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23 September 1966

Crystal Structure of Amylose Triacetate: A Nonintegral Helix

Abstract. *The x-ray diffraction diagram of an oriented fiber of amylose triacetate I, presenting evidence for a nonintegral helical structure, was analyzed by a model and by Fourier transform calculation. The results suggest a helical structure with 4.67 ± 0.02 residues per one turn of the helix, which appears to be left-handed.*

In studying x-ray diffraction diagram of amylose triacetate, whose crystalline form was first observed by Whistler and Schieltz (*1*), we noted evidence of helical conformation of the polymer chain. As fiber diagrams usually contain a minimum of information regarding the structure of the polymer, this indication presented an attractive starting point for an attempt to solve the crystal structure of amylose triacetate.

Amylose, the linear polymer of α-1, 4-D-glucose which occurs in starch, is easily acetylated by means of a nondegradative procedure (*2*). The triacetate can be cast into a film from chloroform solution. The film is partly crystalline and may be oriented by stretching in glycerol at 160°C to an extension of at least 500 percent (*1*). An x-ray diffraction diagram of this structure, termed amylose triacetate I, taken with CuKα radiation on flat film with the x-ray beam perpendicular to the surface of the film (Fig. 1), indicates a high degree of parallel orientation of the crystallites and shows the typical features of scattering from a helical structure: an x-shaped distribution of intensities about the center of the diagram and a single strong reflection on the equator, suggestive of hexagonal close packing. Some degree of translational disorder in the structure is indicated by streaking of reflections on layer lines other than the equator. The lack of streaking on the equator shows the absence of variation in the lateral distance between the chains.

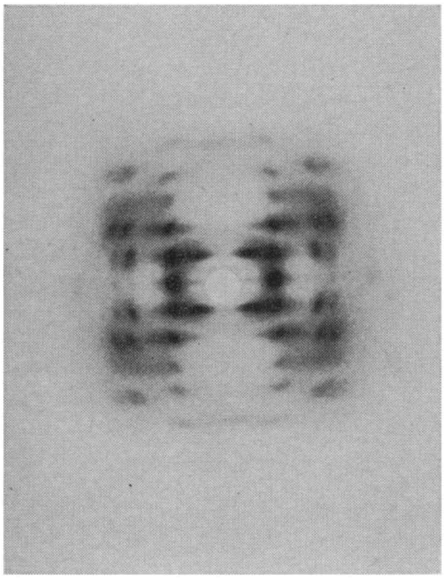

Fig. 1. X-ray diffraction diagram (flat film) of an oriented film sample of amylose triacetate I. CuKα radiation; flat-film vacuum camera; film-to-sample distance, 5 cm; x-ray beam perpendicular to surface of sample; and fiber axis vertical.

Quantitative appraisal of this diagram, as well as of others taken with the sample inclined with respect to the primary x-ray beam, showed the following: (i) the packing of chains is indeed hexagonal, with the lateral distance between chains 10.87 Å; (ii) although all reflections fall on clearly resolved layer lines, the separation of layers in reciprocal space is not constant and cannot be accounted for with a single fiber repeat (Fig. 2A); (iii) there is only one meridional reflection present. These data indicate that the amylose triacetate chain is helical and that the helix is nonintegral; that is, within one turn of the helix there is no structural repeat. The advance (axial thrust) per turn is 17.6 ± 0.2 Å, as obtained from the first-layer line spacing, and the advance per residue is 3.64 ± 0.06 Å, as obtained from the meridional reflection. The ratio 17.6/3.64 indicates that the number of residues per turn of the helix is in the vicinity of 4.8 to 4.9.

Scale models of such a helix were constructed for both the left-handed (*3*) and the right-handed case (the handedness of the helix could not be determined from the x-ray diagram), and both conformations proved stereochemically sound, although the left-handed helix seemed more probable on the basis of better cylindrical symmetry and a higher degree of compactness.

The essential agreement between the scale models and the above interpretation of the fiber diagram prompted a more quantitative examination of the proposed structure, as the monomers-per-turn ratio was still approximate and the handedness of the helix could not be determined from the scale models only. This examination took the form of the calculation of Fourier (or molecular) transforms. Since the molecular transform is essentially the diffraction diagram of one molecule, it is of value in a quick comparison of the scattering from an assumed molecular conformation and the observed diffraction diagram. The calculation of molecular transforms for helical structures is relatively easy, as one needs only the cylindrical coordinates of the atoms of one asymmetric unit of the helix (in most instances one monomer residue) and not the relative positions of the atoms with respect to the crystallographic unit cell, as required by the ordinary structure factor calculations. The intensity, *I*, at any point in the helix transform is given by the following expression (*4*):

$$I \propto F^2 \tag{1}$$

$$F(R, \psi, \zeta) = \sum_n \sum_j f_j J_n(2\pi r_j R) \times \exp\left[i\{n(\psi - \phi_j + \pi/2) + 2\pi z \zeta\}\right] \tag{2}$$

where $F(R, \psi, \zeta)$ is the Fourier transform at a point in reciprocal space with cylindrical coordinates R, ψ, ζ; r_j, ϕ_j, z_j are the cylindrical coordinates of the jth atom; $J_n(2\pi r_j R)$ is the nth-order Bessel function (whose value is determined by the argument in parentheses); and f_j is the scattering factor for the jth atom.

The calculation of the above transform is facilitated by casting it in the following form which is suitable for computer calculation (5):

$$A_n = \sum_j f_j J_n(2\pi r_j R)\cos[n(\pi/2 - \phi_j) + 2\pi z\zeta] \quad (3)$$

$$B_n = \sum_j f_j J_n(2\pi r_j R)\sin[n(\pi/2 - \phi_j) + 2\pi z\zeta] \quad (4)$$

$$F^2_{\bar{\psi}}(R,\zeta) = \Sigma(A^2_n + B^2_n)$$

$\bar{\psi}$ represents angular independence of (F^2). Since the transform is finite only in planes at height

$$\zeta = n/P + m/p \quad (5)$$

where P is the axial translation of one turn of the helix, p is the axial translation of one monomer, and n and m are appropriate integers (4), the transform need be calculated only for those planes. As the values of P and p, previously determined from single-layer lines, were not sufficiently reliable, they were redetermined by a least-squares fit of the experimental values of ζ for all layers, the integer combinations $m = 0$, $n = 1, 2, 3$, for the first three layers, and $m = 1$, $n = -2, -1, 0, 1$ for the next four layers. The resulting values were $P = 17.51 \pm 0.06$ and $p = 3.75 \pm 0.07$, from which the monomer ratio per turn of the helix is 4.67 ± 0.02. This is almost exactly 14 monomers per 3 turns of the helix; consequently, for convenience the transforms were calculated for exact 14/3 helices.

The coordinates of the atoms were calculated by assuming standard bond lengths and angles (6) and the chair conformation for the glucose ring (7). The most probable positions of the ring and the acetate groups were chosen by visual inspection of scale models. All coordinates were calculated on the computer, and those used for the calculation of the left-handed 14/3 helix are given in Table 1. The calculated transform for the same helix is shown in Fig. 2B.

Table 1. Cylindrical coordinates of the atoms of one glucose triacetate residue in a 14/3 left-handed helix.

Atom*	r (Å)	Ø (degrees, relative to x-axis)	z (Å)
C1	2.712	−26.214	3.220
C2	3.199	2.245	3.027
C3	2.630	22.866	2.043
C4	2.079	5.880	.781
C5	1.808	−38.305	1.193
O5	2.945	−38.624	1.993
O2	3.404	13.146	4.251
C2′	4.706	18.764	4.264
O2′	5.406	16.391	3.287
C2″	5.362	25.832	5.512
O3	3.843	33.303	1.689
C3′	4.330	46.328	2.558
O3′	3.712	53.765	3.472
C3″	5.827	50.012	2.389
O4	1.508	38.571	0.000
C6	2.224	−60.753	−.067
O6	1.638	−96.905	−.498
C6′	2.401	−101.789	−1.611
O6′	3.144	−83.944	−2.069
C6″	2.874	−130.365	−2.295

* The nomenclature of the atoms in one residue is the following. Ring carbons are numbered from 1 to 5, with all side-group atoms bearing the same number as the ring carbon atom to which the side group is attached. The primes and double primes indicate the atoms of the acetate groups.

From the comparison of the transform and the x-ray diffraction diagram (or the schematic in Fig. 2A), almost all features of the x-ray diagram are correctly predicted by the transform. Unfortunately, the right-handed transform predicts the same features equally well, thus a conclusion regarding the handedness of the helix could not be reached. Otherwise, in view of the good correspondence in the gross features of the diagram and the transform it may be concluded that the 14/3 helix model is a reasonable model for the structure of amylose triacetate I.

The atomic parameters given in Table 1 are only approximate in that they were arrived at by use of several assumptions; thus the substitution of correct atomic parameters would change the appearance of the transform significantly along the layer lines. Such a change in the parameters would not, however, significantly change the appearance of the helix.

In all likelihood the true structure is not a strict 14/3 helix; as in the latter case one might expect some intensity in the x-ray diagram between the observed layer lines, as predicted by the transform; however, in no case was such intensity observed. Probably the true structure is really nonintegral in the sense that there is no repeat whatsoever in the direction of the fiber. This assumption is substantiated in part by the finding that the amylose triacetate I helix is readily and irreversibly transformed to a new crystalline polymorph—amylose triacetate II—by heating in glycerol to 240°C. This crystal form has a true fiber repeat of 16.95 Å, and since the transformation occurs with little gross sample shrinkage a related molecular helix must be also involved (8).

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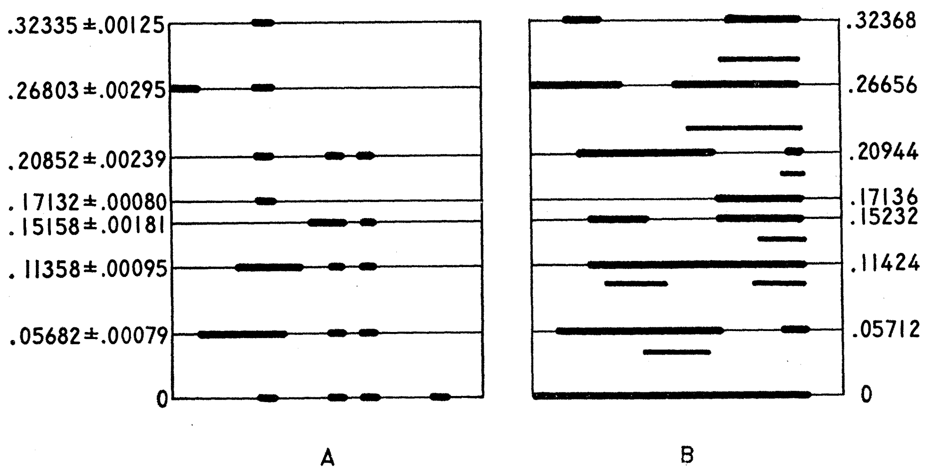

Fig. 2. (A) Schematic of the x-ray diagram of Fig. 1 (only the upper right quadrant is shown). The lines indicate the positions of the layer lines, with the corresponding experimental ζ values (in $Å^{-1} \pm$ S.D.) shown on the left of each line. (B) Calculated helix transform for a left-handed 14/3 helix (only the quadrant corresponding to part A is shown). Computed ζ values are given on the right of the layer lines, and the areas of significant predicted intensity are shown in black.

References and Notes

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