Supporting information

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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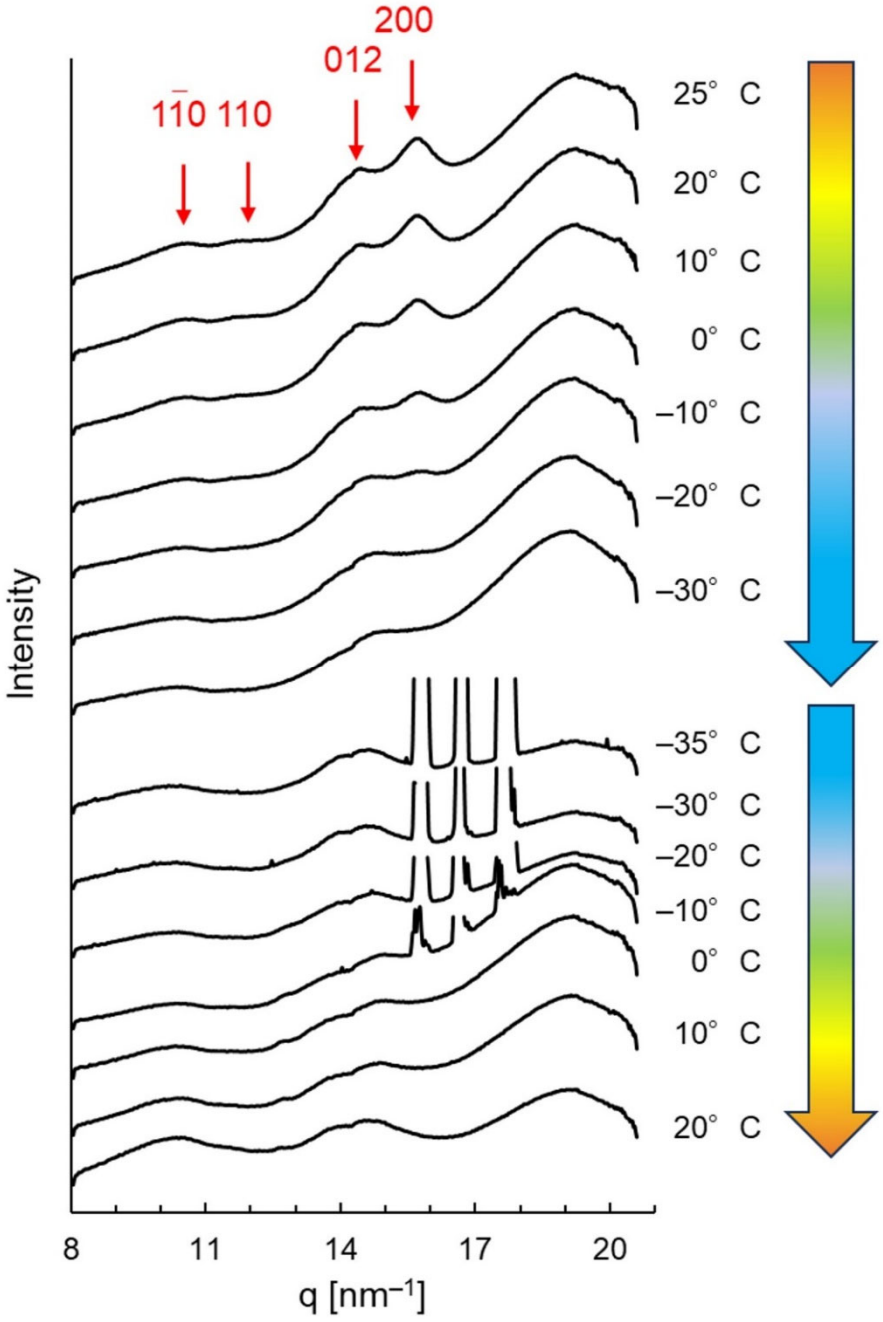
Results

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

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



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

29 35 °C > 20 °C).

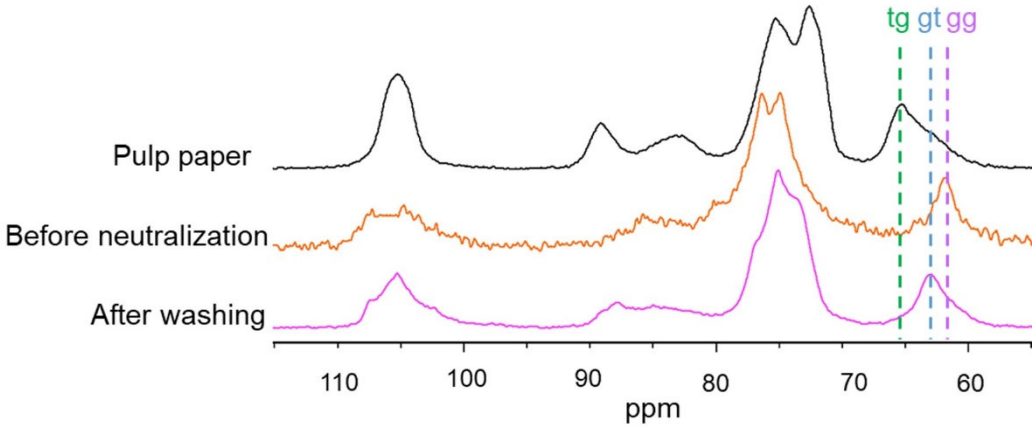

Fig. S2. Solid-state ^{13}C CP/MAS NMR spectra before neutralization and after drying of the 10 wt% NaOH-soaked pulp paper samples used for the in situ WAXS measurements. *Color code:* black line, pulp paper; orange line, before neutralization; pink line, after washing. *Abbreviations*: *tg*, trans-gauche;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

^{23}Na NMR relaxation time measurements

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

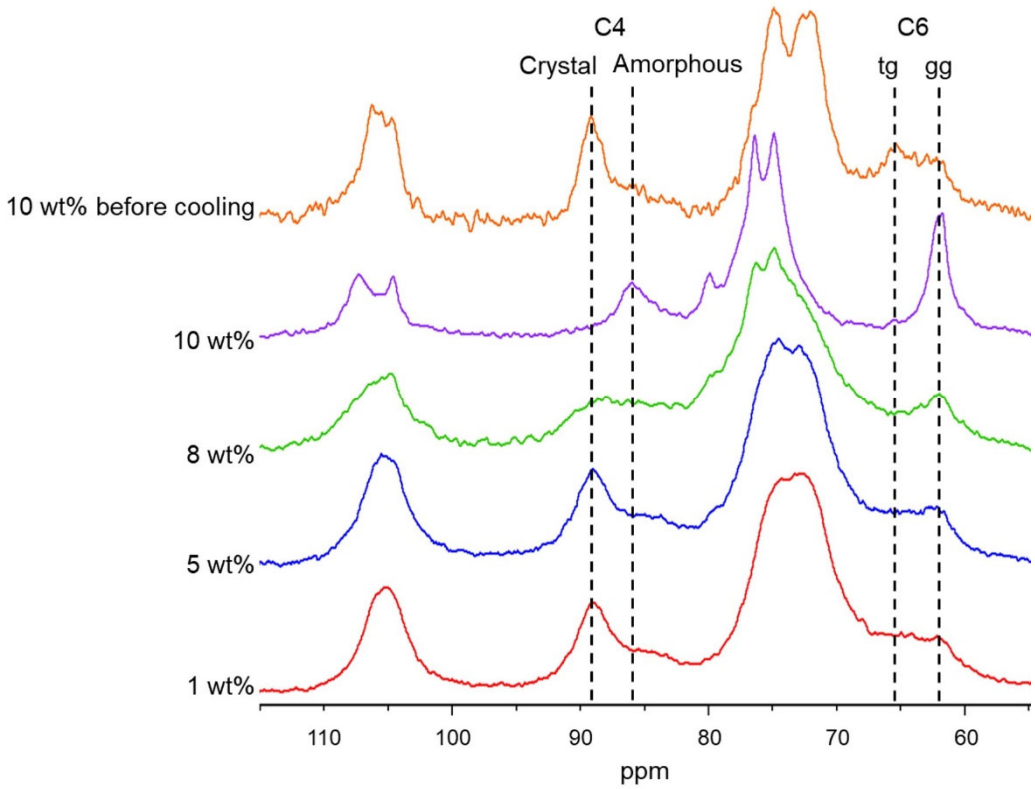

Fig. S3. Solid-state ^{13}C CP/MAS NMR spectra of 1–10 wt% NaOH-soaked cellulose powders used for the ^{23}Na NMR relaxation measurements. These spectra were recorded at 24 °C. The samples were cooled from room temperature to low temperatures and subsequently warmed back to room temperature. *Color code:*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

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

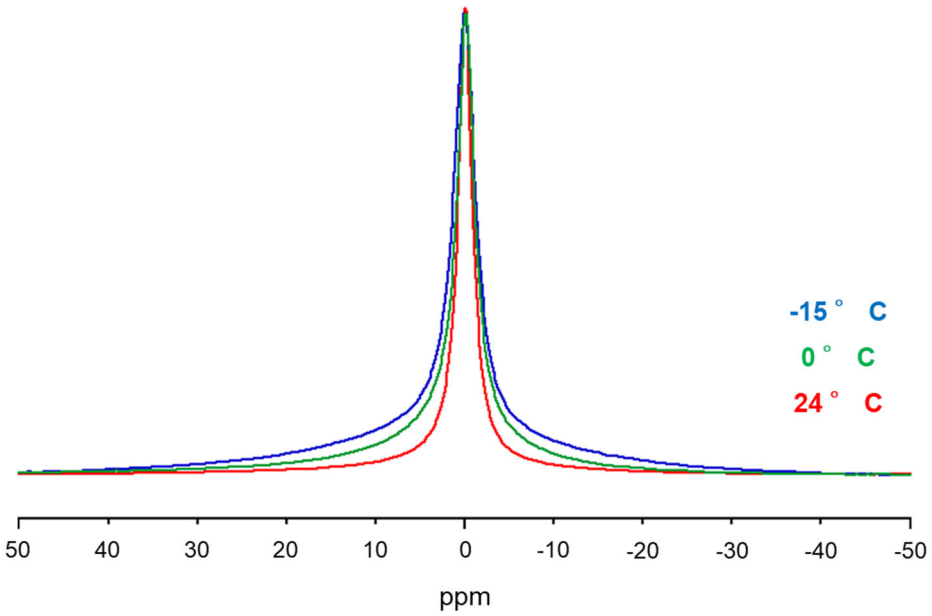

Fig. S4. ^{23}Na NMR spectra of 10 wt% NaOH-soaked cellulose powder recorded at 24 °C, 0 °C, and –15 °C during temperature decrease process.