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Ring Opening Polymerization of Cyclic Oligoesters and their
Cyclodepolymerization for a Circular Economy**

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Synthesis of Aromatic-Aliphatic Polyesters by Enzymatic Ring Opening Polymerization of Cyclic Oligoesters and their Cyclodepolymerization for a Circular Economy

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KEYWORDS: Aromatic-aliphatic polyesters, Enzymatic cyclization, Enzymatic polymerization,
Enzymatic cyclodepolimerization, Entropically driven ROP, Cyclic oligoesters, Furanoate
polyesters, Terephthalate polyesters.

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3 ABSTRACT: Cyclic oligomers of hexamethylene furanoate and hexamethylene terephthalate
4 were obtained from 1,6-hexanediol and the corresponding methyl esters using *Candida*
5 *antarctica* Lipase B (CALB) enzyme catalyst. HPLC, MALDI-TOF MS and NMR analyses
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7 showed that mixtures composed from cyclic dimer up to heptamer were obtained almost
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9 quantitatively. Subsequently, these cycles were polymerized by ring opening polymerization
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11 (ROP) mediated by CALB to obtain semi-crystalline polymers. In addition, we demonstrated that
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13 the polymers obtained from the ROP process could be transformed into cyclic oligomers in high
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15 yields using enzymatic cyclodepolymerization, thereby recycling the polymer in a circular
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17 biosynthetic path.
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25 TEXT:
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30 The production of plastics obtained from petrochemical resources is not sustainable.¹ Physical
31 or chemical recycling is among the possible solutions associated with the disposal of plastic
32 waste. In the latter case, after the recycling process, monomers are obtained which can be used
33 again to obtain the polymers, allowing a circular alternative for these residues.² In the case of
34 aromatic-aliphatic polyesters such as PET, different chemical recycling methods have been
35 proposed to obtain the monomers such as methanolysis, glycolysis, hydrolysis or aminolysis.³
36 For aliphatic polyesters Chen *et al.*⁴ developed a method in which changing the reaction
37 conditions could select the direction of the chemical equilibrium towards the formation of cyclic
38 monomer or polymer, allowing the preparation of polyesters with infinite recyclability. A similar
39 idea was used by Shaver *et al.*⁵ to prepare a new biodegradable aromatic-aliphatic polyester by
40 ROP that could be easily depolymerized to monomer using a very active aluminium salen
41 catalyst.
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3 One of the most interesting approaches where the reaction conditions can be used to select the
4 direction of the monomer-polymer equilibrium is the entropically driven ring opening
5 polymerization of macrocycles (ED-ROP). Macrocycles with 14 or more atoms have very small
6 transannular interactions so that the negative Gibbs free energy required for their opening is
7 mainly due to the positive entropy generated by the increase in conformational flexibility
8 entailed in the polymerization. This situation can be reverted at high dilutions where the
9 translational entropy of the macrocycles prevails and the equilibrium shifts to the formation of
10 the cycles.⁶⁻⁸ For instance, the ROP of cyclic oligoesters, which is mainly entropically driven,
11 has been explored as a clean route for the synthesis of high molecular weight polyesters. The
12 almost athermal character of these reactions has been corroborated by the work of He *et al.*⁹
13 which reported small values of ΔH_P between -1 and -2 kJ·mol⁻¹ and values of ΔS_P between 10
14 and 17 J·mol⁻¹·K⁻¹ for some alkylene terephthalate cyclic oligomers, which were calculated from
15 cycles/polymer equilibrium concentrations at different polymerization temperatures. In this
16 reaction, as opposed to polycondensation, no by-products are generated, and high molecular
17 weight polymers can be obtained in short reaction times.¹⁰ The reaction can be catalyzed by
18 metallic,¹¹ organometallic¹² and organic¹³ catalysts or enzymes.¹⁴⁻¹⁶ The main drawback of this
19 methodology is that, the synthesis of the cyclic oligomeric precursors is laborious, affords low
20 yields and in some cases acid chloride derived reagents are used to obtain the initial
21 macrocycles.¹⁷

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Cyclic oligoesters derived from aliphatic diols such as ethylene glycol, 1,4-butanediol or 1,6-hexanediol and aromatic diacids, such as terephthalic or furandicarboxylic acids, have been usually obtained by high dilution condensation (HDC) of diols and acid dichlorides or by cyclodepolymerization (CDP) in solution at high temperatures.^{12, 17-20} In these cases the final

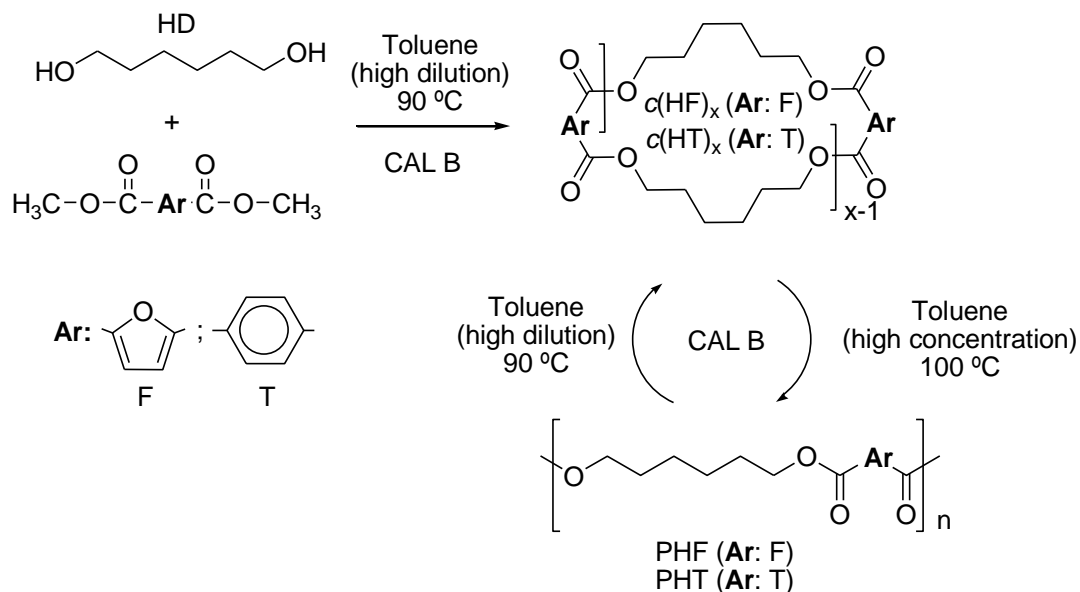
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3 products are contaminated by linear oligomeric species that have to be removed by column
4 chromatography or by other techniques, such as selective precipitation, if high molecular weight
5 polyesters want to be produced by ROP.¹⁷⁻²⁰
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10 Although the enzymatic synthesis of cyclic aliphatic oligoesters,¹⁶ and the use of enzymes for
11 preparation of aliphatic polyesters from different macrolactones, such as globalide or
12 pentadecalactone has been reported in the literature,^{21,22} the use of enzymes for the production of
13 more interesting technological aliphatic-aromatic cyclic oligoesters or polyesters has been
14 scarcely studied.²³ Only a few reports mention the possibility of formation of cyclic oligomeric
15 species as side products in the enzymatic polymerization of dimethyl furanoate and diols of
16 different lengths.²⁴
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26 In this contribution, we would like to report the synthesis of cyclic oligomers of
27 hexamethylene terephthalate and hexamethylene furanoate by enzymatic reaction using *Candida*
28 *antarctica* Lipase B enzyme avoiding the use of acid chloride derived reagents. These cycles
29 were obtained in high yields and they were found to be able to polymerize with the concurrence of
30 the same enzyme. Additionally, we have shown the ability of CALB to favour the
31 cyclodepolymerization of the polyesters upon selection of the appropriate conditions and
32 corroborating that these cycles could be recovered in high yields, opening a recycling pathway
33 for further polymerization.
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44 The chemical route followed for the synthesis of hexamethylene furanoate and hexamethylene
45 terephthalate cyclic oligomers, their cyclopolymerization, and their recovery by
46 cyclodepolymerization is depicted in Scheme 1.
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51 **Scheme 1.** Enzymatic synthesis of $c(\text{HF})_x$ and $c(\text{HT})_x$ cyclic oligomers, their
52 cyclopolymerization and the cyclodepolymerization of their respective polyesters.
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24 The cyclization reaction was carried out in toluene solution under mild and high dilution
25 conditions in the presence of enzymes. Its evolution was followed by HPLC and ^1H NMR
26 analysis of aliquots taken at scheduled times.
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30 The presence of small amounts of cyclic oligomers mixed with other species, such as short
31 linear oligomers, was detected after 7 hours of reaction. However, after 1 day of reaction, the
32 non-cyclic structures fully disappeared (Figures S1 to S4). ^1H NMR spectra showed the almost
33 complete disappearance of signals corresponding to the methyl and hydroxymethylene protons
34 after 1 day of reaction. To further confirm the non-presence of linear structures, HPLC and GPC
35 analysis were performed, confirming that only cyclic species were present. In order to evaluate
36 the thermodynamics of the process, the reaction was maintained for 7 days and we did not
37 observe any ROP, and any change in the content of the different cyclic species indicating that the
38 thermodynamic equilibrium was achieved from the first day of reaction (Figures S5 and S6). The
39 presence of CALB was essential because not reaction was observed in the absence of this
40 enzyme after 7 days of reaction (Figures S7 and S8).
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3 More detail evaluation of HPLC crude reaction products after 7 days (Figure 1) reveals that
4 cyclic oligomeric species from dimer to hexamer for the hexamethylene furanoate and to
5 heptamer for the hexamethylene terephthalate derivatives were the main products. In addition, it
6 is clearly observed that their relative contents rapidly decreased with cycle size in both cases in
7 accordance with a thermodynamically controlled process as described by Jacobson-Stockmayer
8 model, in which the concentration of cyclics obtained is proportional to approximately the 5/2
9 power of cyclic size.²⁵ It has to be mentioned that the content of cyclic dimer was clearly
10 superior for the $c(\text{HF})_x$ cycles than for $c(\text{HT})_x$. It seems that the furanoate 2,5 substitution, as
11 compared to the terephthalate 1,4 substitution favours the ring closure of smaller cycles for the
12 former. A similar effect has been observed for PBT cycles obtained by CDP, where the content
13 of cyclic dimer was lower than predicted by both, a modified Jacobson/Stockmayer²⁶ and RIS
14 theories and attributed to its high ring strain.²⁷ No linear oligomers were detected at longer
15 retention times. The assignment of different HPCL peaks was carried out by comparison with the
16 MALDI-TOF MS spectra obtained from these samples (Figures S9 and S10). On the other hand,
17 the content of the different oligomeric $c(\text{HT})_x$ cycles was not far from that obtained by
18 cyclodepolymerization of PHT in solution at high temperatures as it was carried out by us using
19 organometallic catalyst.¹⁸
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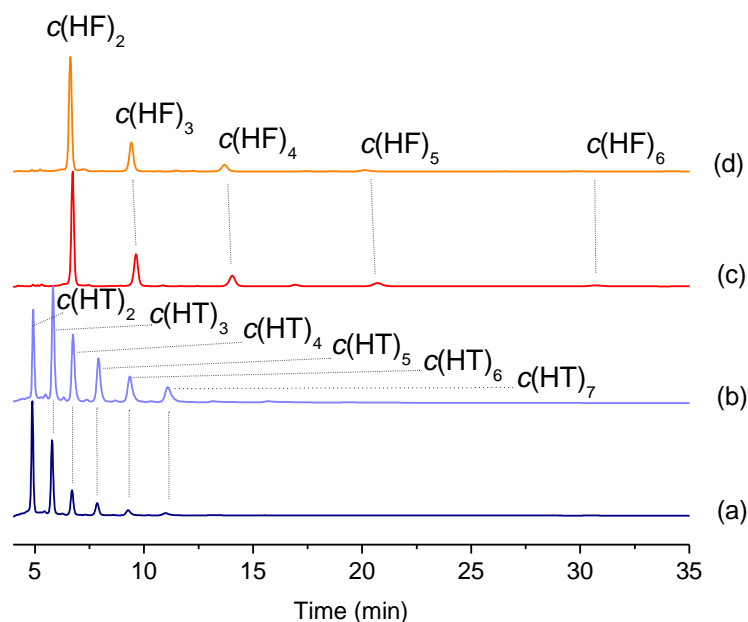


Figure 1. HPLC chromatograms of the crude product obtained after 7 days of enzymatic HDC: a) $c(\text{HT})_x$ and c) $c(\text{HF})_x$, and after 3 days of enzymatic CDP: b) $c(\text{HT})_x$ and d) $c(\text{HF})_x$.

The results obtained by HPLC were corroborated by ^1H NMR (Figure 2). In these spectra, signals due to small cyclic species, such as dimer, appeared clearly resolved and downfield and upfield shifted for the interior methylenes (3) and aromatic protons (4,5) respectively. Such displacements were, most probably due to the magnetic anisotropy effects caused by the electrons circulation in the aromatic rings, an effect that has been observed in other related cycles.^{17,28}

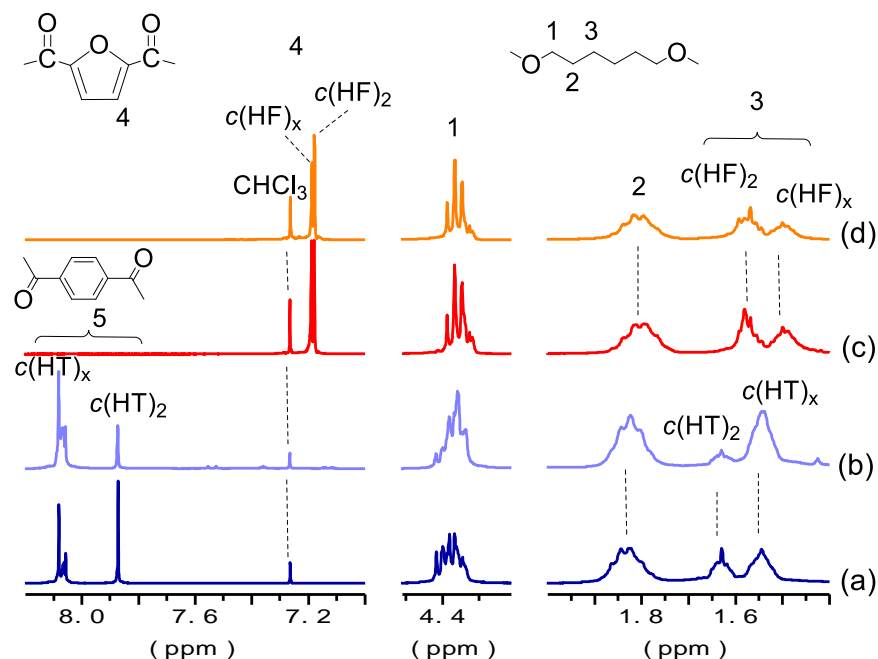


Figure 2. ^1H NMR of the crude product obtained after 7 days of enzymatic HDC (down) and 3 days of enzymatic CPD (up). a) and b) $c(\text{HT})_x$, c) and d) $c(\text{HF})_x$.

The thermal stability of the synthesized cycles was evaluated by TGA analysis under inert atmosphere. The TGA thermograms in Figure 3 show that both types of cycles were thermally stable up to around 250-270 °C. They decomposed in a single step with temperatures of maximum decomposition rate at 379 and 389 °C for $c(\text{HF})_x$ and $c(\text{HT})_x$ respectively, and with remaining weights at 600 °C about 3 wt% (Table S1).

DSC data recorded from as synthesized samples showed that both types of cyclic oligomers display endotherms at around 92-93 °C. These peaks are broad due to the melting of the different size crystallites belonging to different cyclic species and showed melting enthalpies of 24 and 41 J g^{-1} for $c(\text{HF})_x$ and $c(\text{HT})_x$ respectively (Figure 4).

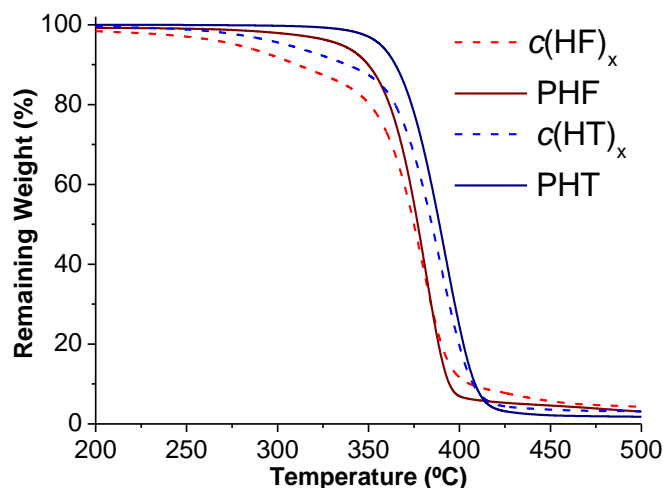


Figure 3. TGA analysis of $c(\text{HF})_x$, $c(\text{HT})_x$, and PHF, PHT derived polymers.

After the first heating treatment both type cycles were not able to crystallize and flat thermograms were observed in the second heating scans (Figure S11). The thermal properties observed allow concluding that these cycles could be processed for bulk polymerization by ROP at temperatures between 100-250 °C in the presence of a catalyst.

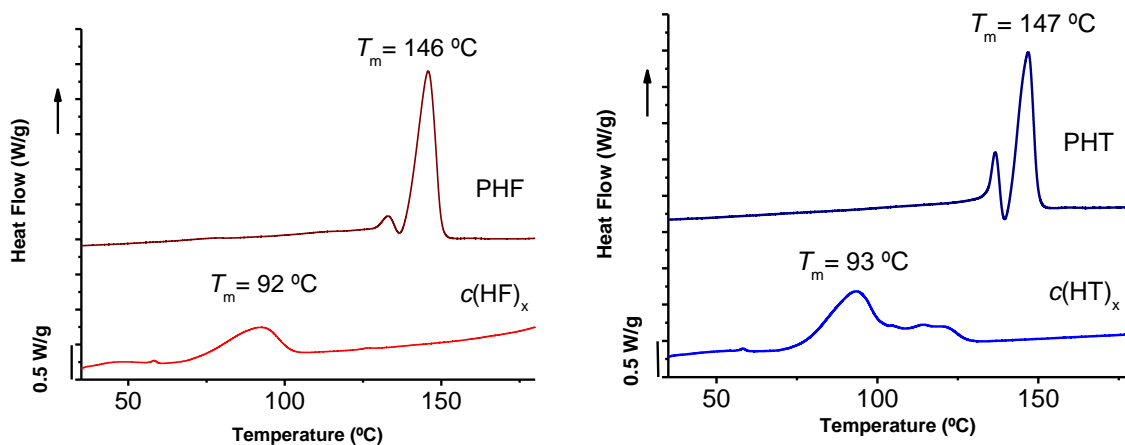


Figure 4. DSC thermograms of $c(\text{HF})_x$ and $c(\text{HT})_x$ cyclic oligomers (1st heating) and their PHF and PHT derived polymers (2nd heating).

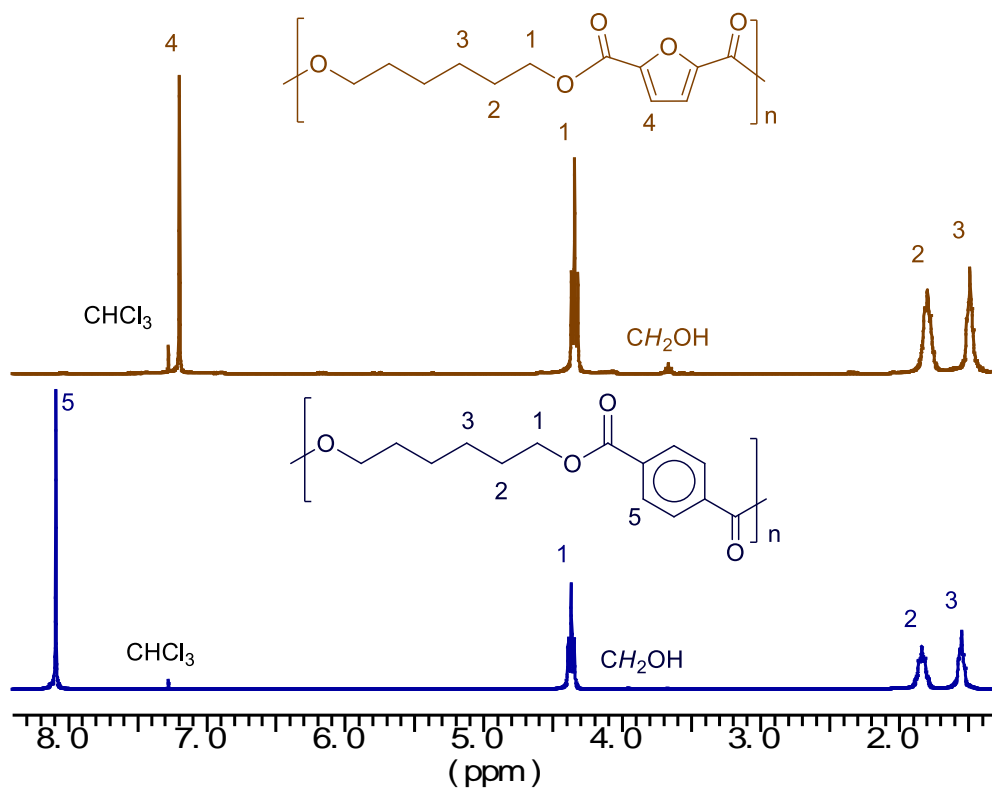
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3 The suitability of $c(\text{HT})_x$ and $c(\text{HF})_x$ to be polymerized by ROP in the presence of CALB to
4 give PHT and PHF polyesters respectively was then evidenced. As most of ED-ROP, the
5 polymerization could be carried out at higher monomer concentration. Hence, the reaction was
6 accomplished at 100 °C using higher cycles concentration.¹⁶ After 24 hours polymers with
7 weight average molecular weights of 8.9 and 15 Kg mol⁻¹ were attained for PHT and PHF
8 respectively (Table S1). Control test carried out without enzymes showed that no reaction took
9 place under same conditions and the cyclic oligomers were recovered at the end of reaction. The
10 polyesters showed dispersities around 1.7-2.5, which are in accordance with the values observed
11 for polymers obtained by entropically driven ring opening polymerization.^{6, 7}

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24 PHT and PHF polyesters were recovered as white powders and characterized by ¹H NMR
25 (Figure 5). Signals due to cyclic oligomers disappeared whereas new signals characteristic of
26 linear species were detected. Moreover, a small triplet at 3.6 ppm was observed and assigned to
27 the -CH₂OH end group.
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The thermal stability of PHT and PHF polyesters here obtained was found to be slightly higher
than that of their respective cyclic oligomers (Figure 3). The onset temperature increased around
50 °C and the maximum decomposition rate temperature around 3 °C in both cases (Table S1). In
accordance with data reported for these polymers in the literature, PHT showed better thermal
stability than PHF.^{18, 23} DSC scans recorded for these polyester samples are depicted in Figure 4
and showed that both of them were semicrystalline polymers with melting temperatures of 147
and 146 °C for PHT and PHF, respectively, not far from those observed for the same polyesters
obtained by melt polycondensation.^{23, 29, 30}

The two melting peaks observed for PHT may be due to the presence of different polymorphs
or to a crystalline reorganization process taking place during the heating scan.³⁰ Samples

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3 recorded at different heating rates showed these two peaks with almost no differences in both
4 melting temperatures and enthalpies (Figure S11). Further experiments are needed to ascertain
5 their precise origin (e.g., WAXS as a function of temperature). The glass transition temperatures
6 determined from rapidly melt quenched samples were around 11 and 15 °C for PHT and PHF
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45 **Figure 5.** ¹H NMR of PHF (top) and PHT (bottom) obtained by enzymatic ROP of *c*(HF)_x, and
46 *c*(HT)_x respectively.
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51 In order to determine if this enzymatic process could be used as a recycling tool, a preliminary
52 essay with samples of previously synthesized polyesters were subjected to
53 cyclodepolymerization in solution in the presence and absence of CALB. This CDP reaction,
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3 carried out under conditions similar to those used for enzymatic cyclization, was followed by ^1H
4 NMR (Figures S12 and S13). Both ^1H NMR (Figure 2b and 2d) and HPLC data showed that, in
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6 the presence of CALB, oligomeric cycles were obtained almost quantitatively after 72 hours of
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8 reaction, being the dimer the predominant species for PHF and the trimer for PHT (Figure 1b and
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10 1d). The linear polymer was recovered at the end of reaction in the absence of CALB enzyme,
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12 showing its biocatalytic effect for the intramolecular transesterification reaction.
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17 In summary, it can be concluded that cyclic oligoesters derived from dimethyl terephthalate
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19 and dimethyl furanoate and 1,6-hexanediol can be obtained in high yields by enzymatic
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21 cyclization. The successful polymerization of these cycles by enzymes has been proven, and
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23 even more interestingly, the cyclodepolymerization that converts the polyester into cyclic
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25 oligoesters has been also demonstrated. The approach here described can be extrapolated to the
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27 synthesis of other cycles of higher industrial interest, such as those derived from ethylene glycol
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29 or 1,4-butanediol and aromatic diesters which are usually obtained by HDC or CDP. One
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31 drawback of these enzymatic reactions is that longer reaction times are required to be
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33 accomplished if compared with those assisted by metallic or organometallic catalysts. This
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35 limitation is susceptible to be solved by using a more efficient enzyme able to work at higher
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37 temperatures.
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44 ASSOCIATED CONTENT

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47 **Supporting Information.** Materials and methods, HPLC, NMR and MALDI-TOF MS figures
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49 and GPC, DSC and TGA data.
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52 AUTHOR INFORMATION

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9 **Author Contributions**

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11 The manuscript was written through contributions of all authors. All authors have given
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26 **Notes**

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28 The authors declare no competing financial interest.
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38 sample used throughout in this work.
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