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Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part I. Spectra of Lattice Types I, II, III and of Amorphous Cellulose*

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Synopsis

The infrared spectra of highly crystalline samples of cellulose containing the lattice types I, II, and III were compared with one another and with the spectrum of amorphous cellulose in the 850–1500 cm.$^{-1}$ region. The spectra of cellulose II and of amorphous cellulose showed interesting similarities at 1420, 893–897, and 1111 cm.$^{-1}$, three bands which others have used to follow changes in crystallinity and lattice type because the spectrum of cellulose I differs distinctly at these points from that of amorphous cellulose or cellulose II. The similarity between amorphous cellulose and cellulose II prevents the use of these bands for crystallinity determination in samples with mixed lattice types—for instance, partly mercerized cotton. An explanation is offered for the resemblance of the two spectra, based on the hypothesis that a rearrangement of intramolecular hydrogen bonds, tending to stabilize a different conformation of the cellulose chain, occurs upon destruction of the native cellulose I crystal lattice.

INTRODUCTION

The quantitative relationship between infrared spectral bands of cellulose in the 800–1500 cm.$^{-1}$ region and the fine structure (degree of crystallinity and crystal lattice type) has needed further exploration for some time. The separate evaluation of spectral changes due to lattice transition and those due to decrease in crystallinity, if such is possible, would be of considerable value to those engaged in studies of fine structure.

Qualitative studies have been made by a number of workers. Forziati and Rowen[1] observed that conversion of cellulose I into cellulose II or into amorphous cellulose produced a decrease in the sharpness and definition of the spectrum as well as changes in intensity at certain wavelengths. Tsuboi[2] used polarized infrared radiation to examine native celluloses and one "amorphous" cellulose (prepared by dissolving in cuprammonium hydroxide and reprecipitating) before and after deuteration and made struc-

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tural assignments for most of the bands in the cellulose I spectrum. He commented that the spectral differences between the amorphous and crystalline celluloses were very slight, especially in the 1200–1500 cm.$^{-1}$ region. It has subsequently been pointed out[3] that some of Tsuboi's material contained small quantities of cellulose II due to his method of purification.

In a series of papers, Mann and Marrinan[3–5] compared by means of polarized infrared radiation and deuteration the spectra of the crystal modifications cellulose I, II, III_I, and III_{II} in the OH-stretching region (3000–3600 cm.$^{-1}$). At about the same time Liang and Marchessault,[6–8] also using polarized infrared radiation, described the spectra of crystalline cellulose I and II in detail and discussed the structural assignments of bands in both the OH-stretching region and the longer wavelength region (640–1700 cm.$^{-1}$).

A quantitative study which "enables the crystallinity of a cellulose, defined as the fraction of OH groups which are hydrogen-bonded in a regular crystalline manner, to be estimated by infrared spectroscopy" was published by Mann and Marrinan.[9] The relative intensities of the OD- and OH-stretching bands were used to calculate the fraction of hydroxyl groups which were inaccessible to deuterium exchange. The application of their technique is, however, severely limited by the experimental conditions which require the use of a cellulose film mounted in a gas-tight cell and, therefore, would not be useful for cotton. O'Connor and co-workers[10] developed for native cottons an empirical but serviceable "crystallinity index"—the ratio of absorptivities at 1429 cm.$^{-1}$ and 893 cm.$^{-1}$*—from the observation that in mechanically (vibratory ball-milled) and chemically (ethylamine-swollen) decrystallized cottons the absorption band at 1429 cm.$^{-1}$ decreased or disappeared while the band at 893 cm.$^{-1}$ increased in intensity as the crystallinity decreased. They pointed out, however, that this crystallinity index was not applicable to mercerized cottons.

McKenzie and Higgins[11] studied the influence of alkali on the infrared spectra of various native celluloses. They reported that bands located at 1429, 1111, 990, and 893 cm.$^{-1}$ showed regular changes with increasing concentration of sodium hydroxide and therefore were infrared spectroscopic criteria of the transition from cellulose I to cellulose II. In another paper[12] they discussed the spectral changes occurring upon transition from cellulose I to cellulose II with respect to the structural assignments of some of the bands which are altered. Recently, Higgins, Stewart, and Harrington[13] published a comprehensive survey of the spectra of polysaccharides, simple sugars, and derivatives closely related to cellulose, as well as spectra of the several cellulose crystal modifications. Their purpose was to examine qualitative differences in the infrared spectra related to crystal lattice type, type of anomeric linkage, position of glycosidic linkage on the sugar residue, and deuteration, in an attempt to clarify some

* For uniformity, locations of all infrared bands are given in wavenumbers (cm.$^{-1}$) regardless of the units employed in the paper cited.

controversial assignments of absorption bands. They showed that when simple sugars were put into an amorphous state by freeze-drying, the infrared bands lost sharpness and intensity. When cellulose I was converted to an amorphous state by high-speed dry milling, a spectrum resembling that of cellulose II was eventually produced.

Hurtubise and Krässig[14] used the absorbances at 3333, 1163, and 900 cm.$^{-1}$ to follow the transformation of cellulose I to cellulose II in a variety of materials. They observed that O'Connor's crystallinity index was dependent not only on crystallinity but also on degree of mercerization. They suggested that a more appropriate designation was "infrared lateral order index." By making synthetic mixtures of unmercerized and mercerized cotton linters, birch pulp, and spruce pulp, they showed that this lateral order index varied linearly with the percentage of mercerized cellulose in the mixture, but that the lateral order index of the original unmercerized materials differed from one another considerably.

Although the studies of both Higgins and co-workers and of Hurtubise and Krässig demonstrated that certain infrared bands are excellent criteria for the extent of mercerization of a particular type of cellulosic material, both groups found differences in the absorptivities at the selected wavelengths which appeared to be related also to the degree of crystallinity of the original samples. The difficulty with Hurtubise and Krässig's study was that both crystallinity and extent of mercerization were varying simultaneously. As they stated, "One of the important experiments that remains to be done is a quantitative study of the effect of crystallinity on the lateral order index. Actually, a detailed study of the changes occurring in the cellulose spectrum during decrystallization has yet to be made. This should provide valuable information and would certainly increase the usefulness of infrared spectroscopy for fine structure investigations on cellulose."[14]

The purpose of the present study was to attempt to evaluate separately the spectral changes due to decrystallization and those due to changes in lattice type, particularly the cellulose I–cellulose II transition. The study resolved itself into two phases. The first was a comparison of the spectra of highly crystalline celluloses I, II, and III with the spectrum of highly amorphous cellulose. Particular attention was given to those spectral bands which have been used by other workers to assess crystallinity, lateral order, and lattice transitions. The second phase was an attempt to find other spectral bands which could be used as criteria of the crystallinity where mixtures of cellulose I and II were present, as well as for samples containing either lattice type. This phase will be the subject of a separate paper.[15]

EXPERIMENTAL

Materials

Starting materials were: for cellulose I, a stock lot of purified cotton yarn; for cellulose II, Fortisan rayon, which is already of moderately high

crystallinity; and for cellulose III, a portion of ethylamine-treated cotton yarn. To obtain materials of high crystallinity, portions were acid-hydrolyzed (refluxed 30 min. in 4*N* hydrochloric acid), washed, and dried to produce powdery hydrocelluloses. The highly amorphous cellulose was obtained by vibratory ball-milling a portion of the purified cotton yarn.

METHODS

Infrared spectra were obtained with a Beckman IR-7 spectrophotometer using the potassium bromide pellet technique.[16] X-ray diffractograms were run with a Norelco high-angle precision x-ray diffractometer equipped with proportional counter and pulse-height analyzer.[17]

The deuterated and rehydrogenated samples were prepared by soaking in deuterium oxide (99.5% D_2O) for 1 hr. and drying, then soaking in water for 1 hr. and drying.

RESULTS

Comparison of Spectra of "Crystalline" and "Amorphous" Celluloses

The x-ray diffractograms of the experimental materials were first evaluated for crystallinity and purity of lattice type. As may be seen from Figure 1, the cellulose I and cellulose II were highly crystalline and showed no traces of a mixed lattice type. The cellulose III was probably of somewhat lower crystallinity and contained a small amount of cellulose I, as indicated by the residual peaks in the diffractogram at approximately 14.6, 16.2, and 22.6° (2θ). The ball-milled sample was highly amorphous, as indicated by the absence of peaks in the diffractogram.

The infrared spectra in the 850–1500 cm.$^{-1}$ region are shown in Figure 2. Absorption bands in this region which have been used by other workers for estimation of crystallinity and detection of extent of mercerization occur at 1429, 1163, 1111, and 893 cm.$^{-1}$. A brief summary of the structural assignments found in the literature for these bands will be given, and the relative intensities and shifts in frequency to be observed in Figure 2 will be noted:

1429 cm.$^{-1}$. This band in cellulose I and the corresponding one at 1420 cm.$^{-1}$ in cellulose II were assigned by Liang and Marchessault[6,8] to the CH_2 scissoring motion. This would imply that changes in intensity or location are related to alterations in the environment of the C_6 group. In Figure 2 it is seen that this band is strong in cellulose I; very weak and shifted to 1420 cm.$^{-1}$ in cellulose II and amorphous cellulose; and of moderate intensity, located at 1425 cm.$^{-1}$, in cellulose III.

1163 cm^{-1}. The assignment by Liang and Marchessault[6,8] of this band to the antisymmetrical bridge C—O—C stretching mode has been questioned by Higgins, Stewart, and Harrington.[13] They noted that their data, showing diminished intensity upon deuteration, were more consistent with the data of Segal et al.,[18] which confirmed O'Connor's assignment of

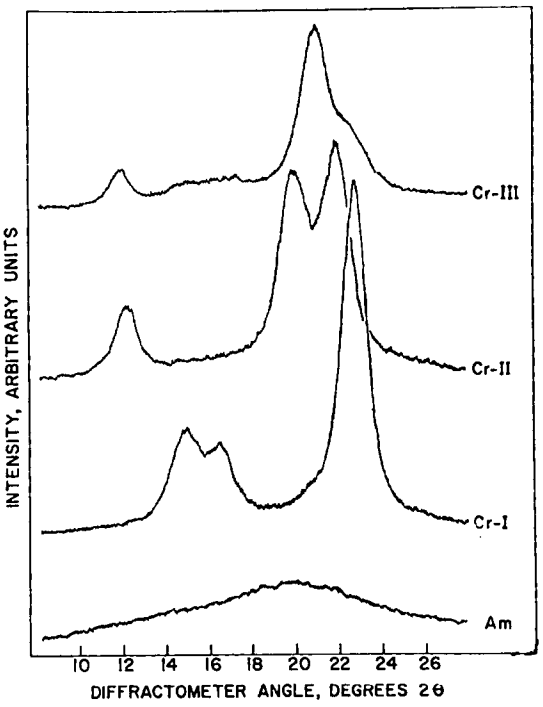


Fig. 1. X-ray diffractograms of hydrocelluloses prepared from cotton cellulose III (Cr-III), fortisan rayon (Cr-II), and native cotton (Cr-I), and of vibratory ball-milled cotton (Am).

this band to C-O stretching or O-H bending of the C-OH group; but they also mentioned that Marchessault (private correspondence) felt it was easier to explain the decreased intensity upon deuteration as being due to a change in the hydrogen-bonding of the bridge oxygen than to explain their data by this other band assignment.

In the spectra of Figure 2, this band appears at the same location (1163 cm.$^{-1}$) in cellulose I and cellulose III but is shifted slightly (to 1156 cm.$^{-1}$) in cellulose II and amorphous cellulose. The intensity does not differ greatly among the four spectra, although there is a slight reduction in the spectrum of amorphous cellulose.

1111 cm.$^{-1}$. Liang and Marchessault[6,8] tentatively assigned this band to the ν_{at} mode of ring stretching. Higgins et al.[13] believe that this assignment is more appropriate for the adjacent residual band at 1120 cm.$^{-1}$ and conclude, therefore, that the 1111 cm.$^{-1}$ band may be an "association" band analogous to those found near 1111 cm.$^{-1}$ in primary and secondary alcohols. The association band in alcohols has been attributed to the effect of hydrogen bonding on the skeletal vibrations which involve stretching of the C–O bond. Higgins et al.[13] noted that the change in intensity in going from cellulose I to cellulose II or III also indicated an intimate connection with the hydrogen-bonding system.

In Figure 2, this band is seen to be strong in the spectrum of cellulose I, weak and shifted to 1102 cm.$^{-1}$ in cellulose III, and appears only as a shoulder in cellulose II and amorphous cellulose due to the development of a strong, broad band near 1090 cm.$^{-1}$.

893 cm.$^{-1}$. Higgins, Stewart, and Harrington[13] have recently summarized the experimental facts upon which an assignment of this band

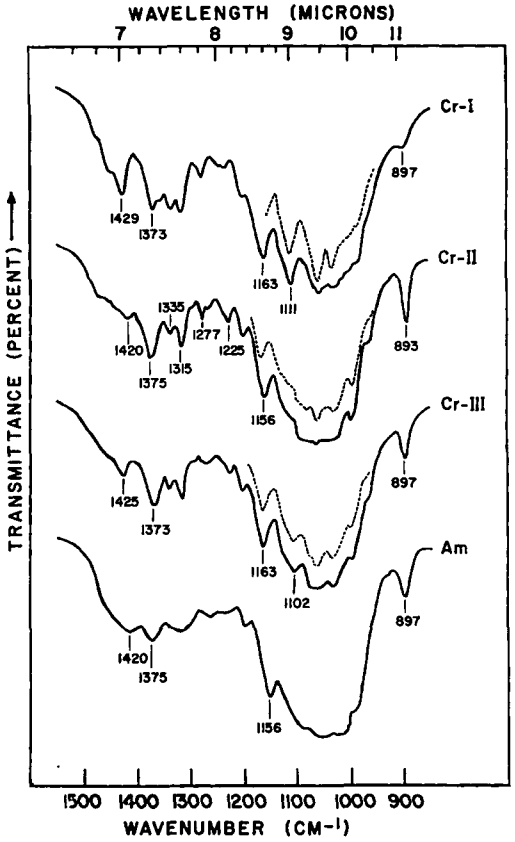


Fig. 2. Infrared spectra of hydrocelluloses prepared from native cotton (Cr-I), Fortisan (Cr-II), and cotton cellulose III (Cr-III), and of vibratory ball-milled cotton. The dotted line indicates reduced concentration.

in cellulose can be based: It is characteristic of β-anomers or β-linked glucose polymers, it shows weak parallel polarization, and it is sensitive to deuteration and to the nature of the hydrogen-bond system. They concluded that the suggestion of Stacey (private communication, quoted by Liang and Marchessault[6]), that it was due to a vibrational mode involving C_1 and the four atoms attached to it, was the most plausible assignment. They pointed out that if the oxygen atoms attached to C_1 participate in this vibration, then changes in hydrogen bonding could affect its

intensity. They noted that mercerization approximately doubles the absorbance.

In Figure 2 it is seen that this band in cellulose I is weak and broad, centered at about 897 cm.$^{-1}$; in cellulose II it is strong and sharp, located at 893 cm.$^{-1}$; while in cellulose III it is less strong and located at 897 cm.$^{-1}$ as in cellulose I. In the spectrum of amorphous cellulose, it is less strong and sharp than in cellulose II, and is located at about 897 cm.$^{-1}$. The cellulose II curve is in agreement with the observation of Higgins et al., except that in this spectrum from highly crystalline cellulose II the absorbance is much more than double that in the cellulose I spectrum.

Summarizing, the spectra of cellulose II and of amorphous cellulose are quite similar in the presence and strength of bands at 1420 cm.$^{-1}$ and

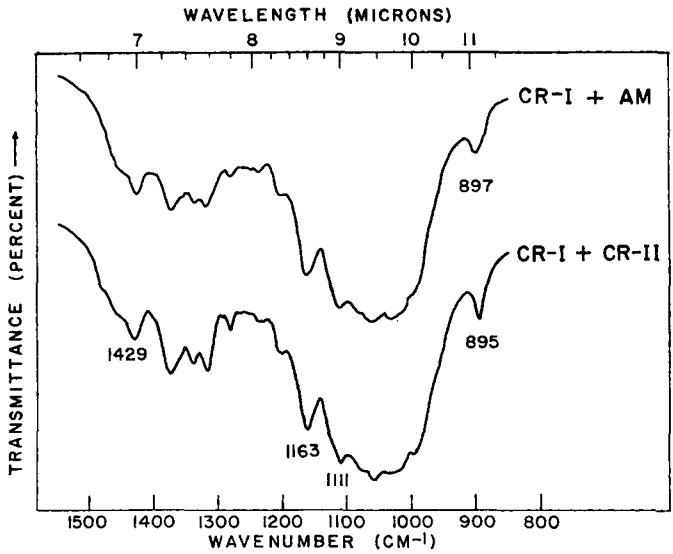


Fig. 3. Infrared spectra of 1:1 mixtures of cotton hydrocellulose with ball-milled cotton (Cr-I + Am) and of cotton hydrocellulose with Fortisan hydrocellulose (Cr-I + Cr-II).

1156 cm.$^{-1}$, the absence of a discrete band at 1111 cm.$^{-1}$, and the presence of a strong band at 893–897 cm.$^{-1}$. The band at 893 cm.$^{-1}$ is, however, sharper and more intense in cellulose II than in amorphous cellulose. The spectra of cellulose II and of amorphous cellulose differ in the 900–1500 cm.$^{-1}$ region chiefly in the resolution and intensity of bands at 1375, 1335, 1315, 1277, and 1225 cm.$^{-1}$. These are well resolved in the spectra of high crystallinity cellulose II but in that of ball-milled amorphous cellulose the 1375 cm.$^{-1}$ band is much less intense, the 1335 and 1315 cm.$^{-1}$ bands are merged into a diffuse region centered near 1310 cm.$^{-1}$, and the small, sharp bands at 1277 and 1225 cm.$^{-1}$ are weak and diffuse. Interpretations of these bands as given by Marchessault and Liang[8] and by Higgins et al.[13] are: 1375 cm.$^{-1}$, C-H bending; 1335 cm.$^{-1}$, O-H in-plane bending; 1315

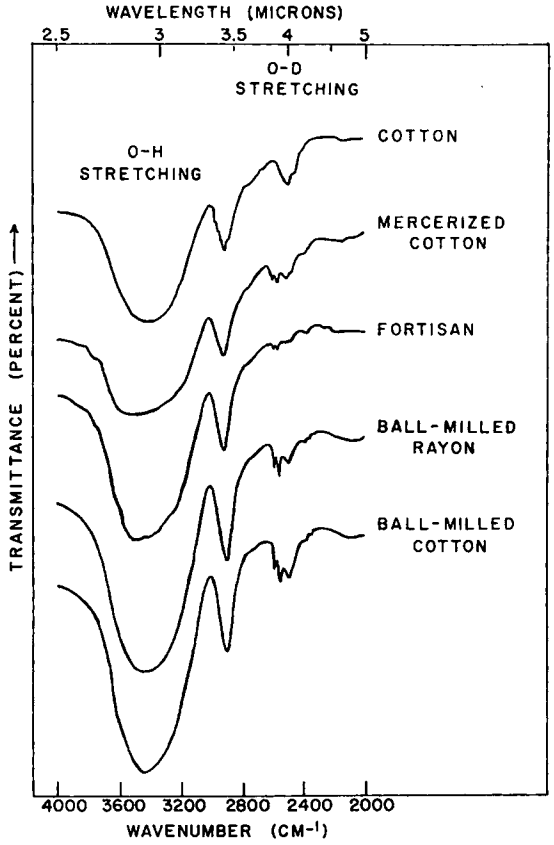


Fig. 4. Infrared spectra of deuterated and rehydrogenated cotton, mercerized cotton, Fortisan, ball-milled rayon, and ball-milled cotton.

cm.$^{-1}$, CH_2 wagging; 1277 cm.$^{-1}$, C-H bending; and 1225 cm.$^{-1}$, possibly O-H in-plane bending.

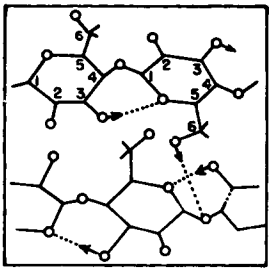
To further show the similarity in the spectra of cellulose II and amorphous cellulose, two 1:1 mixtures were made: (*a*) highly crystalline cellulose I with amorphous cellulose, and (*b*) highly crystalline cellulose I with crystalline cellulose II. The spectra of these mixtures (Fig. 3) show that mixing cellulose II with cellulose I has approximately the same effect on certain regions of the spectrum as mixing an equal quantity of amorphous cellulose with cellulose I. The relative intensities of the bands at 1429 cm.$^{-1}$ and 893 cm.$^{-1}$ (used for calculating the crystallinity index of O'Connor or the lateral order index of Hurtubise and Krässig) and the band at 1111 cm.$^{-1}$ (shown by McKenzie and Higgins to change with alkali treatment) are affected to about the same extent in the two spectra shown in Figure 3. It is noted, however, that the bands at 1375, 1335, 1315, 1277, and 1225 cm.$^{-1}$ are reduced in intensity by a mixture of amorphous cellulose but are not decreased by adding high crystallinity cellulose II.

Howsmon and Marchessault[19] have already shown that amorphous cellulose produced by ball-milling has a tendency to recrystallize as cellulose II. They found that when such material is placed in water at room temperature and then dried, its x-ray diffractogram revealed the presence of some cellulose II. We have confirmed this observation by another method. Vibratory ball-milled cotton was moistened with deuterium oxide to exchange the accessible hydroxyl hydrogens with deuterium. The sample was dried and remoistened with water to rehydrogenate the accessible deuteroxyl groups. The presence of sharp absorption bands in the 2400–2650 cm.$^{-1}$ region of the infrared spectrum (O-D stretching) showed that some deuteroxyl groups were still present, trapped by partial crystallization during the first drying period. Retention of deuterium also occurs to a limited extent when cotton, mercerized cotton, and Fortisan are deuterated and rehydrogenated under the conditions employed. The positions and intensities of these bands in the 2400–2650 cm.$^{-1}$ region, assigned to O-D stretching vibrations, are distinctly different in the spectra of cellulose I and cellulose II, as may be seen in Figure 4 by comparing this portion of the top curve (cotton cellulose I) with the second and third curves (mercerized cotton and Fortisan), and furnish a sensitive means of determining which lattice type is present. Examination of this region of the curve for ball-milled cotton (bottom curve of Fig. 4) shows quite clearly that this material derived from cellulose I recrystallized as cellulose II. The ball-milled sample derived from rayon (second curve from bottom) also recrystallized as cellulose II, but this would be expected.

DISCUSSION

The strong similarity of the spectra of amorphous cellulose and of highly crystalline cellulose II at 1420 and 893 cm.$^{-1}$ and the dissimilarity to that of highly crystalline cellulose I at these frequencies requires explanation. Since the regularity of the crystal lattice is disrupted by the process of producing the amorphous state (whether by grinding, strong swelling, or solution and reprecipitation), no organized system of interchain hydrogen bonding should exist, although undoubtedly many interchain bonds are randomly dispersed. Some intrachain hydrogen bonding of a regular character could, however, be present in amorphous material, especially if a particular chain conformation were sterically favorable for the formation of these intrachain bonds. Cellulose I and cellulose II are currently believed to differ in chain conformation, although the exact nature of the difference has yet to be determined.[20–24] One postulated difference involves a rotation about the glucosidic linkage to give a "bent" or a "bent and twisted" alignment of adjacent anhydroglucose units.

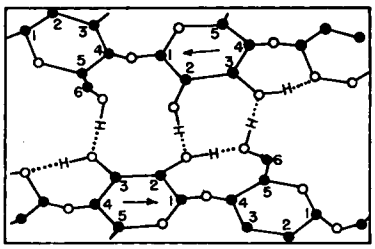
Such a change in molecular conformation might be dependent upon or concurrent with a rearrangement of intramolecular hydrogen bonds. As noted above, the intermolecular hydrogen-bonding system must be drastically disrupted when the native cellulose I lattice is destroyed by grinding



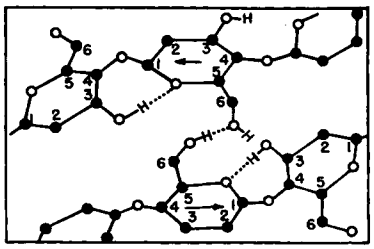
CELLULOSE I
(1$\bar{1}$0 PLANE)

INTRAMOLECULAR: $O_3H \rightarrow O'_5$
INTERMOLECULAR: $O_6H \rightarrow O^*_4$
(after Liang and Marchessault, 7)

CELLULOSE II (1$\bar{1}$0 PLANE)



INTRAMOLECULAR $O_3H \rightarrow O'_5$
$O_2H \rightarrow O'_6$
(after Mann and Marrinan, 4)



INTRAMOLECULAR $O_3H \rightarrow O'_5$ (2 KINDS)
(after Marchessault and Liang, 8)

Fig. 5. Intramolecular hydrogen bonds in cellulose I and II according to Liang and Marchessault[7,8] and Mann and Marrinan.[4] Subscripts indicate carbon atom to which the OH group is attached. O′ is in the same chain but in an adjacent ring; O* is in a different chain.

or strong swelling. Sufficient energy is probably also supplied by these processes to disturb the intramolecular system as well. This would permit rotation of anhydroglucose units about the glucosidic linkage into positions favorable for the formation of a different set of intramolecular hydrogen bonds. Such a rearrangement of intramolecular bonds would tend to stabilize the new conformation, even in the amorphous state. If the sterically most favorable conformation were that found in the cellulose II crystal lattice, then this would be the one tending to be formed in the amorphous state, and to be stabilized by the new intramolecular bonds. This could be an explanation for the similarity in the spectra of amorphous cellulose and cellulose II. The band at 893 cm.$^{-1}$, assigned to motions of atoms attached to C_1, would be expected to reflect changes in molecular conformation due to rotation about the C_1—O—C_4 (glucosidic) linkage. The band at 1420 cm.$^{-1}$ (CH_2 symmetrical bending) should respond to changes in the environment of the C_6 group, such as the formation (or breaking) of an intramolecular hydrogen bond involving O_6.

Perhaps the stabilization, by intramolecular hydrogen bonds, of a chain conformation characteristic of the cellulose II lattice could also explain why it has so far been impossible to effect the reverse transformation of cellulose II to cellulose I. If a complexing agent could be found that would force the cellulose molecule into the native conformation and if the agent could then be removed in such a way that the original system of intramolecular hydrogen bonds would be re-established, then perhaps this transformation could be effected.

That the hydrogen-bonding system is different in the two crystal lattice types (celluloses I and II) is clearly shown by the intensities and frequencies of the infrared absorption bands in the O—H stretching region.[8] The bands definitely assigned[7,9] to intrachain hydrogen-bonded hydroxyls are at 3350 cm.$^{-1}$ in cellulose I (in ramie, and by inference, cotton) and in cellulose II at 3488 and 3447 cm.$^{-1}$. The specific intramolecular bonds which these represent have been discussed at length by Liang and Marchessault[6-8,25] and by Mann and Marrinan.[3-5] Figure 5 summarizes diagrammatically the postulated intramolecular bonds and some of the intermolecular bonding. An O_3—O_5' bond (the prime indicates the oxygen atom is in an adjacent anhydroglucose unit of the same chain) in both cellulose I and II is generally assumed, but the second intramolecular bond in cellulose II has been assigned either to a second O_3—O_5' bond with a different environment[8] or to an O_6—O_2' bond.[4] The single O_3—O_5' bond would make a six-membered ring which would include the bridge oxygen; an O_3—O_5' bond plus an O_6—O_2' could involve the bridge oxygen in two hydrogen-bonded rings. Such a double ring system could probably stabilize the chain conformation even in the amorphous state.

Liang[26] and Marchessault and Liang[8] have presented considerable evidence against the existence of the O_6—O_2' bond in either cellulose I or cellulose II. For cellulose I, Liang[26] has stated that a careful study of a model of the cellulose chain led to the conclusion that the infrared CH_2 symmetrical stretching and bending bands would not show parallel polarization if the O_6—O_2' hydrogen bond were formed. Since in cellulose I the CH_2 symmetrical stretching band near 2850 cm.$^{-1}$ and the CH_2 symmetrical bending band near 1430 cm.$^{-1}$ were observed to be highly parallel, the O_6—O_2' intramolecular hydrogen bond was quite unlikely. Saksena et al.[27] have recently reviewed the published data. From calculations based on the Meyer and Misch ("straight") conformation of the cellobiose unit, they maintained that an O_6—O_2' intrachain bond would be in accord with the observed polarizations. Recent crystallographic studies of cellulose[22,23,24] indicate, however, that the Meyer and Misch conformation is no longer tenable, at least without some modification. This casts some doubt on the validity of Saksena's conclusions.

For cellulose II, Marchessault and Liang[8] have presented the same arguments as for cellulose I against the existence of the O_6—O_2' intrachain bond. However, the observed dichroisms of the CH_2 stretching and bending frequencies are much lower in cellulose II than in cellulose I, tending to weaken

this objection. Collateral evidence proposed by Liang (private communication) is the fact that the O_6—O_2' bond is not assumed in a careful x-ray study[28] of the crystal structure of cellobiose, which is closely related in structural detail to cellulose II. This line of reasoning is not completely valid because the infrared spectrum of cellobiose recently published by Mann[29] is appreciably different from that of cellulose II in the OH stretching region, and because in the crystal structure of cellobiose the molecules are not lined up parallel to one another (as are the cellulose molecules) but are alternately perpendicular.

It is not possible, on the basis of existing data, to determine definitely the kinds of intramolecular hydrogen bonds in the two cellulose crystal lattice types. The marked resemblance of the amorphous cellulose spectrum to that of crystalline cellulose II at frequencies related to the C_1 and C_6 groups, and its dissimilarity to that of cellulose I at these frequencies, suggests that the conformation of the chain might be similar in amorphous cellulose to that in cellulose II and different from that in cellulose I. Since crystal lattice forces are at a minimum in the amorphous state, intrachain hydrogen bonding seems the logical explanation for maintaining a particular conformation in that state.

CONCLUSIONS

Comparison of the infrared spectra of highly crystalline samples of cellulose containing the lattice types I, II, and III with one another and with the spectrum of amorphous cellulose in the region from 850 to 1500 cm.$^{-1}$ showed some strong similarities and some marked differences. All three crystal modifications had fairly strong, sharp bands in the 1315–1375 cm.$^{-1}$ region, in contrast to the weak, diffuse bands in amorphous cellulose in that region. The spectrum of cellulose III resembled that of cellulose II more closely than that of cellulose I, although the positions of some bands were nearer to the corresponding ones in cellulose I.

With respect to three bands previously used to follow changes in crystallinity and lattice types, the spectra of cellulose II and amorphous cellulose showed some interesting similarities; namely, a very weak band at 1420 cm.$^{-1}$, a strong band at 893–897 cm.$^{-1}$ (somewhat stronger and sharper in the crystalline cellulose II), and the presence of the 1111 cm.$^{-1}$ band of cellulose I as only a shoulder, due to development of strong, poorly resolved adjacent bands.

An explanation for the similarity of the spectra of cellulose II and amorphous cellulose at these points was based on the hypothesis that rotation of glucose units about the glucosidic bond to give a somewhat different molecular conformation in cellulose II than that found in native cellulose actually occurs when the native crystal lattice is destroyed (by grinding or swelling); and that the new conformation is stabilized sufficiently to give rise to changes in the infrared absorption, even in the amorphous state, by formation of a different set of intramolecular hydrogen bonds. The system

of hydrogen bonding proposed by Mann and Marrinan could have such a stabilizing effect, and could affect both the 1420 and the 893 cm.$^{-1}$ bands.

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Use of trade names does not imply endorsement by the United States Department of Agriculture over other similar instruments or products.

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Résumé

On a comparé entre eux et avec le spectre de la cellulose amorphe dans la région de 850 à 1500 cm^{-1} les spectres infra-rouges d'échantillons fortement cristallins de cellulose contenant les types de réseau I, II et III. Le spectre de la cellulose II et de la cellulose amorphe montrent des intensités intéressantes à 1420, 893, 897 et 1111 cm^{-1}, trois bandes que d'autres ont utilisées pour suivre les changements de cristallinité et du type de réseau parce que le spectre de la cellulose I diffère nettement en ces points de la cellulose amorphe et de la cellulose II. La ressemblance entre la cellulose amorphe et la cellulose II empêche l'usage de ces bandes pour déterminer la cristallinité d'échantillons à types de

réseaux mélangés, par example, du coton partiellement mercérisé. On propose une explication pour la ressemblance des deux spectres. Elle se base sur l'hypothèse qu'un réarrangement des liens hydrogène intramoléculaires, qui tendent à stabiliser une conformation différente de la chaîne cellulosique, a lieu lors de la destruction du réseau cristallin primitif de cellulose I.

Zusammenfassung

Die Infrarotspektren hochkristalliner Celluloseproben der Gittertypen I, II und III wurden sowohl miteinander als auch mit dem Spektrum von amorpher Cellulose im Bereich von 850–1500 cm^{-1} verglichen. Die Spektren von Cellulose II und von amorpher Cellulose weisen bei 1420, 893–897 und 1111 cm^{-1} interessante Ähnlichkeiten auf. Diese drei banden wurden von anderen Autoren zur Untersuchung von Änderungen der Kristallinität und des Gittertyps verwendet, da sich das Spektrum von Cellulose I in diesen Bereichen deutlich von denjenigen von amorpher Cellulose und von Cellulose II unterscheidet. Wegen der Ähnlichkeit von amorpher Cellulose und von Cellulose II können jedoch diese Banden nicht zur Bestimmung der Kristallinität von Proben mit gemischtem Gittertyp wie etwa teilweise mercerisierte Baumwolle herangezogen werden. Auf Grund der Hypothese, dass bei der Zerstörung des Kristallgitters von nativer Cellulose I eine Umlagerung intramolekularer Wasserstoffbindungen und damit eine Stabilisierung einer anderen Konformation der Cellulosekette auftritt, wird eine Erklärung für die Ähnlichkeit der beiden Spektren gegeben.

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