10.2-3 **X-RAY FIBER DIFFRACTION ANALYSIS OF SOME POLYSACCHARIDE AND NUCLEIC ACID STRUCTURES**

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X-ray diffraction can be used to help determine the molecular geometries of polymers that form long helices rather than globular structures. Specimens can usually be prepared in which the molecules are aligned with their long axes parallel and often further lateral organization occurs in the form of microcrystals. Since the crystallites are randomly rotated about their long axes, the diffraction patterns recorded are cylindrically averaged. Also, their tendency to disorder makes it difficult to obtain heavy-atom derivatives without multiple site occupancy. Therefore, the well-trodden paths that lead from diffraction intensities to a unique solution of molecular structure are not available. These difficulties are circumvented by building a stereochemically plausible model of a residue that fits into a helix of appropriate pitch and symmetry as determined from the spacings and symmetry of the diffraction pattern. Thereafter the problem is one of refinement. If fundamentally different initial models are possible, each must be refined and the optimized models of each kind tested for significant differences. Refinement processes that involve simultaneous optimization against diffraction data and stereochemical restraints are well established (P.J.C. Smith & S. Arnott, Acta Cryst., 1978, A34, 3-11). Recent advances in intensity measurement (R.P. Millane & S. Arnott, J. Macromol. Sci. Phys., 1985, B24, 193-227) have made continuous diffraction data also available for quantitative analysis. We have used these techniques to analyze the structures of industrially useful gel-forming polysaccharides, and nucleic acids containing biologically important sequences.

Gellan is a recently discovered polytetrasaccharide produced by the bacterium Auromonas elodea that forms gels at very low concentrations. Analysis of diffraction data to 3 Å resolution from well oriented polycrystalline fibers shows that the molecule forms a double helix containing two identical left-handed 3-fold chains of pitch 56·4 Å. The chains are parallel and translated axially relative to each other by exactly half the pitch.

Kappa-carrageenan is a polydisaccharide of the marine algae Rhodophyceae, and is widely used in the food industry. Continuous diffraction data to approximately 4 Å resolution show that it forms either (non-half-staggered) parallel or antiparallel double helices containing right-handed 3-fold chains of pitch 25·0 Å. The structure is distinct from that of iota-carrageenan (S. Arnott et. al., J. Mol. Biol., 1974, 90, 253-267).

The recently characterized capsular polyhexasaccharide from the bacterium Rhizobium trifolii strain TA-1 also forms gels at very low concentrations. Molecular models consistent with its diffraction pattern symmetry and spacings are 2-fold single helices of pitch 19·6 Å and double helices containing parallel half-staggered 4-fold chains of pitch 39·2 Å.

The DNA duplex poly d(A)·poly d(T) has properties uniquely different from B-DNA. A candidate (H-DNA) for the secondary structure of the low humidity (<77%) β-form has previously been visualized (S. Arnott et. al., Nucl. Acids Res., 1983, 11, 4144-4155) which has C2'-endo furanoses on one strand and C3'-endo on the other. We have now performed a detailed refinement of the high humidity (>77%) screw-disordered α-form of poly d(A)·poly d(T). We find that the two polynucleotide chains are conformationally similar (with C2'-endo rings on both strands) but different enough to provide a duplex rather like the earlier H-DNA and distinct from classical B-DNA. This is reinforced by independent analyses of similar diffraction patterns from poly d(AI)·poly d(CT) and poly d(A)·poly d(U). The resulting bending of the helix axis at junctions between H-DNA and B-DNA would lead to curvature of DNA when appropriately phased tracts of oligo d(A)·oligo d(T) occur in the midst of more general sequences as has recently been observed.