Structure of potassium bromide–amylose determined by accurate X-ray diffraction intensities

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This communication relates the determination of the structure of the fibrous polymer KBr–amylose by X-ray diffraction techniques to a reliability index of 0.68.

This system has been studied previously by Senti and Witnauer[1] using intensity values estimated from diffraction films. They were able to determine the space group, $P4_32_12$ (D_4^8) and approximate cell constants and determined approximate positions of the potassium and bromine atoms from Patterson section calculations. Fourier projections failed to show individual ring atoms but did disclose the helical chain conformation of the polymer.

Jackobs, Bumb and Zaslow[2] re-evaluated the same film data, establishing a more uniform and wide range of intensity values. The K and Br positions were re-determined. Fourier maps again failed to show individual atoms. Space-filling CPK models were constructed and packing criteria used to reject all but a single model. X-ray diffraction intensities were calculated and compared with observed values. The reliability index

$$R = \frac{\Sigma ||F_{\text{obs}}|-|F_{\text{calc}}||}{\Sigma |F_{\text{obs}}|}$$

was used as the criterion for selecting helix orientation. A single temperature factor, $B = 2.00$ was assigned to all atoms. The final value of R was 0.41.

For our study, we obtained a small amount of the original sample batch prepared by Senti and Witnauer. A fibre bundle of parallelopiped shape 79 μ x 79 μ x 300 μ was mounted on a Buerger precession camera. Intensity data were collected for 48 h in a He atmosphere (Cu target, Ni filter, 35 kV, 15 mA) to a distance of $\sin\theta/\lambda = 0.3$ Å^{-1} in reciprocal space. From measurements on the films as developed, the space group of Senti and Witnauer was confirmed. The films were measured by step-scan on a microphotometer. The transmission of a quadrant of a film was measured at a resolution of 10 μ x 10 μ in steps of 500 μ. The quadrant of data was stored on disc file as a 101 x 101 data array. Background values (from data array locations between intensity maxima) were used to fit a Gaussian background scatter function[3]. Values of the function, calculated at all array points, were subtracted from the array, effectively removing the background. Lorentz, polarization and absorption corrections (all calculated to an accuracy greater than the 4 parts in 5000 accuracy of the microphotometer) were applied to each data array value. A fibre rotation factor was applied to each array value (a precession camera samples a planar slice (the meridion lies in the plane) of the cylindrical diffraction transform). Data arrays for three quandrants were then averaged. A least-squares determination of cell constants was made at this stage of calculation. These were $a = b =$ 10.55 Å and $c = 16.12$ Å.

Individual intensity maxima in the data array were isolated in sub-arrays of about 18 x 18. A final background removal calculation was performed on each. A double plane function was fitted to the values at the sub-array perimeter. Values calculated from the double-plane function were subtracted from each sub-array point value. The sub-array was smoothed by fitting cubic splines across rows and columns to a least-squares residual of 0.0075 and numerically integrated to a residual of 0.01. From the large data array, 55 accurate reflection intensities were determined. The set includes 11 intensities not listed by Senti and Witnauer. Some, i.e. (116), (126) and (127), all quite strong, appear on their diffraction photograph (their Figure 3). The (004), very strong, was unobservable by their measurement technique. Some 20 intensities, 1 W$^+$, 14 W and 25 W$^-$ were not observable in our precession photographs. A few, (010), (110), (011) and (111), are obscured by our beamstop. The rest could not be extracted from background.

Patterson sections calculated at the $z = 0$, 0.25 and 0.5 levels accurately determined the potassium position as 0.56, 0.56, 0.00 and the bromine position as 0.25, 0.25, 0.00. These positions were used to calculate E-sections. As poly-

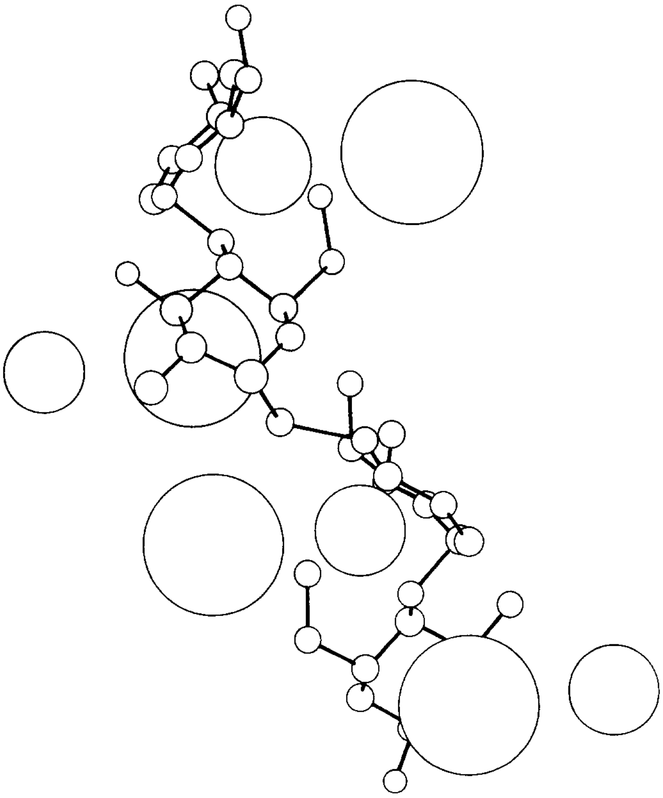

Figure 1 View of amylose chain and KBr along the *b* axis. The chain atoms are drawn to 50% probability thermal circles. The K and Br atoms are drawn at half their atomic radii so as not to obscure the chain

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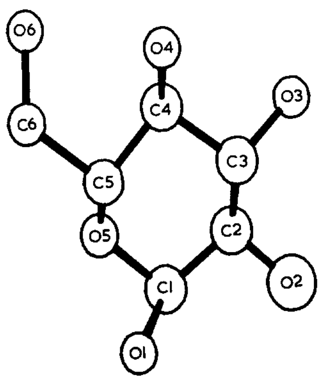
Table 1 Isotropic temperature factors, bond angles and bond lengths



Isotropic temperature factors	(Å)	Bond angles	(degrees)	Bond lengths	(Å)
C_1	4.00	$O_1-C_1-C_2$	111	C_1-O_1	1.53
C_2	4.00	$O_5-C_1-O_1$	110	C_1-C_2	1.50
C_3	4.00	$O_5-C_1-C_2$	108	C_2-O_2	1.44
C_4	4.00	$C_1-C_2-O_2$	108	C_2-O_3	1.52
C_5	3.62	$C_1-C_2-C_3$	119	C_3-O_3	1.44
C_6	3.19	$O_2-C_2-C_3$	120	C_3-C_4	1.54
O_1	3.00	$C_2-C_3-O_3$	106	C_4-O_4	1.53
O_2	5.48	$C_2-C_3-C_4$	112	C_4-C_5	1.55
O_3	3.00	$O_3-C_3-C_4$	106	C_5-C_6	1.53
O_5	3.21	$C_3-C_4-O_4$	108	C_6-O_6	1.44
O_6	3.00	$C_3-C_4-C_5$	105	C_5-O_5	1.47
K	1.50	$O_4-C_4-C_5$	108	O_5-C_1	1.40
Br	1.37	$C_4-C_5-O_5$	115		
		$O_5-C_5-C_6$	109		
		$C_4-C_5-C_6$	102		
		$C_5-C_6-O_6$	118		
		$C_5-O_5-C_1$	114		

mer chain atoms were located, the positions were included with K and Br in the *E*-section calculation. All non-hydrogen chain atoms were found. A crude value of scale factor, applied to intensities calculated from these atom locations, gave an *R* value of 0.19.

The coordinates of all non-hydrogen atoms were refined (isotropic temperature factors, 37 parameters) by full-matrix least-squares (program SFLS[4]) to an *R* value of 0.068. The reflections observed by Senti and Witnauer, but unobserved by us, were not included specifically in the SFLS data. However, SFLS checks were made to see if inclusion of unobserved data would substantially alter the fit. No such indication resulted.

The molecular configuration is shown in *Figure 1*. The positions of the Br and K atoms are close to those reported by Jackobs *et al.*[2], but shifted slightly along the base diagonal away from the origin. The polymer chains are shifted into the cell along the diagonal from their positions[2]. *Table 1* lists atom positions, isotropic temperature factors, bond lengths and bond angles. End-bond angles $C_2-C_1-O_5$ and $C_3-C_4-C_5$ seem to be at the bottom of the range for other amylose derivatives[5,6], whereas side-ring angles seem larger than average. The $O_1O_4(O_1-O'_1)$ distance is 4.8 Å, at the top of the observed range.

The structure, although accurately derived, *is* in violation of commonly accepted stereochemical criteria for fibrous polymer bond lengths and angles. Nonetheless, it shows that single crystal methods can achieve a correct structure with sufficiently accurate data. The subsequent applications of sterochemical constraints can obtain the lowest possible *R* value consistent with the constraints. These constraints are now being applied in further SFLS refinements. There is also need to rationalize the C_4-O_4 and C_1-O_1 bond lengths (they are at present slightly different) and to see if the introduction of hydrogen atoms into the refinement has any effect on the reliability index.

The data acquisition and reduction methods will be described elsewhere[7]. A more complete discussion of the structure determination including application of constraints will follow.

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