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SOLID STATE NMR OF CELLULOSE, WOOD AND PULP

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ABSTRACT

High resolution ^{13}C NMR of crystalline celluloses is both complementary and supplementary to x-ray diffraction analysis because it is effective both for crystalline and non-crystalline materials. Good spectral quality has been achieved for a range of cellulose samples and spectral elements related to lateral order are observed but some interpretational details are still evolving.

The spectrum of a complex material such as wood, shows morphological and conformational features for each chemical component. The resolution achieved is sufficient to allow identification of carbohydrate resonances, methoxyl and aromatic resonances and methyl and carbonyl resonances of hemicellulose acetyls. The effect of solid state chemical treatments such as acetylation and prehydrolysis are readily detected. The use of interrupted decoupling allows one to separate the lignin and cellulose components of the spectrum.

The potential of the technique for rapid ^{13}C NMR analysis of paper debris, coated sheets and insoluble resins is now becoming well-established. More complex biosubstances such as grasses, bark and plant cell wall are being molecularly examined in their true nascent state for the first time. In this paper, a series of spectra are presented covering the various physical states of Esparto grass: native, holocellulose, alkali extracted, pulp; these spectra are compared to Esparto xylan. The line broadening effect of the latter on the C-1 resonance of cellulose demonstrates the difficulty in interpreting effects of fine structure vs. heterocomposition.

INTRODUCTION

No single physical tool has been as valuable to carbohydrate chemists over the past decade as high-resolution ^{13}C NMR spectroscopy. New experimental methods for obtaining structural and conformational information continue to be developed. In the case of (1 → 4)-linked glucans, for example, high-resolution studies of C-1/H-4' coupling and C-4'/H-1 coupling (1,2) yield parameters directly related to the interglycosidic dihedral angles ϕ and ψ. Similarly, proton relaxation methods can provide data on specific intramolecular proton distances which lead to detailed conformational analyses of both simple carbohydrates and complex polysaccharides. (3,4)

Perhaps the most promising new NMR method for studies of polysaccharide fine structure is magic-angle spinning (MAS) for recording the ^{13}C spectra of solid samples. (5-8) This technique is also invaluable for studying insoluble composite materials such as lignocellulosics, whose complex three-dimensional structure is part of their molecular signature. Wood, for example, is composed of fiber-shaped cells embedded in a matrix of lignin. The latter, a polyphenolic, permeates the fiber cell wall by surrounding the crystalline microfibrillar elements of the polysaccharide. Once dissolved, wood cellulose no longer exists in its nascent form; hence, an NMR spectrum of the solid material provides a complete molecular characterization of the cellulose native state.

For those unfamiliar with solid-state NMR techniques, a brief review of the principles involved will be presented and applications of the method to cellulose and wood chemistry subsequently discussed.

HIGH-RESOLUTION ^{13}C NMR SPECTROSCOPY OF SOLIDS

There are several differences between ^{13}C NMR spectra of materials in the solid state and in solution due to differences in the rates and amplitudes of molecular motion in the two states. It is generally necessary to employ special techniques for line

narrowing and sensitivity enhancement to obtain high resolution spectra for solids. Since these techniques are well described in several recent review articles, (5-8) only a brief overview will be given here.

Dipolar Decoupling

An important source of line-broadening in ^{13}C NMR spectra of solids is the dipolar coupling between ^{13}C and ^{1}H nuclei. The magnitude of the interaction is such that the resonance lines in the spectrum of a solid may be broadened over a frequency range greater than the entire range of ^{13}C chemical shifts (i.e., 10-40 kHz). Thus, it is generally impossible to resolve separate ^{13}C resonances for individual nuclei in a molecule. This problem may be overcome by the application of strong radio-frequency (rf) irradiation at the resonance frequency of the ^{1}H nuclei. This dipolar decoupling is analogous to the well-known heteronuclear scalar decoupling used in liquid-state ^{13}C NMR, except that for solids, the intensity of the rf irradiation must be much greater.

Magic-Angle Spinning

A second source of line-broadening in solid-state spectra is the anisotropic nature of the chemical shift. The chemical shift of a given nucleus is largely determined by its associated electron-density distribution. This distribution is generally not spherical; consequently, the shift of a nucleus in a solid depends on the orientation of the molecule in the spectrometer magnetic field. For a single crystal, a single orientation-dependent shift is observed for each chemically distinct nucleus. For a polycrystalline material, however, where the molecular orientations are random, an envelope of signals (powder pattern) corresponding to the distribution of molecular orientations in the powder is observed. This shift envelope may span the whole ^{13}C chemical-shift range, so that spectra remain broad even when the ^{13}C-^{1}H dipolar interaction is eliminated.

This source of line-broadening, referred to as chemical shift anisotropy (CSA), can be removed by mechanically rotating the sample. Rapid sample rotation (2-5 kHz) results in a continuous variation of the molecular orientations with respect to the magnetic field direction, producing a time-averaging of the CSA. The extent of this averaging scales with $(3\cos^2\theta - 1)$, where θ is the angle between the field direction and the sample rotation axis. At the so-called magic angle ($\theta = 54.7°$) the value of $(3\cos^2\theta - 1)$ is zero. The anisotropic part of the chemical shift is thus removed, leaving only the isotropic shift, as observed in solution. It should be noted, however, that the actual value of the shift may differ from that in solution, due to solid-state effects. The resolution obtained by combining magic-angle spinning with dipolar decoupling allows the observation of resolved resonances from individual nuclei in solid samples; in favourable cases, linewidths may approach those found in ^{13}C spectra of liquids.

Cross Polarization

The NMR method is an inherently insensitive spectroscopic technique since the observed transitions are between closely spaced nuclear Zeeman levels. The ground and excited states are almost equally populated; i.e., the nuclear levels are weakly polarized. This polarization is particularly weak for ^{13}C relative to ^{1}H nuclei, leading to a lower detection sensitivity of ^{13}C compared to ^{1}H. However, it is possible to improve the sensitivity of ^{13}C NMR in solids by a technique which increases the polarization of the ^{13}C levels. In this method, referred to as cross polarization (CP) or proton enhancement (PE), contact is established between the abundant, stongly polarized ^{1}H nuclei and the dilute, weakly polarized ^{13}C nuclei by the simultaneous application of matched (5-8) ^{1}H and ^{13}C rf fields. The two nuclear spin systems achieve equilibrium during this contact; the result

is an increase in the polarization of the ^{13}C system at the expense of the ^{1}H system. Properly applied, this polarization transfer scheme can yield up to a four-fold improvement in the ^{13}C detection sensitivity for solids.

There is an additional improvement in detection sensitivity due to the application of cross polarization. Fourier transform NMR spectra are acquired by averaging repetitive scans. The rate at which individual scans can be collected is limited by the spin relaxation properties of the NMR nucleus. In solid materials, ^{13}C spin relaxation can be very slow so that long equilibration periods are required between successive scans. In the cross polarization experiment, the repetition rate is determined by the relaxation properties of the ^{1}H nuclei. The ^{1}H relaxation rate is generally much greater than the ^{13}C rate, so that more scans can be acquired in a given time in the cross polarization experiment.

APPLICATIONS TO CELLULOSE

Native Cellulose

There are many areas of research where a rapid analytical method for solid cellulosic materials is required. Although x-ray diffraction and infrared spectroscopy are useful, both are deficient in that x-ray diffraction examines only the crystalline regions of the sample and infrared spectroscopy relies on an interpretation of OH and other vibrational frequencies. CP/MAS NMR, however, can probe the entire sample (both crystalline and amorphous regions) and, moreover, spectral features can be directly related to structure and conformation through the characteristic chemical shifts of specific carbon atoms. Spectra of Valonia, cotton and wood pulp celluloses are shown in Figure 1. The close similarity of the three spectra reflects their common structure (i.e., cellulose I) but the progressive broadening of C-1 and increasing shoulders for C-4 and C-6 are indicative of decreasing order/crystal size. A more comprehenisve treatment of these data can be found in a recent review. (9)

As summarized in Table 1, there are specific chemical shift differences between the polymorphs of cellulose. Not included in the table are the elements of fine structure for the C-1 and C-4 signals of native cellulose whose interpretation is still controversial. (10-12) The interpretation of the intensity of the shoulder on C-4 as a measure of degree of crystallinity is generally accepted. (13) The fact that with decreasing crystallinity all resonance lines become broad and featureless with the C-4 absorption eventually merging with the central C-2, C-3, C-5 peak has also been demonstrated in a study of a series of ball-milled samples. (14)

Table 1: ^{13}C NMR chemical shifts (ppm relative to TMS) from the 22.6 MHz CP/MAS spectra of solid cellulose polymorphs (9).

	C-1	C-2, C-3, C-5	C-4	C-6
Cellulose I	105.0	74.1, 72.0	90.0	67.0
Cellulose II	107.9, 106.2	77.7, 76.0, 73.4	88.9	64.0
Cellulose IV	103.3	72.3	82.2	62.3

Regenerated Celluloses

When textile rayon is hydrolyzed, a clear enhancement in the sharpness of the x-ray diffractometer trace is produced. Similarly, the linewidths of the C resonances in the solid-state CP/MAS spectrum of a solution-hydrolyzed hydrocellulose II are narrower than those in the spectrum of microcrystalline rayon (Figure 2). Furthermore, the degree of crystalline perfection correlates with the presence or near absence of C-1 splitting in these regenerated celluloses. (11)

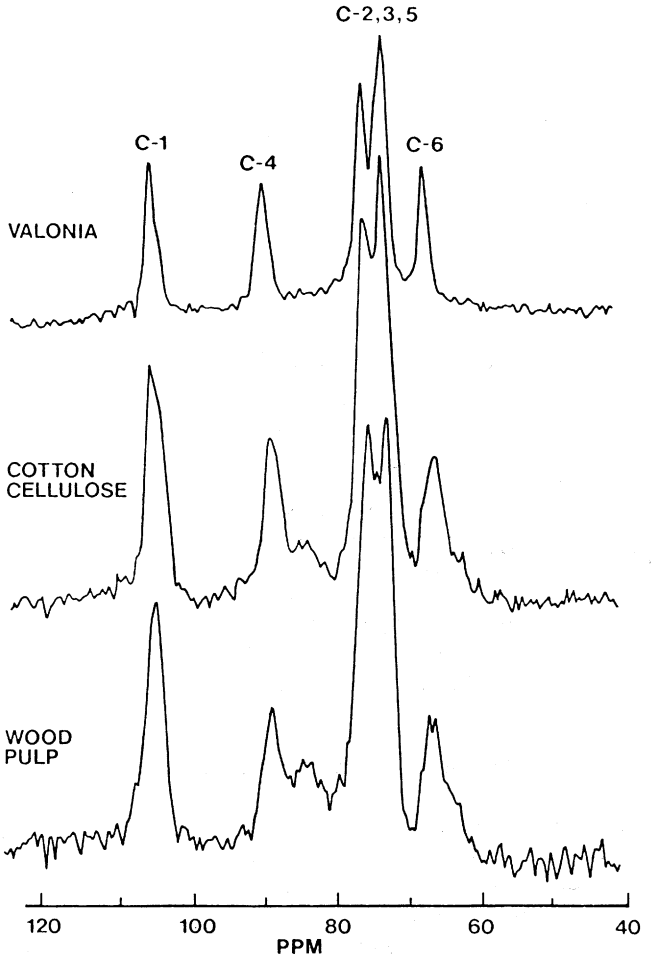

Fig 1— ^{13}C CP/MAS NMR spectra of native cellulose samples derived from **Valonia ventricosa**, cotton and wood pulp

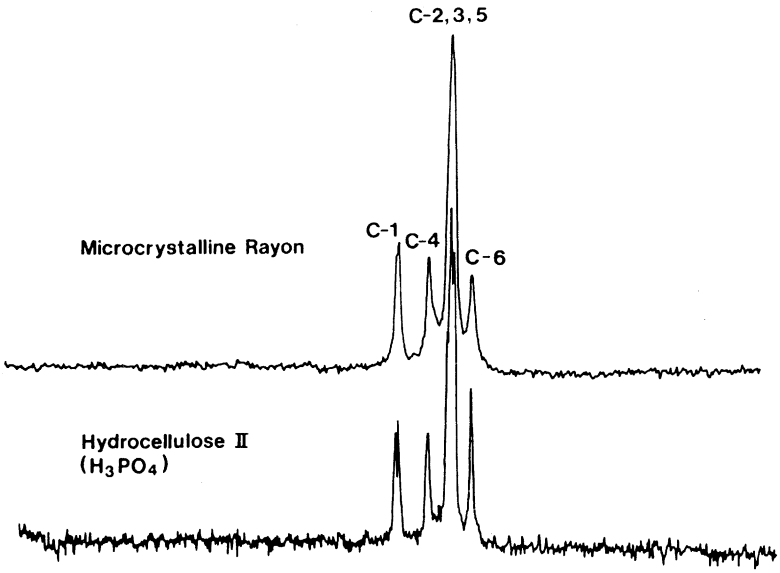

Fig 2— ^{13}C CP/MAS NMR spectra of microcrystalline rayon and hydrocellulose II (homogeneous hydrolysis in H_3PO_4 followed by precipitation from solution)

The clear splitting of the C-1 signal for well-crystallized cellulose II has led solid-state specialists to attempt to use ^{13}C CP/MAS data to complement x-ray diffraction analysis. The latter technique resorts to modelling in order to find a proposed structure whose calculated intensities match the observed. (15) In the case of cellulose II, an antiparallel-chain model has been favoured by x-ray crystallographers. (16,17) The origin of the C-1 splitting has led to extensive discussion and further experimentation, with spectra of the quality shown in Figure 3 being consistently reported. (9) From the spectra of Figure 3 one can see that both C-1 and C-4 signals are split as is C-1 in the model compound cellotetraose. Except for small peaks from the end residues, the cellotetraose spectrum is essentially the same as that of cellulose II. (18)

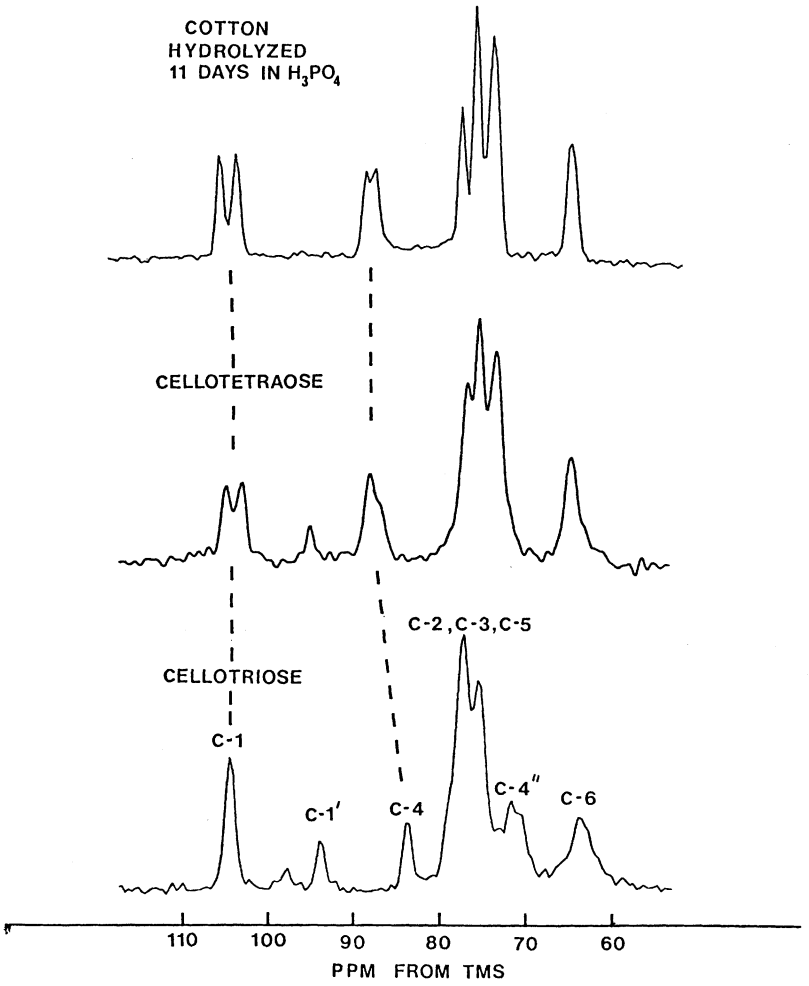

Fig 3— ^{13}C CP/MAS NMR spectra of cellutriose, cellotetraose and a cellulose II sample from the homogeneous H_3PO_4 hydrolysis of cotton

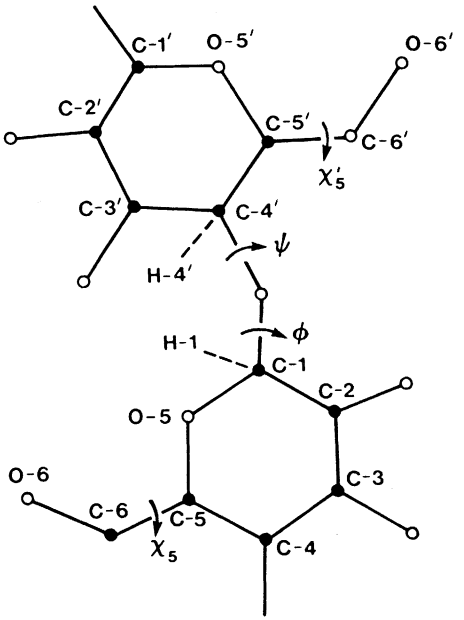

Fig 4—Diagram showing the glycosidic dihedral angles ϕ and ψ and the torsional angle χ in the cellobiose repeat unit

The published x-ray data for cellotetraose show a cellulose II type of conformation and unit cell, (19) but the full three-dimensional x-ray based structure is not available. The following comments refer to the Hermans conformation (fig. 4) for the cellobiose entity in crystalline cellulose where ϕ and ψ represent the rotatable dihedral angles whose regular repetition generate a regular helical array of the anhydroglucose units in the cellulose chain; the torsional angle χ controls the position of the O-6 oxygen with respect to the anhydroglucose unit.

The close similarity between the spectra of cellotetraose and cellulose II suggests that the C-1 splitting arises from two independent chains in the unit cell rather than alternating dihedral-angle pairs (ϕ,ψ) along a single chain, as has recently been proposed.(12) Cellotetraose has only three sets of ϕ, ψ dihedral angles per molecule which would predict a 2:1 intensity ratio for the C-1 doublet; since the two C-1 signals are essentially of equal intensity, one cannot account for the cellotetraose result except in terms of two independent chains with uniform ϕ , ψ pairs in a given chain.(18)

Additional conformational information concerning the preferred rotameric position of O-6 will probably be forthcoming. In Table 1 there is an indication that the cellulose I C-6 chemical shift is sufficiently different from that of cellulose II to suggest that O-6 rotameric positions are not identical in the two polymorphs. What is lacking at present, is a full understanding and calibration of the solid-state chemical shift of C-6 as a function of χ. A promising approach to the problem has recently been reported. Using x-ray diffraction and ^{13}C CP/MAS data for crystalline small-molecule carbohydrates (mono- and disaccharides) Horii, Hirai and Kitamaru (13) have constructed approximate linear correlations between ϕ , ψ and χ and C-1, C-4 and C-6 chemical shifts. With these correlations, it should be possible to derive semi-quantitative ϕ , ψ and χ values directly from ^{13}C solid-state chemical shifts.

In the case of simple carbohydrates, crystal-structure effects on chemical shifts and multiplicities are being actively investigated.(20-22) Here also, model studies are helpful. For example, the molecules methyl-β-xylopyranoside and methyl-α-xylopyranoside gave respectively 6 and 12 signals for the CP/MAS spectra of the crystalline solids.(20) These observations are consistent with 1 and 2 molecules per unit cell, respectively, and provide some support for our interpretation (18) that the C-1 and C-4 signal splitting in cellulose II is related to the presence of two independent molecules in the unit cell. In general, peak multiplicities will be seen if the site symmetry in the crystal is less than the molecular symmetry for the isolated molecule and if the unit cell contains more than one chemically equivalent molecule.

Wood, Grass and Process Chemistry

A number of publications have focussed on the use of ^{13}C CP/MAS NMR for the characterization of wood, holocellulose and grasses,(23-25) all of which contain a complex mixture of cellulose, hemicellulose and lignin. The spectra are all rather similar and changes in chemistry due to solid state reactions are usually interpretable in a straightforward way (e.g., partial acetylation of wood markedly increases the acetyl C=0 and CH_3 signals at 175 and 25 ppm). Strict quantitative interpretation should not be expected from the technique at this time, however.

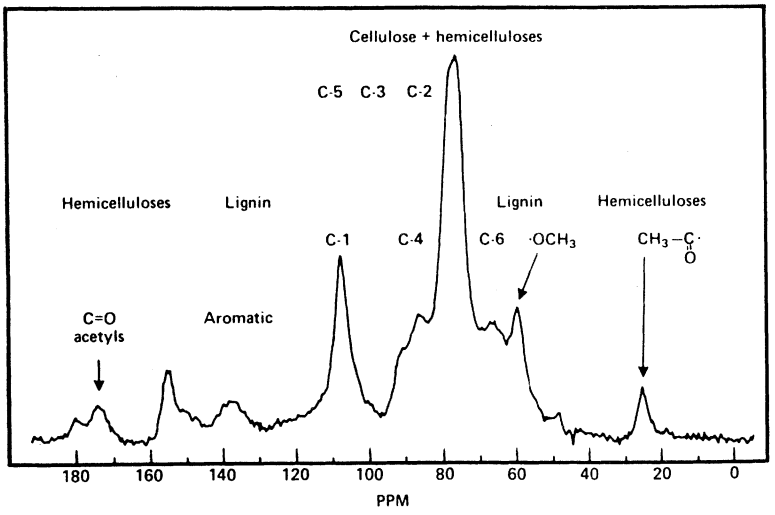

Fig 5— ^{13}C CP/MAS NMR spectrum of solid ash wood

Figure 5 shows the CP/MAS spectrum of a typical hardwood; all of its chemical components (cellulose, hemicellulose, lignin) may be associated with one or more resonances. Thus some overlap of peaks is inevitable leading to several broad resonances rather than the sharp, well-resolved lines usually observed in the NMR spectra of liquids or solutions. The resolution obtained, however, is sufficient to identify the several major components of wood. The spectrum is dominated by resonances arising from cellulose and hemicellulose components. The peaks between 65 and 110 ppm. can be assigned as indicated by comparison with solution spectra of hemicelluloses and celluloses.

Several other less intense signals are observed for hemicellulose components. The acetyl groups of the O-acetyl (4-O-methyl-glucururono) xylan give rise to signals for the acetyl methyl group at 26 ppm and the acetyl carbonyl group at 175 ppm. In addition, the minor peak at 180 ppm may result from the carboxyl groups of 4-O-methy-glucuronic acid residues attached to the xylan chain. The observed chemical shift suggests that at least some of the glucuronic acid residues occur as salts in the wood.

In the case of a composite such as wood, which contains a polyphenolic and carbohydrate components, a technique called interrupted or delayed decoupling (7) is useful for separating the two components. Figure 6a shows the spectrum of spruce wood after a short but severe explosive prehydrolysis treatment.(25) In Figure 6b, where delayed decoupling was used, carbohydrate components are removed from the spectrum because these components contain only protonated carbons.(7) In addition to non-protonated carbon resonances, the interrupted-decoupling technique leaves attenuated methoxyl signals at 56 ppm. Finally, the difference spectrum, Figure 6a minus 6b shows the carbohydrate component of the composite. Spectral manipulations of this type are starting to be explored extensively in biomass studies.(26)

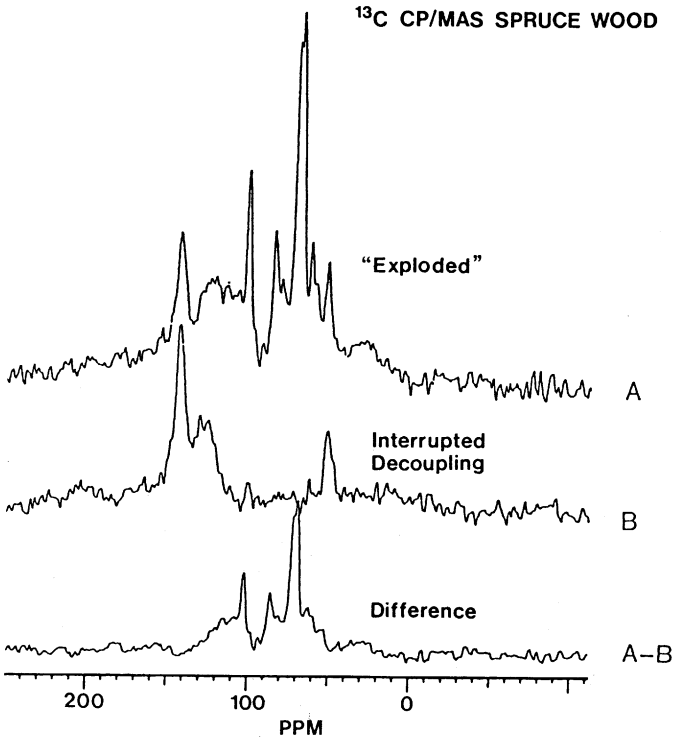

Fig 6— ^{13}C CP/MAS NMR spectra of "exploded" spruce wood. Spectrum A is the normal spectrum, while spectrum B was obtained using the interrupted decoupling technique

The ability to examine composite materials in their nascent forms can be exploited in the study of processing chemistry of lignocellulosics. This application is illustrated by following the processing of Esparto grass from the native material through to the pulp stage. A collection of spectra is presented in Figure 7.

The first spectrum, 7a, was obtained with Esparto grass washed with ethanol/benzene to remove waxes, etc. This spectrum can be compared with that of solid ash wood, Figure 5. Resonances due to the cellulose and hemicellulose components are readily observed in the Esparto spectrum. Lignin component resonances are indicated with asterisks above the 4X expansion inset in Figure 7a. The indicated bands at approximately 150 ppm and 55 ppm are due to oxygen substituted aromatic and methoxyl lignin components respectively. The relative weakness of the intensities of the lignin resonances reflects the low concentration of lignin in the Esparto grass in comparison to wood.

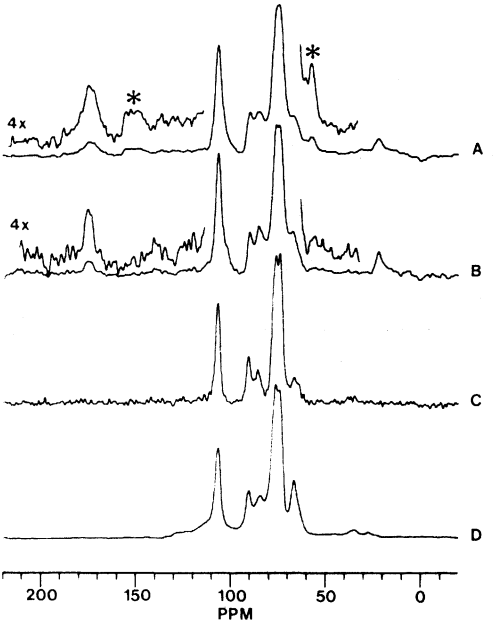

Fig 7— ^{13}C CP/MAS NMR spectra of Esparto grass derived samples. Spectrum A corresponds to the native material after ethanol/benzene washing. Spectrum B is shlorite holocellulose. Spectrum C is holocellulose extracted with 1% NaOH. Spectrum D is a commercial Esparto grass pulp.

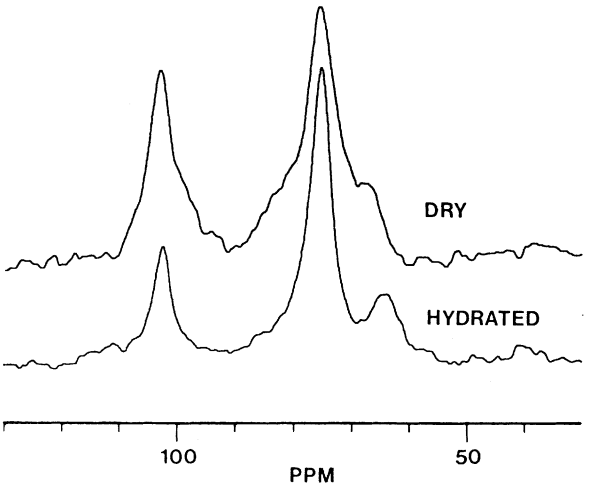

Fig 8— ^{13}C CP/MAS NMR spectra of Esparto grass xylan corresponding to the "dry" and "hydrated" polymorphs.

The spectrum of holocellulose prepared by the chlorite method is shown in Figure 7b. It can be seen that the lignin resonances mentioned above are absent, while the carbohydrate component resonances are still prominent. Treatment of this holocellulose with aqueous NaOH results in the saponification of hemicellulose acetyl functions and extraction of the xylan component. The spectrum of the extracted material is shown in Figure 7c. The acetyl resonances (approximately 175 ppm, carbonyl; appproximately 25 ppm, methyl) are absent and a careful examination of the carbohydrate C-1 region, at approximately 105 ppm, reveals a sharpening and loss of a high field shoulder in the C-1 peak of the extracted material as compared to the holocellulose. This observation is related to the extraction of the xylan component as will be illustrated below.

Finally, a spectrum of pulp derived from the Esparto grass was obtained (Figure 7d). With the high signal/noise ratio of this spectrum, one can observe spinning sidebands in the 25-40 ppm region. The pulp spectrum is typical of those observed for other pulps and for paper. The resonance at 85 ppm is associated with non-crystalline cellulose and is broader in the pulp than in the xylan-extracted holocellulose. This suggests that mild alkali-treatment of holocellulose is a pseudo annealing process for cellulose.

The ^{13}C spectrum of the xylan component extracted from the holocellulose was also obtained. The dry xylan first obtained in a lyophilized form was hydrated by exposure to an atmosphere of 100% relative humidity at room temperature for four days. As was noted previously for other carbohydrates, (27) hydration often results in a sharpening of the ^{13}C resonance lines due to improved conformational homogeneity in the solid carbohydrate. The effect of hydration on the ^{13}C spectrum of the Esparto xylan is illustrated in Figure 8. The spectra are shown before (upper) and after (lower) hydration. Sharpening of the resonances is observed resulting in improved resolution. This effect is not as spectacular as has been noted with other polysaccharides, such as $\beta(1\rightarrow3)$ glucan (27, 28, 29), perhaps because the crystalline xylan hydrate contains more than one polymorph. (27, 28)

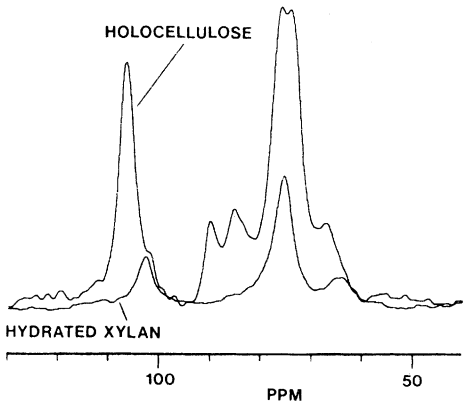

Fig 9— ^{13}C CP/MAS NMR spectra of Esparto grass holocellulose and hydrated xylan.

The influence of the xylan component on the ^{13}C spectrum of the holocellulose material is seen in Figure 9, where the spectra for holocellulose and the xylan hydrate are superimposed. In the holocellulose spectrum, a high field shoulder is observed on the C-1 peak at approximately 102 ppm. This shift corresponds to the location of the xylan C-1 peak. Further evidence that this shoulder is due to xylan is obtained from the spectrum of the holocellulose after extraction of the xylan (Figure 7c) where this shoulder is no longer observed.

These and many other applications will undoubtedly make ^{13}C CP/MAS NMR as valuable for materials studies as infrared and UV/visible spectroscopy are already. Correlations between solution- and solid-state NMR data bases should greatly advance the materials scientist's objective of "understanding molecular level influences on macroscopic behaviour". (6)

CONCLUSIONS

The information to be derived from ^{13}C CP/MAS NMR spectroscopy is still being counted and assessed. In the lignocellulosic field, much remains to be understood in terms of nascent morphology of the lignin, cellulose, hemicellulose complex. From changes in the NMR spectrum after delignification in the case of Esparto grass, one hopes to make inferences concerning the relative association of xylan with lignin, with itself and with cellulose. Such information will probably derive from relaxation studies. Certainly the study on Esparto grass and studies of this kind on lignocellulosics are essential if one is to obtain a full understanding of the elements which contribute to spectral broadening in lignocellulosics.

The potential of the technique for following chemical changes which result from pulping, bleaching, extraction and derivitization chemistry is strong. Similarly, information on the physical state of macromolecular components, i.e., crystalline vs. non-crystalline has been demonstrated for cellulose (13). What is only beginning to be explored is the potential for understanding the association of similar glycans such as xylan, mannan and cellulose.

Of great promise for cellulose studies is the information from ^{13}C CP/MAS concerning the population of C-6 rotational isomers. X-ray crystallographers have been completely dependent on modelling studies concerning the choice of rotameric position for O-6 in a given cellulose polymorph. As may be seen from Table 1, the CP/MAS spectrum of cellulose polymorphs would appear to provide information on dihedral angle χ for each polymorph. A correlation between the observed chemical shift and the corresponding χ value is being actively sought by means of model CP/MAS studies on crystalline mono- and oligosaccharides whose crystalline structure has been fully determined such as the cyclodextrins.(32)

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Transcription of Discussion

Solid State NMR of Cellulose, Wood and Pulp

by R.H. Marchessault, M.G. Taylor, G. Hamer and Y. Deslandes

Prof. R.H. Atalla IPC, Appleton, USA

I would like to comment on three items in Dr. Marchessault's published text.

a) In relation to the xylan spectra, we have had the opportunity to record spectra on samples prepared by Dr. Yundt when he was working with Prof. Louis Wise in 1948 at the Institute. You may recollect that he was the first to prepare a polymer single crystal; he did this in 1948, nine years before Keller's preparation of polyethylene single crystals. Those samples give much higher resolution spectra and much narrower lines than you show in your spectra thus supporting your thought that you might have a multiplicity of polymorphs of xylan.

b) The second point is in reference to the spectra shown in Fig. 7 (d) where you observe the spinning sidebands at 25 to 40 ppm, and this is simply a caution to the audience that spinning sidebands associated with the aromatic rings usually overlap with the signals associated with the carbohydrate resonances complicating problem of interpreting the spectra in the case of wood.

c) In relation in the spectra of cellotetraose, I want to report that at the Symposium on Solids State Characterisation of Cellulose held at the ACS meeting on 9th and 10th September, 1985, the group of Perez and Winters and their co-workers from Grenoble reported that their results indicate, on the basis of conformational analysis and recalculation based on Poppleton's intensity data, that the cellotetraose molecule has two glycosidic bond systems similar to those in methy β cellobioside, and the one at the reducing end corresponding to cellobiose, suggesting that there are indeed nonequivalent glycosidic linkages in that molecule.

Dr. R.H. Marchessault The xylan of Esparto grass at one stage was reported to be a very pure xylan. That is apparently a very special preparation. Analysis by Jean Paul Joseleau (Grenoble) of our xylan shows it is typical of hardwood xylan with arabinose and uronic acid attached to it. It certainly wouldn't be as crystalline as the single crystals prepared by Yundt.

Prof W. Scott Miami University, Oxford, USA

I have a question with regard to your technique for conformational analysis; what is the sensitivity of the method to the conformational angles in terms of the O-6 and C-1 and C-4?

Marchessault For the C-6 carbon in CP/MAS NMR spectra of cellulose and other solid carbohydrate polymers the change in chemical shift is 2-3 ppm for 120° change in O-6 i.e. 40-60°/ppm. For C-1 and C-4 the relation is much more sensitive ie. 2-3°/ppm. These conclusions are based on observations with crystalline carbohydrates and model compounds whose full three dimensional crystal structure is known.

Dr. J. Roberts UMIST, Manchester, England

Is the two dimensional NMR technique applicable to the solid state, and if so is it likely to yield conformational data which would give you more information on the organisation of the molecules in the crystal lattice? Also, can you deduce anything about the sites of substitution in acetylation?

Marchessault The exploration of how two dimensional NMR can yield information on the solid state organisation of wood is underway in Prof. Maciel's laboratory (Colorado State University). It is likely to be a useful approach for characterising orientation and lateral order. The use of solid state NMR for following the chemical derivatization of cellulose in the solid state is now being studied for the nitration reaction. It is too early to judge how much information will be provided regarding the sites of substitution. However, it is too early for me to make further comment.

Prof. S.G. Mason McGill University, Montreal, Canada

I would like to ask you two questions:

Firstly, in your C^{13} NMR technique what does CP/MAS designate?

Secondly, I take it that you still reject out of hand R. St. J. Manley's concept of folded structure in native cellulose crystals. He, on the other hand, is more convinced than ever of the correctness of his picture and is about to embark on a collaboration with a theoretical chemical-physicist on a statistical thermodynamical test of the model.

Marchessault The CP stands for cross polarisation and it is part of the technique that essentially allows you to get the spectra in a reasonable length of time and in conditions where the intensity of the carbon signal is manageable. MAS stands for magic angle spinning.

I think that a model which involves extensive chain folding of native cellulose just doesn't stand up to the data. I feel that much more experimental data is required before this concept can be seriously considered. So, I reject it at present through lack of supporting experimental data.