Electronic Supplementary Information for "Cooking Cellulose in Hot and Compressed Water" by Shigeru Deguchi, Kaoru Tsujii, and Koki Horikoshi

Experimental Section

Materials. Cellulose used was α-cellulose obtained from Whatman (microcrystalline cellulose, CF1). Degree of polymerization was found to be 230 by viscometry. Crystallinity index was found by X-ray diffraction to be 73.4 %, showing highly crystalline nature of the sample.

High-temperature and -pressure in situ optical microscopy. Observation was made using an optical microscope equipped with a high-temperature and -pressure cell. The system allows *in situ* microscopic observation of specimen at temperatures and pressures up to 400 ºC and 35 MPa with the optical resolution of 2 μm. Advanced microscopic techniques such as polarized or fluorescence microscopy can also be performed. The cellulose sample was dispersed in water or ethanol at the concentration of 1 %(w/v), and loaded to the cell. The cellulose sample, initially suspended in water, sedimented on the bottom window surface. The sample was then pressurized to 25 MPa for water or 7 MPa for ethanol, and heated to 350 ºC while keeping pressure constant. Heating rate of the sample was almost constant at 11-14 ºC/min in the temperature range reported. Hydrostatic pressure of 25 MPa was applied to maintain water in a liquid state during the observation. The observation was made under crossed polarizers. In this set up, the sample is held between two optical diamond windows. Although diamond is a cubic crystal and is not birefringent in principle, natural diamond usually exhibits birefringence due to inherent distortion in the crystalline lattice. Thus, unlike typical polarized microscopic observations, the background of the images cannot be made completely dark.

Image analysis. The observation was quantified by calculating the brightness of the images, as the images become brighter as cellulose loses birefringence. The images were converted to grayscale, and the average brightness of the whole image was calculated. It was found out that the brightness is also affected by thermal expansion of the cell body that changes the alignment of the two opposing birefringent windows made of diamond. This effect was compensated by measuring the brightness of a

part of the image that was not covered with cellulose, and dividing the average brightness of the whole image by that of the uncovered area. All the image analysis was performed using ImageJ (http://rsb.info.nih.gov/ij/).

Movie captions

Movie 1S. Movie showing crystalline-to-amorphous transformation of cellulose in water between 260 ºC and 350 ºC and at constant pressure of 25 MPa. The movie has been edited to 20 times the original playback rate.

Movie 2S. Movie showing cellulose in ethanol between 240 ºC and 350 ºC and at constant pressure of 7 MPa. The movie has been edited to 20 times the original playback rate.