Polysaccharide physical properties may be traced to various levels of molecular organisation. Individual sugar rings in the covalent sequence, or primary structure, are essentially rigid, and chain geometry (secondary structure) is determined by their relative orientations. Chain flexibility is restricted by non-bonded interactions between adjacent residues, thus leading to extended coil dimensions, and high solution viscosity. In the solid state most polysaccharides adopt ordered tertiary structures such as nested ribbons or double helices. These may persist in solution, or as the fundamental structural unit in gels, and frequently show co-operative order-disorder behaviour. Tertiary structures may further associate to build higher levels of organisation (quaternary structure). Changes in structural organisation may be monitored chiroptically, rheologically, calorimetrically, or by changes in molecular weight or n.m.r. relaxation behaviour, all of which may, in principle, be used as probes for kinetic studies.

INTRODUCTION

Polysaccharides are naturally occurring carbohydrate polymers which represent the principal solid component of most plants, and are also of major importance in many animal and bacterial tissues. In addition to their familiar role as energy reserves the primary biological function of many polysaccharides is in development of structure. This natural ability is widely exploited industrially to create texture in, for example, food and cosmetics. The molecular origin of bulk textural properties may be traced to various levels of polysaccharide organisation.
PRIMARY STRUCTURE

The component sugars of polysaccharides occur in the polymer chain as rings, as shown opposite. Substituents may lie either equatorially (e) in the plane of the ring, or axially (a) above or below the ring. Linkage of adjacent sugars may be either \( \alpha \) (axial) or \( \beta \) (equatorial), as shown. Branching is introduced by disubstitution of a single residue. Polysaccharide primary structures frequently show a simple repeating sequence, as outlined below.

![Agarose and Iota Carrageenan structures](image)

Alginate is a linear block co-polymer of \( 4 \)-linked \( \alpha \)-L-guluronate and \( \beta \)-D-mannuronate residues, arranged in homopolymeric blocks of both types, and in regions which approximate to an alternating structure (1). Plant galactomannans have a linear backbone of \( \beta \)-1,4 linked D-mannose, substituted to different degrees at position 6 by \( \alpha \)-D-galactose residues. In one member of this family, locust bean gum (LBG), galactose substituents are clustered together in 'hairy' regions, interspersed by 'smooth' unsubstituted mannan blocks (2). The bacterial polysaccharide xanthan is based on the \( \beta \)-1,4 linked D-glucose structure of cellulose (see opposite), substituted on every second backbone residue by a charged trisaccharide sidechain (3,4).