical shift difference between the C-1 chemical shifts of internal and β end groups of cellulose models reported by Gast, Atalla, and McKelvey.[6]

In conclusion, the results of this study support the interpretations by Earl and VanderHart,[4] which were based on cellulose samples taken from different biological sources. This work underscores the difficulty of separating

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the concepts of crystallinity, morphology, long-range order, and short-range order and the extent to which each of these is addressed by different physical measurements. Further studies are under way on the nature of cellulose in plants and its interactions with lignin.

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(7) To whom correspondence should be addressed at the Department of Chemistry, Colorado State University.
(8) On leave during 1980–1981 from the Institute of Basic Problems in Chemistry, Warsaw University, Warsaw, Poland.

Gary E. Maciel,*[7] Waclaw L. Kolodziejski,[8]
Maria S. Bertran, and Bruce E. Dale
Departments of Chemistry and
Agricultural and Chemical Engineering
Colorado State University, Fort Collins, Colorado 80523

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