



Title	Elucidating the structural changes of cellulose molecules and dynamics of Na ions during the crystal transition from cellulose I to II in low temperature and low concentration NaOH solution
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1 **Supporting information**

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3 **The structural changes of cellulose molecules and dynamics of Na ions**  
4 **during the crystal transition from cellulose I to II in low temperature**  
5 **and low concentration NaOH solution** *Yuki Kugo<sup>1</sup>, Satoshi Nomura<sup>1</sup>, Takuya Isono<sup>2</sup>,*

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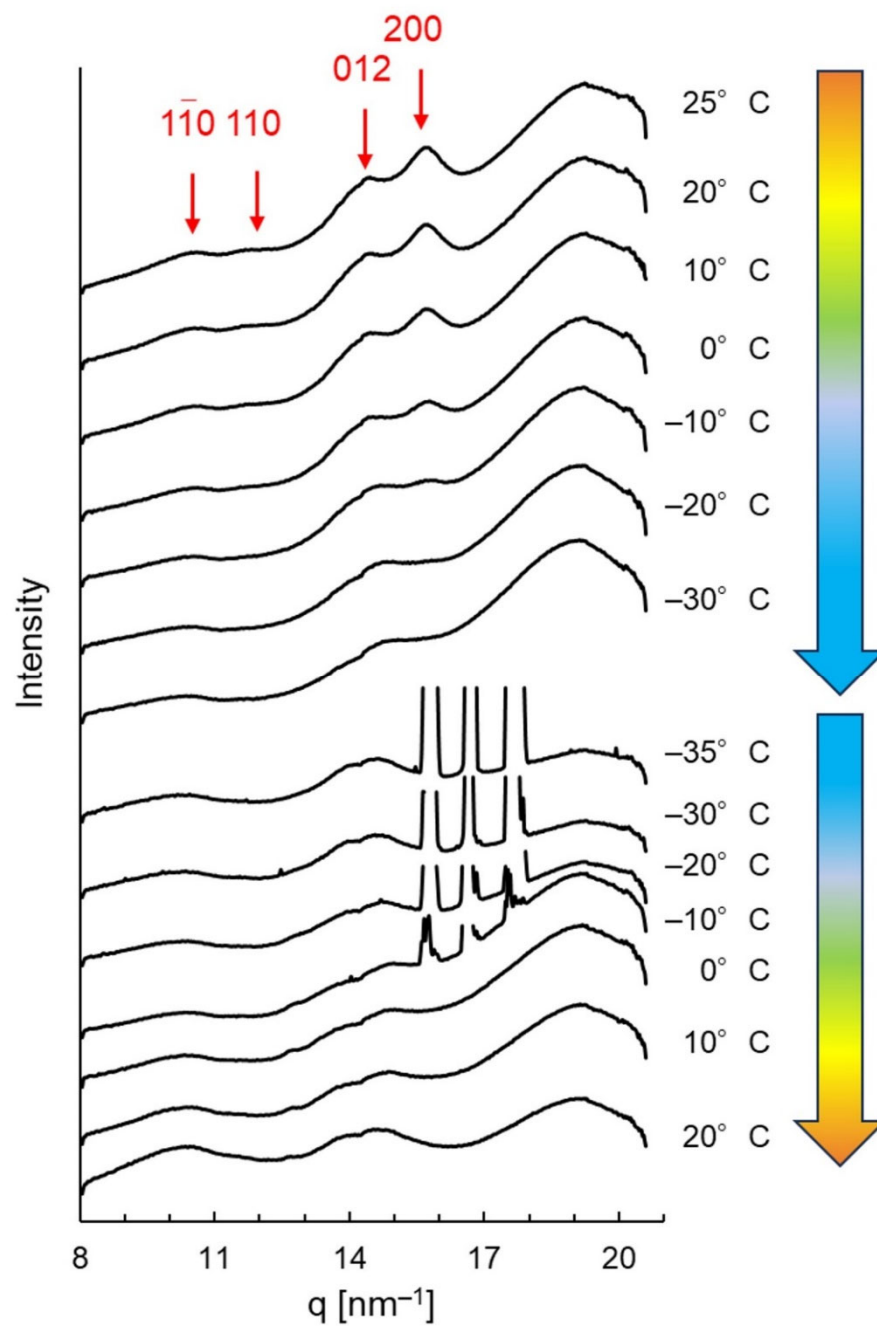
11 <sup>3</sup>ICReDD List-PF, Hokkaido University, N21W10, Kita-ku, Sapporo 001-0021, Japan

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## 13 Results

### 14 In situ wide angle X-ray scattering (WAXS) measurements at different temperatures

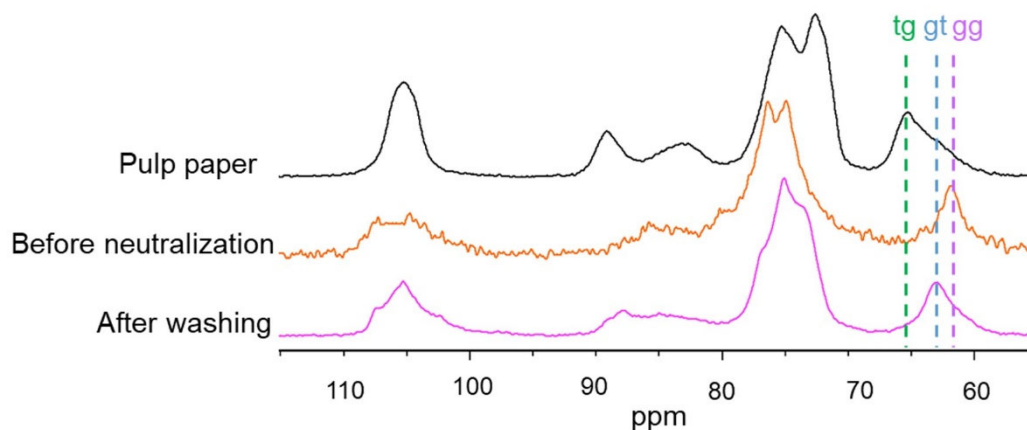
15 Fig. S1 shows the WAXS profiles obtained from the in situ WAXS measurements of the 10  
16 wt% NaOH-soaked pulp paper. The ranges of  $q$  were different (Figs. 6 and S1) because these  
17 measurements were performed at different beamlines. The cellulose I crystal peaks (Fig. S1) were  
18 broad, which is attributed to the lower crystallinity of the pulp paper than that of the cellulose powder.  
19 Similar to that observed for the cellulose powder, as the temperature increased, the intensity of the  
20 cellulose I crystal peak decreased, and the width at half maximum increased. Fig. S2 shows the solid-  
21 state  $^{13}\text{C}$  cross-polarization magic angle spinning (CP/MAS) NMR spectra of the 10 wt% NaOH-  
22 soaked pulp paper sample used in the in situ WAXS measurements before neutralization and after  
23 drying. The sample before neutralization was determined to be alkali cellulose, and the sample after  
24 drying was cellulose II. This indicates that cellulose I crystals disappear and alkali cellulose is formed  
25 as the temperature is lowered, and the crystal morphology does not change as the temperature is  
26 increased, regardless of the cellulose material.



27

28 Fig. S1. Temperature-variable WAXS profiles of the 10 wt% NaOH-soaked pulp paper (25 °C > -

29 35 °C > 20 °C).



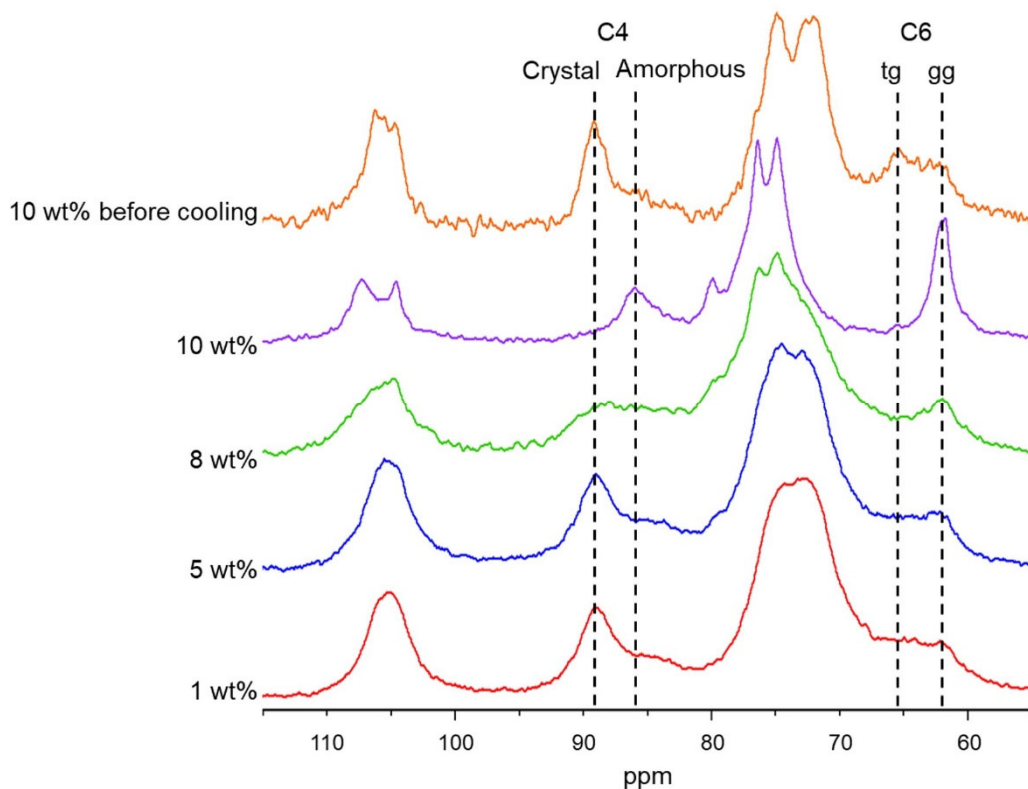
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31 Fig. S2. Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra before neutralization and after drying of the 10 wt%  
 32 NaOH-soaked pulp paper samples used for the in situ WAXS measurements. *Color code*: black line,  
 33 pulp paper; orange line, before neutralization; pink line, after washing. *Abbreviations*: *tg*, trans-  
 34 gauche; *gt*, gauche-trans; and *gg*, gauche-gauche.

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### 36 $^{23}\text{Na}$ NMR relaxation time measurements

37 Fig. S3 shows the solid-state  $^{13}\text{C}$  CP/MAS NMR spectra of the samples used for the  $^{23}\text{Na}$   
 38 NMR relaxation time measurements. These measurements were obtained to confirm the concentration  
 39 of the NaOH solution at which the crystal transition proceeded. The spectra of the samples soaked in  
 40 1 wt% and 5 wt% NaOH were nearly identical to those of the samples soaked in 10 wt% NaOH before  
 41 cooling. Significant C4 peaks were observed in the amorphous region, along with those in the  
 42 crystalline region, for the 8 wt% NaOH-soaked sample, whereas the C4 peak in the crystalline region  
 43 completely disappeared for the 10 wt% NaOH-soaked sample.



44

45 Fig. S3. Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra of 1–10 wt% NaOH-soaked cellulose powders used  
 46 for the  $^{23}\text{Na}$  NMR relaxation measurements. These spectra were recorded at 24 °C. The samples were  
 47 cooled from room temperature to low temperatures and subsequently warmed back to room  
 48 temperature. *Color code*: orange line, 10 wt% NaOH before cooling; purple line, 10 wt%; green line,  
 49 8 wt%; blue line, 5 wt%; red line, 1 wt%. *Abbreviations*: tg, trans-gauche; gt, gauche-trans; and gg,  
 50 gauche-gauche.

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52 Fig. S4 shows the  $^{23}\text{Na}$  NMR spectra of the 10 wt% NaOH-soaked cellulose powder  
 53 recorded at 24 °C, 0 °C, and –15 °C during temperature decrease process. The width of the peak  
 54 increased as the temperature decreased, suggesting that the  $T_1$  of Na ions decreased as the temperature  
 55 decreased.

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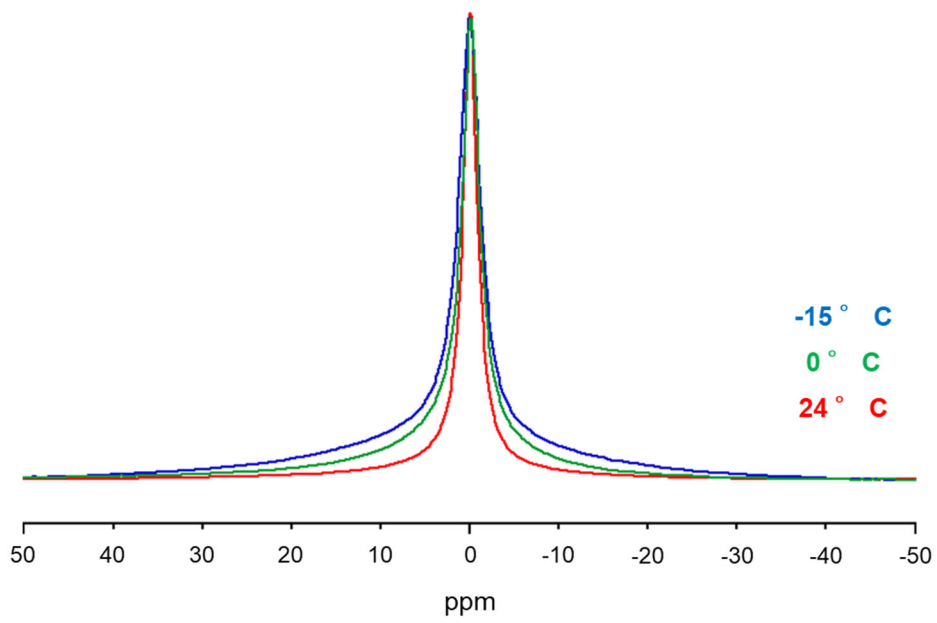
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63 Fig. S4.  $^{23}\text{Na}$  NMR spectra of 10 wt% NaOH-soaked cellulose powder recorded at 24 °C, 0 °C, and –  
64 15 °C during temperature decrease process.