



# Enzymatic synthesis and preliminary evaluation as coating of sorbitol-based, hydroxy-functional polyesters with controlled molecular weights



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## ABSTRACT

By using a combination of bio-based monomers (sorbitol, 1,10-decanediol and a range of dicarboxylic acids), a series of novel sorbitol-based polyesters was prepared by solvent-free enzymatic polycondensation using an immobilized form of *Candida antarctica lipase B* (Novozyme 435). The aim was to prepare linear polyesters with pendant, curable hydroxyl groups along the polymer backbone. To achieve this, the polyester molecular weight was controlled by tuning the reaction time, enzyme loading and reaction stoichiometry. Extensive molecular and thermal characterization was performed, showing that the obtained polyesters were semi-crystalline materials with a low  $T_g$ . The presence of sorbitol in the polyesters was confirmed through a qualitative investigation using MALDI-ToF-MS. The quantification of the sorbitol content in the polymers was achieved by inverse-gated decoupling  $^{13}\text{C}$  NMR spectroscopy, while  $^{31}\text{P}$  NMR provided information regarding the selectivity of CALB for the primary vs. the secondary hydroxyl groups. Moreover,  $^{31}\text{P}$  NMR and potentiometric titration were utilized for the quantitative determination of the amount of carboxylic groups and hydroxyl functional groups present in the polyesters. The obtained hydroxyl-functional polyesters had suitable properties to be applied as solvent-borne coatings in terms of their molecular weight, functionality and thermal characteristics. Cross-linked coatings were prepared using different conventional curing agents, including two renewable diisocyanates (ethyl ester L-lysine diisocyanate and dimer fatty acid-based diisocyanate). The resulting poly(ester urethane) coatings were tested in terms of solvent resistance, hardness and resistance against rapid deformation, showing the beneficial effect of the implemented sorbitol on network formation.

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## 1. Introduction

The use of abundant, naturally occurring renewable compounds for chemical synthesis is an important strategy to reduce our dependence on petroleum-derived raw materials. An expanding range of chemicals can be produced from renewable resources starting from sources

such as starch, cellulose and vegetable oils. Sugar-based biomass has the potential to serve as a widely available source of starting compounds for biobased polymers, as well as for bioenergy and biochemistry purposes [1]. One of the key areas targeted in the development of biomass conversion technologies is the production of new materials from renewable building blocks [2]. Much of the currently ongoing research is focused on utilizing existing building blocks coming from the second generation biomass stream (forestry and agricultural waste) for novel performance polymers.

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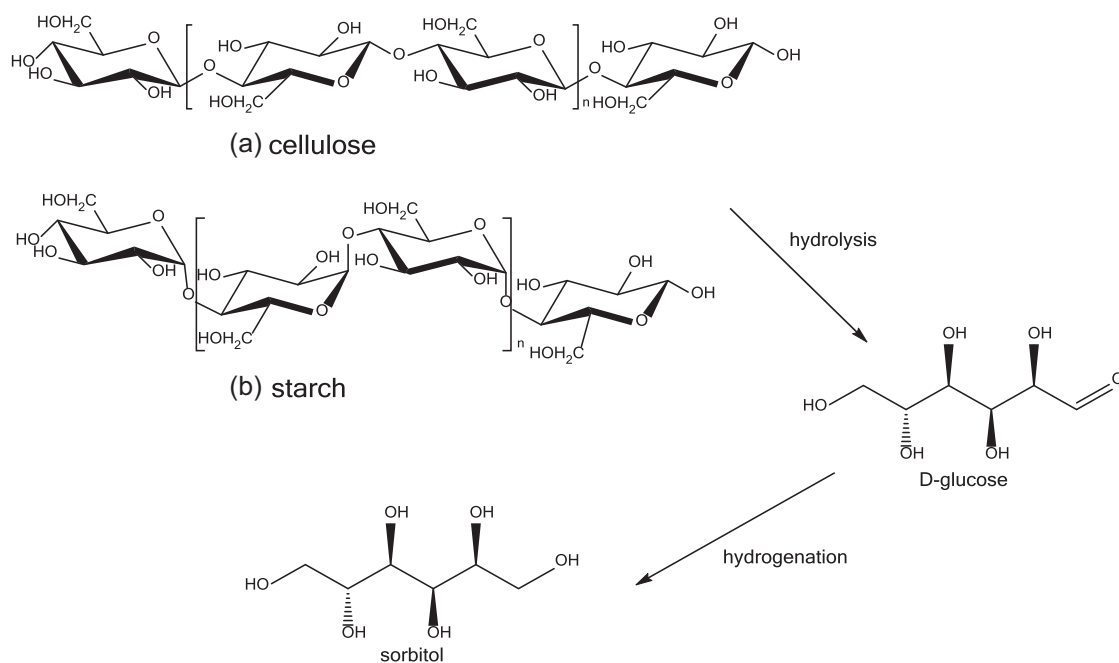
Due to its structural complexity, starch exhibits certain unique properties which are not encountered in other polysaccharides, such as granule swelling under heating. When dispersed in water upon heating, starch shows the particular ability to interact with a number of linear polar and non-polar molecules including fatty acids, fatty alcohols, monoglycerides and others. One of the most studied starch-derived saccharides is glucitol, a natural polyhydric sugar alcohol also known as sorbitol (see Scheme 1), and its derivatives sorbitan, isosorbide and galactitol [3]. Sorbitol is the most extracted sugar from starch [4] and cellulose [5]. It is increasingly utilized in non-food industries for applications such as textiles, packaging and as building block for commodity chemicals and renewable resins [3].

As a polyhydric alcohol monomer, sorbitol can in principle be directly used in polyester synthesis. However, the application of sugar-derived monomers in linear polyesters is challenging due to their multifunctional nature. Still, as sorbitol contains both primary and secondary OH-groups, it is possible to either convert most (or even all) OH-groups to ester moieties, or to selectively convert, e.g., only the primary hydroxyl functionalities. To achieve the introduction of these sugar segments along the polymer backbone without excessive branching or even cross-linking, a good control over selective ester bond formation is required. As a result, residual functional groups can be left available for further modification, functionalization or cross-linking of the obtained polyester, ideally without the use of tedious protection/de-protection chemistries. Common metal-based and organic catalysts can provide good efficiency in converting alcohol monomers to polyesters even at very low loadings, but the selectivity of such systems for either primary or secondary hydroxyl groups is typically moderate. In contrast, it is well known that enzymes may provide

a relatively high selectivity in esterification reactions. The application of enzymes is not limited to their original environment or natural role as such. In fact, their versatility facilitates their use in industrial applications, ranging from the food industry to pharmaceuticals, as well as in organic solvent-based polymerization processes [6].

The most studied enzyme used in polymer synthesis is *Candida antarctica* lipase B (CALB). This enzyme is responsible for the hydrolysis of fatty esters in nature. In anhydrous media, lipases can be active in the reverse reaction [7] and accept water, alcohols and amines as nucleophiles. By combining di(acyl) donors such as dicarboxylic acids with (di)nucleophiles such as diols, a wide range of polyesters can be produced enzymatically. Moreover, lipases do not require any co-catalyst and they can be used for polycondensation and polytransesterification reactions, ring-opening polymerizations, and polymer modification reactions [8]. For synthetic applications, CALB can be physically adsorbed on the macro-porous resin Lewatit VPOC 1600, consisting of poly(methyl methacrylate-co-butyl methacrylate) [9]. This immobilized enzyme is also known as Novozyme 435<sup>®</sup>. Since long chain, apolar alcohols are compounds quite similar to the natural fatty acid substrate, it may be expected that long chain aliphatic monomers are more readily incorporated than polar sugar derivatives [10].

Many polymers have been prepared via one-pot lipase-catalyzed condensation polymerization using a wide range of biobased diols and dicarboxylic acids [11–14]. Especially Gross et al. [9,15–17] have extensively worked with Novozyme 435<sup>®</sup> to synthesize (nearly) linear copolyesters of sorbitol with 1,8-octanediol and adipic acid, while Kobayashi et al. [18] have shown the possibility to prepare polyesters of sorbitol and divinyl sebacate by using CALB as a transesterification catalyst. The strong preference of CALB



**Scheme 1.** Production of sorbitol from starch or cellulose.

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