

Crystallinity of cellulose, as determined by CP/MAS NMR and XRD methods

R. Teeäär^{1*}, R. Serimaa^{2**}, and T. Paakkari²

¹Department of Wood and Polymer Chemistry, University of Helsinki, SF-00170 Helsinki, Finland

²Department of Physics, University of Helsinki, Siltavuorenpenger 20c, SF-00170 Helsinki, Finland

SUMMARY

The crystallinity of six cellulose samples with different origin and treatment was determined using x-ray diffraction (XDR) and nuclear magnetic resonance with cross polarization and magic angle sample spinning (CP/MAS NMR) methods. The numerical results for crystallinity obtained by using curve fitting methods in both cases correlated very well. It was concluded that the values for the crystallinity can be determined from NMR spectra when CP times not exceeding 0.5 ms are used. The range of order of the samples was further characterized calculating the radial atomic density function from the x-ray diffraction patterns and determining the greatest distances with significant deviations from the average density.

INTRODUCTION

Since the first results on high resolution solid state ¹³C NMR of cellulose by Atalla et al. (1) and Earl et al (2) numerous investigators have confirmed the separation of the signals from ordered (crystalline) and disordered (amorphous) regions. To verify the latter statement it has been shown that intensity of 89 ppm line decreases while that of a 84 ppm line considerably increases as a result of ball-milling of the sample. In case of acidic hydrolysis one can follow "intensity flow" from 84 to 89 ppm line in the spectrum of nonhydrolysed residue as a function of the treatment. ¹³C spin-lattice relaxation times indicate much greater molecular movement for 84 ppm carbon atoms than in case of 89 ppm. Although the discussion on the origin of the signals and on the splitting of the lines has continued for long time all of the details are not clear at present. However, large difference of the chemical shifts of anhydroglucose units, situating in the ordered and disordered regions has seemed attractive for quantitative determination of the amount of material in those regions (3-9).

The direct way of determining the degree of order (crystallinity) in a cellulose sample is x-ray diffraction. The crystallinity is defined quantitatively as a weight fraction, x_{cr} , of crystalline material in the sample. The numerical results in the literature, which are often called "index of crystallinity", are much dependent on the data evaluation procedure (cf. 10) and on the perfectness of the sample. Ruland's method (11,12) gives, at least, in principle values for x_{cr} . However, it is rather tedious for practical applications, because it implies great accuracy in data collection and ideal powder sample. The average size of the crystallites can be calculated using the well-known Scherrer

*On leave from Institute of Chemical Physics and Biophysics, Estonian Academy of Sciences, SU-200105 Tallinn, USSR

**To whom offprint requests should be sent

equation (cf. 10). More information can be obtained by calculating the radial atomic density function around an arbitrary atom from the experimental diffraction pattern. For example, the greatest distance, at which the deviations from the average atomic density are still significant, characterizes the range of order in the sample.

Intensities of NMR spectrum should give values for crystallinity, because signals from different nuclei are registered in the same coil at the same time in form of free induction decays of nuclear magnetic moments after radio frequency (RF) excitation pulse. The integral intensities of the lines in cross polarization (CP) ^{13}C NMR spectrum do not necessarily correspond to the number of nuclei in the sample under study because of differences of CP dynamics as well as of proton relaxation differences for the different nuclei or phases in the sample. Fulfilling of condition $T_{CH} \ll T_{CP} \ll T_{1\rho H}$ is usually considered sufficient to get adequate quantitative results, when T_{CH} , T_{CP} and $T_{1\rho H}$ are proton-carbon CP time constant, CP time interval used in the experiment, and proton spin-lattice relaxation time in the rotation frame, respectively. The practical condition is typically $25T_{CH} \leq 5T_{CP} \leq T_{1\rho H}$. Otherwise relative intensity distortions occur in the CP spectrum causing systematic errors. Horii et al. (8) found that in case of ramie relative distortions do not exceed 3% if CP time of 1 ms is used. In their measurements $T_{1\rho H} = 15$ ms in 69 kHz spin lock field (actually 69 kHz was given for carbon H field, but we suppose Hartmann-Hahn condition fulfilled). According to our measurements $T_{1\rho H}$ can be shorter for samples of different origin (and in different conditions of course). Relative intensities of the lines would correspond to the number of the nuclei with different chemical shifts in case of simple ^{13}C NMR without CP. In practice it is impossible to get such a spectrum because of long carbon spin-lattice relaxation times (8,9). Accumulation time for such a spectrum would be several weeks.

Earlier experiments have indicated (13) that a wide range of numerical values are obtained for crystallinity using both XRD and CP/MAS NMR method for the same sample. This is due to the fact that there are several possibilities to separate overlapping spectral lines and to choose the experimental conditions. The purpose of the present study was to minimize the ambiguities between the results obtained by these two methods. Therefore, it was decided to measure the crystallinity of several cellulose samples using both methods independently.

EXPERIMENTAL

^{13}C CP/MAS NMR measurements were carried out using a 50 MHz operating pulse spectrometer. Up to 10 000 free induction decays (FID) were accumulated into 1 K memory before Fourier transform to 4K to get practically noise-free spectra. Sample spinning frequency was about 3.5 kHz. During all of the experiments spin-lock and CP field strength were 50 kHz.

To characterize intensity behaviour a set of NMR spectra of microcrystalline cellulose (LACHEMA, Czechoslovakia) was recorded with different CP times up to 20 ms. Proton spin lattice relaxation times in the rotating frame and proton-carbon CP time constants for "crystalline" lines were found to be $T_{1\rho H} = 11.8$ ms and $T_{CH} = 0.31$ ms and for "amorphous" line $T_{1\rho H} = 6.4$ ms and $T_{CH} = 0.29$ ms for C4 signals. $T_{1\rho H}$ numbers correspond to 50 kHz decoupling field and were calculated from the falling part

of the signal intensity curves in the logarithmic scale as described elsewhere (14). T_{CH} times were determined to get the best fit of the rise-fall exponents with the experimental data points.

The x-ray diffraction measurements were performed using a powder diffraction apparatus and monochromatized CuK_{α} radiation. To study the effects of preferred orientation both reflection and transmission modes were used (10). The width of the receiving slit was 0.6 mm. The measurements were done in two parts. In the scattering angle range $5^{\circ} < 2\theta < 40^{\circ}$ was 0.25° and $40^{\circ} < 2\theta < 100^{\circ}$ the angle step was 0.25° and 0.5° , respectively. The measuring time varied from 20 s to 40 s per point for the first angle range and from 120 s to 180 s for the second range. The maximum counting rate was 2500 counts/second. The samples were in a form of finely divided powder pressed slightly in a form of flat cake of thickness of about 1 mm. The samples were rotated during the measurements in an evacuated chamber.

Crystallinity of the following six samples was determined: 1. microcrystalline cellulose from cotton linters produced as a result of hydrolysis with 2.5N HCl at 100 centigrade during 2 hours, 2. Avicel PH-101 (FLUKA), 3. microcrystalline cellulose from LACHEMA, Czechoslovakia, 4. Sigmacel 100 noncrystalline (SIGMA), 5. moderately well ball-milled (3 h) Czechoslovakian microcrystalline cellulose and 6. extensively ball-milled Czechoslovakian microcrystalline cellulose.

RESULTS AND DISCUSSION

Figure 1 presents the ^{13}C signal intensities as a function of CP time. Intensities are normalized to the same amount of and spin temperature of protons at $t=0$. According to Mehring (14) in this case ^{13}C signal intensity should be described by the formula

$$\beta(t) = \frac{1}{1-\lambda} (1 - e^{-(1-\lambda)/T_{CH}t}) e^{-1/T_{1\rho H}t},$$

where $\lambda = T_{CH}/T_{1\rho H}$. Here depolarization of 1H spins as a result of energy transfer to the ^{13}C spins is assumed to be negligible as well as relaxation of ^{13}C spins in the rotating frame ($T_{1\rho C} = \infty$). It can be seen from the curves that there is practically no relative intensity distortion when CP times are less than 0.5 ms. After that one can notice a monotonically increasing difference between 89ppm and 84ppm CP signals. At 1 ms the deviation is about 5 %. Influence of CP time to spectral shape is clearly seen on the spectra with different CP times. Therefore, for adequate characterization of absolute intensities, CP time should not exceed 0.5 ms (in case of stronger RF fields CP time limit can be correspondingly longer).

The intensities of the spectral lines were determined using a curve fitting procedure (Figure 2). It could be thought *a priori* that NMR spectral lines in solid samples have a Gaussian shape because they consist of many narrower lines with slightly different chemical shifts. However, the best fit was achieved using combinations of Gaussian and Lorentzian functions by varying the shape of the lines. After the fitting 89 and 84 ppm signals were calculated. As a result NMR factor of crystallinity was determined as a portion of 89ppm line to the total intensity of C4 carbons signals (at 89 and 84 ppm) in the simulated spectrum.

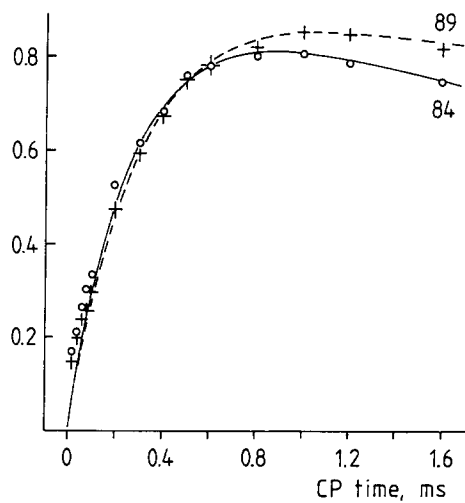


Figure 1. ^{13}C CP NMR spectral signal intensities of 84 and 89 ppm lines upon CP time for microcrystalline cellulose (LACHEMA). Curves are normalized to equal spin temperature and number of protons at $t = 0$.

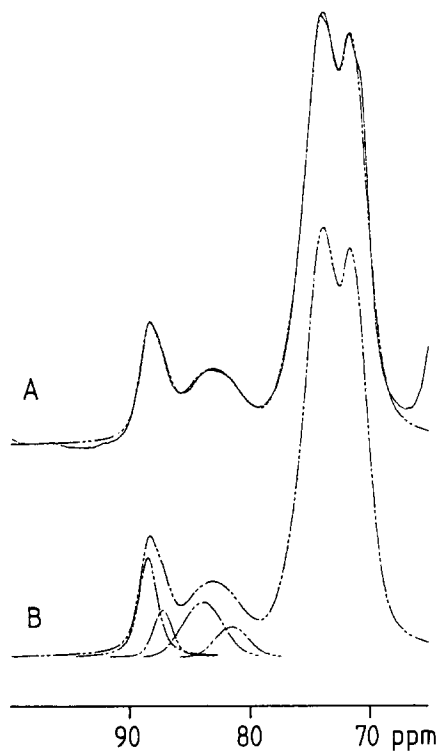


Figure 2. a) The experimental (solid line) and fitted (broken line) spectra for C4 carbon. b) Fitted components of 89 and 84 ppm lines.

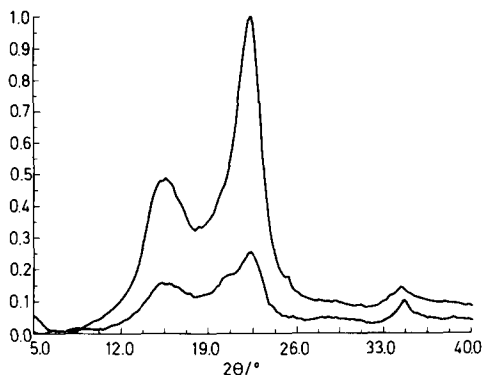


Figure 3. The diffraction patterns of Sigmacel sample. The upper curve is measured using the symmetrical reflection mode and the lower one using the symmetrical transmission mode.

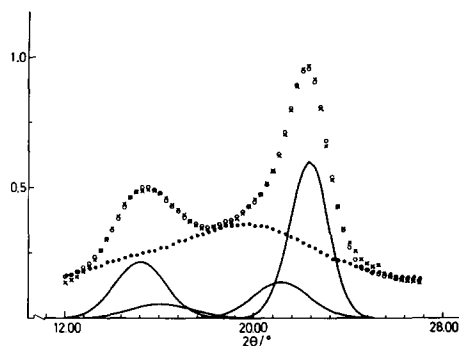


Figure 4. The curve fitting in the case of Sigmacel, measured using the symmetrical reflection mode. The experimental curve is denoted by crosses and the superposition of the model curves by open circles.

The x-ray diffraction results for crystallinity were obtained from diffraction patterns by separating the reflections from the background by a fitting procedure. The reflections were simulated by Gaussians and the model function for the background was a scattering curve of a totally amorphous cellulose sample (10). The results were normalized to correspond to the value of crystallinity of a standard Avicel sample determined by Ruland's method (11,12) by Fink (15). The final results were calculated as an weighted average of the ones obtained by reflection and transmission measurements to minimize the effects of preferred orientation (10). Examples of the diffraction patterns and of the curve fitting procedure are given in Figures 3 and 4.

The final comparison of results is given in Table 1 and Figure 5 where the crystallinity obtained by CP/MAS NMR is plotted against the crystallinity by XRD. The agreement between the results is very good. It is to be noted that the XRD method resulted in the values of crystallinity of 0.54 and 0.67 for Avicel and cotton linter, respectively. The earlier values used for the normalization of the data are 0.55 and 0.66 measured for different samples using Ruland's method. The small deviation proves the precision of the XRD method.

To characterize the range of order in the samples the radial atomic density function (RDF) was calculated (16):

$$RDF(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty k \frac{I(k) - \langle f^2 \rangle}{\langle f \rangle^2} \sin kr dk,$$

where $I(k)$ is the experimental coherently scattered intensity, k is the magnitude of the scattering vector, ρ_0 is the average atomic density and $\langle f \rangle$ is the averaged scattering factor. The first term describes the average radial atomic density of the sample and

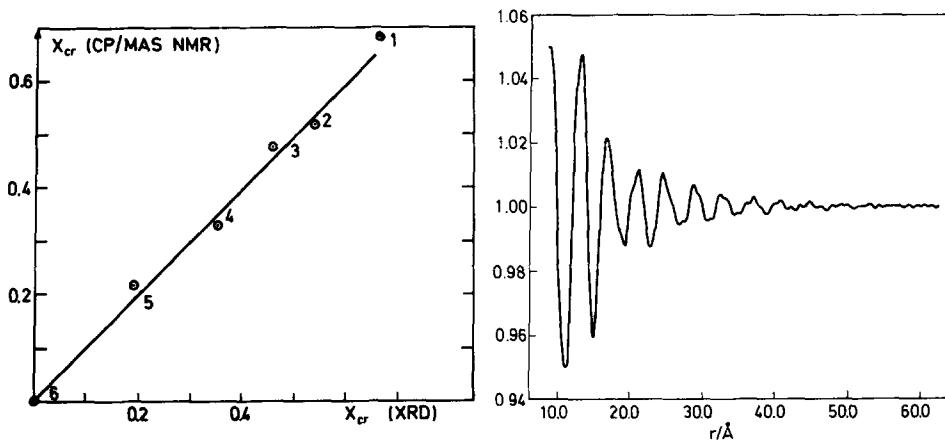


Figure 5. The crystallinity obtained by CP/MAS NMR against the crystallinity by XRD. Numbers refer to the samples.

Figure 6. The pair correlation function, $PCF(r)$, of Sigmacel sample.

Table 1. The XRD parameters which characterize the crystalline state of three cellulose samples.

sample	greatest distance from PCF [Å]	crystallinity x_{cr}		cryst. size from refl. 002 [Å]
		XRD	NMR	
1. cotton		0.67	0.69	64
2. Avicel	55	0.54	0.52	45
3. LACHEMA		0.46	0.48	49
4. Sigmacell	45	0.35	0.33	44
5. milled 3h	35	0.19	0.22	43

the second term the deviations from the average density. For practical use the so called pair correlation function (PCF) were calculated dividing RDF by the average radial atomic density of the sample: $PCF(r) = RDF(r)/4\pi r^2 \rho_0$. The resolution in real space is limited as the largest k reached by $CuK\alpha$ radiation is not very high, so the features of functions cannot be discussed in detail, but the range of order in the sample can be characterized by determining the distance after which the deviations vanish in PCF. One of the functions obtained is presented in Figure 6 and the results are compared in Table 1 with the values of crystallinity obtained by XDR method and the average linear dimensions of crystallites perpendicular to the fibre axis. These values have been calculated from the halfwidth of the 002 reflection using Scherrer's equation. There is a linear dependency of the crystallinities and the greatest distances from the PCFs, but the average linear dimension obtained by curve fitting from the 002 reflection seems not to be sensitive to the changes in the range of order in the samples.

ACKNOWLEDGEMENTS

The authors appreciate very much Mr. R. Kaila's help in the experimental work (XRD) and analysis of the data.

REFERENCES

1. R. H. Atalla, J. C. Gast, D. W. Sindorf, V. J. Bartuska and G. E. Maciel, *J. Am. Chem. Soc.*, 102, 3249 (1980).
2. W. L. Earl and D. L. VanderHart, *J. Am. Chem. Soc.*, 102, 3251 (1980).
3. G. E. Maciel, W. L. Kolodziejcki, M. S. Bertran and B. E. Dale, *Macromolecules* 15, 686 (1982).
4. C. A. Fyfe, R. L. Dudley, P. J. Stephenson, Y. Deslandes, G. K. Hamer and R. H. Marchessault, *J. Macromol. Sci., Rev. in Macromol. Chem. and Phys.*, C23, 187 (1983).
5. W. L. Earl and D. L. VanderHart, *Macromolecules* 14, 570 (1981).
6. D. L. VanderHart and R. H. Atalla, *Macromolecules*, 17, 1465 (1984).
7. J. Kunze, G. Scheler, B. Schröter and B. Philipp, *Polym. Bull.* 10, 5 (1983).
8. F. Horii, A. Hirai and R. Kitamaru, *J. Carbohydr. Chem.*, 3, 641 (1984).
9. R. Teeäär and E. Lippmaa, *Polym. Bull.*, 12, 315 (1984).
10. T. Paakkari, R. Serimaa and M. Blomberg, To be published.
11. W. Ruland, *Acta Cryst.* 14, 1180 (1961).
12. C. G. Vonk, *J. Appl. Cryst.* 6, 148 (1973).
13. R. G. Zbankov et al., *Khimija Drevesiny* 4, 3 (1986), (in Russ.).
14. M. Mehring, *Principles of High Resolution NMR in Solids*. Springer-Verlag, Berlin, Heidelberg, New York, (1983).
15. H.-P. Fink, Private communication.
16. C. N. J. Wagner, *Liquid Metals, Chemistry and Physics*, ed. Beer S. Z., Marcel Dekker, New York 257 (1972).

Accepted January 31, 1987 C