

# The Impact of Diethyl Furan-2,5-dicarboxylate as an Aromatic Biobased Monomer toward Lipase-Catalyzed Synthesis of Semiaromatic Copolyesters

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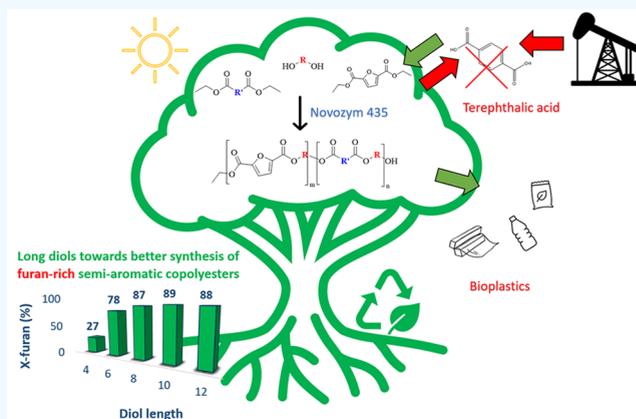
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**ABSTRACT:** Furan-2,5-dicarboxylic acid has been introduced in recent years as a green aromatic monomer toward the design of aromatic (co)polyesters with enhanced properties, i.e., polyethylene furanoate (PEF) that can definitely compete with its petroleum-based counterpart, i.e., polyethylene terephthalate (PET). In an attempt to produce biobased semiaromatic copolyesters in an efficient eco-friendly approach, we report herein the polycondensation of diethyl furan-2,5-dicarboxylate (DEFDC) with different aliphatic diols and diesters of variable chain length catalyzed by an immobilized lipase from *Candida antarctica* using a two-step polymerization reaction carried out in diphenyl ether. The influence of diol and diester chain length, the molar concentration of DEFDC, and the effect of enzyme loading were assessed via nuclear magnetic resonance (NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and wide-angle X-ray scattering (WAXS). With high quantities of DEFDC, significant differences in terms of  $\bar{M}_n$  buildup were noticed. Only longer diols starting from octane-1,8-diol successfully reacted with up to 90% DEFDC as opposed to only 25% DEFDC reacting with short diols such as butane-1,4-diol. While varying the chain length of the diester, it was evident that shorter diols such as hexane-1,6-diol have better reactivity toward longer diesters, while dodecane-1,12-diol was reactive toward all tested diesters. The incorporation of long chain fatty dimer diols such as Pripol 2033 led to polyesters with higher  $\bar{M}_n$  and was successfully used to overcome the limitations of poor reactivity observed in the case of short diols in the presence of high furan content. The DSC results showed a pseudoeutectic behavior as a function of increasing the mol % of DEFDC, and a change in the crystalline phase was confirmed via WAXS analysis. Finally, this work showed the successful enzyme-catalyzed synthesis of several DEFDC biobased semiaromatic copolyesters with variable interesting properties that can be further optimized for possible applications in food packaging as well as other possibilities.

**KEYWORDS:** enzymatic polymerization, polycondensation, lipase, furan, aromatic copolyesters, time course profile



## INTRODUCTION

The increasing environmental concerns of fossil fuel-based materials and their pronounced negative impact on our environment has been shifting the research focus toward a more sustainable synthetic pathway to develop polymers with adequate properties and a low carbon footprint. Such an approach is strongly supported with the increasing research works on the valorization of biomass to produce biobased polymeric materials.<sup>1–5</sup> In this respect, furan-2,5-dicarboxylic acid (FDCA) has been given a lot of attention in recent years as a (co)monomer, due to its ease of production from biomass and its aromaticity. FDCA is a biobased monomer synthesized by oxidation of 5-hydroxymethylfurfural, which is by turn the dehydration product of hexoses such as fructose and

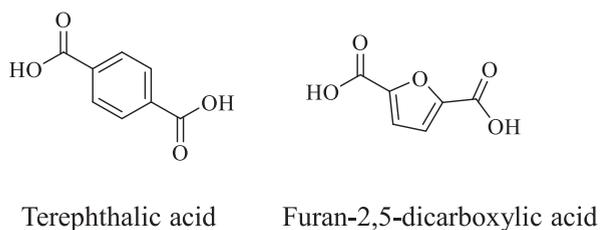
glucose.<sup>6–8</sup> There are many new research works that implement FDCA as an alternative (co)monomer to petroleum-based terephthalic acid (TPA), which is vastly used in the synthesis of aromatic polyesters, notably polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). This trend favoring FDCA stems from the structural similarities between both monomers as both are aromatic rings

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53 with two oppositely positioned carboxylic groups.<sup>9,10</sup> In  
54 addition, the FDCA bioproduction route is easily accessible  
55 when compared to the challenging and inefficient TPA  
56 bioproduction.<sup>11–14</sup> The structures of both TPA and FDCA  
57 are given in Scheme 1. When polymerized, aromatic polyesters

**Scheme 1. Structures of Terephthalic Acid (TPA) and Furan-2,5-dicarboxylic Acid (FDCA)**



58 produced from FDCA instead of TPA show very competitive  
59 properties that are in some cases considered to be far superior  
60 to TPA-based polyesters.<sup>15–19</sup>

61 In general, semiaromatic polyesters are structurally designed  
62 on the basis of both aliphatic and aromatic (co)monomeric  
63 units. The incorporation of aromatic units into the polymer  
64 structure helps increase the rigidity, hydrophobicity, and  
65 thermal properties of the polymeric backbone, whereas the  
66 aliphatic units in the form of aliphatic diacids or diols serve to  
67 enhance the flexibility of the polymeric structure and lower its  
68 glass transition temperature ( $T_g$ ).<sup>20,21</sup> Accordingly, the  
69 combination of aliphatic and aromatic groups in semiaromatic  
70 polyesters such as PET and PBT has shown a great  
71 enhancement of properties and expanded the scope of their  
72 applications, ranging from plastic bottles to synthetic fibers and  
73 food packaging.<sup>22,23</sup>

74 In recent years, many furan-based polyesters and polyamides  
75 have been synthesized,<sup>21,24</sup> and many research works have  
76 focused on comparing them to their TPA-based counter-  
77 parts.<sup>25–27</sup> For example, via a two-step polycondensation  
78 process in the presence of titanium isopropoxide ( $\text{Ti}(\text{O}-i\text{-Pr})_4$ )  
79 as catalyst, Knoop et al.<sup>16</sup> synthesized a series of polyethylene  
80 furanoates (PEFs), polypropylene furanoates (PPFs), and  
81 polybutylene furanoates (PBFs) with medium molecular  
82 weights that are comparable to their TPA analogues and  
83 show less coloration. Moreover, furan-based polyesters have  
84 been shown to present enhanced gas barrier properties when  
85 compared to their TPA counterparts.<sup>28,29</sup> Regarding their  
86 mechanical properties, PEF was found to be similar to PET in  
87 terms of its Young's modulus and maximum stress values. In  
88 contrast, PEF was shown to be significantly more brittle than  
89 PET.<sup>30</sup> In another interesting study, the PBF ductility was  
90 found to significantly increase as a function of the molecular  
91 weight, reaching Young's modulus and elongation values  
92 comparable to the reported values of commercial PBT when  
93 the  $\bar{M}_n$  was  $>16\,000\text{ g}\cdot\text{mol}^{-1}$ . In contrast, lower values of  
94 Young's modulus and elongation at break were reported when  
95 the  $\bar{M}_n$  was  $\sim 7000\text{ g}\cdot\text{mol}^{-1}$ . This difference was suggested to  
96 originate from the insufficient number of entanglements at  
97 lower molecular weight values.<sup>17</sup> Although FDCA-based  
98 polyesters show great promising properties, they are still  
99 prone to limitations, especially in regard to their fragility, slow  
100 crystallization, and in some cases, poor biodegradability. To  
101 address these issues, researchers have been trying to tune the  
102 properties of FDCA-based polymers using an array of different

diols and diacids (cyclic, secondary, etc.).<sup>21</sup> For example, the  
incorporation of cyclic diols such as 1,4-cyclohexanedimethanol  
along with propane-1,3-diol and FDCA has been shown to  
increase the thermal stability of the polyesters produced.<sup>31</sup>  
Moreover, the copolymerization of FDCA-based polyesters  
such as PEF, PPF, and PBF with rigid cyclic diols such as 1,4-  
cyclohexanedimethanol and 2,2,4,4-tetramethyl-1,3-cyclobuta-  
nediol resulted in polymers with enhanced tensile strength yet  
a lower elongation at break.<sup>32,33</sup> Enzymatic catalysis has been  
introduced as a greener synthetic approach toward the  
production of polyesters, owing to its nontoxic nature, high  
selectivity, and the possibility of processing under mild  
conditions.<sup>34–36</sup> When compared to current metal catalysts  
used for polyester synthesis, they are advantageous by avoiding  
any residual traces of harmful metals after synthesis and by  
preventing any discoloration and side reactions that can occur  
with metallic catalysis due to the elevated temperatures  
required.<sup>37</sup> In addition, the high selectivity of some enzymes  
can allow one to perform some reactions with minimal steps by  
avoiding additional steps like protection/deprotection chem-  
istries that would otherwise be required via these conventional  
catalyses.<sup>38,39</sup> Although the literature is rich in examples of  
enzyme-catalyzed polyesterification to produce aliphatic  
polyesters, the synthesis of aromatic polyesters remains less  
studied mainly due to the need to use elevated reaction  
temperatures when dicarboxylic aromatic (co)monomers are  
used. Nevertheless, several promising attempts depicted in  
multiple excellent review articles<sup>18,19</sup> have been noted to  
synthesize aromatic and semiaromatic polyesters via enzymatic  
catalysis, which can be manageable at lower temperatures by  
substituting diacid monomers with their methyl or ethyl diester  
analogues. However, such polyesters were ill-defined with their  
low molecular weights, mainly due to side reactions such as  
ether formation as well as to the low temperature used, leading  
to phase separation of the end-product and limited polymer  
growth.<sup>40,41</sup> In an attempt to overcome this limitation, Jiang et  
al.<sup>34</sup> performed a two-step polycondensation reaction in  
diphenyl ether using Novozym 435 (N435) as a catalyst,  
which is a *Candida antarctica* lipase B (CALB) immobilized on  
an acrylic resin. The results obtained showed that for the  
polyesterification reaction between dimethyl furan-2,5-dicar-  
boxylate (DMFDCA) and different aliphatic diols, specifically  
hexane-1,6-diol, octane-1,8-diol, and decane-1,10-diol, at a  
temperature of  $140\text{ }^\circ\text{C}$ , the polyesters obtained possessed a  
high  $\bar{M}_n$  of 41 100, 41 000, and 51 600  $\text{g}\cdot\text{mol}^{-1}$ , respectively.  
However, the high temperature used significantly impacted the  
activity of the recycled enzyme. Those values exceeded the  
values obtained at  $80\text{ }^\circ\text{C}$  by more than 10-fold. As enzymatic  
catalysis proved to be better suitable for oligomer production,  
several attempts to synthesize furan-based oligomers via  
enzymatic catalysis have been made in recent years, where  
different aromatic and semiaromatic oligomers were pro-  
duced.<sup>42,43</sup> Other attempts to synthesize semiaromatic diesters  
via enzymatic catalysis were reported by Pellis et al.<sup>44</sup> Aliphatic  
diols varying in chain length between  $\text{C}_4$ – $\text{C}_8$  were reacted with  
several aromatic monomers such as diethyl furan-2,5-  
dicarboxylate, diethyl terephthalate, and diethyl isophthalate  
in addition to different isomers of pyridine dicarboxylic acid.  
The results showed that the reaction between 2,4-diethyl  
pyridine dicarboxylate and octane-1,8-diol in diphenyl ether  
led to the highest molecular weight ( $\bar{M}_n = 14\,300\text{ g}\cdot\text{mol}^{-1}$ ). In  
another research work, Pellis et al.<sup>45</sup> conducted the enzyme  
catalyzed synthesis of furan and pyridine diol-based polyesters

166 such as 2,5-bis(hydroxymethyl)furan (2,5-BHMF), 3,4-bis-  
167 (hydroxymethyl)furan (3,4-BHMF), and 2,6-bis-  
168 (hydroxymethyl)pyridine using diphenyl ether as solvent. Via  
169 a two-step polycondensation reaction maintained for 96 h at  
170 85 °C, and apart from 3,4-BHMF polymers that gave low  
171 yields and  $M_n$ , all reactions tested with varying chain-length  
172 aliphatic diesters were successful with yields > 65% and  $M_n$   
173 reaching 5000 g·mol<sup>-1</sup>.

174 Although semiaromatic polyesters such as PET and PBT or  
175 their furan counterparts possess good physical properties, they  
176 are resistant to biodegradation.<sup>46,47</sup> To tackle this, semi-  
177 aromatic terpolyesters such as polybutylene adipate tereph-  
178 thalate (PBAT) were developed, consisting of aromatic and  
179 aliphatic units and showing adequate mechanical properties  
180 while being biodegradable at the same time.<sup>48</sup> In fact, the  
181 biodegradation of such copolyesters was due to the presence of  
182 aliphatic repeating units such as butylene adipate (BA) in  
183 PBAT, which were more susceptible to hydrolysis and  
184 microorganism attacks than the semiaromatic butylene  
185 terephthalate (BT).<sup>48,49</sup> In a study conducted by Herrera et  
186 al.,<sup>50</sup> PBAT with an adipate/terephthalate ratio of 60/40 was  
187 found to degrade at a faster rate than PBAT with a higher  
188 terephthalate content (40/60). Such findings could allow for  
189 adequate control over the properties and degradation time of  
190 semiaromatic copolyesters such as PBAT simply by tuning the  
191 adipate/terephthalate ratio. With the biodegradability advant-  
192 age of such copolyesters, in addition to the advantages of  
193 furan-based polyesters, researchers have been focusing in  
194 recent years on developing furan-based copolyesters such as  
195 polybutylene adipate furanoate (PBAF) aiming to produce  
196 biobased polymers, which are also biodegradable and possess  
197 adequate properties, allowing them to compete with TPA-  
198 based polymers.<sup>51–56</sup>

199 Although the enzymatically catalyzed synthesis of furan-  
200 based polyesters such as PBF, among other types, was recently  
201 reported in the literature,<sup>24,34,41</sup> the enzymatic synthesis of  
202 furan-based terpolyesters, on the other hand, is less studied.  
203 Morales-Huerta et al.<sup>57</sup> synthesized poly(butylene furan-2,5-  
204 dicarboxylate-co-succinate) via the ring-opening polymer-  
205 ization of cyclic butylene furan-2,5-dicarboxylate and butylene  
206 succinate oligomers yielding copolyesters with a  $\bar{M}_n$  ranging  
207 between 16 000 and 31 000 g·mol<sup>-1</sup> where Novozym 435 was  
208 loaded at 40% w/w relative to the totality of the concentration  
209 of the monomers. On the other hand, the enzymatic  
210 polycondensation approach toward semiaromatic copolyesters  
211 was reported by Maniar et al.<sup>58</sup> by reacting DMFDCA and 2,5-  
212 bis(hydroxymethyl)furan (BHMF) with aliphatic linear diols  
213 and diacid ethyl esters. The highest  $\bar{M}_n$  determined for the  
214 precipitated polymers was achieved when using 1,8-octanediol  
215 and reached 16 000 g·mol<sup>-1</sup> after 72 h under vacuum with  
216 temperature varying between 80 and 95 °C.

217 Previously, we introduced a statistical approach that allowed  
218 us to predict the  $\bar{M}_n$  of poly(hexylene adipate) simply by  
219 tuning the values of certain parameters such as vacuum,  
220 enzyme loading, and temperature.<sup>59</sup> In our current work and  
221 on the basis of the promising properties of furan-based  
222 terpolyesters, such as their excellent mechanical properties and  
223 biodegradability, we investigate the enzyme-catalyzed synthesis  
224 of furan-based semiaromatic terpolyesters by reacting diethyl  
225 furan-2,5-dicarboxylate (DEFDC) with variable aliphatic linear  
226 dicarboxylic esters and primary diols. A special emphasis was  
227 made on the influence of furan loading and the chain length of  
228 the diols and diesters and how such factors can influence the

229 reactivity, molecular weight, and thermal properties of the end-  
230 product. In addition, an amorphous fatty dimer diol, Pripol  
2033, was tested for its influence on improving the reactivity in  
231 the system where enzymatic catalysis was limited and its effect  
232 on the thermal behavior of such polymers. Such polymers can  
233 be used for applications in food packaging.  
234

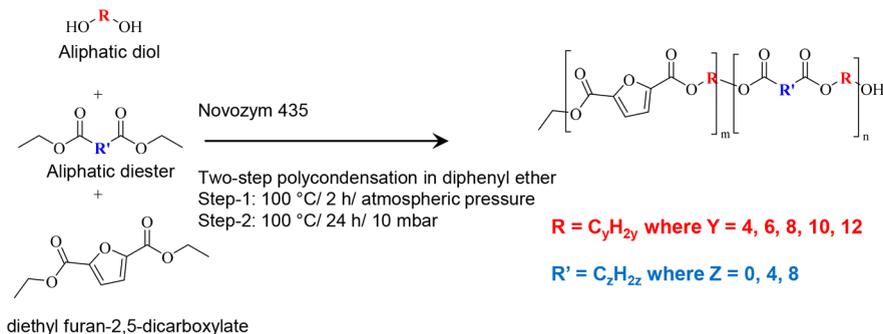
## 235 MATERIALS AND METHODS

**Materials.** Hexane-1,6-diol (97%), diethyl adipate (99%), sebacic  
236 acid (99%), and diphenyl ether (99%) were purchased from Sigma-  
237 Aldrich. Butane-1,4-diol (99%), octane-1,8-diol (98%), and dodecane-  
238 1,12-diol (98%) were purchased from Acros Organics. Decane-1,10-  
239 diol (97%) and diethyl oxalate were purchased from Alfa Aesar.  
240 Furan-2,5-dicarboxylic acid (99.7%) was purchased from Satachem  
241 Co. Pripol 2033 fatty dimer diol ((9Z,12Z)-18-[(6Z,9Z)-18-  
242 hydroxyoctadeca-6,9-dienoxy]octadeca-9,12-dien-1-ol) (≥96.5) was  
243 kindly provided by Croda Chemicals. Analytical grade methanol,  
244 absolute ethanol, and chloroform (99%) were purchased from VWR.  
245 All the reagents and solvents were used as received. Novozym 435  
246 (N435), a *Candida antarctica* lipase B (CALB) immobilized on an  
247 acrylic resin, was kindly provided by Novozymes. Chloroform D  
248 (CDCl<sub>3</sub>) (99.8%) and deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>)  
249 were purchased from Euriso-Top.  
250

**Synthesis of Diethyl Furan-2,5-dicarboxylate (DEFDC).** In  
251 general, 5 g of furan-2,5-dicarboxylic acid (FDCA) was added to 60  
252 mL of absolute ethanol and 2 mL of sulfuric acid and refluxed  
253 overnight under continuous stirring at 100 °C. The mixture was  
254 allowed to cool, followed by evaporation to remove the excess amount  
255 of ethanol. The solution was added dropwise into distilled water  
256 under continuous stirring, resulting in FDCA precipitation. The  
257 product was washed multiple times with distilled water before being  
258 suspended in 100 mL of a H<sub>2</sub>O solution, neutralized by adding 5%  
259 NaCO<sub>3</sub>, and finally filtered using a Buchner funnel under vacuum  
260 application. The white crystalline powder obtained was dried  
261 overnight under high vacuum, and the yield by weight achieved was  
262 >75% w/w. <sup>1</sup>H NMR analysis confirmed the structure of diethyl  
263 furan-2,5-dicarboxylate (DEFDC) with no detectable impurities; <sup>1</sup>H  
264 NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.20 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 4H),  
265 1.39 (t, *J* = 7.1 Hz, 6H) ppm (see Figure S1).  
266

**General Procedure for the Enzymatic Synthesis of Poly-  
(alkylene alkanooate-co-alkylene furan-2,5-dicarboxylate).** *Ef-*  
267 *fect of Diol Length (C<sub>4</sub> to C<sub>12</sub>) and DEFDC Molar Ratio.* Furan-based  
268 semiaromatic copolyesters were prepared by reacting DEFDC and  
269 diethyl adipate with diols of different chain lengths varying from C<sub>4</sub>  
270 to C<sub>12</sub>. As an example, the synthesis of poly(hexyleneadipate-co-  
271 hexylene-2,5-furandicarboxylate) containing 50 mol % furan relative  
272 to the total diesters was as follows: hexane-1,6-diol (4 mmol), diethyl  
273 adipate (2 mmol), and DEFDC (2 mmol) were weighed and added  
274 into a Schlenk tube. A predetermined amount (20% w/w) of N435  
275 relative to the total weight of hexane-1,6-diol (4 mmol) and diethyl  
276 adipate (4 mmol) was weighed and added to the mixture. Precisely, 1  
277 mL of diphenyl ether (6.3 mmol) was added as the solvent of choice.  
278 The reaction proceeded under atmospheric pressure for 2 h at 100 °C  
279 (using an oil bath with continuous stirring kept constant at 350 rpm).  
280 Afterward, the Schlenk tube was attached to a vacuum line, and the  
281 pressure was decreased gradually within 1 h to reach a predetermined  
282 value of 10 mbar to remove the byproduct (ethanol). The reaction  
283 was left to proceed for 24 h; then, it was stopped by adding an excess  
284 amount of chloroform under atmospheric pressure after a cooling  
285 step, followed by direct filtration to remove the N435 beads. The  
286 filtrate was then partially evaporated and then added dropwise to an  
287 excess amount of cold methanol under stirring to precipitate the  
288 obtained polymer. The mixture was then filtered, and the obtained  
289 product was left to dry at room temperature for 24 h before being  
290 collected and weighed. The percentage yield was calculated by  
291 dividing the actual yield (816 mg) by the theoretical yield (932 mg).  
292

*Effect of Diester Length (C<sub>2</sub>–C<sub>6</sub>–C<sub>10</sub>) and DEFDC Molar Ratio.*  
293 Following the same procedure as before, the influence of diester  
294 length was examined by performing the copolymerization reaction  
295

Scheme 2. Polycondensation Reaction of Variable Diols, Diethyl Adipate, and DEFDC in the Presence of N435 as Catalyst<sup>a</sup>

<sup>a</sup>Where  $n$  varied between 4 and 12 depending on the diol used.

297 between hexane-1,6-diol and different chain-length diesters, specifi-  
 298 cally diethyl oxalate ( $\text{C}_2$ ), diethyl adipate ( $\text{C}_6$ ), and diethyl sebacate  
 299 ( $\text{C}_{10}$ ), at variable DEFDC molar feed percent (0–90%). The same  
 300 approach was used starting from dodecane-1,12-diol.

301 **Effect of Diol Length on DEFDC Conversion during Oligomeriza-**  
 302 **tion: "A Comparison between Hexane-1,6-diol- and Dodecane-**  
 303 **1,12-diol-Based Copolyesters".** In the first part of this study and  
 304 following the same procedure as before, different samples containing  
 305 either hexane-1,6-diol or dodecane-1,12-diol in addition to diethyl  
 306 adipate and DEFDC were prepared by keeping an equimolar ratio  
 307 between the diol and diesters while varying the DEFDC content from  
 308 10% to 75%. The conversion of DEFDC into alkylene furanoate was  
 309 monitored by withdrawing samples at different time intervals and  
 310 exploiting the  $^1\text{H}$  NMR signals at  $\delta = 4.32$ – $4.34$  of the methylene  
 311 ( $-\text{O}-\text{CH}_2-\text{C}_n\text{H}_{2n}-\text{CH}_2-\text{O}-$ ) of the alkylene furanoate,  $\delta = 4.06$ –  
 312  $4.07$  of the methylene ( $-\text{O}-\text{CH}_2-\text{C}_n\text{H}_{2n}-\text{CH}_2-\text{O}-$ ) of the alkylene  
 313 adipate, and  $\delta = 3.65$  of the methylene ( $\text{HO}-\text{CH}_2-\text{C}_n\text{H}_{2n}-\text{CH}_2-$   
 314  $\text{OH}$ ) of the residual diol represented in eq S3. The X-furan amount  
 315 (%) representing the evolution of furan content in the oligomers  
 316 produced is given via eq S1

317 In the second part of this study, hexane-1,6-diol and dodecane-  
 318 1,12-diol were added into the same reaction in equimolar amounts  
 319 and reacted against 75% DEFDC and 25% of diethyl adipate while  
 320 maintaining an equimolar ratio between the diols and diesters. The  
 321 conversion of DEFDC into either hexylene furanoate or dodecylene  
 322 furanoate was monitored via  $^1\text{H}$  NMR in the same fashion as  
 323 previously mentioned and by taking advantage of the global spectral  
 324 deconvolution technique to distinguish between overlapping signals of  
 325 hexylene furanoate and dodecylene furanoate. The aim was to  
 326 monitor how two different chain-length diols could compete in the  
 327 same reaction media.

328 **Effect of N435 % Loading.** Hexane-1,6-diol was chosen as a model  
 329 monomer to see the effect of enzyme loading on the polymerization  
 330 reaction. Similar to the general procedure mentioned above, hexane-  
 331 1,6-diol was reacted with diethyl adipate and DEFDC at different  
 332 molar percentages (10%, 25%, 50%, and 75%), and the N435 %  
 333 loading was varied between 10% and 20% while maintaining similar  
 334 reaction conditions.

335 **Effect of Fatty Dimer Diol (Pripol 2033).** The effect of Pripol 2033  
 336 was tested in two experimental parts. In the first experimental  
 337 approach, octane-1,8-diol and Pripol 2033 were reacted with DEFDC  
 338 in equimolar (diol-diesters) ratios (4 mmol). Pripol 2033 was added at  
 339 10 and 20 mol % relative to the total diols in the reaction (or 13.7 and  
 340 25 wt % relative to the total monomers), and the reactions proceeded  
 341 for 2 h at 100 °C in 1 mL of diphenyl ether and 20% w/w N435  
 342 loading, followed by 24 h under vacuum (10 mbar). The polyesters  
 343 synthesized were compared in terms of conversion, X-furan,  $\bar{M}_n$ , and  
 344 their thermal properties.

345 In the second experimental procedure, butane-1,4-diol and Pripol  
 346 2033 were reacted against diethyl adipate (25 mol %) and DEFDC  
 347 (75 mol %). Pripol 2033 was added at 10, 25, and 50 mol % relative to  
 348 the diesters while maintaining an equimolar (diol-diesters) ratio (4

mmol). The reactions proceeded for 2 h at 100 °C in 3 mL of 349  
 diphenyl ether and 20% w/w N435 loading, followed by 72 h under 350  
 vacuum (10 mbar). The synthesized polyesters were compared in 351  
 terms of conversion, X-furan,  $\bar{M}_n$ , and their thermal properties. 352

353 **Analytical Methods. Nuclear Magnetic Resonance (NMR)**  
 354 **Analysis.** The  $^1\text{H}$  NMR spectra of the monomers and the recovered 354  
 polymer were recorded at room temperature on a Bruker Avance 300 355  
 instrument (delay time = 3 s, number of scans = 32) at 300.13 MHz 356  
 using either  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as solvents. Chemical shifts (ppm) 357  
 are given in  $\delta$  units and were calibrated using the residual signal of 358  
 $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  at 7.26 and 2.5 ppm, respectively. Additionally, 359  
 $^1\text{H}$  NMR was used to determine the furan content in the 360  
 microstructure of the polymer, confirm conversion, and determine 361  
 its rate (eqs S1, S2, and S3). DOSY spectra were recorded on an 362  
 Avance II 400 Bruker spectrometer (9.4 T) regulated at 298 K in 363  
 $\text{CDCl}_3$  and toluene- $d_8$ . Data acquisition and analysis were performed 364  
 using Bruker TopSpin 3.2 and MestReLab 6.0. 365

366 **Gel Permeation Chromatography (GPC) Analysis.** Gel permea-  
 367 tion chromatography (GPC) analysis was performed in chloroform 367  
 as eluent (flow rate of 1 mL/min) at 23 °C using an Alliance e2695 368  
 (Waters) apparatus and with a sample concentration of around 10–15 369  
 mg/mL. A refractive index detector Optilab T-REX (Wyatt 370  
 Technology) was used as a detector, and a set of columns, HR1, 371  
 HR2, and HR4 (Water Styragel), was utilized. The molecular weight 372  
 calibration curve was obtained using monodisperse polystyrene 373  
 standards. 374

375 **Differential Scanning Calorimetry (DSC).** The thermal transition 375  
 was recorded with differential scanning calorimetry (DSC) on a TA 376  
 Discovery DSC 25 using a cooling–heating–cooling–heating 377  
 method. First, samples of  $\sim 10$  mg were sealed in aluminum pans; 378  
 the temperature was equilibrated at  $-90$  °C, followed by a heating 379  
 ramp of 10 °C/min to 200 °C, then a cooling ramp of 10 °C/min to 380  
 $-90$  °C, and a second heating ramp of 10 °C/min to 200 °C. The 381  
 thermograms were analyzed using TA Instruments TRIOS software. 382

383 **Wide-Angle X-ray Scattering (WAXS).** Wide-angle X-ray scattering 383  
 (WAXS) analysis were performed on a Xeuss 2.0 apparatus (Xenocs) 384  
 equipped with a micro source using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54$  Å) and 385  
 point collimation (beam size:  $500 \times 500 \mu\text{m}^2$ ). The sample to 386  
 detector distance, around 15 cm, was calibrated using silver behenate 387  
 as standard. Through view 2D diffraction patterns are recorded on a 388  
 Pilatus 200k detector (Dectris). Integrated intensity profiles were 389  
 computed from the 2D patterns using the Foxtrot software. The 390  
 exposure time was 15 min. 391

## RESULTS AND DISCUSSION

392  
 393 Following the general procedure above, the polycondensation 393  
 of different diols with diethyl adipate and DEFDC in the 394  
 presence of N435 (see Scheme 2) was conducted in diphenyl 395  
 ether, as it was previously reported to be the more suitable 396  
 solvent to achieve high conversion and molecular weights.<sup>60–62</sup> 397  
 While maintaining the equimolarity between the diols and the 398

**Table 1. Molecular Structure Analysis (X-furan), % Conversion, % Yield,  $\bar{M}_n$ ,  $\bar{D}_M$ , and DP of Furan-Based Copolyesters with Variable Furan Content and Aliphatic Diols**

entry	diol <sup>a</sup>	DEFDC feed (%) <sup>b</sup>	X-furan (%) <sup>c</sup>	conversion (%) <sup>d</sup>	yield by weight (%)	$\bar{M}_n$ (g mol <sup>-1</sup> ) <sup>e</sup>	$\bar{D}_M$ <sup>f</sup>	DP <sup>g</sup>
1	C <sub>4</sub>	0	0	98	85	16 000	1.80	80
2	C <sub>4</sub>	10	12	86	68	4900	1.93	24
3	C <sub>4</sub>	25	27	95	62	1300	6.9	6
4	C <sub>4</sub>	50						
5	C <sub>6</sub>	0	0	97	91	9200	1.80	40
6	C <sub>6</sub>	10	12	95	77	9400	1.61	41
7	C <sub>6</sub>	25	27	98	82	11 100	2.13	48
8	C <sub>6</sub>	50	51	98	87	9600	2.09	41
9	C <sub>6</sub>	75	75	96	90	3800	1.91	16
10	C <sub>6</sub>	90	78	48	0			
11	C <sub>8</sub>	0	0	94	88	9000	1.94	35
12	C <sub>8</sub>	10	12	95	87	10 900	1.82	42
13	C <sub>8</sub>	25	27	95	86	8900	1.75	34
14	C <sub>8</sub>	50	49	91	74	9900	1.91	38
15	C <sub>8</sub>	75	75	96	84	7500	2.14	28
16	C <sub>8</sub>	90	87	96	87	4700	1.85	18
17	C <sub>10</sub>	0	0	95	98	9100	2.05	32
18	C <sub>10</sub>	10	12	95	93	8300	1.91	29
19	C <sub>10</sub>	25	27	95	92	8600	1.78	30
20	C <sub>10</sub>	50	50	94	83	10 300	1.84	35
21	C <sub>10</sub>	75	74	95	92	7300	2.04	35
22	C <sub>10</sub>	90	89	97	99	8500	2.27	29
23	C <sub>12</sub>	0	0	95	98	7700	2.07	25
24	C <sub>12</sub>	10	11	95	97	9900	2.01	31
25	C <sub>12</sub>	25	26	96	93	9700	2.21	31
26	C <sub>12</sub>	50	50	95	95	8700	1.97	27
27	C <sub>12</sub>	75	74	95	89	6300	1.98	20
28	C <sub>12</sub>	90	88	97	100	7300	2.19	23

<sup>a</sup>C<sub>4</sub> = butane-1,4-diol, C<sub>6</sub> = hexane-1,6-diol, C<sub>8</sub> = octane-1,8-diol, C<sub>10</sub> = decane-1,10-diol, and C<sub>12</sub> = dodecane-1,12-diol. <sup>b</sup>DEFDC feed (%) represents the molar percentage of diethyl 2,5-furandicarboxylate added, relative to the total diester amount. <sup>c</sup>X-furan (%) is defined as the molar fraction of the alkylene furan-2,5-dicarboxylate repeating unit in the copolymer and determined via <sup>1</sup>H NMR per eq S1. <sup>d</sup>Conversion (expressed in %) represents the total amount of reacted diols relative to the overall diols in the system and was calculated by <sup>1</sup>H NMR via eq S2. <sup>e</sup>The number-average molecular weight ( $\bar{M}_n$ ) was obtained from GPC analyses (CHCl<sub>3</sub>, 23 °C, polystyrene standards).  $\bar{M}_n$  values might be skewed to higher values for longer chain comonomers. <sup>f</sup>Molar mass dispersity ( $\bar{D}_M = \bar{M}_w/\bar{M}_n$ ) was obtained from GPC analyses (CHCl<sub>3</sub>, 23 °C, polystyrene standards).  $\bar{D}_M$  might be skewed to lower values due to fractionation (precipitation). <sup>g</sup>DP (degree of polymerization) =  $\bar{M}_n/M_0$ , where  $M_0$  is the molecular weight of the repeating unit.

399 diesters, the molar percent of DEFDC relative to the aliphatic  
400 diester was varied between 0 and 90%. Different aliphatic diols  
401 tested as (co)monomers were butane-1,4-diol, hexane-1,6-diol,  
402 octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol.

403 The impact of the diol length and furan content on the final  
404 copolymer properties were both assessed in terms of  
405 copolymer composition (X-furan), total conversion (%),  
406 yield by weight (%),  $\bar{M}_n$ , dispersity ( $\bar{D}_M$ ), and degree of  
407 polymerization (DP) (Table 1). Peak assignments and the  
408 respective calculations are given in Figure S2 and eqs S1 and  
409 S2.

410 From Table 1, it was observed that the increase in DEFDC  
411 content had a negative impact on X-furan, conversion, yield,  
412  $\bar{M}_n$ , and DP of copolymers synthesized from shorter diols. The  
413 maximum quantities of furan successfully incorporated into  
414 copolymers based on butane-1,4-diol and hexane-1,6-diol were  
415 27 and 75 mol %, achieving yields of 62% and 90% (as  
416 observed in entries 3 and 9), respectively. The increase of the  
417 feed molar percentage of DEFDC with these short diols  
418 limited the copolymer growth and led to a failure in  
419 precipitation, which was assumed to result from the low  
420 reactivity and the formation of short oligoesters that did not  
421 precipitate in methanol. No detectable conversion or yield was

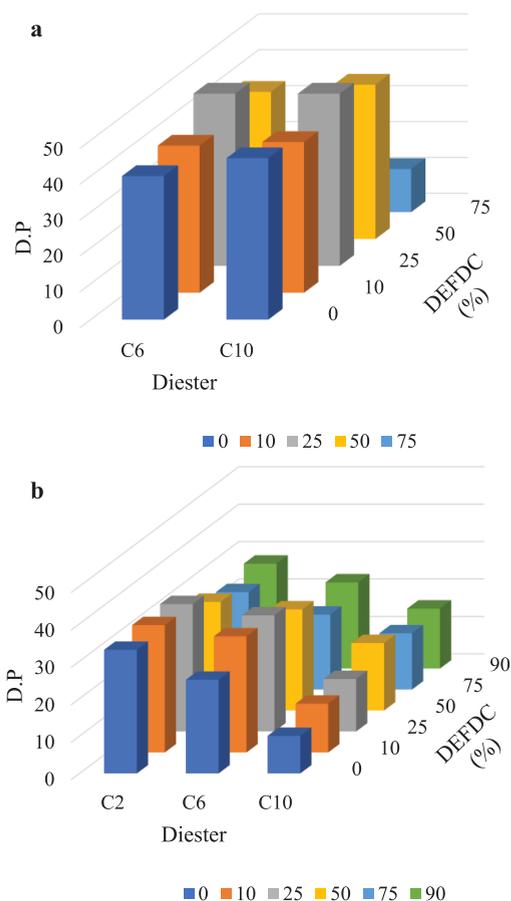
observed (see entry 4) when the DEFDC feed was increased to 422  
50%, while only 48% conversion was calculated when the 423  
DEFDC feed was increased to 90% (as observed in entry 10) 424  
without any detectable yield. Similarly, the DP of the 425  
copolymers prepared with butane-1,4-diol was highly influ- 426  
enced by DEFDC feed, where increasing the DEFDC feed by 427  
only 10% led to a drop in DP from 80 (entry 1) to 24 (entry 2) 428  
and further decreased to 6 (entry 3) with 25% DEFDC. On the 429  
other hand, copolymers based on octane-1,8-diol, decane-1,10- 430  
diol, and dodecane-1,12-diol showed a stable conversion 431  
(>90%) and high yields without any noticeable variations as 432  
a function of the DEFDC feed increase. The DP of the 433  
copolymers based on octane-1,8-diol was partially affected at 434  
high DEFDC content, decreasing from 38 to 28 to 18 with the 435  
increase in DEFDC feed from 50% to 75% to 90%. Longer 436  
diols were not significantly affected by the increase in DEFDC 437  
feed %, where copolymers based on decane-1,10-diol and 438  
dodecane-1,12-diol maintained a relatively stable DP at high 439  
DEFDC feed. The formation of poly(alkylene alkanoate-co- 440  
alkylene furan-2,5-dicarboxylate) rather than poly(alkylene 441  
alkanoate) and poly(alkylene furan-2,5-dicarboxylate) homo- 442  
polymers was confirmed by performing DOSY NMR scans. 443  
The spectrum provided in Figure S3 shows a single diffusion 444

445 coefficient for the produced poly(dodecylene adipate-co-  
446 dodecylene furan-2,5-dicarboxylate) representing entry 26.

447 What was generally noticed from these results is that the  
448 limitation imposed by the increase in DEFDC feed became less  
449 significant as a function of the increase in the diol length,  
450 where up to 90% DEFDC was successfully incorporated into  
451 the copolyesters based on octane-1,8-diol, decane-1,10-diol,  
452 and dodecane-1,12-diol. The superior catalytic efficiency of  
453 N435 or CALB catalysts toward longer diols in the presence of  
454 high furan content agreed well with the previously documented  
455 results by Jiang et al.<sup>34</sup> They suggested that, besides the better  
456 selectivity of CALB toward longer diols, furan-based polyesters  
457 based on longer diols showed higher solubility in the reaction  
458 media (diphenyl ether) and lower melting points compared to  
459 those produced from shorter diols, which precipitated rapidly  
460 due to the reasons mentioned above and prevented polymer  
461 growth. In another study, Bazin et al.<sup>63</sup> assumed that the  
462 limited polymer growth detected in terpolymers synthesized in  
463 diphenyl ether based on hexane-1,6-diol, diethyl adipate, and  
464 dimethyl furan-2,5-dicarboxylate was mainly a solubility  
465 limitation, rather than a catalytic one, where high furan  
466 content (90%) leads to early precipitation and limited polymer  
467 growth. Surprisingly though, in our work, and contrary to  
468 previous results in the literature (performed under similar  
469 conditions in diphenyl ether or bulk),<sup>61</sup> an increase in the diol  
470 length in the absence of DEFDC did not seem to cause any  
471 increase in the DP of the corresponding aliphatic polyesters.  
472 On the contrary, the polymer based on butane-1,4-diol and  
473 diethyl adipate (entry 1) was found to possess the highest DP  
474 (80) among the aliphatic polyesters, while the DP was  
475 maintained within a range of 25–40 for polymers based on  
476 hexane-1,6-diol (entry 5), octane-1,8-diol (entry 11), decane-  
477 1,10-diol (entry 17), and dodecane-1,12-diol (entry 23).  
478 However, it should be noted that the limitations in polymer  
479 growth could have stemmed from the diminishing mixing  
480 speed due to the increase in the viscosity of the samples, which  
481 might have posed a negative effect on the heat and mass  
482 transfer. In fact, it was observed that the mixing efficiency  
483 decreased rapidly in the reactions containing long diols, while  
484 it took more time to notice the same decrease when shorter  
485 diols were used. This observation could further justify the  
486 limited DP values with long diols.

487 The influence of the diester length was examined by  
488 comparing 1,2-diethyl oxalate ( $C_2$ ), 1,6-diethyl adipate ( $C_6$ ),  
489 and 1,10-diethyl sebacate ( $C_{10}$ ). The results showing the  
490 evolution of DP as a function of diester length are given in  
491 Figure 1, and further results concerning the X-furan,  
492 conversion (%), yield (%),  $\bar{M}_n$  ( $\text{g mol}^{-1}$ ),  $\bar{D}_M$ , and DP are  
493 stated in Table S1.

494 With the exception of 1,2-diethyl oxalate that did not yield  
495 any polymers when reacted against hexane-1,6-diol, the  
496 increase in the diester length from  $C_6$  to  $C_{10}$  did not have a  
497 significant impact on the molecular weight of the copolymers  
498 produced, as observed in Figure 1a. On the other hand, in  
499 Figure 1b, the reaction of dodecane-1,12-diol with diethyl  
500 oxalate ( $C_2$ ) in the presence or absence of DEFDC led to  
501 copolymers with a DP ranging between 26 and 34. The DP  
502 decreased on average with an increase in the diester length  
503 down to a DP of 20–31 with diethyl adipate ( $C_6$ ) and a further  
504 decrease in DP down to 10–18 with diethyl sebacate ( $C_{10}$ ).  
505 However, as mentioned before, the decrease in DP with longer  
506 diesters could have resulted from the high viscosity built up in  
507 the system that could have limited polymer growth. Moreover,

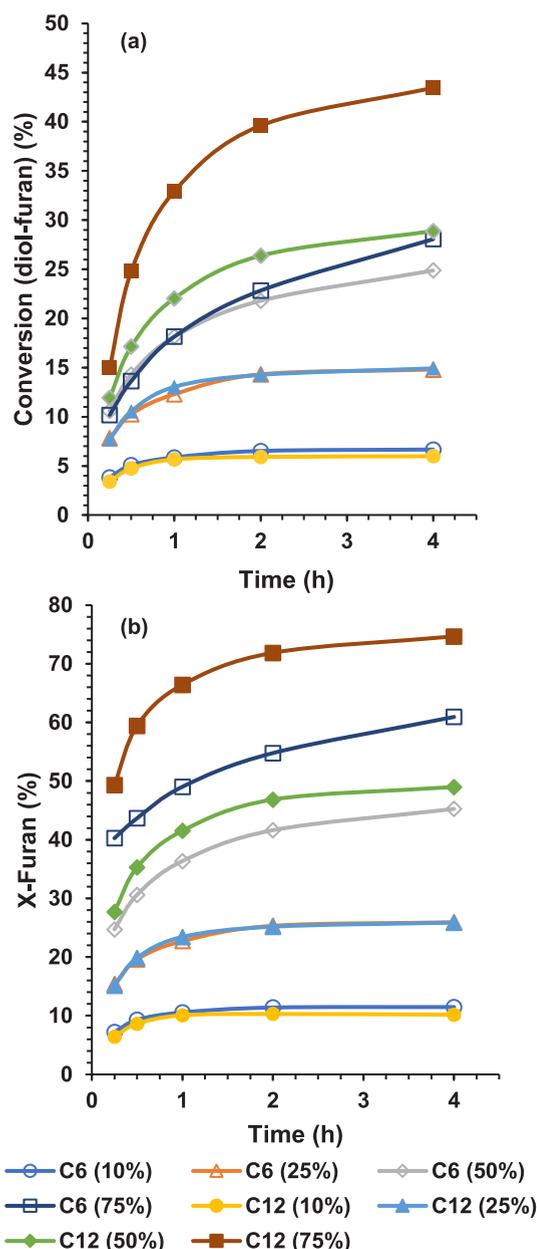


**Figure 1.** (a) Variation in DP of furan-based copolyesters with variable furan content based on hexane-1,6-diol and different aliphatic diesters. (b) Variation in DP of furan-based copolyesters with variable furan content based on dodecane-1,12-diol and different aliphatic diesters, where  $C_2$  = 1,2-diethyl oxalate,  $C_6$  = 1,6-diethyl adipate, and  $C_{10}$  = 1,10-diethyl sebacate.

508 unlike copolyesters based on hexane-1,6-diol, copolyesters  
509 based on dodecane-1,12-diol and regardless of the aliphatic  
510 diester used did not show significant variations in terms of  
511 conversion, yield, and DP as a function of increasing the  
512 DEFDC feed.

513 Taking advantage of the difference in reactivity between  
514 different chain-length diols, a time course study was performed  
515 comparing hexane-1,6-diol and dodecane-1,12-diol in terms of  
516 conversion during the oligomerization step as a function of  
517 DEFDC content in the feed. The results showing the evolution  
518 of conversion in addition to X-furan representing the furan  
519 content (%) in the produced oligomers are given in Figure 2.

520 From Figure 2, the reactions of two diols showed similar  
521 time course profiles at 10% and 25% DEFDC in the feed,  
522 where in both cases, the conversion representing the total  
523 amount of diols that reacted with DEFDC reached within a 2 h  
524 interval a constant value of 6% with  $C_6$  (10%) and  $C_{12}$  (10%)  
525 and 14% with  $C_6$  (25%) and  $C_{12}$  (25%). Similarly, the amount  
526 of furan (X-furan) in the copolymer structure was similar to  
527 both diols reaching 10% with  $C_6$  (10%) and  $C_{12}$  (10%) and  
528 25% with  $C_6$  (25%) and  $C_{12}$  (25%), respectively. Such values  
529 accurately represented the DEFDC in the feed. However, as  
530 the DEFDC feed content increased to 50% and 75%, variations  
531 in terms of conversion and X-furan were observed when  
532 comparing hexane-1,6-diol to dodecane-1,12-diol-based oli-



**Figure 2.** (a) Conversion of diols to furan-esters (expressed in mol %) during oligomerization, determined via  $^1\text{H}$  NMR. Medium: diphenyl ether; N435: 20% w/w; temperature: 100  $^\circ\text{C}$ . (b) Composition of copolyesters during oligomerization showing the evolution of furan content in the produced oligomers determined via  $^1\text{H}$  NMR. Medium: diphenyl ether; N435: 20% w/w; temperature: 100  $^\circ\text{C}$ .

533 goesters, where at 50% DEFDC feed content, the conversion  
 534 calculated for  $\text{C}_6$  (50%) and  $\text{C}_{12}$  (50%) reached values of 25%  
 535 and 29% and the X-furan values were 45% and 49%,  
 536 respectively. The superior reactivity of dodecane-1,12-diol  
 537 with DEFDC was further confirmed at higher DEFDC content  
 538 (75%), where for  $\text{C}_6$  (75%), conversion did not increase  
 539 beyond 29% after 4 h of oligomerization time compared to  
 540 43% with  $\text{C}_{12}$  (75%) within the same time limit. Similarly, the  
 541 X-furan was limited to 61% with  $\text{C}_6$  (75%) but was equivalent  
 542 to the DEFDC feed percentage with  $\text{C}_{12}$  (75%) with a X-furan  
 543 value of 75%. These results further confirmed the results  
 544 obtained in Table 1, suggesting that, in the presence of N435  
 545 as a catalyst, longer diols were more reactive toward DEFDC

than their shorter counterparts. However, at low DEFDC 546  
 content (<25%), and in the presence of diethyl adipate, the  
 conversion of both seemed to proceed at a very similar rate 547  
 regardless of the diol length. 548  
 549

As the reactivity differences between hexane-1,6-diol and 550  
 dodecane-1,12-diol appeared to be more significant in the 551  
 presence of high amounts of DEFDC, another time course 552  
 study was performed to compare hexane-1,6-diol and 553  
 dodecane-1,12-diol reactivity using the same system as detailed 554  
 under the Materials and Methods. The evolution of X-furan 555  
 and X-adipate for both hexane-1,6-diol and dodecane-1,12-diol 556  
 is given in Figure S4. 557

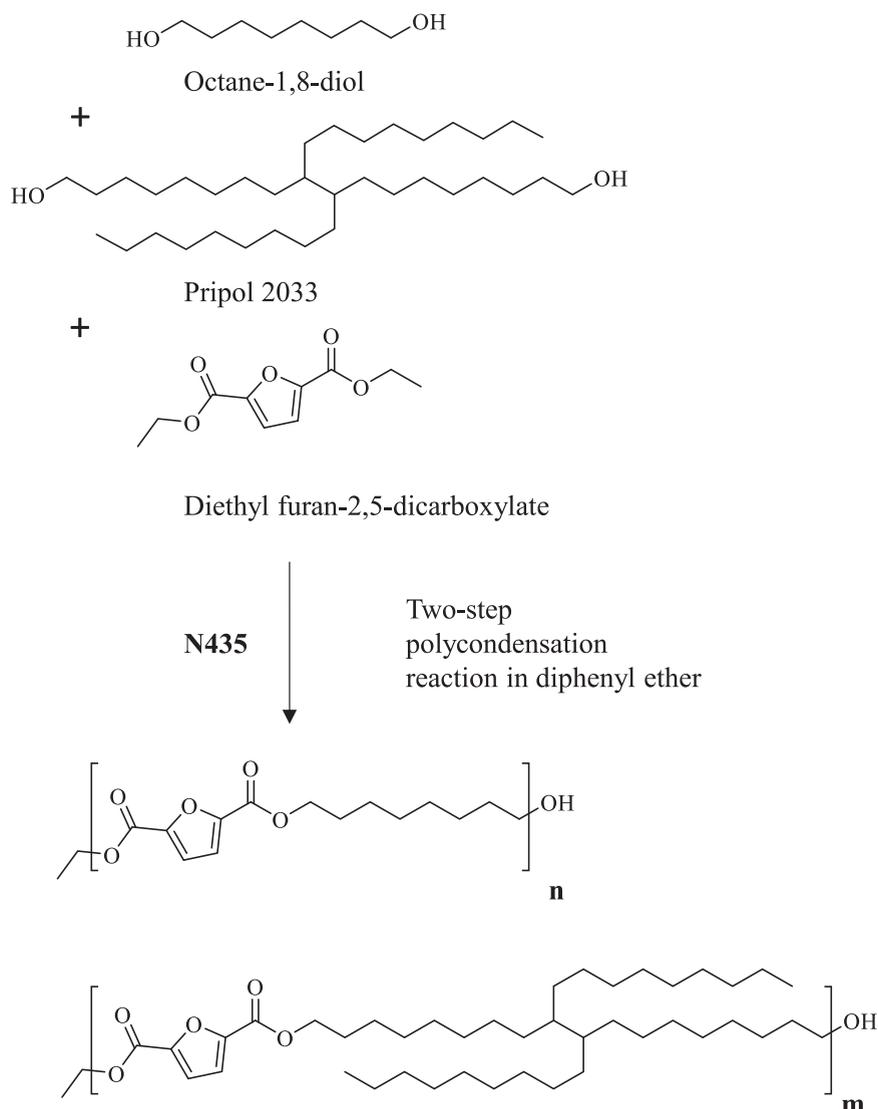
It was evident from Figure S4 that, after only 15 min from 558  
 the start of the reaction, the oligoester structures were 559  
 dominated by hexanediol-adipate and dodecanediol-adipate 560  
 ester units recording 32% and 36%, respectively, relative to the 561  
 total esters formed in the system, while hexanediol-furan and 562  
 dodecanediol-furan esters were limited to 13% and 19%, 563  
 respectively. The domination of diol-adipate esters during the 564  
 first minutes of the reaction resulted from the higher reactivity 565  
 of diols toward aliphatic diesters under N435 mediated 566  
 catalysis. As the reaction proceeded, the X-adipate for both 567  
 diols started to decrease gradually while the X-furan increased 568  
 simultaneously, where after 4 h, X-adipate(hexane-1,6-diol) 569  
 and X-adipate(dodecane-1,12-diol) decreased to reach values 570  
 of 13% and 18%, whereas the X-furan(hexane-1,6-diol) and X- 571  
 furan(dodecane-1,12-diol) increased to reach 33% and 37%, 572  
 respectively. Unlike what was observed in Figure 2 in the case 573  
 of hexane-1,6-diol, where the X-furan was limited to 61% after 574  
 4 h, the presence of the two diols in the same system allowed 575  
 the oligoesters' composition to rearrange as the reaction 576  
 proceeded to reach, after 4 to 6 h, a composition that 577  
 accurately represents the feed ratio of diols and esters based on 578  
 the summation of X-furan of both hexane-1,6-diol and 579  
 dodecane-1,12-diol. 580

These two time course studies showed how N435 showed 581  
 minimal catalytic differences between hexane-1,6-diol and 582  
 dodecane-1,12-diol at low DEFDC content, which is evident 583  
 from the conversion profiles presented in Figure 2. On the 584  
 other hand, it was also clear how, in the presence of an 585  
 aromatic group such as DEFDC, N435 tended to catalyze the 586  
 transesterification reaction between dodecane-1,12-diol and 587  
 DEFDC at a faster rate compared to similar reactions with 588  
 hexane-1,6-diol. These observations suggest that, in enzymatic 589  
 catalysis based on N435, longer diols are better suitable to 590  
 react against high furan content. 591

The impact of % w/w N435 loading was tested by 592  
 comparing the polycondensation reaction of hexane-1,6-diol 593  
 with diethyl adipate and DEFDC at 10 and 20% w/w N435 594  
 enzyme loading. The results in Table S2 showed modest 595  
 variations in the results at low DEFDC % (entries 22' and 596  
 26'). However, as the DEFDC feed content increased, it 597  
 became evident that a higher enzyme loading was necessary to 598  
 conduct the reaction, where copolymers based on 10% N435 599  
 (see entries 24' and 25' in Table S2) had a minute amount of 600  
 furan in their structures (3–4%) and a low conversion of 24 601  
 and 17%, respectively. While elevated conversions and yields 602  
 were persistent in copolymers based on 20% N435 loading. 603

As the reactivity of diols and the  $M_n$  of the copolyesters 604  
 tended to decrease with high amounts of DEFDC, especially 605  
 with shorter diols, small amounts of Pripol 2033 were 606  
 incorporated in the reaction media as mentioned in the 607  
 Materials and Methods and observed in Scheme 3 in an 608 s3

## Scheme 3. Enzyme-Catalyzed Polycondensation Reaction of Octane-1,8-diol, Pripol 2033, and DEFDC



**Table 2.** X-furan, % Conversion, % Yield, and  $\bar{M}_n$  of Copolyesters Based on Butane-1,4-diol and DEFDC with or without Pripol 2033

entry	Pripol 2033 (%) <sup>a</sup>	X-furan (1,4-BD) (%) <sup>b</sup>	X-furan (Pripol) (%) <sup>c</sup>	X-furan (total) (%) <sup>d</sup>	conversion (%) <sup>e</sup>	yield by weight (%)	$\bar{M}_n$ (g mol <sup>-1</sup> ) <sup>f</sup>
29	0	0	0	0			
30	10	0	0	0			
31	25	56	19	75	99	88	7700
32	50	37	38	75	99	91	12 000

<sup>a</sup>Pripol 2033 (%) represents the molar percentage of Pripol 2033 added, relative to the total diester amount. <sup>b</sup>X-furan (1,4-BD) (%) = molar percent of the butylene furandicarboxylate unit in the copolymer, calculated via eq S1. <sup>c</sup>X-furan (Pripol) (%) = molar percent of the Pripol-furandicarboxylate unit in the copolymer, calculated via eq S1. <sup>d</sup>X-furan (total) (%) = molar percent of the alkylene furandicarboxylate unit in the copolymer, equal to the summation of X-furan (1,4-BD) and X-furan (Pripol). <sup>e</sup>Conversion (expressed in %) is calculated via <sup>1</sup>H NMR using eq S2. <sup>f</sup>The number-average molecular weight ( $\bar{M}_n$ ) is obtained from GPC analyses (CHCl<sub>3</sub>, 23 °C, polystyrene standards).

609 attempt to overcome the limitations of producing copolyesters  
610 with high aromatic content via enzymatic catalysis.

611 As observed in Table S3, the yield by weight and  $M_n$   
612 increased significantly with the addition of Pripol 2033 from  
613 68% and 2700 g·mol<sup>-1</sup> up to 90% and 5300 g·mol<sup>-1</sup> upon the  
614 addition of 10% and 20% of Pripol 2033 relative to DEFDC.  
615 The formation of a single copolyester rather than two  
616 homopolymers was confirmed by performing a DOSY NMR

analysis for entry 32'; the spectrum showing a single diffusion  
617 coefficient for the concerned peaks is provided in Figure S5. 618

As semiaromatic copolyesters based on small diols such as  
619 butane-1,4-diol were limited to small amounts of DEFDC 620  
621 (~25%) and to small molecular weights and yields, Pripol  
622 2033 was used in a similar approach as before to enhance the  
623 polycondensation reaction in the presence of butane-1,4-diol.  
624 The reactions proceeded as observed in Scheme S1 in  
625 equimolar ratios between the diols and the diesters, where

626 Pripol 2033 was added at 10%, 25%, and 50% relative to the  
 627 diesters. Similar to what was observed before in the case of  
 628 butane-1,4-diol at high DEFDC loading and even after  
 629 extending the reaction time to 72 h and increasing the volume  
 630 of diphenyl ether up to 3 mL to avoid mixing issues, butane-  
 631 1,4-diol did not react with DEFDC when the latter was added  
 632 at 75% relative to the total diesters in the reaction, and no  
 633 copolyesters were collected (entry 40, Table 2). In fact, the  $^1\text{H}$   
 634 NMR of the sample collected from the reaction media after 72  
 635 h did not show any peaks representing the formation of an  
 636 ester bond between butane-1,4-diol and DEFDC. The same  
 637 observation continued upon the addition of 10% Pripol 2033  
 638 (entry 41, Table 2) with no detected changes in the reactivity  
 639 toward DEFDC whether for butane-1,4-diol or for Pripol 2033.  
 640 However, upon a further increase in Pripol 2033 molar loading  
 641 up to 25%, the X-furan detected in the  $^1\text{H}$  NMR sample was  
 642 equivalent to the DEFDC molar feed percent (75%) with 56%  
 643 resulting from the esterification of butane-1,4-diol and DEFDC  
 644 and 19% of Pripol 2033 and DEFDC and a high conversion of  
 645  $\sim 99\%$  (entry 42, Table 2). Likewise, when butane-1,4-diol and  
 646 Pripol 2033 were in equimolar amounts, the reaction  
 647 proceeded to reach a high conversion, and the X-furan reached  
 648 75% divided equally between butane-1,4-diol and Pripol  
 649 2033 (entry 43, Table 2). The increase in the Pripol 2033  
 650 feed ratio had a positive impact on reactivity, and as a result, a  
 651 higher  $\bar{M}_n$  was achieved, reaching 7700 and 12 000  $\text{g}\cdot\text{mol}^{-1}$   
 652 with 25% and 50% Pripol 2033.

653 The DSC profiles of the prepared polymers were determined  
 654 following the protocol stated in the Materials and Methods.  
 655 The results given in Figure 3 representing the entries in Table  
 656 1 showed the evolution of major melting endotherms ( $T_m$ ) and  
 657 crystallization enthalpies ( $\Delta H_m$ ) during the second heating  
 658 cycle as a function of DEFDC molar ratio and diol length. For

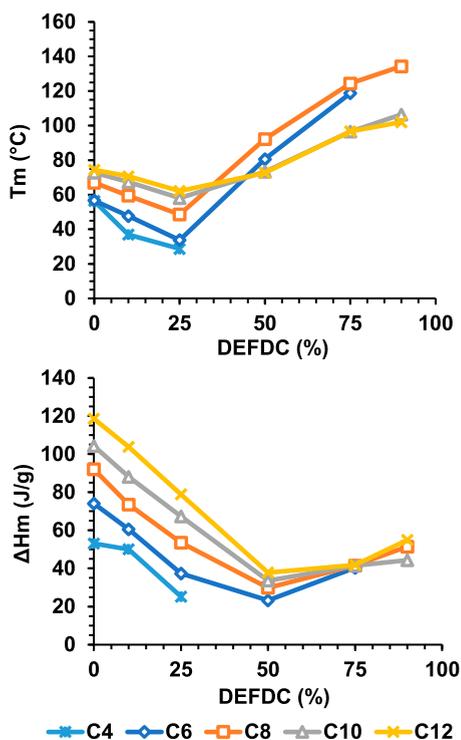


Figure 3. Variations in melting endotherms ( $^{\circ}\text{C}$ ) and crystallization enthalpies ( $\text{J/g}$ ) as a function of diol length and furan content.

up to 25 mol % DEFDC feed, the melting endotherms of the  
 copolymers showed a gradual decrease as a function of the  
 increase in DEFDC molar content, where longer diols showed  
 higher melting endotherms. However, as the DEFDC content  
 increased beyond 25 mol %, the melting endotherms started  
 increasing. Copolymers based on hexane-1,6-diol showed an  
 increase in their melting endotherms from 34  $^{\circ}\text{C}$  at 25 mol %  
 DEFDC up to 81 and 119  $^{\circ}\text{C}$  at 50 and 75 mol % DEFDC  
 content. Similarly, copolymers based on octane-1,8-diol  
 showed a similar increase in their melting endotherms  
 exceeding that of hexane-1,6-diol based copolymers, where  
 $T_m$  increased from 49  $^{\circ}\text{C}$  at 25 mol % DEFDC up to 92, 124,  
 and 134  $^{\circ}\text{C}$  for 50, 75, and 90 mol % DEFDC feed ratios.  
 Although the increase in DEFDC molar content also resulted  
 in a positive shift in the melting endotherms of copolymers  
 based on  $\text{C}_{10}$  and  $\text{C}_{12}$  diols, this increase was not as significant  
 as those for shorter diols. It should be noted that copolymers  
 based on  $\text{C}_8$ ,  $\text{C}_{10}$ , and  $\text{C}_{12}$  diols showed a second but minor  
 melting endotherm at 50 mol % DEFDC, which appeared to  
 fall within close proximity to the main endothermic peaks,  
 suggesting the coexistence of two crystalline structures. In fact,  
 the thermal behavior of these copolyesters represented in  
 Figure 3 and showing a decrease followed by an increase in the  
 melting endotherms and the coexistence of two crystalline  
 phases at certain molar ratios suggest a pseudoeutectic  
 behavior and isodimorphic cocrystallization.<sup>64,65</sup> The crystal-  
 lization enthalpy, which was higher for aliphatic copolymers  
 based on longer diols, showed a gradual decrease as a function  
 of DEFDC feed ratio until reaching a transitional point ( $\sim 50$   
 mol % DEFDC), followed by an increase upon further DEFDC  
 addition ( $>50\%$  DEFDC). In fact, the pseudoeutectic point in  
 copolymers that is usually characterized by the coexistence of  
 two crystalline phases and represents the minimal crystalline  
 value usually falls around equimolar monomer ratios, but it can  
 vary according to the nature of the repeating unit.<sup>64,66</sup> The  
 different crystal phases were later confirmed via WAXS  
 analysis.

Regarding the glass transition temperature ( $T_g$ ), Table S4  
 depicts its evolution as a function of diol length and DEFDC  
 molar content. Due to the high crystallinity in some samples,  
 the  $T_g$  was not detected in all copolyesters. As observed in  
 Table S4, the  $T_g$  appeared to increase as a function of  
 increasing DEFDC mol % with all tested copolymers, but no  
 specific pattern that relates the length of the tested diols to the  
 value of  $T_g$  was observed. During the first heating cycle and at  
 50 mol % DEFDC feed, the polymer based on  $\text{C}_6$  (entry 8)  
 showed a glass transition temperature at  $-47$  and a premelting  
 point at 43  $^{\circ}\text{C}$ , belonging to adipate-rich and furan-rich blocks,  
 respectively. However, during the second heating cycle, the  
 premelting point at 43  $^{\circ}\text{C}$  disappears and only a  $T_g$  at  $-40$   $^{\circ}\text{C}$   
 is observed. The same observation was noticed at 75 mol %  
 DEFDC (entry 9). Similarly, polymers based on  $\text{C}_8$  diol  
 showed a similar behavior at 50 and 75 mol % DEFDC feed  
 (entries 14 and 15), but at 90 mol % DEFDC (entry 16), only  
 a premelting point at 45  $^{\circ}\text{C}$  appeared during the first heating  
 cycle, while no changes were observed during the second  
 heating cycle. The polymers based on  $\text{C}_{10}$  diol showed a  $T_g$  of  
 $-44$  and  $-35$   $^{\circ}\text{C}$  at 50 and 75 mol % DEFDC during the  
 second heating cycle, while polymers based on  $\text{C}_{12}$  did not  
 show any  $T_g$  with 75 and 90 mol % DEFDC (entries 27 and  
 28). What was noticeable from these results was that, although  
 changes in the melting endotherms as a function of furan  
 content were observed for all copolymers, their change was

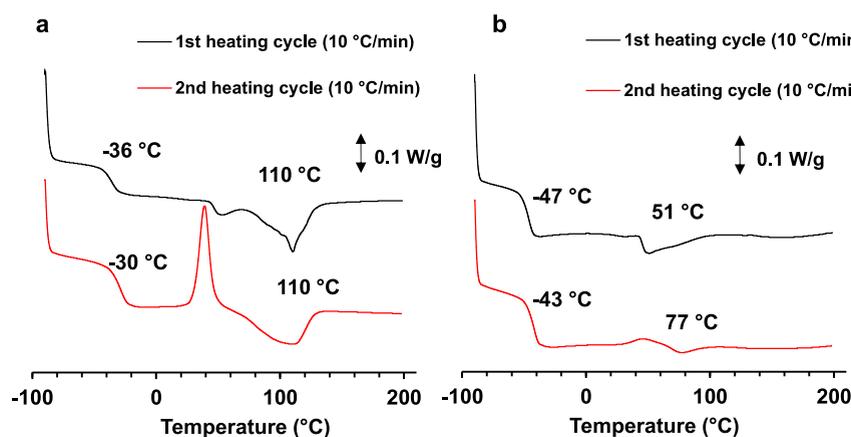


Figure 4. DSC profiles of entries 31 (a) and 32 (b) showing the first and second heating cycle.

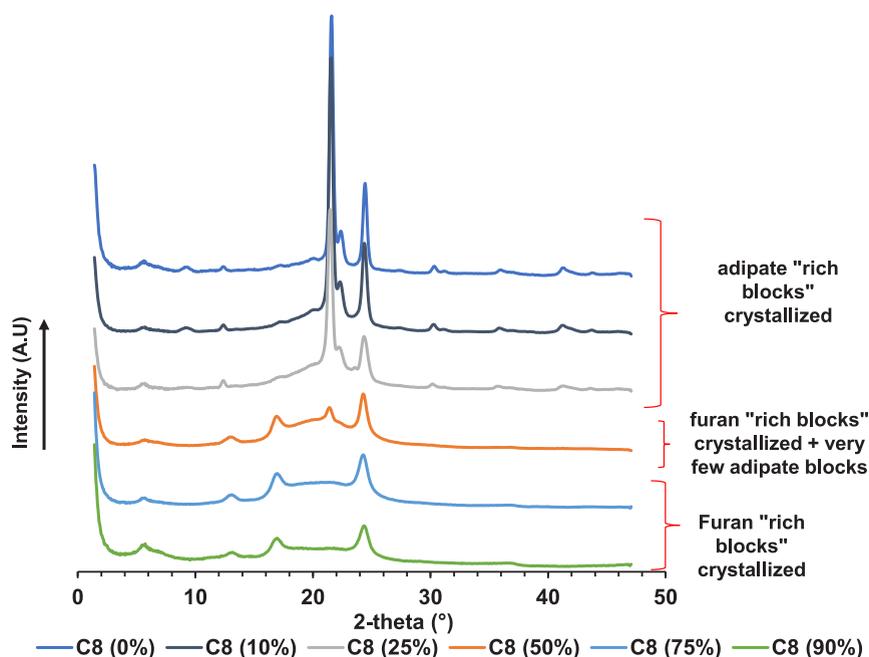


Figure 5. WAXS profiles of poly(octyleneadipate-co-octylenefuranoate) as a function of increasing the DEFDC content.

722 more pronounced with copolymers based on shorter diols  
 723 achieving higher  $T_m$  values at high DEFDC content, which is in  
 724 agreement with previous reports in the literature associating  
 725 the decrease in  $T_m$  to the increase in the number of methylene  
 726 groups.<sup>10,34</sup> Regarding the influence of diester length on the  
 727 DSC profiles of the copolymers produced, Figure S6 shows the  
 728 evolution of both the melting endotherms and crystallinity as a  
 729 function of both DEFDC mol % and diester length. The  
 730 increase in mol % DEFDC showed a similar effect on the DSC  
 731 profiles as what was observed in Figure 3. However, no direct  
 732 relation was found relating the evolution of the DSC profiles as  
 733 a function of the diester length.

734 Regarding the thermal properties of the copolyesters based  
 735 on Pripol 2033, octane-1,8-diol, and DEFDC depicted in  
 736 Scheme 3 and during the second heating cycle (see Table S3),  
 737 all polymers showed an endothermic peak that gradually  
 738 decreased as a function of increasing Pripol 2033 content from  
 739 140 °C in entry 30' in the absence of Pripol 2033 down to 135  
 740 and 129 °C with 10% and 20% Pripol 2033, respectively.  
 741 Similarly, the crystallinity also decreased from 66 to 38 J/g.

The incorporation of Pripol 2033 at 25% along with butane- 742  
 1,4-diol, diethyl adipate, and DEFDC as depicted in Table 2 743  
 resulted in a highly viscous yellow sticky liquid, which during 744  
 the first heating cycle of the DSC (Figure 4), the copolymer 745 f4  
 given in entry 31, showed a  $T_g$  at  $-36$  °C and a broad melting 746  
 endotherm peaking at  $110$  °C with an enthalpy of  $16$  J/g. The 747  
 cooling cycle did not show any recrystallization peaks. During 748  
 the second heating cycle, the first  $T_g$  increased by  $6$  °C up to 749  
 $-30$  °C, followed by a cold crystallization peak at  $39$  °C. The 750  
 $T_m$  peaked at  $109$  °C with a slight decrease in enthalpy from  $16$  751  
 to  $12$  J/g. The decrease in crystallinity might have risen from 752  
 the incomplete crystallization during the second heating cycle 753  
 and the close proximity between the crystallization and melting 754  
 point. Regarding entry 32, the increase in Pripol 2033 feed to 755  
 50 mol % led to the formation of a copolyester with a  $T_g$  756  
 appearing at  $-47$  °C during the first heating cycle and a  $T_m$  at 757  
 $51$  °C with an enthalpy not exceeding  $5.5$  J/g. During the 758  
 second heating cycle, the  $T_g$  shifted slightly toward  $43$  °C, 759  
 followed by a cold crystallization peak at  $46$  °C. Directly after 760  
 crystallization, the  $T_m$  peaked at  $77$  °C with minimal enthalpy 761  
 that did not exceed  $1$  J/g. The big shift in the  $T_m$  peak from  $51$  762

763 °C during the first heating cycle to 77 °C on the second cycle  
764 could have resulted from the presence of the cold  
765 crystallization and the melting peaks in very close quarters,  
766 masking any melting that might have occurred at similar  
767 intervals. The copolymer in entry 32 appeared as a white  
768 flexible film. The decrease in  $T_g$  as a function of increasing  
769 Pripol 2033 content reflects an increase in the flexibility of the  
770 polymer structure and increases the distance between the rigid  
771 blocks, which subsequently decreases the crystallinity and the  
772 crystallization rate.<sup>67</sup>

773 To further study the influence of the DEFDC molar content  
774 and diol length on the crystallinity of the copolymers, wide-  
775 angle X-ray scattering (WAXS) was employed following the  
776 protocol stated in the [Materials and Methods](#). Regarding the  
777 influence of DEFDC feed %, copolymers based on octane-1,8-  
778 diol with DEFDC content varying between 0 and 90% were  
779 examined and compared (see [Figure 5](#)). For  $C_8$  (0%), the  
780 WAXS profile was dominated by two major peaks at 22° and  
781 25°, which appeared to be very similar to the profiles of similar  
782 aliphatic polymers tested in the literature such as the case of  
783 poly(hexylene succinate).<sup>68</sup> For up to 25% DEFDC feed, the  
784 crystallinity continued to be dominated by poly(octylene  
785 adipate) crystals. However, upon the increase in DEFDC to  
786 50%, a new peak started appearing at 17° with a significant  
787 decrease in the intensity of the peak at 22°, suggesting a  
788 mixture of poly(octylene adipate) and poly(octylene fur-  
789 anoate) crystal phases. Upon further increase in DEFDC up to  
790 75 and 90 mol %, the peak at 20° completely disappears. These  
791 WAXS profiles of furan rich copolymers were very similar in  
792 pattern to what was previously reported in the literature with  
793 poly(octylene furanoate), suggesting that, at high furan  
794 content, regardless of the presence of small amounts of diethyl  
795 adipate, the crystalline structures of the copolymers are  
796 dominated by the poly(octylene furanoate) crystal phase.<sup>34</sup>  
797 The pseudoeutectic behavior of these copolyesters is thus  
798 confirmed by the WAXS results and is a characteristic of  
799 isodimorphic copolymers showing an adipate-rich crystalline  
800 phase at one side of the pseudoeutectic region, furan-rich  
801 crystalline phase at the other, and the coexistence of both  
802 crystalline phases at the pseudoeutectic point, which is  
803 observed in the case of  $C_8$  (50 mol %) in [Figure 5](#). This  
804 does not mean that only one of the crystalline phases can exist  
805 at either sides of the pseudoeutectic region but rather that the  
806 two crystalline phases coexist at any given ratio of the two  
807 repeating units; however, they appear as a single crystalline  
808 phase resembling that of the repeating unit present in  
809 abundance.<sup>21,64,69</sup>

810 The influence of diol length was studied by comparing the  
811 WAXS profiles of copolymers based on hexane-1,6-diol,  
812 octane-1,8-diol, decane-1,10-diol, and dodecane-1,12-diol at a  
813 constant 50 mol % DEFDC ratio as observed in [Figure S7](#). All  
814 tested copolymers appeared to be semicrystalline in nature,  
815 where  $C_6$  (50 mol %) showed dominating peaks at 17° and 25°  
816 belonging to furan-rich blocks, in addition to a minor peak at  
817 14° that appeared to move gradually to lower  $\theta$  angles as a  
818 function of increasing the diol length, reaching 10° with  $C_{12}$   
819 (50 mol %), while maintaining a stable intensity. As the diol  
820 length increased, peaks at 17° started to diminish and new  
821 crystalline peaks at 21° belonging to the adipate-rich blocks  
822 started appearing; where  $C_8$  (50 mol %) showed a mixture of  
823 both poly(octylene adipate) and poly(octylene furanoate)  
824 crystal blocks,  $C_{10}$  (50 mol %) was dominated by poly-  
825 (decylene adipate) crystals and small quantities of poly-

(decylene furanoate). However, with the longer dodecane- 826  
1,12-diol, the peak belonging to poly(dodecylene furanoate) 827  
disappeared, and the WAXS spectra was dominated with peaks 828  
at 21° and 25°, suggesting the domination of the poly- 829  
(dodecylene adipate) blocks. From these results, it appeared 830  
that, at an equimolar DEFDC/diethyl adipate ratio, copoly- 831  
mers based on longer diols had a stronger tendency to form 832  
poly(alkylene adipate) rather than poly(alkylene furanoate) 833  
crystals, as opposed to copolymers based on shorter diols that 834  
had a quicker tendency to form the opposite. What was 835  
generally observed in our work was that shorter diols reach the 836  
pseudoeutectic transitional point at lower quantities of 837  
DEFDC, whereas as evident in [Figure S7](#), at 50 mol % 838  
DEFDC, polymers based on smaller diols such as hexane-1,6- 839  
diol had already shifted toward furan-rich crystalline structures, 840  
and octane-1,8-diol-based polymers appeared to be in very 841  
close proximity to the pseudoeutectic point, while polymers 842  
based on decane-1,10-diol and dodecane-1,12-diol maintained 843  
adipate-rich crystalline structures even at 50% DEFDC. 844

## 845 CONCLUSION

846 The polycondensation reactions of different chain-length 846  
aliphatic diols and diesters at a variable content of diethyl 847  
furan-2,5-dicarboxylate (DEFDC) were studied using Novo- 848  
zym 435 as biocatalyst. In agreement with previous reports in 849  
the literature, an increase in the diol length was essential to 850  
allow better reactivity toward DEFDC. However, the addition 851  
of aliphatic diesters to synthesize terpolymers rather than 852  
biopolymers was found to be better suited for CALB-mediated 853  
catalysis, yielding polymers with  $M_n$  as high as 10 000 g·mol<sup>-1</sup> 854  
even at elevated DEFDC content without the need for extreme 855  
temperatures and long reaction times. On the other hand, the 856  
reaction of dodecane-1,12-diol with different aliphatic diesters 857  
in the presence of DEFDC showed no variations as a function 858  
of DEFDC feed. Surprisingly though, copolymers produced in 859  
the presence of long aliphatic diesters such as diethyl sebacate 860  
had a low  $M_n$  when compared to reactions with diethyl oxalate 861  
and diethyl adipate that had relatively similar results. The 862  
introduction of the amorphous Pripol 2033 improved the 863  
polymerization reaction in the systems containing high furan 864  
content and butane-1,4-diol, which otherwise did not yield any 865  
polymers without the long chain fatty dimer diol. The use of 866  
such long fatty acid diols adjacent to the short chained diols 867  
could be a promising approach, playing an important role in 868  
future work to overcome some major limitations in enzymatic 869  
catalysis toward the synthesis of semiaromatic polymers. Such 870  
polymers can be used for food packaging, and this work has 871  
introduced a green method to produce semiaromatic furan- 872  
based copolyesters that could be further optimized, studied, 873  
and compared with other semiaromatic copolyesters already on 874  
the market such as polybutylene adipate terephthalate. 875

## 876 ASSOCIATED CONTENT

### 877 Supporting Information

878 The Supporting Information is available free of charge at 878  
<https://pubs.acs.org/doi/10.1021/acsapm.1c01777>. 879

880 Additional <sup>1</sup>H and DOSY NMR spectra; additional 880  
experiments; evolution of the composition of the 881  
copolyesters vs reaction time; additional reaction 882  
schemes; thermal properties of the copolyesters; 883  
WAXS profiles of the copolyesters (PDF) 884

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921 ology: K.N.; formal analysis: K.N.; WAXS analysis: G.S.;  
922 DOSY analysis: M.B.; writing, original draft preparation: K.N.;  
923 writing, review and editing: K.N., A.F.-H., J.-M.R., and P.Z.;  
924 supervision: A.F.-H., J.-M.R., and P.Z.; project administration:  
925 J.-M.R. and P.Z.; funding acquisition: J.-M.R. and P.Z. All  
926 authors have read and agreed to the published version of the  
927 manuscript.

## 928 Notes

929 The authors declare no competing financial interest.

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