JOURNAL OF APPLIED POLYMER SCIENCE VOL. 18, PP. 3373-3377 (1974)

An Electron Diffraction Study of the Crystal Structure of Native Cellulose

JACQUES J. HEBERT and LINDA L. MULLER, *Southern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

Synopsis

The crystal lattice of native cellulose from four sources has been investigated by electron diffraction techniques. The four sources were: cotton, ramie, a bacterial cellulose (*Acetobacter xylinum*), and an algal cellulose (*Valonia ventricosa*). Evidence for the existence of at least two different unit cells is provided. There were no systematic absences of odd-order OkO reflections in any of the cellulose patterns, therefore, it was concluded that neither cellulose cell falls into the $P2_1$ space group.

INTRODUCTION

The crystal lattice of native cellulose has been a subject of study for many years. Cellulose I is that form of the crystalline polymorph which normally occurs in natural materials, e.g., cotton, ramie, wood pulp, etc., as opposed to cellulose II, which occurs in many chemical modifications of native cellulose. Examples of this form would be rayon or highly mercerized cotton fibers.

The monoclinic unit cell proposed by Meyer and Misch[1] has for many years been accepted as the unit cell of cellulose I; however, the results of the low-temperature electron diffraction study of *Valonia ventricosa* by Honjo and Watanabe[2] suggested that a modified form, in which the "*a*" and "*c*" axes of the cell are doubled, would be more nearly correct. Fischer and Mann,[3] also working with *Valonia*, confirmed the existence of this "super" lattice and further suggested a different space group symmetry. The Meyer-Misch cell assumes that the space group is $P2_1$ and that the molecular chains have a twofold screw symmetry. This condition requires that all odd-order OkO reflections be absent in the diffraction pattern. Several investigators, though not necessarily agreeing with the space group determination, seem to accept these systematic absences in the diffraction patterns of their materials.[4,6]

Ellis and Warwicker[6] also suggested a different unit cell, one based on the diagonals of the Meyer-Misch cell and having "*a*" and "*c*" axes with lengths similar to those in the Sponsler-Dore unit cell.[7] Variations in unit cell dimensions of cellulose samples from different sources were reported by Wellard[8] even before the advent of these so-called "super" lattices.

The purpose of the present report is to present evidence that verifies the existence of at least two unit cells in native cellulose. One, found in ramie and raw cotton fibers, closely approximates the classical model of Meyer and Misch; the other, evident in algal and bacterial cellulose, seems to indeed possess a superlattice. The data also clearly establish the presence of the odd-order OkO reflections regardless of type of sample or lattice.

EXPERIMENTAL

The celluloses studied were cotton, ramie, an algal cellulose (*Valonia ventricosa*), and a bacterial cellulose (*Acetobacter xylinum*). The cotton fibers were purified according to the ethanol extraction method of Conrad,[9] followed by boiling in 1% NaOH under nitrogen. The ramie was extracted with ethanol, then refluxed with monoethanolamine, and boiled in 1% NaOH. The *Valonia* was boiled in the caustic solution and then acid rinsed in 0.05*N* HCl. The bacterial cellulose was prepared according to the method of Colvin.[10] After purification, all specimens were washed with water and air dried.

Samples of each specimen were beaten in water in a laboratory blender until the fibers were fragmented into discrete bundles of fibrils in a slurry. Drops of this slurry were placed on uncoated copper 500-mesh electron-microscope grids and dried at room temperature under vacuum. The grids were studied in a Philips electron microscope (Model EM 300) equipped with a rotating and tilting stage and a specimen holder cooled

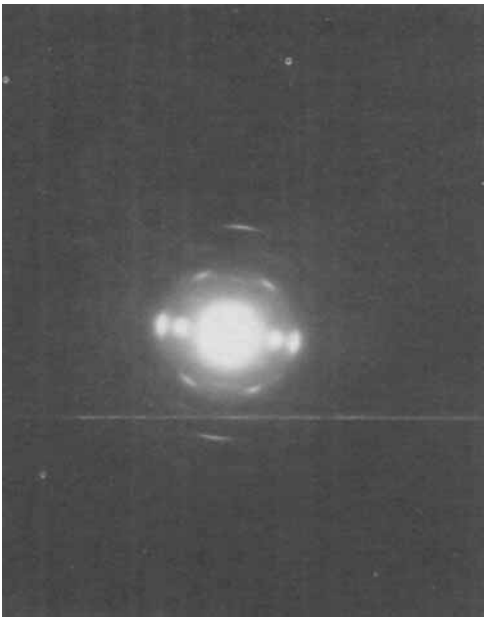

Fig. 1. Electron diffraction pattern of fragment of ramie cellulose fiber.

with liquid nitrogen. Each specimen was cooled to −130°C before exposure to the electron beam. Diffraction patterns were recorded photographically on glass plates. Spacings were measured with a glass ruler equipped with a dial indicator.

DISCUSSION

The electron diffraction diagrams of cellulose contain many more reflections than are normally found in x-ray patterns. In our original patterns of the four celluloses studied (photographic reproductions shown in Figs. 1, 2, 3, and 4), discrete reflections were visible out to the ninth layer line and, in many cases, numbered 50 or more per quadrant.

In all patterns, the reflections were smooth arcs reflecting the statistical distribution of the crystallites about the fiber axis.[11] As can be seen in the figures, this distribution is broader in the algal and bacterial celluloses than in the cotton and ramie. This indicates that the ramie and cotton celluloses are probably more highly oriented than the others.

Odd-order OkO reflections of significant intensity were found in patterns from all samples. In fact, the 030 reflection could easily be identified and indexed in all patterns. No systematic absences of odd-order OkO reflections could be discerned in any of the cellulose diffraction diagrams. Evidently, the requirements of a twofold screw axis are not met, and the cellulose space group is probably not $P2_1$.

As regards unit cell dimensions, the ramie and cotton reflections could be indexed by a unit cell quite similar to Wellard's[8] which closely approximates

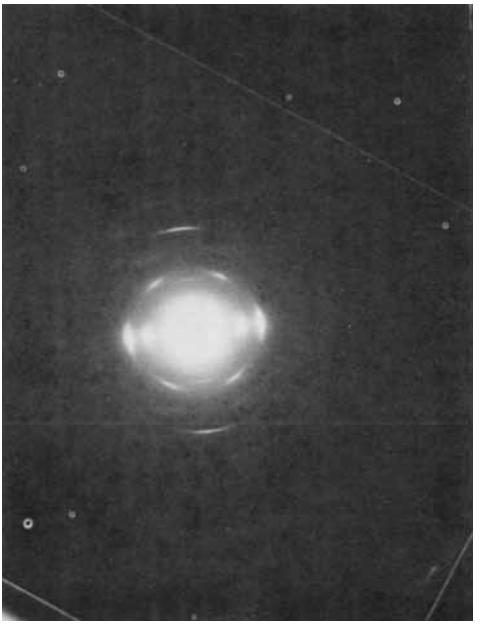

Fig. 2. Electron diffraction pattern of fragment of cotton cellulose fiber.

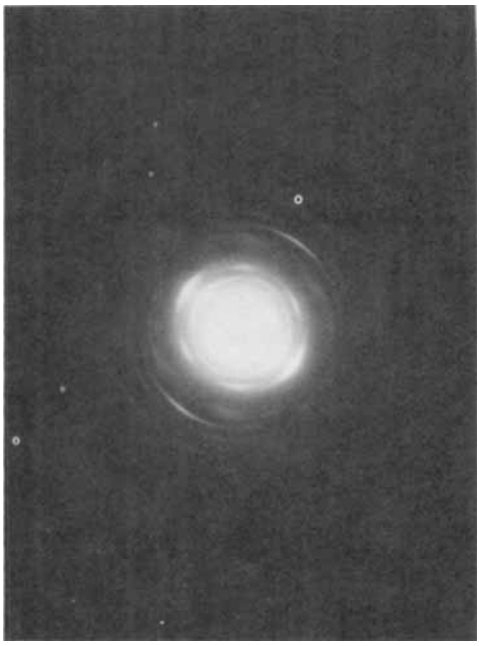

Fig. 3. Electron diffraction pattern of fragment of algal cellulose fiber (*Valonia ventricosa*).

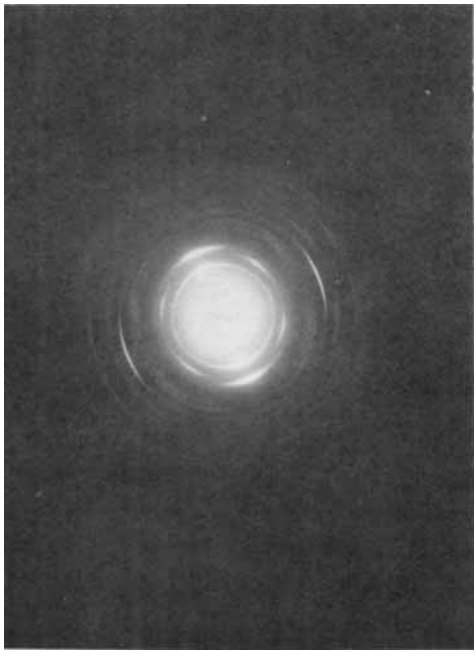

Fig. 4. Electron diffraction pattern of fragment of bacterial cellulose fiber (*Acetobacter xylinum*).

that of Meyer and Misch.[1] There were no arcs which could not be accounted for in either of these specimens by this unit cell. On the other hand, the algal pattern contained many reflections that could only be indexed by the lattice proposed by Nieduszynski and Atkins[12] for the algal cellulose *C. melagonium*. The bacterial cellulose patterns exhibited these same reflections, primarily about the third layer line and are, therefore, grouped with those of the algal cellulose. The reflections in these two types of cellulose patterns were completely indexed by this "super" lattice cell, which incidently coincides with the structure proposed for *Valonia ventricosa* by Honjo and Watanabe.[2]

The data from the present study indicate the existence of at least two polymorphs of cellulose in nature. One, which has a unit cell with a = 8.35 Å, b = 10.3 Å, c = 7.9 Å, and β = 84°, comprises the structure of ramie and cotton fibers. The other, which has the "a" and "c" axes doubled, is found in the algal cellulose *Valonia ventricosa* and the bacterial cellulose *Acetobacter xylinum*. Neither polymorph belongs to the space group $P2_1$.

The authors wish to express their appreciation to Dr. A. D. French for his valuable aid in measuring of spacings in the diffraction patterns, and to R. J. Schmidt for his help in obtaining the patterns.

Use of a company or product name by the Department of Agriculture does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

References

1. K. H. Meyer and L. Misch, *Helv. Chim. Acta*, **20**, 232 (1937).
2. G. Honjo and M. Watanabe, *Nature*, **181**, 326 (1958).
3. D. G. Fisher and J. Mann, *J. Polym. Sci.*, **42**, 189 (1960).
4. A. J. A. Van der Wyk and K. H. Meyer, *J. Polym. Sci.*, **2**, 583 (1947).
5. N. Norman, *Text. Res. J.*, **33**, 711 (1963).
6. K. C. Ellis and J. O. Warwicker, *J. Polym. Sci.*, **56**, 339 (1962).
7. O. L. Sponsler and W. H. Dore, *J. Amer. Chem. Soc.*, **50**, 1940 (1928).
8. H. J. Wellard, *J. Polym. Sci.*, **13**, 417 (1954).
9. C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **16**, 745 (1944).
10. J. R. Colvin, *J. Cell. Biol.*, **17**, 105 (1963).
11. J. J. Hebert, J. H. Carra, C. R. Esposito, and M. L. Rollins, *Text. Res. J.*, **43**, 260 (1973).
12. I. A. Nieduszynski and E. D. T. Atkins, *Biochim. Biophys. Acta*, **222**, 109 (1970).

Received May 6, 1974