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Analysis

High Resolution Solid State ^{13}C-NMR Study of Heterogeneous Reactions on Cotton Cellulose

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Summary

High resolution solid state ^{13}C NMR spectra of cellulose of different origins present complexe features : thin multiplets and broad lines. Chemical substitution of accessible hydroxyl groups by $-OCD_3$ and -OTMS groups of cotton fibers has been achieved in mild conditions by means of heterogeneous reactions.

The observed modifications of the solid stage ^{13}C spectra of modified cotton celluloses are related to morphological substituted sites.

Introduction

Previous works on solid state analysis of cellulose by means of ^{13}C NMR CP/MAS spectroscopy, have shown various interesting features about the structure of this natural polymer (1-5). One of the main characteristic of the cellulose solid state ^{13}C NMR spectrum is the fine structure observed for each kind of carbon atom of the constitutive unit. Cellulose is a poly ß-(1→4) D-glucopyranosyl polymer which should give six signals corresponding to the D-glucopyranosyl repeating unit, as observed for its solution ^{13}C NMR spectrum (6,7). In the solid state, the sequence obtained by X-ray diffraction along the c axis (chain axis) is 10.4 A and corresponds to a D-cellobiosyl unit with a twofold screw axis along the chain. In that case, providing a magnetic inequivalency of the two D-glucopyranosyl units carbon nuclei, a twelve signal pattern should be expected as solid state ^{13}C NMR spectrum. It also presents a change of signal multiplicity with the crystalline polymorphism state of cellulose, either native cellulose I with parallel chains or regenerated cellulose II with antiparallel chains. The last important remark concerning the cellulose ^{13}C CP/MAS solid state spectra, is the presence of broad signals accompanying thin ones, especially for well separated signals corresponding to C-4 and C-6. The broad signals are mainly observed for cellulose I form (3) and for amorphous cellulose (1,4). It has been shown by relaxation time measurement, that these broad signals correspond to more mobile nuclei and thus were assigned to surface atoms (3).

The work presented here has been conducted on cotton cellulose, which presents the highest ratio of broad/thin signals. A heterogeneous labelling of surface cotton fibrills has been achieved, in order to observe the modification of the solid state ^{13}C NMR spectrum.

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Methyl and trimethylsilyl (TMS) groups have been used as labelling agents, and chemically linked by using the reactivity of the accessible hydroxyl groups of cellulose.

Experimental :

Labelling of cotton cellulose by methyl-d_3-groups :

Natural cotton was sonicated four hours in water, suspension, then freezedried. Treated cotton (1 g) in suspension in 100cm^3 of DMSO was then activated by using the HAKAMORI methylation method (12) with 4.5 cm^3 of active reagent obtained by dissolving sodium hydride in dimethyl sulfoxyde (2.08 mole NaOH/cm^3 of dimethylsulfoxyde). The activation step proceeds 12 hours at room temperature under nitrogen atmosphere. 0.5 cm3 of CD_3I was then slowly added (0.5 mole CD_3I per cellulose hydroxyl group) and the reaction time varied from 2 to 8 hours. Methylated cotton samples were isolated by washing with water, acetone and then dried. Degree of substitution were determined from elementary methoxyl analysis.

Sample	Reaction time (hours)	OCD_3 %	DS
I	2	2.35	0.11
II	4	8.45	0.41
III	8	14.13	0.71

Cotton cellulose labelling by trimethylsilyl groups :

Gaz-solid heterogeneous silylation :

It was achieved by impregnating 0.7 g of treated cotton by 9 cm3 of N,O bis(trimethylsilyl)acetamide. The reaction was carried out in a closed stainless steel bomb at 150°C under pressure, during 2 hours. After cooling, the silylated cotton was washed with anhydrous acetone and dried under vacuum.

Infrared : Si-C streching at 1250 and 845 cm^{-1}; % Si : 0.5 DS = 0.1

Liquid-solid heterogeneous silylation :

This was done by a modified method for obtaining trimethylsilyl derivatives of polysaccharides (15). 5.18 g of treated cotton in suspension in 350 cm3 of formamide was heated at 50°C during 3 hours. After cooling to room temperature, 50 cm3 of hexamethyldisilazane was slowly added. The suspension was vigorously stirred and solid cotton was periodically sampled.

After 24 hours at room temperature, the temperature was raised to 70°C.

Each sample was washed with dry aceton and dried under vacuum. Silicon analysis and calculated degrees of substitution are given below :

Sample	Reaction time (hours)	Temperature	Silicon content (%)	DS
1	15	20	< 0.1	0.
2	24	20	2.9	0.18
3	28	70	4.85	0.32
4	32	70	6.45	0.45

Solid state CP/MAS high resolution ^{13}C NMR spectroscopy :

All the NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Bruker CXP 200 spectrometer. Cross polarization times of 1 to 2 ms and repetition times of 4 s were used. There were 2k data points in the FID, followed by a 8k data transformation. The spinning rate was set at 3.1 kHz. The number of scans per spectrum was generaly of 2000. Solid polyethylene was used as an internel reference at 33.6 ppm (3).

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Results and discussion :

Chemical modification of cellulose has been widely used to obtain cellulose derivatives. This study is only concerned with low substitution degrees - typically $0.1 < DS < 0.5$ - corresponding to less than 20% of substituted hydroxyl groups, in order to minimize the destructuration of the original cotton morphology. Penetration and reaction of the reagents has been facilitated : 1- by sonicating the natural coton in water suspension and then freeze-drying, 2- by swelling the freeze-dried cotton with a polar solvent (dimethylsulfoxyde or formamide). In all cases, the reaction proceeds in heterogeneous conditions (liquid-solid otherwise mentioned). It is not the aim of this study to look at the different hydroxyl reactivities of cotton cellulose as it has been done elsewhere (9).

The heterogeneous reaction conditions used in this study have been chosen so as to discriminate between microfibrills surface and interior hydroxyl groups of cotton cellulose. Cotton cellulose has been shown by the X-ray cristallography method to be approximately 80% crystalline with elementary fibrills having a cross section of 3.5 x 3.5 nm (10,11). First step heterogeneous reactions occur on accessible surface hydroxyl groups situated either on the highly ordered microfibrills or in disrupted microfibrills (amorphous regions), which have been shown to exist owing to preferential acid hydrolysis at these fragile points.

Surface labelling by methyl groups :

Surface labelling of cotton cellulose has been carried out by using the methylation method of Hakamori (13). In this method, the substract is activated by the methylsulfinyl ion obtained by dissolving sodium hydride in dimethylsulfoxyde. Then methylation was achieved via a deficiency of deuterated methyl iodide (0.5 mole per hydroxyl group). A deuterated reagent was used to avoid an important $O\text{-}CH_3$ signal in the C-6 region of cellulose ^{13}C NMR spectrum. Average degrees substitution from 0.11 to 0.71 were obtained by varying the reaction time and the step number.

Figure 1 indicates the results of the methoxyl labelling of cotton. Figure 1A shows the ^{13}C NMR solid state reference spectrum of native cotton. It is identical to the previous published one, which indicates that sonication has no visible effect on the ^{13}C NMR spectrum nor on the X-ray diffraction diagram. Figures 1B, C, D show the evolution of the spectra when increasing the substitution amount from 3.6% (DS = 0.11) to 23% (DS = 0.71). The main feature of these spectra is the noteworthy stability of the thin signals which are rather more resolved in the case of labelled cotton than the original one. This fact implies a non destructurated crystalline lattice, as it has been shown that the destruction of crystallinity dramatically reduces the resolution of the solid state NMR spectrum of cotton (4).

The second feature of these spectra is the expected increase of the large signals occuring at 86. and 61.5 ppm. The signal at 61.5 ppm is due to the presence of OCD_3 carbon, which is observed by cross polarization with neighbouring protons. Signals situated at 86 ppm are due to substituted carbon atoms (C-2 and C-3). The ^{13}C NMR study of cellulose and trimethylcellulose in solution have shown that methylation of hydroxyl bearing carbon atoms induces a downfield shift ($\Delta\delta$ = +9 to +10 ppm) of these signals. Methylation also induces a small downfield shift for C-1 ($\Delta\delta$ = + 1 ppm) while C-4 is shifted upfield ($\Delta\delta$ = -3 ppm) (13). This methylation shift has also been observed by the solid state CP/MAS ^{13}C NMR spectrum of trimethylcellulose. In that case, C-4 resonates at 86 ppm while substituted C-2 and C-3 appear at 87.5 ppm. These carbon signals are thus assigned to the large signal centered at 86 ppm as shown on figure 1.

On Figure 1, the upper trace is the difference spectrum obtained by substracting spectrum A (natural cotton cellulose) from spectrum C (DS = 0.71). The positive signals correspond to trimethylcellulose signals, while negative signals correspond to substituted cotton signals.

From these results we can assume that cotton methylation, in our experimental conditions, mainly proceeds via accessible reactive hydroxyl groups up to an amount of 20 % of the total hydroxyles. That tends to show that D-glucopyranosyl units on the surface of the microfibrills are mainly trisubstitued. The fact that methoxyl signals are not resolved in three signals as for solid trimethylcellulose (δ = 59.5, 61.9 and 62.7) must be related to a structural disorder in the surface regions of fibrils, bringing about a distribution pattern of the magnetic environment.

Methoxyl groups are interesting labelling groups for the discrimination of interior and accessible reactive hydroxyl groups of cellulose. However, methylation induces strong shift for the substituted carbon signals and the adjacent ones. These shifts overlap since some signals are shifted "low-field" while others are shifted "upfield". The methoxyl carbon signals, though deuterated, are situated in the 60-65 ppm region, which does not facilitate the observation of C-6 cellulose signals.

Surface labelling by trimethylsilyl groups :

Trimethylsilyl groups due to their bulky nature, are expected to be more specific of a surface reaction than the one occuring towards the interior of cotton fibrills. Furthermore, as shown by the solid state ^{13}C NMR spectrum of tri-(TMS)-cellulose (DS = 2.4), signals of the substituted units (C-1 at 103, C-4, C-5, C-3, C-2 at 78, C-6 at 61.5 ppm and TMS carbon atoms at 2.5 ppm) will not be superimposed to those of original cotton, except for the main signal at 78 ppm. This labelling group has another advantage inherent to the high variety of silylating agents which allowed us to conduct both gazeous-solid and liquid-solid reactions.

Figure 2 shows the results brought about by different silylation amounts of cotton cellulose samples, on their high resolution ^{13}C NMR spectra. Sample B was silylated by using N,N-bis(trimethylsilyl)-acetamide in gazeous phase as silylating agent. Samples C, D and E were silylated by using hexamethyldisilazane in the liquid state at different times and temperatures.

The presence of TMS labelling groups was checked by infrared spectroscopy using the Si-C streching vibrations at 1250 and 845 cm^{-1}. Degrees of substitution were determined via silicon elemental analysis.

On Figure 2 only the low field part of the spectrum is shown, since no TMS signal around 2 ppm were visible, for weak degrees of substitution.

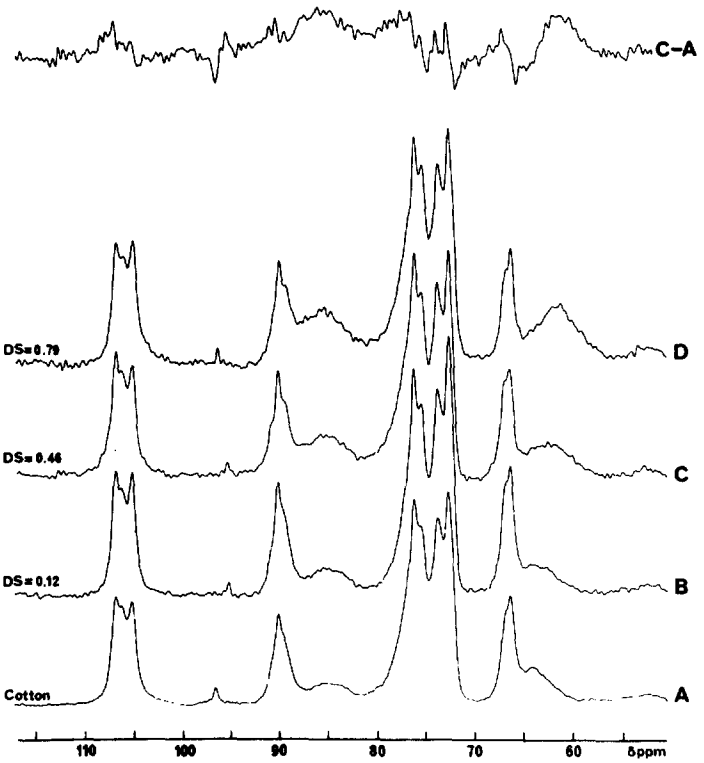

Figure 1 : High resolution solid state CP/DD/MAS ^{13}C NMR spectra of : A, Cotton cellulose ; B, C, D, Cotton samples surface labelled by $-OCD_3$ groups at different DS.

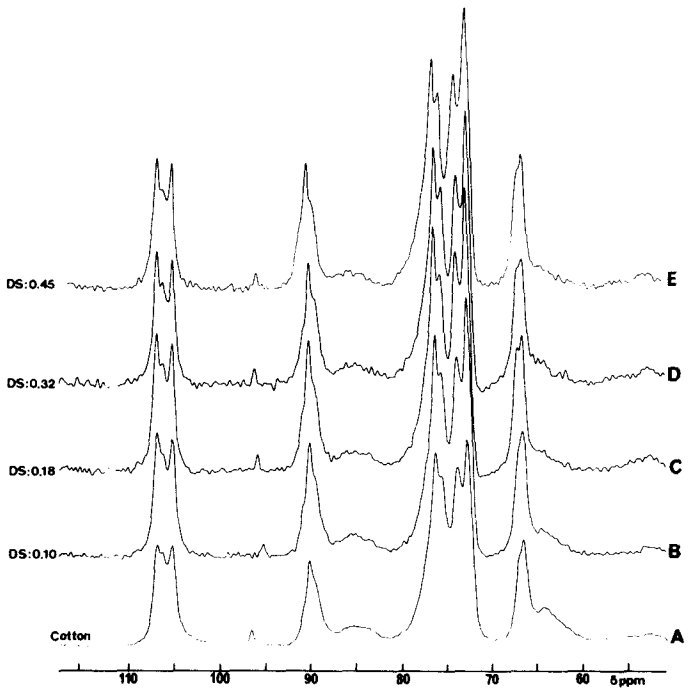

Figure 2 : Solid state high resolution ^{13}C NMR spectra of :

A, Cotton cellulose ; B, C, D, E, Cotton cellulose surface labelled by trimethylsilyl groups at different DS.

This is the first information given by this experiment. As solid state high resolution ^{13}C NMR spectra are obtained by cross polarization of carbon nuclei with proton ones, the absence of TMS signals could indicate a lack of cross polarization related to the small value of T_1 CH of TMS groups. However the use of various contact time values from 0.1 ms to 2 ms does not significantly alter the spectra. Another possibility could arise from the inefficiency of dipolar decoupling, coming from the rotation of the TMS groups at a frequency in the range of ^{13}C-H dipolar interactions. In any case, the absence of TMS signals should be related to their high mobility, as it has already been observed for dimethylsiloxy groups of polysiloxane (16). The observation of TMS signals for tri TMS cellulose (DS = 2.4) would indicate a lowering of this rotation frequency due to steric hindrance of the substituents. This is corroborated by the fact that a labelled TMS cotton cellulose of an intermediate DS = 1.5 - prepared in more drastic conditions - shows effectively the presence of a TMS signal together with a clear destructuration pattern.

The second feature is the disappearance of the upfield large signals of carbon C-4 and C-6, which indicates that surface labelling highly modifies these signals. We can also notice a decrease in the intensity of

the C-1 central line situated at 106.5 ppm. The decrease of these signals should be compensated by the apparition of new signals at the tri-TMS cellulose chemical shift, (103 and 61.5 ppm for C-1 and C-6) which is not observed.

As well as for heterogeneous methylation, silylation leads to a more resolved ^{13}C spectrum, which means a labelling without destructuration of the internal crystalline fibrils.

We can conclude from these labelling experiments that broad signals observed on the solid state ^{13}C NMR spectra of natural cellulose (valonia ventricosa, bacterial, cotton) are due to signals from disorder D-glucopyranosyl carbon units situated either on the surface of microfibrils or in three-dimensional disorder regions. In both experiments, difference spectra allow to observe negative signals corresponding to these regions, not only on the upfield side of C-4 and C-6 signals, but also of C-1, C-2 and C-3 too. C-1 complex signals of cotton is composed at least from three lines, the two lateral ones coming from the interior of the crystal lattice while the central one is affected by labelling and thus superimposed to broad signals coming from disorder regions. Methyl and TMS labelling groups used here seem to be specific of the crystalline/non crystalline regions. However, the discrimination of the surface/amorphous internal sites, cannot thus be obtained.

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