

# Mercerization of Cellulose. II. Alkali-Cellulose Intermediates and a Possible Mercerization Mechanism\*

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## Synopsis

Continued study of the five crystalline Na-celluloses, previously shown to occur as intermediates during the mercerization of cellulose and exhibiting two types of crystallographic fiber repeats, further indicates that they fall into three classes based on their unit cells and NaOH contents. In one class are Na-celluloses I and III, both containing up to 34% NaOH; in the second class are Na-celluloses IIA and IIB, marked by ca. 15 Å fiber repeat and containing up to 65% NaOH; and in the third class is Na-cellulose IV which is likely to be a hydrated form of cellulose II. Na-cellulose I was found to be the common first alkali-cellulose structure produced in the NaOH treatment of both cellulose I and cellulose II. Further study of this conversion step suggested a mercerization mechanism in which the alkali begins the conversion of cellulose to Na-cellulose I in the amorphous parts of the fiber. The conversion of the parallel-chain cellulose I structure to an antiparallel one is likely to occur already in this first step.

## INTRODUCTION

In the previous report of this series, it was shown that five crystalline alkali-celluloses (Na-celluloses) occur as intermediates during the mercerization of ramie cellulose.<sup>1</sup> The five structures could be generated reproducibly by slowing down the mercerization process, and it was shown that their interconversions followed definite paths which depended on the concentration of the alkali. Of particular interest was the observation that the conversions appeared to proceed, for the most part, through crystal-to-crystal phase transformations. Another interesting feature of the transformations was the presence of a class of Na-celluloses with a crystallographic fiber repeat of ca. 15.4 Å, suggesting a threefold helical chain conformation. The latter would be considerably at variance with the usual, 10.3 Å, twofold conformation common to all crystalline cellulose polymorphs.

Further study of the Na-cellulose structures and their interconversions was undertaken to provide information leading to the understanding of the mechanism of mercerization. Specifically, information was sought regarding the possible reversibility of some of the conversion steps, and the role of the degree of crystallinity of the starting material. Of interest was the

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question regarding the point during the mercerization process when the parallel-chain structure of cellulose I begins to transform to the antiparallel structure of cellulose II. Also of interest was how alkali treatment of cellulose II, that is, an already antiparallel chain structure, would differ from that of cellulose I.

As before, x-ray diffraction was the primary experimental method of study. In preparation for an eventual full crystal structure determination of all Na-celluloses, an accurate determination of their unit cell characteristics was needed.

## EXPERIMENTAL

**Materials.** Purified native ramie cellulose, a microcrystalline cellulose prepared from cotton, and a cellulose II obtained by mercerization of ramie cellulose were the starting materials. A commercial Fortisan cellulose II (a regenerated cellulose) was also used in some experiments. The purification of ramie cellulose has been previously described.<sup>1</sup> The microcrystalline cellulose I was prepared by subjecting commercial cotton to a hydrolytic treatment with 2*N* HCl at 100°C for 2 h. The acid was neutralized with 0.1*N* NaOH, and the cellulose was washed thoroughly with distilled water. The mercerized cellulose II starting material was prepared by treating ramie fibers with 8*N* NaOH at room temperature for several days, followed by thorough washing and air-drying.

**Mercerization and Diffraction Studies.** As previously described, all mercerizations were carried out with the starting material packed into glass capillary tubes normally used in x-ray diffraction experiments.<sup>1</sup> This was done for two reasons: (1) lateral constraining of the sample by the tube allowed slowing down the process of mercerization to a desired degree, and (2) x-ray diffraction exposures could be obtained during the entire process without disturbing the sample. The slowing down of the mercerization process was apparently caused by the swelling of the cellulose within the confined space and the consequent reduction of molecular mobility. In this, the effect of lateral compression mimicked a similar slowing down observed with fibers kept under longitudinal tension.

All x-ray diffraction diagrams were recorded in a Searle toroidal focusing camera mounted on a Rigaku RU-100 rotating anode x-ray generator, operated at 50 kV and 100 mA. Suitable diffraction diagrams were obtained under these conditions in 20 min, using Kodak SB x-ray film and a film-to-sample distance of 3 cm.

**Density Measurements.** The densities of the Na-celluloses were measured by the buoyancy method, in which the samples were weighed both in air and when submerged in an NaOH solution of known concentration. Knowing the density of the latter, the density of the sample could be calculated.

## RESULTS

**Irreversibility of Transformations.** It was previously observed that during the first transformation step in the mercerization sequence—the conversion of cellulose I to Na-cellulose I—the crystal structure of cellulose

I disappeared gradually while the crystal structure of Na-cellulose I appeared simultaneously.<sup>1</sup> The conversion did not require an apparent decrystallization of cellulose I prior to its recrystallization as Na-cellulose I, nor was there a significant amount of an amorphous phase present at any time. At all intermediate stages during this conversion step, the crystal structures of both cellulose I and Na-cellulose I were present at the same time, as illustrated by the diffraction diagram in Figure 1. (Also cf. Fig. 3 in Ref. 1). Since it is known that cellulose I possesses a parallel-chain crystal structure which is converted to an antiparallel structure at some stage during mercerization,<sup>2</sup> these observations raised a question of the chain polarity of Na-cellulose I. Short of attempting a full crystal structure analysis of the latter, this question was addressed by investigating the possibility of reversing the cellulose I to Na-cellulose I conversion. If the structure of the latter was parallel, the reversibility of the conversion should be demonstrable, as is possible for the cellulose I  $\leftrightarrow$  cellulose III<sub>1</sub> transformation. On the other hand, an antiparallel Na-cellulose I should not revert to cellulose I.

The starting material for the reversibility experiments was in all cases a partially converted cellulose I whose diffraction diagram showed the presence of both cellulose I and Na-cellulose I crystal structures. The NaOH was removed from such samples either by neutralization with HCl followed by washing in water, or by simple washing in water, or by a nonaqueous wash (with methanol). The diffraction patterns obtained after drying showed no evidence of reversion to the structure of cellulose I, even in samples containing only a very small amount of Na-cellulose I. As illustrated by

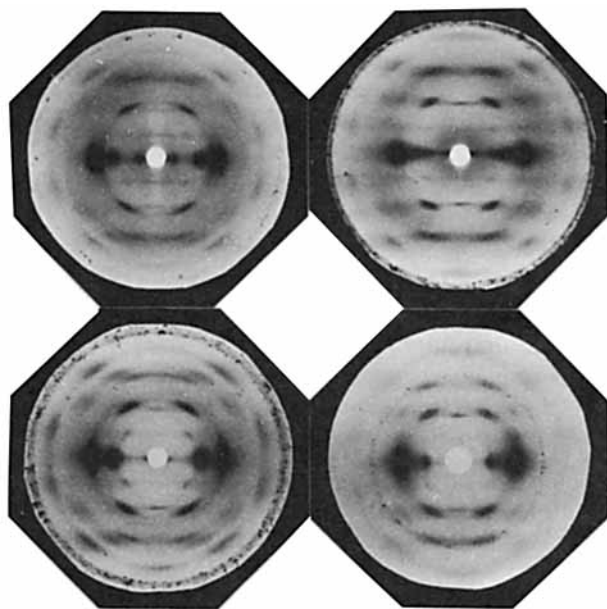


Fig. 1. X-ray fiber diffraction patterns of: (top, left to right) cellulose I + Na-cellulose I, cellulose I + cellulose II obtained from the latter mixture; (bottom, left to right) cellulose I and cellulose II, shown for comparison. Fiber axis is vertical.

the diffraction diagrams in Figure 1, a mixed cellulose I–Na-cellulose I crystal structure in roughly equal proportions gave a mixture of cellulose I and cellulose II in about the same proportions. These observations strongly suggest that Na–cellulose I is an antiparallel-chain crystal structure.

**Conversion and the Crystallinity of Cellulose I.** It is well known that highly crystalline cellulose I, such as of *Valonia*, is difficult to mercerize.<sup>3</sup> In order to determine how increased crystallinity of the starting cellulose might affect the conversion, the mercerization experiments conducted with ramie were repeated with a microcrystalline cellulose I prepared from cotton. Treatment with 3.5*N* NaOH—which easily converts ramie cellulose to Na–cellulose I in all but the most severely compressed samples—did not produce conversion of microcrystalline cellulose even after a long time, or after grinding the samples, or even after ultrasonic treatment of the cellulose (in water, prior to adding the alkali). A conversion could be effected only after ultrasonic treatment of the sample while in suspension in 8.0*N* NaOH solution. However, once formed, the Na–cellulose I from microcrystalline cellulose behaved indistinguishably from the Na–cellulose I obtained from ramie. These results suggest that either an amorphous phase in the cellulose or an imperfectly crystalline morphology are necessary for the conversion to Na–cellulose I to begin.

**Na–Cellulose Formation from Cellulose II.** The irreversibility of cellulose I to Na–cellulose I transformation, which had suggested that the latter structure is antiparallel, also suggested that cellulose II should be converted by alkali to Na–cellulose I. The results obtained with microcrystalline cellulose had further suggested that such conversion should proceed easily, in view of the generally lower degree of crystallinity of cellulose II as compared with cellulose I. Both a mercerized cellulose II (from ramie) and a regenerated cellulose II (Fortisan) were consequently treated with NaOH, in the same laterally constrained manner and with the same alkali concentrations as had previously been used with ramie cellulose I. As expected, the same Na–celluloses were obtained, i.e., the first stage was Na–cellulose I, followed by other Na–celluloses shown in the sequence in Fig. 4 of Ref. 1. The only significant differences between the results obtained with cellulose I and cellulose II were in the rates of conversion to Na–cellulose I, and in the treatment conditions necessary to produce the conversion. For example, in the case of ramie cellulose I the formation of Na–cellulose I with 3.5*N* NaOH could be entirely prevented by the use of sufficiently high lateral compression of the fibers. Cellulose II, however, under the same conditions always converted to Na–cellulose I in less than 1 h, and the conversion with this NaOH concentration could not be prevented under any circumstances. Lower concentrations of NaOH, including those that were ineffective in converting cellulose I, were effective in producing conversion of cellulose II. The subsequent transformations of Na–cellulose I to other Na–celluloses proceeded exactly as with Na–cellulose I obtained from cellulose I, without any differences with regard to either the degree of lateral compression of the fibers or the concentration of the alkali.

These results clearly support the view that Na–cellulose I may be the common first alkali–cellulose produced by the action of NaOH on any cel-

lulose. Furthermore, these results agree with the conclusion that the conversion to Na-cellulose I proceeds much more easily with celluloses of a lower degree of crystallinity. It is also probable that in the case of cellulose II its antiparallel crystal structure further facilitates the conversion to an antiparallel Na-cellulose I.

**Preliminary Crystallographic Characteristics of Na-Celluloses.** The x-ray fiber diagrams of all five Na-celluloses (cf. Fig. 2 in Ref. 1) indicate a varying degree of crystallinity among the different structures, but a high degree of fibrous orientation. As a consequence, the unit cell parameters of most structures could be readily determined and are shown in Table I. (However, at this stage, these unit cells should still be considered preliminary because parameters may change during the course of a full structure refinement).

The NaOH contents of the unit cells, also shown in Table I, are based on density measurements and should be considered approximate. In addition, there may be undetermined amounts of water present in the unit cells. The exact number of NaOH and water molecules in the unit cell may be determined only after a full crystallographic structure analysis has been completed. Nonetheless, the indicated approximate NaOH contents serve to compare the relative polysaccharide densities of the crystal structures.

Based on the structural characteristics shown in Table I, it is clear that the five Na-celluloses, although showing two types of probable chain conformations, fall into three distinct classes. In the first class are Na-celluloses I and III, both having similar unit cells, same approximate NaOH contents, and, most likely, the same ca. 10 Å, twofold helical chain conformation possessed by all cellulose polymorphs. The unit cells are large, containing six chains in both cases. The similarity of the unit cell parameters suggests that only minor changes in the crystalline packing occur during the Na-cellulose I to Na-cellulose III transformation. This is consistent with the observation that the latter structure can only be obtained by drying the former.<sup>1</sup>

The second class of structures is comprised of Na-celluloses IIA and IIB whose unit cells are considerably different from those of any known cellulose polymorphs, as well as other Na-celluloses. The main difference resides in the fiber repeat of the two structures—at approximately 15 Å about 50% larger than the normal cellulose fiber repeat. Because the maximum ex-

TABLE I  
Probable Crystallographic Properties of Na-Celluloses

Na-cellulose	Unit Cell Parameters				Number of chains in unit cell	Density (g/cc)	% NaOH in unit cell <sup>a</sup>
	<i>a</i>	<i>b</i> (Å)	<i>c</i>	$\gamma$ (deg)			
I	11.70	25.70	10.12	94	6	1.8	33
IIA	12.9	10.5	15.48	112	2	—	—
IIB	14.94	14.94	15.39	120	2	1.4	65
III	12.54	26.40	10.28	115	6	1.8	34
IV	9.88	9.65	10.28	126	2	1.5	0

<sup>a</sup> Maximum content, assuming no additional water present in the cell.

tension of a  $\beta$ -1,4-linked D-glucose residue is of the order of 5.5 Å, the ca. 15 Å fiber repeat clearly points to a threefold helical chain conformation. As shown in Figure 2, both left- and right-handed threefold conformations are possible, not differing a great deal from one another. However, a comparison with a twofold chain conformation (cf. Fig. 2) suggests considerable differences in the crystalline packing of the two types of conformations. The maximum NaOH contents of the Na-cellulose IIA and IIB unit cells is also (probably) considerably higher than that of the Na-cellulose structures in the previous class. This difference, along with the threefold chain conformation, suggests that the structures of Na-celluloses IIA and IIB are determined more by interactions between NaOH and the cellulose molecules, rather than by interactions between the latter.

Finally, in the third class is the structure of Na-cellulose IV. Its unit cell resembles that of cellulose II into which it is converted simply by drying. This observation, coupled with the fact that Na-cellulose IV can only be obtained by washing Na-celluloses IIA, IIB, and III, strongly suggests that Na-cellulose contains no NaOH and that it is a hydrated, unstable form of cellulose II. In fact, there are indications that even before drying and during prolonged washing the unit cell parameters of Na-cellulose IV slowly change toward cellulose II and that, during this change, the structure is becoming more crystalline. Therefore, it is likely that the hydration is not permanent and that the hydrated crystal structure possesses a higher energy in comparison with cellulose II.

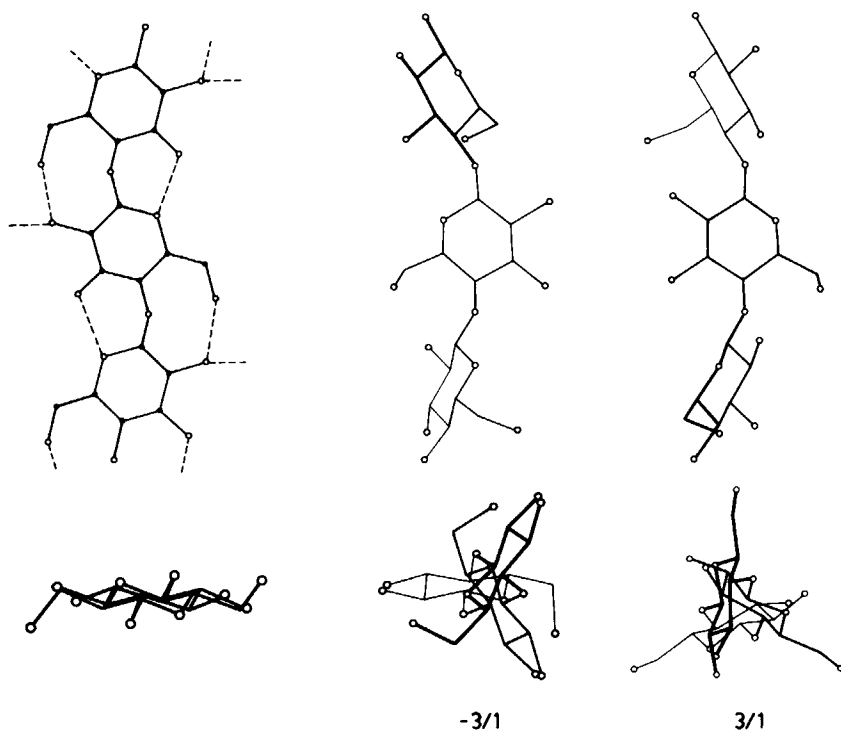


Fig. 2. (Left) Twofold helical cellulose chain conformation, in two projections. (Center and right) Probable threefold chain conformations of Na-cellulose IIB, in two projections. Both left-handed ( $-3/1$ ) and right-handed ( $3/1$ ) conformations are shown.

## DISCUSSION

The combined observations of the irreversibility of the cellulose I to Na-cellulose I conversion, the Na-cellulose I as the common first intermediate in the conversion of both cellulose I and cellulose II to alkali-cellulose, the difficulty of converting the more crystalline celluloses, and the apparently crystalline phase transformation during the first step of conversion, all suggest the mechanism of mercerization illustrated in Figure 3. In the first step, the alkali solution readily enters the amorphous regions that exist as the interface regions between the crystallites. Because a normal fiber of ramie cellulose is composed of a large number of crystallites less than 100 Å in diameter in which the chain directions are parallel but which are distributed along the fiber axis with equal probability for "up" and "down" directions—as is illustrated in Figure 4—the amorphous interface regions contain chains arranged along both directions. The NaOH solution entering such regions can thus cause the formation of an antiparallel Na-cellulose I with very little movement of the segments of chains and, initially, very little effect on the crystalline regions. Because the alkali generally swells the cellulose that it enters, chain segment mobility within the swollen regions is expected to be sufficiently high. In a normally completely antiparallel cellulose, such as cellulose II, the formation of Na-cellulose I can be expected to proceed with increased ease. In the native, parallel cellulose, as the formation of Na-cellulose I proceeds, the energetic and entropic factors probably favor the formation of the latter structure; thus the crystalline regions of cellulose I gradually diminish in size while the crystallites of Na-cellulose I increase. This process is likely to proceed through the removal, by the action of the alkali, of individual chains from the surface of cellulose I crystallites and their incorporation onto the surface of Na-cellulose I crystallites. The chain conformation in Na-cellulose I is probably close to a twofold one because of the constraints exerted by such a conformation in the adjacent unconverted cellulose I (or II) crystallites. When the first conversion step is completed, and all constraints due to the unconverted crystalline cellulose phase have been removed, Na-cellulose I is free to absorb more NaOH and, in the process, convert to a crystal structure based on a threefold helical chain conformation and one in which all contacts between adjacent chains in the unit cell are removed. The resulting structure—Na-cellulose IIA or IIB—is probably the lowest energy alkali-cellulose intermediate that occurs during the mercerization process. It is stable both when in contact with the NaOH solution and when dried. (The Na-cellulose IIB structure is probably the more stable of the two as it forms when the fibers are under the least amount of lateral constraint<sup>1</sup>).

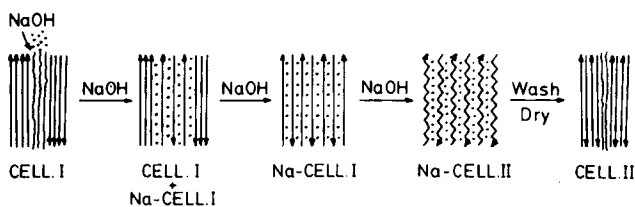


Fig. 3. Possible mechanism of mercerization. (Chain directions are indicated by arrows.)

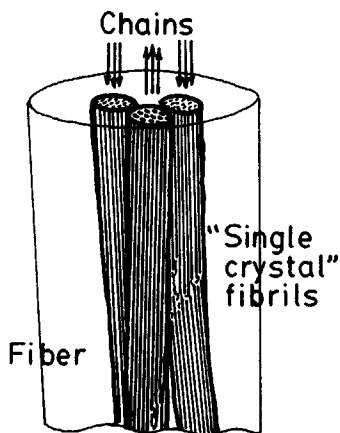


Fig. 4. Random up-down arrangement of parallel-chain crystallites in the fiber.

Finally, after the NaOH has been washed out of the structure, the cellulose chains again revert to a twofold helical conformation which represents a lower energy structure in the absence of NaOH, and the structure crystallizes in the lowest-energy, cellulose II polymorphic form. This process is temporarily interrupted by the presence of water, in the form of Na-cellulose IV; however, the water molecules leave the structure spontaneously as hydrogen bonds between the chains are reestablished.

The above mechanism agrees with the observations of both the retarding effect of high crystallinity (microcrystalline cellulose, *Valonia* cellulose) and the difficulties of mercerizing wood.<sup>4</sup> In the latter, lignin is present within the fiber, presumably restricting the motion of cellulose chains, hindering the access of NaOH, and generally altering the nature of the interfacial, amorphous regions between the crystallites. Under such conditions, the first conversion step in the mercerization process would understandably be more difficult.

In order to test the validity of the proposed mechanism, further characterization of both the crystal structures of various Na-celluloses and the morphology of the cellulose fibers are necessary. Of particular value would be a better understanding of the amorphous regions of cellulose. Some of the characterization studies are in progress, and will be reported on in due course.

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