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

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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 $^{13}$C 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. $^{13}$C 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, $x_c$, 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 $x_c$. 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
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 $T_{CH} < < T_{CP} < < T_{pH}$ is usually considered sufficient to get adequate quantitative results, when $T_{CH}$, $T_{CP}$ and $T_{pH}$ 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 $25 T_{CH} < < T_{CP} < < T_{pH}$. 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 $T_{pH} = 15$ 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 $T_{pH}$ 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 $T_{pH} = 11.8$ ms and $T_{CH} = 0.31$ ms and for "amorphous" line $T_{pH} = 6.4$ ms and $T_{CH} = 0.29$ ms for C4 signals. $T_{pH}$ numbers correspond to 50 kHz decoupling field and were calculated from the falling part