In Situ Observation of the Crystalline Transformation from Cellulose III_I to I_β

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ABSTRACT: An oriented, crystalline film of cellulose I was transformed into cellulose III_I by supercritical ammonia treatment. These oriented, crystalline cellulose III_I films were converted into cellulose I_β crystalline film by heating in air for 1 h at 230 °C. This transformation process, from cellulose III_I to I_β, was studied by differential scanning calorimetry and X-ray diffraction methods. During the heating, an endothermic peak was observed at 200 °C. This suggests that some hydrogen bonds are broken, which might trigger the transformation from cellulose III_I to I_β, at this temperature. Analysis of the X-ray diffraction results revealed that cellulose III_I transforms into I_β in the temperature range 200−217 °C. At 217 °C, the intrasheet and intersheet distances between cellulose chains in both the cellulose III_I and I_β crystalline phases are almost identical. Thus, we propose a mechanism account for the cellulose III_I transformation into I_β by shear of the hydrogen-bonded cellulosic sheets in the *bc*-plane.

Introduction

Cellulose I is a natural form of cellulose, and there are two crystalline polymorphs: I_α and I_β.[1,2] The structures of cellulose I_α and I_β are assigned to the triclinic and monoclinic crystalline systems, respectively.[3] The I_β phase is considered to be more stable than the I_α phase, because I_α transforms into I_β after hydrothermal treatment.[4] Furthermore, Debzi et al.[5] reported that most of the I_α phase could be converted into I_β under an atmosphere of helium. This suggests that the important factor is temperature and not existence of water for the transformation between cellulosic polymorphs.

Another polymorph, cellulose III_I, is obtained by treatment of cellulose I in liquid ammonia[6,7] or various amines[8−10] followed by removal of these reagents. Cellulose III_I can be reverse transformed into cellulose I_β by treatment in hot water.[11−14] The above finding by Debzi et al.[5] was the motivation to check whether the cellulose III_I transformed into I_β by heating without water, based on the reasoning that if the conversion occurs by heating alone, it would be possible to observe in situ the phase transformation process by physical means.

Recently, Nishiyama et al.[15] developed a way to make uniaxial oriented cellulose I films from crystalline cellulose samples. Also, Yatsu et al.[16] prepared crystalline cellulose III samples with supercritical ammonia. Using these methods, oriented crystalline cellulose III_I films were prepared using a supercritical ammonia treatment on oriented cellulose I films. Thereafter, by using the prepared films, cellulose III_I was found to be transformed into cellulose I_β by heat treatment. In this report, the result of monitoring the phase transformation process by differential scanning calorimetry (DSC) and X-ray diffraction are described, and a phase transformation mechanism is proposed.

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Experimental Section

Materials. The sample used in this study was crystalline cellulose from green marine alga *Cladophora*. The alga sample was repeatedly purified with 5% KOH and 0.3% $NaClO_2$ solution according to the method previously reported.[17] The purified sample was homogenized into small fragments using a double-cylinder type homogenizer, and these fragments were treated with 65% sulfuric acid at 70 °C for 30 min with continuous stirring. The samples were washed with deionized water by successive dilution and centrifugation at 3200*g* for 5 min until the supernatant became turbid. The turbid supernatant was collected and concentrated by a high-speed centrifuge at 18 800*g* for 40 min and further dispersed into a small amount of distilled water. The concentrated suspension was sonicated with a rod-type sonicator for 1 min. The suspension was finally treated by placing it in contact with a mixed-bed ion-exchange resin.

Thin films of cellulose microcrystals with random orientation were obtained by casting the suspension on a glass plate followed by drying in air for several days. The films were further dried at 50 °C for 24 h and stored in a desiccator over P_2O_5 until used.

Oriented films of cellulose microcrystals were prepared from the suspension by the shearing method as previously reported.[15] In short, the suspension with a small amount of sulfuric acid was put into a glass vial, and the vial was then kept horizontal and rotated around its center. After a few hours, the gel layer attached on the inner surface of the glass vial was dried into a film by repeated treatment of rinsing with ethanol and drying with a warm air flow. The films of oriented microcrystals were further dried at 105 °C for 8 h and stored in a desiccator over P_2O_5 until used.

Supercritical Ammonia Treatment. The films were placed in a steel pressure vessel, which was cooled in a dry ice/methanol bath. By introducing the NH_3 gas into the cooled vessel, the sample was immersed in liquid NH_3. The vessel was hermetically sealed and maintained at room temperature for 30 min. The vessel was then heated at 140 °C, which is above the critical temperature of ammonia: 132.5 °C, for 1 h in an oil bath. After the vessel was taken out of the oil bath, the NH_3 gas was immediately vented. The treated samples were thoroughly washed with dry methanol and dried under high vacuum at 50 °C.[16,18,19] Oriented cellulose III_I films with high degree of crystallinity were obtained.

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X-ray Fiber Diffraction. The oriented cellulose III_I films were heated at 230 °C in air for 1 h. X-ray fiber diffraction diagrams of the films before and after heat treatment were obtained using a vacuum camera mounted on a Rigaku RU-200BH rotating anode X-ray generator. Ni-filtered Cu Kα radiation ($\lambda = 0.154\ 18$ nm) generated at 50 kV and 100 mA was used. These samples was irradiated using an incident X-ray beam that was collimated by a pinhole 0.3 mm diameter, and the fiber diffraction patterns were recorded on Fuji film imaging plates (BAS-IP SR 127). The camera length was calibrated using NaF ($d = 0.231\ 66$ nm).

FT-IR Spectroscopy. The randomly oriented thin films treated with ammonia were heated at 230 °C in air for 1 h. FT-IR spectra of the films before and after heat treatment were obtained using a Nicolet Magna 860. All spectra were recorded with an accumulation of 64 scans, resolution of 4 cm^{-1}, in the range from 4000 to 400 cm^{-1}.

DSC Measurements. DSC was performed with a Perkin-Elmer Pyris1. About 3 mg of ammonia treated cellulose sample was sealed in an aluminum pan. The sample was then heated from 150 to 250 °C at a rate of 5 °C/min. After holding the temperature at 250 °C for 5 min, the samples were cooled at a rate of −5 °C/min to 150 °C.

X-ray Diffractometry under Heat Treatment. Equatorial X-ray diffraction profiles were obtained using a sample heating holder and a position-sensitive proportional counter (PSPC) mounted on a Rigaku RINT 2200 goniometer. Ni-filtered Cu Kα radiation ($\lambda = 0.154\ 18$ nm) generated at 36 kV and 50 mA was collimated by a pinhole of 1.0 mm diameter. The oriented cellulose III_I film sample was positioned at the center of the goniometer as the film surface was perpendicular to the incident X-rays ($\theta = 90°$), and the PSPC was placed to cover the range of 2θ from 8° to 30°. After the sample was placed in the heating holder, the atmosphere in the holder was completely replaced with helium. The diffraction pattern was recorded for the initial sample at room temperature. The sample was heated to a specific temperature at a rate of 5 °C/min and kept there for 2 min while the diffraction pattern was recorded. The measurement and heating process was repeated up to 250 °C. After holding the temperature at 250 °C for several minutes, the sample was cooled to room temperature at a rate of −5 °C/min. Finally, the pattern at room temperature was recorded.

Results and Discussion

An X-ray fiber diagram of the supercritical ammonia treated film is shown in Figure 1A. The pattern is typical of highly crystalline cellulose III_I with two strong reflections (a) and (b) located on the equator at $d = 0.759$ and 0.427 nm and an intense reflection (c) on the meridian at $d = 0.518$ nm. According to a one chain unit cell with $P2_1$ symmetry,[20,21] reflection (a) was indexed as 010, (b) was the overlapping of the two reflections 100 and 110, and (c) was 002.

Figure 1B is an X-ray fiber diagram of the annealed film of Figure 1A at 230 °C for 1 h. This pattern, the resolution of which is poorer than that of the initial cellulose III_I, closely resembles the fiber diagram of ramie cellulose.[22] Three crystalline reflections (d), (e), and (f) with broader width appeared on the equator at $d = 0.597$, 0.538, and 0.394 nm, respectively. A weak reflection (g), which was comparable with intense reflection (c) of cellulose III_I, was observed on the meridian. Furthermore, all reflections in the diagram were indexed according to the I_β monoclinic unit cell,[3,22] there being no observed characteristic I_α reflection. Therefore, the diagram was of cellulose I_β, the same as ramie, indicating that cellulose III_I transformed into cellulose I_β by heat treatment without water.

To confirm the X-ray fiber diffraction results, FT-IR measurements of thin films were performed. Figure 2

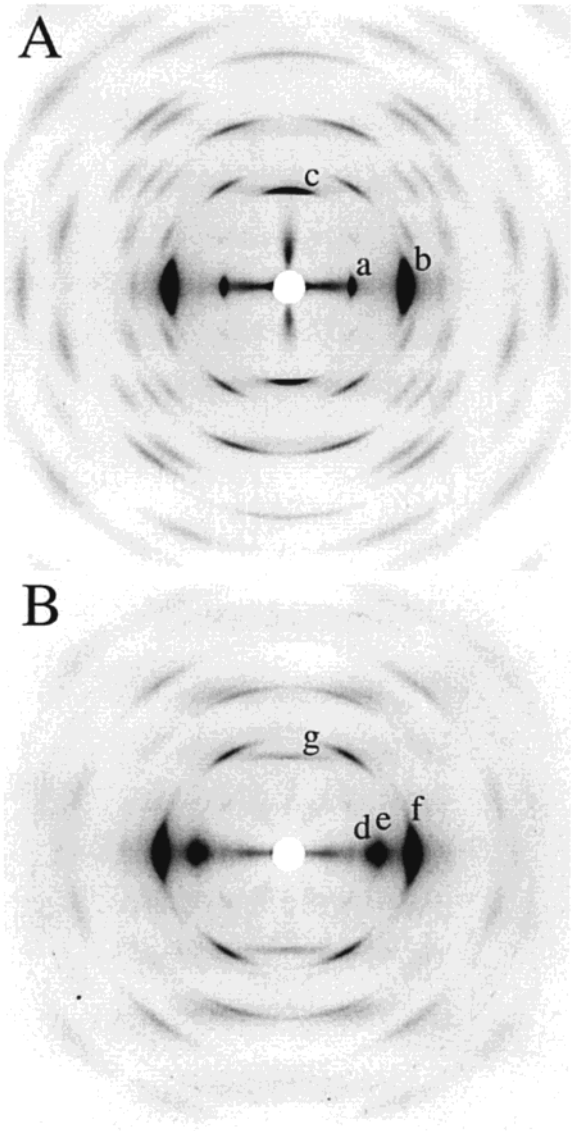

Figure 1. X-ray fiber diagrams of crystalline cellulose III_I (A) and heat-treated cellulose, held at 230 °C for 1 h (B). Diagram B is a typical cellulose I_β pattern.

shows the FT-IR spectra of before (A) and after (B) heat treatment of cellulose III_I films in the OH stretching region recorded with a resolution of 4 cm^{-1}. Only three bands, one sharp band at 3480 cm^{-1} and two broad bands at 3300 and 3150 cm^{-1}, exist in the spectra of cellulose III_I. On the other hand, the annealed spectrum is the same as that of *Halocynthia*, ramie, and cotton cellulose, which are I_β type cellulose. In accordance with Sugiyama et al.,[17] the bands at 3240 and 3270 cm^{-1} were assigned to I_α and I_β, respectively. In the spectrum of the annealed film, the band at 3270 cm^{-1} is clearly observed, but no band is present at 3240 cm^{-1}. Thus, the annealed sample is cellulose I_β. From the FT-IR results, we confirmed that the III_I to I_β transformation was induced by heat treatment.

The above X-ray and FT-IR results were the motivation to monitor the crystalline phase transformation process. First, the monitoring process was undertaken by in situ DSC measurements. Figure 3 is a DSC thermogram of cellulose III_I for the heating and cooling processes. In the heating process, an endothermic peak, whose onset was 195 °C, was observed at 200 °C.[23] This

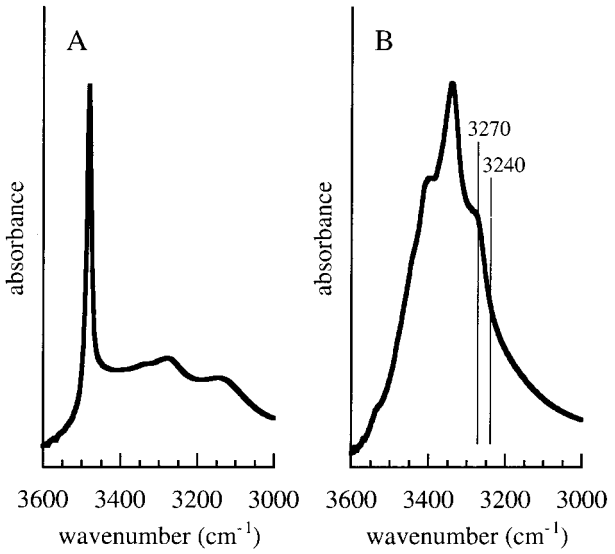

Figure 2. FT-IR spectra in the OH stretch region of cellulose III_I (A) and cellulose I_β (B), which was converted from the cellulose III_I sample by heat treatment at 230 °C for 1 h.

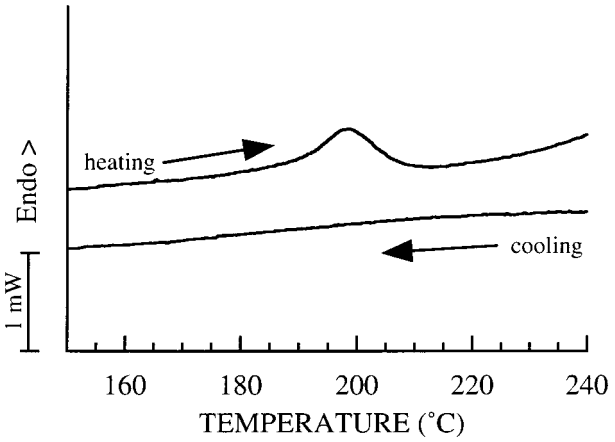

Figure 3. DSC thermogram of the crystalline phase transition process from cellulose III_I to cellulose I_β.

result indicates that release of some hydrogen bonding may occur at this temperature. Above this temperature, cellulose chains may move more flexibly to relax into the more stable I_β structure. With increasing temperature, thermal vibration of the molecular chains increases, and as a result, the amount of transformation to the I_β phase would be expected to increase. However, in the cooling process no peak was observed. After DSC measurements, the sample was removed from the pan and X-ray diffraction undertaken. The observed diffraction profile was that of cellulose I_β, suggesting that the cellulose III_I completely transformed into I_β by this thermal treatment.

To observe in situ the crystalline phase transition from cellulose III_I to I_β, X-ray diffraction was performed at specific temperatures. Figure 3 shows the equatorial X-ray diffraction profiles for the crystalline phase transformation process from cellulose III_I to I_β. Three equatorial reflections of cellulose III_I, symbolized 1, 2, and 3, which were indexed at 010, 100/1$\bar{1}$0, and 110, respectively, were observed at room temperature before heating. As the sample was heated to 192 °C, peak 2 shifted noticeably to smaller angles because of thermal expansion, while peaks 1 and 3 shifted only to a small extent. When the temperature increased to 200 °C, the

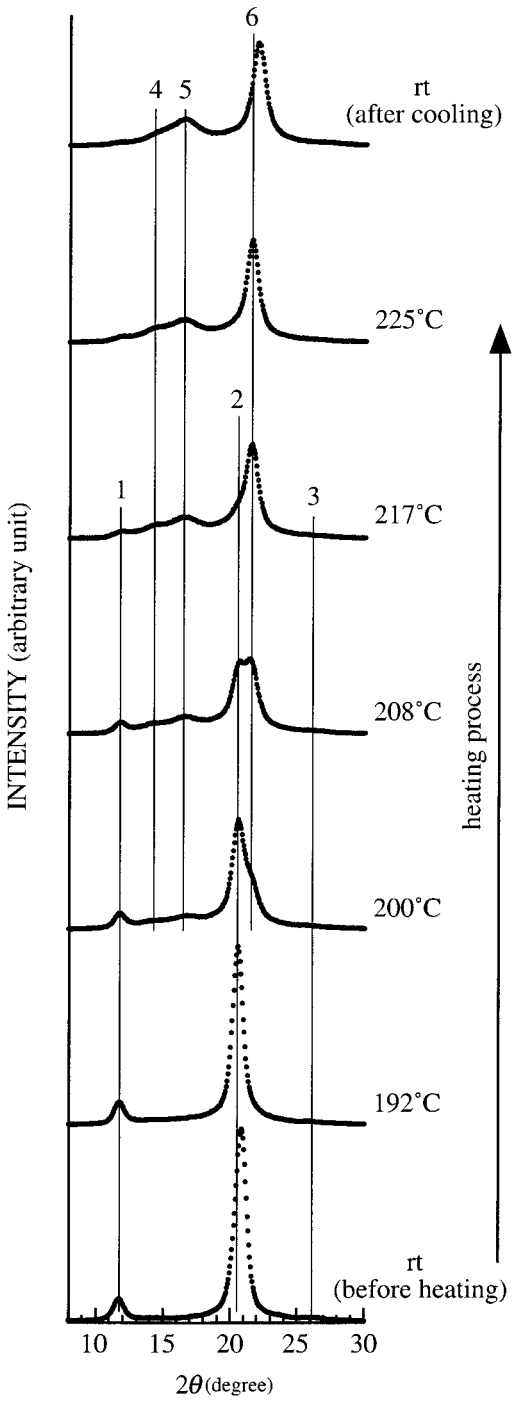

Figure 4. Equatorial X-ray diffraction profiles in the crystalline phase transformation process from cellulose III_I to I_β at specific temperatures in an atmosphere of helium.

three peaks (4, 1$\bar{1}$0; 5, 110; 6, 200) that correspond to cellulose I_β appeared, and the intensity of peaks 1, 2, and 3 assigned to cellulose III_I diminished. At 208 °C, the cellulose III_I and I_β phases were approximately 50:50. The cellulose III_I phase was almost completely converted into cellulose I_β phase at 225 °C. After heating to 250 °C, the sample was cooled to room temperature. Although the peaks shifted to wider angles by thermal shrinkage, the profiles remained as the I_β pattern. These X-ray results indicate that cellulose III_I directly transformed into I_β at 200−217 °C during the heating process.

To consider how the transformation from cellulose III_I to I_β proceeded, peak fitting of the X-ray diffraction

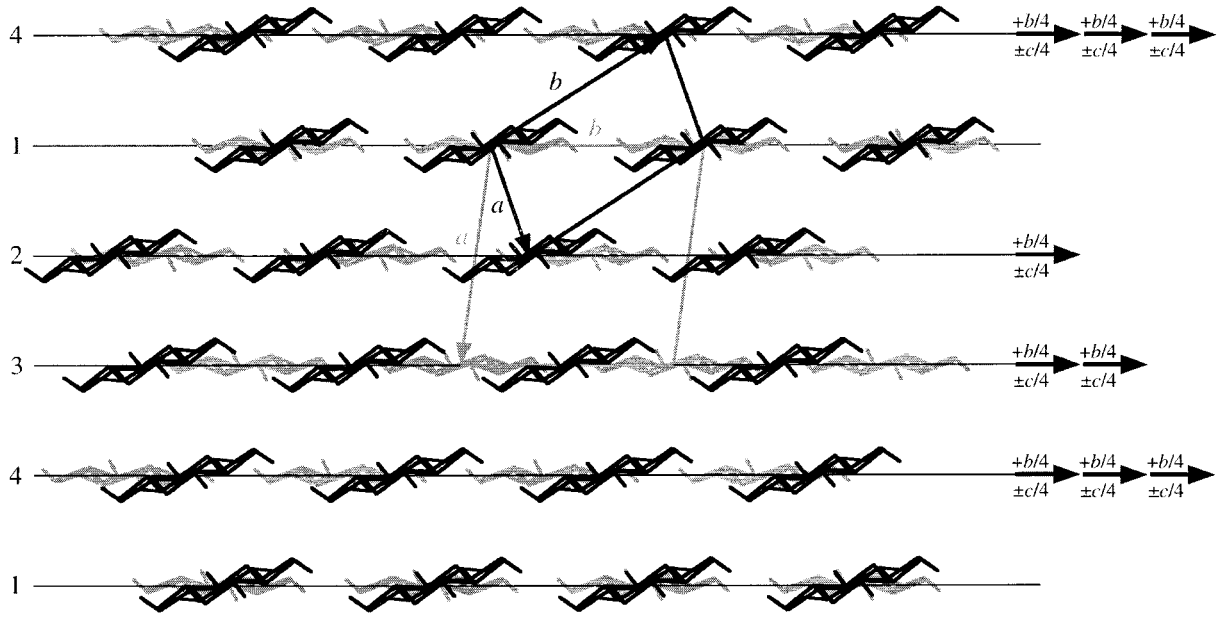

Figure 5. Schematic representation of the crystalline transformation from cellulose III_I to I_β. The black and gray lines represent the *ab* projection (*c*-axis projection) of the unit cell and cellulose chains of cellulose III_I and I_β at 217 °C, respectively. The hydrogen-bonded cellulose molecular sheets (1, 2, 3, and 4) translate $+b/4$ to the *b*-axis direction of the I_β phase and $+c/4$ progressively (or $-c/4$ progressively) to the *c*-axis direction.

profile at 217 °C was undertaken. In the fitting process, a fifth-degree polynomial function for a background profile was used, a pseudo-Voigt function for each crystalline reflection,[24] and the Levenberg−Marquardt algorithm applied. The *d*-spacings of each reflection were $d010$ III_I (1) = 0.752 nm, $d100$ III_I/$d1\bar{1}0$ III_I (2) = 0.433 nm, $d110$ III_I (3) = 0.342 nm, $d1\bar{1}0$ I_β (4) = 0.617 nm, $d110$ I_β (5) = 0.538 nm, and $d200$ I_β (6) = 0.413 nm. From these *d*-spacings, the unit cell parameters were determined for the *a*- and *b*-axes and monoclinic angle γ for the two phases at 217 °C: $a = 0.453$ nm, $b = 0.782$ nm, and $\gamma = 105.8°$ for cellulose III_I and $a = 0.833$ nm, $b = 0.805$ nm, and $\gamma = 97.8°$ for cellulose I_β.

Figure 5 shows the arrangement of molecular chains (*c*-axis projection) and unit cells in the *ab* plane of cellulose III_I and I_β at 217 °C. The distance between cellulose chains in a hydrogen-bonded sheet, corresponding to the length of the *b*-axis of cellulose I_β, is almost the same for the two phases. Furthermore, both crystalline phases have similar intersheet distances; precisely the *d*-spacing (200) of the I_β phase is a 4.3% smaller than that of the *d*-spacing (1$\bar{1}$0) of III_I phase. These results suggest the following transformation mechanism. Consider the four types of sheet numbered as 1, 2, 3, and 4 in Figure 5. In the first step of transformation, sheet 1 does not move, but sheets 2, 3, and 4 translate $+b/4$ in the *b*-axis direction of the I_β phase. In the next step, sheets 1 and 2 do not move and sheets 3 and 4 translate together $+b/4$. Finally, only sheet 4 translates $+b/4$. When the sheets translate $+b/4$ to the *b*-axis direction, they also have to translate $+c/4$ or $-c/4$ in the *c*-axis direction. Because the sheets of cellulose I_β are staggered by $c/4$ relative to one another, those of cellulose III_I are not staggered because of the displacement of the one-chain unit cell.[20] For the transformation, all molecular chains also have to rotate approximately 15° about their chain axis, as shown in Figure 5. Cellulose III_I probably transforms into cellulose I_β while keeping the sheet structure constant.

The model proposed here was for the case of perfect transformation occurring. In fact, however, cellulose III_I transforms into I_β with reducing crystallite size. This was easily recognized from the broadness of the equatorial peak width of converted cellulose I_β compared with cellulose III_I (Figure 4). It has been reported that when cellulose III_I microcrystals prepared from *Valonia* undergo a transition to cellulose I_β in hot water, the crystals become subfibrillated into subelements 3−5 nm wide.[13,14] Decrease of crystallite size by the transformation is caused by the fibrillation of microcrystals. Why does the fibrillation occur? One suggestion is that, during the phase translation, a large number of defects are created between the cellulosic sheets due to imperfection of the intersheet sheet translation. Thus, the defects between the sheets might be the beginning of the microcrystalline fibrillation.

Conclusions

Cellulose III_I can be transformed into cellulose I_β by heating above 200 °C without water. With increasing temperature, thermal vibration of the cellulose molecule becomes more active with thermal expansion of the lattice occurs. Breakage of hydrogen bonds may occur at about 200 °C, which could be the trigger for the crystalline phase transformation into cellulose I_β. At the phase transformation temperature, the intrasheeet and intersheet interchain distances is almost the same for both phases. Therefore, an intersheet translation mechanism, in which the sheet structure is retained, is proposed for the phase transformation of cellulose III_I to cellulose I_β.

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