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Short communication

Mechanism of cellulose gelation from aqueous alkali-urea solution

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ABSTRACT

Molecular process of regeneration-gelation of cellulose from aqueous alkali-urea solvent was monitored by synchrotron-radiation X-ray. The wide-angle diffraction from cellulose during regeneration, both by coagulant and heating, gave information on behavior of cellulose molecules, i.e. the glucopyranoside rings first stack by hydrophobic interaction to form monomolecular sheets, which then line up by hydrogen bonding to form Na–cellulose IV type crystallites (hydrate form of cellulose II). While such a process in regeneration of cellulose has been hypothesized and supported by molecular dynamics or monitoring of mercerization process, our observation finally confirmed it experimentally. This knowledge will be useful in understanding behavior of cellulose molecules during regeneration, leading to better controls of resulting structure and properties.

1. Introduction

Cellulose has long attracted much attention for material usage because of its abundance, renewability, and useful mechanical properties (Klemm, Heublein, Fink, & Bohn, 2005). Besides its uses in native forms such as paper and textiles, regenerated cellulose prepared by coagulation of solution has been used in many ways such as artificial fibers and films. While most types of regenerated cellulose have crystal form of cellulose II, having antiparallel chain packing (Kolpak & Blackwell, 1976; Langan, Nishiyama, & Chanzy, 1999; Stipanovic & Sarko, 1976), their mechanical and surface-chemical properties are known to depend strongly on the type of cellulose solvent and coagulant (Fink, Weigel, Purz, & Ganster, 2001; Inamoto, Miyamoto, Hongo, Iwata, & Okajima, 1996; Isobe, Kimura, Wada, & Kuga, 2011; Isobe, Kim, Kimura, Wada, & Kuga, 2011; Takahashi, 1968a, 1968b; Yamane, Mori, Saito, & Okajima, 1996).

Much effort has been paid to understand the nature of regenerated cellulose, and its primary structure formation has been investigated from old days. Hermans (1949) and Hayashi, Masuda, and Watanabe (1974) separately reported that structural disorders lie mainly in the hydrogen-bonded intermolecular region, and both assumed the primary structure as a monomolecular sheet formed by stacking of glucopyranoside planes by van der Waals force (see Fig. 1B). This sheet was named as “sheet-like structure” (Hermans) or “plane lattice structure” (Hayashi). Recently, Miyamoto et al. (2009) simulated regeneration of cellulose by molecular dynamics (MD), reproducing hypothesized formation of the sheet-like structure. While these studies gave a consistent picture of the primary structure formation of regenerated cellulose, they were either deduced from the resulting structure or based on computer simulation. Although development of hydrophobically stacked monomolecular sheets at the early stage of washing process during mercerization was observed by Nishiyama, Kuga, and Okano (2000), no in situ observation has been given for the molecular process in cellulose regeneration from solution.

Recently, a new class of cellulose solvent based on aqueous caustic alkali and urea was found by Cai and Zhang, which represents a potential alternative for viscose process (Cai & Zhang, 2005). In addition to the economic and environmental advantages, this solvent has a notable feature of giving highly transparent hydrogel on regeneration (Cai, Kimura, Wada, Kuga, & Zhang, 2008). This gel has a nanoporous network composed of nanometric cellulose fibrils, and offers many possibilities as separation material and substrate for composites (Isobe, Kimura, et al., 2011; Isobe, Kim, et al., 2011; Mao, Zhou, Cai, & Zhang, 2006). Since the gelation from this solvent proceeds with minimal shrinkage, it is suited for monitoring by X-ray diffraction from a properly arranged sample. As such, we chose here a glass capillary containing the cellulose solution, which is contacted by coagulant supplied from one end of capillary. As the coagulant penetrates the solution by diffusion, dissolved cellulose molecules will undergo transformation to gel. With this capillary arrangement, synchrotron X-ray radiation was effectively used to monitor the time-dependent phenomenon in the capillary.

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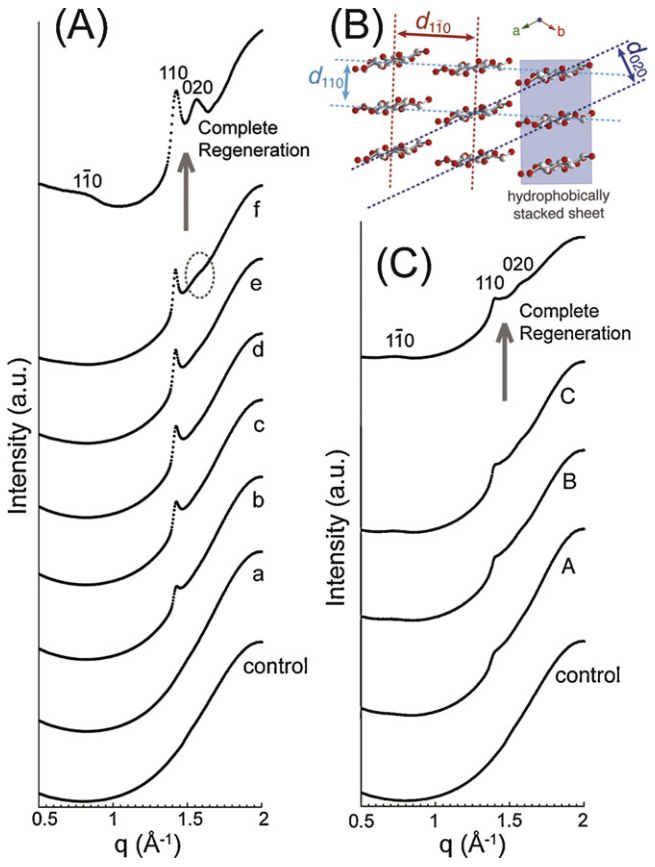

Fig. 1. (A) Synchrotron X-ray diffraction profiles of cellulose solution under regeneration by 5 wt% aq. Na_2SO_4, control: 10 wt% cellulose solution without coagulant, a: measured at 2 mm away from boundary with coagulant and 180 min after coagulant introduction; b: 2.5 mm, 195 min; c: 1.75 mm, 190 min; d: 1.5 mm, 185 min; e: 1.5 mm, 200 min; f: 1.5 mm, 270 min, and complete regeneration: 1.5 mm, 1 week. q denotes the scattering vector ($2\pi/d$). (B) Crystal structure of Na–cellulose IV viewed parallel to c-axis. Na–cellulose IV is a hydrate form of cellulose II (Kobayashi et al., 2011; Nishimura & Sarko, 1991) and indexation follows Kobayashi et al. Water molecules are not depicted here. (C) Synchrotron X-ray diffraction profiles of cellulose solution under regeneration with heat, control: 10 wt% cellulose solution, and A: cellulose solution heated for 5 s at 105 °C, B: for 15 s, C: for 30 s, and complete regeneration: for 3 min.

2. Experimental

2.1. Materials

CF11 (Whatman, USA) was used as cellulose sample. LiOH·H_2O, urea, sodium sulfate, were of reagent grade (Wako Pure Chemicals, Japan) and used without further purification. Deionized water was used for all experiments.

2.2. X-ray diffractometry

Ten-wt% cellulose solution was prepared as reported by Cai and Zhang (2005). Briefly, aqueous solution of 4.6% LiOH and 15% urea by weight was cooled to −15 °C, desired amount of dry cellulose was added, and the mixture was stirred vigorously for 10 min, resulting in a transparent solution. This cellulose solution was kept at 4 °C until use. A glass capillary, 2 mm bore and 80 mm long, was half filled with the cellulose solution, and on top of it 5 wt% aqueous Na_2SO_4 solution was added as coagulant. The capillary was mounted on a goniometer head, and the synchrotron X-ray (λ = 1.0 Å) was irradiated at several points for 60 s each by moving the capillary vertically. The diffraction patterns were recorded by a camera system equipped with a flat imaging plate (IP) (R-AXIS V, Rigaku). The sample-to-IP distance (L) was calibrated by Si powder (d = 0.31355 nm), and the L was 159.208 mm. The X-ray diffraction profiles were obtained by analyzing the diffraction diagrams using the R-Axis display software package (Rigaku).

In addition, the thermal gelation of cellulose solution was observed after heating the fresh cellulose solution in capillary by a small gas burner 5 cm away (105 °C with digital thermometer) up to 3 min, followed by synchrotron X-ray measurement.

We determined the regeneration process was “complete” when the X-ray profiles did not show any discernible change. Also, with the cellulose solution kept at room temperature for 4 h, it was checked that the change at room temperature was negligible.

3. Results and discussion

Fig. 1A shows a series of diffraction profiles selected from such measurements showing discernible changes during coagulation by sodium sulfate aqueous solution. A large broad peak centered at around q = 2 was diffuse scattering of water. The top profile is from the completely regenerated cellulose gel formed in the capillary after 2 weeks. It shows the pattern of Na–cellulose IV, which is actually the hydrate form of cellulose II containing water between hydrophobically stacked sheets (Kobayashi, Kimura, Togawa, & Wada, 2011; Nishimura & Sarko, 1991). From a to f, the profiles show gradual formation of cellulose hydrogel. At first, the peak of (1 1 0) plane of Na–cellulose IV appeared and grew gradually (a to e), and then a very weak peak of (0 2 0) appeared (dotted circle in f). As shown in Fig. 1B, the reflection of (1 1 0) plane comes from the lattice spacing of the hydrophobically stacked cellulose molecules, and that of (0 2 0) plane comes from the lattice spacing transverse to the ring planes. Therefore, the changes in the X-ray profile indicates that the cellulose molecules first form hydrophobically stacked monomolecular sheets, followed by their mutual association via hydrogen bonding.

This cellulose solution also forms gel by heating (Cai & Zhang, 2006). LiOH/urea system has stronger dissolution power and higher thermal stability of resultant cellulose solution than NaOH/urea system (Cai & Zhang, 2005). To obtain the thermally coagulated hydrogel within limited time, it was necessary to apply rather high temperature over 80 °C; therefore we used a small gas burner for quick gelation in the capillary. Fig. 1C shows the change in the X-ray profile in the course of heat-induced gelation. The change is basically similar to that in Fig. 1A, but all peaks are much weaker. Therefore, the molecular process must be similar to those in gelation by coagulant (the formation of hydrophobically stacked monomolecular sheet in the initial stage), but the resultant crystalline order must be very limited. It is likely that the enhanced thermal motion causes more random association and entanglement of cellulose molecules than in the coagulant-induced gelation. Thermally coagulated cellulose hydrogel is known to have inferior mechanical property to that of cellulose hydrogels prepared with coagulants (Cai & Zhang, 2006; Chang & Zhang, 2011). The cellulose hydrogel by solvent-induced coagulation consists mainly of Na–cellulose IV type crystalline region, which is thought to give higher mechanical property to the hydrogel (Cai et al., 2008). Therefore, the situation observed here, i.e. poor growth of Na–cellulose IV crystalline region, is likely to be one of the reasons of the inferior mechanical property of thermally coagulated cellulose hydrogel.

On the basis of these analyses, a schematic image of cellulose regeneration in the present system can be drawn as in Fig. 2. Namely, the cellulose molecules stack with hydrophobic interaction to form monomolecular sheets, which then line up by hydrogen bonding.

Such a mode of molecular association can be understood as resulting from that both of the solvent and coagulant used

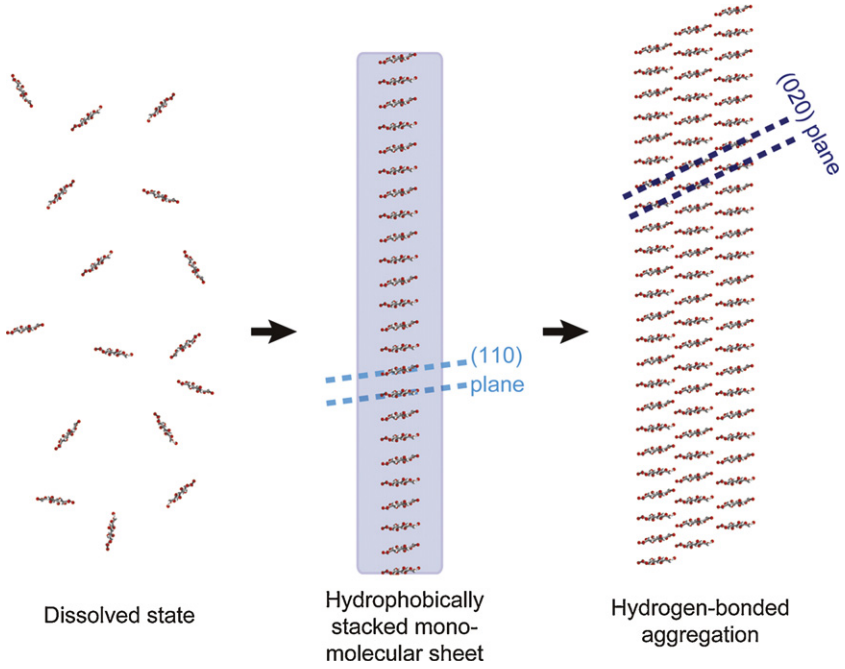

Fig. 2. Schematic image of cellulose hydrogel formation. Cellulose molecules are depicted as cross-section and water molecules are not depicted here.

here were aqueous, i.e. when the medium surrounding the cellulose molecule becomes unfavorable for molecular dispersion, they would aggregate to hide the glucopyranoside's ring planes, which are hydrophobic and unfavorable to be exposed to the polar medium.

4. Conclusion

Synchrotron X-ray diffraction gave detailed information on the molecular process and resulting structure of cellulose regeneration. The wide-angle diffraction profiles lead to a consistent picture of the molecular process involving hydrophobic stacking of cellulose molecules into monomolecular sheets, followed by their binding by hydrogen bonding. These findings will be useful in controlling structure and properties of regenerated cellulose, as well as in understanding biogenetic process of native cellulose (Cousins & Brown, 1995).

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