INTERACTIONS OF ORDERED WATER AND CATIONS IN THE GEL-FORMING POLYSACCHARIDE GELLAN GUM

R. Chandrasekaran

Whistler Center for Carbohydrate Research, Smith Hall
Purdue University, West Lafayette, Indiana 47907

ABSTRACT

Gellan gum, useful to the food industry, is chosen as a model system for the investigation of the structural role of water molecules and cations in its gel-forming properties. X-ray fiber diffraction technique has been used to determine the crystal structure of potassium gellan. This gives the three-dimensional structure of the polysaccharide, the locations of ordered water molecules, and of potassium ions. The precise interactions among the three components at molecular level reveal that the water molecules are essential for the stability of the polysaccharide chains, for the binding of cations with the polymer molecules, and for the aggregation of the polymers, all of which are crucial for the gelation process. Computer modeling shows how the calcium ions can directly crosslink adjacent gellan molecules, but the potassium ions cannot, and this explains the stronger gelation properties of calcium gellan, even at very low ionic concentrations. L-glycerate, but not acetyl, groups interfere with the intermolecular association of native gellan molecules and are thus responsible for its weak and rubbery gels.

INTRODUCTION

Flavor, texture, and taste are some of the prominent features of any food product which are usually controlled by an appropriate combination of a set of raw materials. Water is an integral part of almost every food system, and it provides the essential means of keeping together the variety of ingredients which would otherwise be independent entities. In this context, polysaccharides and proteins are two of the most important constituents of food. Many of them exhibit excellent ability to form aqueous gels which can hold a substantial amount of water. Carrageenans and pectates are good examples of gel-forming polysaccharides which are extensively used in ice cream and fruit jam, respectively. Examples of protein gels include food products such as yoghurt and tofu.

A proper understanding of the gelling mechanism of these polymers is not possible without a detailed knowledge of the molecular architecture of the material. This includes the three-dimensional structure of the polymer, the interactions between the polymer chains, and those between the polymers and water molecules.
Gel-forming polysaccharides have been the subject of investigation in our laboratory for over twenty years. These polymers have the tendency to adopt long helical structures and thus cannot be grown as single crystals. Therefore, they are not amenable to traditional analysis by x-ray crystallography. On the other hand, it is often possible to produce polycrystalline and oriented specimens from these polymers. Such a fibrous specimen generally consists of microcrystallites which are aligned preferentially with their molecular axes approximately parallel to the fiber axis, but are otherwise randomly organized. X-ray diffraction from these fibers enables us to establish the molecular structures of the polymers and, in favorable cases, the crystal structures also. The details of solving polymer crystal structures using fiber diffraction data are given elsewhere.1

Gellan

Gellan gum is an exciting new bacterial polysaccharide. It is an excellent gelling agent for use in candies, dessert gels, dairy products, frostings and icings, puddings and pie fillings, jams and jellies, structural foods, and pet foods. The gum is so versatile that it can be used to match the existing texture of these products, or vary it predictably over a wide range. Consequently, for the first time, it provides great opportunities for the food technologist to create a spectrum of new products.

The primary structure2 of gellan gum consists of a linear, anionic, tetrasaccharide repeating unit (A-B-C-D) as shown below:

\[\beta-D-Glc-(1 \rightarrow 4)\beta-D-GlcA-(1 \rightarrow 4)\beta-D-Glc-(1 \rightarrow 4)\alpha-L-Rha(1 \rightarrow)\]

Solutions are viscous and become gels even at concentrations of the polymer as low as 0.05%. Cations are required for gel formation. Divalent ions, such as calcium, can produce firm and brittle gels at a much reduced concentration compared to that of monovalent ions, such as sodium or potassium. Moreover, products using gellan gum are stable over a wide pH range (3.5-8.0). The gels can be made resistant to heating up to 100°C and can be combined with other hydrocolloids, notably xanthan gum, locust bean gum, starch, or gelatin, so as to achieve any desired texture. Because of its water-holding properties and due to its low use level, gellan gum also exhibits an outstanding flavor release.

Native gellan, secreted by the bacterium Pseudomonas elodea, contains additional substituents on the gellan gum backbone: acetate at C6 on approximately 50% of the O-3 linked glucose residues and L-glycerate at C2 on every one of them.3 In contrast with gellan gum, this material gives only weak and rubbery gels.

We have conducted detailed x-ray fiber diffraction studies on polycrystalline and oriented specimens of two different monovalent salt forms of gellan.4,5 We have also carried out computer modeling6 to evaluate the influence of calcium ions on the aggregation properties of gellan molecules and determine the morphology of native gellan. These studies reveal not only the molecular features and their robustness under different cationic situations, but also the precise details of a) the interactions within and between the polymer molecules, b) those between the polymer molecules and the cations and water molecules, and c) the structural roles of the glycerate and acetate groups and their influences on the surrounding water molecules, and hence on the gelation properties of native gellan.

Crystal Structure of Potassium Gellan

A high quality diffraction pattern used in the structure analysis of