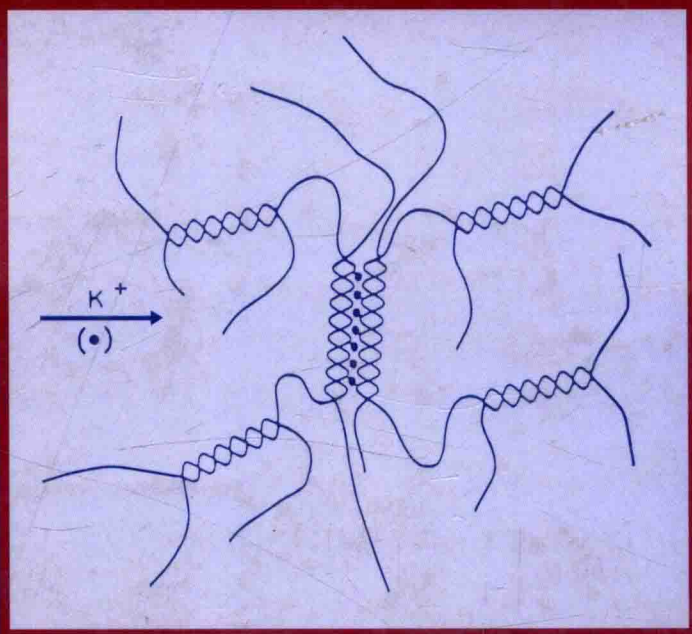# Polysaccharide Association Structures in Food

edited by
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Polysaccharide Association Structures in Food

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Preface

Polysaccharides are the basic skeletal component of plant tissues. Inasmuch as polysaccharides do not depolymerize substantially during extraction and purification, isolated polysaccharides, through their macromolecular assemblies, are exploited in the creation of structure and texture, in vitro, in aqueous media, with particular applications in fabricated foods. They frequently perform interchangeably, although subtle differences may elicit different, sometimes unique, behavior among members and isomers, under identical combinations of stimuli. The spontaneous tendency of dispersed polysaccharide solutes to aggregate cohesively and adhesively with other molecules impels them toward the creation of supramolecules. This treatise focuses on the physicochemical origins and structures formed by the association of aqueous, dispersed polysaccharides with like and unlike chemical species.

Reginald H. Walter

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Origin of Polysaccharide Supramolecular Assemblies

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I. INTRODUCTION

Nature is adept at weaving (practically) one-, two-, and three-dimensional structures (Fig. 1) from aqueous, dispersed polysaccharides, through whose instrumentality it imparts form and function to living plant tissues, to wit, the cellulose skeleton of fruits and vegetables. This biopolymer is deposited naturally in bundles of microfibrils that constitute the fibrous and ribbonlike suprastructures of vegetable matter. Native starch is deposited mostly as spheroidal granules. Arguably, macromolecular assemblies with aquatic and microbial polysaccharides, in vivo, have teleological significance. Polysaccharide supramolecules may also be the product of purely chemical synthesis. The natural and chemically synthesized polysaccharides and their derivatives are collectively called *gums*. This unconventional class of substances is increasingly relied on to impart coherence, body, and texture to fluid substrate, in vitro. The singular property common to its members is their amphiphilicity, albeit to different degrees, which enables them to associate with polar and nonpolar molecules alike in water (surfactancy). The extent of the surfactant associations is determined by the net force generated as a result of solute–solute, surfactant–solute, and surfactant–solvent interac-

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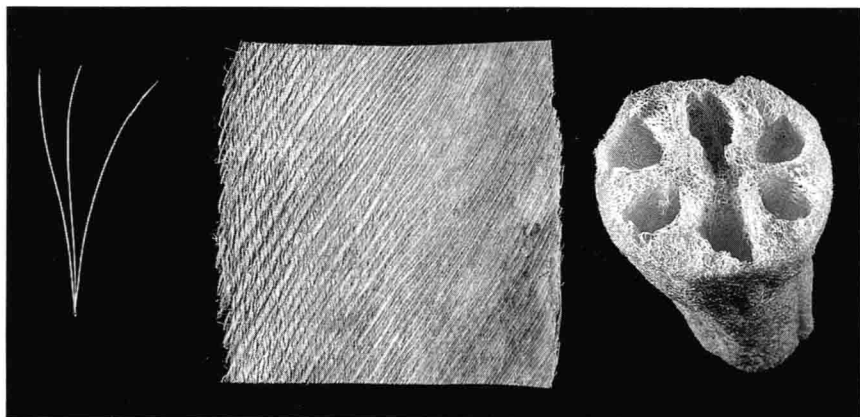
Figure 1   Natural plant structures: (left to right) partial fascicle of white pine (*Pinus stobus*), a portion of the leaf base of the coconut palm (*Cocus nucifera*), and the loofah of a gourd (*Luffa aegyptiaca*).

tions and by thermal energy [1]. Ionic polysaccharides experience additional coulombic attraction and repulsion.

Aqueous polysaccharides display a continuum of disorder–order–disorder and order–disorder–order transitions that ultimately yield flocs, pastes, aggregates, gels, and precipitates. The final outcome is dictated more by the solute's aqueous environment and external stimuli than by its chemistry. It is not unusual for different gums to exhibit the same response under a given set of conditions and for the same gum to respond differently to different combinations of stimuli.

II.   DEFINITIONS

Some definitions are a necessary precedent to elaborating the tendency of gums to associate in aqueous media. A polymer, synonymously called *macromolecule*, is a molecule, $10–10^3$ nm diameter, containing $10^6–10^{12}$ chain atoms [2]. Thus, size is conventionally characterized by the degree of polymerization (DP) as well as by the molecular weight. The DP, then, is the length of a polymer's unsubstituted primary chain, counted in monomer units. Oligosaccharides are differentiated from polysaccharides by a cutoff molecular weight of 10–20 monomers [3,4].

Chemically, polysaccharides are mostly linear polyhydric alcohols, polyacids, or polyesters, consisting of a primary structure that is subject to various configurations (the secondary structure), depending on bond lengths

and angles, the DP, branching, heterogeneity, and sensitivity to the dispersion medium. The topology of a linear polymer is the average of multiple equilibrium geometries of the primary structure. Long, single-bonded chains are conducive to flexibility, and short chains, to rigidity. Unsubstituted primary chains facilitate parallel orientations and contacts between segments of different chains.

An amphiphile, containing hydrophobic and hydrophilic groups in the same molecule, enables amphiphilicity to be empirically referenced against a quantifiable tendency to promote oil-in-water and water-in-oil emulsions; this is the hydrophile–lipophile balance [5]. Amphiphilic chain segments result in ordered micellar aggregation in solution or bulk [6]. Dispersed polysaccharide solutes are prone to micellar aggregation, as a consequence of the high incidence of polar groups [hydroxyl ($-OH$), carboxyl ($-COOH$), and/or sulfonic ($-OSO_3H$) groups]: $-COOH$ is common in uronans, and $-OSO_3H$ in carrageenans. A *micelle* is defined as a spontaneously formed aggregate of tens to hundreds of surfactant molecules or ions [7]. Trifunctionality in a polysaccharide monomer accommodates aggregation by three-dimensional crosslinking.

The association tendency of some polysaccharides is altered by chemical derivatization, notably esterification and etherification, and that of others by deesterification. Starch and cellulose, for example, are alkylated and hydroxyalkylated to improve performance over the parent molecules'. Pectin is a deesterified biopolymer of protopectin, the native precursor. Neither the original nor the derivatized species is truly water-soluble in the classical sense of a monophase; instead, they disperse to a macromolecularly heterogeneous system [8].

A polymer molecule in a flow field devoid of adsorbed solvent, traveling at a different rate from the bulk solvent, is said to be *free-draining*. A *non-free-draining* polysaccharide molecule has an adsorbed envelope of water traveling at the same rate as the solid core. Non-free-draining water (water of hydration) is therefore an integral part of the discrete colloidal nucleus. *Hydrodynamic interaction* refers to the influence of the motion of a molecule or segment and its water of hydration on other molecules or segments. Free-draining water is the overwhelming volume of solvent in a solution or dispersion. Inasmuch as free-draining water is not in colloidal association with the discrete nucleus, and therefore almost always travels with a different velocity from it, any identicalness of transport of the discrete nucleus and free-draining water is purely coincidental. Free-draining water is not affected by hydrodynamic interaction.

Water of hydration has a stabilizing effect on dispersed gums, through a number of different mechanisms [8].

Dispersed polysaccharides structure water at the solid–liquid interface where the water becomes non-free-draining. The influence of a polysaccharide is exercised at concentrations as low as fractions of a percent, where at the binary dispersion can assume the character of either a liquid or a solid, under the influence of solvent conditions and temperature. A *dilute* dispersion is considered to be one in which there is no solute–solute interaction; in such a "dilute" regime, dispersion properties are additive of the contribution of single molecules. At the highest weight or volume percentages—the concentrated regime—each property loses its concentration dependence, and, behaving like a polymer melt, the dispersion displays thixotropy, viscoelasticity, or elasticity. At intermediate concentrations, linear dispersed solute entangles and interpenetrates and hence exhibits unique properties. The critical micelle concentration (c^*) is that concentration at which gross macromolecular properties of a dispersion cease to be concentration-dependent, and the properties obtain from clusters of molecules acting as single hydrocolloidal units.

Molecules and segments of a dispersed polysaccharide occupy an excluded volume (v_{ex}) that is inaccessible to other segments and molecules. The v_{ex} effect is the net of divers forces acting on the segment or molecule in v_{ex}. The free volume (v_f) is that vacant volume available for occupancy by any segment or molecule. The volume of a dispersion (V_i) is the sum of the excluded volume and the free volume:

$$V_i = v_f + v_{ex} \qquad (1)$$

A large v_f is indicative of much space for independent molecular motion; conversely, a small v_f suggests a higher probability of polymer–polymer contacts. At the macromolecular level, Eq. (1) is temperature-dependent. The glass transition temperature (T_g) is the temperature where v_f is zero or constant and translational and rotational motions cease, relative to the expanded chain's motion above T_g where Brownian activity engenders increasing v_f with increasing temperature. Below T_g, v_{ex} expands only as a result of the higher amplitudes of the thermal vibrations [9].

Ordered polysaccharide assemblies (e.g., rods and helices) show a lower c^* than do the disordered assemblies (random coils). Cellulose and cellulose derivatives are inherently stiff rods, because of the β-glycoside bonding and the steric hindrance resulting from the substituents, thereby initiating resistance to segmental rotations. Starch and noncellulose gums freely adopt flexible shapes, because of widespread amorphism.

Random coils, rigid rods, stiff chains, etc., define a tertiary structure (conformation). In the vicinity of c^* at a critical temperature, modulated by solution conditions, tertiary structures grow into quaternary structures, insofar as points of contact or junction zones multiply into micelles, aggre-

gates, clusters, vesicles, gels, films, and crystals. Clusters of ordered surfactants in oil/water emulsions are typically 100 molecules [10]. Vesicles are self-ordering closed bilayers wherein amphiphiles are sandwiched between two liquid layers thousands of angstroms apart [11]. Gels are given many definitions, but the common feature is elasticity in the semisolid structure. Gels are the most common form of food polysaccharides. A *hydrogel* is a dispersion structured as a discontinuous, solid phase in a continuous water phase; a *xerogel* is a dehydrated hydrogel. *Films* are two-dimensional xerogels. The mechanics of the macromolecular associations initiating these structures include interpenetration of random coils, multiple coupling of single and double helices, orientation of rods, and electrostatic crosslinking in homogeneous and mixed junction zones.

The quaternary ordering of rods and stiff chains along the molecular axis eventuates into mesomorphic phases that are intermediate between a liquid and a crystalline solid. These mesomorphs, or liquid crystals, remarkable for their appearance as a solid at rest and as a liquid when disturbed, possess unique features, e.g., dichroism and birefringence. Their c^* generally depends on chain rigidity [12] that in turn is a complicated function of side- and main-chain lengths, side-chain chemistry, and temperature [13]. Mesophases are classified as *lyotropic*, if the self-organization results from interaction with an amphiphilic surfactant cosolute, which enables them to be disordered by solvent action; they are classified as *thermotropic*, if the self-organization develops in an usually narrow temperature interval.

A linear, random-coil polymer has been theoretically modeled after a sphere. It should be recalled that a sphere has the lowest area/volume ratio of all known geometries. The normally hydrated polysaccharides are preferably represented by an equivalent hydrodynamic sphere that is assumed to have properties and exhibit responses identical to those of its linear counterpart. Spherical [14] and circular [15] polysaccharide suprastructures have been observed experimentally. The volume of this equivalent hydrodynamic sphere is delimited by the hydrodynamic radius, R_h, the radius of gyration, R_g, or the root mean square end-to-end distance, $(r^2)^{1/2}$, i.e., the average distance between the two ends of a chain. The relationship between R_h, R_g, and $(r^2)^{1/2}$ is as follows [9,16]:

$$R_h = 0.665 R_g \tag{2}$$

$$(r^2)^{1/2} = (6R_g^2)^{1/2} \tag{3}$$

The squared function averages the distances of all solute molecules in a positive and negative direction from the center of mass. Water of hydration creates long distances between non-free-draining coils, giving a longer R_h and R_g. Rodlike polysaccharides are dimensionally thicker, i.e., give a shorter