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Bark Suberin as a Renewable Source of Long-Chain ω-Hydroxyalkanoic Acids

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Summary: Polycondensations of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid, isolated from birch outer bark, were performed at 75 °C in toluene as solvent and at 85 °C in bulk using immobilized *Candida antarctica* lipase B as catalyst. The polycondensation performed in toluene in presence of molecular sieves gave a polyester with DP 50 after 24 h. The same DP was obtained at much shorter reaction time (3 h) by bulk polymerization in an open vial without any drying agent present.

Keywords: enzymes; MALDI MS; NMR; polyesters; suberin

Introduction

Production of paper pulp and timber results in by-product streams of which some have potential commodity values. One example is bark, a low value by-product today mainly used for energy production. The outer bark of birch species in northern Europe contain about 30% of the natural polyester aliphatic suberin. *cis*-9,10-Epoxy-18-hydroxyoctadecanoic acid is the principal monomer comprising about 100 g/kg dry outer bark in *Betula verrucosa*.[1] The highly crystalline *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid (mp 79–81 °C) can be isolated in a nearly quantitative yield from alkali hydrolyzed outer bark together with a mixture of straight-chain even numbered C_{16} to C_{24} ω-hydroxy fatty acids.[2,3]

Lipase catalyzed polymerizations may sometimes allow straightforward synthesis strategies for polyesters from sensitive monomers that do not survive more conventional polymerization catalysts and this has, for example, been used for the preparation of polyesters from epoxy containing monomers. In this paper we summarize results from a recent study on polycondensations of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid isolated from birch outer bark using immobilized *Candida antarctica* lipase B (Novozyme 435) as catalyst.[4]

Birch Suberin Monomers

Suberin is a natural polyester which could be used for further chemical or enzymatic conversions. The chemical composition varies with the origin and upon depolymerisation mixtures of different fatty acids are obtained, typically C_{16} to C_{24} (even-numbered) α,ω-dicarboxylic acids and ω-hydroxy fatty acids, some with additional functional groups in the middle of the chain. One interesting source for suberin fatty acids is the outer bark of birch which has one principal monomer, *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid, in contrast to many other sources, for example, cork from the cork oak, Figure 1.[1,5]

Lipase-Catalyzed Synthesis of Polyesters

Candida antarctica lipase B immobilized on a macroporous acrylic acid resin (Novozym 435) was chosen as catalyst as it has been shown to be a highly efficient catalyst for polymerization of long chain aliphatic ω-hydroxy acids.[6] Toluene has been shown

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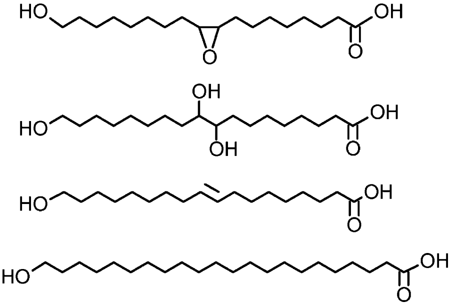

Figure 1.

Examples of ω-hydroxy fatty acids isolated from the outer bark of birch. From top to bottom: 9, 10-epoxy-18-hydroxyoctadecanoic acid (36 wt-%), 9, 10,18-trihydroxyocta-decanoic acid (9 wt-%), 18-hydroxy-octadec-9-enoic acid (11 wt-%), 22-hydroxydocosanoic acid (14 wt-%).

to be an efficient solvent for Novozym 435 catalyzed polymerizations.[7] In Figure 2 polymerization with toluene as solvent in presence of molecular sieves is compared with bulk polymerization without any drying agent present. The temperature used for the toluene polymerization was 75 °C. For the bulk polymerizations a higher temperature of 85 °C was needed in order to melt the epoxy acid (m.p. 79–81 °C). A DP of 50 was obtained after 24 h reaction time when toluene was used as solvent. The same DP of 50 was obtained in the bulk polymerizations at a much shorter reaction time (3 h). It should be mentioned that in the bulk polymerization the polymer started to form an insoluble gel at reaction times longer then 24 h probably due to side reactions involving cross-linking by the epoxide group.[4]

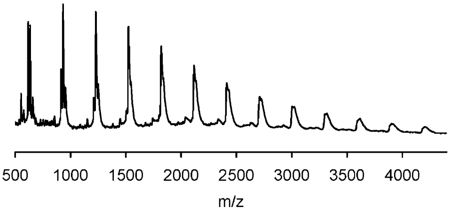

Figure 3.

MALDI-TOF MS spectrum from a 30 minutes polymerization of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid in toluene.

Characterization of Products

Positive ion MALDI-TOF MS spectra were recorded for products larger than 600 Da since the range below was dominated by peaks from matrix. Figure 3 shows a mass spectrum of the products from a 30 minutes polymerization in toluene.

There are two product distributions in the mass spectrum both with a repeat unit of 296 Da. The first minor peak distribution starting at 615 Da with very low intensities indicates the formation of small amounts of Na$^+$-cationized cyclic oligomers in the initial phase of the reaction. The second major peak distribution starting at 633 Da represents Na$^+$-cationized oligomers. ^{1}H NMR analyses were performed on the monomer and the polymer purified by precipitation from methanol. The ^{1}H NMR

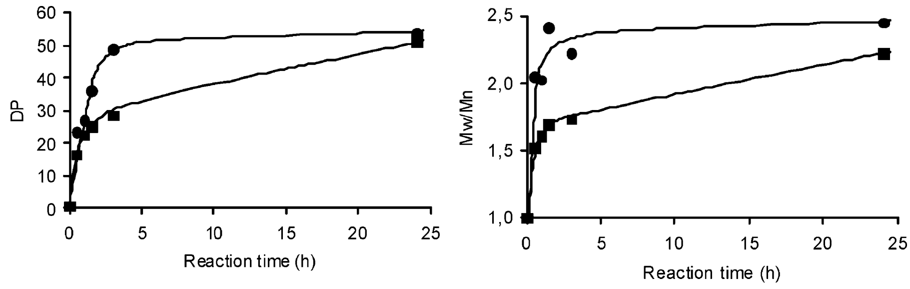

Figure 2.

Degree of polymerization (DP) and polydispersity index (M_w/M_n) in Novozym 435 catalyzed polycondensations determined by GPC of *cis*-9,10-epoxy-18-hydroxyoctadecanoic in toluene with molecular sieves (■) and in bulk without any drying agent (●).

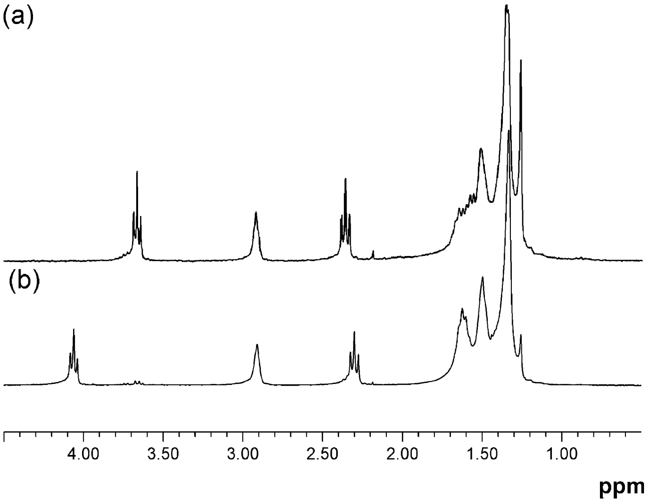

Figure 4.
^{1}H NMR spectra of (**a**) *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid and (**b**) poly(9,10-epoxy-18-hydroxyoctadecanoic acid).

spectra of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid and the corresponding polyester are shown in Figure 4 and it should be noted that in the polyester the *cis*-epoxy group (δ 2.9 ppm) is still intact.

Conclusion

Immobilized *Candida antarctica* lipase B (Novozym 435) is an efficient catalyst for the polycondensation of *cis*-9,10-epoxy-18-hydroxyoctadecanoic acid to give epoxy functionalized polyesters. A high molecular weight polyester with (M_w 15 000, M_w/M_n 2.2) was obtained by an uncomplicated bulk polymerization for 3 h in an open vial without any drying agent present.

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