SUMMARY OF Ph.D. DISSERTATION

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Title

Studies on the synthesis of sulfur containing polymers using enzymes

Abstract

Environmentally benign methods for synthesis of polymer are needed in order to establish green and sustainable chemistry. Such methods may include the use of enzymes, which exhibit high catalytic activities and also high selectivities under mild reaction conditions. This report focuses on the enzymatic syntheses of novel sulfur containing polymers, polythioester and polyester with free pendant mercapto groups.

In Chapter 1, green chemistry, enzymatic polymerization, recycling of polymers and sulfur containing polymers were explained as the introduction of this thesis.

In Chapter 2, enzymatic syntheses of a series of polythioesters with various methylene lengths by the direct polycondensation were introduced. Higher T_m values were shown for the synthesized polythioesters compared to those of the corresponding polyesters. Polythioester-assimilating microbes were isolated from culture broth that contained polythioester as a sole carbon source, suggesting their biodegradability.

In Chapter 3, enzymatic ring-opening polymerization of cyclic(thioester) was studied as an objective to synthesize polythioesters with higher molecular weight. Using this method, polythioester with M_w of over 100,000 was obtained, which could not be synthesized by the direct polycondensation method. Furthermore, the enzymatic ring-opening polymerization behavior of cyclic(thioester) was compared with the corresponding cyclic(ester) and studied in detail. It was found that the rate-determining step for ring-opening polymerization of cyclic thioester was the deacylation of the enzyme-activated monomer by the propagating thiol chain.

In Chapter 4, aliphatic polyester with free pendant mercapto groups was prepared by direct lipase-catalyzed polycondensation. The polycondensation reaction was carried out without any formation of disulfide or thioester linkages to produce the corresponding polyester with excellent selectivity. The obtained polyester was easily cross-linked to form gels by the air oxidation of pendant thiols to disulfides into DMSO.

In Chapter 5, the conclusions for this thesis were shown.