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^{13}C High Resolution Solid State NMR Studies on Cellulose Samples of Different Physical Structure

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Summary

^{13}C high resolution solid state NMR spectra of cellulose samples differing in lattice type, crystallinity and gross morphology (pulp, filament, film, bead) are presented and discussed with regard to the above mentioned parameters of physical structure.

Introduction

Conformational, supermolecular and morphological structure of cellulose is relevant to the material properties as well as to the reactivity of this polymer. In spite of the ample work already published, especially on WAXS data and computer modeling in connection with the various polymorphs of cellulose, many open questions and some contradictions still exist in this field. Further progress is achieved now by the application of ^{13}C high resolution solid state NMR spectroscopy using the cross polarization magic angle spinning (CP/MAS) technique /1/. While X-ray diffraction methods are sensitive mainly to geometric parameters of cellulose physical structure, ^{13}C CP/MAS NMR spectroscopy yields additional information on the "electronic environment" (shielding of C-atoms by electrons) of the different C-atoms of the anhydroglucose unit (AGU) (comp. 2-6).

In this contribution, ^{13}C CP/MAS NMR spectra of cellulose samples of different physical structure are discussed.

Experimental

A survey of samples studied is given in Table 1. The commercial samples of cellulose powders were obtained by partial hydrolysis of cotton linters and subsequent mechanical desintegration (comp. /7/), the samples Filtrak (R) FNA and FND showing a length average particle size of 120 µm, and 32 µm, respectively. The bead cellulose was prepared by coagulation of viscose spinning dope according to /8/. Samples of "neutralized alkali cellulose" were obtained by steeping of linters with an aqueous solution of NaOH of the concentration specified for 2 h at room temperature, neutralizing with

aqueous HCl, washing and air-drying. Transformation of cellulose I to cellulose III was achieved by treatment of linters with liquid NH_3 at -50 °C, evaporation of the liquid and air-drying at room temperature (comp. /9/).
A homebuilt ^{13}C NMR pulse spectrometer, operating at 15.087 MHz has been used for our measurements /10/. The proton decoupling field strength was 1.5 mT. Spectra were recorded with magic angle sample spinning at a rate of ≈ 2 kHz /10/. WAXS diagrams were taken by the technique reported in /11/.

Results

Our spectra summarized in Table 1 and Figures 1-3 will be evaluated with regard to line position, evidence of shoulders or line splitting, and overall line-width resp. line resolution.

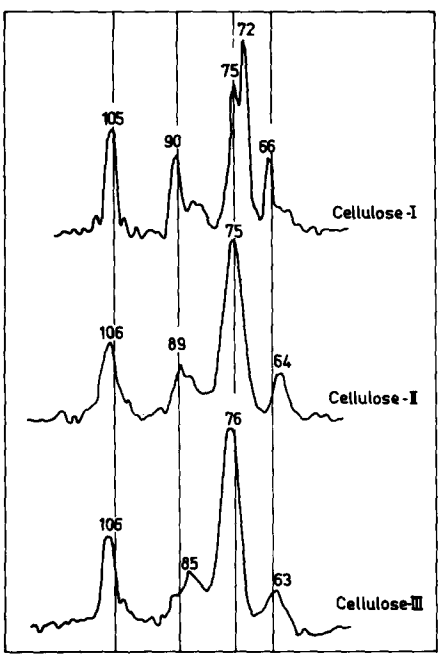

Figure 1.
CP/MAS ^{13}C NMR spectra of cellulose polymorphs

In Figure 1 the spectra of lattice modifications I, II and III of cellulose obtained from our linters-based samples are compared. The spectrum of cellulose I is in good agreement with that reported in /2/, while our spectrum of cellulose II (mercerized linters) shows broader and less resolved lines, especially in the C-1 and C-2, 3, 5 region, than that obtained by ATALIA /2/ who used a cellulose II sample of very high crystallinity. The spectra of our samples of cellulose II and III show some difference only in the position of the C-4 signal (comp. Table 1). The line width of the C-4 and C-6 signals increases in the order:
cellulose I < cellulose II < cellulose III
As already demonstrated in /2, 4/ and /5/ for cellulose I, NMR spectra may differ somewhat even between cellulose samples of the same lattice type, due to changes in "morphology". Our spectra obtained with various samples of cellulose I are summarized in Figure 2. Supermolecular order of these samples as revealed by WAXS patterns decreased according

TABLE 1 Line positions for cellulose samples in ppm relative to TMS = 0

Sample	Lattice type	Carbon atoms C-1	C-4	C-2, 3, 5	C-6
cotton, bleached and scoured	I	105	89	75/72	66
acetate grade cotton linters, $DP_{Cu} \sim 1600$	I	106	90	75/72	66
cellulose powder Filtrak(R) FNA	I	106	90/84	75/72	66
cellulose powder Filtrak(R) FND	I	105	89	75/72	66
beech sulphite dissolving pulp	I	105	89/84	74	66
cellobiose, reagent grade, for comparison	-	104/96[a]	84	75	63
viscose film	II	106	87	74	63
bead cellulose	II	108	89	75	64
neutralized alkali cellulose (12 % NaOH)	I + II	106	89/86	75	66/64
neutralized alkali cellulose (18 % NaOH)	II	106	89	75	64
viscose reyon staple from beech pulp (normal grade)	II	106	89/82	75	64
viscose reyon staple from beech pulp (high wet modulus grade)	II	106	87[b]/84	75	65/61
cuprammonia reyon	II	106	88/85	75	63
cellulose III from linters	III	106	87[b]/85	76	63

a) - C-1ß resonance;
b) - shoulder

to: FNA and FND powder > linters > cotton > beech pulp. Differences in the NMR spectra are visible mainly in the C-4 and to a smaller extend also in the C-6 region. The C-4 and mostly the C-6 lines are accompanied by upfield (lower ppm value) shoulders increasing in intensity in the order

linters < cotton < FNA < FND

In the spectrum of sample "FND", i.e. the powder of smaller average particle size as compared to sample FNA, the additional upfield shoulder on C-6 is evident. In compari-

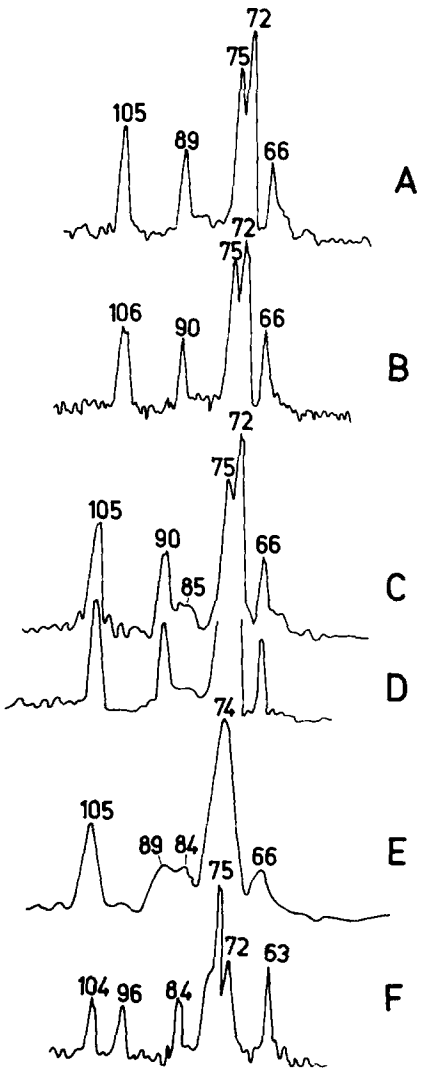

Figure 2.
CP/MAS ^{13}C NMR spectra of various samples of cellulose I

A - cotton (bleached and scoured)
B - acetate grade cotton linters
C - cellulose powder Filtrak(R) FND
D - cellulose powder Filtrak(R) FNA
E - beech sulphite dissolving pulp
F - cellobiose, for comparison

son to the cotton resp. linters based samples, the beech pulp spectrum shows broader and poorly resolved signals especially in the C-2, 3, 5 region, and a broad and intense line is found upfield the C-4 signal.

As to be expected for this coarse crystalline compound, cellobiose gives a spectrum with rather small and well resolved lines. The line positions of C-1 and C-2, 3, 5 are about the same as with cellulose I. The position of the C-4 and C-6 lines of cellobiose, however, does not coincide with that of the appropriate signals of cellulose, but is shifted upfield and agrees well with the "broad shoulders" in the C-4 and C-6 region of the spectrum of some samples of cellulose I.

NMR spectra of our cellulose II samples are compiled in Figure 3. Overall line width decreases in the order:

HWM-fibre > staple fibre > cuprammonium rayon > cellophane film > mercerized linters > bead cellulose

This ranking is in general aggrement with that of an increasing supermolecular order according to WAXS pattern,

except the observation that no significant difference has been observed between the WAXS patterns of normal grade and HWM staple fibre, both samples being manufactured from beech pulp.

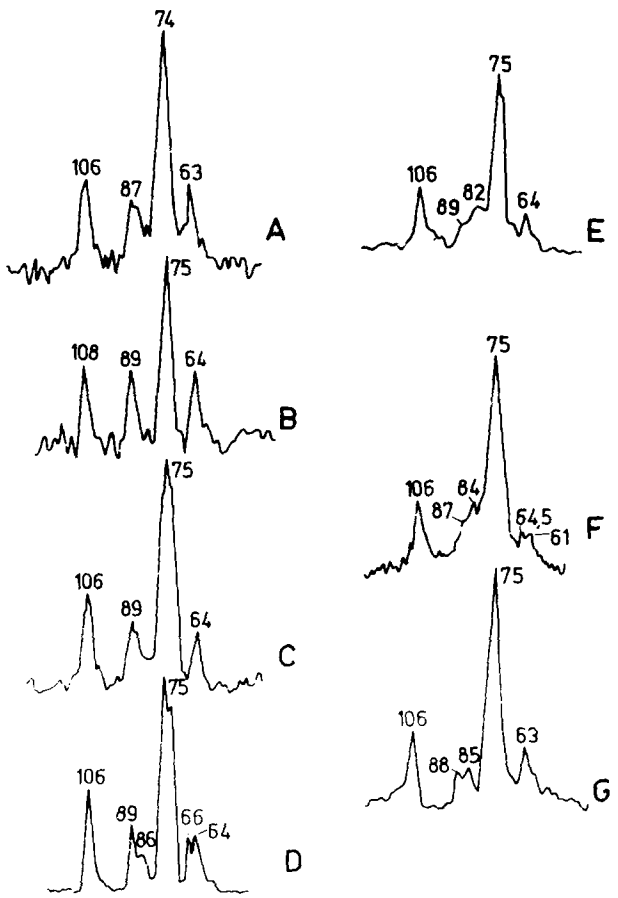

Figure 3.
CP/MAS ^{13}C NMR spectra of various samples of cellulose II

A - viscose film
B - bead cellulose
C - neutralized alkali cellulose (18 % NaOH)
D - neutralized alkali cellulose (12 % NaOH)
E - viscose reyon staple from beech pulp (normal grade)
F - viscose reyon staple from beech pulp (high wet modulus grade)
G - cuprammonia reyon

The line splitting especially on C-6 observed in the spectrum of neutralized alkali cellulose steeped at a lye concentration of 12 % NaOH can easily be traced back to the presence of cellulose II as well as of cellulose I in this sample, as revealed by the WAXS pattern. In agreement with this reasoning, no line-splitting of this kind is observed with the sample mercerized at a lye concentration of 18 % NaOH, consisting of cellulose II only. Special spectral features of our verious cellulose II samples are again found mainly in the C-4 and to a lesser extend in the C-6 region, while no differences became visible with regard to line position of the C-2, 3, 5 signals. Also the C-1 line

generally remained at the same position of 106 ppm, a small downfield shift to 108 ppm being observed with the bead cellulose sample only. In contrast to bead, film and neutralized alkali cellulose, where the C-4 signal consists of a single line only, a splitting into two lines situated at 87 ... 89 ppm and at 83 ... 84 ppm is observed with all the filament and fibre samples obtained by wet spinning from viscose or cuprammonium cellulose solution. An additional line splitting in the C-6 region probably occurs in the spectrum of the HWM staple fibre. Finally, it may be accentuated once more that morphological variability of viscose-based products of "regenerated cellulose" is reflected also by remarkable differences in the NMR spectra, if beads, film and the two samples of staple fibre are compared.

Discussion and Conclusions

Differences in the NMR spectra of samples of cellulose I and II varying in morphology within each of these two lattice types have been observed mainly with regard to overall line-width of the signals and with regard to signal position and signal form in the C-4 and C-6 region.

A decrease in overall line width of the spectrum generally correlates rather fairly to an increasing supermolecular order as revealed by the WAXS pattern. This correlation is in agreement with interpretations in /12/ and results on cellulose I samples discussed in /4/.

Obviously, with some types of samples (cellulose powders, viscose reyon fibres) the NMR spectrum responds more sensitive to small changes in physical structure than the WAXS pattern. Differences in the NMR spectra of cellulose I as well as of cellulose II samples are found mainly in the C-4 and to a minor extend also in the C-6 region. To our opinion, the line splitting of the C-4 signal observed in the spectra of our solution-spun threads, may be correlated to the existence of different conformations of the anhydroglucose units within the ordered regions of these samples, as both of the split lines are rather narrow and well resolved. The "broad shoulder" in the C-4 region of some of our cellulose I samples is assumed by us to be caused also by the existence of two conformations and, as already proposed in /3, 5/ by some "non-uniformity" in the state of structural order.

According to our interpretation proposed here, which of course needs further experimental proof, the change in line position is associated with a conformational change of the anhydroglucose units, while a broadening of a line or shoulder reflects an increasing "non-uniformity" of packing resp. supermolecular order. The C-4 line of cellulose I is shifted some ppm downfield as compared to the C-4 signal of cellobiose, probatly due to a conformational distortion caused by the H-bond system along the chain, while the shoulder at C-4 of cellulose I resp. the second, upfield line in the C-4 region of cellulose II might reflect a conformation very similar to that of cellobiose. Obviously, by this conformational distortion due to H-bonding in cellulose, the environment of the C-4 atom usually is affected much more than that of C-6, line splitting or shoulder formation at C-6 thus being rather more an exception than the rule.
Finally it may be accentuated again that obviously the O-C (4)-bond of the glycosidic linkage shows a much larger compliance to conformational stress than the C(1)-O-bond, as in contrast to the C-4 region no changes in line position, resp. line splitting or shoulder formation have been observed at the C-1 signal of our various cellulose samples, in agreement with our earlier observations on alkali cellulose (comp. /13/).

Acknowledgement

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