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Preliminary communication

Raman-spectral evidence for differences between the conformations of cellulose I and cellulose II

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One of the questions outstanding with regard to the structure of cellulose centers on the conformation of the molecular chains in the ordered regions and whether the chains possess the same conformation in cellulose I and cellulose II[1,2]. The evidence that a twofold screw-axis is an element of the symmetry of the unit cell is thought convincing by many; there is uncertainty, however, concerning its coincidence with the chain axis. Conformational-energy computations have indicated that two-fold screw conformations have energies somewhat higher than those of immediately neighboring conformations that depart from this symmetry[3]. Extensive analyses of electron-density distributions from X-ray diffractometric studies have suggested that the chain conformations of celluloses I and II are indeed different[4], whereas others, equally comprehensive, have been interpreted as indicating that the conformations are similar[5]. The differences between the infrared spectra of the two polymorphs above 700 cm^{-1} can, and have been, rationalized in terms of differences between hydrogen-bonding patterns[6]. We present preliminary results of studies of the Raman spectra of celluloses I and II which we believe can only be interpreted in terms of different conformations involving different orientations about the β-D-(1→4)-glycosidic linkage.

Raman spectra of highly crystalline samples of celluloses I and II* are compared in Fig. 1. The outstanding feature in the comparison is the occurrence of significant differences between the spectra in the low-frequency region. The changes in the spectra upon conversion from form I into II are quite consistent, and have been used as the basis for developing an index of the degree of conversion in partial mercerization experiments[8]. In contrast, the changes in the region between 800 and 1500 cm^{-1} are relatively minor.

The low-frequency region of the spectra, where most of the changes occur, is associated

*The cellulose I sample was regenerated by the procedure reported in ref. 7. Its Raman spectrum is very similar to those of highly crystalline native celluloses; it is used in the present comparison because the spectral features are somewhat better resolved. The cellulose II was a low-d.p. sample selected because of its high crystallinity and its very low level of residual cellulose I.

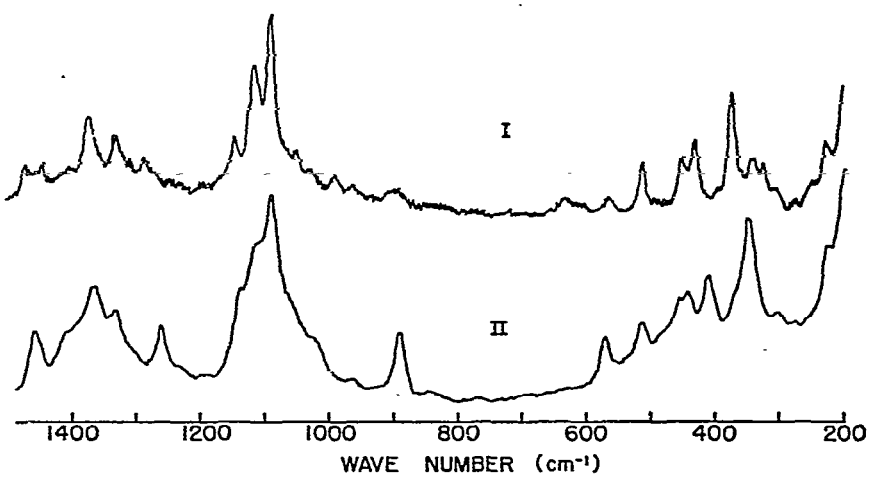

Fig. 1. Raman spectra of highly crystalline samples of celluloses I and II.

with skeletal-angle bending vibrations[9]. Studies of the effects of conformation on the spectra of carbohydrate molecules indicate that changes similar to those indicated in Fig. 1 may be anticipated when conformational changes occur[10]. Thus, a difference in conformation is suggested by the differences between the spectra of the two celluloses. The basic ring-structure is not expected to change. Nor is rotation of the CH_2OH side-chain likely to contribute to the spectral changes below 500 cm^{-1}. It appears, therefore, that change in the orientation of the glycosidic linkage relative to the D-glucose residues is the only credible explanation. The plausibility of this explanation has been explored by examination of the G matrix in the formulation of the normal-coordinate problem for analysis of the vibrations of cellulose, based on the Wilson GF matrix-method[11]. The matrix elements affected by changes in the dihedral angles about the two bonds in the glycosidic linkage are indeed those related to coupling of angle-bending vibrations. Furthermore, calculations on model compounds indicate that changes in the dihedral angles, which are consistent with other structural data, can result in spectral changes of the magnitude observed. In contrast, effects on the stretching vibrations are secondary, and occur through other coupling terms. This, in turn, is consistent with the observation that changes in the skeletal stretching-vibration region of the spectra are relatively minor.

The suggestion of different conformations for celluloses I and II does not preclude the differences in hydrogen-bonding patterns inferred from the infrared spectra. It must be emphasized, however, that differences in the hydrogen-bonding patterns cannot explain the spectral differences appearing in Fig. 1 in the low-frequency regions.

The studies under way, to be reported in the near future, cover quite broadly the effect of polymorphic changes on the Raman spectra of celluloses. In no instance have the results been inconsistent with the interpretation suggested here.

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