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RESEARCH ARTICLE



Cyclic and linear poly(L-lactide)s by ring-expansion polymerization with Bu₂SnO, Oct₂SnO, and Bu₂SnS

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| Steffen M. Weidner²

Abstract

To elucidate the usefulness of commercial Bu₂SnO as catalyst for syntheses of linear and/or cyclic polylactides L-Lactide was polymerized in bulk with variation of the LA/Cat ratio, temperature and time. Based on a ring-expansion polymerization (REP) mechanism cyclic polylactides (PLAs) with weight average molecular weights in the range of 200,000–300,000 are obtained at the highest temperature (180 °C). Polymerizations at 150 °C yielded crystalline, mainly cyclic polylactides which, after annealing, showed high melting temperatures (up to 197.5 °C) and high crystallinities (>80%). Polymerization at 120 °C confirmed the trend towards more linear chains with lower temperatures but yielded extended-ring crystals showing a "saw-tooth pattern" in the mass spectra. Oct₂SnO gave similar results as Bu₂SnO. Bu₂SnS proved a sluggish polymerization catalyst, but a good transesterification catalyst in solid PLA.

K E Y W O R D S

cyclization, lactide, MALDI TOF mass spectrometry, ring-expansion-polymerization, transesterification

1 | INTRODUCTION

Over the past 50 years the interest in synthesis and properties of cyclic polymers has rapidly increased and new synthetic strategies were developed.^{1–5} A versatile and particularly successful approach to syntheses of cyclic polymers is ring-expansion polymerization (REP). First examples of REPs were published by the first author in 1994 based on the polymerization of lactones with a cyclic tin catalyst; 2,2.dibutyl-2-stanna-1,3-dioxane (Scheme 1).^{6,7}

In the following years, the REPs of cyclic esters (incl. L-lactide and trimethylene carbonate) with cyclic dibutyltin bisalkoxides were studied by the research groups of Kricheldorf and Albertsson in much detail.^{8–11} Characteristic for REPs catalyzed by cyclic tin bisalkoxides is the finding that the catalyst remains fixed via Sn-O bonds in the cyclic polyester, so that it plays in fact the role of an initiator and the ring size increases indeed with the monomer/catalyst ratio. The Sn-O bonds are highly reactive and are easily hydrolyzed or react with various electrophilic compounds such as acid chlorides, anhydrides or thioesters, and in this way numerous linear, telechelic or branches branched polyesters and biodegradable networks can be prepared.⁹ About 20 years later the author found that cyclic tin compounds derived from dimercaptanes or diphenols (Scheme 2) initiate a REP which involves elimination pf the catalyst, so that cyclic polyesters become the main reaction product (Scheme 3).^{12–15}

In this context the question remained open, how dibutyltin sulfide and dibutyltin oxide react with lactide and

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SCHEME 1 REP of lactones initiated with cyclic dibutyl tin bisalkoxides (first published in Ref. 6).



SCHEME 2 Structures and acronyms of cyclic polymerization/ transesterification catalysts discussed in this work.

other cyclic esters. Both compounds are commercial, stable, non-hygroscopic and relatively inexpensive chemicals. Furthermore, the toxicity of Bu₂SnO is well documented (see various internet sources). It is registered in Europe according to REACH standards and its world-wide production amounts to many thousand tons per year. This tin oxide has found numerous technical applications for example as transesterification catalyst in the production of coatings and insulating lacquers, or as additive to paints and machine wash liquids (numerous sources of information are available from the internet). Dioctyl-tin oxide which has a somewhat lower toxicity than dibutyltin oxide has found an even broader range of applications, and a few experiments with this tin oxide were also included in this study.

Dibutyltin sulfide is a trimeric cycle, and one may assume that it reacts with L-lactide analogously to the cyclic dibutyltin sulfides DSTL and DSTD (2,2-dibutyl-2-atanna-1,3-dithiolane and 2,2-dibutyl-2-stanna-1,3dithiane, Scheme 2), so that cyclic polylactides are the main reaction products. However, dibutyltin oxide is a solid insoluble in common inert solvents due to 3D donor-acceptor interactions between oxygen and tin. It is not quite clear, whether its basic structure is that of a cyclic dimer, trimer or liner oligomer. Its reaction with lactides may yield rather stable tin containing cycles (Ca in Scheme 4) in analogy to the cyclic tin bisalkoxides (Scheme 1), so that upon hydrolytic work up linear chains having one CH—OH and one CO_2H end group are the final reaction products (La in Scheme 4).

Alternatively, elimination of all Bu_2SnO groups may result in formation of cyclic polylactides (PLAs) (Cb in Scheme 4). Hence, it was the purpose of this work to elucidate the polymerization process of Bu_2SnO - or Oct₂SnO-initiated REPs and to compare the results with those obtained from Bu_2SnS -initiated REPs.

Finally, it should be mentioned that syntheses and properties of cyclic PLAs and other cyclic polyesters have attracted much interest over the past 15 years, and only papers dealing with cyclic PLAs which are directly related to the present work, should be cited here.^{12–35} Almost all the catalysts described by other research groups are not useful for polymerizations in bulk at elevated temperatures (>130 °C) due to side reactions, above all racemization, caused by their basicity. It is a particular advantage that tin catalysts do not cause racemization of L-lactide even when used at 180 °C for several hours. This statement is based on nearly academic studies^{36,37} and on the fact that the racemization-free technical polymerization of PLA with tin(II) 2-ethylhexanoate requires temperatures up to 180 °C and even 200 °C for extrusion from the reactor.

2 | EXPERIMENTAL

2.1 | Materials

L-Lactide, a product of Corbion-Purac, was kindly supplied by Thyssen-Uhde SE (Berlin, Germany). It was recrystallized from toluene (99.98% extra dry, Fisher-Scientific, Schwerte, Germany). Dibutyltin oxide, dioctyltin-oxide and dibutyl-tin-sulfide were purchased from Alfa-Aesar (Kandel, Germany) and used as received. 2,2-dibutyl-2-stanna-1,3-dithiane (DSDT) was prepared from dibutyltin oxide and 1,3-dimercaptopropane as described previously.¹³

2.2 | Polymerizations with dibutyl-tinoxide

Dibutyltin oxide (0.08 or 0.04 mmol) and L-lactide (40 mmol) were weighed into a flame-dried 50 mL Erlenmeyer flask under a blanket of argon and a magnetic bar was added. The reaction vessel was immersed into an oil bath thermostated at one of the temperatures listed in Tables 1–3. Finally, the reaction vessel was destroyed, the SCHEME 3 REP

mechanism involving







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Exp. no.	LA/cat	Time (h)	$M_{ m n}$	$M_{ m w}$	Dispersity D
1A	200/1	1.5	35,000	76,000	2.2
1B	200/1	4.0	21,500	51,000	2.4
2A	500/1	1,5	99,500	255,000	2,6
2B	500/1	4.0	81,500	202,000	2.5
3A	1000/1	1.5	99,000	245,500	2.5
3B	1000/1	4.0	91,000	284,000	3.1
4	2000/1	4.0	51,000	102,000	2.0

TABLE 1 Bu₂SnO-catalyzed polymerizations at 180 °C.

TABLE 2 Bu₂SnO-catalyzed polymerizations at 150 $^{\circ}$ C.

Exp. no.	LA/cat	Time (h)	$M_{ m n}$	$M_{ m w}$	Dispersity D	T _m ("C)	$\Delta H_{ m m}$ (J g ⁻¹)	Crystallinity ^a (%)
1A	200/1	24	41,000	96,000	2.4	190.7	99.4	87
1B	200/1	96	39,000	93,000	2.4	195.1	100.9	88
2A	500/1	24	47,000	115,000	2.5	190.8	87.0	76
Rep.	500/1	24	45,000	109,000	2.5	190.9	83.5	72
2B	500/1	96	34,500	81,000	2.4	190.0	90.8	79
3A	1000/1	24	51,000	109,500	2.2	190.2	86.6	75
3B	1000/1	96	42,500	98,000	2.4	197.5	88.8	78
4	2000/1	96	72,000	148,000	2.1	191.5	88.7	78

 aCalculated from ΔHm with $\Delta Hm^0 = 115$ J $g^{-1}.$

TABLE 3	Bu ₂ SnO-cata	lyzed po	lymerizations	at 120 °C.
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Exp. no.	LA/cat	Time (h)	M _n	$M_{ m w}$	Dispersity Đ	<i>T</i> _m (°C)	$\Delta H_{ m m}~({ m J~g^{-1}})$	Crystallinity (%) ^a
1X	200/1	24	35,500	70,000	2.0	181.0	78.8	68
1Y	200/1	24	34,500	68,500	2.0	-		-
2AX	500/1	24	47,000	87,500	1.9	186.4	89.0	77
2AY	500/1	24	46,500	79,000	1.7	-	-	
2A	1000/1	24	58,000	160,000	2.7	185.1	87.2	76
2B	1000/1	96	50,000	139,000	2.7	182.3	81.4	71

^aCalculated from $\Delta H_{\rm m}$ with $\Delta H_{\rm m}^{0} = 115 \text{ J g}^{-1}$.

isolated crystalline plaque of PLA was cut or broken into four or five pieces two of which were used for characterization. The remaining two pieces were annealed under an atmosphere of argon for a longer time (see Tables 2 and 3).

In the case of the 180 $^{\circ}$ C experiments, part of the molten PLA was removed with spatula or pincer and the remaining part was annealed for two more hours at 180 $^{\circ}$ C.

2.3 | Polymerizations with dioctyltin oxide or dibutyltin sulfide

The catalyst (0.08 mmol) and L-lactide (40 mmol) were weighed into a flame-dried 50 mL Erlenmeyer flask and polymerized as described above.

2.4 | Measurements

The 400 MHz 1 H NMR spectra were recorded on a Avance 400 FT NMR spectrometer (Bruker, Germany) in 5 mm sample tubes using CDCl₃ as solvent and TMS as internal shift standard.

The MALDI TOF mass spectra were measured with an AutoflexMax mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a Smartbeam laser ($\lambda = 355$ nm). All spectra were recorded in the positive ion linear mode. The MALDI stainless steel targets were prepared from chloroform solutions of poly (L-lactide) and DCTB matrix (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile, Sigma, Germany). Typically, 20 µL of the sample solution (5 mg mL⁻¹) and 50 μ L of the matrix solution (20 mg mL⁻¹) were pre-mixed in an Eppendorf vial. This solution was spiked with 5 μ L potassium trifluoroacetate (2 mg mL⁻¹ in THF). Finally, 1 μ L of the corresponding solution was deposited on the MALDI target by a pipette. After solvent evaporation the target was inserted. 2000 spectra were recorded on one spot region. For better reproducibility, this procedure was recorded on 4 different regions, and all spectra were accumulated to the final spectrum. For fractionation experiments fractions were taken manually every minute. These solutions were concentrated by evaporation of the solvent and mixed with DCTB/K solutions. Calibration of the mass spectrometer was achieved by using polymer standards and biopolymers with known isotopic masses.

The GPC measurements were performed using a HPLC 1200 system (Agilent, USA) running at 40 °C with a flow rate of 1 mL min⁻¹. A refractive index detector was used. Samples (100 μ L, 2–4 mg mL⁻¹) were injected by an autosampler. For instrument control and data calculation WinGPC software (Polymer Standards Service-PSS, Mainz, Germany) was used. The calibration was performed using polystyrene standard sets (Polymer Standards Service-PSS, Mainz) covering a mass range of 500–1,200,000 g mol⁻¹.

The DSC heating traces were recorded on a freshly calibrated (with indium and zinc) DSC-1 (Mettler-Toledo, Berlin, Germany) equipped with Stare Software-11 using a heating rate of 10 K min⁻¹. Only the first heating traces were evaluated. The crystallinities were calculated with a Δ Hm max of -115 J g^{-1.38}

3 | RESULTS AND DISCUSSION

3.1 | Polymerizations with dibutyltin oxide at 180 °C

All polymerizations were conducted in bulk. The main purpose of these polymerizations was to explore the influence of temperature and time on molecular weight and architecture (topology) of the resulting polylactides (PLAs). The results were listed in three Tables, depending on the polymerization temperature used for the experiments. At 180 °C (Table 1), the highest molecular weights were obtained as demonstrated by comparison with the data of Tables 2 and 3. The variation of the LA/Cat ratio also revealed that the molecular weights vary only by a factor around 1.3, when the LA/Cat ratio varies by a factor of 10. Such a correlation is characteristic for a REP with elimination of the catalyst according to the mechanism outlined in Scheme 4 (equations (a) and (c)). In contrast, the polymerization mechanism outlined in





FIGURE 1 MALDI TOF mass spectra of (A) a PLAs prepared at 180 $^{\circ}$ C/4 h with Bu₂SnO, (LA/Cat = 500/1 (2B, Table 1) and (B) SEC fraction 7 (out of 9) of this sample.

equations (a) and (b) of Scheme 4 should result in a perfect parallel between number average molecular weight (M_n) and LA/Cat ratio.

The MALDI TOF mass spectra confirmed this interpretation, because only peaks of cycles were detectable or at least a large predominance of cycles as illustrated by the spectrum of Figure 1A, which is typical for all polymerizations conducted at 180 °C. These mass spectra do, of course not allow for a quantitative determination of the cycles. In order to get more information about the presence of linear chains, samples 2A, 2B and 3A, 3B (Table 1) were fractionated by SEC and the MALDI TOF spectra of the fraction above m/z 10,000 were recorded. In all cases a small fraction of linear chains was detected as illustrated in Figure 1B.

The presence of linear chains having HO-CH(CH₃) end groups was confirmed by 400 MHz ¹H NMR spectra, which were recorded with a signal-to-noise ratio > 10,000/1. When the amplitude was enhanced to such an extent that the noise became detectable, a quadruplet signal at 4.35 ppm became visible, which is characteristic for the methine proton of this end group (as illustrated in



FIGURE 2 400 MHz ¹H NMR spectra of the PLA prepared with Bu_2SnO at 150 °C/4 d (3C, Table 2).

Figure 2 for a PLA prepared at 150 °C). In the case of the high molar mass samples prepared at 180 °C, the end group signal was barely detectable, what means that intensity of the end group signal was around or below 0.01% relative to the signal of the methine proton of the PLA backbone. These low values certainly indicate a high extent of cyclization, but these end group signals do not allow for a quantification of the linear chains because a separate determination of the molecular weights of cyclic and linear PLAs is not feasible.

Since any elimination is combined with a gain in entropy, the elimination of Bu_2SnO is kinetically and thermodynamically favored by higher temperatures and should be complete after 4 h at 180 °C. Hence, it may be assumed that the incomplete elimination of the catalyst at 180 °C might be a consequence of its reversibility as indicated by the dotted arrow in Scheme 4.

3.2 | Polymerizations with Bu₂SnO at 150 °C

When the polymerizations were conducted at 150 °C with reaction times of 1 d or longer, all PLAs crystallized and conversions >99% were achieved, because the crystalline chains and cycles do not participate in the ring chain equilibration which limits the conversion of LA for thermodynamic reasons to values around 97%, when the PLAs stay in the melt or in solution. Despite reaction times up to 7 days, the molecular weights were significantly lower than those obtained at 180 °C. With cyclic tin catalysts the inverse pattern was observed, and a straightforward explanation of the lower molecular



FIGURE 3 MALDI TOF mass spectra of PLAs prepared with Bu_2SnO at 120 °C, (A) LA/Cat = 500/1, 1 day (2A, Table 2), (B) LA/Cat = 1000/1, 1 day (3A, Table 2), (C) LA/Cat = 2000/1 (4 days, Table 2).

weights cannot be given at this time. The molecular weights did again not parallel the LA/Cat ratio, but a broader scattering of the M_n and M_w data was observed. Whereas the MALDI mass spectra exclusively reveled peaks of cycles the ¹H NMR spectra displayed the CHCH₃-OH end group peak with intensities in the range of 0.03–0.2 ppm, which were somewhat more intensive than those observed for the high molar mass PLAs obtained at 180 °C. Hence, one may conclude that the faction of cycles is lower than that of the "180 °C samples", presumably in the range of 90–96%.

The most interesting result of the MALDI mass spectra is the appearance of the so-called "saw-tooth pattern" (STP) of the mass peaks (Figure 3). STPs were observed for numerous cyclic PLAs prepared under various conditions, when the PLAs were annealed in the presence of the catalyst in the temperature range of 120–160 °C, but the STP was never observed for linear PLAs.³⁸⁻⁴¹ A detailed interpretation of the STP and its origin has been presented in several recent publications and thus should

not be repeated here again.³⁸⁻⁴¹ However, it should be mentioned that the underlaying phenomenon is formation of extended-ring crystallites in the mass range below 15,000 Da. These extended-ring crystals represent a rather perfect, thermodynamically favorable kind of crystallites, and smoothing of their surface by transesterification reactions yielding the STP further improves their thermodynamic optimization. What is new and surprising here is the finding that the STP increases with the LA/Cat ratio. Higher LA/Cat ratios mean lower catalyst concentration, and since the formation of the STP is based on transesterification reactions of loops on the surface of the crystallites, one may expect that a higher catalyst concentration is favorable for the development of a STP. Why SnO differs from other tin catalyst in this regard cannot be explained at this time.

The DSC measurements yielded $T_{\rm m}$ values around or above 190 °C indicating the formation of the thermodynamically controlled high $T_{\rm m}$ morphology. The DSC traces did not show any unusual feature, the endotherms were monomodal without shoulders, and due to the high crystallinity of the samples even glass-transition steps were absent. It has been shown in previous publications for dozens of cyclic PLAs samples that formation of the high $T_{\rm m}$ morphology is based on increasing crystal thickness in combination with smoothing of the surface, which reduces the surface free energy and allows for a more perfect 3D ordering of the crystallites.^{40–43} Hence, the finding of the STP and formation of the high m morphology in the present work are in good agreement with each other.

3.3 | Polymerizations with Bu₂SnO at 120 °C

The polymerizations conducted at 120 °C (see Table 3) still showed a relatively rapid conversion, and the 200/1 or 500/1 experiments showed beginning crystallization after 1.5 or 2.0 h, and complete crystallization after ca. 4 h (meaning that the entire reaction volume was filled with spherulites). Yet, when the experiments were repeated (Y experiments), nucleation appeared later, and crystallization was somewhat slower than in the first series of experiments. The following trends were found. First, the molecular weights were similar to those obtained at 150 °C. Second, the melting temperatures were lower, a normal result for annealing at lower temperatures. Third, with exception of the 200/1 experiment (1A), the melting enthalpies were similar to those recorded at 150 °C. This latter result is not trivial, because annealing at a higher temperature usually results in higher crystallinities. Fourth, the mass spectra

7



FIGURE 4MALDI TOF mass spectra of PLAs prepared with Bu_2SnO at 120 °C: (A) LA/Cat = 200/1: (1×, Table 3,(B) LA/Cat = 200/1 (1Y, Table 3), (C) LA/Cat 1000/1 (3B, Table 3).

proved again a large predominance of cyclic PLAS, but the fraction of linear species was now significantly higher than in the case of the $150 \,^{\circ}\text{C}$ experiments (Figure 4).

A closer inspection of the mass spectra revealed that he peaks of the linear chains display a relatively narrow molecular distribution with a maximum around 4000 m/z regardless of the catalyst concentration (Figure 4). A satisfactory explanation of this phenomenon cannot be forwarded at this time. Furthermore, it was observed that when the experiments were repeated with another batch of LA in another reaction vessel (X vs. Y experiments) the intensities of the "linear peaks" relative to those of the cycles varied a little and the perfection of the STP varies (s. Figure 4A vs. B). Faster nucleation and spherulite growth favored a more pronounced STP, because the catalyst has a longer time to modify the surface of the crystallite. The most perfect STP was obtained with a LA/Cat ratio of 1000/1 (Figure 4C). Considering that a SP became detectable within 20 h regardless of LA/Cat ratio, SnO was the best transesterification catalyst for the solid state of PLA found by the authors so far.

Exp. no.	Temperature (°C)	Time (h)	$M_{ m n}$	$M_{ m w}$	Dispersity D	$T_{\rm m}$ (°C)	$\Delta H_{ m m}$ (J g ⁻¹)	Crystallinity (%) ^a
1A	180	1.5	75,000	220,000	2.9	-	-	-
1B	180	4	84,000	211,000	2.5	-	-	-
2A	150	24	44,000	94,000	2.1	183.3	79.5	69
2B	150	96	59,000	136,000	2.3	188.7	91.4	79

TABLE 4 Oct₂SnO-catalyzed polymerizations in bulk; LA/Cat = 500/1.

^aCalculated from $\Delta H_{\rm m}$ with $\Delta H_{\rm m}^{0} = 115$ J g⁻¹.

8 JOURNAL OF BUILEY- POLYMER SCIENCE

3.4 | Polymerizations with dioctyl tin oxide

Four experiments were conducted with Oct₂SnO (Table 4), which revealed the following trends. The highest molecular weights and the lowest percentage of CHCH₃—OH end groups were again achieved at 180 °C. The mass spectra exclusively displayed peaks of cyclic PLAs even for the PLSAs prepared at 150 °C (Figure 5) indicating a high efficiency of cyclization in analogy to the Bu2SnO catalyzed polymerizations. Neither a maximum of the mass peaks above m/z 2000 nor a saw-tooth pattern were detectable. The lower molecular weights and the absence of a STP in the mass spectra of the 150 °C samples suggest that Oct₂SnO is less reactive as transesterification catalyst than Bu₂SnO. This result may be explained by a higher steric hindrance of all transesterification reactions due to the higher steric demands of the octyl group compared to the butyl group.

3.5 | Polymerizations with Bu₂SnS or DSDT

The main result of the three experiments conducted with Bu₂SnS (Table 5) was the finding that this catalyst is extremely sluggish. After 1 day at 150 °C the melt had still a low viscosity. Nonetheless, a crystalline PLA with a M_w above 120,000 was obtained after 4 days indicating a slow but steady continuation of the polymerization process over a period of several days. The slow polymerization is most likely a consequence of a slow initiation, where the relatively stable Sn-S bond is replaced by the weaker Sn-O bond. Due to this slow polymerization, it is obvious that Bu₂SnS is no attractive catalyst for preparative purposes. However, the mass spectrum of the PLA prepared at 150 °C displayed a clear STP in the range of m/z 3000-5000 and 8000-13,000 (Figure 6) indicating that Bu₂SnS is a good transesterification agent in solid PLA, nearly as good as SnBiph, although the latter catalyst is at least 100 times more active as polymerization catalyst. This surprising finding has a parallel, when DSTL is compared with SnBiph. DSTL is about 10 times less active as polymerization catalyst,^{12,15} but slightly



FIGURE 5 MALDI TOF mass spectra of PLAs prepared with $Oct_2SnO:$ (A) at 180 °C/4 days (1B, Table 4), (B) at 150 °C/4 days (2B, Table 4).

more efficient as transesterification catalyst in solid PLA. $^{\rm 38-41}$

To provide a broader basis for a comparison of Sn–O and Sn–S type catalysts, two more experiments were performed with DSDT (Scheme 2 and Table 5). From previous experiments¹³ it was known that DSDT is somewhat less active as polymerization catalyst than DSTL, a conclusion confirmed by the experiment listed in Table 5. However, it was found to be significantly more reactive than Bu₂SnS, because nearly quantitative conversion (based on ¹H NMR spectra) and crystallization was found after 1 d. Therefore, the activity of the polymerization catalysts discussed in this work (Scheme 2) can be arranged in the following order:

Bu₂SnS << DSDT < DSTL < Bu₂SnBiph < SnBiph

The MALDI mass spectra of Figure 7 demonstrate that DSDT is less efficient than Bu_2SnS as transesterification catalyst in solid PLA.

The STP is less pronounced. However, the mass spectra of the PLAs prepared with DSDT are remarkable for another reason. In Figure 7A, the peaks of the cycles with DP 18, 22 and 26 were marked, because they are slightly

9

TABLE 5 Bu₂SnS and DSDT-catalyzed polymerizations in bulk: LA/Cat = 500/1.

Exp. No.	Catalyst	Temperature (°C)	Time (h)	M _n	$M_{ m w}$	Dispersity Đ	<i>T</i> _m [°C]	$\Delta H_{ m m}$ (J g ⁻¹)	Crystallinity (%) ^a
1	Bu ₂ SnS	180	4	31,000	54,000	1.8	-	-	_
2A	Bu ₂ SnS	150	24	Low conversion		-	-	-	-
2B	Bu ₂ SnS	150	96	54,500	135,000	2.5	190.8	100.8	88
3A	DSTD	150	24	91,000	160,000	1.7	192.7	92.5	81
3B	DSTD	150	96	66,000	124,000	1.9	190.8	81.0	70

^aCalculated from $\Delta H_{\rm m}$ with $\Delta H_{\rm m}^{0} = 115 \text{ J g}^{-1}$.



FIGURE 6 MALDI TOF mass spectrum of a PLA prepared with Bu₂SnS at 150 °C/4 days (2B, Table 5).



FIGURE 7 MALDI TOF mass spectra of PLAs prepared with DSTD at 150 °C: (A) after 1 day (3A, Table 5), (B) after 4 days (3B, Table 5).

more intensive than their neighbors. At first glance this comment may look like an overinterpretation of this spectrum, but the authors dare to present it for two reasons. First, in Figure 7B, meaning after longer annealing, the intensity of these three cycles is even more pronounced. Second, the authors observe an analogous STP with a periodicity of 4 in almost all mass spectra of cyclic polyglyco-lides (ongoing research, which will be published soon).

In this connection it worth mentioning that in the ${}^{1}\text{H}$ NMR spectra of the Bu₂SnS and DSDT samples isolated after 4 days, the end group signal was extremely weak indicating a higher elimination efficiency than Bu₂SnO at identical temperature. This observation and conclusion agree with the high elimination efficiency of DSTL (according to the mechanism of Scheme 3) when compared to dibutyltin bisalkoxides which, as mentioned above, initiate the polymerizations according to Scheme 1. The higher thermodynamic stability of the Sn—S bond relative to the Sn—O bond is the driving force behind the high elimination tendency of the cyclic Sn—S catalysts.

In a previous publication the authors have hypothesized that DSTL is more mobile in solid PLA and thus more efficient as transesterification catalyst than the bulky SnBiph.⁴¹ Yet, this argumentation is not convincing for the trimeric Bu₂SnS, which is certainly a more space-filling molecule than SnBiph. In other words, an explanation, why cyclic Sn-S compounds are poor polymerization catalysts but excellent transesterification catalysts in solid PLA cannot be forwarded at this time.

4 | CONCLUSIONS

The results of this work allow for the following conclusions. First, all three dibutyl tin compounds catalyze a ring-expansion polymerization involving elimination of the catalyst according to the mechanism outlined in Scheme 4 (Equations (a) and (c)). Second, higher temperatures favor elimination of the catalyst due to a gain in entropy and a faster reaction. Third, Bu₂SnO enables rapid syntheses of medium and high molecular weight cyclic PLAs by REP in bulk at temperatures around 180 °C. Since Bu₂SnO is a commercial rather inexpensive

non-hygroscopic compound, stable on storage, it is an attractive catalyst for preparative purposes, in as much as polymerization in bulk is the most sustainable procedure and better suited for upscaling than polymerization in solution. Fourth, Bu₂SnO is an excellent transesterification catalyst in solid PLA. Fifth, despite an extremely low activity as polymerization catalyst, Bu₂SnS is also a good transesterification catalyst in solid PLA.

Finally, it may be concluded that Bu₂SnO may also be useful as catalyst for syntheses of cyclic polyesters from other cyclic monomers.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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KRICHELDORF and WEIDNER

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