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

3

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12

13 Keywords: enzymatic polymerisation, biobased polyesters, solventless synthesis, *Candida*
14 *antarctica* lipase B, enzymatic selectivity

15

16 Abstract

17 The sustainable synthesis of polymers is a field with growing interest due to the need of
18 modern society to preserve the environment whilst making used products and food
19 sustainable for the future generations. In this work we investigate the possibility of
20 synthesizing aliphatic polyesters derived from various dicarboxylic acid diesters and diols
21 in a solvent-free reaction system. *Candida antarctica* lipase B was selected as biocatalyst
22 and its selectivity towards the carbon and ester chain length were elucidated. The selected
23 enzyme was able to synthesize various polyesters combining C₄-C₁₀ diesters and C₄-C₈
24 diols. All combinations led to monomer conversions above 90% in 24 h with the best
25 number average molecular weights (M_n) being obtained through the combination of
26 dimethyl adipate and 1,8-octanediol leading to a M_n of 7141 Da. Differential scanning

27 calorimetry analysis shows a clear trend with an increase in melting temperature of the
28 polymers that correlates with both the increase of the M_n or of the polymer's constitutional
29 repeat unit carbon chain length. Thermogravimetric analysis and rheology measurements
30 performed on selected samples also confirm the trend showing a variation of the polymer's
31 degradation temperatures and viscosity profiles.

32

33 Introduction

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

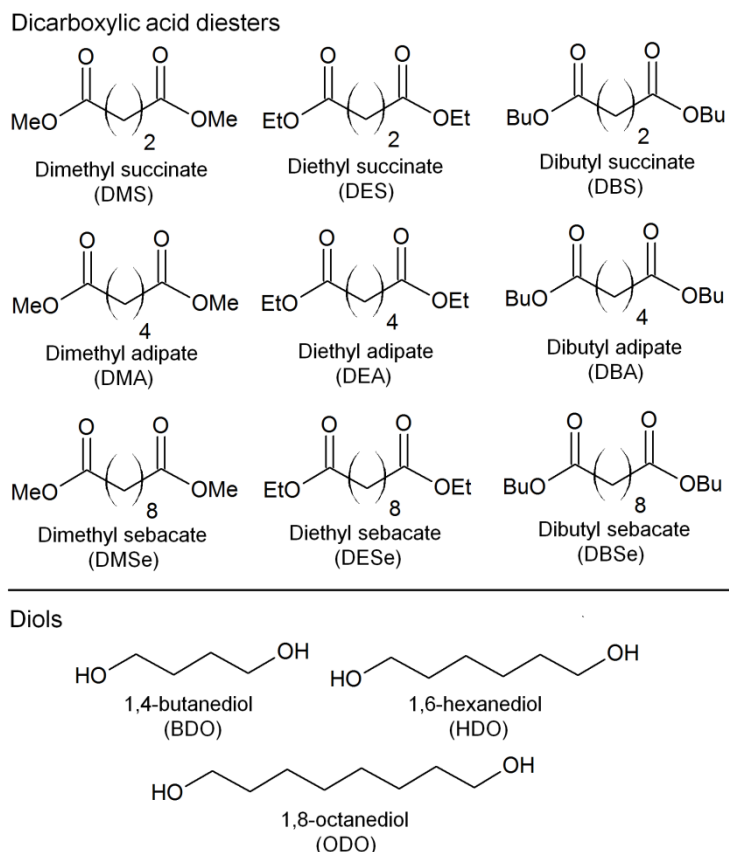
42 Despite studies focused on the use of glycosidases for the synthesis of natural and
43 unnatural polysaccharides [2], as well as oxidoreductases for the polymerisation of phenol
44 derivatives [3] and vinyl monomers [1] (mainly using laccases and peroxidases), the most
45 investigated area of enzymatic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

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

59 Despite several other enzymes belonging to the hydrolases family, namely cutinases from
60 *Humicola insolens* [15], *Fusarium solani pisi* [16] and *Thermobifida cellulosilytica* [17],
61 being reported to be active for the synthesis of various polyesters and polyamides in their
62 lyophilized and immobilized forms (ranging from cross-linked enzyme aggregates to
63 covalent binding [18, 19]), the choice of the chemist is still often the readily available CaLB
64 adsorbed on a methacrylic resin known under the tradename of Novozym® 435. This
65 biocatalyst has been shown to be active and stable in several different conditions ranging
66 from water-based to anhydrous organic media and up to temperatures of ~100 °C.

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

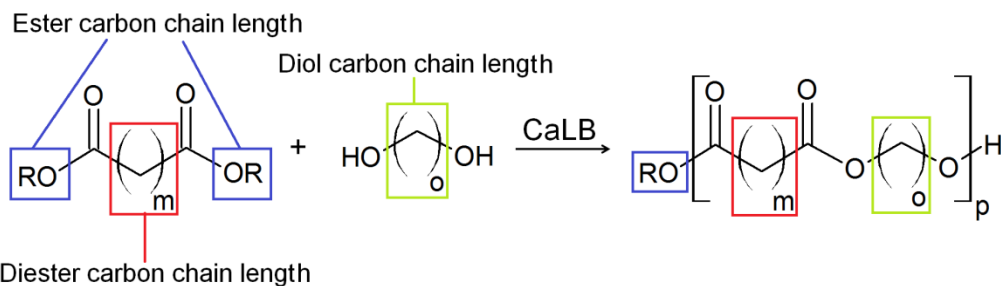
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72
73 Scheme 1. Dicarboxylic acid diesters (top) and linear diols (bottom) used in this study for the enzymatic
74 synthesis of aliphatic polyesters in solvent-free systems using *Candida antarctica* lipase B as biocatalyst.
75

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

85



86
87 Scheme 2. The three parameters that were investigated in the present study, namely 1) ester carbon chain
88 length; 2) diester carbon chain length and 3) diol carbon chain length.
89

90 Materials and methods

91 Chemicals and enzymes

92 1,4-butanediol (BDO) was purchased from Alfa Aesar. Dimethyl adipate (DMA) and 1,8-
93 octanediol (ODO) were purchased from Acros Organics. Dimethyl succinate (DMS) was
94 purchased from Fluka. All other chemicals and solvents were purchased from Sigma-
95 Aldrich and used as received if not otherwise specified. *Candida antarctica* lipase B
96 (CaLB) immobilized onto methacrylic resin was purchased from Sigma-Aldrich (product
97 code L4777) (N435). The enzyme was dried under vacuum for 96 h at 25 °C and stored in
98 a desiccator prior to use.

99 Enzymatic polycondensation of aliphatic polyesters

100 0.006 mol of dicarboxylic acid ester (A) and 0.006 mol of linear diol (B) (diester:diol ratio=
101 1.0:1.0) were accurately weighted in a 25 mL round bottom flask. The mixture was then
102 stirred at 85 °C until a homogeneous melt was obtained. 10% w w⁻¹ (calculated on the total
103 amount of the monomers) of N435 was then added and the reaction was run for 6 h at
104 1 Atm. A vacuum of 20 mbar was subsequently applied for an additional 18 h maintaining
105 the reaction temperature at 85 °C (total reaction time: 24 h). The reaction product was
106 recovered by adding THF (or DCM in the case of the 24 h succinate-BDO polymers) in
107 order to dissolve the solid reaction products. The biocatalyst was then removed via a
108 filtration step and the solvent evaporated under vacuum. The polymers were then
109 characterised without additional purification steps.

110 Nuclear Magnetic Resonance (NMR) Spectroscopy

111 ^1H -NMR analyses were performed on a JEOL JNM-ECS400A spectrometer at a frequency
112 of 400 MHz. CDCl_3 was used as NMR solvent for all synthesized polymers.

113 Gel Permeation Chromatography (GPC)

114 GPC was carried out using a PSS SDV High set composed of 3 analytical columns ($300 \times$
115 8 mm , particle diameter $5 \mu\text{m}$) of 1000, 1000×10^5 and 10^6 \AA pore sizes, plus guard column
116 (Polymer Standards Service GmbH, PSS) installed in a PSS SECcurity SEC system.
117 Elution was with THF at 1 mL min^{-1} with a column temperature of $23 \text{ }^\circ\text{C}$ and detection by
118 refractive index. $20 \mu\text{L}$ of a $\sim 2 \text{ mg mL}^{-1}$ sample in THF, adding a drop of toluene as
119 reference standard, was injected for each measurement and eluted for 50 min. Calibration
120 was carried out in the molecular weight range 370-2520000 Da using the ReadyCal
121 polystyrene standards supplied by Sigma Aldrich and referenced to the toluene peak.

122 Differential Scanning Calorimetry (DSC)

123 Traditional DSC analyses were performed on a TA Instruments Q2000 under nitrogen
124 atmosphere. The heating rate used was $5 \text{ }^\circ\text{C min}^{-1}$ over a T range of -60 - $200 \text{ }^\circ\text{C}$. Cooling
125 rate was set at $5 \text{ }^\circ\text{C min}^{-1}$ over the same T range. Sample mass was of 5-10 mg for all
126 measured samples. The polymer's melting ranges were calculated from the second
127 heating scan using the value at peak maximum option.

128 Thermogravimetric analysis (TGA)

129 TGA was performed on a PL Thermal Sciences STA 625 thermal analyzer. $\sim 10 \text{ mg}$ of
130 sample was weighted in an aluminium pan. The sample was then placed into the furnace
131 with a N_2 flow of 100 mL min^{-1} and heated from 21 to $625 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}$
132 min^{-1} . From the TGA profiles the temperatures at 5% and 50% mass loss (TD5 and TD50)
133 were subsequently determined.

134 Rheology measurements

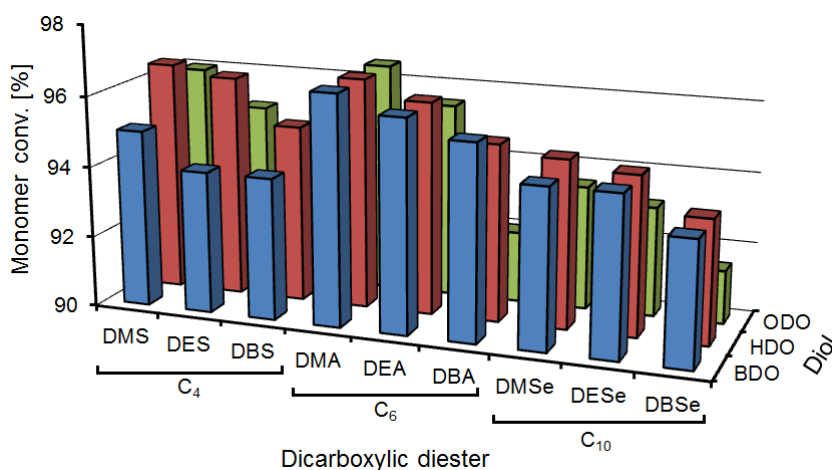
135 Rheological rotational measurement under controlled shear rate were recorded using a
 136 Brookfield R/S-CPS+ Rheometer fitted with a Peltier P-TS2 temperature controller and
 137 cone-plate geometry where the cone used had a 25 mm diameter, 2° angle and 0.045 mm
 138 gap height. The polymer samples were ground with a pestle and mortar prior to being
 139 loaded onto the pre-heated (80 °C) bottom plate. In all cases, a constant shear rate of 100
 140 s⁻¹ was maintained throughout the experiments with each polymer melt being initially held
 141 at 80 °C (under shear) for 120 s before the temperature was decreased by 0.01 °C s⁻¹.

142

143 Results and Discussion

144 The CaLB-catalysed polycondensation of methyl-, ethyl- and butyl- succinic (C₄), adipic
 145 (C₆) and sebacic (C₁₀) dicarboxylic acids esters with linear diols having a carbon chain
 146 length of 4, 6 or 8 atoms were investigated. In order to be environmentally friendly, all
 147 reactions were performed in bulk (i.e. solvent-less). All monomers were melted at 85 °C
 148 before adding the biocatalyst that allowed the initiation of the step-growth
 149 polycondensation. From the ¹H-NMR spectra analysis it is possible to observe that for all
 150 reactions excellent monomer conversion values (>90%) were obtained with the methyl and
 151 ethyl esters consistently giving slightly higher conversions than the equivalent butyl esters
 152 for all the dicarboxylic diesters investigated (Figure 1).

153



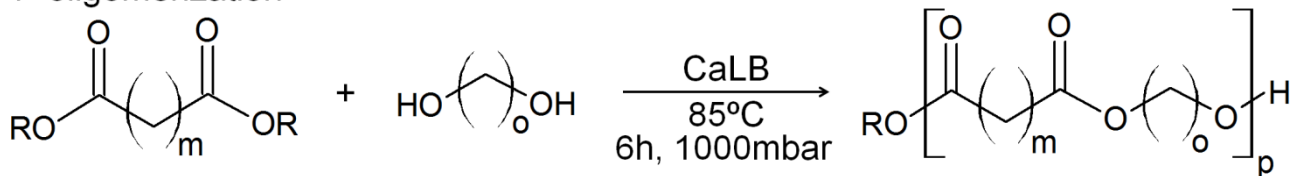
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155 Figure 1. ¹H-NMR analysis of the crude polycondensation products after CaLB-catalyzed polycondensation
 156 reactions after 24 h. Reactions without catalyst led to no detectable transesterification products. All reactions
 157 were performed in duplicates. Statistical analysis reporting the mean value ± standard deviation for all
 158 reactions can be found in ESI, Figure S1 and the complete spectra assignment in Figure S5.
 159

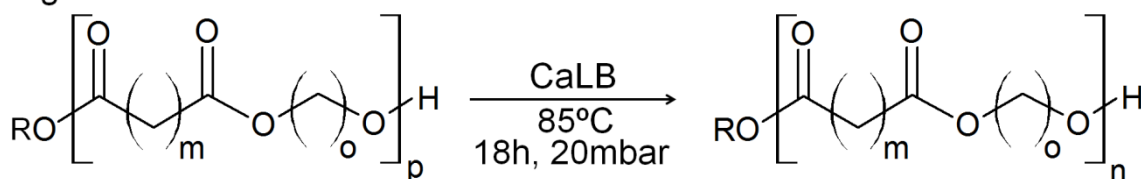
160 The 2-step polycondensation protocol (1st-oligomerization and 2nd-chain elongation)
 161 reported in Scheme 3 was found suitable for all the reactions (see Table 1). The
 162 polycondensation reactions occur via transesterification of dicarboxylic acids diesters with
 163 aliphatic diols and follow a step-growth polymerisation mechanism (the same as some
 164 other similar synthetic polymers such as polyamides and polyurethanes). In fact with low
 165 DP (~5-10) the conversion is already >80-90% and further increase in DP (two fold)
 166 influences only minor the monomer conversion. This allows the initial oligomerisation of
 167 most of the monomers without loss of any of the starting compounds. After oligomerisation
 168 is achieved, vacuum is applied to effectively remove the alcohol by-product and enables
 169 the elongation of the polymeric chain length. The biocatalyst is indeed able to catalyse
 170 synthetic reactions starting from long polymeric chains as recently reported by Vastano et
 171 al. who coupled dimethyl itaconate and poly(ethylene glycol) to poly(hydroxyalkanoates)
 172 having M_n of 50188 Da and M_w of 117720 Da produced using an engineered strain of
 173 Escherichia Coli [21].

174

1- oligomerization



2- elongation



R= -methyl, -ethyl or -butyl

o= C₄, C₆ or C₈

m= C₂, C₄ or C₈

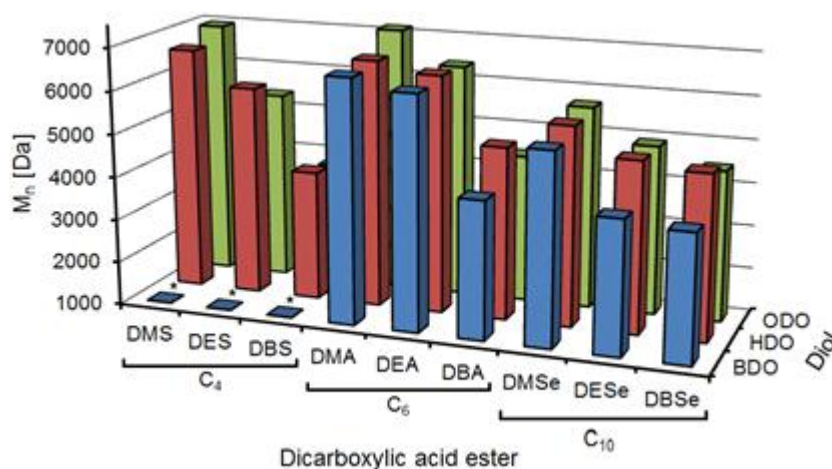
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 177

Scheme 3. The 2-step polycondensation protocol used for the synthesis of various aliphatic-aliphatic polyesters via enzymatic catalysis in bulk (n>p).

178

179 The number average molecular weight (M_n) (Figure 2) and the weight average molecular
180 weight (M_w) (see Figure S2 in ESI) of the polymers were determined via GPC analysis.
181 The M_n trend reported in Figure 2 agreed well with the $^1\text{H-NMR}$ spectroscopy monomer
182 conversion analysis reported in Figure 1. The methyl and ethyl diesters lead to the
183 synthesis of polymers having higher molecular weight relative to the butyl diesters. This
184 effect of the size of the alkyl group of the diester (-methyl, -ethyl and -butyl) becomes less
185 marked when increasing the diester internal chain length from C_6 to C_{10} . The lower
186 conversions and molecular masses obtained using butyl diesters is most probably due to
187 the relative boiling points of the alcohol by-products with methanol (BP= 64.7 °C) and
188 ethanol (BP= 78.4 °C) being significantly less volatile than butanol (BP= 117.7 °C) and
189 therefore easier to remove from the reaction system, especially when considering a
190 reaction temperature of 85 °C was used. The polymers synthesized using the shortest
191 dicarboxylic esters, dimethyl succinate (DMS), diethyl succinate (DES) and dibutyl
192 succinate (DBS) together with 1,4-butanediol (BDO) were not soluble in the GPC mobile
193 phase (THF) and therefore were not characterised using this technique.

194



195
196 Figure 2. Number average molecular weights (M_n) calculated via GPC analysis of the crude
197 polycondensation products using a 370-2520000 Da polystyrene calibration curve. Reactions without
198 catalyst did not lead to detectable polyesterification products. All reactions were performed in duplicates.
199 Statistical analysis reporting the mean value \pm standard deviation for all reactions can be found in ESI,
200 Figure S2. *=reactions non soluble in the GPC mobile phase (THF).

201

202 The generally observed trend for the synthesised polymers based on HDO and ODO
203 having higher molecular masses than the BDO equivalents (with the exception of the
204 adipate-based polyesters that showed similar molecular masses) reflects very well the
205 data reported by Feder and Gross for the polycondensation of sebacic acid and various
206 diols using N435 at 70 °C. [15] In this previous work, a comparison between adipic and
207 sebacic acid was made and fully agrees with our observation that the adipic acid diesters
208 lead to higher molecular weight products than the sebacic diesters when methyl and ethyl
209 esters were used while no significant differences were observed when butyl esters were
210 used. It was noticed that CaLB, when operating in a solventless reaction system, led to
211 smaller differences between the different ester chains than when using cutinases and
212 serin-hydrolase enzymes belonging to the same family. [22] In fact, whereas CaLB leads
213 to similar conversions with BDO, HDO and ODO, cutinases have a preferred substrate.
214 Cutinase from *Humicola insolens* (70 °C, in bulk, diol diacid 1:1 mol/mol, 1% w/w of
215 enzyme-to monomer, application of vacuum after 2 h) produces polyesters with higher
216 molecular weight when ODO is used as a diol [15] while cutinase 1 from *Thermobifida*
217 *cellulosilytica* (Thc_cut1) (70 °C, in bulk, diol diacid 1:1 mol/mol, 10% w w⁻¹ CaLB
218 immobilized onto methacrylic resin-to monomer, application of vacuum for 24 h) prefers
219 BDO, leading to only short oligomers when HDO and ODO are used in combination with
220 dimethyl adipate. [23] For Thc_cut1, it was recently reported that the structure of the diol is
221 relevant for the chain length, but the conversion is not much affected. [17]

222 In order to be able to analyze the differences between all reactions, including the formation
223 of aforementioned insoluble poly(butylene succinate), some selected reactions (reported in
224 Table 1) were run for only 6 h at 85 °C and atmospheric pressure in order to stop the
225 reaction after the initial oligomerisation phase.

226

Table 1. Comparison of the CaLB-catalyzed polycondensation reactions after 6 h at 85 °C and 1000 mbar and 24 h.

Diester	Diol	Time [h]	Conv. [%] [#]	M _n [*] [Da]	M _w [*] [Da]	Đ [*]	M ₀	DP _n	
DES	BDO	6	89	851	1094	1.29	172.2	4.9	
		24	94	ns	ns	ns		x	
	HDO	6	92	2164	2398	1.26	200.2	9.8	
		24	96	5853	10439	1.79		29.2	
DMA	BDO	6	89	2227	2843	1.31		200.2	10.1
		24	97	6626	11549	1.71			33.1
DBA	HDO	6	83	2018	2247	1.07	228.3	9.5	
		24	95	4978	8018	1.62		21.8	

[#] Calculated via ¹H-NMR based on the conversion of the diol.

^{*} Calculated via GPC using a - Da polystyrene calibration curve and toluene as internal standard.

ns= non soluble in THF

227

228 From the collected data it is possible to see that the insolubility of poly(butylene succinate)
 229 in THF, even after stirring for several days, is not due to the high molecular weight of the
 230 polymers. It is well known that the dissolution of polymers depends not only on their
 231 physical properties, but also on their polarity, molecular weight, branching, crosslinking
 232 degree and crystallinity. [24] In this particular instance, given the crystalline nature of all
 233 produced polymers it is probable that the insolubility of the succinate-based aliphatic
 234 oligoesters after 24 h reaction was indeed a result of high crystallinity rather than the
 235 oligomers as evidenced by the molecular masses data reported in Table 1 (and the DSC
 236 data reported later). The calculation of the DP of the reactions after 6 and 24 h fully
 237 confirms the trend previously reported via ¹H-NMR spectroscopy and GPC for all of the
 238 other reactions carried out (Table 1).

239 In addition to monomer conversion and molecular weight analysis, differential scanning
 240 calorimetry analysis for the determination of the polymers' melting points and
 241 thermogravimetric analysis for the determination of the mass loss were performed. Figure
 242 3 reports the melting temperatures of all the synthesized polymers when the standard
 243 protocol (6 h at 1000 mbar, 18 h at 20 mbar, 85 °C, 10% w w⁻¹ CaLB, 24 h total reaction
 244 time) was applied. It is possible to observe a general trend where an increase in polymer
 245 melting point aligns with increasing carbon chain length of the diester, where C₄-based

246 polymers have lower melting points than the C₁₀-based polymers. This is due to the
 247 crystallinity of the C₄-based polymers as discussed above. A similar increase is also
 248 observed when increasing the diol carbon chain length from C₄ (BDO, blue) to C₈ (ODO,
 249 green). In this case, increasing the dicarboxylic ester length from C₄ to C₈ reduces the
 250 melting point differences among the produced polymers, analogous to number average
 251 molecular weight observations plotted in Figure 2.

252

Table 2. Calculated percentage of M_n reduction for any diethyl ester chain in relation to the alkyl group in relation to 1,8-octanediol.

		Diester end group		
		Me	Et	Bu
Diester carbon chain length	C4	6959 g mol ⁻¹ * 100%	5380 g mol ⁻¹ * 23%	3796g mol ⁻¹ * 45%
	C6	7141g mol ⁻¹ * 100%	6390 g mol ⁻¹ * 11%	4413 g mol ⁻¹ * 38%
	C10	5677 g mol ⁻¹ * 100%	4908 g mol ⁻¹ * 14%	4478 g mol ⁻¹ * 21%

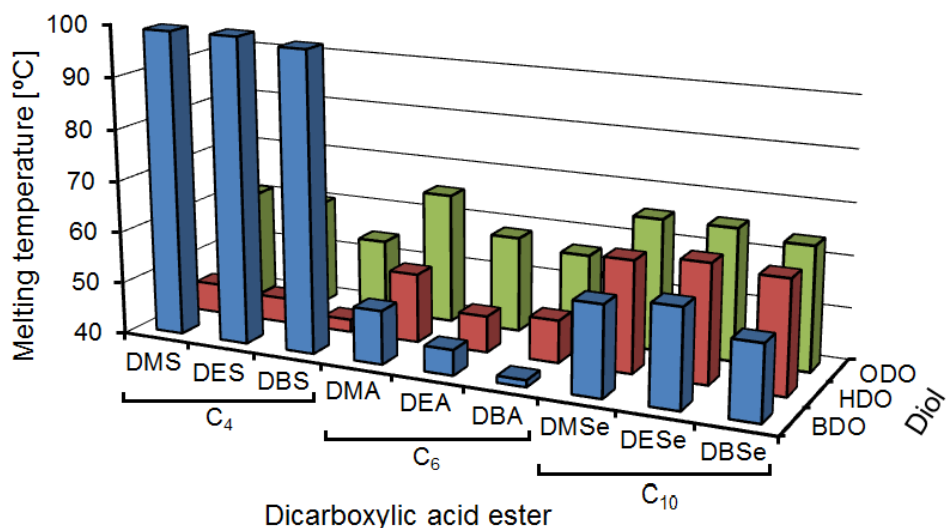
* Calculated via GPC using a - Da polystyrene calibration curve and toluene as internal standard.

253

254 In Table 2 we reported the % of M_n reduction for any diethyl ester chain in relation to the
 255 alkyl group in relation to 1,8-octanediol. As we can see from the collected data, the methyl
 256 ester (Me) (taken as 100%) is always the best performing one, followed by the diethyl (Et)
 257 and the dibutyl (Bu) ones. Also to notice that the differences in the M_ns decrease for the
 258 Bu end group are lower with the increase of the carbon chain length of the diester for the
 259 considered reaction.

260 Further to this, the difference in polymer melting temperature between the different diol
 261 chain lengths becomes less pronounced when increasing the diester chain length (Figure
 262 3).

263

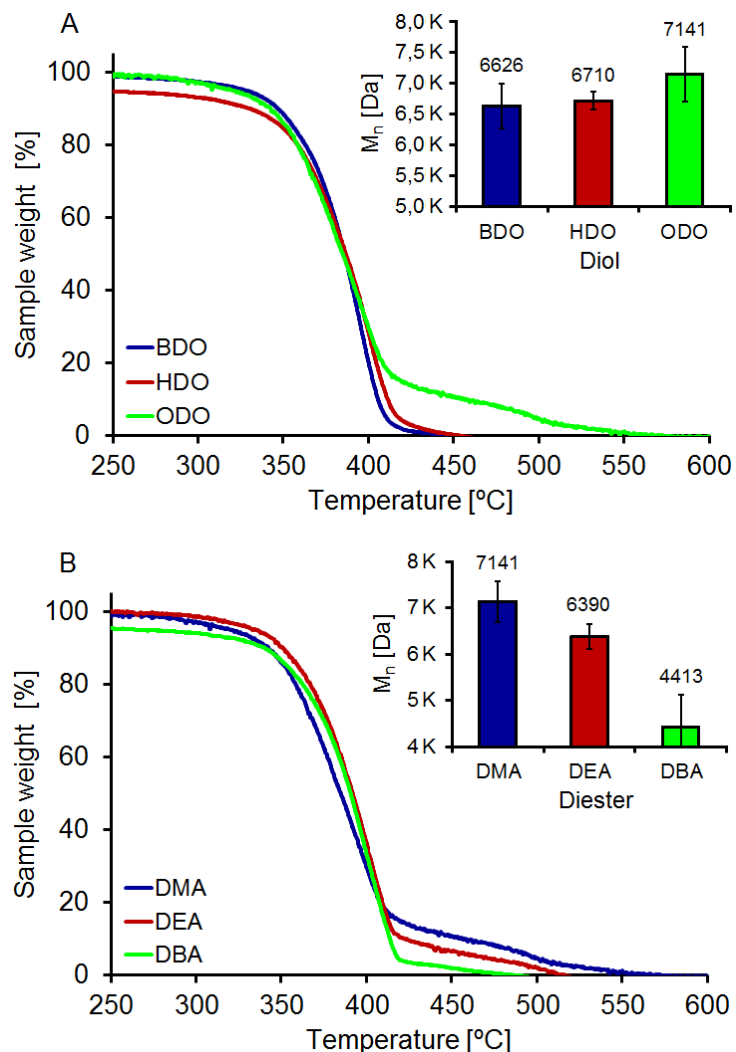


264 Figure 3. DSC determination of the polymer's melting points (see Table S1 for details).
 265
 266

267 The inert atmosphere (N₂) thermogravimetric profile of the polymers presented in Figure 4
 268 is also consistent with the previously discussed molecular mass data. In fact, with the
 269 increase of the polymer's M_n and the increase of the diol's carbon chain length (see Figure
 270 4a insert) the degradation temperature increases accordingly (Figure 4a).

271 A comparison of the polymerisations conducted using the same diol (1,8-octanediol, ODO,
 272 C₈) with three different diesters having methanol, ethanol or butanol alkyl groups on the
 273 monomers also show a remarkable difference in the obtained M_n (see discussion above
 274 and Figure 4b insert), with the dimethyl adipate-derived polyester proving more thermally
 275 stable than the diethyl equivalent, with this being more stable than the dibutyl. This
 276 indicates that the selection of the diester remains highly important for these
 277 transesterification reactions since the volatility of the leaving group proved to be a key
 278 point in determining the extent to the which the polyester chain grows. From the TGA
 279 profiles the temperatures at 5% and 50% mass loss (TD5 and TD50) were subsequently
 280 determined and are reported in Table S2 in ESI.

281



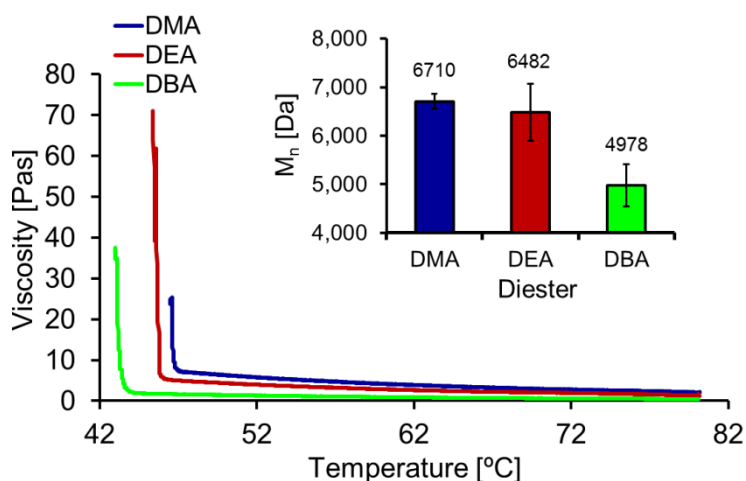
282
 283 Figure 4. TGA analysis of A) polymers obtained from the polycondensation of dimethyl adipate and the three
 284 different aliphatic diols 1,4-butanediol (C4, BDO), 1,6-hexanediol (C6, HDO) and 1,8-octanediol (C8, ODO)
 285 and B) polymers obtained from the polycondensation of ODO with three different diesters dimethyl adipate
 286 (DMA), diethyl adipate (DEA) and dibutyl adipate (DBA).
 287

288 Rheology was used to further characterise the polymers and identify differences in their
 289 viscosity. Figure 5 shows the viscosity change of the polymer melts based on a decrease
 290 of temperature for poly(1,6-hexylene adipate) synthesized from dimethyl adipate (blue),
 291 diethyl adipate (red) and dibutyl adipate (green). In all cases, viscosity steadily rose with
 292 decreasing temperature until the onset of freezing was reached, at which point viscosity
 293 increased rapidly. This further exemplifies how the differing molecular weights (see Fig.5
 294 insert) lead to different viscosity profiles. The shorter chain polymer behaves remarkably
 295 different compared with the other two polymers with similar M_n values. Comparative
 296 studies of the presented reactions in organic media are needed in order to better elucidate

297 the effect of viscosity on the reaction progression. Moreover, we noted that the viscosity of
298 any initial mixture appeared to be below the lower detection limit (ca. <0.2 Pa.s) of the
299 apparatus when used under the same conditions.

300 The produced polyesters can find applications that range from the biomedical field (as
301 carriers in protein- and peptide-delivery systems) [25] and, if further coupled with
302 poly(ethylene glycol), for the production of eco-friendly water-soluble polymers and
303 coatings [26].

304



305

306 Figure 5. Change of the polymer's viscosity relative to the temperature decrease over time for different
307 poly(hexamethylene adipate) polyesters whose chain length alters due to the chose dialkyl adipate monomer
308 (dimethyl adipate – DMA, diethyl adipate – DEA and dibutyl adipate – DBA).
309

310 Conclusions

311 From the collected data we can conclude that CaLB is an effective catalyst for the
312 synthesis of a range of aliphatic polyesters using a solventless reaction system. Polyesters
313 based on diesters with an internal carbon chain length between 4 (succinate) and 10
314 (sebacate) and diols with a carbon chain length between 4 (1,4-butanediol) and 8 (1,8-
315 octanediol) were successfully synthesized via transesterification. A strong effect of the
316 selected alkyl group of the diester (dimethyl, diethyl and dibutyl) was observed for all
317 polyesters. Lower molecular weights and monomer conversions were obtained using
318 dibutyl esters since it proved more difficult to remove the butanol by-product during the

319 reaction due to its higher boiling point (relative to methanol and ethanol). DSC, TGA and
320 rheology measurements confirm the trend showing a large difference in degradation
321 temperatures and viscosity of the melts due to the polymers' molecular weight. This work
322 has sets the basis for efficient biocatalyzed syntheses of aliphatic polyesters having M_n of
323 ~ 6 and M_w of ~ 13 KDa and with monomers conversions $>94\%$. This also represents the
324 first systematic study of different dialkyl aliphatic diesters with various diols under identical
325 reaction conditions.

326

327 Conflicts of interest

328 The authors declare no conflicts of interest.

329

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337

338 Notes and references

339 Electronic Supplementary Information (ESI) available: Details of: $^1\text{H-NMR}$ spectroscopy
340 conversions (Fig. S1), M_n (Fig.S3) and M_w (Fig. S2 and S4) GPC data, DSC-determined
341 polymer's melting temperatures (Table S1) and TD5 and 50 (Table S2) are reported in
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343 contained within the manuscript or the ESI.

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