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Mechanism of mercerization revealed by X-ray diffraction

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Abstract We studied the crystalline conversion of cellulose fiber from cellulose I to cellulose II (mercerization) by X-ray diffraction, focusing on the putative chain-polarity conversion from parallel to antiparallel. The structural change of Na-cellulose was examined during stepwise changes in NaOH concentration. Either Na-cellulose I or Na-cellulose II was formed depending on the initial NaOH concentration. Once formed, both structures were stable and did not inter-convert to each other when the NaOH concentration was changed. Such stability indicates that the parallel-to-antiparallel conversion is not likely to take place in the crystalline region of Na-cellulose. Regeneration of cellulose II from both forms of alkali cellulose proceeded with the formation of 0.44 nm lattice plane corresponding to the sheet of $(1\ \bar{1}\ 0)$ plane of cellulose II, showing that the molecular stacking due to van der Waals' interaction is the driving force of the formation of cellulose II. A mechanism was proposed whereby the geometry of the cellulose molecule allows close fitting of the hydrophobic faces only in the antiparallel arrangement, thus driving formation of the antiparallel structure of cellulose II.

Key words Cellulose · Mercerization · Crystal structure · Alkali-cellulose · X-ray diffraction

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Introduction

The mechanism of mercerization has long been studied in relation to the basic structure of cellulose I and cellulose II. The constrained least-square refinements against X-ray diffraction data during the 1970s resulted in a parallel structure for cellulose I and an antiparallel structure for cellulose II,[1,2] but not everyone accepted these models as conclusive. In support of the "parallel cellulose I–antiparallel cellulose II" scheme, Okano and Sarko[3] proposed an interdigitation scheme: mingling of chains between microfibrils with opposite polarities. Meanwhile, Hayashi et al.,[4] Atalla,[5] and Fink and Philipp[6] placed more importance on conformation change as the basic nature of mercerization.

Since then, the parallel structure of cellulose I was established by electron microscopy[7] together with the one-chain unit cell in a particular type of cellulose I.[8] Afterward, even the direction of synthesis was elucidated.[9] For cellulose II, studies on a single crystal of cellotetraose[10–12] and a neutron fiber diffraction study[13] gave a model that has antiparallel arrangement and different conformations for the two chains. Thus, the basic structures of cellulose I and cellulose II seem to be settled now, although some skepticism persists because the mechanism of cellulose I–cellulose II conversion has not been clarified. For example, some recent computer simulation studies were in favor of a parallel structure of mercerized cellulose II.[14,15] The mercerization process, however, involves interaction with alkali and water molecules that are not considered in simulations. To understand the mechanism of mercerization, we need more detailed knowledge on the nature of the alkali-swollen state of cellulose.

Okano and Sarko suggested that the irreversible step of mercerization took place at the stage of Na-cellulose I formation.[3] However, Hayashi et al.[4] demonstrated that the alkali cellulose complex of Na-cellulose I-type unit cell could be categorized into two types: Na-cellulose I_I (which regenerates into cellulose I) and Na-cellulose I_{II} (which regenerates into cellulose II). This phenomenon was interpreted as showing the possibility that a certain confor-

Table 1. Summary of the experiments

Experiment	Initial moistening	NaOH concentration	Temperature	Observation
1	Yes	8 N (Figs. 1, 2)	20°C	Na-cellulose I
2	Yes	5 N → 0 N	20°C	Na-cellulose I
3	Yes	3 N → 0 N (Figs. 4, 5)	0°C	Regeneration from Na-cellulose I
4	Yes	3 N	25 → 0°C	Cellulose I + Na-cell I → Na-cellulose I
5	No	8 N → 0 N (Fig. 3)	25°C	Regeneration from Na-cellulose II
6	No	5 N, 3 N	20°C	Na-cellulose I

mational change, without parallel-to-antiparallel rearrangment, was the cause of mercerization.[4,6] Later, Kim et al.[16,17] also observed that cellulose I could be recovered from Na-cellulose I and concluded that the polarity change took place at the stage of Na-cellulose.

In this study we examined the structural changes of alkali-swollen cellulose using X-ray diffraction. We present plausible interpretations and molecular mechanisms of the conversion.

Material and methods

Cellulose sample

Purified ramie fibers donated by Teikoku Boseki Co. were used. A bundle of 100–200 single fibers was used for the experiments outlined in Table 1.

X-ray diffraction

The Na-cellulose samples were prepared in a Teflon specimen holder that can be fitted to the X-ray camera. The fiber bundle was sandwiched between a pair of thin polyethylene films and placed vertical in the sample holder. The specimen was kept vertical by hanging a 2-g weight at the lower end. This condition can be considered slack mercerization, as the weight does not prevent shrinkage of the fiber on swelling. A small silicone tube was inserted between the films to supply NaOH solution by a peristaltic pump. In most cases the sample was first wetted with water for facilitating penetration of the alkali solution into the fibers (preliminary moistening). The NaOH swelling behavior was examined at room temperature and at 0°C; the latter condition was provided by cooling the specimen chamber by cold nitrogen flow.

Nickel-filtered Cu kα from a Rigaku 200 rotating anode X-ray generator was used. The generator was operated at 50 kV and 100 mA. The beam was collimated by two pinholes of 0.3 mm diameter. Diffraction patterns were recorded on an imaging plate, BAS UR (Fuji Film), with an exposure time of 5–10 min. Digitized data of the diffraction image at 50 μm resolution was obtained by a Rigaku RAXIS IID imaging plate reader. Equatorial profiles were obtained from the two-dimensional data by accumulating the gray value over an arc of 10° in a fan-shaped area.

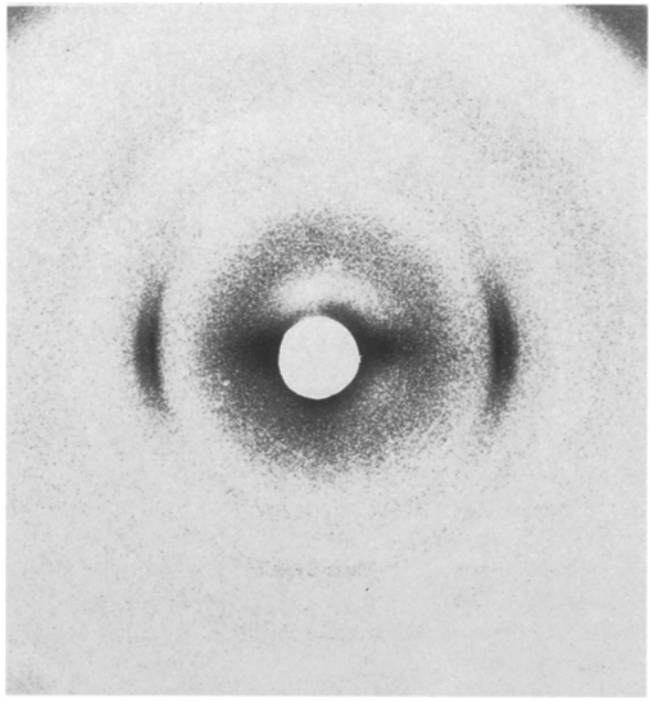

Fig. 1. X-ray diffraction pattern of Na-cellulose I formed after 80 min in 8 N NaOH, with preliminary moistening. The halo background was removed

Subtraction of the background

To enhance the contrast of the crystalline reflection, background scattering resulting from the liquid was removed by an algorithm of Sonneveld and Visser[18] extended to two dimensions. Sampling points were chosen for every 15–30 points. When the value exceeded the mean value of its two neighboring points, it was replaced by the mean. These values were then interpolated by a bicubic spline curve. The sampling and interpolation was done in polar coordinates.

Results

Figure 1 shows the X-ray diffraction diagram of Na-cellulose prepared by treating the moistened ramie fiber with 8 N NaOH at room temperature with preliminary moistening. The diagram is that of well-defined Na-

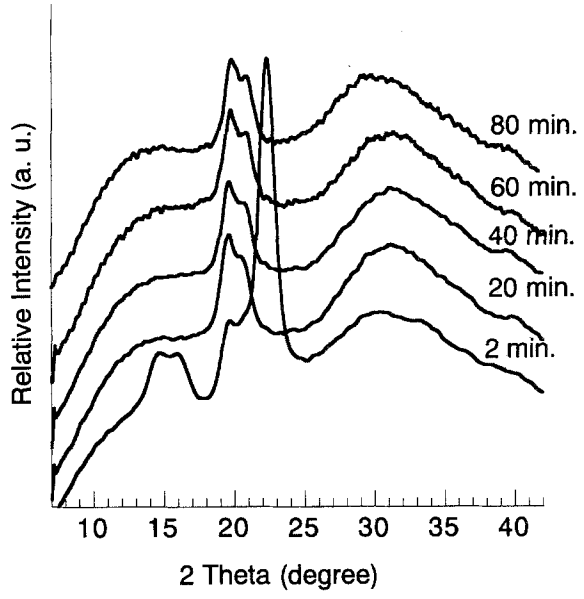

Fig. 2. Time course change of the equatorial profile of ramie fibers swollen with 8 N aqueous NaOH (0–80 min after swelling)

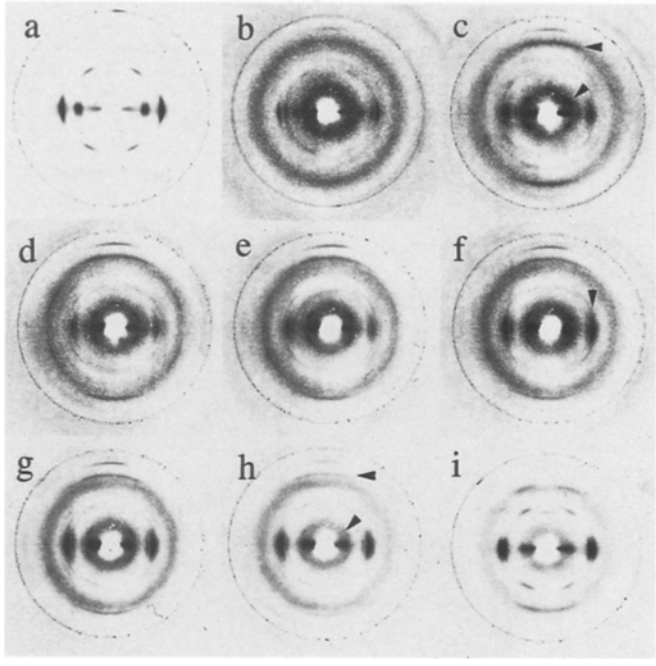

Fig. 3. Formation of Na-cellulose II and regeneration into cellulose II. Ramie fibers were swollen with 8 N aqueous NaOH without preliminary moistening. Then the surrounding liquid was diluted stepwise toward regeneration. **a** Dry. **b** 10 min in 8 N. **c** 40 min in 8 N. **d** 12 h in 3 N. **e** 2.5 N. **f** 2 N. **g** 1.5 N. **h** 0.5 N. **i** 0 N. Na-cellulose II was gradually converted to cellulose II, without forming Na-cellulose I (**b**, **c**). Equatorial reflection corresponding to 4.4 Å becomes strong at about 1.5 N (**f**, *arrowhead*)

cellulose I showing a broad inner spot and a doublet on the equator, corresponding to 1.26, 0.43, and 0.45 nm respectively. Figure 2 shows the time course change in equatorial profile. The pattern of the original cellulose I disappeared completely during the first 20 min. The pattern did not change for the following 60 min, as shown in Fig. 2, and remained the same after 2 days at 80°C (data not shown).

On the other hand, a typical Na-cellulose II pattern was obtained after 40 min of treatment of the same specimen with 8 N NaOH (Fig. 3c) without preliminary moistening. Na-cellulose II is characterized by the 1.5 nm fiber repeat, with strong reflections in the first and fifth layer lines (arrowheads, Fig. 3c). Once Na-cellulose II formed, it did not convert to Na-cellulose I by changing the immersing solution to 3 N NaOH (Fig. 3d); however, the Na-cellulose II pattern after going to 3 N NaOH was sharper than at 8 N NaOH. Figures 3e–h show that the stepwise decrease in NaOH concentration from 3 N to 1.5 N did not affect the basic structure of Na-cellulose II (note the 1.5 nm layer lines marked by arrowheads in Fig. 3h). The dilution resulted in a gradual increase in intensity of the equatorial reflection at 0.44 nm (arrowhead, Fig. 3f). Finally the exchange of 0.5 N NaOH with water (Fig. 3h, i) resulted in disappearance of the 1.5 nm repeats and the formation of cellulose II.

The treatment of cellulose with 3–5 N NaOH, with or without preliminary moistening, resulted in the formation of Na-cellulose I. The 3 N NaOH is a critical concentration and resulted in a mixture of cellulose I and Na-cellulose I at room temperature. This sample was completely converted to Na-cellulose I by cooling to 0°C. Figure 4 shows the diffraction pattern of Na-cellulose I formed by 3 N NaOH at 0°C (Fig. 4a) and the subsequent change caused by a stepwise decrease in NaOH concentration at 0°C. Figure 5

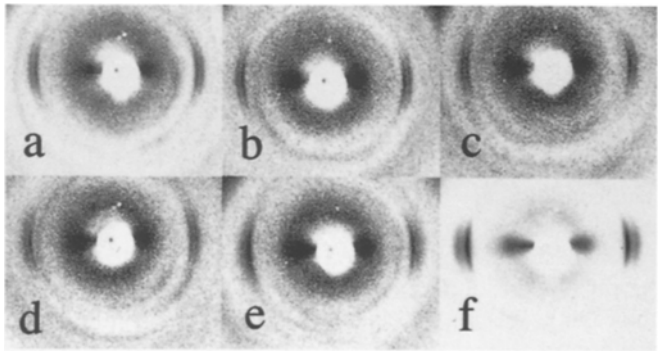

Fig. 4. X-ray diffraction patterns during regeneration from Na-cellulose I. The NaOH solution was diluted stepwise from 3 N to 0 N at 0°C. **a–f** 3 N, 2 N, 1.5 N, 1.0 N, 0.5 N, 0 N

shows the corresponding equatorial profiles. No change can be seen between 3.0 N and 1.0 N NaOH (Fig. 5a–d). At 0.5 N NaOH, the 0.43 nm reflection becomes weak (Fig. 5e). The same behavior was observed with Na-cellulose I samples prepared by an initial concentration of 5 N or 8 N NaOH, at 0°C or 25°C. The only difference between the processes at 0°C and 25°C was that the change in the 1.0 N to 0.5 N NaOH dilution at 0°C occurred in the 1.5 N to 1.0 N NaOH dilution at 25°C.

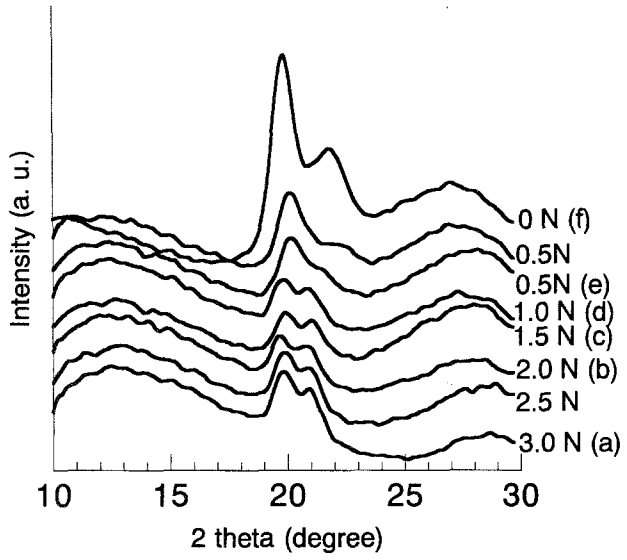

Fig. 5. Equatorial profiles corresponding to Fig. 4

Discussion

Earlier studies indicated the existence of many types of alkali cellulose based on the alkali concentration, temperature, and subsequent treatments; but the most important forms are Na-cellulose I and Na-cellulose II. Na-cellulose I is usually formed by 3–5 N NaOH at room temperature; Na-cellulose II is formed by more than 7 N NaOH at higher temperatures (60–100°C).[19] Our results showed that the type of Na-cellulose formed by 8 N NaOH treatment is affected by whether the cellulose sample is moistened with water before aqueous NaOH treatment. That the moistened sample gave Na-cellulose I and the dry sample gave Na-cellulose II, both by 8 N NaOH treatment, is considered to be the result of dilution of the solution by water in the specimen. When Na-cellulose I is formed from a moistened sample, subsequent complete immersion with 8 N solution did not cause conversion of Na-cellulose I to Na-cellulose II. Also Na-cellulose II, once formed, could not be converted to Na-cellulose I by changing the surrounding solution from 8 N to 5 N or 3 N.

These observations show that the formation of Na-cellulose is a history-dependent phenomenon and involves a rather immobile state of cellulose molecules. Therefore we here conclude that if mercerization involves rearrangements of cellulose molecules leading to interdigitation such movements are not likely to take place in the crystalline part of alkali cellulose. Such a dynamic process should take place (1) on the formation of Na-cellulose, (2) on regeneration from Na-cellulose, or (3) in the amorphous or solution-like region of Na-cellulose, depending on the condition of swelling (e.g., the tension or lateral compression applied).

Hayashi et al.[4] and later Kim et al.[16,17] demonstrated that Na-cellulose I partly reverts to cellulose I when washed at high temperature, and that the amount of recovered cellulose I decreased during aging as Na-cellulose I. This effect of aging implies that case (2) above is the most likely situation for the conditions employed by these authors.

On the other hand Yokota et al.[20] concluded that Na-cellulose is composed of crystalline regions only, based on the observation of narrow peaks of ^{13}C solid-state nuclear magnetic resonance (NMR) spectra and X-ray diffraction. This seems to contradict our understanding, but attention should be paid to the condition of the sample. Our result shows that even in an excess of solution the gel-like sample contains a crystalline region that is not readily affected by ambient condition. Yokota et al.[20] observed two components for the spin-lattice relaxation time (T_1) of Na-cellulose, typically 1.5 s and 5.5 s. We can tentatively interpret that finding as the faster component being from the paracrystalline region, which is stable only in the absence of excess solution.

The regeneration from Na-cellulose I into cellulose I is possible only under specific conditions (i.e., when swelling of cellulose is restricted and when the sample is washed at high temperatures). Even if the critical step of interdigitation had not taken place in Na-cellulose I, washing at low temperature results in regeneration to cellulose II.

We could clearly observe the mode of lattice plane formation in this process. When the ambient solution was diluted stepwise, regeneration of cellulose from both Na-cellulose I (Fig. 4) and Na-cellulose II (Fig. 3) starts with growing intensity of equatorial reflection of 0.44 nm spacing. This spacing is close to that of the (1 1 0) plane of cellulose II, which represents stacking of pyranose rings by van der Waals' interaction.

This behavior strongly suggests that the hydrophobic interaction is the driving force in formation of the cellulose II crystal. The importance of van der Waals' interaction has been noted in many instances related to cellulose complexe.[21,22] The crystal growth driven by hydrophobic stacking is also observed during the growth of low-DP (degree of polymerization) cellulose crystals,[23,24] and should be a general phenomenon in the regeneration of cellulose from aqueous media.

Now we consider why the antiparallel arrangement is necessary during cellulose II formation based on molecular geometry. The stable conformation of glucopyranoside is characterized by three equatorial hydroxyl/methylol groups and five axial C—H groups. These C—H groups form three and two bumps on the top and the bottom faces of the pyranose ring, respectively. These faces appear alternately on one side of the extended cellulose molecule (two-fold helix). Figure 6a shows the projection of a pair of antiparallel chains in the established structure of the cellotetraose crystal,[10] which is generally accepted as a low-molecular-weight analogue of cellulose II. It can be seen that the two chains are closely overlapping. To see the effect of the gross structure, we took the coordinate from the cellulose II model of Langan et al.[13] and emphasized the C—H bumps (Fig. 6b) in Fig. 7a. The bumps on the top face of the lower molecule are shown as black circles and those on the bottom face of the upper molecule as gray circles. The two molecules have identical conformation.

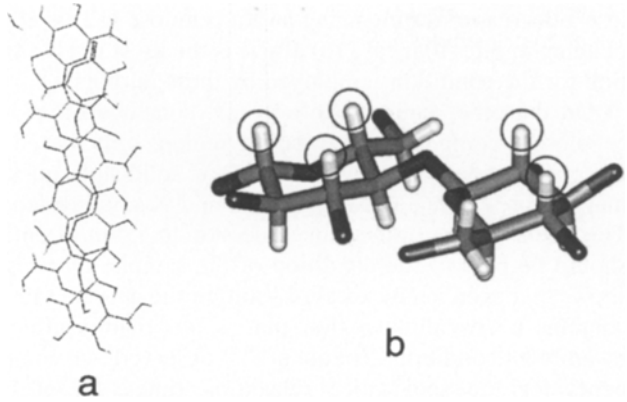

Fig. 6. **a** Projection of a stacked pair of cellotetraose molecules. **b** Perspective view of a cellobiose unit. Hydrogen atoms stretching out from pyranose rings are marked with *circles*

We then superposed these molecules, keeping the "quarter-staggered" relative position, trying to avoid close contacts of the black and gray circles. Figure 7b shows stacking of the two molecules, as in Fig. 6a. If we allow longitudinal relative translation, a more favorable position is found, as shown in Fig. 7c. Before the final locking of molecules into the cellulose II crystal, this form of stacking is likely to prevail. On the other hand, the parallel (cellulose I type) superposition of the same pair of molecules (Fig. 7d) results in several close contacts between black and gray circles (arrows, Fig. 7e). Any longitudinal relative displacement to avoid these contacts results in new contacts in other positions. Thus the only way to avoid contacts during parallel stacking is lateral displacement. This results in rather poor stacking, as shown in Fig. 7f. One can see that this arrangement is similar to that of neighboring chains in (1 $\bar{1}$ 0) plane of cellulose I.

Summarizing the situation, we can conclude that the antiparallel arrangement is selected by the geometry of the cellulose molecule, when each molecule is free to choose its neighbors in polar environments. Our present observations indicate that such a condition arises during the process of regeneration from alkali cellulose, and that this stage is critical for the parallel-to-antiparallel conversion.

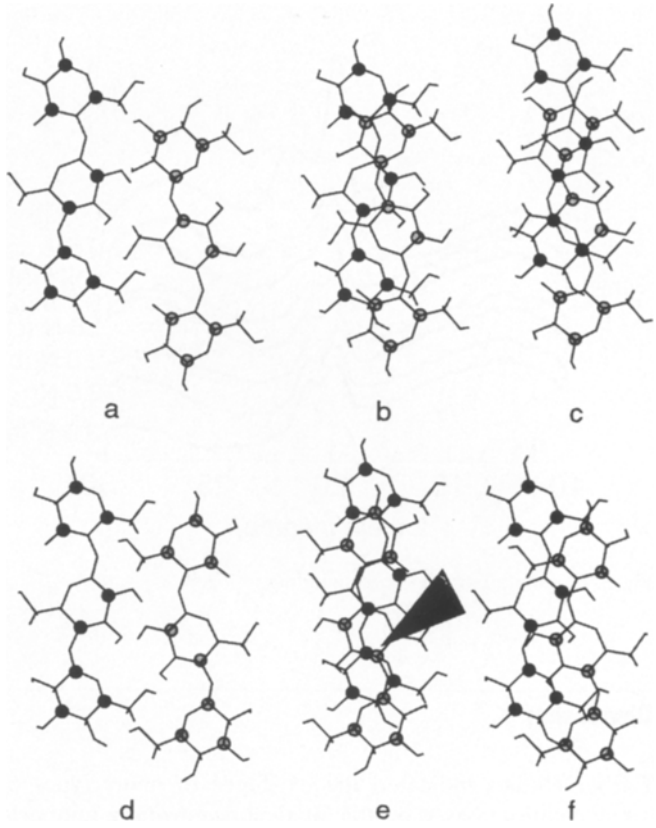

Fig. 7. C—H bumps of cellulose are shown by *circles*. *Black circles* are those of the top face of lower molecule, and *gray circles* are those of the bottom face of the upper molecule. **a** Two equivalent chains placed in antiparallel arrangement. **b** Antiparallel stacking with quarter-stagger. [It is not the same as (that in Fig. 6a) because the two molecules in cellotetraose or cellulose II have a different conformation, whereas here we used a unique type of molecule for both chains to compare with parallel case.] **c** Improved stacking by longitudinal translation. **d** Two equivalent chains placed in parallel arrangement. **e** Parallel stacking with quarter-stagger. Note the hitting (*arrow*). Any longitudinal translation causes new contacts. **f** After lateral translation to avoid contacts

Conclusions

The stability of the crystal structure of Na-cellulose I and Na-cellulose II indicates that the parallel-to-antiparallel rearrangement of cellulose chains is not likely to occur in the crystalline region of Na-cellulose. Regeneration of cellulose II from Na-cellulose proceeds by the formation of 0.44 nm period stacking via mutual attraction of hydrophobic planes. We propose that the molecular geometry of cellulose be such that the antiparallel arrangement is preferable for stacking of the hydrophobic planes, leading to the antiparallel structure after mercerization.

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