Molecular Conformations of Chitin and Chitosan

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Summary
Molecular and crystal structures of chitin and chitosan analyzed so far by x-ray diffraction method are introduced. The crystal structure of chitin I (α-chitin) was reconfirmed by an electron diffraction study. Inclusion complexes of chitin II (β-chitin) with alcohols and other materials are also presented. Two crystalline polymorphs of chitosan have been analyzed. One, the most abundant and termed the tendon chitosan polymorph, is a hydrated form. The second, annealed chitosan prepared by heating the tendon chitosan in the presence of water at a high temperature around 200°C, is anhydrous. With both polymorphs the chitosan molecule adopts the same conformation, an extended two-fold helix which is stabilized by an intramolecular O(3)---O(5) hydrogen bond, similar to those of chitin and cellulose. Three chitosan conformations other than the 2/1 helix have been found with crystals of chitosan-acid salts. In the salts with L-ascorbic acid and some other acids, so called type I salts, the chitosan molecule retains the extended two-fold helical conformation. On the other hand, chitosan salts of type II take up a relaxed two-fold helix composed of an asymmetric unit of tetrasaccharide. This conformation appears to be unstable because of the lack of any strong intramolecular hydrogen bond like that in the extended two-fold helix. Type II salts demonstrate change to a similar crystal structure as annealed chitosan (the extended two-fold helix) by spontaneous loss of the acid accompanied by a water molecule. Chitosan molecule of HI salt prepared at low temperature (4°C) exhibits a 4/1 helix with an asymmetric disaccharide unit. The fourth chitosan conformation has been demonstrated to be a 5/3 helix, observed with medical organic acid having phenyl groups such as salicylic, gentisic or acetylsalicylic (aspirin) acid. This conformational flexibility of chitosan is clearly due to the presence of the free primary amino groups on the molecule.