Coil to Double Helix Transition for a Polysaccharide

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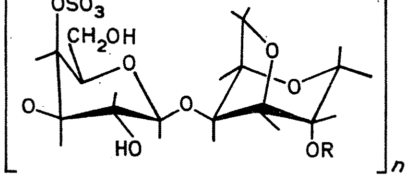
Summary ι-Carrageenan segments can achieve an ordered conformation in a process which resembles the polypeptide and nucleic acid transitions already known, thereby showing for the first time that intramolecular cohesion between sugar residues can be sufficient to outweigh solvation and polymer-conformational entropy in aqueous solution.

The carrageenans, κ- (I) and ι- (II), have masked repeating structures[1,2] and can exist as double helices in the solid state.[3] In solution, κ-carrageenan shows optical rotation changes which can be attributed to formation of these helices but which are complicated by secondary changes and by irreversibility, gel formation, and the possibility of stress birefringence.[4] We now report results which are simpler and should be more amenable to precise interpretation, using alternating copolymer segments (III) of ι-carrageenan from *Aghardhiella tenera*. These were prepared by splitting the polysaccharide by Smith degradation[5] followed by 6-sulphate elimination[6] with alkaline borohydride. The conditions are mild enough to avoid nonspecific removal of sulphate which would lead to a product of irregular primary structure, and the segments were evidently too short to form networks of the type which complicated previous investigations because the solution did not gel when cooled.



(I) R = H (*ca.* 95%) and SO_3^-(*ca.* 5%); the 3,6-anhydride residue is replaced partly by galactose 6-sulphate and partly by galactose 2,6-disulphate.

(II) R = SO_3^- and the 3,6-anhydride residue is replaced partly by galactose 2,6-disulphate and to a very small extent by galactose 6-sulphate.

(III) R = SO_3^- and the chains are terminated by 2-linked tetritol derivatives.

After dialysis to remove material of low molecular weight, an aqueous solution of the potassium salt showed large changes in optical rotation with temperature (Figure).

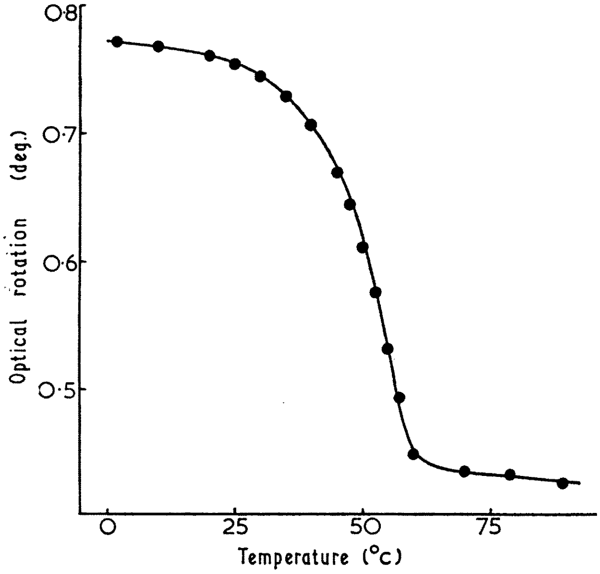


FIGURE. *Optical rotation changes with temperature for ι-carrageenan segments in distilled water* (5·6%, *w/v*), *at* 546 *nm. using a cell of path length* 1·99 *cm. The readings* (●) *were independent of thermal history.*

These are attributed to formation of double helices on the cooling curve and their dissociation on heating because:

(i) the shifts are very similar to those which parallel the onset of chain association in the intact polymer.[4]

(ii) *X*-ray diffraction and other evidence[1-3] indicates that this association involves double helix formation.

These results represent the first example of a transition to an ordered polysaccharide conformation in solution.† The reversible and sigmoidal change (Figure) is strikingly similar to classical transformations of polypeptides and DNA[7] and evidently is not linked to the separation of a quasi-solid phase such as might occur in the gel.[4] Intramolecular cohesion between sugar residues, as between purine and pyrimidine bases and between amino-acid residues, can therefore[8] cause co-operative stabilisation of ordered conformations in aqueous solution and outweigh solvation and the drive to disorder owing to polymer-conformational entropy. For reasons given elsewhere,[1] electrostatic interactions with counterions are not thought to be necessary to cohesion, although they probably contribute to solubility after the transition. The rather broad temperature range of transition for the present sample (Figure) is attributed in part to heterogeneity because the end of the transition is less abrupt than the beginning. The system is now simple enough for quantitative estimates of energy parameters to be attempted, especially if subfractions can be obtained with sharp molecular weight distributions.

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† Such transitions can of course be observed for the amylose–iodine complex but the ordered conformation is stabilised by special interactions with complexed cosolute (see D. A. Rees, "The Shapes of Molecules: Carbohydrate Polymers," Oliver and Boyd, Edinburgh, 1967, pp. 100—104, 113; F. W. Schneider, C. L. Cronan, and S. K. Podder, *J. Phys. Chem.*, 1968, **72**, 4563; there is no evidence that the conformations below and above the pK_a of pectic acid (R. W. Stoddart and K. F. Tipton, *Biochem. J.*, 1968, **109**, 21P) or amylose and carboxymethylamylose (V. S. R. Rao and J. F. Foster, *J. Phys. Chem.*, 1965, **69**, 636; *Biopolymers*, 1965, **3**, 185) are other than different fluctuating conformations, differing, for example, in degree of expansion.

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