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Synthesis of poly(butylene succinate) through oligomerization–cyclization–ROP route

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The preparation of cyclic butylene succinate lactone *via* catalytic depolymerization of poly(butylene succinate) oligomers (OPBS) and conversion to high-molecular weight poly(butylene succinate) (PBS) *via* ring-opening polymerization (ROP) is described. OPBS was first synthesized by two-stage melt polycondensation, purified and characterized by size exclusion chromatography (SEC). Then, it was depolymerized under reduced pressure in a glass oven and the volatile fraction (VF) was collected and characterized. The butylene succinate lactones obtained by intramolecular transesterification were characterized by nuclear magnetic resonance (^{1}H NMR) and mass spectrometry (MS). Their further successful ROP polymerization within 24 hours afforded the desired PBS with $\overline{M_w}$ of 65 000 g mol^{-1} and $Đ$ of 2.2.

Introduction

Nowadays, aliphatic polyesters are among the most promising materials to replace conventional plastics for several reasons. In addition to their high performance, they can be processed using conventional equipment at conventional temperature. Those polyesters exhibit controllable biodegradability and their monomers are more and more produced from renewable feedstock. One of these, poly(butylene succinate) (PBS) is a white crystalline thermoplastic exhibiting melting point and toughness similar to low-density poly(ethylene) (LDPE), glass transition temperature and tensile strength between poly(ethylene) (PE) and poly(propylene) (PP) and stiffness between LDPE and high-density polyethylene (HDPE).[1,2] PBS is synthesized through a two-stage melt polycondensation process (esterification and polycondensation) of 1,4-butanediol and succinic acid. As these step-growth polymerizations usually reach oligomers, chain extenders, *e.g.* hexamethylene diisocyanate, are required to reach processable polymers with $\overline{M_n}$ and $\overline{M_w}$ respectively of about 40 000 and 100 000 g mol^{-1}.[2–4] An alternative to the condensation polymerization followed by extension step is the chain-growth polymerization from lactone monomer: ring-opening polymerization (ROP). This polymerization procedure is known to give both higher controlled molecular weights and higher monomer conversions without byproducts. The synthesis of cyclic mono- or multi-mer of aliphatic polyester (PLA, PET, PBT…) were reported using different chemical reactions such as condensation or thermal catalytic depolymerization[5–7] and are daily used in industry to produce high molecular weight polymer PLA.[8,9] The cyclic oligomers production from the thermal depolymerization of polyesters could also be a way to recycle them.[10] In the special case of PBS, mono- and multi-mer lactones were already observed in literature. Indeed, they have been known for some time, being formed in the parent condensed polymers at concentrations of 1–3%[11–13] and they were observed as byproduct of (thermal, thermo or photo-oxidative) degradation of PBS.[4,14–20] Nevertheless, they were not much isolated and their potential for polymerization was not studied. To date, and as far as we know, only Matsumura's laboratory[20–23] has investigated the synthesis of butylene succinate cycles with the aim of polymerizing them. Matsumura obtained oligomeric lactones with different size by lipase-catalyzed degradation of oligo-PBS and re-polymerized them by ROP with the same enzyme.

In this study, for the first time PBS lactone monomers were successfully chemically synthesized and further polymerized by ROP in bulk.

Materials and methods

Chemicals

Succinic acid (99%, Merck), 1,4-butanediol (p.s., Merck), ZnO (99.9%, Sigma-Aldrich), acetone (p.a., Merck), toluene (technical grade, VWR), chloroform (technical grade, VWR), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) (96%, Alfa Aesar), titanium(IV) tetraisopropoxide (97%, Sigma-Aldrich), GC derivatization agent (BSTFA + TMCS, 99 : 1; Supelco, Aldrich) were used as received without further purification.

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Synthesis of poly(butylene succinate) oligomers (OPBS)

Synthesis of aliphatic oligomeric polyesters was performed following the two-stage melt polycondensation method (esterification and polycondensation) in a steel batch reactor. Succinic acid (SA) and 1,4-butanediol (BDO) in a molar ratio 1/1.12 and the catalyst titanium(IV) tetraisopropoxide (5.2×10^{-3} mol mol_{SA}^{-1}) were charged into the stainless steel vessel equipped with a condenser. After three vacuum–argon cycles to remove oxygen, the reaction mixture was heated at 185 °C under argon and stirring at a constant speed (50 rpm) was applied. This first step (esterification by condensation of monomers) is considered to be complete after the collection of theoretical amount of H_2O (2 h), which was removed from the reaction mixture by distillation and collected in a graduated cylinder. In the second step of polycondensation, a vacuum was applied slowly over a time period of about 3 h at 220 °C. After the end of the polycondensation reaction, the OPBS (solubilized in $CHCl_3$) was purified by extraction with HCl solution (1 M) and precipitated in THF and finally characterized by SEC.

Synthesis of butyl succinate lactone (BSL)

OPBS was depolymerized in a Glass Oven B-585 Kugelrohr (bulb to bulb distillatory) supplied by Büchi at 290 °C under controlled reduced pressure (10 mbar) during 1 h. Typically, 8 g of polymer and ZnO (1 wt%), both previously dried 16 h at 60 °C under reduced pressure, were introduced in the 20 mL end-bulb placed in the oven and the volatile fractions (VF) were collected in 20 mL mid-bulb placed outside. The compositions of the volatile fractions were evaluated by GC-(FID or MS) (on BSTFA derivatized samples), MS, and proton nuclear magnetic resonance (^{1}H NMR). The butylene succinate lactone monomers were purified from the other by-products of VF by solubilization in toluene.

The spectral data of butyl succinate cyclic dimer (DBSL) cyclic butylene succinate ester are shown to be representative. ^{1}H NMR ($CDCl_3$, δ in ppm): 4.05 (triplet, 4H, $-CH_2OCO$), 2.64 (triplet, 4H, $-CH_2-COO-$), 1.71 (quintuplet, 4H, $-OCH_2-CH_2\ CH_2\ CH_2O-$).

Polymerization of BSL by ROP

Typically, 0.15 g of BSL dimer (0.4×10^{-3} mol), previously dried 16 h at 80 °C under reduced pressure, $Sn(Oct)_2$ (10 μL of a 0.015 M toluene solution) octanol (0.1 mL of a 0.3 M toluene solution) and toluene (2 mL) were introduced in a two-necked flask equipped with a three-way stopcock and a magnetic stirring bar in a glove box. The mixture was then heated at 115 °C (the temperature was kept at rather low level to avoid the transesterification issues) under stirring to homogenize the medium then the solvent was evaporated. After 24 hours, the polymerization mixture was cooled down to room temperature and dissolved in chloroform, then the solution was precipitated in excessive acetone. The obtained polymer was characterized by SEC and ^{1}H NMR.

Analyses

Size-exclusion chromatography (SEC) was performed in $CHCl_3$ at 30 °C using an Agilent liquid chromatograph equipped with an Agilent degasser, an isocratic HPLC pump (flow rate = 1 mL min^{-1}), an Agilent autosampler (loop volume = 200 μL, solution conc. = 2.5 mg mL^{-1}), an Agilent-DRI refractive index detector and three columns: a PL gel 10 μm guard column and two PL gel Mixed-D 10 μm columns (linear columns for separation of $\overline{M_w}$ PS ranging from 500 to 10^6 g mol^{-1}). Polystyrene standards were used for calibration.

^{1}H-NMR spectrum were recorded on solutions prepared in $CDCl_3$ using a Bruker AMX-500 apparatus at a frequency of 500 MHz.

Gas chromatography system (Shimadzu, GC-2010) equipped with a flame ionization detector (GC-FID) and a fused silica capillary separation column (Macherey Nagel, Optima 5; 30 m long × 0.25 mm). The identification of the peaks on the chromatograms was carried out using a gas chromatography-mass spectrometry (GC-MS) system (Shimadzu, QP2010) with an electron impact ionization (EI) at 70 eV and separation column (Macherey Nagel, Optima 5 MS; 30 m long × 0.25 mm). Carrier gas is Helium. The temperature program on both GC was inspirited from literature:[14] temperature of the injector set at 340 °C, of the column set at 50 °C for 5 min, then programmed up to 340 °C at a rate of 5 °C min^{-1}, and held at 340 °C for 25 min.

The MS experiments were performed on a Waters QToF2 mass spectrometer at the University of Mons – Mass Spectrometry Research Group. The sample solutions were delivered to the ESI source by a Harvard Apparatus syringe pump at a flow rate of 5 μL min^{-1}. Typical ESI conditions were: positive ion mode; capillary voltage, 3.1 kV; cone voltage, 40 V; source temperature, 80 °C; desolvation temperature, 120 °C. Dry nitrogen was used as the ESI gas. The quadrupole was set to pass ions from *m*/*z* 100 to 1500 and all ions were transmitted into the pusher region of the time-of-flight (TOF) analyzer for mass-analysis with 1 s integration time. Data were acquired in continuum mode until acceptable average data were obtained (typically 20 scans). The sample solutions were prepared as follow: 1 mg of solid sample was dissolved in 1 mL of acetonitrile (HPLC grade) and 5 μL of a NaI solution (1 mg mL^{-1}) in acetonitrile were added to the acetonitrile solution before direct infusion.

Results and discussion

Synthesis and characterization of polyesters

The OPBS used in this study was prepared by a two steps melt polycondensation process. In the first stage (esterification), succinic acid reacted with 1,4-butanediol (DBO) catalyzed by titanium(IV) tetraisopropoxide to form oligomers and water was eliminated as byproduct. As DBO is rather volatile, it was used in a small excess in order to produce alcohol/acid α,ω-terminated PBS.

In the second stage (polycondensation), the prepared oligomers condensed at a higher temperature with the application of vacuum. To prevent the risk of overestimating the yield in volatile fraction (VF) in the following degradation reaction, the OPBS was successfully purified through extraction with acid and precipitation in THF. The crude oligomer was light yellow and became white after purification. Characterization by size-exclusion chromatography (SEC) of the OPBS shows that it contains less small molecules as succinic acid and 1,4-butanediol (Fig. 1) after purification ($\overline{M_{\mathrm{n}}} = 6600$ g mol^{-1} and $Đ = 1.62$).

Synthesis and characterization of BSL

The oligo-PBS was decomposed in a bulb to bulb distillatory with ZnO (1 wt%) at 290 °C and 10 mbar. This bulb tube oven really suits for this kind of reaction: the polymer is decomposed in the end-bulb placed in the oven and the vapor phases are collected in the mid-bulb placed outside the oven and cooled down by the air (Fig. 2). The VF is a white crystalline solid and the weight yield is around 14 wt%.

The composition of the VF was obtained by ^{1}H NMR spectrum (Fig. 3). It contains an important quantity of succinic anhydride (SAN) (2.9 ppm) (4.7 mol mol^{-1} of BS unit) and products including butylene succinate groups (4.1; 2.6 and 1.6 ppm). The SAN could be the result of the direct dehydration of the succinic acid formed as byproduct of degradation. The analysis supports the cyclic structure of butylene succinate molecules. Indeed, linear molecules should show a peak at 3.6 ppm for terminal hydroxyl methylene proton (CH_2-OH) or an integration value of peak at 2.6 superior to those of peaks at 4.1 and 1.6 ppm for terminal succinic acid proton (CH_2-COOH) but none of those observations can be made at the above mentioned spectrum. However, NMR spectroscopy provides structural information only on functional groups or segments of molecules and not on the full molecule. It is so inappropriate to detect the different lactones as a function of their size. Mass spectrometry (MS) is more adapted to identify these molecules including butylene succinate functions. Indeed, it reveals (Fig. 4) that the VF is composed of several products listed in Table 1: SAN and butylene succinate lactones with 1 to 3 butylene succinate groups. In the present publication, we call them MBSL, DBSL, TriBSL and TetraBSL for mono-; di-; tri- or tetra-butylene succinate lactone (IUPAC nomenclature would be 1,6,11,16-tetraoxacycloeicosane-2,5,12,15-tetraone[13] for DBSL). Because of the principle of analysis and of the sensibility of MS, the proportion of components of the VF observed by MS is different from these observed in ^{1}H NMR spectrum.

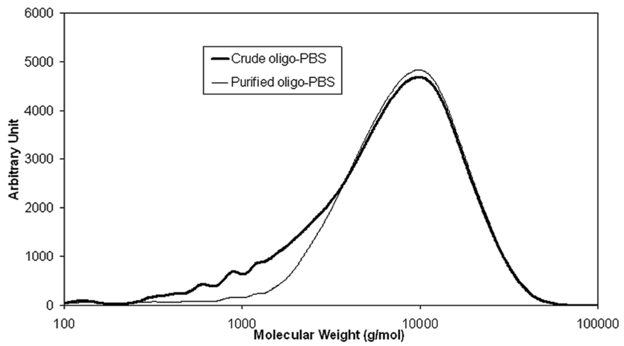


Fig. 1 Chromatogram of crude and purified oligo-PBS.

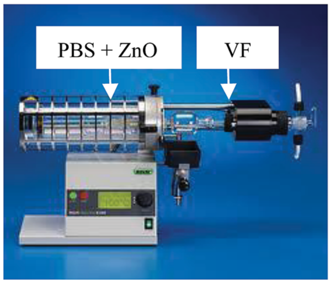


Fig. 2 Glass Oven B-585 Kugelrohr and localization of reagents and products.

These lactones are obtained by intramolecular transesterification (Fig. 5) of the oligo(butylene succinate) chains (several mechanisms can be involved concomitantly, including alcoholysis or acidolysis by chain ends, as well as ester–ester exchange reactions, all leading to the same products; Fig. 5 only illustrates the latter). They are produced in different proportion due to their ease of formation and to their stability; in the present case the dimer is predominant. Spanagel and Carothers[24] already observed this phenomenon and concluded that for repeat unit lengths of 8, 9, 10 or 11 chain atoms the dimeric esters tended to predominate in oligomer mixtures obtained. Stoll and Stoll-Comte[25] have suggested that this is due to a steric hindrance caused by mutual repulsions of peripheral hydrogens which are crowded against one another.

The crude VF was also analyzed by gas chromatography (GC) because this technique is more adapted to individually quantify the components of the VF. GC-MS was first used to attribute molecules to elution peaks then GC-FID was done to improve quantification (Fig. 6). All the peaks up to 12 minutes are

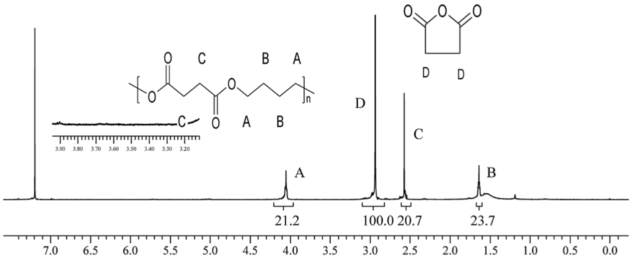


Fig. 3 ^{1}H NMR spectrum of VF of depolymerization of OPBS ($CDCl_3$).

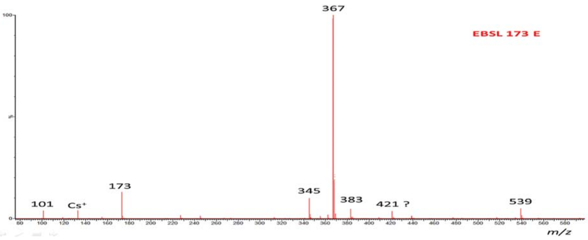
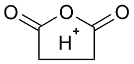
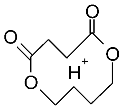
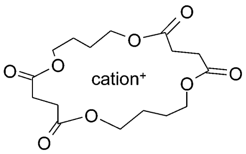
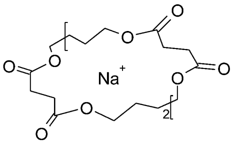


Fig. 4 ESI-ToF analyses of VF of depolymerization of oligo-PBS.

Table 1 Identification of ions observed in ESI-ToF analyses of VF

m/*z*	Identification	Chemical structure
101	Succinic anhydride/H^+	
173	MBSL/H^+	
345	DBSL/H^+	
367	DBSL/Na^+	
383	DBSL/K^+	
539	TriBSL/Na^+	

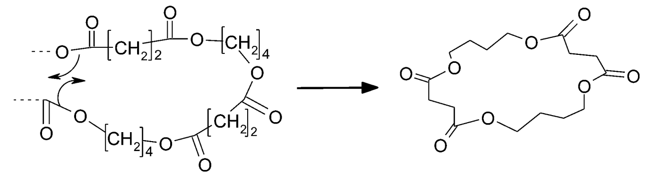


Fig. 5 Intramolecular transesterification leading to dibutylsuccinate lactone DBSL.

attributed to the solvent and the derivatization agent. The product observed at 22 minutes is succinic acid (obtain by reaction of succinic anhydride with the derivatization agent) and the DBSL appears at 46 minutes. The other cycles are not observed because of their small quantities.

By using several catalysts (*e.g.* 1,8 diazabicyclo-undec-7-ene, titanium(IV) tetraisopropoxide, $Sn(Oct)_2$), volatile fractions of various compositions were obtained and analyzed. By comparison of results of MS and GC-FID, the different molecules were identified and classified in function of their retention time (Table 2). The order of this classification is in agreement with information found in literature.[14]

According to the catalyst used, the butylene succinate lactone content varies (Table 3). Some catalysts are inefficient and produce lower yields than non-catalyzed reactions. The tin(II) 2-ethylhexanoate is the most efficient one and the yield increase with the ratio of this catalyst. This yield in lactones is rather small in comparison to those obtained for polylactic acid.

The DBSL was separated from the succinic anhydride by precipitation in diethyl ether followed by solubilization in toluene and characterized by GC-FID (Fig. 6). The global recovery weight yield of DBSL for reactions catalyzed with zinc oxide is around 2 wt% in good correlation with values calculated from GC-FID analyses.

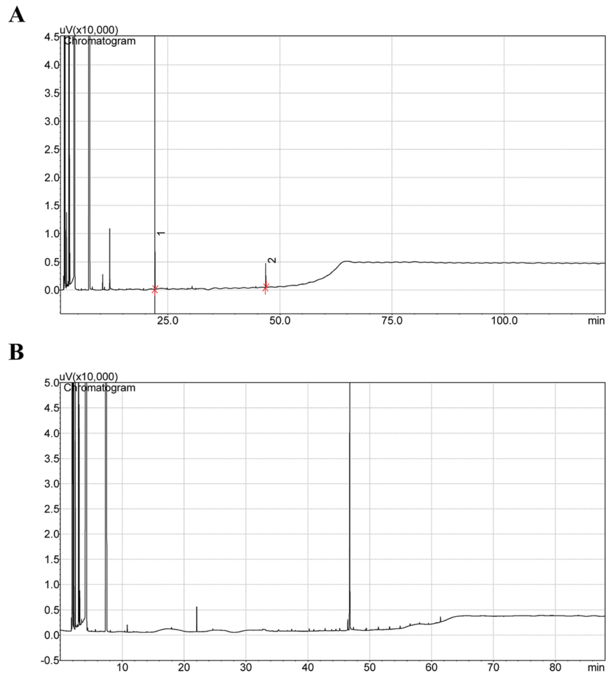
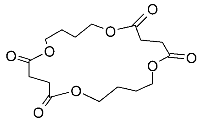
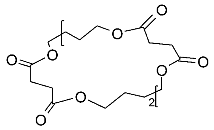
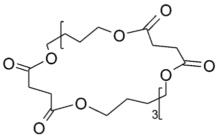


Fig. 6 GC-FID chromatograms of crude VF (A) and purified lactone (B).

Polymerization of DBSL by ROP

After purification, the butyl succinate cycles were polymerized by ROP catalyzed with $Sn(Oct)_2$ and initiated with octanol at

Table 2 Identification and retention time of molecules observed in VF

Chemical structure	Abb.[a]	R.t.[b] (min)
$HOOC(CH_2)_2COO(CH_2)_4OH$	HSBH	13.7
$HO(CH_2)_4OH$	HBH	17.9
$HO(CH_2)_4OOC(CH_2)_2COO(CH_2)_4OH$	HBSBH	18.7
$HOOC(CH_2)_2COO(CH_2)_4OOC(CH_2)_2COOH$	HSBSH	20.2
$H[OOC(CH_2)_2COO(CH_2)_4]_2OH$	$H[SB]_2H$	22.1
$HOOC(CH_2)_2COOH$	HSH	22.4
$HO(CH_2)_4[OOC(CH_2)_2COO(CH_2)_4]_2OH$	$HB[SB]_2H$	33.2
$H[OOC(CH_2)_2COO(CH_2)_4]_2OOC(CH_2)_2COOH$	$H[SB]_2SH$	42.1
$H[OOC(CH_2)_2COO(CH_2)_4]_3OH$	$H[SB]_3H$	44.6
	DBSL	46.8
$H[OOC(CH_2)_2COO(CH_2)_4]_3OOC(CH_2)_2COOH$	$H[SB]_3SH$	50.4
	TriBSL	61.6
$H[OOC(CH_2)_2COO(CH_2)_4]_4OOC(CH_2)_2COOH$	$H[SB]_4SH$	67.5
	TetraBSL	81.5

[a] Abbreviated name. [b] Retention time.

Table 3 Global weight yield in DBSL observed in VF according to the catalyst

Catalyst	Catalyst ratio	Global yield in DBSL (wt%)
Sc (triflate)$_3$	1 wt%	0.7
TBD		1.1
DBU		1.2
—		1.8
Ti(OisoProp)$_4$		2.5
ZnO		2.5
Sn(Oct)$_2$		4.1
Sn(Oct)$_2$	2 wt%	12.1

115 °C in bulk during 24 h. For the calculation of reagents, we considered the cyclic lactones to be exclusively dimeric as they are majority in the purified VF. The ^{1}H NMR analysis (Fig. 7) confirms that the obtained product contains linear PBS as terminal functions were observed (3.7 ppm).

The chromatogram (Fig. 8) of the obtained product attests of the polymerization of the butylene succinate lactones: a monomodal distribution of polymers ($\overline{M_w} = 65\,000$ g mol^{-1}; $Đ = 2.2$) was obtained. This is the first time that poly(butylene succinate) is polymerized from cyclic monomer by chemical catalysis. In addition, the obtained dispersities are lower with ROP.

Several kinds of cyclic monomers, such as lactones,[26] anhydrides,[27] or carbonates[28] can be used for ROP. Several kinds of catalysts were also already reported, *e.g.* metallic complexes[29] and enzymes.[30] The size of the ring of the cyclic monomer used is another important parameter to consider, it should be both, stable and reactive, enough to allow successful polymerization. Thus, the 6-membered lactide for the synthesis of PLA or the 7-membered ε-caprolactone for the synthesis of PCL are nice examples of suitable cyclic monomers. In our case, the 20-membered DBSL was found to be the major product of the depolymerization process. This macrocycle is less easy to handle for both its production and purification; however the results obtained for its first ROP polymerization show that it worth the effort.

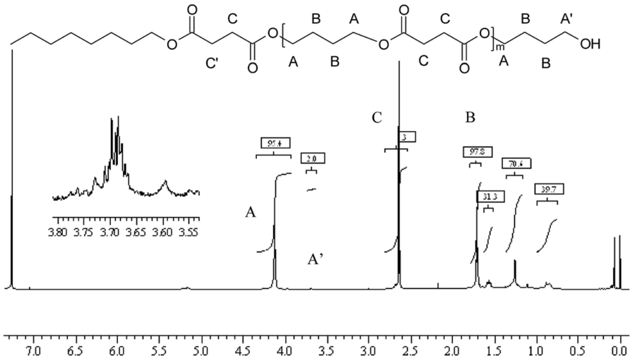


Fig. 7 ^{1}H NMR spectrum of the synthesized PBS (CDCl$_3$).

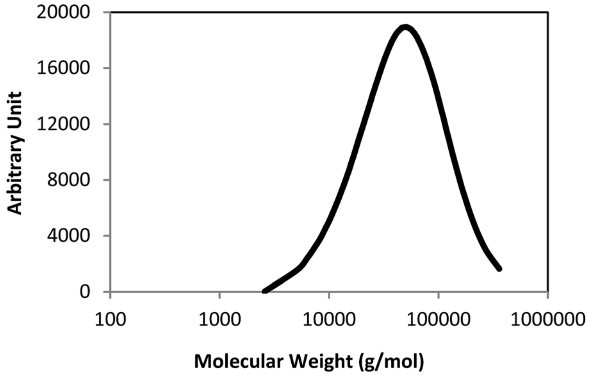


Fig. 8 Chromatogram of PBS obtained by ROP.

Conclusions

The development of valuable routes for the synthesis of high molecular weight PBS is crucial to reach desired properties of this bioplastic. In this study, and for the first time, PBS was obtained by chemically catalyzed ROP from previously prepared, through oligomers depolymerization, cyclic precursors. This first attempt of ROP polymerization for the preparation of PBS reached the $\overline{M_w}$ of 65 000 g mol^{-1}, which is comparable to the best results obtained after chain extension for the polycondensation route.[2]

The elucidation of the depolymerization process of oligomers and the identification of the cyclic precursors represent the main pavement on the road to the widespread usage of the ROP technique for the preparation of higher molecular weight PBS in the near future.

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Notes and references

1 Y. F. Shih and Y.-C. Chieh, *Macromol. Theory Simul.*, 2007, **16**, 101.
2 J. Xu and B.-H. Guo, *Biotechnol. J.*, 2010, **5**, 1149.
3 N. Jacquel, *et al.*, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 5301.
4 P. Rizzarelli and S. Carroccio, *Polym. Degrad. Stab.*, 2009, **94**, 1825.
5 F. D. Kopinke, *et al.*, *Polym. Degrad. Stab.*, 1996, **53**, 329.
6 D. J. Brunelle, *et al.*, *Macromolecules*, 1998, **31**, 4782.
7 N. González-Vidal, *et al.*, *Macromolecules*, 2008, **41**, 4136.

8 P. Coszach and P. A. Mariage, Method for obtaining lactide, US 2011/0155557 A1, Futerro S.A., 2011.

9 T. P. Coupin, P. Coszach and D. Hottois, Isotactic polylactic acid and method for producing same, JP2012515245, Futerro S.A., 2010.

10 N. Berezina, N. Landercy, P. A. Mariage and B. Moreau, *World J. Org. Chem.*, 2013, **1**, 20.

11 T. Yashiro, H. R. Kricheldorf and S. Huijser, *Macromol. Chem. Phys.*, 2009, **210**, 1607.

12 A. C. Davis, *Polymer*, 1977, **18**, 305.

13 K. Noguchi, H. Kondo, Y. Ichikawa, J. Washiyama and K. Okuyama, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2006, **62**, 528.

14 H. Sato, *et al.*, *Polym. Degrad. Stab.*, 2001, **73**, 327.

15 D. N. Bikiaris, *et al.*, *Polym. Degrad. Stab.*, 2007, **92**, 525.

16 K. Chrissafis, K. M. Paraskevopoulos and D. N. Bikiaris, *Polym. Degrad. Stab.*, 2006, **91**, 60.

17 S. Carroccio, *et al.*, *Macromolecules*, 2004, **37**, 6576.

18 S. Carroccio, P. Rizzarelli and C. Puglisi, *Rapid Commun. Mass Spectrom.*, 2000, **14**, 1513.

19 K. Chrissafis, K. M. Paraskevopoulos and D. N. Bikiaris, *Thermochim. Acta*, 2005, **435**, 142.

20 Y. Tsuneizumi, *et al.*, *Polym. Degrad. Stab.*, 2010, **95**, 1387.

21 A. Kondo, *et al.*, *Macromol. Biosci.*, 2008, **8**, 533.

22 S. Okajima, *et al.*, *Biomacromolecules*, 2003, **4**, 1514.

23 S. Sugihara, K. Toshima and S. Matsumura, *Macromol. Rapid Commun.*, 2006, **27**, 203.

24 E. W. Spanagel and W. H. Carothers, *J. Am. Chem. Soc.*, 1935, **57**, 929.

25 M. Stoll and G. Stoll-Comte, *Helv. Chim. Acta*, 1930, **13**, 1185.

26 J. F. Carpentier, *Macromol. Rapid Commun.*, 2010, **31**, 1696.

27 S. Ren, J. Ling and Z. Shen, *Eur. Polym. J.*, 2004, **40**, 647.

28 K. S. Bisht, *et al.*, *Macromolecules*, 1997, **30**, 7735.

29 C. Jerome and P. Lecomte, *Adv. Drug Delivery Rev.*, 2008, **60**, 1056.

30 S. Kobayashi, *Macromol. Symp.*, 2006, **240**, 178.