Texture of cellulose crystallized from hydrazine

E. D. T. Atkins*, J. Blackwell and M. H. Litt
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA

(Received 1 August 1978; revised 18 August 1978)

X-ray diffraction studies of cellulose fibres extruded from hydrazine solution indicate that the chain axes are arranged perpendicular to the fibre direction. The observed Bragg reflections index in the cellulose II lattice and the data is consistent with ribbon-like lamellae which have their $(1\bar{1}0)$ surfaces parallel to the fibre axis. The implication of these results to chain folding are commented upon.

INTRODUCTION

It has been reported by Litt[1] that cellulose will dissolve in hydrazine at elevated temperature and pressure. This finding offers scope to examine the recrystallization behaviour of cellulose together with the morphology, texture and properties of the regenerated material. A recent Note[2] from this laboratory describes the morphology of the regenerated material as seen using transmission electron microscopy. Two distinct types of morphology were reported: the majority of the regenerated cellulose occurred as mats of short, rod-like units together with a small proportion of thin fibres. Frequently these small units exhibited widths of 2 or 6 nm and lengths in the range 25–50 nm. Such units appeared to be quite novel and distinct compared with previously reported morphologies for other regenerated cellulosic systems and it was suggested that they may well be single crystals of cellulose. Kolpak and Blackwell[3] have recorded X-ray diffraction rings from unoriented hydrazine celluloses. Some of the reflections are characteristic of the cellulose II X-ray pattern[4], in particular the strong 110 and 020 reflections, at spacings of approximately 0.44 and 0.40 nm. However other reflections with observed spacings of 1.51, 0.92 and 0.51 nm seem to bear little relationship to any of the cellulosic polymorphs. In this contribution we report on attempts to orient regenerated cellulose from hydrazine and the discovery of a novel and interesting texture.

MATERIALS AND METHODS

A convenient starting material was a wood pulp preparation obtained from ITT – Rayonier, which had been delignified, bleached, and purified to remove hemi-cellulose. The preparation gave a powder X-ray diffraction pattern typical of cellulose I[5] and the assay reported a degree of polymerization (*DP*) of ~980. A 10% solution was prepared in hydrazine at 180°C under endogenous pressure for 90 min in a sealed glass pressure vessel. Fibres suitable for X-ray diffraction were prepared by allowing the hot viscous solution, at a pressure of approximately 60 p.s.i., to be forced through a long, narrow metal tube (internal bore 1 mm and arranged with its axis vertical) into air. The fibres emerging from the thin tube stretched and tapered under their own weight before hardening. Examination of the whole apparatus after cooling revealed films of regenerated cellulose deposited on the inner walls of the larger diameter tube connecting the thin tube and the pressure vessel. X-ray diffraction patterns were recorded for both the extruded fibres and the films using Ni-filtered CuKα radiation using conventional flat-plate cameras.

Once the fibres had cooled and the majority of the hydrazine dispersed they became quite brittle and attempts at further stretching were unsuccessful. In addition on some occasions the fibres were allowed to drop into water immediately after extrusion from the thin tube. Although these 'wetted' fibres remained flexible, no improvement in orientation was observed in the X-ray diffraction patterns from such fibres held under tension.

RESULTS AND DISCUSSIONS

A typical X-ray diffraction pattern, obtained with the X-ray beam directed perpendicular to the fibre axis, is illustrated in *Figure 1a*. At first glance the orientation is less than might be expected for drawn fibres. Unfortunately the difficulties of working with toxic and dangerous hydrazine at elevated temperature and pressure allowed little scope for further improvement in orientation with the apparatus available for these experiments. However, we hasten to add that the diffraction information is sufficient to measure the Bragg reflections with accuracy and to establish the relative orientations with confidence. Essentially three reflections dominate the X-ray pattern, the Bragg spacings and azimuthal orientations of which are given in *Table 1* together with the values reported for cellulose II[4]. These data clearly indicate that the cellulose crystallized from hydrazine correlates directly with the cellulose II crystal lattice. The interesting feature is that the three reflections are of the form *hk*0 and

---

* Visiting Professor 1977–78. Permanent address: H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, UK.

0032–3861/79/020145–04$02.00

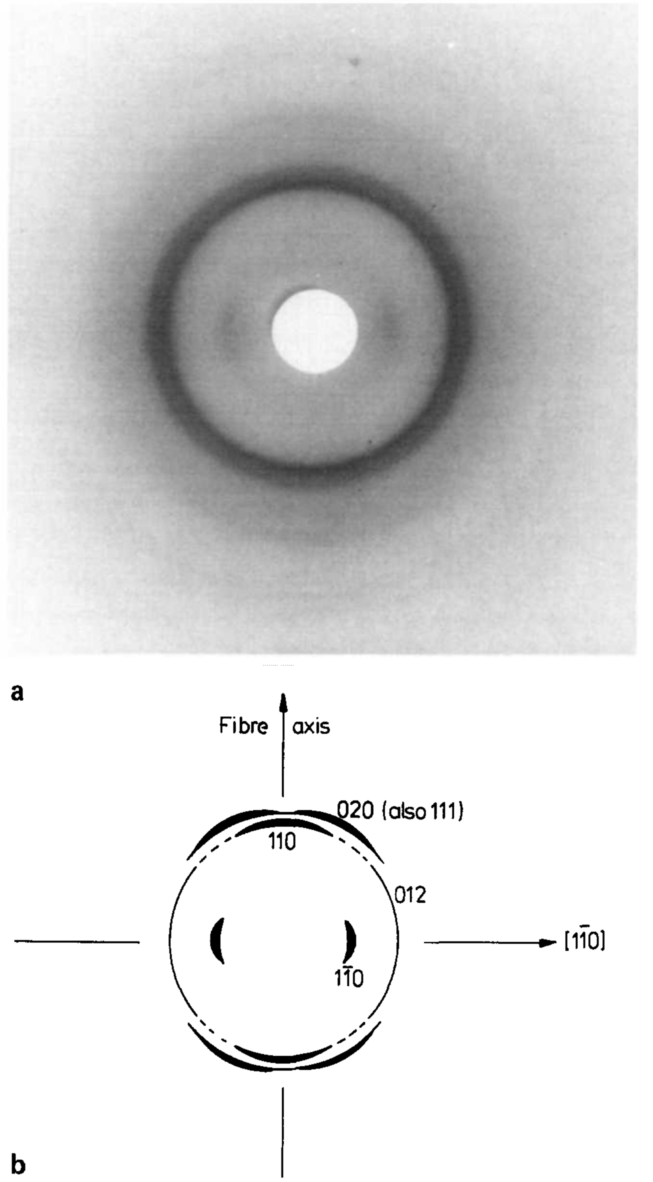

Figure 1 (a) X-ray diffraction pattern obtained from a fibre of cellulose hydrazine. The X-ray beam is directed perpendicular to the fibre axis which in this case is vertical. Similar patterns were obtained from films released from surfaces within the apparatus; (b) schematic version of (a) showing the relative azimuthal orientation of the three prominent reflections which index as the $1\bar{1}0$, 110 and 020 of cellulose II lattice[4]

lie at different azimuths about the direction of the incident beam (perpendicular to *Figure 1*)†.

The accuracy to which we can measure the Bragg spacings of these arcs leaves us in no doubt that they can be assigned as the dominant $1\bar{1}0$, 110 and 020 basal plane reflections of the cellulose II lattice[4]. The assignment of indices to these reflections means that the problem is one of orientation or texture, rather than of a structural nature. Thus the quality of the X-ray diffraction pattern (*Figure 1*) is quite sufficient to support the discussion presented in this paper. The relative orientations, although measured with less accuracy, support this assignment especially the angle between $1\bar{1}0$ and 110, which is close to 90°. This angle is 84° in the structure of cellulose II as may be seen in the *hk*0 reciprocal lattice net as shown in *Figure 2*. The above evidence favours a crystal geometry in which the cellulose chains run perpendicular to the fibre direction, or to the film surface for those samples stripped from the internal walls of the pressure vessel (see Materials and Methods). Two aspects of this novel discovery deserve attention. First, we need to consider the relationship between the crystal geometry and the overall fibrous texture of the fibres and films in a relatively straightforward manner. Secondly, questions arise concerning the possibility of chain folding and we wish to comment upon this topic.

Fibrous textures in which the molecular chains present themselves perpendicular to the stretch (or fibre) direction

Table 1 Comparison of the interplanar spacings of partly oriented cellulose crystallized from hydrazine with cellulose II

Cellulose crystallized from hydrazine		Cellulose II		
Spacings (nm)	Azimuthal orientation relative to equator	Spacings (nm)	Relative intensity	Lattice index
0.721	0°	0.718	S	$1\bar{1}0$
0.443	90°	0.444	VS	110
0.402	65°	0.405	VS	020

VS = very strong; S = strong

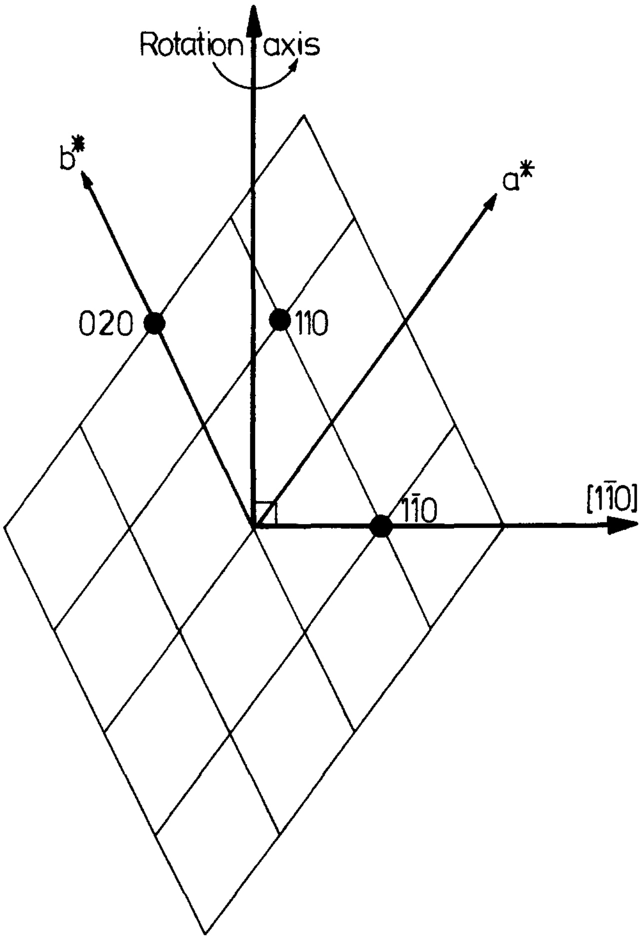

Figure 2 *hk*0 reciprocal lattice net for the cellulose II structure. The three principal reflections $1\bar{1}0$, 110 and 020 are marked. The lattice, when rotated about the perpendicular bisector of the [$1\bar{1}0$] direction represents the randomization of the lamellae about the fibre axis. The *c*,*c** axes and the direction of the X-ray beam pass through the origin perpendicular to the plane of the diagram. The diagram can also be used to judge where other reflections, in particular the 012 reflection, will intersect the Ewald sphere

---

† A schematic diagram providing the indexing and some fine detail lost in the reproduction from the original is shown in *Figure 1b*.

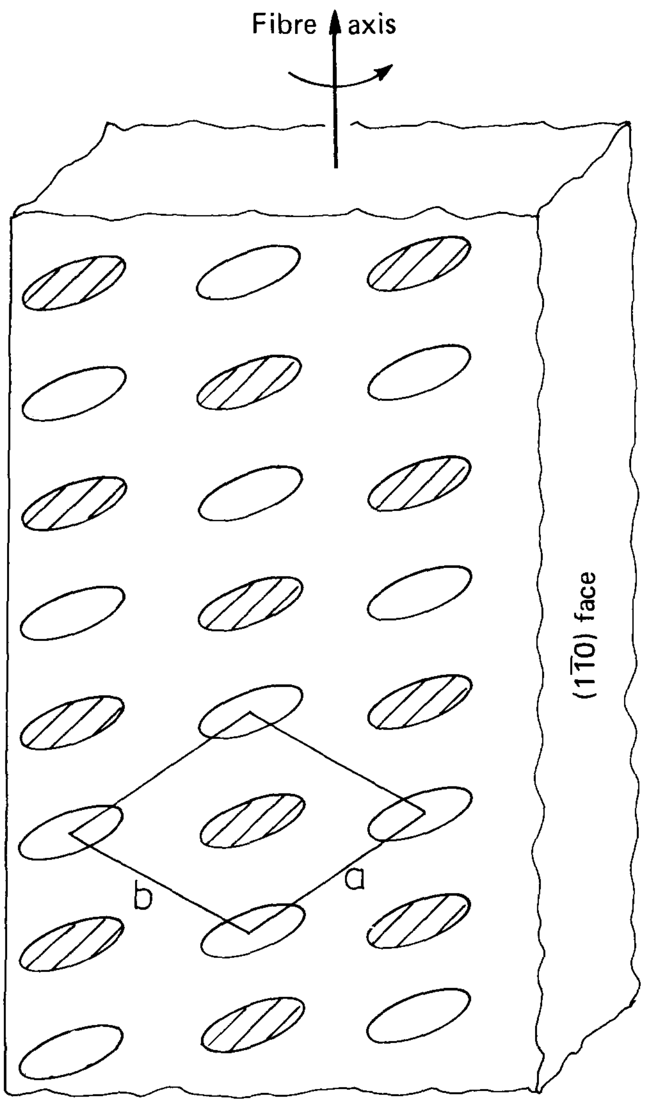

Figure 3 Schematic diagram showing the arrangement of chains within a ribbon-like lamella. The ellipses represent a view along the chain axis and the cross-hatching indicates chains of opposite polarity relative to the open ellipses

have been observed before in other polymeric systems[6–8]. Perhaps the most relevant to the present observation is the 'cross-β' protein structure discovered in the fibres drawn naturally by the green lace-wing fly *Chrysopa*[6]. In this case the polypeptide chains pack together to form long, thin ribbon-like lamellae. These lamellae are in random azimuthal orientation about their long azes which align parallel to the fibre direction, yet the polymer chains run transverse to the lamellar surfaces, i.e. perpendicular to the fibre axis.

Examination of the X-ray diffraction pattern (*Figure 1*) shows that the $1\bar{1}0$ reflection lies on the equator (the horizontal bisector). If the crystals are randomized about a direction perpendicular to the [$1\bar{1}0$], the positions of the other two arcs fall at predictable sites. The [110] direction is 84° (close to 90°) to the [$1\bar{1}0$] direction and would give rise to two closely spaced arcs, which would merge into one due to the poor orientation, centred on the meridian (see *Figure 2*). The 020 reflection would centre at an angle of ~65° to the equator in accordance with the observation. This seems the most straightforward explanation of the observed information and readily accounts for the longer arc length of the 110 reflection relative to the $1\bar{1}0$ and 020 reflections. The X-ray beam direction in *Figure 2* is perpendicular to the *hk*0 reciprocal net and the Ewald sphere will make contact at the origin and curve slowly away out of the plane at a radius of $1/\lambda$. Randomization about the fibre axis (*Figure 2*) will ensure that all three reflections cut the Ewald sphere and give rise to diffraction spectra.

So far we have only considered *hk*0 reflections. In addition we need to consider general *hkl* reflections, particularly those exhibiting strong intensity. The cellulose II structure[4] predicts a medium intense 012 reflection at 0.436 nm. This reflection would occur at an azimuth of 30° and offers an explanation for the slight intensification of the 0.44 nm ring as indicated in *Figure 1b*. In addition the 111 reflection with spacing 0.407 nm happens to fall on approximately the same site on the Ewald sphere as the 020 reflection and is therefore masked by that reflection. The 002 and 004 reflections at spacings 0.518 nm and 0.259 nm would be expected to fall on the equator, but no such reflections are observed. These absences are not too unexpected since in this particular case these reflections do not enjoy the large Lorentz correction factors that are applicable in the normal extended chain fibrous texture.

This texture correlates well with some recent electron microscopy and electron diffraction work by Buleon and Chanzy[9]. They have shown that single crystals grown from cellulose solutions exhibit ribbon-like lamellar morphology with the ($1\bar{1}0$) planes as the growth face. In fact *Figure 2* of ref 9 shows an electron micrograph of a ribbon-like single crystal with a shape and crystal geometry identical to what we envisage from our own independent analysis of the cellulose hydrazine pattern; in our case, however, such units are randomized about the perpendicular bisector of the [$1\bar{1}0$] direction. *Figure 3* shows the arrangement of the cellulose chains within a ribbon-like lamella. The morphological results of Kolpak and Blackwell[2] support rod- or ribbon-like units which we would expect to be the units which orient on extrusion.

In summary the X-ray diffraction results favour ribbon-like lamellae aligned with their long axes in the fibre (extrusion) direction. The molecular chains run perpendicular to the lamellar surfaces and therefore the fibre axis. The X-ray diffraction evidence alone is unable to distinguish between the two possible models:

(a) where the cellulosic chains fold within the lamellae, a morphology encountered in other polymers[7,8,6], or

(b) where straight chains traverse the lamellae, the thickness of which is a measure of the *DP*.

ACKNOWLEDGEMENTS

This research was supported by NSF (Polymer Program) Grant No. DMR 76-82768 (to J. B.).

REFERENCES

1 Litt, M. paper presented at the American Chemical Society, New York City, March 1978, Litt, M., Kumar, N. G., Hughes, D. A. and Shimko T. in preparation
2 Kolpak, F. J., Blackwell, J. and Litt, M. H. *Polym. Lett.* 1977, **15**, 655–658
3 Kolpak, F. J. and Blackwell, J. 1978 in press
4 Kolpak, F. J. and Blackwell, J. *Macromolecules* 1976, **9**, 273–278
5 Gardner, K. H. and Blackwell, J. *Biopolymers* 1974, **13**, 1975
6 Geddes, A. J., Parker, K. D., Atkins, E. D. T. and Beighton, E. *J. Mol. Biol.* 1968, **32**, 343–358
7 Geil, P. H. 'Polymer Single Crystals', Interscience, New York, 1963
8 Keller, A. *Rep. Prog. Phys.* 1968, **31**, 623–704
9 Buleon, A. and Chanzy, H. *J. Polym. Sci. (Polym. Phys. Edn)* 1978, **16**, 833–839