JOURNAL OF APPLIED POLYMER SCIENCE VOL. 16, PP. 1305–1308 (1972)

Chain Conformations in Cellulose I and Cellulose II*

B. R. MANJUNATH† and N. PEACOCK, *Department of Fibre Science, University of Strathclyde, Glasgow, C.1, Scotland*

Synopsis

There is strong evidence in the literature that cellulose chains have different conformations, as well as forming different crystalline lattices, in cellulose I and cellulose II. New data on the birefringence of amine-treated fibers (cellulose III) support this view.

INTRODUCTION

Cellulose is polymorphous; at least five modifications have been distinguished by x-ray diffraction patterns. The irreversible crystallographic change which takes place upon alkali swelling of native cellulose has often been held to be the result of a simple skewing of the original lattice involving individual chains[1] or coherent "sheets,"[2] and resulting in a less dense packing. On recrystallization from solution, however, the formation of cellulose II is most favored, and formation of cellulose I starting from cellulose II has never been observed. Furthermore, Marrinan and Mann[3,4] have shown that cellulose III and cellulose IV, prepared from cellulose I, are similar to their parent; and likewise, when prepared from cellulose II, they are similar to cellulose II, in certain bondings. It therefore appears that there is some inherent difference between cellulose I and cellulose II, of which the differences between their lattices is a reflection and not a cause. This difference is most probably one of chain conformation.

The two models proposed are shown in Figure 1: (a) the straight-chain Meyer and Misch model[5] and (b) the bent-chain Hermans model.[1] Both conform to the accepted axial repeat of 10.3 Å, but the Hermans model is the one of lower energy,[6] and, because it also agrees well with evidence for intrachain hydrogen bonding,[4] it has often been preferred for both modifications. However, Petitpas et al.[7] have concluded from x-ray evidence that cellulose I may contain chains of type a, and cellulose II, chains of type b. From energy considerations, Chü[8] has also concluded that there are different chain conformations in the two modifications.

The birefringences of native and mercerized fibers have been shown to be different.[9] Hermans observed that, at the same orientation, the bire-

* This work forms part of a thesis submitted to the University of Strathclyde for the degree of Ph.D. by B. R. M. in 1969.

† Present address: The Bombay Textile Research Association, Agra Road, Ghatkopar, Bombay 86 (AS), India.

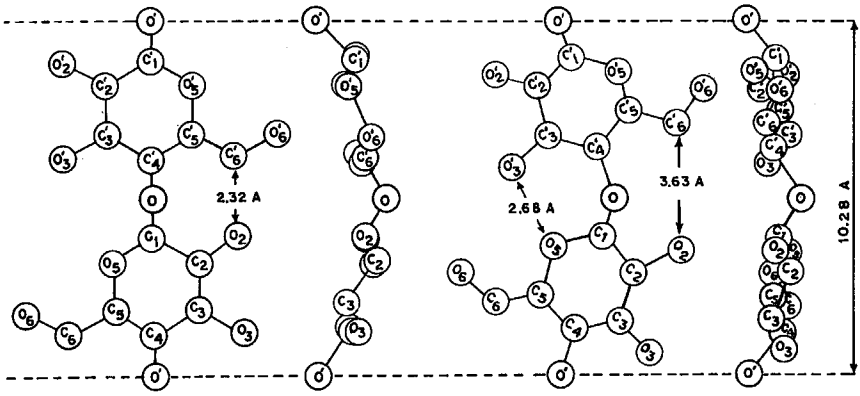

Fig. 1. Proposed models: (a) straight-chain from Meyer and Misch[5]; (b) bent-chain from Hermans.[1]

fringence of cellulose I fibers was 0.071 and that of cellulose II fibers was 0.055. Even after reducing these values to correspond to the standard density of 1.520 g/cc, their difference was 0.014. Since the difference in density between the two lattices is only 0.009 g/cc and there is no difference in chemical composition, this large difference in polarizability most probably results from differences in chain conformation. Therefore, the ideal solution to the problem is to impart the same lattice to native and mercerized fibers without changing their orientation and to compare their respective optical constants. Conversion of native and mercerized cellulose to the cellulose III modification appears to fulfil this condition.[3,4]

EXPERIMENTAL

Native cotton fibers (Sea Island type) and repeatedly mercerized fibers were treated with anhydrous ethylamine at 0°C for 4 hr. The amine was then allowed to evaporate slowly under reduced pressure for 2 hr at 0°C, and later at a higher temperature. The orientations of the two lots of fibers, measured before and after treatment, did not alter significantly, the Ψ^{-1} value being around 0.034 (Ψ is the 40% x-ray angle). Some workers are of the opinion that the azimuthal dispersion of the interferences in the x-ray diagram is an index of the orientation in the crystalline regions only and that this may differ from the overall orientation, which is indicated by the birefringence.[1] For a paracrystalline lattice, however, this ambiguity does not arise, and our own studies on cotton cellulose indicate that the x-ray measurements may be used to characterize the overall orientation. In this instance, therefore, it remains constant.

Refractive index measurements were made on the fibers using the Becke line method; the results are presented in the Table I. It will be seen that the difference between the birefringences of the two amine-treated samples is quite considerable. Certainly the x-ray patterns indicated that some cellulose I and cellulose II remained in the respective samples, but these

TABLE I
Refractive Indices of Native and Mercerized Fibers Before and After Ethylamine Treatment

Sample	$\eta_\parallel$	$\eta_\perp$	$\eta_\parallel - \eta_\perp$
Native cotton (cellulose I)	1.5782	1.5306	0.0476
Mercerized cotton (cellulose II)	1.5635	1.5285	0.0350
Amine-treated native cotton (cellulose III_I)[a]	1.5705	1.5282	0.0423
Amine-treated mercerized cotton (cellulose III_{II})[a]	1.5565	1.5225	0.0340

[a] Following the notation of Mann and Marrinan.[4]

remnants could not have produced this difference in birefringence. Therefore, it appears that cellulose III_I and cellulose III_{II} do differ in birefringence.

DISCUSSION

If the cellulose I conformation were that of the straight-chain Meyer and Misch model, and the cellulose II conformation that of the bent-chain Hermans model, it would be expected that the birefringence of cellulose III_I would be greater than that of cellulose III_{II}, and also that $\eta_\parallel$ would be greater for the former than for the latter. To this extent the present results support this assignment of conformations. But without knowledge of the bonds involved, it is difficult to proceed with any quantitative discussion. Chu[8] argues in favor of a difference in the orientation of the C-6 hydroxyl groups, which might create differences in the hydrogen bonding in the two conformations. However, the work of Sprague et al.[10] shows that native cellulose, even on complete acetylation, may retain a "memory" of the cellulose I lattice, which reappears on saponification. This implies that any conventional type of intrachain hydrogen bonding scheme involving the hydroxyl groups will not suffice to stabilize the cellulose I conformation. The two forms of cellulose III provide suitable material for further physical investigations into these conformations.

References

1. P. H. Hermans, *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949.
2. J. O. Warwicker and A. C. Wright, *J. Appl. Polym. Sci.*, **11**, 659 (1967).
3. H. J. Marrinan and J. Mann, *J. Polym. Sci.*, **21**, 301 (1956).
4. J. Mann and H. J. Marrinan, *J. Polym. Sci.*, **32**, 357 (1958).
5. K. H. Meyer and L. Misch, *Helv. Chem. Acta*, **20**, 232 (1937).
6. D. A. Rees and R. J. Skerrett, *Carbohyd. Res.*, **7**, 334 (1968).
7. T. Petitpas, M. Oberlin, and J. Mering, *C. R. Acad. Sci. Paris*, **244**, 346 (1957).

8. N. J. Chu, *J. Appl. Polym. Sci.*, **14**, 3129 (1970).
9. P. H. Hermans, *Contribution to the Physics of Cellulose Fibres*, Elsevier, New York, 1946.
10. B. S. Sprague, J. L. Riley, and H. D. Noether, *Tex. Res. J.*, **28**, 275 (1958).

Received August 16, 1971
Revised December 19, 1971