POLYSACCHARIDE CONFORMATION IN SOLUTIONS AND GELS.

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Introduction

Possible conformational states for polysaccharides in solutions and gels are: (i) Ordered: (ii) Disordered; (iii) A mixture of (i) and (ii); (iv) An equilibrium between (i) and (ii). This lecture will outline the extent to which methods are available for distinguishing between these four conformational states, the characteristic physical properties that are associated with each, and the possible biological relevance.

Characterization of Conformational States

The traditional approach for polysaccharides has been to infer the overall form of the chain from the hydrodynamic properties in terms of such models as the random coil, rigid rod, sphere or ellipsoid.[1] Other methods used more recently and which are more sensitive for the detection of ordered domains, include the investigation of cooperative transitions, particularly when these are induced by change of temperature[2] and the measurement of a nuclear magnetic resonance parameter, T_2, which is the spin-spin relaxation time.[3,4]

When an ordered state is present, the characterization of its detailed geometry must rely heavily on correlation with solid state conformations that have been characterized by X-ray diffraction. This correlation may be achieved in favourable cases, for example[5] by comparison of the observed and calculated values for specific optical rotation, comparison of circular dichroism spectra in the solution and solid states, and analysis of the stoichiometry of the order-disorder transition.

Types of Ordered Conformation

The wealth of information now available from X-ray diffraction studies,[6] confirms the general conclusion suggested earlier from model building calculations[7] that linear carbohydrate chains having a periodic sequence of sugar residues can usually be classified into the ribbon family (sub-types: flat, twisted, buckled, twist-buckled) and the helix family (sub-types: hollow, entwined, and nested). All of these require inter- as well as intramolecular interactions for stability. Among the most important[8] of these interactions are:

(i) Flat ribbons and twisted ribbons packed in dense fibrous aggregates and are particularly common in extra cellular composites, e.g. cellulose, chitin, xylan, mannan.

(ii) Buckled ribbons formed by uronic acid polymers can be stabilised by inter-chain egg-box complexes with suitable divalent cations, e.g. alginate, pectin.

(iii) Hollow helices are stabilised in inclusion complexes, e.g. amylose-iodine, palmitate-CoA binding polysaccharides of Mycobacterium smegmatum.

(iv) Entwined helices are stablised by inter-strand interactions in double (carrageenan, agarose, probably hyaluronate) or triple (β-1,3-glucan, β-1,3 xylan) helices.

(v) Nested helices stabilised by side-to-side packing as in most of the glycosaminoglycan structures in oriented films.

In contrast, it seems that at least some branched polysaccharides can achieve stability through intramolecular interactions between side chains

and backbone.[3,9] In this sense, the function of chain branching in polysaccharides can be analogous to that of chain folding in globular proteins. This raises the exciting possibility that will be discussed further in this lecture, that such principles may extend to carbohydrate-carbohydrate and carbohydrate-peptide interactions in some glycoproteins.

Properties associated with Conformational States.

The characteristic property of a disordered chain in solution, particularly of a polyelectrolyte, is of course an expanded domain in which is extrained a large volume of solvent.

For linear, periodic polysaccharides in ordered conformations, the requirement for intermolecular stabilisation (see above) often implies insolubility unless, as happens in relatively rare cases, chain association is limited to two or three strand.

For periodic polysaccharides with interrupted sequences, the tendency to complete phase separation can be arrested if the "interruption segments" are more stable as soluble random coils. Such a mixture of ordered and disordered conformations along the length of each chain can therefore lead to the gel state.

When fast equilibrium exists between a disordered state and an ordered chain-associated state, the result is the appearance of marked visco-elastic properties at concentrations much lower than would be expected from the mere entanglement of random coils. Evidence will be discussed that the conformation of hyaluronate is to be explained in terms of such a model which involves the fleeting appearance of an ordered state which may be formed from nested helices.

References

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