Single-step lipase-catalyzed functionalization of medium-chain-length polyhydroxyalkanoates

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Abstract

BACKGROUND: Functionalization of aliphatic biopolymers such as bacterial polyhydroxyalkanoates (PHA) using biologically active hydrophilic moieties like sugars helps to improve the hydrophilicity and biodegradability of the biomaterial.

RESULTS: The effects of reaction variables on variable time, temperature, enzyme concentration and substrate ratio on reaction rate and yield in the synthesis of poly(1-3-hydroxyacyl sucrrose) using Candida antarctica lipase B (EC 3.1.1.3) were studied. Using H2O2 as micro-initiator, enzyme-mediated synthesis yielded reaction rate, vH2O2 of 0.076 x 10−3 mol L−1 s−1. The biodegradability of the functionalized polymer was observed to increase by 1.5 fold compared with the non-functionalized material apart from showing better compostability. Increasing the reaction temperature (≥ 50°C), enzyme concentration (≥ 15 g L−1) and reactant ratio (w/w) of sucrrose:PHA (≥ 2) did not increase further the rate or yield. The sucrrose-functionalized mcl-PHA was characterized with respect to the non-functionalized material.

CONCLUSIONS: Novozym® 435 can be used effectively to synthesize poly(1-3-hydroxyacyl sucrrose) in micro-aqueous medium bypassing the need for chemo-synthetic steps. The synthesized biomaterials have potential applications in biomedical and industrial niches.

Keywords: biopolymer; Candida antarctica; lipase; polyhydroxyalkanoates; sugar-ester; sucrrose

INTRODUCTION

Polyhydroxyalkanoates (PHA) are known to have important industrial and biomedical applications as a result of their biodegradability, biocompatibility, compostability and versatile structural composition. In fact, the current concerns over environmental pollution and degradation, favor the application of these biodegradable polymers over their petrochemical counterparts. Despite their applications in the biomedical field spanning from surgical sutures, drug delivery devices to tissue engineering scaffolds, the biopolymers may exhibit slow degradability and resorbability especially within the extracellular matrices. For instance, the in vivo degradability of poly-2-oxepanone was reported to take about 3–4 years in tissue in addition to lack of total elimination of the degraded monomers out of the body. Among the reported strategies employed to address this issue is the functionalization of the polymer. One such approach is functionalization by transesterification via sugar-acylation, which not only improve the hydrophilicity of these carbohydrate esters but also impart novel properties for specialty applications such as antimicrobial activity, lectins interaction, galactosyl transferase inhibition, specific ligands to the ASGPR receptor that is overexpressed in hepatocellular carcinoma, water repelling and oil absorption.

The use of conventional chemical catalysis in polymer functionalization and modification processes is viewed as unfavorable due to byproduct(s) formation that are complicated to control particularly when the main products are intended for use in biomedical and environmental applications. Alternatively, enzymatic catalysis offers excellent enantiomeric selectivity, specificity and catalytic activity under mild reaction conditions, making the enzyme catalyzed functionalization process highly desirable. Lipases (EC 3.1.1.3) were among the most commonly used triacylglycerol hydrolases that catalyze the synthesis of ester bonds in micro-aqueous media. A wide range of biodegradable functionalized polymers has been produced using enzymatic catalysis. Most reported polymer functionalization was based on polyvinyl, polyacrylate and polycaprolactone esters. In addition, most of the synthetic process is not solely enzymatic but a hybrid system (chemo-enzymatic) where enzymatic transesterification of the vinyl or acrylic ester with the sugar moiety is followed by chemical radical polymerization. In most cases, the functionalized polymer obtained through this approach has toxic chemical impurities, which may make it less attractive for biomedical applications. Secondly, the pendant carbohydrate moiety is attached to the main polymeric chain.