Mercerization of Cellulose. III. Changes in Crystallite Sizes*

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Synopsis

When cellulose is mercerized slowly, the initial conversion is from the cellulose I crystal structure to that of Na-cellulose I. The conversion is a crystal-to-crystal phase transformation, without passage through an amorphous state. The analysis of crystallite sizes of cellulose I and Na-cellulose I during this transformation has shown that the process takes place in two steps. The first is a rapid step, occurring in approximately 1/7 (or less) of the total conversion time, resulting in a conversion ratio of ca. 65%. The measured crystallite sizes of both cellulose I and Na-cellulose I remain constant during this stage, at ~ 62 and ~ 35 Å, respectively. In the following slow step, complete conversion to Na-cellulose I takes place, and the crystallite size of cellulose I decreases steadily until disappearance. The crystallite size of Na-cellulose I increases steadily at the same time, to a final value of ~ 50 Å. Simultaneously, the unit cell parameters of cellulose I change significantly. The observation of a two-step conversion is consistent with a proposed mercerization mechanism in which the conversion is assumed to begin in the amorphous phase of the cellulose fiber.

INTRODUCTION

The well-known process of alkali mercerization of cellulose results in an irreversible change of the native cellulose I crystal structure to that of cellulose II. In this process, alkali penetrates the cellulose fiber, swells it, and in some fashion causes a change of a parallel-chain crystal structure (cellulose I) to an antiparallel one (cellulose II). This can occur without a remarkable change in the outward appearance or morphology of the fiber. Although the crystal structures of both cellulose I and cellulose II are known in reasonable detail from X-ray structure analyses[1-5] and the difference in their chain polarity has been established, little information is available concerning the mechanism of the transformations that occur during mercerization.

In previous studies of this series it was shown that during a controlled mercerization of cellulose I, a series of crystalline alkali-celluloses (Na-celluloses) could be observed.[6,7] A total of five Na-cellulose structures were reproducibly obtained, and a well-defined transformation scheme was shown to exist. The first structure in this series—Na-cellulose I—was shown to be the first crystal structure that formed as a result of treating either cellulose I

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or cellulose II with NaOH. Several interesting features of this transformation were observed. For example, the formation of Na–cellulose I was generally facilitated by a lower crystallinity of the original cellulose. In the case of cellulose II, which is considerably less crystalline compared with cellulose I, the formation of Na–cellulose I was both more rapid and occurred at a lower alkali concentration than with cellulose I. Conversely, microcrystalline cellulose I could not be converted to Na–cellulose I without resorting to ultrasonication. Another observation was that the cellulose I to Na–cellulose I transformation appeared to be a crystal-to-crystal phase transformation, occurring without an intervening amorphous phase. This is an important observation, in that it shows that decrystallization of cellulose I is not necessary prior to its conversion to Na–cellulose I. Finally, the Na–cellulose I crystal structure, once formed from cellulose I, could not be made to revert to the structure of cellulose I, and in all cases resulted in the structure of cellulose II upon removal of the alkali. This was true even when only a minor fraction of Na–cellulose I was present. In the latter cases, the result was always a mixture of the crystal structures of cellulose I and cellulose II, in approximately the same proportions as the mixture of cellulose I and Na–cellulose I prior to the removal of NaOH.

These observations suggested a mechanism in which the conversion of cellulose I begins in the amorphous or disordered phase of the cellulose fiber. Once Na–cellulose I is formed in this phase, the transformation of the crystalline structure follows.

In further study of the proposed mechanism, the crystallite sizes of cellulose I and Na–cellulose I were measured as a function of conversion time. As previously, X-ray fiber diffraction methods were used in this study.

EXPERIMENTAL

X-Ray Diffraction. Refined ramie fibers, purified as previously described, were used as the starting material.[6] Specimens for X-ray diffraction were prepared by packing bundles of parallel fibers into 1 mm diameter capillary tubes, normally used as sample containers in X-ray diffraction experiments. After adding an aqueous NaOH solution of the desired concentration, the tubes were sealed. Preparing samples in this fashion had two advantages: (1) The same sample could be observed throughout the entire conversion, and (2) the fixed volume constraint imposed by the tube on the swelling fibers slowed down the conversion process, permitting diffraction patterns to be obtained at convenient intervals. (The sample preparation procedure has previously been described in detail.[6]) A 5.5*N* NaOH solution was used in the present study. Under such conditions, complete conversion of cellulose I to Na–cellulose I took place in approximately 60 days. Na–cellulose I was converted, when necessary, to cellulose II by washing the fibers for 3 days with distilled water without removal from the capillary tube, followed by drying.

X-ray diffraction diagrams were recorded in an evacuated, flat-film camera with pin-hole collimation, using Ni-filtered CuKα radiation. The X-ray film used was CEA Reflex 25; typical exposure times at a film-to-sample distance of 5 cm and with power settings of 40 kV and 25 mA ranged from 5 to 18 h. An exact film-to-sample distance was calculated from diffraction diagrams re-

corded from specimens dusted on the outside with finely powdered NaF (principal reflection at $d = 2.319$ Å).

Crystallite Size Determination. Intensity profiles of equatorial reflections were obtained by recording the optical density of the diffractogram along the equatorial direction, using a Joyce-Loebl Recording Microdensitometer. Only diffraction patterns exposed to a suitable, approximately equal level of density were used for this purpose. The intensity profiles were digitized and resolved into individual reflection components using a least-squares, curve resolution computer program.[8] Further details of this procedure and the subsequent analysis are described in the following section.

RESULTS AND DISCUSSION

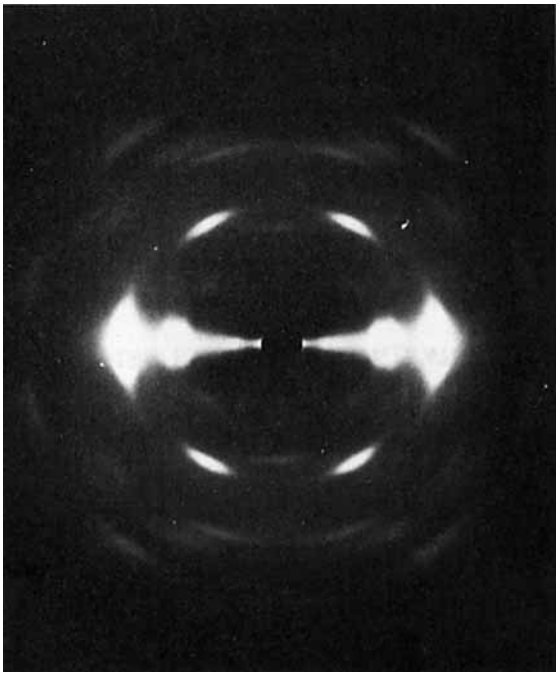
Conversion and Crystallite Size. Typical diffraction patterns of the original cellulose I, of a mixed crystal structure of cellulose I and Na–cellulose I, and of pure Na–cellulose I (i.e., after complete conversion of cellulose I), are shown in Figure 1. The microdensitometer tracings obtained from diffraction diagrams corresponding to different conversion times, complete with curve resolution results, are reproduced in Figure 2.

The resolution of tracings was performed in three different fashions, depending on the amounts of cellulose I and Na–cellulose I present. In group A were all diagrams in which the proportion of Na–cellulose I was small and that of cellulose I was large [see Fig. 2(A)]. The three reflection intensities of Na–cellulose I [reflections 1, 2, and 3, see Fig. 2(D)] were regarded as a single, broad peak, and the three cellulose I reflections ($\bar{1}10$, 110, and 200) were completely resolved. (The best resolutions were obtained with individual components having approximately equal contributions from both Gaussian and Lorentzian line shapes.) In group B were the diffractograms in which all three Na–cellulose I reflections and the three cellulose I reflections could be clearly discerned. A complete resolution into six peaks was performed in this group, as shown in Figure 2(B). Finally, in group C were all diffraction patterns in which the cellulose I contribution was small. The weak $\bar{1}10$ and 110 intensities of cellulose I were neglected and the total intensity profile was resolved into four peaks: The three Na–cellulose I reflections (1, 2, and 3) and the 200 reflection of cellulose I [cf. Fig. 2(C)]. The resolution of tracings in groups B and C was considerably facilitated by fixing the positions of the three Na–cellulose reflections on the 2θ scale. The validity of this procedure was substantiated by direct measurements of the corresponding d-spacings on the diffraction diagrams.

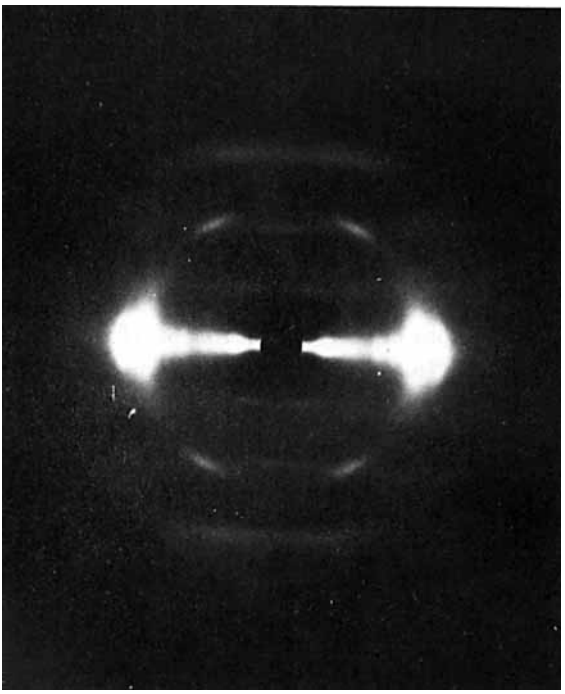
The areas under the resolved intensity components were used to calculate the conversion ratio R, defined as follows:

$$R = 1 - \frac{\int I(2\theta)_{\text{cell I}} d(2\theta)}{\int I(2\theta)_{\text{total}} d(2\theta)} \tag{1}$$

In this equation, $I(2\theta)_{\text{cell I}}$ represents the combined intensities of cellulose I reflections, and $I(2\theta)_{\text{total}}$ represents the combined intensities of all reflections

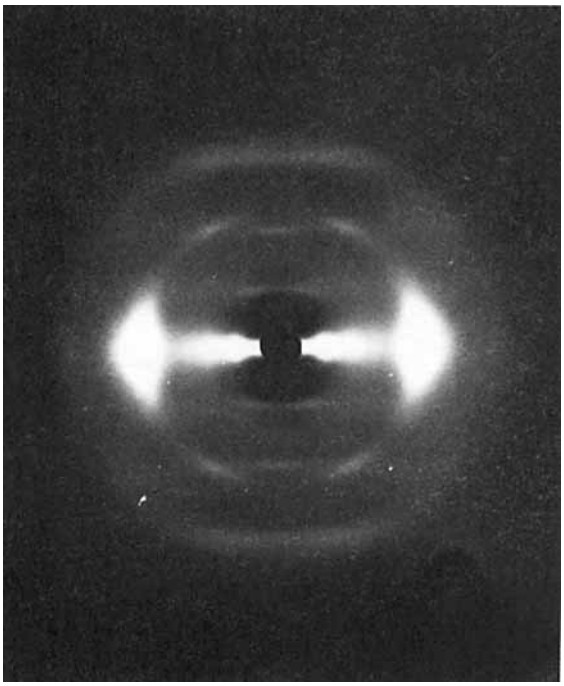


(a)



(b)

Fig. 1. X-ray fiber diffraction diagrams of: (a) cellulose I; (b) cellulose I + Na–cellulose I; (c) Na–cellulose I. Fiber axis is vertical.



(c)

Fig. 1. (*Continued from the previous page.*)

of cellulose I and Na–cellulose I. The value of R is thus a convenient index for the measure of conversion, ranging in value from 0 for pure cellulose I to 1 for pure Na–cellulose I. It should be noted that R does not measure the volume ratio of Na–cellulose I to cellulose I in the sample.

The crystallite sizes of cellulose I and Na–cellulose I were calculated from the widths of the resolved components at half-height, using the 200 reflection of cellulose I and reflection 1 of Na–cellulose I, respectively. The conventional line broadening formula was used for the calculation:

$$L(hkl) = K/dS_p \tag{2}$$

In this equation, $L(hkl)$ represents the crystallite size normal to the hkl plane, K is the Scherrer parameter, equal to 0.9 for half-width measurements, and dS_p is the pure half-width of the hkl peak in units of $S = 2\sin\theta/\lambda$. (The term "half-width" is henceforth used to denote peak width measured at half-height.) The values of dS_p were obtained from the observed half-widths dS_0 by applying the corrections for the $K\alpha_1, \alpha_2$ doublet and instrumental broadening effects. (The derivations of the corrections are shown in the Appendix.)

The results of these measurements are shown in Figures 3 and 4. The relationship between the conversion ratio R and the conversion time is shown in Figure 3, while Figure 4 shows the crystallite dimensions of both cellulose I and Na–cellulose I as a function of conversion ratio.

It is clear from Figure 3 that the conversion of cellulose I to Na–cellulose I proceeds in two stages: a rapid stage up to R of approximately 0.65 (or 65%)

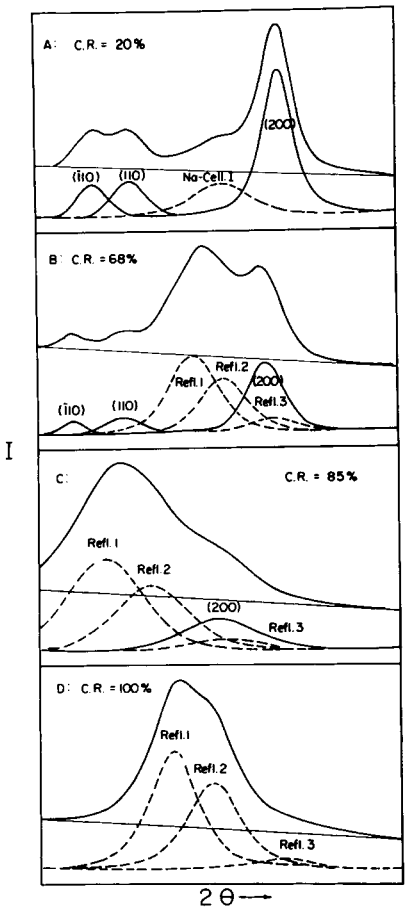


Fig. 2. Resolved equatorial intensity profiles for increasing conversion ratios: (A) 20%; (B) 68%; (C) 85%; (D) 100%. The observed intensity profiles and baselines are shown above the resolutions. The sum curves of the resolved peaks and the observed profiles coincide exactly in all cases: (—) cellulose I reflections; (- - -) Na–cellulose I reflections. (The individual 2θ scales do not coincide.)

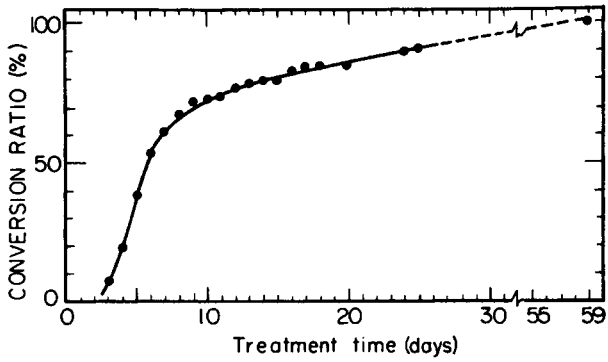


Fig. 3. Conversion ratio as a function of conversion time.

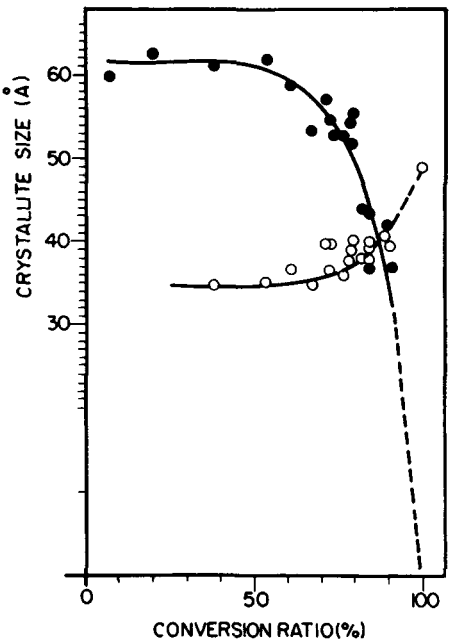


Fig. 4. Lateral crystallite dimensions of cellulose I and Na–cellulose I as a function of conversion ratio.

and a slow stage from that point to $R = 1$ (or 100%). As is evident from Figure 4, the crystallite sizes of both cellulose I and Na–cellulose I remain essentially constant during the rapid conversion stage, at ~ 62 Å for cellulose I and ~ 35 Å for Na–cellulose I. However, during the following slow conversion stage, the crystallite size of cellulose I decreases sharply with increasing R and the crystallite size of Na–cellulose I increases, although less sharply, to a value near 50 Å. These results suggest that the conversion process follows two different, consecutive mechanisms, proceeding at different rates.

During the first, rapid stage, the unvarying crystallite sizes suggest that a crystalline Na–cellulose I phase is forming predominantly in the noncrystalline regions of cellulose I. Even though our understanding of the amorphous phase of ramie cellulose is still incomplete, the degree of chain orientation in it can be assumed to be similar to that in the crystalline phase. The latter is composed of discrete crystallites whose weight-average diameter is ~ 62 Å, as indicated by the present measurements. Within these crystallites ("elementary fibrils"), the chain directions are parallel, as shown by previous crystal structure analyses.[1-3] A fiber whose diameter is ~ 20 μm, contains a large number of such elementary fibrils, divided approximately equally between "up" and "down" directions. The interfaces between discrete crystallites can be considered as the amorphous or noncrystalline regions, containing chains running in both directions. (A model based on this concept is illustrated in Figure 5.) It is within these interfacial regions, where NaOH can be expected to enter with relative ease, that the initial conversion to Na–cellulose I should occur. The rate of conversion of these regions should be relatively rapid because little crystallinity is present.

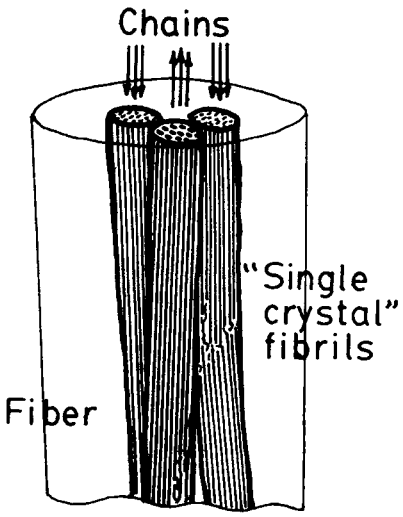


Fig. 5. Probable arrangement of elementary fibrils in a ramie fiber.

It is also possible that the smallest crystallites of cellulose I are transformed at a relatively rapid rate during the fast conversion stage. Crystallites of small diameter possess a large surface-to-volume ratio and are, therefore, much less stable than the large crystallites. It is not clear how much the small crystallites contribute to the fast conversion step, because their contribution to the weight-average size measurement is relatively small and may be difficult to discern in overall size measurements.

During the slow conversion step, a different mechanism must be in operation, as suggested by the crystallite size changes shown in Figure 4. By this time, all of the oriented amorphous regions have been converted, and the only interfaces that exist are those between the respective crystalline phases of cellulose I and Na–cellulose I. The presence of NaOH at these interfaces probably creates both entropic and energetic forces that lead to an irreversible conversion of the cellulose I crystal to that of Na–cellulose I. The simultaneous decrease in the size of the cellulose I crystallites and the increase in the size of Na–cellulose I crystallites suggests that chains from the former are deposited on the surfaces of the latter. At the same time, competition for the

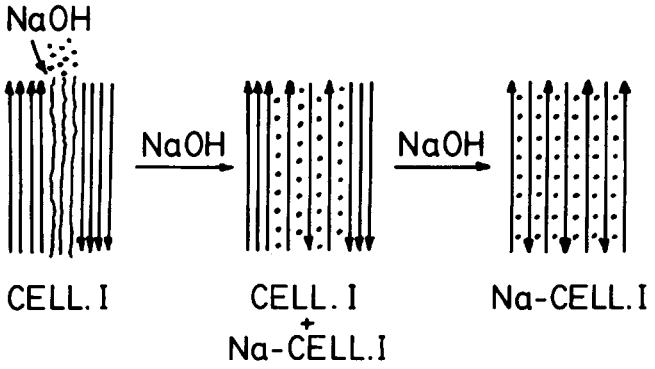


Fig. 6. Probable mechanism of cellulose mercerization (initial stages).

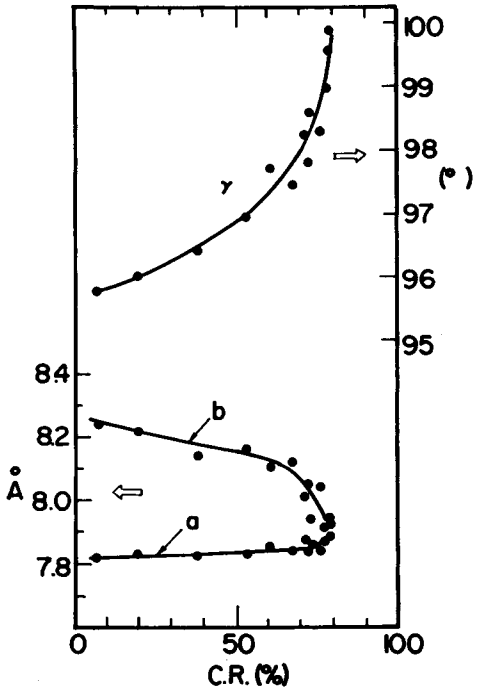


Fig. 7. Changes in unit cell parameters of cellulose I as a function of conversion ratio.

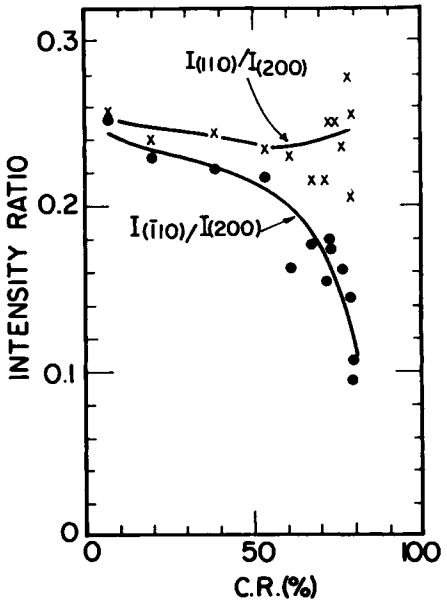


Fig. 8. Ratios of intensities $I_{(110)}/I_{(200)}$ (×) and $I_{(\bar{1}10)}/I_{(200)}$ (●) as a function of conversion ratio.

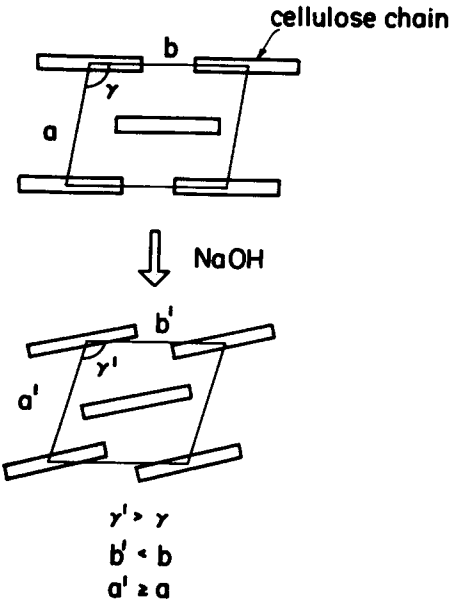


Fig. 9. Shearing deformation and chain rotation likely to occur in the unit cell of cellulose I during conversion to Na–cellulose I (exaggerated).

cellulose I chains by different neighboring crystallites of Na–cellulose I may create strains and discontinuities in the crystalline regions of the latter. Because of this, the average crystallite size of Na–cellulose I can be expected to be smaller in comparison with cellulose I, as is observed. Considering that the presence of NaOH in the crystal lattice of Na–cellulose I causes the separation between adjacent chains in it to be considerably larger than in cellulose I, the ~ 50 Å crystallite size of Na–cellulose I may, in fact, correspond to considerably fewer chains per crystallite than in the ~ 62 Å diameter crystallite of cellulose I.

The two-part mechanism is consistent with the previously advanced hypothesis for the conversion of cellulose I to cellulose II, part of which is schematically illustrated in Figure 6. It is also in agreement with the experimental observations that microcrystalline cellulose and the highly crystalline *Valonia* cellulose I are very resistant to mercerization.[9]

In *Valonia* mercerization it has been observed that a shish-kebab morphology can occur.[10] Although our results are not inconsistent with such morphology, it is not known at the present time whether it occurs in Na–cellulose I.

Conversion and Unit Cell Parameters of Cellulose I. The unit cell parameters a, b, and γ of cellulose I were measured during the entire process of conversion to Na–cellulose I. All parameters changed systematically as shown in Figure 7. In addition, the ratios of the intensities $I_{(\bar{1}10)}/I_{(200)}$ and $I_{(110)}/I_{(200)}$ showed significant changes (cf. Fig. 8) as a function of the conversion ratio.

As can be seen in Figure 7, little change in the unit cell base-plane dimensions a and b occurred prior to $R = 65\%$, i.e., during the fast stage of the conversion. Of the two dimensions, b—which reflects the distance between the chains within the sheets—changes more than a, the distance

between the sheets. A more significant change occurs in the angle γ which increases by almost 2° during the conversion to $R = 65\%$. After the latter point, the changes in b and γ are larger and even a increases more. As illustrated in Figure 9 (in an exaggerated fashion), these changes suggest a shearing deformation of the unit cell.

The intensity ratios, plotted in Figure 8, show considerable change in the $\bar{1}10/200$ ratio, and a far smaller change in the 110/200 ratio. Although it has not been quantitatively substantiated, these changes in the intensity ratios suggest a rotation of the chains about the helix axis, as shown in Figure 9. The shearing deformation of the unit cell, in the form of a sliding of sheets of chains relative to one another, may thus be accompanied by a rotation of the chains within the sheets. The significance of these changes in the unit cell of cellulose I is not clear at this time; however, the fact that they occur in a more pronounced fashion during the slow phase of conversion indicates that they may be connected with the destruction of the crystalline phase of cellulose I.

CONCLUSIONS

Although the changes in crystallite sizes as a function of the conversion ratio support a probable mercerization mechanism in which conversion of cellulose I begins in the amorphous phase, some questions remain. For instance, it is assumed for the purpose of this mechanism that the amorphous phase is an interface region between the crystallites. In it, the chains are well ordered, but possess an undefined polarity. This is plausible, but, in the absence of an accurate characterization of the amorphous regions in cellulose, it must remain only an assumption. It is likely that the smallest crystallites of cellulose I are also transformed during the first conversion stage, along with the amorphous regions and with equal ease. (This possibility is investigated in the following paper.)

Another assumption that has been made considers the crystal structure of Na–cellulose I to be based on antiparallel chains. In view of all of the data accumulated on the conversions, this is a very reasonable assumption. It cannot, however, be definitely proven until the crystal structure of Na–cellulose I has been determined by diffraction analysis.

APPENDIX

The observed intensity profiles were fitted by the following equation, using a least-squares curve resolution program[8]:

$$I(S) = \sum^{N} \left(fA_{0i} \exp\left(-\ln 2 \left[\frac{2(S - S_{0i})}{dS_{0i}} \right]^2 \right) + \frac{(1 - f)A_{0i}}{1 + \left[2(S - S_{0i})/dS_{0i} \right]^2} \right) \tag{3}$$

in which f = the profile function parameter, A_{0i} is the peak intensity of the ith reflection, S_{0i} is the peak position of the ith reflection, and dS_{0i} is the observed half-width of the ith reflection. [The two terms in this equation describe Gaussian and Lorentzian peaks, respectively; thus f is a fraction of the former and $(1 - f)$ is a fraction of the latter.] As many as necessary peaks N were included in the resolution.

In order to obtain a pure diffraction profile, it is necessary to correct the observed profile for instrumental broadening factors such as wavelength distribution, slit width, and sample geometry. The instrumental profile may, in general, be obtained by recording a standard sample that is presumed to be free of any size and distortion broadening effects. The standard sample should exhibit a diffraction peak in the same angular region as the sample under study. The absorption

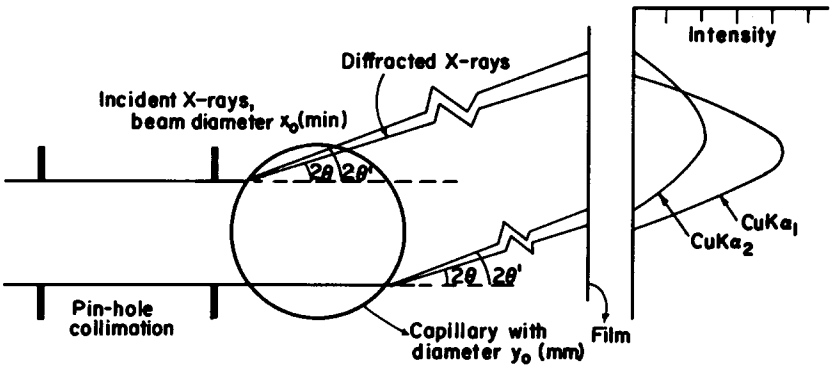


Fig. 10. Geometry of diffraction of X-rays by normal beam transmission technique. (The view is down the sample capillary and perpendicular to the X-ray beam.)

coefficient of the standard sample should also match that of the sample. In most instances, a standard sample fulfilling these conditions cannot be easily found, as was the case here. In the present study, therefore, the instrumental profile was calculated on the basis of the collimation system employed, the sample geometry, and the wavelength distribution, as illustrated in Figure 10. In the calculation, it was assumed that the incident X-ray was a parallel beam with a diameter x_0, the $K\alpha_2$ component (λ = 1.54433 Å) was one-half as intense as the $K\alpha_1$ component (λ = 1.54051 Å), and that the sample with linear absorption coefficient μ was placed in a capillary tube of circular cross section and of diameter y_0. A comparison of the observed and calculated diffraction profiles for the d = 2.319 Å diffraction line of NaF, for which the linear absorption coefficient μ = 66.4 cm^{-1}, proved this model to be valid.

For celluloses, values of $2\theta = 18°$ and μ = 10 cm^{-1} were used for the position of the diffraction peak and the linear absorption coefficient, respectively. (The value of μ is 12.7 cm^{-1} for completely crystalline cellulose I.) The resultant half-width of the calculated instrumental profile was thus 0.00562 A^{-1}, and the correction for instrumental broadening was calculated from the equation:

$$dS_p = f\left(dS_0^2 - 0.00562^2\right)^{1/2} + (1 - f)(dS_0 - 0.00562) \quad (4)$$

where dS_p is the pure half-width, dS_0 is the observed half-width, and f is the profile function parameter.

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