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Solid-State High-Resolution ^{13}C-NMR Studies of Regenerated Cellulose Samples with Different Crystallinities

Fumitaka Horii, Asako Hirai and Ryozo Kitamaru

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Summary

CP/DD/MASS ^{13}C-NMR spectra have been obtained for regenerated cellulose samples with different crystallinities as well as for cotton, β-D-glucose, β-D-cellobiose, and cellopentaose. The spectra of the regenerated cellulose samples exhibit broad multiplicities of the C-4 and C-6 resonance lines in a similar manner as those of native cellulose samples such as cotton and ramie, and, in addition, another broad tailing of the C-1 resonance. Since these multiplicities change linearly with crystallinity, it is concluded that they are ascribed to the contributions from the crystalline and noncrystalline components. Effects of hydrogen bonds and conformations of the β-1,4-glycosidic linkage on the chemical shifts are also discussed.

Introduction

Recent solid-state high-resolution ^{13}C-NMR studies of cellulose by the cross-polarization/dipolar decoupling/magic angle sample spinning(CP/DD/MASS) technique have shown fine splittings of the order of 1-2 ppm for the resonance lines of C-1 and C-4 carbons involved in the glycosidic linkage and additional larger splittings of about 3-5 ppm for the C-4 and C-6 resonances (ATALLA et al. 1980, EARL and VANDERHART 1980, 1981). Since these splittings may be attributed to nonequivalent conformation of the cellulose chains in the solid state, the clarification of their origin will give new information of the crystalline and noncrystalline structure of cellulose.

The broad-line ^{1}H-NMR analysis suggests that the noncrystalline chains of cotton are highly constrained in conformation whereas those of rayon fibers are relatively relaxed (HIRAI et al. 1980a, 1980b). In order to know more clearly the chain conformation of these cellulose samples, we have begun to study the origin of the splittings mentioned above. This is the first report dealing with the effect of crystallinity on the larger splittings associated with morphology.

Experimental

Sample preparation β-D-glucose and β-D-cellobiose were prepared from commercial sources by the purification method used for β-D-glucose (HUDSON and DALE 1917). Cellopentaose, which was kindly supplied by Dr. Azuma of Wood Research Institute,

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Kyoto Univ., was crystallized by precipitation from the aqueous solution in ethanol. Egyptian cotton and cuprammonium rayon fibers were purified according to the methods reported previously (HIRAI et al. 1980a, 1980b). These fibers were also hydrolyzed to change crystallinities; "hydrolyzed cotton" was obtained by hydrolysis with 2.5N HCl at 100°C for 1 h and "hydrolyzed rayon A and B" by hydrolysis with 2.5N HCl at 50°C for 10 and 42 h, respectively. Single crystals of cellulose II were prepared by means of method 3 of Buleon and Chanzy (1978), and a cellulose sample of low crystallinity was obtained by dissolution of Whatman cellulose powder CF-1 in dimethyl sulfoxide-paraformaldehyde followed by precipitation in ethanol. All samples were well dried at 50°C under vacuum before and after packing in a rotor.

^{13}C-NMR spectroscopy CP/DD/MASS ^{13}C-NMR spectra were recorded with a JEOL JNM FX-100 spectrometer(25.05MHz for ^{13}C) equipped with a CP/MAS unit operating with JEOL CP/MAS software which includes temperature-inversion techniques (STEJSKAL and SCHAEFER 1975). The matched field strength ν_{1C} and ν_{1H} of 69.4kHz were applied to ^{13}C and ^{1}H for 2.0 ms, and ν_{1H} remained on during the signal acquisition period. The magic angle sample spinning was carried out at a rate of about 3.2kHz by use of a modified Andrew-type rotor of polychlorotrifluoroethylene whose volume was about 0.5cm^3. Chemical shifts relative to TMS were determined using a narrow crystalline resonance peak at 33.6 ppm (EARL and VANDERHART, 1981) for polyethylene inserted in all samples, though the value was somewhat low compared with the value obtained by us (KITAMARU et al. 1982).

Results

CP/DD/MASS ^{13}C-NMR spectra of different cellulose samples are shown in Figure 1(the dotted lines in each spectrum will be explained below) and the chemical shifts of their respective carbons are compiled in Table I together with the values of β-D-glucose, β-D-cellobiose, and cellopentaose in the solid state and in solution. As already reported (EARL and VANDERHART 1980), in the spectrum of cotton(Figure 1d) the C-4 and C-6 resonance lines are apparently split into narrow downfield and broad upfield components, suggesting the existence of two kinds of morphologically different carbons. On the other hand, the spectrum of rayon fibers(Figure 1a) is somewhat different; the C-4 resonance is split in a similar manner but the relative intensity of the downfield component is very low in comparison with that of cotton. The splitting of the C-6 carbon, which is observed as an upfield shoulder in the case of cotton, disappears for this sample, probably because the sharp downfield line at 66.2 ppm is shifted upfield and overlaps with the upfield component at 63.5 ppm. In addition, a new multiplicity is observed for the C-1 resonance as an upfield tailing which is not recognized for cotton.

These findings that are probably related to the different morphology of the rayon fibers drastically change upon hydrolysis of the glycosidic bonds as shown in Figures 1b and 1c. Thus, with increasing hydrolysis time the relative intensity of the upfield C-4 resonance distinctly decreases and the C-1

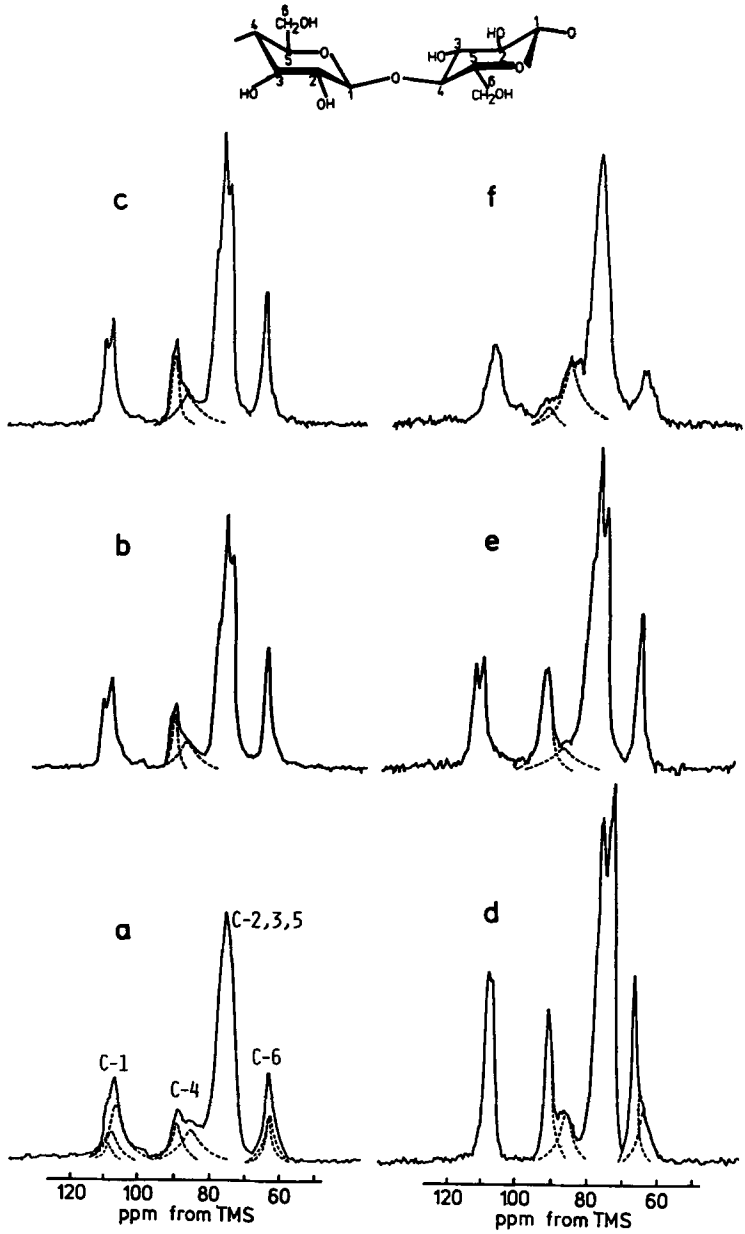

Figure 1 CP/DD/MASS ^{13}C-NMR spectra of different cellulose samples. a: cuprammonium rayon fibers, b: hydrolyzed rayon A, c: hydrolyzed rayon B, d: cotton, e: single crystals, f: low-crystalline cellulose. For the dotted lines in each spectrum, see text

TABLE I

^{13}C-Chemical Shifts of Different Cellulose Samples and Related Compounds in the Solid State and in Solution.

Sample	chemical shifts/ppm from TMS					
	C-1	C-4	C-6	C-2	C-3	C-5
cotton	106.3 105.2	89.8 85.1	66.2 63.8		72.4 73.5 75.3	
hydrolyzed cotton	106.3 105.7	90.2 85.0	66.5		72.7 73.8 75.6	
rayon fibers	105.8	88.4 85.6	63.5		75.4	
hydrolyzed rayon						
A	108.2 106.0	88.6	63.9		74.0 75.8 77.6	
B	108.1 106.0	89.5 88.6	63.8		74.0 75.9 77.6	
single crystals	107.7 105.5	89.4 88.4	63.3		73.4 75.4 76.8	
low-crystalline cellulose	104.6	89.2 85.1	63.3		75.7	
β-D-glucose						
solid	97.4	70.2	61.9		75.1 76.3[b]	
solution[a]	95.7-97.4	69.4-71.3	60.4-62.5	73.9-75.9	74.8-77.4	75.7-77.4
β-D-cellobiose						
solid NR[c]	104.9	72.9	63.8	73.9	77.5	78.9
R[c]	98.0	84.8	63.8		75.9[b] 76.7	
solution[a] NR[c]	102.4-103.9	69.3-71.1	60.5-62.4	73.0-74.7	75.8-77.2	75.4-77.6
R[c]	95.6-97.1	78.5-80.4	59.8-61.8	73.8-75.7	74.6-76.6	74.1-76.0
cellopentaose[d]						
solid	106.8	89.0	63.9		73.7 75.7 77.2	
solution[e]	103.3	79.6 79.7	61.2	74.1	75.2	75.9

a Reported data in D_2O or H_2O at 22-90°C(AZUMA and KOSHIJIMA 1981, GORIN 1981). b Two resonance lines are superposed upon each other. c R and NR indicate the reducing and nonreducing residues, respectively. d Values for the carbons in the internal residues. e Reported data in D_2O at 60°C(HEYRAUD et al. 1979).

upfield tailing and the C-6 overlapping broad components tend to disappear. Since the noncrystalline component of regenerated cellulose is thought to be more easily hydrolyzed than the crystalline component, such changes will be due to the increase in crystallinity which was confirmed by X-ray analysis.

However, a spectrum devoid of the C-1 tailing, C-4 splitting, and C-6 overlapping could not be obtained even by longer or more vigorous hydrolysis(for instance, at 100°C for 10h). As a highly crystalline model single crystals were, therefore, prepared according to the published method (BULEON and CHANZY 1978). The spectrum of these crystals is shown in Figure 1e. In this case such broad multiplicities as tailing, splitting, and overlapping(referred to as broad multiplicities hereafter) almost disappear and the resolution of each line is improved considerably. As a result, fine multiplicities of the C-1 and C-4 resonances, which are ascribed to their nonequivalences in crystals (EARL and VANDERHART 1980), are clearly observed at 107.7 and 105.5 ppm and at 89.4 and 88.4 ppm, respectively. On the other hand, Figure 1f shows the spectrum of the cellulose sample with low crystallinity. Interestingly, the intensity of the upfield resonance line of the C-4 carbon is enhanced, whereas its downfield component appears only as a small shoulder.

Based on the results described above, the broad multiplicities of the C-1, C-4, and C-6 carbons are assumed to be associated with the crystalline and noncrystalline components. In order to confirm this assumption, we first resolved the C-4 resonance into two Lorentzian curves with a curve resolver(du Pont 310) as indicated as dotted lines in each spectrum of Figure 1. In Figure 2, the integrated fraction f_{nmr} of the downfield resonance with respect to the total resonance of the C-4 is plotted against the degree of crystallinity $f_{x\text{-}ray}$ determined from X-ray diffraction analysis based on the Hermans' method (HERMANS and WEIDINGER 1948, 1949, HIRAI et al. 1980a). A linear relationship apparently exists between the f_{nmr} and $f_{x\text{-}ray}$. It is therefore concluded that the C-4 downfield and upfield components are the contributions from the crystalline and noncrystalline components for the regenerated cellulose samples, respectively. Since the data of cotton and hydrolyzed cotton(indicated as closed circles in Figure 2) fit the same relationship, this conclusion seems also plausible for cotton. Nevertheless, more detailed studies are necessary for cotton or other native cellulose samples because a controversial conclusion has been reported (EARL and VANDERHART 1981, MACIEL et al. 1982).

We also tried to split the C-1 and C-6 resonances into crystalline and noncrystalline components by assuming their crystalline contributions to be nearly equal to the f_{nmr} obtained for the c-4 resonance. As shown in Figure 1a, their resonances are also well split into two components if the fine splitting appearing in the C-1 sharp downfield resonance is considered to be composed of two Lorentzian curves. Therefore, the C-1 tailing and C-6 overlapping broad components are also the contributions from the noncrystalline component of regenerated cellulose. In addition, as shown in Figure 1d, the C-6 tailing observed for cotton is also well decomposed into two

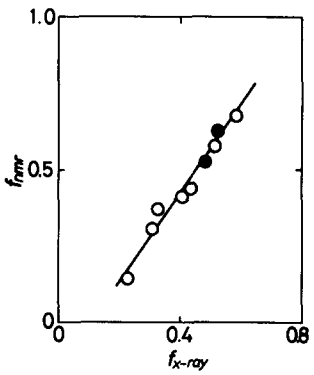

Figure 2 Integrated fraction f_{nmr} of the downfield component of the C-4 resonance line vs. degree of crystallinity $f_{x\text{-}ray}$ determined by X-ray analysis.
o: *regenerated cellulose,*
●: *cotton and hydrolyzed cotton*

components in a similar manner, suggesting that the cause of the C-6 tailing is the same as that of the C-4 splitting.

Compared with complicated spectra of cellulose samples, the spectra of solid β-D-glucose and β-D-cellobiose are simple. Each resonance line of β-D-glucose is very sharp even in the solid state and the chemical shifts are in accord with those in solution as shown in Table I. In β-D-cellobiose, however, the chemical shifts of the C-1, C-4, and C-6 carbons in both residues are appreciably higher than those in solution and, in addition, some of them are very close to the corresponding values of the noncrystalline components of cellulose samples. This suggests that the conformation of the noncrystalline chains may be related to that of cellobiose. The chemical shifts of cellopentaose are almost identical with those of the crystalline component of regenerated cellulose.

Discussion

As described above, there are two kinds of multiplicities in the spectra of regenerated cellulose samples: fine multiplicities associated with the crystal structure* which is observed for the C-1 and C-4 carbons of highly crystalline samples and broad multiplicities related to the crystallinity, which is observed for the C-1, C-4, and C-6 carbons of samples of low crystallinity. The chemical shifts of these multiplicities are much higher than the corresponding values of cellopentaose (Table I) or cello-oligosaccharides (INOUE and CHUJO 1978, GAST et al. 1980) in solution. Similar findings have already been reported for the carbons involved in the glycosidic linkages of (1→3)-β-D-glucans, (1→4)-α-glucans, chitin, and N-acyl chitosans (SAITO and TABETA 1981, SAITO et al. 1981a, 1981b). Since these high chemical shifts as well as the multiplicities in the solid state may stem from hydrogen bonds and different conformations of glycosidic linkages, we briefly discuss here the effects of these factors on chemical shifts by using the data of β-D-glucose and β-D-cellobiose.

* The difference in the crystal structure between cellulose I and II is also reflected in the difference in chemical shift. Compare, for instance, the chemical shifts of cotton with those of the single crystals in Table I.

Hydrogen bonds: The intermolecular oxygen distances are 2.69-2.77Å for the hydrogen-bonded pairs O_5-O_3', O_6-O_2', O_2'-O_3'' and O_6-O_1 in the β-D-glucose crystal (FERRIER 1960, 1963). Since the chemical shifts of all carbons of this crystal are almost identical with those in solution(Table I), such hydrogen bonds do not seem to affect the chemical shifts of these carbons. This is in good accord with a recent CP/DD/MASS ^{13}C-NMR study (IMASHIRO et al. 1982) which reveals that the intermolecular hydrogen bond with an O-O distance of 2.754Å does not change the chemical shifts of the carbons chemically bound to those oxygen atoms. In addition, they have found that the downfield shifts appear for the corresponding carbons in the formation of stronger hydrogen bonds and increase with decreasing O-O distance. For instance, the downfield shift is 10.6 ppm for solid dimedone containing intermolecular hydrogen bonds with an O-O distance of 2.593-2.595Å.

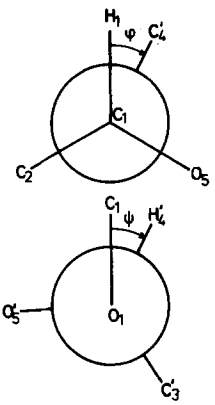

Figure 3 Torsion angles φ and ψ about the β-1,4-glycosidic linkage

According to their results, the relatively high chemical shift of the C-6 carbons of the β-D-cellobiose crystal should not be ascribed to the effect of hydrogen bonds. The reason is as follows; though the O_6'-O_3 distance(2.808Å) is longer than the O_6-O_3 distance(2.711Å) (CHU and JEFFREY 1968), the downfield shift(2.0-4.0 ppm) for the C-6' carbon in the reducing unit is larger than that(1.4-3.3 ppm) for the C-6 carbon in the nonreducing unit. A possible cause may be the different conformation of the (C-5)-(C-6) bond in the solid state and in solution. Since there is no shorter O-O distance than 2.711Å in the β-D-cellobiose crystal (JACOBSON et al. 1961, CHU and JEFFREY 1968), the downfield shifts for other carbons cannot be attributed to the hydrogen bonds, either.

Conformation of β-1,4-glycosidic linkage: The large downfield shifts of the carbons in the glycosidic linkage of the β-D-cellobiose crystal may be caused by the different conformation of this linkage in the solid state and in solution, as pointed out for other glucans (SAITO et al. 1981b). The torsion angles φ and ψ, which are defined as shown in Figure 3 (SANDARAJAN and RAO 1969) and which determine the conformation of the linkage together with the bond angle (C-1)-O-(C-4'), are 44.6° and -13.7° in the crystalline state, respectively (CHU and JEFFREY 1968, LEUNG et al. 1976). However, at present, there is no reliable data on studies made in solution, though a preliminary analysis of the $^3J_{C-H}$ coupling for the (C-1)-(H-4') and (C-4')-(H-1) pairs suggests that the φ and ψ are about ±60° in solution (PERLIN et al. 1974). On the other hand, calculations (REES and SKERRETT, 1968) indicate that there are two minima in the van der Waals energy map for cellobiose, the values of φ and ψ being 41° and -5° at one minimum and 0° and -37° at the other, respectively. Since the former values are close to the values in the crystalline state, it is difficult at present to conclude that the values of φ and ψ affect the chemical shifts of the carbons in the glycosidic linkage. We

are now studying the effects of the angles ϕ and ψ as well as of the glycosidic bond angle on the chemical shifts, using different oligomers the crystal structures of which have been determined. The conformation of cellulose chains in the solid state will be discussed elsewhere.

Acknowledgments

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