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Transformation of *Valonia* Cellulose Crystals by an Alkaline Hydrothermal Treatment

Even though cellulose has been one of the most studied polymers, its crystalline structure remains only partially understood. As early as 1937, the work of Meyer and Misch[1] led to the proposal that native cellulose or cellulose I was crystallized in a two-chain monoclinic unit cell, each of the chains being positioned on one of the monoclinic 2-fold screw axes. This structure was questioned in 1958 when Honjo and Watanabe[2] started to investigate the highly crystalline *Valonia* cellulose by electron diffraction analysis. Their diagrams contained a series of extra reflections, which could not be accounted for by the two-chain monoclinic unit cell, but required a larger eight chain cell. The occurrence of "extra" reflections was confirmed by X-ray diffraction analysis[3,4] but, to date, the exact significance of such reflections remains to be determined. At any rate, *Valonia* cellulose I is the widely accepted native cellulose standard, having the highest crystallinity and perfection. The more common celluloses, being of lower crystallinity than *Valonia*, display diffraction spectra that are not as well-defined. For most of them (in particular for ramie and cotton cellulose), the extra reflections of Honjo and Watanabe are not resolved. Thus, the two-chain monoclinic cell seems acceptable for such samples.

The debate on the crystal structure of native cellulose has been revived recently when the first CP/MAS ^{13}C NMR spectra of cellulose became available.[5] Atalla and VanderHart[6,7] were the first to analyze in detail such spectra. From their work came the new proposal that each native cellulose was a composite of two different crystalline modifications, namely Iα and Iβ. In such a scheme, *Valonia* and bacterial cellulose would be rich in Iα, whereas ramie and cotton cellulose would be dominated by Iβ.[8] Pure Iβ cellulose was isolated from animal cellulose.[9] On the other hand, no pure Iα has been found or prepared so far.

In the two-phase model Iα/Iβ, Iβ is the most stable form. In particular, it is invariably obtained from *Valonia* cellulose after either a selective swelling of cellulose[10] or an acetylation treatment followed by saponification.[11] Quite recently, it was discovered by Horii et al.[12,13] that well-resolved Iβ ^{13}C NMR spectra could be obtained when *Valonia* cellulose was subjected to a hydrothermal annealing. In such spectra, a well-resolved multiplicity of two was found for the signals of the carbon atoms at C1, C4, and C6 of the glucose moieties. This is opposed to the initial *Valonia* spectra where at least three signals were observed for these carbons. The multiplicity of 2 for the carbon atoms in the annealed *Valonia* samples indicates that in the corresponding "annealed" unit cell there are only two glucose residues that are magnetically nonequivalent. Therefore, the corresponding crystal structure should be simpler than that of the unannealed sample. To test this hypothesis, we have compared the diffraction diagrams of *Valonia* cellulose before and after hydrothermal annealing. This report confirms unambiguously that there is indeed a substantial modification of the diffraction diagram of such cellulose when an hydrothermal annealing treatment is applied. This modification is not due to any loss in crystalline perfection but to a solid-state transformation.

In order to study the hydrothermal treatment of *Valonia* cellulose, purified vesicles of *Valonia macrophysa* were introduced in glass vessels containing a solution of 0.1 N NaOH in water. The vessels were tightly sealed, and each of them was subjected to annealing. For this, they were inserted in an autoclave, which was immersed in an oil bath where the temperture could be set in the range 220–260 °C. After 30 min at a given temperature, the autoclave was cooled under tap water and the vessel opened. The resulting annealed *Valonia* vesicles were then thoroughly washed with distilled water and delaminated under a stereomicroscope. Thin cellulose layers were floated off and mounted on carbon-coated grids. In other experiments the specimen was mounted across the holes of gold-sputtered micronet grids. The grids were observed with a JEM-2000 EXII electron microscope operated at 200 kV. A number of electron diffraction diagrams were recorded on never observed areas of the specimen ranging from 1 to 4 μm in diameter. These diagrams were obtained with various electron doses but never exceeding 300 electrons/nm^2 for the recording (this dose is half of the dose that leads to total disappearance of the electron diffraction diagram). Calibration of the diffraction diagrams was performed with the gold diffraction ring d_{111} = 0.235 nm. The unit cell refinements were obtained after a computer least-square fitting, using d spacings measured from each single reflection.

The above hydrothermal annealing treatment had no effect on the physical appearance of the *Valonia* fragments, which could be delaminated with equal ease in

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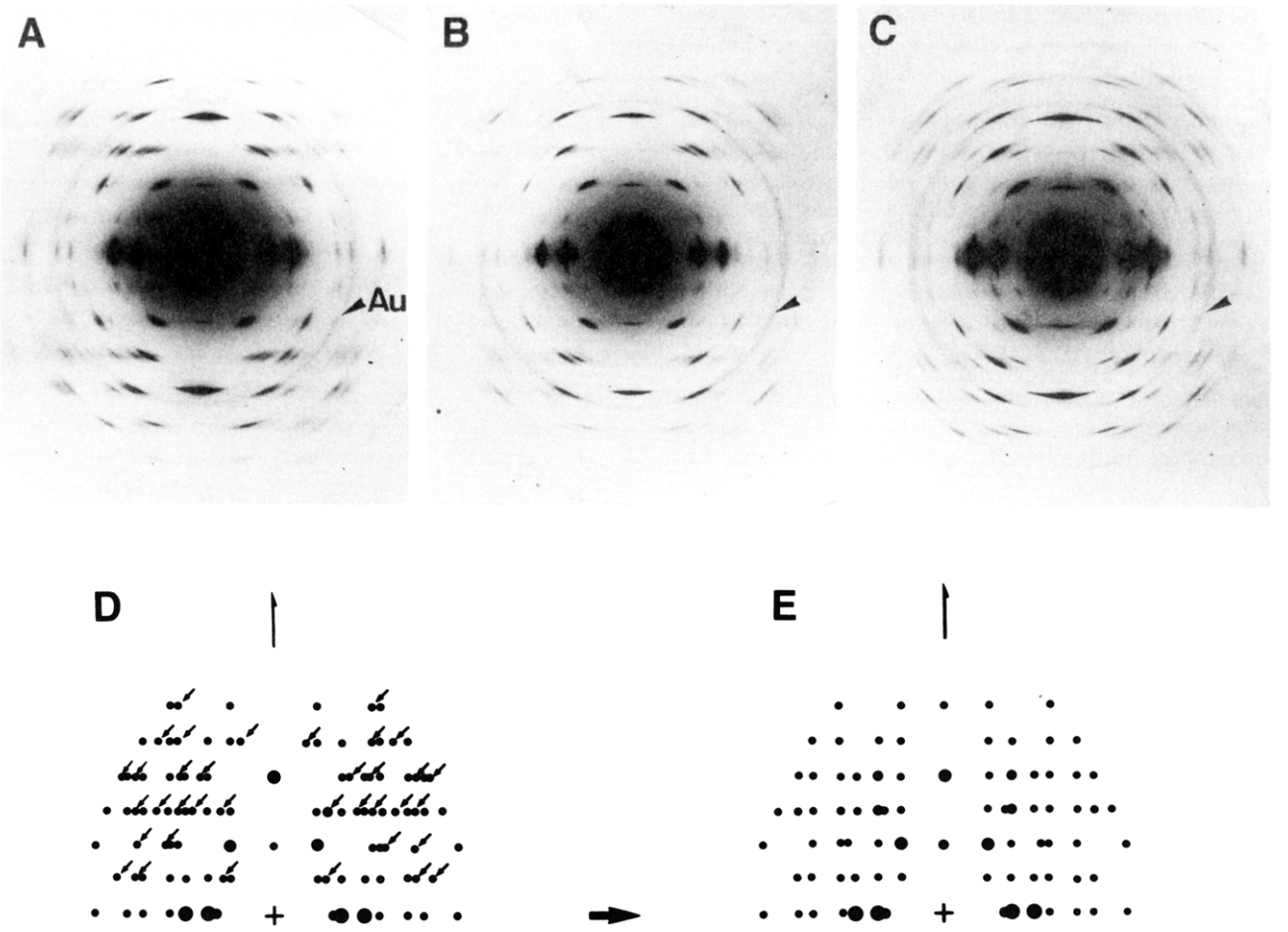

Figure 1. Typical electron diffraction diagram of *Valonia* cellulose before and after its annealing: (A) initial sample; (B) after annealing at 240 °C; (C) after annealing at 260 °C. D and E are schematic drawings of the diagrams in A and C. The arrowed spots in D correspond to the reflections that disappear during the annealing treatment.

all cases. When imaged by transmission electron microscopy, a bundle of annealed microfibrils was not distinguishable from an untreated bundle. In diffraction, however, the pattern of the annealed sample was substantially different from that of the initial material. This is clearly seen when one compares the electron diffraction diagrams of the samples before and after annealing. Typical diffraction diagrams are shown in Figure 1 where A corresponds to the diagram of the initial unannealed sample B is the diagram of a specimen annealed at the intermediate temperature of 240 °C, whereas in C the specimen was treated at 260 °C. In Figure 1 are also represented two schematic drawings D and E, corresponding to the diagrams in A and C.

The diffraction diagram in A is identical with all *Valonia* patterns published so far and in particular to the classical patterns reported by Honjo and Watanabe.[2] This diagram is highly resolved as it extends to the ninth layer line. Its triclinic character is clearly observed especially on the third layer line where the spots occurring in the upper left-hand quadrant have different intensities from those in the upper right-hand quadrant. The diagram in Figure 1B resembles that in Figure 1A in the sense that all the reflections in A are also present in B. However, there are substantial differences in the distribution of the diffraction intensities when one compares the two diagrams. Again this is particularly noticeable on the third layer line of the pattern.

In similarity with A and B, the diagram in C is also well resolved as it extends also to the ninth layer line. However, in contrast with A and B, the diagram in C contains a smaller number of reflections (in particular, all the arrowed reflections in D have disappeared). In addition, in C, all the diffraction spots in the upper left quadrant have intensities identical with those of the corresponding spots in the upper right quadrant. The diagram in C can be totally indexed with a two-chain $P2_1$ unit cell with $a = 0.792$ nm, $b = 0.822$ nm, $c = 1.036$ nm, and $\gamma = 97.3°$. Therefore, the above hydrothermal annealing treatment of *Valonia* cellulose converts the complicated crystalline form of this as grown material into a simpler and more symmetric crystalline structure. This transformation occurs in the solid state and without any apparent loss of crystalline perfection.

The results presented in this study bring a new dimension to the general knowledge of cellulose. In particular, the characterization of a true monoclinic two-chain cellulose structure is a remarkable result that will undoubtedly lead to substantial advances in the understanding of the structure of cellulose I. In the annealed crystalline structure that is now emerging for cellulose, two situations can be envisaged for positioning the cellulose chains within the unit cell. In one situation, there are two independent cellulose chains, located at the corner and center of the unit cell, exactly on one of the 2-fold screw axes: this implies that all the glucose residues are equivalent along a given chain. In the other situation, the cellulose chains are in between one of the screw axes: this requires that the two chains are identical, but in a given chain, two successive glucose moieties are no longer connected by a 2-fold screw symmetry. Either situation leads to two nonequivalent glucose units per unit cell. This is

in full agreement with the ^{13}C NMR data recorded on such a sample where high-resolution spectra are obtained with a multiplicity of 2 at C1, C4, and C6.

The explanation of the diffraction diagram of the initial *Valonia* is less straightforward. From the analysis of the ^{13}C NMR spectrum of *Valonia* cellulose, Atalla and VanderHart[6,7,14] have demonstrated that *Valonia* was composed of two distinct crystalline phases: the dominant Iα and the minor Iβ. The above experiment has demonstrated that Iβ corresponds to a monoclinic phase. Therefore, the pure Iα diffraction diagram can be obtained by substracting the Iβ fraction from this diagram. Such substraction is, however, not very accurate as one does not know the exact proportion of the Iα and Iβ phases. Nevertheless, the Iα diffraction spectrum can be interpreted in at least two ways: (a) It may correspond to a two-chain triclinic cell with a = 0.954 nm, b = 0.825 nm, c = 1.036 nm, α = 90°, β = 57.0°, and γ = 96.6°. Such a cell would account for almost all the extra reflections arrowed in Figure 1D. (b) It may also correspond to an eight-chain triclinic cell similar to that of Honjo and Watanabe[2] with a = 1.584 nm, b = 1.644 nm, c = 1.036 nm, $\alpha = \beta$ = 90°, and γ = 97.3°. Our favor goes toward the first hypothesis, but unless a pure Iα form is prepared or pure Iα diagram is obtained, it is difficult to give a clear answer on the unit cell or crystal structure of Iα cellulose.

One may speculate as to why a highly crystalline native cellulose sample such as *Valonia* is found in the form of such a composite crystalline structure. It is likely that such occurrence results from the cellulose biogenesis mechanism. During such a biosynthetic process, cellulose is synthesized, spun, and crystallized almost simultaneously at a temperature far below the glass transition or the melting point of cellulose. This undoubtedly leads to a structure where strains and stresses are built in. We suggest that the triclinic Iα phase, which is more or less abundant depending on the specimen origin, corresponds to this strained crystalline form. The strains would be released when the tempertaure is raised, in particular, above the cellulose softening temperature, to give the relaxed monoclinic Iβ form.

The crystalline composite features observed for native cellulose are not unique in the world of either "nascent" or deformed crystalline polymers. This had been well documented in the case of crystalline polyethylene where a triclinic phase was also found in nascent samples, especially those prepared at a very low temperature.[15] Such a triclinic phase is also found in stretched polyethylene as for instance in the gel spun samples.[16] In both cases, the triclinic phase is metastable as opposed to the stable orthorhombic crystalline polyethylene. Upon annealing, the triclinic metastable form relaxes and disappears readily when the temperature of the specimen is brought in the vicinity of the melting point.[17] This is very similar to what happens in the present cellulose experiment.

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Size-Quantized, Semiconductor Particle Mediated Photoelectron Transfer in Ultrathin, Phosphonate-Functionalized, Polymer-Blend Membranes

Size and dimensionality reductions of semiconductor particles result in altered mechanical, chemical, electrical, electrooptical, and magnetic properties, which could be profitably exploited in a variety of applications, including solar energy conversion.[3-5] Carefully controlled experimental conditions are required, however, for the preparation and stabilization of ultrasmall colloidal semiconductor particles. Inspired by the ability of commercially available Nafion membranes to incorporate colloidal semiconductors and catalysts,[6-9] we have developed functionalized, ultrathin, polymer-blend membranes (PBMs) as matrices for size-quantized semiconductor particles. Our work shows that miscible polymer blends provide an excel-

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