European Polymer Journal 106 (2018) 79–84

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Elucidating enzymatic polymerisations: Chain-length selectivity of *Candida antarctica* lipase B towards various aliphatic diols and dicarboxylic acid diesters

Alessandro Pellis[a,*], James W. Comerford[a], Andrew J. Maneffa[a], Mika H. Sipponen[b], James H. Clark[a], Thomas J. Farmer[a]

[a] *University of York, Department of Chemistry, Green Chemistry Centre of Excellence, YO10 5DD Heslington, York, UK*
[b] *Aalto University, School of Chemical Engineering, Department of Bioproducts and Biosystems, Espoo, Finland*

ARTICLE INFO

Keywords:
Enzymatic polymerisation
Biobased polyesters
Solventless synthesis
Candida antarctica lipase B
Enzymatic selectivity

ABSTRACT

The sustainable synthesis of polymers is a field with growing interest due to the need of modern society to preserve the environment whilst making used products and food sustainable for the future generations. In this work we investigate the possibility of synthesizing aliphatic polyesters derived from various dicarboxylic acid diesters and diols in a solvent-free reaction system. *Candida antarctica* lipase B was selected as biocatalyst and its selectivity towards the carbon and ester chain length were elucidated. The selected enzyme was able to synthesize various polyesters combining C_4-C_{10} diesters and C_4-C_8 diols. All combinations led to monomer conversions above 90% in 24 h with the best number average molecular weights (M_n) being obtained through the combination of dimethyl adipate and 1,8-octanediol leading to a M_n of 7141 Da. Differential scanning calorimetry analysis shows a clear trend with an increase in melting temperature of the polymers that correlates with both the increase of the M_n or of the polymer's constitutional repeat unit carbon chain length. Thermogravimetric analysis and rheology measurements performed on selected samples also confirm the trend showing a variation of the polymer's degradation temperatures and viscosity profiles.

1. Introduction

The application of biocatalysts in organic synthesis offers several advantages compared with traditional chemo-catalysts such as milder reaction conditions with regards to temperature (usually $T < 100\,^{\circ}C$), pressure and pH (normally 3–8). Such conditions often lead to remarkable energy efficiency, high enantio-, regio- and chemo-selectivities as well as controlled stereochemistry. These features allow the development of new functional compounds for pharmaceuticals, agrochemicals and polymers using nontoxic natural catalysts with a significant "green" appeal having commercial benefits and satisfying ecological requirements [1].

Despite studies focused on the use of glycosidases for the synthesis of natural and unnatural polysaccharides [2], as well as oxidoreductases for the polymerisation of phenol derivatives [3] and vinyl monomers [1] (mainly using laccases and peroxidases), the most investigated area of enzymatic synthesis is the production of polyesters via both polycondensation (transesterification) and ring opening polymerisations (ROPs) [4,5]. These areas have predominantly emerged thanks to the discovery and commercial availability of *Candida antarctica* lipase B (CaLB). Over recent years the extraordinary properties of this enzyme were brought to light from several research teams in the kinetic resolution of organofluorine rac-alcohols [6], the synthesis of glucoside esters [7] and the enantioselective synthesis of a β-amino acid ester via a solvent-free chemo-enzymatic reaction among others [8].

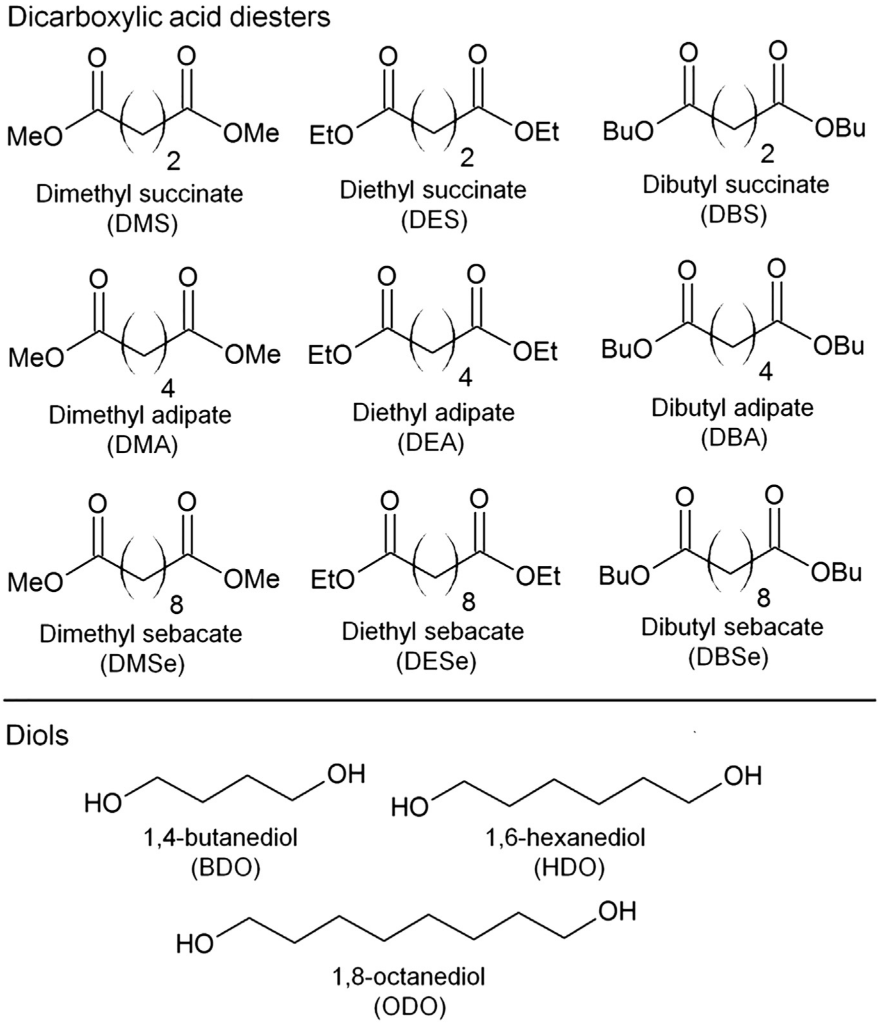
Further to this, CaLB has been shown to be an active catalyst for the synthesis of a wide range of aliphatic [9], aliphatic functional [10,11] (e.g. polyesters containing lateral functionalities such as vinyl and hydroxy groups) and aliphatic-aromatic polyesters [12,13] and polyamides [14]. In recent years these polyesters and polyamides have been derived preferentially from renewable monomers such as 2,5-furandicarboxylic, adipic and succinic acids and 1,4-butanediol among others [5].

Despite several other enzymes belonging to the hydrolyses family, namely cutinases from *Humicola insolens* [15], *Fusarium solani pisi* [16] and *Thermobifida cellulosilytica* [17], being reported to be active for the synthesis of various polyesters and polyamides in their lyophilized and immobilized forms (ranging from cross-linked enzyme aggregates to

---

[*] Corresponding author.
E-mail address: ale.pellis@york.ac.uk (A. Pellis).

https://doi.org/10.1016/j.eurpolymj.2018.07.009
Received 3 May 2018; Received in revised form 6 July 2018; Accepted 7 July 2018

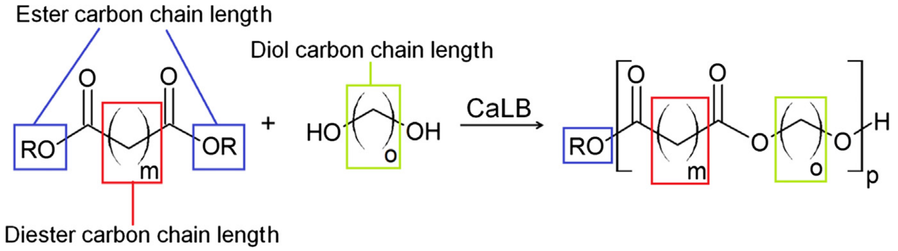


Scheme 1. Dicarboxylic acid diesters (top) and linear diols (bottom) used in this study for the enzymatic synthesis of aliphatic polyesters in solvent-free systems using Candida antarctica lipase B as biocatalyst.

covalent binding [18,19]), the choice of the chemist is still often the readily available CaLB adsorbed on a methacrylic resin known under the tradename of Novozym® 435. This biocatalyst has been shown to be active and stable in several different conditions ranging from water-based to anhydrous organic media and up to temperatures of ~100 °C.

Among the many synthesis studies both on polycondensation and ROPs that were performed over the years using this enzyme, we found there is a lack of comparative studies on the range of monomers shown in Scheme 1 (most of which bio-based) [20] for the synthesis of aliphatic polyesters.

Despite the many studies on the topic, there remains an absence of any detailed systematic study into the implications of changing the diester and/or diol whilst applying identical methodologies for the polymerisation. In the present study we investigated the CaLB-catalyzed polycondensation of various methyl-, ethyl- and butyl- dicarboxylic acid esters with various linear diols having a carbon chain length of 4, 6 or 8, shedding light on how reactive different size diesters are when employing enzymatic catalysis in a solvent-free reaction system (Scheme 2). These results will/have help(ed) us to understand the strengths and weaknesses of using this, until now, sporadically investigated enzyme for polyester synthesis.



Scheme 2. The three parameters that were investigated in the present study, namely (1) ester carbon chain length; (2) diester carbon chain length and (3) diol carbon chain length.