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Thesis Outline

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Title of the thesis:
Poly(butylene succinate) with periodic main chain acetal or hemiacetal ester linkages for tunable degradability

Outline of the thesis:

Poly(butylene succinate) (PBS) is an important sustainable polyester with steadily increasing applications as single use plastics. Commercial PBS has good biodegradability in soil, but its poor and inconsistent marine biodegradability is a cause for concern. In this work, attempts were made to address this issue by developing novel PBS derivatives with periodically distributed acetal and/or hemiacetal ester linkages along the polymer backbone for tunable main chain degradability. The periodicity of the labile linkages in the polymer backbone was realized by utilizing discrete oligo(butylene succinate)s as telechelic macromonomers. Chapter 1 is a prelude to this thesis which explains concepts of degradable polymers and the necessity for designing molecularly defined polymers.

Chapter 2 describes the two iterative methodologies employed to synthesize discrete oligo(butylene succinate)s (OBS) with dihydroxy end groups and dicarboxylic acid end groups. The author explored iterative linear growth approach which enabled synthesis of OBS oligomers with precise control over the number of repeat units, whereas exponential growth approach resulted in multigram synthesis with better efficiency. High purity of the obtained oligomers was confirmed using ^{1}H NMR and ^{13}C NMR analyses. SEC analysis and MALDI-TOF mass spectra analysis corroborated to the monodisperse nature and discreteness of the oligomers. OBS oligomers were also characterized by DSC, TGA, SAXS and WAXS analyses, and found that the

trends in their thermal and crystalline properties could be accurately correlated to their chain length and end groups.

In chapter 3, OBS oligomers with dihydroxy end groups were polymerized in solution with divinyl ethers using acid catalyzed step-growth polyaddition, to yield PBS analogues with periodically distributed main chain acetal linkages. The polymerization reaction was performed under mild conditions to efficiently furnish high molecular weight poly(OBS-acetal)s (M_n > 100000 Da) in multigram scale (~10 g) with varying acetal spacers. This strategy allowed synthesis of PBS like semi-crystalline polymers with well-defined crystallizable OBS segments, joined together by acetal spacers of different lengths. The polyacetals showed good hydrolytic stability between pH of 6-8 but were readily degraded into parent OBS 4.5-mer, acetaldehyde and diol upon treating with aqueous HCl under mild conditions. In accelerated BOD analysis, OBS 4.5-mer and poly(OBS 4.5-mer-TEG acetal) showed good marine biodegradation in 40 days whereas OBS 8.5-mer, poly(OBS 4.5-mer-BD acetal), and commercial PBS had poor biodegradability under the test conditions. This observation indicated that the penetration of water into polymer bulk could induce acetal cleavage to produce the biodegradable low molecular weight of OBS oligomers.

Chapter 4 describes synthesis of PBS analogues with periodically distributed hemiacetal ester linkages along the backbone. Melt polyaddition of dicarboxylic OBS oligomers and 1,4-butnaediol divinyl ether at 100 °C without any additional catalyst and solvent was utilized to furnish poly(OBS-hemiacetal ester)s. OBS oligomers with varying molecular weights were used to tune the length of crystallizing segments and their influence on the crystalline properties of the polymers was studied. The consequences of the presence of weaker main-chain hemiacetal ester linkages on the thermal and degradation properties of the polymers were discussed.

In chapter 5, the author illustrates synthesis and properties of the copolymers of PBS analogues which contain both acetal and hemiacetal ester linkages. The copolymers were furnished by polyaddition of OBS macromonomers containing dihydroxy end groups and dicarboxylic acid end groups with 1,4-butanediol divinyl ether using either melt polyaddition without added catalysts or acid catalyzed solution polymerization. TGA and DSC analysis were carried out to study the effects of varying the ratio of backbone acetal to hemiacetal ester linkages on the thermal properties of copolymers. Finally, the author showed that the degree of hydrolysis of the polymer backbone and the molecular weight of the formed degradation products could be tuned by the extent of incorporation hemiacetal ester linkages and their distribution along the polymer backbone.