LINEAR AND CYCLIC AMYLOSES: BEYOND NATURAL

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This presentation outlines the progress of recent studies on synthetic linear and cyclic amyloses. Unlike linear amylose, which has a long history [1], cyclic amylose (large-ring cyclodextrins, referred to as cycloamylose in this paper) was discovered recently as a result of the action of recombinant potato D-enzyme (4-α- glucanotransferase, EC 2.4.1.25) on linear amylase [2]. The degree of polymerization (dp) of cycloamylose isolated from reaction mixtures has been found to range from 17 to several hundred. Available information on the conformation and molecular characteristics of cycloamylose are limited [3].

Linear amylose has been widely studied, largely because of its interesting solution properties, which include complex formation with iodine, butanol, and other organic reagents, as well as a tendency for molecular association (retrogradation). Synthetic linear amylose can be produced using either glucan phosphorylase or coupling of sucrose phosphorylase and glucan phosphorylase [4]. The chain length can be controlled by changing the reaction conditions. These amyloses are strictly linear molecules and have a narrow molecular-weight distribution. While aqueous solutions of linear amylose are very unstable over a range of from dp 20 to 200, shorter and longer molecules are much more soluble. Linear synthetic amyloses with dp > 4000 can be soluble in water and stable for a long time. For example, a 1% aqueous solution of amylase (dp 5200) is stable for more than one month at room temperature.

Members of this group of ring polymers (cycloamylose) are stable in water even over a range of from dp 20 to 100. SAXS measurements and simulations demonstrate that a cycloamylose in dilute solution can be modeled as a circularized single helix and that the scattering functions that are computed for pseudo-cyclic amylose chains when using the Monte Carlo method agree well with the experimental curves for cycloamylose. Cycloamylose has the potential to function as a host molecule for a variety of organic reagents, and with iodine, in a manner that is different from linear amylose and different from the more common cyclodextrins (α-,β-, γ-CDs). It is likely that cycloamylose has a cavity geometry that differs from those of linear amylose and these CDs. We studied the complex formations of cycloamylose with iodine and surfactants in aqueous solution by isothermal titration calorimetry, and compared these results with those obtained for linear amylose.

These synthetic amylases are now commercially available and many applications are now in development. I will show some examples that display these characteristic physical properties.

[1] S. Kitamura, in Polymeric Materials Encyclopedia, Vol.10, p.7915, J.C. Salamone Ed. (CRC Press, Florida, 1996).
[2] T. Takaha, M.Yanase, H. Takata, S. Okada, S.M. Smith, J. Biol. Chem., **271**, 2902 (1996).
[3] S. Kitamura, in Cyclic Polymers, Chapter 4, p125 J.A.Semlyen Ed. (Kluwer Academic Publishers, Dordrecht, 2000) .
[4] H. Waldmann, D. Gygax, M. D. Bednarski, W. R. Shangraw, G. M. Whitesides, *Carbohydrate Research*, **157**, c4-c7, (1986).