

1 **Supporting information:**
2 **Comparative analysis of molecular weight determination**
3 **techniques for cellulose oligomers**

4 **Wei Li · Yu Ogawa · Gérard Mortha · Issei**
5 **Otsuka · Yoshiharu Nishiyama**

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W. Li
School of Materials Science and Engineering, Beijing Institute of Technology, 100081, Beijing,
P.R. China
Univ. Grenoble Alpes, CNRS, CERMAV, 38000 Grenoble, France
E-mail: weili2021@bit.edu.cn

Y. Ogawa · Y. Nishiyama · I. Otsuka
Univ. Grenoble Alpes, CNRS, CERMAV, 38000 Grenoble, France

G. Mortha
CNRS, Grenoble INP, Institute of Engineering Univ. Grenoble Alpes, LGP2, 38000, Grenoble,
France

1 Rehydration of cellulose

Figure S1 shows the solid-state ^{13}C CP/MAS NMR spectra of the freeze-dried fraction A and rehydrated fraction A. Both of the spectra showed typical spectral features of cellulose II crystal (Isogai et al., 1989). The resonance lines of the rehydrated sample were narrower without change in chemical shifts when compared with those of freeze-dried one. The reason behind this phenomenon was previously described by Horii et al.. Water might relax mechanical constraints of cellulose crystals caused by drying and the non-crystalline or surface chains to a relatively ordered state. Peak deconvolution was easier with sharper and more obvious peaks, so in this consideration, all the samples were in a rehydrated state for the solid-state ^{13}C CP/MAS NMR measurements.

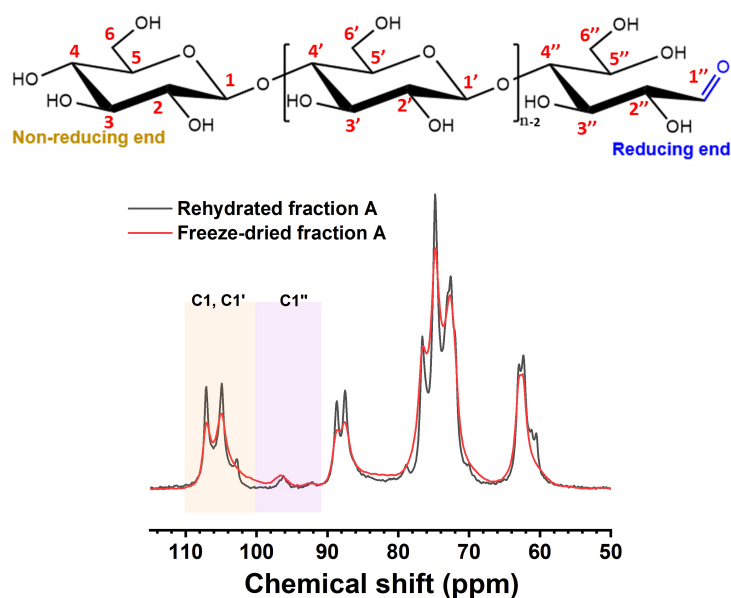


Fig. S1 Solid state ^{13}C CP/MAS NMR spectra of rehydrated fraction A and freeze-dried fraction A. The colored regions corresponded to specific carbon bonds that were annotated on the chemical structure of the cellulose molecule.

2 Kinetics of cross-polarization between ^1H and ^{13}C

The ^{13}C CP/MAS NMR spectrum should be considered semi-quantitative. In a solid-state CP experiment, the ^{13}C signal detection does not depend on the slow ^{13}C spin-lattice relaxation, but on ^1H spin lattice relaxation time, thanks to the cross polarization. However, a solid-state NMR spectrum loses its quantitative nature due to the kinetics effect involved in the cross-polarization process. In the cross-polarization event, three constants of time are involved: T_{1H} , proton spin-lattice relaxation time, T_{CH} , magnetization transfer time constant from ^1H spin reservoir to ^{13}C spin reservoir, and

¹ T_{1C} , carbon spin-lattice relaxation time. respectively. The rate of change of ^{13}C mag-
² netization (Ms) in the CP experiment as function of a contact time t is given as follows
³ (Hill et al., 1994),

$$M_S(t) = \frac{M_0}{T_{CH}} \times \left(\frac{1}{T_{CH}} + \frac{1}{T_{1C}} - \frac{1}{T_{1H}} \right) \times \left(e^{-\frac{t}{T_{1H}}} - e^{-t \times \left(\frac{1}{T_{CH}} + \frac{1}{T_{1C}} \right)} \right) \quad (1)$$

⁵ where M_0 is the initial 1H spin temperature, corresponding to the maximum
⁶ magnetization. Generally, T_{1C} is very long compared with T_{1H} and T_{CH} , as well
⁷ as CP contact time, and its influence on the relaxation dynamics during the cross-
⁸ polarization can be ignored. If the conditions of (1) $T_{1C} \gg T_{1H}$ and (2) $T_{1H} \gg T_{CH}$
⁹ can be satisfied, the above equation can be simplified as follows,

$$M_S(t) = M_0 \times \left(e^{-\frac{t}{T_{1H}}} - e^{-\frac{t}{T_{CH}}} \right) \quad (2)$$

¹¹ This indicates that, for instance, apparent intensity of mobile methylene carbon
¹² should be smaller than that of rigid ring carbon due to the different 1H spin-lattice
¹³ relaxation time. Quantitative analysis based on ^{13}C CP/MAS spectra is possible only
¹⁴ when one compares M_0 values based on the above-mentioned consideration of the CP
¹⁵ kinetics. To estimate these time constants in the equation (1), two sets of solid-state
¹⁶ NMR measurements were conducted. First one is with a normal CP pulse sequence
¹⁷ with a variable CP contact time from 0.001 ms to 10 ms. Another one is for ^{13}C T1
¹⁸ measurement described by Torchia (Torchia, 1978).

¹⁹ The evolution of peak intensities of different C1 contributions as a function of CP
²⁰ contact time (left column of each figure) and delay time for ^{13}C T1 (right column)
²¹ are shown in Figures S2-4. The fitted curves are shown as green lines together with
²² fitted parameters. As described by Hill et al. (Hill et al., 1994), The ^{13}C T1 decay
²³ could not be expressed by a single exponential function. There are two relaxations,
²⁴ fast (in the order of c.a. 100 ms) and slow ones (in the order of tens to a hundred of
²⁵ seconds). Nevertheless, even the shorter T1 was significantly larger than the T_{CH} and
²⁶ CP contact time.

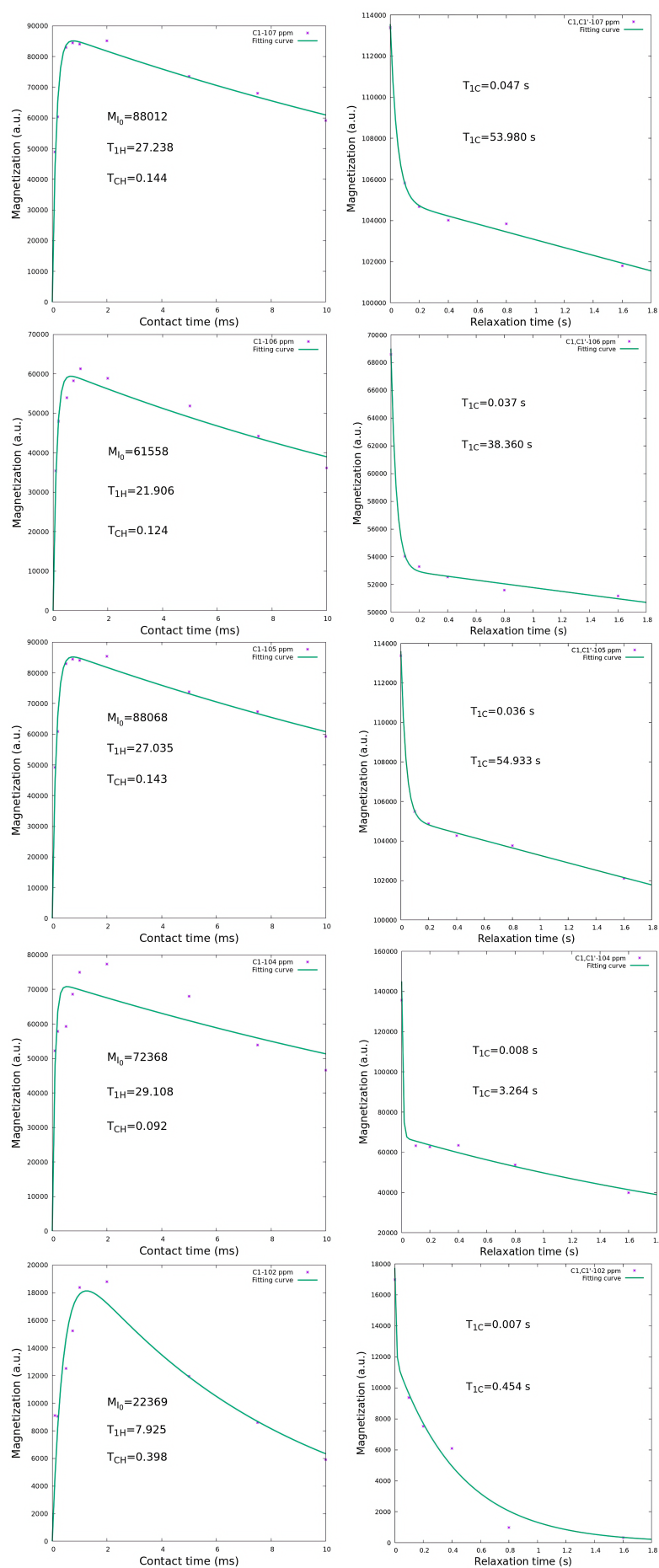


Fig. S2 Variation of ^{13}C signal intensity with CP contact time (left) and ^{13}C spin-lock time (right) for the C1 & C1' region of rehydrated fraction A.

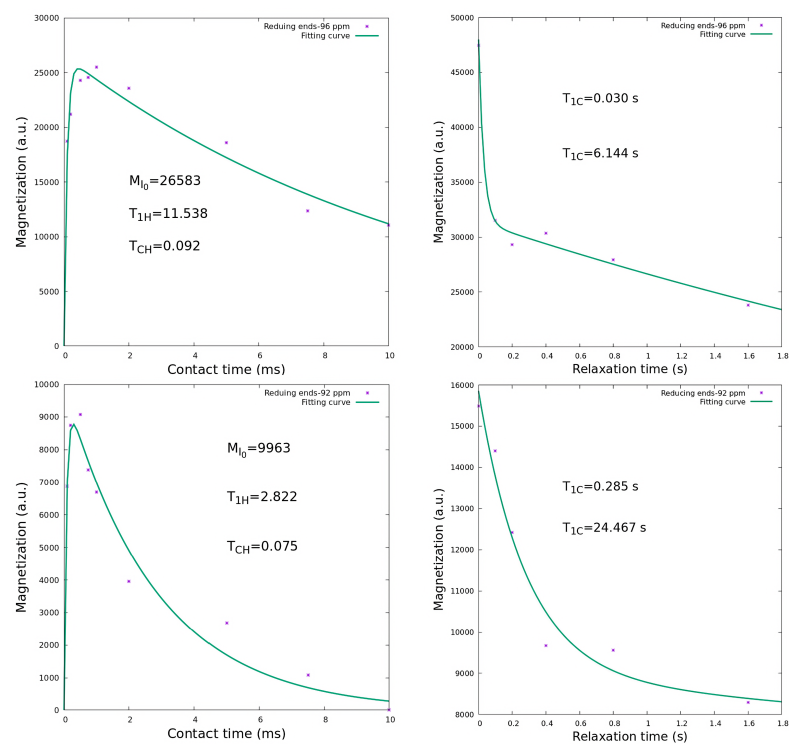


Fig. S3 Variation of ^{13}C signal intensity with CP contact time (left) and ^{13}C spin-lock time (right) for the reducing end (C1'') region of rehydrated fraction A.

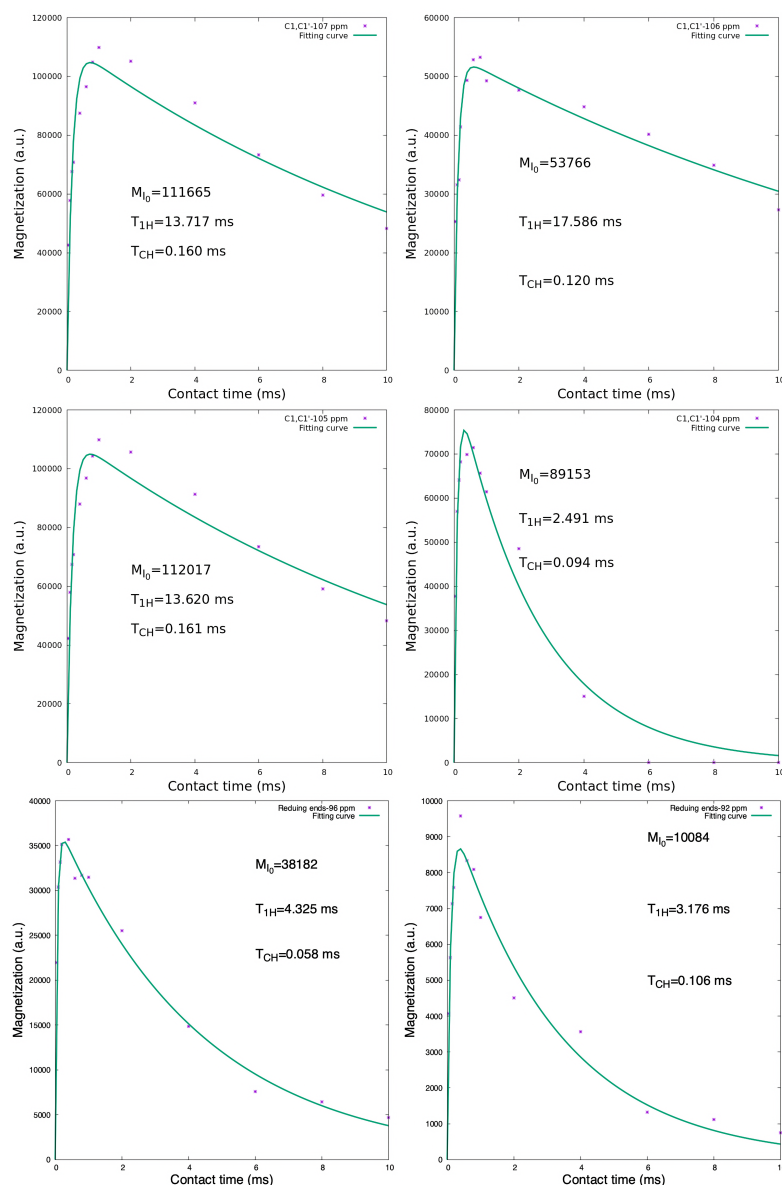


Fig. S4 Variation of ^{13}C signal intensity with CP contact time for the C1 & C1' region and reducing end (C1'') region of rehydrated fraction B.

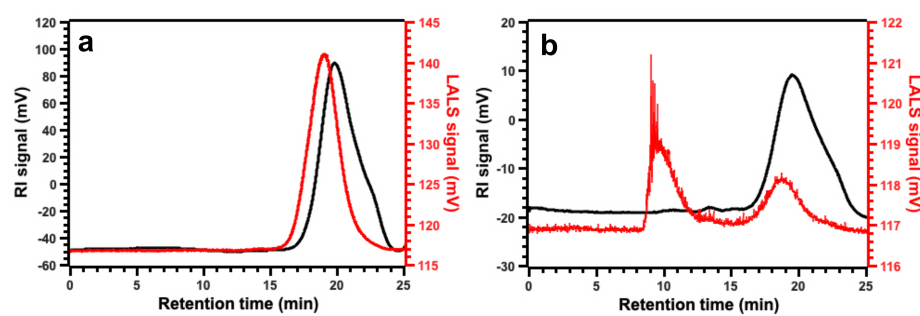


Fig. S5 Refractive index (RI) signals and low-angle light scattering (LALS) signals of (a) carbanilated and (b) nitrated MCC, and the eluent solvent was THF.

References

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