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A NEW LOOK AT THE CHAIN POLARITY PROBLEM OF CELLULOSE

*By Mitsuo Takai, Yoshihito Yaginuma, Hiroshi Kon,
Mitsuhiro Murata and Jisuke Hayashi*

(Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo, Hokkaido, 060 Japan.)

Synopsis

It is suggested that the chain polarity of native cellulose, cellulose I, is preserved in the course of the transformation to cellulose II by mercerization as a reasonable interpretation of following results. The selective uniplanar orientation of (1 $\bar{1}$ 0) plane of original bacterial cellulose is maintained during and after mercerization to provide cellulose II pattern resulted in the preferential orientation. Furthermore, when the air-dried or never-dried spherulite of bacterial cellulose was immersed in 18% NaOH, the Maltese cross pattern and the color correlation are the same as those of the original. There are several other evidences for the same polarity of cellulose I and II. It was proved that cellulose triacetate (CTA) I can be formed by the heterogeneous acetylation of cellulose II as well as cellulose I when the swelling in the pretreatment media is low. It seems that parallel arrangement is not necessarily correct structure of CTA I. It is possible to transform CTA I to CTA II without any dissolving process but by a comparatively simple treatment with superheated steam. These mean that CTA I and CTA II have the same polarity in their crystal structures. The transformation of cellulose I to cellulose II through cellulose III₁ which is hydrolyzed by 20N H₂SO₄ without dissolution has been newly observed in the present study. Completely amorphous wood pulp decrystallized by the mechanical milling is recrystallized to cellulose II with water or 1% NaOH. It seems to be difficult to reverse the chain or to attain antiparallel arrangement from parallel one during the mechanical milling. On the other hand, the chain polarity problem has been solved by the direct TEM observation of LODP cellulose reacted with hydrazine. Characteristic microfibril of the LODP cellulose are observed with uniform width and length of about 200A and 2000A, respectively. In contrast with this, the reacted microfibril is long but has irregular pattern in shape. The possibility of antiparallel arrangement in ramie cellulose has been directly proved by the microphotographs.

Introduction

One big problem for cellulose remains unsettled; whether the chains within the unit cell of the microfibril have the same polarity (all oriented in the same direction) or they alternate in polarity as in the Meyer-Misch structure?

The fundamental difference between the structures of cellulose I and cellulose II has been the subject of debate for many years. Recent x-ray analysis on *Valonia* cellulose¹⁾ has favored a

parallel packing for the cellulose chain in the native microfibril, implying an extended chain model for the cellulose crystals, whereas adjacent chains in regenerated or mercerized cellulose are antiparallel²⁻⁷⁾. It seems that parallel packing is true for *Valonia* cellulose as a special case, but there has been a doubt as to whether this packing is applicable to other native cellulose such as cotton, flax, ramie or bacterial cellulose⁸⁾. Blackwell has suggested that polarity change would happen by interdigitation of parallel sheets of

($1\bar{1}0$) plane in a course of mercerization of *Valonia* cellulose. This change should involve crystallographical change of ($1\bar{1}0$) to (020) in the lattice of cellulose II. The rearrangement is impossible during mercerization of native cellulose because the selective uniplanar orientation of ($1\bar{1}0$) plane is kept during and after mercerization^{9,10}.

On the other hand, Chanzy observed the fibrous mercerization of *Valonia* cellulose microfibrils involving an extensive, transient, "shish-kebab" lamellar crystallization in which lamellae contain cellulose II recrystallized by epitaxial growth on the backbone of the cellulose I microfibril¹¹. They suggested that the cellulose II part of the mercerized microfibrils might be obtained after dissolution or swelling in alkali followed by recrystallization during subsequent washing, and also suggested the possibility of chain back-folding and change in chain polarity in *Valonia* cellulose. Although "shish-kebab" formation of lamellar cellulose II certainly takes place in *Valonia* cellulose microfibrils in which defects have been created by acid hydrolysis, no similar changes take place during the straight-forward conversion of cotton or bacterial cellulose I to cellulose II by 18% NaOH at room temperature^{12,13}. The fibrous mercerization of cellulose by the "shish-kebab" mechanism would seem to depend on creation of initial defects by prior degradation of the microfibril and therefore this mechanism is not applicable to the ordinary conversion of cellulose I to cellulose II.

We have concluded that the difference between cellulose I and cellulose II is due to the chain conformation, that is, the former is bent form while the latter is bent and twisted form, and also suggested that the mechanism of mercerization of cellulose involves the sliding of (020) sheets of chain from one potential minimum to another. This sliding does not involve changes in the original polarity of the cellulose chains or require the solution of the cellulose. This mechanism may be applied equally well to those types of native cellulose with an antiparallel structure and to those with parallel structure like *Valonia*. The present suggestion does not repudiate or invalidate previous ideas of conformational change taking place during mercerization. It simply broadens and extends our understanding of the cause of such a confor-

mational change at molecular level. The purpose of the present study is to give an additional insight into the chain polarity problem and to show some circumstantial and direct evidences that the chain polarity of cellulose I is identical to that of cellulose II.

Experimental

Cellulose Samples. Bacterial cellulose pellicles composed of cells of *Acetobacter xylinum* were grown under the condition described by Hestrin and Schramm¹⁴. After removal from the medium, the pellicles were immersed for several hours in 1% NaOH and then washed overnight in distilled water. Finally, they were immersed in 1% AcOH to neutralize the last traces of alkali and then washed with water. A bacterial cellulose membrane dried on a glass plate showed a preferential orientation, i.e., selective uniplanar orientation with respect to the membrane surface. Spherulites of bacterial cellulose were grown in more dilute medium than usual as described in the previous paper¹⁵. The spherulites were washed with a series of 1% NaOH, 1% AcOH, and water. All washings were done as gently as possible to avoid mechanical distortion of the spherulites, and then dried on glass slides. The ramie phloem fibers refined by Toyo Menka Industrial Company were also used as a cellulose sample; they were extracted with 2:1 benzene-ethanol and then dried under vacuum. Whatman cellulose powder, CF 11, was also used as native cellulose. Cellulose III was prepared from ramie and Fortisan (provided by American Celanese Fiber Company) by treatment with liquid ammonia at -80°C for 24hr followed by slow evaporation of ammonia at about -15°C . Cellulose IV was prepared from cellulose III by heating in glycerol at 260°C for 30min. Amorphous cellulose was prepared by milling native cellulose, wood pulp. Rod milling was performed for a given period by a vibratory mill, model TI-100 of Heiko Mfr. Co. Ltd., which consists of pot and rod fully lined by tungsten carbide.

Mercerization, Acetylation, and Acid Hydrolysis of Cellulose. Mercerization for the membranes and spherulites of bacterial cellulose was observed in the following two ways. One was that water of the swollen, undried samples was substituted with 18% NaOH. The other was that the samples were

first dried on a glass plate and then treated with 18% NaOH. These two kinds of specimens were subjected to x-ray and polarized optical-microscopic analyses.

Heterogeneous acetylation involved pretreating of the cellulose materials in glacial acetic acid at 20°C for 24hr. Then the pretreated materials were acetylated by using 1% of nascent sulfonic acetic acid as a catalyst in a mixture of 25 parts of acetic anhydride and 75 parts of benzene at 20°C for 48hr. The products were washed with benzene to be free from acid and then immersed in 75% neutralized ethyl alcohol at 50°C for 1hr to remove sulfonic acetic acid thoroughly. Finally they were washed exhaustively with distilled water. To recrystallize the product it was heat-treated in silicone oil at 210°C for 15min. Superheated-steam treatment of the products was also carried out in an autoclave at 170°C for 2hr.

The cellulose materials were hydrolyzed in constantly boiling 2.4N HCl by refluxing for 3hr. After hydrolysis the residues were trapped on a glass filter of 1G4. The products were then dried at room temperature in a vacuum desiccator over P₂O₅. Cellulose III and cellulose IV were hydrolyzed in 20N H₂SO₄ at room temperature for 1 to 24hr. After the hydrolysis each product was dialyzed in Visking tubing (36/32) against water for 5–7days with repeated changes of the exterior phase until no indication of acidity was apparent. Each dialyzed product was then dried on a glass plate at 60°C in an electric oven.

X-ray Diffraction. The general fiber diffractograms with the x-ray beam perpendicular and parallel to the surface of the dried membrane were obtained by a flat film camera with nickel-filtered CuK α radiation of Rigaku Denki High Power RU-200S system. An x-ray diffractometer trace of membranous or powdery sample was obtained by the reflection method with Rigaku Denki automatic diffractometer operated in the $w-2\theta$ scanning mode between 5° and 30° (2θ).

Electron Microscopy. TEM or SEM observations of cellulose microfibril were carried out to see morphological changes in fine structure in the course of mercerization or reaction with hydrazine. About 50mg of the residue ($\overline{DP}=200$) hydrolyzed by sulfuric acid were reacted at pH 8.5 with a half mole of hydrazine at room temperature with

constant shaking for 2 to 5hr. After the reaction, the solution was allowed to stand for 24hr. Then one or two drops of the supernatant were put on a carbon-coated grid and air-dried, and then shadowed with Pt-Pd metal. TEM specimens were photographed by using a Hitachi H-700H electron microscope at 200KV. SEM samples were mounted on the specimen stubs with a double-side adhesive tape backing and coated with gold. A Hitachi SEM model S-430 was used. Photographs were taken at 10–15KV accelerating voltage.

Results and Discussion

Retention of (1 $\overline{1}0$) Selective Uniplanar Orientation of Bacterial Cellulose during Mercerization Process.

A bacterial cellulose membrane dried on a glass plate resulted in having a preferential orientation, i.e., selective uniplanar orientation with respect to the membrane surface (Fig. 1). When the water of swollen never-dried membranes was substituted for 18% NaOH, vigorous shrinkage of the membranes occurred. This shrinkage appears to be due to loss of a large amount of water from cellulose hydrogel to give cellulose

Fig. 1. X-ray diffraction patterns of bacterial cellulose membrane; $\perp$: perpendicular to the membrane surface, $//$: parallel to the surface.

Fig. 2. X-ray diffraction patterns of mercerized bacterial cellulose; $\perp$: perpendicular to the membrane surface, $//$: parallel to the surface.

xerogel and to the change to the mercerized form. However, even when the sample was allowed to contract freely upon mercerization, it kept a selective uniplanar orientation. If the membrane was first dried on a glass plate and then treated with 18% NaOH, it shrank to only about two-thirds of its former width and length, with a slight increase in thickness (Fig. 2). Anyhow this process tends to retain the original selective uniplanar orientation¹⁰⁾. On the other hand, both ends of a flat strip of the never-dried membrane were clamped to a glass plate in order to prevent the shrinkage by mercerization. This process produces a biaxially oriented sheet of regenerated cellulose, cellulose II⁹⁾. It is clear that the selective uniplanar orientation of $(1\bar{1}0)$ plane of original bacterial cellulose is kept during and after mercerization to provide cellulose II pattern. If the change in chain polarity of cellulose happens in the course of mercerization, it will be difficult that the orientation is to be retained. It is significant to note that the $(1\bar{1}0)$ plane of cellulose, in its influence on the type of orientation obtained, appears to play an important role in the action of intracrystalline swelling agents and complex or derivative reactants. The $(1\bar{1}0)$ plane is mostly occupied by hydroxyl groups. It is also the plane whose lattice constant and sharpness of diffraction line is always affected first when cellulose is exposed either to intracrystalline swelling agents such as sodium hydroxide, or to chemical substitution reactions in fiber form by acetylation and nitration. Shift of position, line broadening, or decrease in total intensity of the $(1\bar{1}0)$ plane usually precedes the changes of the (110) and (020) planes. Therefore, these results suggested that the elementary structure unit of cellulose could be interpreted to be a sheet-like structure consisting of the $(1\bar{1}0)$ plane. The concept of a sheet of cellulose chains has been introduced by Warwicker et al., to explain the swelling reaction of cellulose with sodium hydroxide^{16,17)}. On the basis of x-ray diffraction they proposed that flat sheet of cellulose chains, which lied on top of each other within $(1\bar{1}0)$ plane, acted as the fundamental reacting unit during swelling. In *Valonia* cellulose, Blackwell et al. have suggested that polarity change would be happened by interdigitation of parallel sheets of $(1\bar{1}0)$ plane in the course of

mercerization. This change should involve the crystallographical change of $(1\bar{1}0)$ to (020) in the lattice of cellulose II. The rearrangement is impossible during mercerization of native cellulose, because the selective uniplanar orientation of $(1\bar{1}0)$ plane is kept during and after mercerization.

Retention of the Chain Orientation in the Spherulite of Bacterial Cellulose during Mercerization Process. Two-dimensional spherulites of bacterial cellulose were formed by static and very dilute cultures of *Acetobacter xylinum* (Fig. 3). Polarizing microscopic evidence indicates that the cellulose microfibrils or molecules in the spherulites are mostly radially oriented¹⁵⁾. X-ray diffractogram of air-dried spherulite shows essentially the same pattern of native cellulose, cellulose I. When the air-dried or never-dried spherulities were immersed in 18% NaOH, drastical shrinkage of

Fig. 3. The optical-microscopic appearance of bacterial cellulose spherulite between crossed Nicols over a color plate ($R = 530$ nm). ($\times 20$).

Fig. 4. The optical-microscopic appearance of mercerized bacterial cellulose spherulite between crossed Nicols over a color plate ($R = 530$ nm). ($\times 20$).

the spherulites was observed with a slight increase in thickness. Nevertheless the Maltese cross pattern and the color correlation were the same as those of the original during and after mercerization (Fig. 4). The orientation of the molecules can be assessed by the sign of birefringence of the spherulite. Thus, above evidence has confirmed that the chain polarity of native bacterial cellulose is preserved in the course of transformation to cellulose II.

Cellulose Triacetate I Derived from Cellulose II by the Fibrous Acetylation. It is generally accepted that two stable polymorphic crystalline structures exist in cellulose triacetate (CTA); CTA I and CTA II^{18,19}). They can be distinguished from each other clearly by x-ray analysis. In general, CTA I is obtained by the fibrous acetylation of cellulose I while CTA II arises if the acetylated product is precipitated from solution or swollen with solvent. Heterogeneous acetylation of cellulose II after adequate pretreatment also yields CTA II. In the previous paper²⁰), it was proved that CTA I could be formed by the heterogeneous acetylation of cellulose II when the swelling in the pretreatment media was slight. When mercerized celluloses were acetylated by the pretreatment with glacial acetic acid, they gave mixed patterns of CTA I and CTA II²⁰). However normal rayon or Fortisan fibers were hardly acetylated by the pretreatment with glacial acetic acid. The acetylation requires a severe pretreatment. Thus the acetylated rayon always had CTA II pattern¹⁹). Sakurada et al.²¹) noticed that the reactivity of rayon toward acetylation was markedly enhanced by acid hydrolysis. Whatman cellulose powder or acid-prehydrolyzed Fortisan fiber was subjected to a comparatively mild pretreatment with glacial acetic acid, followed by acetylation. Figure 5 shows x-ray diffractograms of these triacetates before and after heat-treatment. They are generally sharper than those of the triacetate forms of unhydrolyzed celluloses. Whatman cellulose powder yields the typical CTA I, and then prehydrolyzed Fortisan also gives clear CTA I pattern, in which the diffractions characteristic of CTA I are at 11.5 ($2\theta = 7.7^\circ$) and 5.5 (16.6°) Å. It becomes clear that cellulose II, Fortisan, yields CTA I after suitable pretreatment and that there is no substantial difference between mercerized

Fig. 5. X-ray diffractograms of acetylated cellulose. Acetates after heat treatment (210°C , 15min) of: (A) Whatman cellulose powder; (B) prehydrolyzed Fortisan, and those before the heat treatment of: (C) Whatman cellulose powder; (D) prehydrolyzed Fortisan.

cellulose and rayon. This fact contradicts the previous view that CTA I is yielded from cellulose I and CTA II from cellulose II. In the molecular and crystal structure analysis of CTA II, Dulmage²²) proposed an antiparallel structure for it, and Roche et al.²³) recently confirmed it. Stipanovic et al.²⁴) have similarly analyzed CTA I obtained from ramie cellulose, and its structure is proposed to be based on parallel chains. If this is true, CTA I can never be derived from cellulose II of antiparallel chains. However, as mentioned above, a typical CTA I is obtained from cellulose II, prehydrolyzed Fortisan with high crystallinity. At least, it seems that parallel arrangement is not necessarily a correct structure for CTA I. In our previous papers^{25,26}), the main distinction between CTA I and CTA II are not the matter of chain polarity, but of the orientation of acetyl groups and of the chain packing. The crystal structure of CTA I is based on the sheet-like structure of $(1\bar{1}0)$ plane of the original cellulose, which is densely packed by methyl or carbonyl groups. The shape of CTA I lattice markedly resembles that of cellulose II, whereas the chain packing within the sheet is similar to that of cellulose I. On the other hand, the crystal structure of CTA II is also basically a sheet-like structure, but van der Waals contacts

are within the sheet because of a different orientation of acetyl group. The sheet interlocks each other and is difficult to slip in the sheet direction.

Transformation of CTA I to CTA II without Dissolution. It is possible to obtain transformation of CTA I to CTA II by a comparatively simple treatment with superheated steam without any dissolving process. Such a treatment can be regarded as a combination of swelling and heat treatment. Both crystalline and amorphous CTA I were treated with superheated steam at 170°C for 2hr. The transformation of CTA I to CTA II results in the change of the x-ray diffraction patterns as shown in Fig. 6. Both acetylated Whatman cellulose powder and acetylated Fortisan, which are amorphous CTA I, were almost completely transformed from CTA I to CTA II. On the other hand, the acetylated cellulose powder and Fortisan, which are crystalline CTA I after heat treatment, showed about 30% and complete conversion from CTA I to CTA II, respectively. Anyhow this means that there is no change in the polarity of backbone chain during the transformation without dissolution.

Fig. 6. X-ray diffractograms of acetylated cellulose with superheated-steam treatment. Acetates of: (A) Whatman cellulose powder; (B) prehydrolyzed Fortisan. Those with two-step heat treatment in silicone oil at 210°C for 15min and then in superheated steam at 170°C for 2hr. Acetates of: (C) Whatman cellulose powder; (D) prehydrolyzed Fortisan.

Recrystallization of Amorphous Cellulose from Native Cellulose, Wood Pulp to Cellulose II. The x-ray diffractograms of the original cellulose, wood pulp and the cellulose milled for 100min are shown in Fig. 7. The original one is crystalline (Fig. 7A), but the milled one is completely amorphous (Fig. 7B). Figure 7C, D and E show patterns of those recrystallized with distilled water or 1 to 3% NaOH for 24hr at room temperature. They give a pattern of cellulose II unambiguously. The mechanical milling was performed with a vibratory rod mill lined with tungsten carbide. The milling produced a very small sized particles and reduced crystallinity progressively to give a completely amorphous state as judged from the absence of crystalline diffraction peaks. At an early stage of the milling, the sample was partially decrystallized. Then it was recrystallized to cellulose I with water or 1% NaOH. In contrast to it, completely decrystallized, amorphous sample was recrystallized to cellulose II by the same treatment. Therefore the former was degraded to keep the sheet structure of cellulose I, and the latter was completely decrystallized to give the chain packing of cellulose II. So it is difficult to reverse the chain or to attain antiparallel arrangement from parallel one in the course of the milling.

Fig. 7. X-ray diffractograms of the cellulose powder of wood pulp: (A) original wood pulp; (B) mechanically decrystallized by vibratory mill for 100min, (C) recrystallized from (B) with water, (D) with 1% NaOH, and (E) with 3% NaOH.

Transformation of Cellulose I to Cellulose II through Cellulose III_I. Cellulose III_I and III_{II} prepared from ramie and Fortisan, respectively, were hydrolyzed with 20N H₂SO₄ for 24hr at room temperature. The percentage of the residue to the starting material were 15% for cellulose III_I and 10% for cellulose III_{II} in comparison with the case of cellulose I or II under the same hydrolysis condition, which were completely dissolved. The x-ray diffractograms of the residues are shown in Fig. 8. Both of them showed very intensive peaks of (110) plane of cellulose II which showed a typical uniplanar orientation. The SEM observations of the insoluble residues of hydrolyzed cellulose III_I and III_{II} reveal characteristic appearance of fibrillar fiber. In the present study, the transformation of cellulose I to cellulose II through cellulose III_I, which was hydrolyzed with 20N H₂SO₄, has been newly observed without dissolution. Cellulose III_I, in general, will revert to cellulose I by boiling in water or in relatively dilute solution of hydrochloric acid. The difference in the conversion would be explained on the basis of different ability of HCl and H₂SO₄ to swell the substances. Table 1 summarized the resemblance of chain conformation, chain packing and resultant hydrolyzate by 20N H₂SO₄ between various cellulose polymorphs. The patterns of hydrolyzates are mainly governed by the form of

Table 1. Resemblance of chain conformation and chain packing between various cellulose polymorphs.

CELLULOSE POLYMORPH	CHAIN CONFORMATION	CHAIN PACKING	20N-H ₂ SO ₄ HYDROLYZATE
I	I	I	I
III _I	I	II	II
IV _I	I	I	I
II	II	II	II
III _{II}	II	II	II
IV _{II}	II	I	II

chain packing in the cellulose I family, whereas they are governed by the chain conformation in the cellulose II family. Especially, cellulose III_I shows unusual behavior in the cellulose I family. This is the reason why the hydrogen bonding system in cellulose III_I is a specific form as compared with those of others.

TEM Observation of LODP Cellulose Reacted with Hydrazine. In order to get a direct evidence to solve for the chain polarity problem of cellulose, TEM observation of LODP cellulose reacted with hydrazine was carried out. The hydrazine method is generally used for the determination of carbonyl group in hydrocelluloses, which is quite suitable for low carbonyl values. The model reaction with hydrazine and acetone is shown in Fig. 9. In this case, the theoretical amount of hydrazine needed is a half mole of acetone reacted. The first step of reaction yields a hydrazone, and then finally produce adine form. From the point of view, levelling-off DP (LODP) cellulose ($\overline{DP} = 200$) which was prepared by H₂SO₄ hydrolysis was subjected to the reaction. The LODP cellulose has a carbonyl group per one reducing end. Therefore if the microfibril of LODP cellulose has a parallel chain, the reaction would be stopped by dimerization as shown in Fig. 10. In contrast with the parallel chain, the antiparallel chain would continue to react with hydrazine until the theoretical amount is consumed (Fig. 10). The resulting morphology would be expected to be greatly different each other. In the antiparallel case, it would be expected

Fig. 8. X-ray diffractograms of cellulose. (A) Cellulose III_I from ramie, (B) cellulose III_{II} from Fortisan, (C) hydrolyzed product from (A) and (D) that from (B) by 20N H₂SO₄.

Fig. 9. Model reaction scheme between acetone and hydrazine.

Fig. 10. Expected models for cellulose microfibril reacted with hydrazine.

Fig. 11. Electron micrographs of prehydrolyzed ramie cellulose with 20N H_2SO_4 .

that a long microfibril is observed such as a re-polymerized product. A couple of electron micrographs are shown in Fig. 11 and 12. Characteristic microfibrils of the LODP cellulose were observed with uniform width and length of about 200A and over 2000A, respectively (Fig. 11). On the other hand, the shape of reacted microfibril was long but irregular in its pattern (Fig. 12). Although there is some problem to prepare a specimen for TEM, the possibility of antiparallel arrangement in ramie cellulose is apparent from the micrographs.

Mechanism of Transition from Cellulose I to Cellulose II during Mercerization. In the previous sections, it has been suggested that the mechanism

Fig. 12. Electron micrographs of the prehydrolyzed ramie cellulose reacted with hydrazine.

of mercerization of cellulose involves the progressive shift of sheets of polyglucosan chain in the crystallites of the microfibril as shown in Fig. 13. This notion explains qualitatively all the changes observed when cellulose I alters to cellulose II. The shift need not and does not involve changes in the original polarity of the polyglucosan chains. The mechanism may be applied equally well to those types of native cellulose with an antiparallel structure and to those with parallel structure.

The suggested mechanism is also applicable to mercerization of preferentially oriented sheets of

Fig. 13. Schematic model for the transformation of cellulose I to cellulose II by mercerization at various levels.

cellulose. As demonstrated previously⁹⁾, selective, uniplanar orientation of the crystallites of bacterial cellulose takes place when the swollen, gel-like membranes are dried on a glass plate. This orientation tends to be retained even after mercerization. Since the $(1\bar{1}0)$ plane of the crystallites tends to be parallel to the membrane surface as a result of drying, subsequent relative shifting of the sheets in the (020) plane will remain possible during mercerization and the preferential orientation will be maintained.

Relative displacement of the sheets in the (020) plane is also consistent with the observed, initial loss of sharpness and the broadening of the diffraction line of the $(1\bar{1}0)$ plane. Whenever two (020) sheets slide each other there will be a simultaneous disturbance of the periodicity of the corresponding $(1\bar{1}0)$ plane and a concomitant loss in total intensity of the line. Differential shifting of the sheets within a crystallite and different degrees of conversion between crystallites will set up internal strains within the initially straight microfibrils which will be minimized by helix coiling or convolution. Furthermore, in the crystallite level, the spiral angles of the crystallite to the fiber axis will change. For ramie cellulose, the spiral angle is changed from 7.5° to 15.8° by mercerization.

It may be necessary to emphasize that the present suggestion does not repudiate or invalidate

the previous ideas of a conformational change taking place during mercerization. It simply broadens and extends our understanding of the molecular reason of such a conformational change. For instance, when the sheets of cellulose chains shift each other in the crystallite during mercerization, it is certain that the shift must be accompanied by a conformational variation in one or more elements of the chains. Therefore, the present idea is consistent with the previous suggestions and extends them.

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セルロースの分子鎖配列問題に関する一考察

北海道大学工学部 高井光男, 柳沼義仁, 今 博史, 村田満広, 林 治助

天然セルロース, セルロース I (Cell. I) がマーセル化反応でセルロース II (Cell. II) へ転移する際, 分子鎖配列は変わらないと考えた方が以下の実験事実から妥当である。(1) (110)面の選択面配向構造を有するバクテリアセルロースを 18% NaOH, 室温でマーセル化し Cell. II へ転移させても, この面配向を維持している。(2) バクテリアセルロース球晶のマーセル化においても消光パターン及び干渉色の組合せに変化が見られず, 分子鎖の配向が変わらない。(3) Cell. II からでも酢化反応条件次第で Cellulose triacetate I (CTA I) を生じる。(4) CTA I から CTA II への転移が繊維形態を保持したまま過熱水蒸気処理で可能である。(5) ボールミルで粉碎した天然セルロース非晶化物は水処理で Cell. II を再結晶化する。(6) ラミーから得た Cell. III は約 20N H₂SO₄,

室温の加水分解で繊維形態を保持したまま Cell. II へ転移する。(1)において, もし分子鎖の逆転が起るならば, 選択的面配向構造を維持し得ない。(2)において, もし back fold が生じるならば消光パターンや干渉色のコンビネーションに変化を生じる。(3)については, Sarko 及び Chanzy らが X線結晶構造解析を行い, CTA I は平行鎖, CTA II は逆平行鎖を結論している。もしも, これが正しいならば, 逆平行鎖を有する Cell. II から CTA I は決して生じないことになる。(4), (5) および (6) においては, 繊維形態を保持したままで分子鎖の逆転はあり得ないし, Chanzy が観察した様な Shish-kebab 構造は見られなかった。さらに, ラミー加水分解物のヒドラジン反応によりラミーが逆平行鎖構造を有するという直接的証拠も得た。