Branched Starch Molecules: Contribution to Ordered Structures
in
Granular Starch and Dispersed Starch Molecules

A highly branched homopolyglucan of MW up to 200 x 10^6, the branched fraction of starch, amylopectin, occurs in nature in semi-crystalline form. This observation stands in sharp distinction to the behavior of other branched polymers. The highly ordered nature of the starch granule results from the non-random nature of the branching and the non-random distribution of the linear regions. Stable double helices of two linear regions of glucan chains are the basis for the regular packing in a crystalline array. Single helices from linear glucan regions can also form, around iodine (to form the familiar blue color) or around hydrophobic regions of organic molecules, especially monoacyl lipids.

The basis for starch granule and molecular order is the starch synthases and the branching enzymes. The resulting covalent and granule structure determines accessibility to amylolytic enzymes. The granule structure also determines how the granule will behave in industrial use (one important aspect of granule behavior is "gelatinization," which describes the loss of order prior to and during the swelling that occurs with sufficient heat and water, as the granule takes up water). Molecular structure determines granule structure and properties. In addition, molecular structure is responsible for the instability of starch molecules in the dispersed state (leading to subsequent molecular ordering, a phenomenon termed "retrogradation"). By judicious choice of processing conditions and starch source, one can take advantage of the kinetic constraints to reaching thermodynamic equilibrium, producing desirable metastable states of industrial interest.

In our laboratory we study a wide range of molecular architecture in maize starches, using starches obtained from maize endosperm genotypes with single and multiple lesions in the enzymes of the biosynthetic pathway. By comparing the nature of the molecular structure with physical behavior such as the endothermic phase transitions associated with loss of ordered structures, we can gain insight into physical properties of industrial importance, such as turbidity and gelation. Our research initially focused on the branched fractions alone. The *waxy* (*wx*) mutation leads to a starch that is solely amylopectin. In combination with other mutations, amylopectins of varied structure result. We have studied the structure of these amylopectin molecules. This work has continued in collaboration with Mark Guiltinan. We have explored the effects of various combinations of maize starch branching enzyme (SBE) isoforms on the amylopectin produced. We have developed novel enzymatic techniques to explore the nuances of the

branching pattern of these amylopectins, going well beyond a description of the standard chain length distribution to explore structures of the β-dextrins produced by β-amylase.

For the last several years we have worked with starches that have increased levels of the linear component, amylose. The *amylose-extender* (*ae*) mutant produces such starches, and their composition is modified by other mutations in combination. Even for these high-amylose starches, variation in the structure of the branched fraction can have a dominant influence on the behavior of the linear material. These starches are of special interest because they are resistant to digestion in the native state, and they can be manipulated physically and chemically to produce even higher levels of resistance to digestion. These sources of resistant starch (RS) are of great current interest as they appear to have a beneficial effect on colon health and by definition do not contribute to a glycemic response, as they are not digested in the small intestine. We have been awarded a patent for a granular starch high in RS, for which the level of RS is stable to subsequent thermal treatment. We are looking at novel ways to produce thermally stable RS from dispersed starches, a current line of work that has resulted in an invention disclosure.

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