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High Resolution, Magic Angle Sample Spinning ^{13}C NMR of Solid Cellulose I[1]

Sir:

Recent developments in ^{13}C NMR in solids have made it possible to obtain spectra with lines narrow enough to distinguish resonances due to individual carbons in polymers.[2] We have combined the techniques of cross polarization, high power decoupling,[3] and magic angle sample spinning[4] to study a variety of solid samples. This report is a preliminary account of studies aimed at characterizing several preparations of cellulose.

We have measured the ^{13}C NMR spectra of glucose and cellobiose in the solid state and compared the spectra to peak assignments of the solution NMR spectra of the same compounds.[5] By analogy, it is relatively easy to identify the peaks in the solid-state spectrum of cellulose which correspond to carbons 1, 4, and 6. Figure 1 shows the structure of cellulose and the cross polarization/magic angle sample spinning (CP/MASS) spectrum of a sample of microcrystalline cellulose with the assigned peaks marked. This spectrum is virtually identical with other spectra obtained from native celluloses in our laboratory. This spectrum is also the same as the spectrum of Whatman CF-1 reported by Atalla et al.[1] It is significant that the peaks in the ^{13}C CP MASS spectra of glucose and of cellobiose do not have exactly the same chemical shifts relative to Me_4Si as the solution spectra of the same compounds. The differences in shifts might be attributed to packing effects in the solid or, more likely, to hydrogen bonding in the solid which is liable to be quite different from that in solution.

The chemical similarity of carbons 2, 3, and 5 make it reasonable that their resonance peaks should overlap, but, as yet, it has not been possible to make further assignments in this region. Integration of the peaks in Figure 1 gives a ratio of

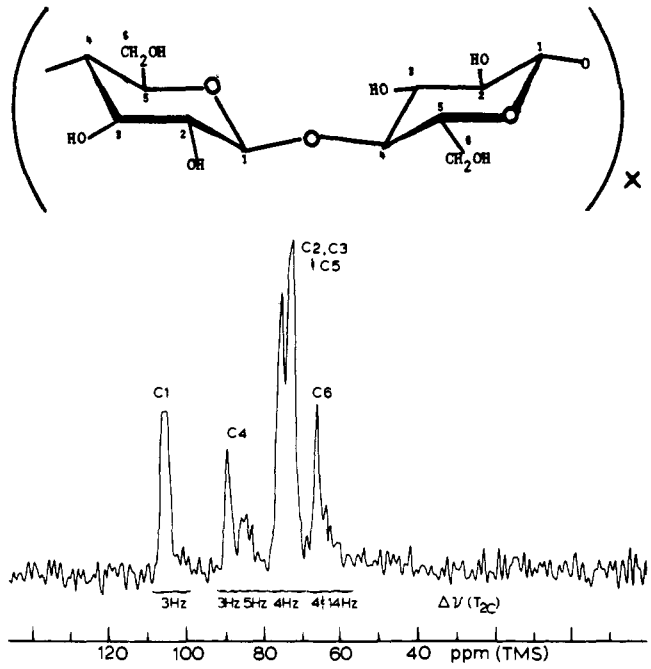

Figure 1. The CP/MASS spectrum of a dried sample of microcrystalline cellulose I. The chemical formula for cellulose is shown above. The transverse relaxation times, T_{2C}, are shown at the bottom of the figure with the regions of the spectrum to which they correspond. This spectrum is the result of 7000 scans with 1024 data points per scan at a dwell time of 50 μs per point. The external applied field was 1.4 T. The ^{13}C and ^{1}H radio frequency fields were matched at 57 kHz. The time between successive scans was 3.6 s and the spinning frequency was 2100 Hz.

1:1:3:1 but, to obtain this ratio, the C-4 resonance was assumed to include both the broad peak located between 81 and 88 ppm and the sharper peak centered at 90 ppm; similarly, the C-6 resonance included the high-field tail.

Two explanations for the broad resonance centered at 85 ppm and the upfield shoulder on C-6 were investigated. The first was that hydration of the cellulose resulted in shifts in C-4 and C-6 resonances due to hydrogen bonding with water molecules. A sample of microcrystalline cellulose[6] was carefully dried by heating to 140 °C for ~40 h under vacuum, followed by careful loading into a rotor which was sealed to prevent atmospheric water from hydrating the sample. The CP MASS spectrum of the dried sample was indistinguishable from that of a hydrated sample. Thus we have concluded that the spectral features are not due to hydration of the cellulose.

The second explanation for the broad resonances is an analogy to polyethylene where we have observed a single sharp resonance with a broad shoulder which could be attributed to noncrystalline carbons.[7] Relaxation time measurements have been used to establish that the noncrystalline regions of polyethylene exhibit much greater mobility than the crystalline regions.[8] We have investigated both the longitudinal, T_{1C}, and transverse, T_{2C}, relaxation times for the peaks observed in the ^{13}C spectrum of the carefully dried sample of cellulose I. Saturation recovery experiments were employed to get a qualitative idea of the longitudinal relaxation times, T_{1C}.[9] The long T_1 values observed in solid ^{13}C NMR in general cause T_{1C} measurements to suffer from poor signal to noise. As a result it was not possible to obtain quantitative values for the T_{1C} values, but several qualitative observations were made. The overall relaxation time for recovery of longitudinal magnetization is tens of seconds. Within the accuracy of the data, all peaks in the observed spectrum relax with the same time constant with the exception of the upfield shoulder on C-6. This shoulder has a somewhat shorter value of T_{1C}, indicating increased molecular mobility.

We have measured the transverse relaxation time, T_{2C}, for the major features in the spectrum of the same dried sample of microcrystalline cellulose. This measurement involves a modification[7] of the original echo sequence discussed by Hahn.[10] Figure 1 includes the values obtained for the T_{2C} values, reported as effective full widths at half-maximum, $\Delta\nu(T_{2C}) = (\pi T_{2C})^{-1}$. The estimated errors in $\Delta\nu(T_{2C})$ are ±2 Hz. Most of these relaxation data were nominally exponential; the decay for C-6 was clearly nonexponential and could be decomposed into two components having associated line widths of 14 and 4 Hz. The faster relaxing component was identified to be the upfield tail of the resonance line.

These relaxation studies permit several qualitative conclusions regarding the structure of cellulose I. The T_{1C} values observed and presumably the molecular motions are in a range between those observed in glassy synthetic polymers and highly crystalline materials.[11] We cannot exclude the possibility that the relaxation is due to motion of water molecules that remain after the drying process or motion of labile protons. Both the T_{1C} and T_{2C} data show a faster relaxation for the carbons in the upfield tail of C-6 relative to the sharp peak. This suggests a greater mobility or more access to labile protons for those carbons in the tail as opposed to the sharp peak of C-6. The corresponding chemical shift may arise from differences in conformation, hydrogen bonding, or crystal packing.

The observed full widths at half height, $\Delta\nu^*$, in the CP MASS spectrum of cellulose I range from 30 to 85 Hz. This can be constrasted with measured $\Delta\nu(T_{2C})$ values of <5 Hz. Since the instrumental broadening is estimated to be <3 Hz, the majority of the $\Delta\nu^*$ is attributed to a dispersion of chemical shifts along with smaller magnetic susceptibility contributions which survive the sample spinning. For comparison, the line widths obtained from a crystalline sample of glucose are <11 Hz. The chemical shift dispersions observed in cellulose I are probably due to irregularities in crystal packing which distort the glucose monomer or change the hydrogen bonding and produce slightly different shifts for different monomers.

From a magnetic resonance point of view, the coarser chemical shift features exemplified by the splitting of C-4 into two separate resonances, the shoulder associated with C-6 and the incipient splitting of the resonance of C-1 into two peaks of nearly equal intensity (in spectra of celluloses derived from cotton an actual splitting is barely resolved) all indicate that the glucose units are found in two magnetically inequivalent environments in dry cellulose I. The resulting picture that one obtains is that the glucose monomers in cellulose are rather rigidly fixed in position but that the crystalline packing is not nearly as regular as one would observe in a crystalline molecular solid or even a highly crystalline synthetic polymer such as polyethylene. It also appears that there exist two types of glucose monomers, one of which allows more freedom of motion or access to labile protons for the pendant C-6. It is not clear what the morphology of these "free C-6's" is, but it is possible that they are in amorphous regions or simply on the outer faces of the elementary fibrils[12] of cellulose. If one interprets the broad peak at 85 ppm to be due to C-4 carbons which are in amorphous regions of the polymer, the relaxation data indicates that the main chain in these amorphous regions does *not* have significantly more motional freedom than those glucose units in the crystalline portion of the sample. Alternatively, if the peak at 85 ppm is due to glucose units on the surface of the elementary fibrils and that at 90 ppm is due to glucose units buried in the center of the elementary fibril or vice-versa, then differences in hydrogen bonding or bond angles will likely be present to account for the observed chemical shifts.

We have measured CP MASS spectra of several different preparations of cellulose and are beginning relaxation studies of these samples. It is hoped that by integrating all of this information we will be able to arrive at a consistent picture of cellulose structure and its relationship to the NMR spectra obtained. It is clear that cellulose is a complicated system and that unambiguous information comes only with the greatest difficulty.

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(1) After this work was in progress, we were informed of similar research by Atalla, Gast, Sindorf, Bartuska, and Maciel (see preceding paper in this issue) concerning the solid state NMR of cellulose. We would like to thank those authors for cordial exchange of information so that not too much effort would be duplicated.
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Detection of "Tension" and Electronic Asymmetry in Imidazole-Appended Iron Porphyrins by NMR Spectroscopy

Sir:

Imidazole-appended iron porphyrins have played an important role in understanding the fundamental chemistry of hemoglobin and myoglobin oxygen binding.[1-4] Such covalently linked models will likely contribute toward elucidation of structure and mechanism in other classes of hemoproteins.[5,6] The first reported and most intensively investigated compounds are based on an amide linkage to a propionic acid side chain of natural-derivative porphyrins.[1,2] Traylor and co-workers have recently demonstrated that such models may simulate the oxygen binding kinetics and thermodynamics, as well as imidazole "tension" effects presumably responsible for the allosteric trigger in hemoglobin.[1] Collman et al. likewise utilized the "picket fence" iron porphyrin and an imidazole-appended analogue to illustrate the sensitivity of oxygen binding thermodynamics to the steric nature of the trans-coordinated imidazole ligand.[3] Additional imidazole-appended tetraphenylporphyrin (TPP) derivatives have recently been prepared via amide linkage to a single aminophenyl group[6,7] or to a pyrrole side-chain residue.[8]

A TPP-appended derivative has been prepared in this laboratory by an alternate synthetic route. An ether linkage is readily formed between the functionalized TPP species, 5-(2-hydroxyphenyl)-10,15,20-tritolylporphyrin, and a dibromoalkane.[9] The isolated bromoalkoxy porphyrin is allowed to react with imidazole using DMF solvent in the presence of a suitable base (K_2CO_3 or triethylamine). Iron insertion and subsequent chromatographic purification yields a product consistent with the structure shown in Figure 1 [isolated as the

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