

## Production of Biodegradable Polyesters via Enzymatic Polymerization and Solid State Finishing

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**ABSTRACT:** The synthesis of aliphatic polyesters (PEs) derived from diols (1,4-butanediol and 1,8-octanediol) and diacids or their derivatives (diethyl succinate, sebacic acid, 1,12-dodecanedioic acid, and 1,14-tetradecanedioic acid) was achieved in order to produce poly(butylene succinate) (PE 4.4), poly(octylene sebacate) (PE 8.10), poly(octylene dodecanate) (PE 8.12), and poly(octylene tetradecanate) (PE 8.14). The herein suggested procedure involved two stages, both sustainable and in accordance with the principles of “green” polymerization. The first comprised an enzymatic prepolymerization under vacuum, in the presence of diphenylether as solvent using *Candida antarctica* lipase B as biocatalyst, whereas a low-temperature postpolymerization step [solid state polymerization (SSP)] followed in order to upgrade the PEs quality. In the enzymatically synthesized prepolymers, the range of number-average molecular weight attained was from 3700 to 8000 g/mol with yields reaching even 97%. Subsequently, SSP of PE 4.4 and 8.12 took place under vacuum or flowing nitrogen and lasted 10–48 h, at temperatures close to the prepolymer melting point ( $T_m - T_{SSP}$  varied between 4°C and 14°C). The solid state finishing led to increase in the molecular weight depending on the prepolymer type, and it also contributed to improvement of the physical characteristics and the thermal properties of the enzymatically synthesized PEs. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40820.

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### INTRODUCTION

Nowadays, plastics have penetrated in daily life, and a growing interest has developed to seek for alternative methods to produce renewable, biodegradable, and biocompatible polymers. To this perspective, aliphatic polyesters (PEs), with poly(lactic acid) (PLA) being a commercially predominant grade, comprise one family of polymeric compounds under study attracting attention for application fields such as packaging, biomedicine, agriculture, electronics, and automotive industry.<sup>1–8</sup> Indicatively, researchers have concluded that biodegradable products for fabrics, fibers, composite materials, and membranes can be designed based on eco-friendly aliphatic PEs of high molecular weight (MW). The fabrics and the membranes present satisfying thermal insulation and resistance; the fibers can be used as bioabsorbable surgical thread; and composite materials have folding resistance, water resistance, and flexibility.<sup>9</sup>

PEs are conventionally produced in the presence of chemical catalysts, such as  $\text{Ti}(\text{O}i\text{Bu})_4$ ,  $\text{ZnAc}$ , dibutyltin oxide, and  $\text{Sb}_2\text{O}_3$  through melt processes, which however may involve significant drawbacks, such as high reaction temperatures, low selectivity, and possibility of side reactions.<sup>10</sup> On the other hand, enzymatic esterification offers many benefits, such as carrying out the reaction under mild conditions, e.g., at low temperatures in the presence of nontoxic media, and resulting in a good-quality polymer due to enzyme high enantio-, chemo-, and regioselectivity and to subsequent restriction of side reactions. These features are the main reasons why enzymatic polycondensation has been regarded as an environmentally friendly synthetic process for polymeric materials and a promising example of green/sustainable polymerization method. The enzymes are big molecular compounds with complex three-dimensional structure and high MW. The activity of the enzyme depends on its structural

configuration and active center where the monomers or the synthesized polymer substrates can be attached. Biocatalysts maintain their chemical and physical structure after the reaction, and therefore, they can be reused.<sup>11</sup> According to literature, most research teams of PEs focus on enzymatic polymerization using lipases in nonconventional media. In nature, lipases catalyze the hydrolysis of esters of fatty acids; nonetheless, in organic medium they show a reverse operation, leading to ester bonds formation.<sup>12,13</sup> The most popular lipase that has been used for the aforementioned purposes is the immobilized lipase B derived from *Candida antarctica* (Novozym 435, N435).<sup>14–17</sup>

In the same concept of “green chemistry,” scientific interest is also centered on supplementary techniques, such as the solid state polymerization (SSP), applied in polycondensates industry (like poly(ethylene terephthalate) and polyamides) for increase in MW and overall quality improvement of the produced polymer. This technique is based on heating a solid starting material to a temperature high enough to initiate and propagate polymerization reactions, but lower than the product melting point, so as to retain the solid phase. SSP starting materials can be both crystalline monomers (direct SSP) and semicrystalline polymers (post-SSP).<sup>18–24</sup> Direct SSP is mainly applied on laboratory scale, presenting however considerable practical interest, because polymerization occurs from the beginning in the solid state. Consequently, all the problems associated with the high temperatures of melt technology, e.g., energy consumption and polymer degradation, as well as the use of any solvent, are completely avoided.<sup>18,25,26</sup> On the other hand, in post-SSP, widely applied on industrial scale, a low-molecular-weight base polymer (prepolymer or precursor), which is derived from solution-melt polymerization technique, reacts to further increase the MW; the relevant step is often stated in overall polymerization layouts as “post-SSP,” “drying,” or “finishing.”<sup>19,20,25–28</sup>

In the current work, a two-step process was suggested to prepare aliphatic PEs, derived from diols and diacids. The examined repeating units were long-chain PEs based on 1,8-octanediol, cited in literature for high reactivity during enzymatic processes,<sup>29,30</sup> with sebacic (poly(octylene sebacate), PE 8.10), 1,12-dodecanedioic (poly(octylene dodecanate), PE 8.12), and 1,14-tetradecanedioic acids (poly(octylene tetradecanate), PE 8.14), which may be derived from renewable resources.<sup>30,31</sup> In addition, the preparation of poly(butylene succinate) (PE 4.4) from 1,4-butanediol and diethyl succinate was examined due to the very limited literature on its enzymatic polymerization,<sup>15,32</sup> combined with its high potential for future development and applications.<sup>33</sup> It can be also considered as a model/reference biopolymer due to its shorter repeating unit and higher melting point ( $T_m = 113^\circ\text{C} - 115^\circ\text{C}$ ) compared with the other studied PEs. The suggested preparation route comprised first an enzyme-catalyzed polymerization step, and then the enzymatically synthesized prepolymers PE 4.4 and PE 8.12 were submitted to SSP in order to improve their properties and to suggest an overall sustainable method for polyesterification. The aforementioned PEs were selected for enduring SSP due to comparatively higher and more stable melting points. Finally, for the first time in similar studies,<sup>17,34</sup>  $^1\text{H-NMR}$  spectroscopy and

viscometry analysis were correlated, and the received results contributed to proper MW determination.

## EXPERIMENTAL

### Materials

1,8-Octanediol (98+ % purity) was supplied by Alfa Aesar (Germany), sebacic acid by DSM (Netherlands), and 1,12-dodecanedioic acid (~98.5% pure) and 1,14-tetradecanedioic acid (~97.0% pure) by Cathay (China). 1,4-Butanediol and diethyl succinate were supplied by ARD (France). The solvents used were diphenylether from Alfa Aesar (Germany), chloroform from Merck (Germany) and Carlo Erba (France), and methanol from Carlo Erba (France). The examined biocatalyst was *C. antarctica* lipase B (CALB) physically adsorbed within the macroporous resin Lewatit VPOC 1600 (Novozym 435, N435) from Novozymes (Denmark). The protein content of nonimmobilized CALB on Lewatit substrate was 0.1 w/w.

### Assay of Lipase Activity

The activity of lipase N435 used in the enzymatic prepolymerization step was determined according to the method of Sigurgisladdottir et al.<sup>35</sup> with slight modifications. Lipase activity was assayed using 9.33 mM *p*-nitrophenol-palmitate in 50 mM phosphate buffer (pH 7) containing 6.8 mM of TritonX and 0.11% (w/v) gum Arabic. The immobilized enzyme was added to the assay solution, and the reaction was carried out at 50°C for 1 h. Afterward, the mixture was centrifuged, and the obtained supernatant was used for the determination of the enzymatic activity by monitoring the release of *p*-nitrophenol at 410 nm. One unit of enzyme activity is defined as the amount of enzyme that liberates 1  $\mu\text{mol}$  of *p*-nitrophenol per minute under standard assay conditions.

### Enzymatic Prepolymerization

Stoichiometric amounts of the diol, the corresponding dicarboxylic acid or derivative, and 10 or 20 wt % N435 (relative to monomers), corresponding to 1% and 2% CALB relative to monomers, were mixed in diphenylether in a round-bottom flask and stirred at 75°C under vacuum. The process involved one or two steps (Table I), with a two-step process applied in the case of PE 4.4 because of 1,4-butanediol's high volatility. At the end of the enzymatic reaction, an amount of chloroform was added in the prepared polymer solution to avoid the solidification of diphenylether that occurred during the cooling step. N435 was filtered off, and the sediment was slowly added in cold stirred methanol. The precipitated product was filtered and dried under vacuum (40°C–50°C, 4 h). The procedure yielded PE prepolymers as colorless solids.

### Solid State Postpolymerization

Prepolymers of PE 4.4 and PE 8.12 were further polymerized via solid state finishing. The postpolymerization involved absence of biocatalyst and was performed in a rotary evaporator (Rotavapor R-210, Buchi) under vacuum (20 mbar). The reaction temperatures ( $T_{\text{SSP}}$ ) were set at the vicinity of the prepolymer melting point ( $T_m - T_{\text{SSP}} = 4^\circ\text{C} - 14^\circ\text{C}$ ), and reaction times varied from 10 to 48 h (Table II).

In the case of PE 8.12, an additional approach was examined regarding by-product removal method that involved passing inert gas through the prepolymer mass. The reaction took place in a

**Table I.** Conditions of Enzymatic Prepolymerization for PE 4.4, 8.10, 8.12, and 8.14

PEs	Steps	T (°C)	t (h)	P (mbar)	Total amount of monomers (g)	N435 (wt %)
PE 4.4A	1	75	4	20	13.3	20
PE 4.4B	2	First step: 75	2	1000 (N <sub>2</sub> )	13.3	20
		Second step: 75	2	20		
PE 8.10A	1	75	4	20	15.6	10
PE 8.12A	1	75	4	20	12.6	10
PE 8.12B	1	75	4	20	12.6	20
PE 8.12C <sup>a</sup>	1	75	4	20	18.8	20
PE 8.14A	1	75	4	20	12.6	10

<sup>a</sup>Use of ca. 0.7 times less solvent compared with PE 8.12B.

bench-scale, cylindrical, stainless steel reactor equipped with a stainless steel gas inlet line of 1/4" in diameter and two thermocouples. The gas line and reactor were heated by immersion in a fluidized sand bath (Techne Corp., Minneapolis, MN). The reaction took place under nitrogen flow and lasted 10, 20, and 48 h. The reaction temperature ( $T_{SSP}$ ) was set at  $T_m - T_{SSP} = 4^\circ\text{C}$ .

### Product Characterization

**Structural Characterization and MW Calculation Through <sup>1</sup>H-NMR.** <sup>1</sup>H-NMR spectroscopy was recorded in CDCl<sub>3</sub> on a Bruker DRX 400 spectrometer equipped with a 5 mm <sup>1</sup>H/<sup>13</sup>C dual inverse broad probe operating at 400 MHz. Based on the derived spectra, the number-average MW ( $\overline{M}_n$ , g/mol) was calculated [eq. (1)]<sup>36</sup>:

$$\overline{M}_n = m_o \cdot [I_{\text{COO-}} / I_{\text{end groups}}] + M_{\text{end group}} \quad (1)$$

where,  $m_o$  is the MW of the repeating structural unit,  $I_{\text{COO-}}$  is the absorbance intensity of the hydrogens that are associated with the methylene (CH<sub>2</sub>) protons next to the ester group inside the repeating structural unit,  $I_{\text{end groups}}$  is the absorbance intensity of the hydrogens next to the end hydroxyl group, and  $M_{\text{end group}}$  is the MW of chain ends.

The <sup>1</sup>H-NMR spectra verified the synthesis of the studied PEs and the relevant shifts were as follows:

**PE 4.4:** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) (ppm): 4.16 (4H, m, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 3.67 (0.20H, t, -CH<sub>2</sub>OH), 2.62 (4H, s, -CH<sub>2</sub>

CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.70 (4H, s, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.26 (0.62H, t, CH<sub>3</sub>CH<sub>2</sub>O-).

**PE 8.10:** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) (ppm): 4.05 (4H, t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 3.64 (0.15H, t, -CH<sub>2</sub>OH), 2.31 (4H, t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.61 (8H, s, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.30–1.32 (18H, m, -CH<sub>2</sub>-).

**PE 8.12:** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) (ppm): 4.05 (4H, t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 3.64 (0.17H, t, -CH<sub>2</sub>OH), 2.28 (4H, t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.61 (8H, s, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.28–1.33 (20H, m, -CH<sub>2</sub>-).

**PE 8.14:** <sup>1</sup>H-NMR (CDCl<sub>3</sub>) (ppm): 4.05 (4H, t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 3.64 (0.28H, t, -CH<sub>2</sub>OH), 2.28 (4H, t, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.61 (8H, s, -CH<sub>2</sub>CH<sub>2</sub>C(O)OCH<sub>2</sub>-), 1.26–1.33 (23H, m, -CH<sub>2</sub>-).

**Solution Viscometry and Estimation of Polymer Intrinsic Viscosity.** Viscosity measurements were performed in PE solutions in chloroform at a concentration of 0.5 dL/g using an Ubbelohde viscometer at 25°C. The relative ( $\eta_r$ ), the specific ( $\eta_{sp}$ ), and the reduced ( $\eta_{red}$ ) viscosity were determined. The intrinsic viscosity ( $[\eta]$ , dL/g) can be calculated using one of the eight expressions reported by Billmeyer<sup>37</sup> (Table III) and the viscosity measurement of a single-concentration polymer solution. More specifically, the interactions in each polymer-solvent system define which equation fits the experimental data best, considering that the calculated  $\eta$  values (assumed equal to  $[\eta]$ ) should

**Table II.** SSP Conditions for PE 4.4 and PE 8.12

Prepolymer and form	Reactor type	Steps	T <sub>SSP</sub> (°C)	T <sub>m</sub> - T <sub>SSP</sub> (°C)	t (h)	N <sub>2</sub> (m <sup>3</sup> /h kg)	P (mbar)
PE 4.4A	Flakes	Rotary evapor.	1	84	7	24	20
PE 4.4B	Flakes	Rotary evapor.	2	First step: 77	10	24	20
				Second step: 90	5	12	20
PE 8.12A	Powder	Rotary evapor.	1	60	14	10	20
	Powder	Rotary evapor.	1	65	9	10	20
	Powder	Rotary evapor.	1	70	4	10	20
	Powder	Rotary evapor.	1	70	4	20	20
PE 8.12B	Flakes	Fixed bed	1	68	4	20	6.3

be the same or slightly lower than  $\eta_{red}$  based on the Huggins's expression ( $\eta_{red} = [\eta] + k_H[\eta]^2C$ ).<sup>38</sup> Because of the lack of literature data for the PEs herein prepared, the fitting of Billmeyer expressions was examined (Figure 1):  $\eta_{red}$  results were found to be higher than the  $\eta$  values in accordance with Huggins equation showing that the formed aliphatic PE solutions at 0.5 g/dL presented acceptable degree of dilution to be able to use the single-point approach for  $[\eta]$  estimation. As a result, one might conclude that any of Billmeyer expressions could be equally selected within the  $[\eta]$  span considered. Therefore, eq. (2) ( $\eta_1$ ), proposed by Solomon and Ciuta<sup>38</sup> was used:

$$[\eta] = \frac{1}{C} \sqrt{2(\eta_{sp} - \ln \eta_r)} \quad (2)$$

Finally, the number-average MW ( $\overline{M}_n$ ) was estimated through eq. (3), using Mark-Houwink constants valid for PLA solutions under the same measurement conditions<sup>39</sup> and polydispersity index equal to 2. Pertinent data are not available in literature for the studied aliphatic PEs.

$$[\eta] = 3.77 \cdot 10^{-4} \overline{M}_n^{0.77} \quad (3)$$

**Correlation of <sup>1</sup>H-NMR and Viscometry Analysis for the Assessment of Aliphatic PEs MW.**  $\overline{M}_n$  values from <sup>1</sup>H-NMR spectra [eq. (1)] and viscosity data [eq. (3)] were compared to establish the suitability and the convergence of both analysis techniques. Figure 2 shows the deviation between the  $\overline{M}_n$  values derived from the two methods, and it can be discerned that in the cases of PE 8.10, PE 8.12, and PE 8.14, they converged satisfactorily. On the contrary, in the case of PE 4.4,  $\overline{M}_n$  derived from <sup>1</sup>H-NMR was found to be significantly higher than the values from viscosity data, which can be attributed to the completely different structure of the short repeating unit of PE 4.4 compared with the other aliphatic long PEs and to the use of PLA Mark-Houwink constants in eq. (3). However, a correction factor can be calculated in order to adjust the PE 4.4 intrinsic viscosity and to be able to use eq. (3) for determination of  $\overline{M}_n$  viscometry (data (•) in Figure 2):

$$[\eta]_{adjusted} = 2.6 \times [\eta]_{measured} \quad (4)$$

The validated  $[\eta]$  and  $\overline{M}_n$  values were used, in order to properly compare polymerization rates of the studied aliphatic PEs.

**Thermal Analysis.** Differential scanning calorimetry (DSC) measurements were performed in a Mettler DSC 1 STARE System through a heating-cooling-heating cycle from 30°C to 150°C, under nitrogen flow (10 mL/min), with heating and cooling rates at 10°C/min. In addition, thermogravimetric analysis (TGA) was conducted in a Mettler TGA/DSC 1 thermobalance from 30°C to 600°C, with heating rate at 10°C/min under nitrogen flow (10 mL/min). Degradation temperatures ( $T_d$ ) were determined at the maximum weight loss. DSC and TGA measurements were performed at duplicates.

## RESULTS AND DISCUSSION

### Enzymatic Prepolymerization

**Effect of Process Parameters on Attained Yield and MW.** Under the selected conditions of enzymatic prepolymerization, the formation of PE 4.4, PE 8.10, PE 8.12, and PE 8.14 repeating units was achieved, identified in <sup>1</sup>H-NMR spectra, and

involved the characteristics shown in Table IV. For reaction conditions of 75°C, 4 h, 20 mbar (Samples A), the attained yields were in the range of 65%–97%, resulting in PE 4.4, PE 8.10, PE 8.12, and PE 8.14 with intrinsic viscosities of 0.180, 0.261, 0.301, and 0.253 dL/g, respectively. Comparatively, previous experiments in toluene at the same temperature and in the presence of molecular sieves<sup>40</sup> provided PE 8.12 and PE 8.14 with lower  $[\eta]$ , i.e., 0.189 and 0.181 dL/g, indicating the higher efficiency of the herein suggested technique with diphenylether and vacuum. This is in accordance with literature because diphenylether has been proven to be the most effective solvent among a variety of substances, e.g., xylene, tetramethylene glycol, 2-methoxyethyl ether, toluene, heptane, 1,4-dioxane, and diisopropyl ether.<sup>15,17,29,41</sup> The herein achieved number-average MWs ( $\overline{M}_{n\text{-NMR}}$ ) were in the range of 3700–8000 g/mol, with PE 4.4A presenting the lower value probably due to lower enzyme affinity with the short chains of the reactants. On the other hand, when comparing 1,8-octanediol-based PEs, 1,14-tetradecanedioic acid resulted in the lowest MW PE, as already shown in our previous work,<sup>40</sup> probably because of its limited purity (97.0% vs. 98.5% for 1,12-dodecanedioic acid) or enzyme's lower selectivity to this monomer.

Following, focus was given on PE 4.4 and PE 8.12 in order to examine some significant enzymatic process parameters. Starting with PE 4.4, because of the volatility of 1,4-butanediol, the enzymatic process was divided in two steps in the presence of 20% N435 (PE 4.4B): (a) 2 h under nitrogen atmosphere (inert conditions) and (b) additional 2 h under vacuum (20 mbar). This two-step process resulted in slightly higher MW value (3900 g/mol), however giving a sticky product. The latter form was significantly improved when prolonging both stages (first stage: 5 h and second stage: 24 h).

Concerning PE 8.12, increasing the enzyme quantity from 10% (PE 8.12A) to 20% (PE 8.12B) for a 4-h reaction had a positive effect on the yield, reaching 97%. This implies that reaction equilibrium regarding monomers conversion was not reached in the time of 4 h for enzyme 10% quantity and based on the fact that enzyme reserved 80% of reactivity (assay of lipase activity) after reaction, increasing polymerization time can be considered feasible. However, MW did not increase with higher amount of enzyme, showing that there is a MW plateau value for the studied conditions. It can be considered that enzyme reacts at different rates as a function of the substrate chain length; it has a higher activity for short and medium chain macromolecules with less sterical hindrance, than for long chain substrates, because of the specific structure of the enzyme binding site. Thus, the polymerization can be found to be slowed down with increase in MW.<sup>42</sup>

Finally, in sample PE 8.12C, condensing monomers suspension was examined, and a significant decrease in yield was observed with a lowering of MW for similar reasons of sterical hindrance and restriction of enzyme activity.

**Thermal Analysis of Enzymatically Synthesized PEs.** Concerning thermal properties, melting points in the range of 67°C–92°C were reached, with enthalpies of fusion between 77 and 150 J/g (Figure 3), both values being higher compared with the

**Table III.** Billmeyer Expressions for the Estimation of Intrinsic Viscosity

$$\eta_1 = \frac{1}{C} \sqrt{2(\eta_{sp} - \ln \eta_r)} = [\eta] + (k_H - 1/3)[\eta]^2 C + \dots$$

$$\eta_2 = \frac{1}{4} \frac{\eta_{sp}}{C} + \frac{3}{4} \frac{\ln \eta_r}{C} = [\eta] + (k_H - 3/8)[\eta]^2 C + \dots$$

$$\eta_3 = \frac{1}{3} \frac{\eta_{sp}}{C} + \frac{2}{3} \frac{\ln \eta_r}{C} = [\eta] + (k_H - 1/3)[\eta]^2 C + \dots$$

$$\eta_4 = \frac{\eta_{sp}}{C} \exp\left(-\frac{\eta_{sp}}{3}\right) = [\eta] + (k_H - 1/3)[\eta]^2 C + \dots$$

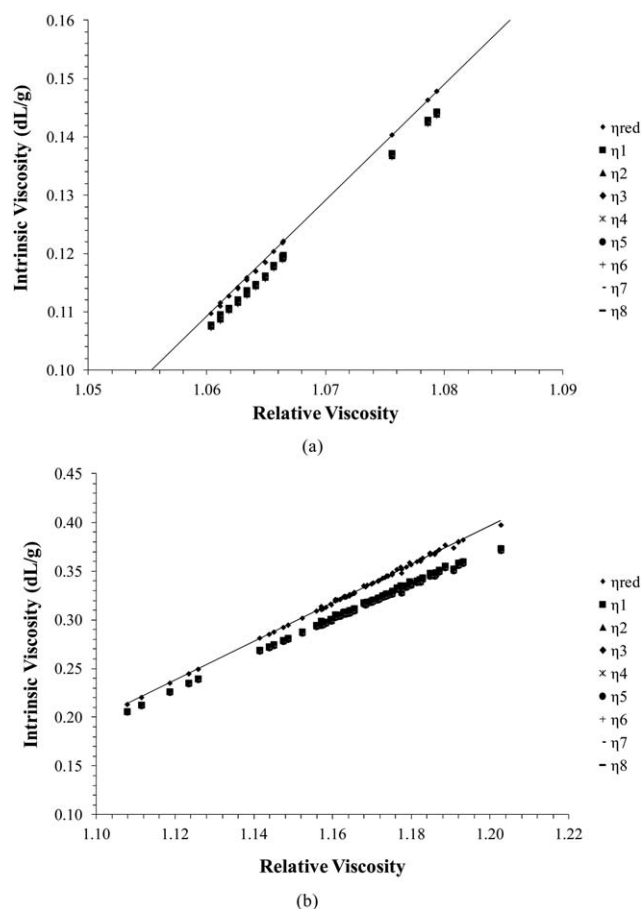
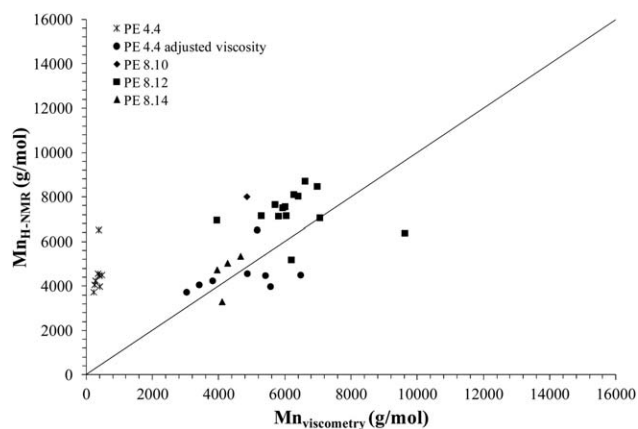
$$\eta_5 = \frac{(1 + 1.5\eta_{sp})^{1/2} - 1}{0.75C} = [\eta] + (k_H - 3/8)[\eta]^2 C + \dots$$

$$\eta_6 = \frac{(1 + 4/3\eta_{sp})^{1/2} - 1}{0.67C} = [\eta] + (k_H - 1/3)[\eta]^2 C + \dots$$

$$\eta_7 = \frac{4}{C} (\eta_r^{1/4} - 1) = [\eta] + (k_H - 3/8)[\eta]^2 C + \dots$$

$$\eta_8 = \frac{3}{C} (\eta_r^{1/3} - 1) = [\eta] + (k_H - 1/3)[\eta]^2 C + \dots$$

results of previous enzymatic polymerization runs in toluene and in the presence of molecular sieves.<sup>40</sup> Values from Ref. 40 concerning PE 8.6 are also quoted for comparison. It should be noted that the melting points of 1,8-octanediol-based PEs were found to be linearly proportional to the carbon atoms of the corresponding diacid (Y) and fitted the empirical equation  $T_m = 2.9Y + 38.55$ . In addition, it can be seen that as the carbon atoms of the diacid segment increases, the melting point of the corresponding PE increases as well, demonstrating higher

**Figure 1.** Assessment of Billmeyer expressions for determining the intrinsic viscosity of (a) PE 4.4 and (b) PE 8.12.**Figure 2.** Correlation between  $\overline{M}_n$  calculated via  $^1\text{H-NMR}$  ( $\overline{M}_{n\text{H-NMR}}$ ) [eq. (1)] and  $\overline{M}_n$  calculated via viscometry ( $\overline{M}_{n\text{viscometry}}$ ) [eq. (3)] for PE 4.4, PE 8.10, PE 8.12, and PE 8.14.

compound cohesive energy. Ester bonds act as defects along the polymer backbone; therefore, for PE 8.10, 8.12, and 8.14, which consist of large macromolecular chains, as the distance between ester groups increases, the number of defects decreases and consequently  $T_m$  and  $\Delta H_m$  raise.<sup>40</sup> However, PE 4.4 was excluded from this rule, showing the higher  $T_m$ , as it was expected. PE 4.4 exhibits balanced performance in thermal and mechanical properties, and its high melting point can be considered a result of its rigid and symmetric short repeating unit.

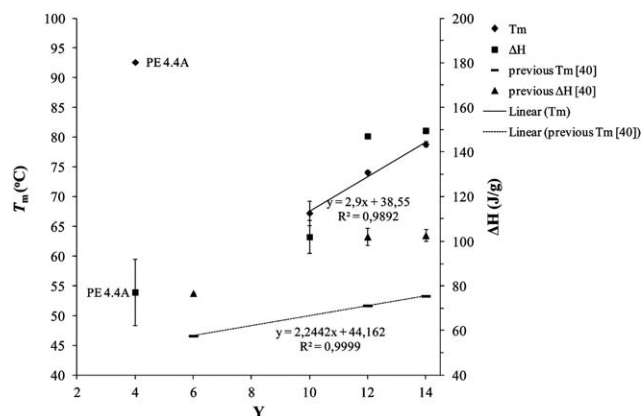
During cooling from melt, crystallization exotherms appeared for 1,8-octanediol-based PEs—PE 8.10, PE 8.12, and PE 8.14—demonstrating that the three PEs had a strong ability to crystallize at temperatures ( $T_c$ ) 50.8°C, 58.9°C, and 61.0°C, respectively (Figure 4). PE 8.14 obtained the higher crystallization temperature, probably due to the higher chain flexibility and thus increased mobility in the molten state and ease of chain folding. Concerning PE 4.4, its  $T_c$  occurred between PE 8.10 and PE 8.12 at 56.4°C. Finally, based on TGA curves, weight loss started at 380°C and lasted up to 480°C, whereas the maximum weight loss was noted at 418°C–420°C ( $T_d$ ). PE 8.10, however, presented a two-step degradation mechanism, starting at 160°C, a phenomenon that has been reported before for PE 8.6,<sup>40</sup> indicating probably that 1,8-octanediol-based PEs with

**Table IV.** Yield and Molecular Weight Properties of Enzymatically Synthesized Polyesters<sup>a</sup>

PEs	Yield (%)	$[\eta]$ (dL/g)	$\overline{M}_{n\text{H-NMR}}$ (g/mol)
PE 4.4A	76	0.180 ± 0.003	3740
PE 4.4B	75	0.218 ± 0.004	3910
PE 8.10A	96	0.261 ± 0.007	8020
PE 8.12A	65	0.301 ± 0.032	7600
PE 8.12B	97	0.346 ± 0.004	7070
PE 8.12C	75	n.d <sup>b</sup>	6400
PE 8.14A	78	0.253 ± 0.015	5360

<sup>a</sup> Samples A: prepared at 75°C, 4 h, 20 mbar.

<sup>b</sup> n.d due to residual diphenylether.



**Figure 3.** Correlation between thermal properties vs. diacid chain length ( $Y$ ) of the enzymatically synthesized prepolymers (75°C, 4 h, 20 mbar).

less than 12 carbon atoms in the corresponding diacid may be less stable than the rest.

### Solid State Postpolymerization

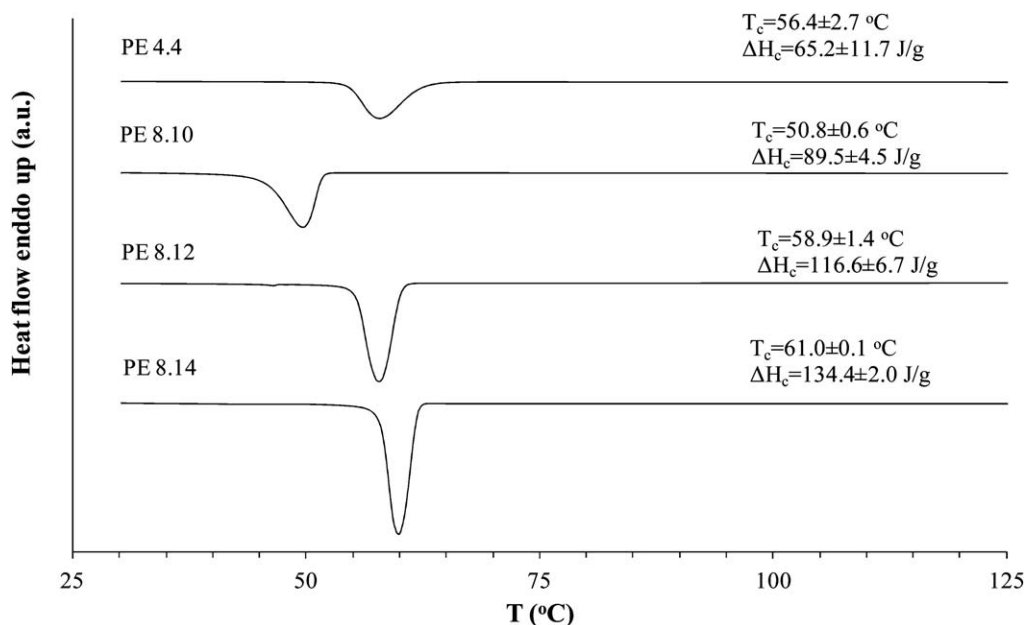
Based on the total properties profile, PE 4.4 and PE 8.12 were selected to be solid state polymerized. In particular, SSP of PE 4.4 prepolymer was examined under reduced pressure for 24 h at 84°C, and a small increase in MW was reached in the range of 14% (Table V). However, a simultaneous increase in  $T_m$  and  $\Delta H$  was evidenced, implying a crystal reorganization/perfectioning during the SSP process (Figure 5). Taking advantage of this  $T_m$  increase, a two-step SSP process was conducted for a total time of 36 h—the first step at 77°C for 24 h serving as a pre-crystallization step. The MW ( $\Delta \overline{M}_n = 67\%$ ) and  $T_m$  (up to 110°C) were significantly enhanced with simultaneous improvement of prepolymer physical characteristics—stickiness disappeared. It should be also highlighted that SSP performance is directly correlated to the suitability of the starting material in terms of COOH and OH end groups balance. Especially for the

**Table V.** Relative Increase in Molecular Weight for Postpolymerized PE 4.4 and PE 8.12 under Vacuum and Nitrogen Flow

Prepolymer	Conditions SSP	$\Delta \overline{M}_{nH-NMR}$
PE 4.4A	84°C, 24 h, 20 mbar	14%
PE 4.4B	First: 77°C, 24 h, 20 mbar	
	Second: 90°C, 12 h, 20 mbar	67%
PE 8.12B	60°C, 10 h, 20 mbar	6%
PE 8.12B	65°C, 10 h, 20 mbar	0%
PE 8.12B	70°C, 10 h, 20 mbar	0%
PE 8.12B	70°C, 20 h, 20 mbar	1%
PE 8.12C	68°C, 20 h, flowing N <sub>2</sub>	23%

case of PE 4.4, often this balance is disturbed in chemically catalyzed processes due to the side reaction of 1,4-butanediol dehydration and tetrahydrofuran formation,<sup>33</sup> affecting the obtained polymer MW and its quality as SSP starting material. In general, it can be said that this deviation from end group balance can be restricted in the case of the enzymatically synthesized prepolymers, due to the lower operation temperatures and to the enzymes selectivity.

On the other hand, the results with PE 8.12 SSP under vacuum were not very encouraging, apparently due to the lower prepolymer melting point and thus to the lower operating temperatures. A slight/insignificant effect on increasing  $\overline{M}_n$  was observed when SSP was performed at 60°C for 10 h (Table V), whereas increasing further the SSP temperature and time had no positive effect on MW build-up. On the other hand, the thermal properties of postpolymerized PE 8.12 presented a significant enhancement (Figure 6): indicatively, maximum increase in  $T_m$  (from 74.1°C to 79.8°C) was reported for  $T_m - T_{SSP} = 4^\circ\text{C}$  and 20 h of reaction. As in the case of PE 4.4, SSP can be considered as a method of upgrading aliphatic PEs in terms of melting



**Figure 4.** DSC crystallization curves of enzymatically synthesized PEs (75°C, 4 h, 20 mbar).

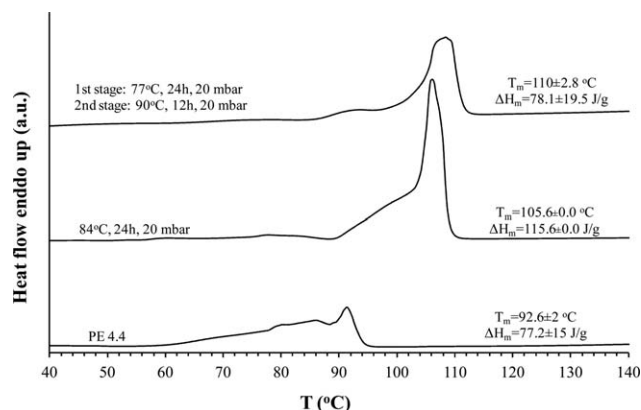


Figure 5. DSC curves of PE 4.4 before and after SSP.

point. Finally, when performing the SSP of PE 8.12 under nitrogen flow at 68°C (20 h), a more pronounced increase in the MW ( $\Delta \overline{M}_n = 23\%$ ) was evidenced, showing that flowing  $N_2$  entailed more promising results, with the need of further studies.

## CONCLUSIONS

This study was focused on the use of CALB as biocatalyst for the synthesis under mild conditions of aliphatic PEs with improved quality. More specifically, enzymatic polymerization of poly(butylene succinate), poly(octylene sebacate), poly(octylene dodecanate), and poly(octylene tetradecanate) was performed in diphenylether for 4 h applying vacuum. The derived yields and MWs were in the range of 65%–97% and 3700–8000 g/mol, respectively. The suggested enzymatic process was also combined successfully with solid state finishing. Prepolymers PE 4.4 and PE 8.12 were applied to SSP by application of vacuum or by passing nitrogen. The solid state finishing under vacuum contributed to increase in MW in the case of PE 4.4 and especially when the process was held in two steps, the first serving as a precrystallization step. Concerning PE 8.12, SSP under flowing nitrogen led to higher increase in MW in comparison with vacuum performance. In addition, it should be mentioned that SSP upgraded thermal properties in all examined conditions for both PE 4.4 and PE 8.12. In conclusion, the herein results suggested that SSP step has the potential to be effective as an extension of the enzymatic polymerization improving

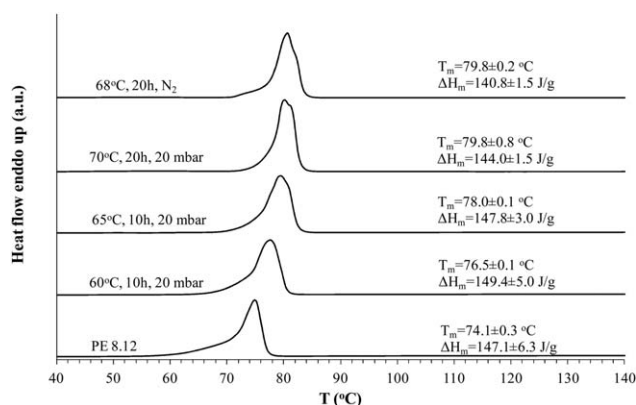


Figure 6. DSC curves of PE 8.12 before and after SSP.

$\overline{M}_n$  and  $T_m$ . However, further research is recommended for more promising future results and better understanding of the pertinent reaction mechanisms.

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