Biocatalytically Synthesized Xylans Self-assemble into Microparticles with Tunable Properties

Background

- Xylan is one of the most abundant polymers found in biomass and can account for up to 30% d.w. of the plant cell wall. Typically, xylans found in nature are complex polymers and branched with abundant glycosyl and acetyl sidechains that decorating a β-1,4 xylose backbone. The enzyme responsible for the polymerization of the xylan backbone, Xylan Synthase 1 (XYS1), was recently identified, and its activity characterized *in vitro*.

Approach

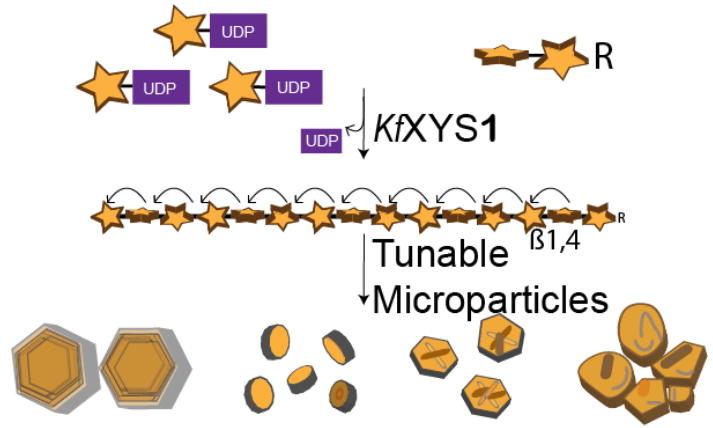
- Using a recombinant xylan synthase as a biocatalyst, we synthesized xylan polymers *in vitro* using UDP-xylose as a donor substrate and small xylan oligosaccharides as glycosyl acceptors. In an attempt to synthesize longer xylan chains, we noticed the formation of insoluble xylan particles and sought to characterize these further using several microscopy, spectroscopic and analytical techniques.

Results

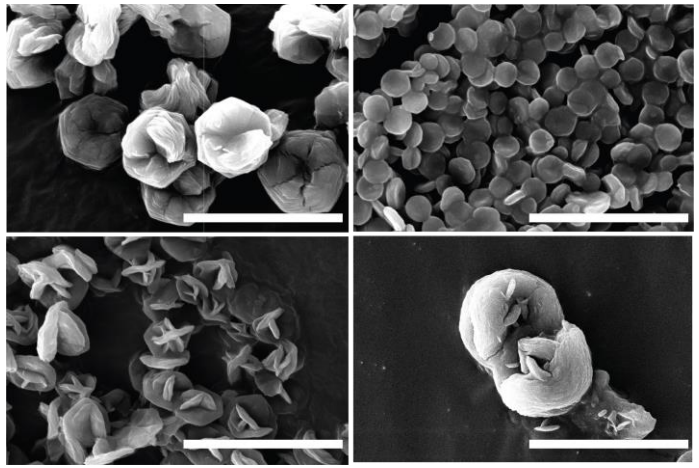
- We found that xylan synthase reactions, resulting in xylan polymers with a DP>14, are prone to self-assemble into microparticles with well-defined morphologies.
- The presence, identity and linkage of sidechain residues on the oligosaccharide acceptor results in differences microparticle morphology (e.g., hexagon vs. circle vs. star).
- We characterized the xylan polymers comprising the microparticles by solid state NMR and found that the xylan topology is consistent with a three-fold helical screw conformation.
- We developed methods to functionalize xylan microparticles both pre- and post-biocatalytic polymerization.
- Finally, we explored the enzymatic deconstruction of xylan microparticles and found that endo-hydrolases can digest the center of some microparticles, and that exo-hydrolases were generally ineffective.

Significance

- Insights gained from this study will help to inform our understanding of xylan synthesis, polymer-polymer interactions and deconstruction. In addition, we foresee the potential of xylan microparticles to be used as biocompatible and biodegradable materials well-suited for several applications in bioindustry.



KfXYS1 is used a biocatalyst to elongate xylan acceptors and form polymers that self assemble into structurally defined microparticles.



SEM images of enzymatically synthesized xylan microparticles. Each image represents microparticles produced from different xylan oligosaccharide acceptors. The scale bar is 10 μm.

Smith, PJ et al. Enzymatic Synthesis of Xylan Microparticles with Tunable Morphologies. *ACS Materials Au* (2022) DOI: 10.1021//acsmaterialsau.2c00006