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Type(English)	Summary

（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 系 応用化学 コース	申請学位（専攻分野）： Academic Degree Requested	博士 （ Engineering Doctor of ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

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 optimized and 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 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.

Overall, the author demonstrated that degradability of the polymer backbone of poly(butylene succinate)s could be tuned by controlling the nature and the spacing of periodically incorporated labile linkages. Polymers with the acetal linkages

were only cleavable under mild acidic conditions while those with backbone hemiacetal ester linkages showed complete hydrolysis even under uncatalyzed conditions (pH = 6-8). Additionally, the copolymers with both of these labile linkages showed increased susceptibility towards hydrolysis at pH = 6-8 and the degree of hydrolysis was controlled by changing the ratio of acetals to hemiacetal esters in the polymer backbone. As a result of the periodic distribution of the labile linkages, the degradation products after selective polymer backbone scission comprised of molecules with discrete molecular weights which were shown to be marine biodegradable. Therefore, the author believes that understanding the interplay between precisely defined backbone OBS segments and the nature of main chain labile linkages could be the key to developing PBS derivatives with tunable and predicable degradation properties.