Communications to the Editor

The Structure of Regenerated Cellulose

The structure of regenerated cellulose has been investigated by crystallographic methods, based on the intensity data for rayon fibers. The X-ray diffraction patterns were recorded on film and the intensities were measured using a scanning densitometer. The unit cell parameters obtained by least-squares refinement from the observed d spacings were a = 8.01 Å, b = 9.04 Å, c = 10.36 Å (fiber axis), and γ = 117.1°. These data are similar to those reported previously.[1]

The 001 and 003 reflections are absent and the space group is $P2_1$. If the individual chains have twofold screw axes, then the space group symmetry is satisfied if the chains have the same (parallel) or opposite (antiparallel) sense. Our strategy was the same as that used by Gardner and Blackwell[2,3] to determine the analogous cellulose I structure. Unit cell structures containing both parallel and antiparallel structures were refined to give the best fit between the observed and calculated structure factors, using the refinement methods of Arnott and Wonacott.[4] Standard bond lengths and angles[5] were used to determine coordinates for the cellulose chain, which had two glucose residues related by a 2_1 screw axis repeating in 10.36 Å. The chain had a glycosidic bond angle of 114.8° and an O3–H···O5′ intramolecular hydrogen bond of length 2.69 Å. This chain was completely rigid except for possible rotation of the $-CH_2OH$ side group about C5–C6.

Gardner and Blackwell[3] showed that in native cellulose, the rotational conformations of the $-CH_2OH$ groups are the same for both chains in the unit cell. For regenerated cellulose, however, study of the stereochemistry soon shows that the $-CH_2OH$ groups must have different conformations on center and corner chains, as was originally pointed out by Jones.[6,7]

For the meridional reflections, the 004 is intense while the 002 is weak, indicating an approximate quarter stagger of the chains. Thus four models need to be considered: (p1) parallel chains oriented "up" in the unit cell (Z(O5) > Z(C5)) with a stagger of approximately $+c/4$; (p2) parallel chains oriented "down" in the unit cell (Z(O5) < Z(C5)) with a stagger of approximately $+c/4$; (a1) antiparallel chains with an up chain at the origin and a down chain through the center, and a stagger of approximately $-c/4$; and (a2) a similar structure to a1 but with a stagger of approximately $+c/4$. The stagger refers to the separation of the glycosidic oxygens of the center and corner chains along the fiber axis.

These models were refined in terms of the following seven parameters: (1) stagger between center and corner chains (S); (2) rotation of the corner chain about the c axis (Φ); (3) rotation of the center chain about the axis through (½, ½, 0) parallel to c (Φ'); (4) rotational conformation of the $-CH_2OH$ group on the corner chain (χ); (5) rotational conformation of the $-CH_2OH$ group on the center chain (χ'); (6) an isotropic temperature factor (B); and (7) a scale factor (K).

These seven variables were refined for each of the four models to produce the best least-squares fit for the 44 observed nonmeridional reflections. This resulted in the following unweighted crystallographic R values: R_{p1} = 0.232; R_{p2} = 0.188; R_{a1} = 0.195; and R_{a2} = 0.171. Inspection of the coordinates for the refined models shows that only model a2 is stereochemically acceptable. Model p1 contains four unacceptable stereochemical contacts, and models p2 and a1 each contain two such contacts. Constraints were included in the refinement of these three models in an attempt to remove these deficiences. This led to some improvement in the stereochemistry (together with an increase in the respective R values), but in all cases the constraints could not be completely satisfied, i.e., some of the bad contacts were still present in each model.

Model a2 is the only structure which is stereochemically acceptable and is compatible with the X-ray data. Inclusion of the unobserved intensity data (for 43 unobserved reflections within the range of the observed data) produced only very minor changes in the model and maintained the good agreement between observed and calculated intensities. The ab and ac projections of the refined a2 model are shown in Figures 1 and 2. The relative stagger between the chains is $+0.216c$. The "down" center chain has the $-CH_2OH$ groups close to the gt position and forms an O6–H···O3 hydrogen bond to the neighboring down chain along the a axis. The O2–H groups on the down chain form O2′–H···O6 intrachain hydrogen bonds. Thus the down chains form sheets which are directly analogous to those in cellulose I. The "up" corner chains, however, have the $-CH_2OH$

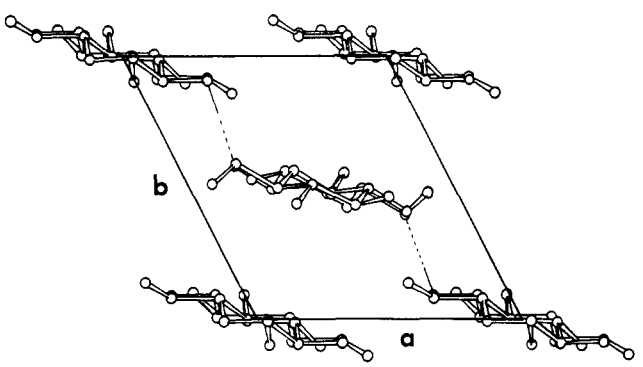

Figure 1. Projection of the cellulose chains down the c axis of the unit cell; the hydrogen bonding along the 110 plane is shown (only carbon and oxygen atoms are drawn in, and the hydrogen bonds are indicated by the partially dashed lines; the hydrogen position is given by the solid portion).

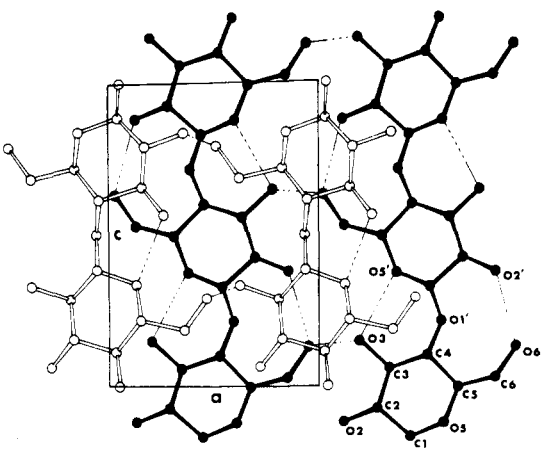

Figure 2. Projection of the chain perpendicular to the ac face of the unit cell. Intramolecular and intersheet hydrogen bonds are indicated by the dashed lines.

groups in the tg position and form O6–H···O2 hydrogen bonds to adjacent chains along the *a* axis. In addition, there is a hydrogen bond between the O2–H of the up chain at (1,0,0) and the O2′ of the center down chain (i.e., hydrogen bonding exists along the 110 diagonal of the unit cell).

Thus regenerated cellulose consists of an array of antiparallel chains, which is consistant with chain folding when the polymer is precipitated from solution, and with packing analyses.[8] Full details of this refinement will be published shortly. Work is currently in progress on mercerized cellulose to check whether the antiparallel chain structure is produced during solid state conversion of cellulose I → II.

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References and Notes

(1) H. J. Wellard, *J. Polym. Sci.*, **13**, 471–476 (1954).
(2) K. H. Gardner and J. Blackwell, *Biochim. Biophys. Acta*, **343**, 232–237 (1974).
(3) K. H. Gardner and J. Blackwell, *Biopolymers*, **13**, 1975–2001 (1974).
(4) S. Arnott and A. J. Wonacott, *Polymer*, **7**, 157–166 (1966).
(5) S. Arnott and W. E. Scott, *J. Chem. Soc., Perkin Trans. 2*, 324–335 (1972).
(6) D. W. Jones, *J. Polym. Sci.*, **32**, 371–394 (1958).
(7) D. W. Jones, *J. Polym. Sci.*, **42**, 173–188 (1960).
(8) A. Sarko and R. Muggli, *Macromolecules*, **7**, 486–494 (1974).

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