



# Polymerization of L-lactide with SnCl<sub>2</sub>: A Low Toxic and Eco-friendly Catalyst

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## Abstract

Polymerizations of L-lactide catalyzed either by neat SnCl<sub>2</sub> or by SnCl<sub>2</sub> + difunctional cocatalysts were conducted in bulk at 180, 160 and 140 °C with variation of the Lac/Cat ratio and time. With neat SnCl<sub>2</sub> poly(L-lactide) having weight average molecular weights (uncorrected M<sub>w</sub>'s) up to 190 000 g mol<sup>-1</sup> were obtained mainly consisting of linear chains. Addition of salicylic acid or 1,1-bisphenol yielded a higher fraction of cyclic polylactides but lower molecular weights. Furthermore, SnCl<sub>2</sub> was compared with Bu<sub>2</sub>SnCl<sub>2</sub> and various other metal chlorides and the best results were obtained with SnCl<sub>2</sub>. With ethyl L-lactate as initiator SnCl<sub>2</sub>-catalyzed ROPs were performed at 120 °C and the lac/initiator ratio was varied. All these experiments were conducted under conditions allowing for comparison with ROPs catalyzed with neat Sn(II)-2-ethylhexanoate. Such a comparison was also performed with ε-caprolactone as monomer.

**Keywords** ε-Caprolactone · Cyclization · Lactide · Ring-opening polymerization · Tin(II)chloride

## Introduction

Poly(L-lactide) has become the most widely produced biodegradable and biosourced polymer with a worldwide production of approximately 700 000 ton per year estimated for the year 2021 [1]. The technical production of almost all commercial poly(L-lactide) is based on ring-opening polymerization (ROP) of L-lactide catalyzed by Sn(II) 2-ethylhexanoate (SnOct<sub>2</sub>). The predominant role of this catalyst is a consequence of its excellent performance, its low costs and the fact that it has been admitted as food stabilizer by the American Food and Drug Administration (FDA). This decision considers that SnOct<sub>2</sub> combines a high toxicity for a broad variety of microbes and fungi with a rather low toxicity for humans.

Over the past 50 years the toxicity of tin(II) ions has intensively been studied, because billions of cans were produced from steel with an interior wall plated by tin [2–4].

For this reason, the term “tin” became a synonym for can in British English. Therefore, it is not surprising that also other tin(II) salts containing nontoxic anions were admitted as food stabilizers, for example SnCl<sub>2</sub>. Since the chloride ions belong to the human metabolism in contrast to 2-ethylhexanoate, SnCl<sub>2</sub> may be even less toxic than SnOct<sub>2</sub>. Its broad application as food stabilizers is highlighted by the fact, that almost all tomato soups, tomato sauces and tomato juices are stabilized against fouling by SnCl<sub>2</sub>. Considering the hundred thousand of liters of tomato juice served on board of airlines every year, millions of people were exposed to SnCl<sub>2</sub> consumption. After a careful review of previously published data Blunden and Wallace concluded that less than 200 mg of SnCl<sub>2</sub> per kilogram human body may be considered to be harmless [3–5]. Nonetheless several research groups have recommended highly reactive tertiary amines (incl. amidines) as nontoxic substitute of tin(II) salts [6–11]. As example, the LD<sub>50</sub> doses of pyridine has been found to be 500 mg Kg<sup>-1</sup> and 4-N,N-dimethylamino pyridine is even ten times more toxic than pyridine [12, 13]. On the other hand, the increasing delivery of Sn(II) salts to the environment due to decomposition of polylactides or their hydrolysis in oceans, does not cause concern about environmental pollution. Sn(II) is a reducing agent, which is oxidized by oxygen or Fe(III) ions to SnO<sub>2</sub>. This extremely insoluble

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and harmless tin salt has been known as Cassiterite to the mankind for more than 5 000 years.

Whereas numerous patents and papers deal with application and polymerization mechanism of SnOct<sub>2</sub>, rather little is known about SnCl<sub>2</sub> as polymerization catalyst. A first short study of SnCl<sub>2</sub> (and SnCl<sub>4</sub>) catalyzes ROPs of L-lactide was published by Kricheldorf and Sumbel in 1989 [14]. At that time MALDI-TOF mass spectrometry did not exist yet, and SEC was not used. Tin(II)chloride hydrate in combination with toluene sulfonic acid was used by Kimura and coworkers as catalyst for polycondensation of L-lactic acid [15]. Three papers describing the oligomerization of L-lactide with isosorbide as initiator followed by in situ polycondensation with isophthalic or terephthalic acid dichloride were recently published by the authors [16–18]. Quite recently, the authors have unexpectedly discovered that neat SnOct<sub>2</sub> catalyzes the formation of high molar mass cyclic poly lactides and not of linear chains as believed by many researchers (incl. the first author) for almost 50 years [19]. In this context, the present work had the purpose to study ROPs of L-lactide catalyzed by neat SnCl<sub>2</sub> and by combinations of SnCl<sub>2</sub> with either difunctional cocatalysts or with ethyl lactate as initiator under conditions allowing for direct comparison with analogous polymerizations catalyzed by SnOct<sub>2</sub>. Furthermore, a comparison with ε-caprolactone (CL) was also intended.

## Experimental

### Materials

L-Lactide, a product of Corbion Purac, was kindly supplied by Thyssen-Uhde AG (Berlin) and recrystallized once from “Toluene 99.89%, extra dry” purchased

from ACROS Organics (Geel, Belgium). Tin(II)acetate and anhydrous SnCl<sub>2</sub> were purchased from Alfa Aesar (Karlsruhe, Germany) and used as received. SnOct<sub>2</sub> (purity > 96%) was also purchased from Alfa Aesar and used as received, since no water was detected upon azeotropic drying with toluene. Salicylic acid, 4-tert.butylcatechol, 1,1-diphenol, ethyl L-lactate, anhydrous zinc chloride, magnesium chloride, ferrous(III)chloride, bismuth chloride and hafnium chloride THF complex were all purchased from Sigma-Aldrich and used as received.

### Polymerizations of L-lactide

#### With Neat SnCl<sub>2</sub> at 180, 160 or 140 °C (Tables 1, 2, and 3)

Anhydrous SnCl<sub>2</sub> was weighed into a flame-dried 50 mL Erlenmeyer flask, L-lactide (50 mmol) and a magnetic bar were added under a blanket of argon. The reaction vessel was immersed into an oil bath preheated to 140 or 160 °C. The resulting polylactide was isolated by means of spatula and pincer and characterized without purification. For lac/cat ratio of 2 000/1 100 mmol of L-lactide was used.

#### With SnCl<sub>2</sub> and Difunctional Cocatalyst (Table 4)

The cocatalyst (0.05 mmol) and SnCl<sub>2</sub> (0.05 mmol) were weighed into a flame-dried Erlenmeyer flask, L-lactide (50 mmol) and a magnetic bar were added under a blanket of argon. The reaction vessel was immersed into a preheated oil bath and the resulting polylactide was finally isolated by means of spatula and pincer.

**Table 1** Polymerizations catalyzed with neat SnCl<sub>2</sub> in bulk at 160 °C

Exp. No	Lac/Cat	Time (h)	M <sub>n</sub>	M <sub>w</sub> (meas.)	Đ (meas.)	Color
1	200/1	1.0	50 000	111 000	2.1	Colorless
2	400/1	1.0	107 000	166 000	1.5	Colorless
3	600/1	1.0	108 000	170 000	1.5	Colorless
4A	1 000/1	1.0	73 000	125 000	1.8	Colorless
4B	1 000/1	2.0	65 000	176 000	2.7	sl. tan
4C	1 000/1	4.0	57 000	142 000	2.5	sl. brownish
4D	1 000/1	8.0	32 000	96 000	3.0	Brownish
5A	2 000/1	1.0	113 000	191 000	1.7	Colorless
5B	2 000/1	2.0	71 000	161 000	2.3	sl. tan
5C	2 000/1	4.0	51 000	147 000	2.9	sl. brownish
5D	2 000/1	8.0	38 000	120 000	3.2	Brown

<sup>a</sup>These colors were observed for amorphous samples

**Table 2** Polymerizations catalyzed with neat SnCl<sub>2</sub> at 180 °C

Exp. No	Lac/Cat	Time (h)	M <sub>n</sub>	M <sub>w</sub>	Đ	Color
1	1 000	0.5	22 000	46 000	2.1	Colorless
2	1 000	1.0	68 000	134 000	2.0	sl. brownish
3	1 000	1.5	50 500	101 000	2.0	Brownish
4	1 000	2.0	35 000	83 000	2.4	brownish

**Table 3** Polymerizations catalyzed by SnCl<sub>2</sub> in bulk at 140 °C without and with addition of ethyl L-lactate (Lac/Cat = 1000/1, Lac/In = 200/1)

Exp. No	Initiator	Time (h)	M <sub>n</sub>	M <sub>w</sub>	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J g <sup>-1</sup> )	Cryst (%) <sup>b</sup>
1	–	2	44 000	71 000	–	–	–
2	–	4	72 000	140 000	– <sup>a</sup>	– <sup>a</sup>	–
3	–	16	51 000	149 000	188.0	68.5	64
4	–	48	45 000	117 000	190.0	81.0	76
5	EtLac	16	27 000	35 000	183.0	77.0	72

<sup>a</sup>Beginning crystallization<sup>b</sup>Calculated with a ΔH<sub>m</sub> max of 106 J g<sup>-1</sup>[20, 21]**Table 4** Polymerizations catalyzed by SnCl<sub>2</sub> at 160 °C in bulk with addition of ortho-diphenols or ortho-hydroxy acids (Lac/Cat = 1000/1, Time 1 h)

Exp. No	Cocatalyst	Time(h)	M <sub>n</sub>	M <sub>w</sub>	Đ
1	4-tert-Butyl-catechol	1	77 000	140 000	1.8
2	2,2'-Dihydroxy-biphenyl	1	61 000	97 000	1.6
3	Salicylic acid	1	40 000	67 000	1.6
4	o-Hydroxyphenoxy-acetic acid	1	54 000	81 000	1.5

**With SnCl<sub>2</sub> in Combination with Ethyl Lactate as Initiator (Table 5)**

SnCl<sub>2</sub> (0.05 mmol) and neat ethyl L-lactate (1 or 0.5 mmol) were weighed into a flame dried 50 mL Erlenmeyer flask, L-lactide and a magnetic bar were added under a blanket of argon. The reaction vessel was immersed into an oil bath thermostated at 20 °C and the polylactide was isolated approx. 0.5 h after its crystallization. For the Lac/Cocat

**Table 5** ROPs catalyzed with SnCl<sub>2</sub> + EtLac at 120 °C (Lac/Cat = 1 000/1)

Exp. No	Lac/In	Time (h)	M <sub>n</sub> (theor.)	M <sub>n</sub> (corr.) <sup>a</sup>	M <sub>n</sub> (meas.)	M <sub>w</sub> (meas.)	Đ
1	40	3	5 800	4 900	7 100	8 000	1.14
2	60	4	8 700	8 100	11.800	12 900	1.10
3	100	5	14 500	10 000	16 200	18 200	1.13
4	200	5	28 500	20 000	28 500	34 500	1.23

<sup>a</sup>Measured GPC values multiplied with a correction factor of 0.68**Table 6** Comparison of ROP of L-lactide catalyzed by neat SnCl<sub>2</sub> or Bu<sub>2</sub>SnCl<sub>2</sub> in bulk at 160 °C/4 h

Exp. No	Catal	Lac/Cat	M <sub>n</sub>	M <sub>w</sub>	Đ
1	SnCl <sub>2</sub>	100/1	41 000	95 000	2.3
2	SnCl <sub>2</sub>	200/1	46 000	110 000	2.4
3	SnCl <sub>2</sub>	400/1	71 000	166 000	2.3
4	Bu <sub>2</sub> SnCl <sub>2</sub>	100/1	28 000	57 000	2.0
5	Bu <sub>2</sub> SnCl <sub>2</sub>	200/1	22 000	43 000	2.0
6	Bu <sub>2</sub> SnCl <sub>2</sub>	400/1	16 500	37 500	2.2

ratios > 60/1 the L-lactate was added in form of a 2 M solution in toluene.

**With Neat Bu<sub>2</sub>SnCl<sub>2</sub> at 160 °C (Table 6)**

Bu<sub>2</sub>SnCl<sub>2</sub> (0.1, 0.2 or 0.4 mmol) was weighed into a flame-dried 50 mL Erlenmeyer flask, L-lactide (40 mmol) and a magnetic bar were added under a blanket of argon. The reaction vessel was immersed into an oil bath preheated

to 160 °C and the reaction product was isolated by means of spatula and pincer.

### Comparison with Other Metal Chlorides

The catalyst ( $\text{SnCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{HfCl}_4 + 2\text{THF}$ , 0.1 mmol) was weighed into a 50 mL Erlenmeyer flask, and L-lactide (40 mmol) was added under a blanket of argon. After addition of a magnetic bar, the reaction vessel was immersed into an oil bath thermostated at 160 °C. In the case of  $\text{SnCl}_2$ , part of the colorless reaction product was removed with a spatula after 1 h. In the case of  $\text{MgCl}_2$  80 mmol of L-lactide was polymerized with 0.2 mmol of catalyst.

### Polymerizations of $\epsilon$ -Caprolactone (Table 7)

$\text{SnCl}_2$  (0.1 mmol) was weighed into a flame-dried 50 mL Erlenmeyer flask, a magnetic bar and CL (40 mmol) were added under a blanket of argon. The reaction vessel was immersed into an oil bath thermostated at 160 °C. Finally part of the viscous reaction product was removed by means of a spatula and characterized in the virgin state. Analogous experiments were conducted with  $\text{SnOct}_2$  as catalyst, so that a 1.0 M or a 0.4 M solution in toluene was injected into the reaction vessel.

### Measurements

The 400 MHz  $^1\text{H}$  NMR spectra were recorded with a Bruker Avance 400 in 5 mm sample tubes.  $\text{CDCl}_3$  containing TMS served as solvent and shift reference. The 150 MHz  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance 600 MHz spectrometer again in 5 mm sample tubes with  $\text{CDCl}_3$  as solvent. The DSC measurements were conducted with a Mettler-Toledo DSC-1 equipped with Stare Software version 11.00. Matrix-assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometry was performed using an Autoflex Max (Bruker Daltonik GmbH, Bremen) equipped with a Nd-YAG laser (355 nm). Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile

(DCTB) dissolved in chloroform (20 mg  $\text{mL}^{-1}$ ) was doped with potassium trifluoroacetate and served as matrix. Matrix solution was premixed with the analyte solution (chloroform, 4 mg  $\text{mL}^{-1}$ ) in a ratio of 50/20  $\mu\text{L}$ . A droplet (1  $\mu\text{L}$ ) of this solution was pipetted on the sample target. At least 6 000 single spectra recorded at 3 different spot positions were accumulated in the positive linear positive mode. The instrument was previously calibrated with PEO standards.

For the GPC experiments a modular LC system kept at 40 °C (isocratic pump, 1  $\text{mL min}^{-1}$ , refractive index detector, RI-501 -Shodex) was applied. Samples were manually injected using a Rheodyne valve (100  $\mu\text{L}$ , 2–4 mg  $\text{mL}^{-1}$ ). For instrument control and data calculation Clarity software (GPC extension, DataApex) was used. The calibration was performed using polystyrene standard sets (Polymer Standards Service – PSS, Mainz, Germany). For the determination of the Mark-Houwink-Sakurada (MHS) relationship a viscometer (Viscostar, Wyatt, Germany) and a multiangle laser light scattering (MALS) detector (Dawn EOS, Wyatt, Germany) were used. Astra 6.1 software (Wyatt) served for calculating the MHS curves.

## Results and Discussion

### Polymerizations with Neat $\text{SnCl}_2$ at 160 and 180 °C

A first series of polymerizations was performed at 160 °C in bulk with variation of Lac/Cat ratio. This temperature was selected, because reaction times of several hours do not cause degradation, racemization or crystallization, and because this standard temperature was also used in numerous previous studies, so that these results were comparable. The initially insoluble catalyst dissolved in the course of 5–20 min at Lac/Cat ratios around 200 and higher. At lower Lac/Cat ratios the rapid polymerization stops stirring before the catalyst has completely dissolved, and therefore the evaluation of the experiments summarized in Table 1 begins with a Lac/Cat ratio of 200/1. The polymerizations were

**Table 7**  $\text{SnCl}_2$ - and  $\text{SnOct}_2$ -catalyzed polymerizations of  $\epsilon$ -caprolactone in bulk at 160 °C

Exp. No	Catalyst	CL/Cat	Time (h)	Mn	Mw	$\bar{D}$
1A	$\text{SnCl}_2$	200/1	0.5	26 000	68 000	2.6
1B	$\text{SnCl}_2$	200/1	1.0	26 500	67 000	2.5
2A	$\text{SnCl}_2$	400/1	0.5	35 000	87 000	2.5
2B	$\text{SnCl}_2$	400/1	1.0	37 500	84 000	2.2
3	$\text{SnCl}_2$	1 000/1	1.0	64 500	133,000	2.1
4	$\text{SnOct}_2$	200/1	1.0	65 500	134 000	2.1
5	$\text{SnOct}_2$	400/1	1.0	90 000	178 000	2.0
6	$\text{SnOct}_2$	1 000/1	1.0	98 000	190 000	2.0

fast, so that the melt viscosity raised dramatically within 5–15 min. at Lac/Cat ratios  $< 2\,000/1$ .

The SEC measurements revealed four trends. First, the weight average molecular weights ( $M_w$ ) vary little, when the Lac/Cat ratio increases by a factor of 10. Second, the number average molecular weights ( $M_n$ 's) obtained at Lac/Cat ratios of 1 000/1 and below are significantly higher than expected from a stoichiometric initiation of ROPs. As demonstrated in Table 1, this deviation is also true when the measured  $M_n$  value are modified by a correction factor of 0.68 (relevant for chloroform solutions [22] but 0.58 for THF [23]), which is based on the fact that calibration of SEC measurements with polystyrene overestimates the real molecular weights of polylactide and other aliphatic polyesters due to its lower hydrodynamic volume. A third trend is a significant decrease of the molecular weight with longer polymerization times and the fourth trend consists in increasing dispersities with longer times. This pattern is typical for a polymerization process, where an initial rapid and kinetically controlled propagation is followed by slower equilibration reactions. In this connection it should be mentioned that ring chain equilibration resulting from reversible “back-biting” automatically involves ring-ring and chain-chain equilibration.

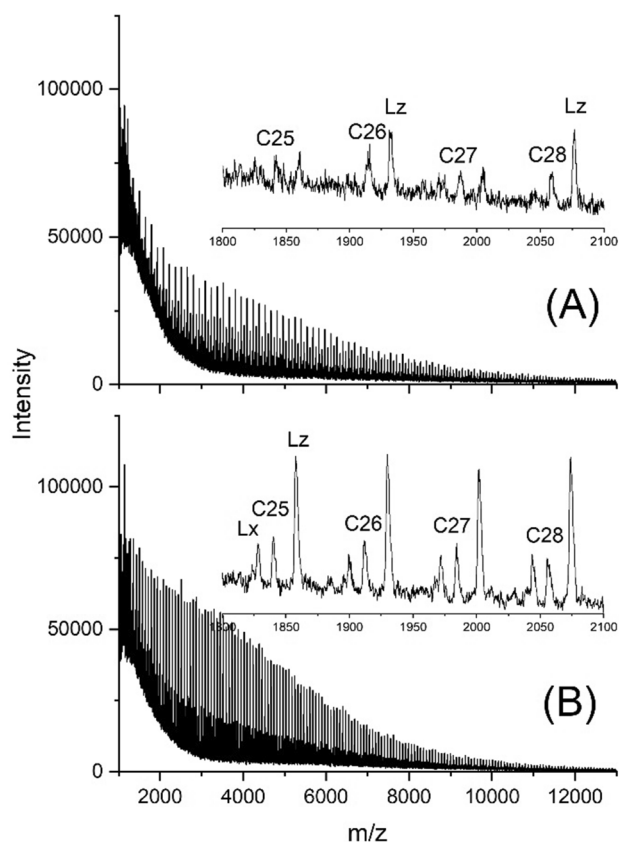
From the preparative point of view, it is a positive result that  $M_w$  values above  $150\,000\text{ g mol}^{-1}$  were achieved, values which are satisfactory for any application as engineering plastic with thermal processing from the melt. Commercial poly(L-lactide)s produced for injection molding typically have (uncorrected)  $M_w$  values in the range of  $100\,000 - 150\,000\text{ g mol}^{-1}$  [24].  $M_w$ 's in the range of  $150 - 200\,000\text{ g mol}^{-1}$  are even too high for injection molding but good for extrusion of films. However, it is also noteworthy that under identical conditions higher molecular weights were achieved ( $M_w$ 's up to  $320\,000\text{ g mol}^{-1}$ ) when  $\text{SnOct}_2$  was used as catalyst [19]. One more positive result is the observation that the polylactides isolated after 2 h at  $160\text{ }^\circ\text{C}$  were colorless, whereas after extension up to 4 h (see Table 2) a slight brownish discoloration was detectable.

The MALDI-TOF spectra revealed two general trends. First, peaks of three species were detectable, namely peaks of cycles (labeled C in the mass spectra) and peaks of two linear types of chains (Lx and Lz) having masses of 16 Da below that of the next cycle and 18 Da above. The authors have observed these peaks in numerous mass spectra of polylactides prepared by various tin catalysts at temperatures around or above  $140\text{ }^\circ\text{C}$ . Hence, the Lx and Lz peaks are not characteristic for  $\text{SnCl}_2$  catalyzed ROPs. By repetition of several MALDI-TOF measurements with Na-doping it was confirmed that the Lx peaks in the K-doped spectra originate from doping with coexisting Na ions. However, in all mass spectra of samples listed in Table 1 (and Table 2) the Lz chains were the predominant species, and in this regard the results obtained with  $\text{SnCl}_2$  are different from those

obtained with  $\text{SnOct}_2$  or  $\text{Sn(II)acetate}$ . Unfortunately, the authors were not able to identify the end groups of the Lz peaks. At Lac/cat ratios  $> 400/1$  those latter catalysts yielded polylactides almost exclusively consisting of cycles.

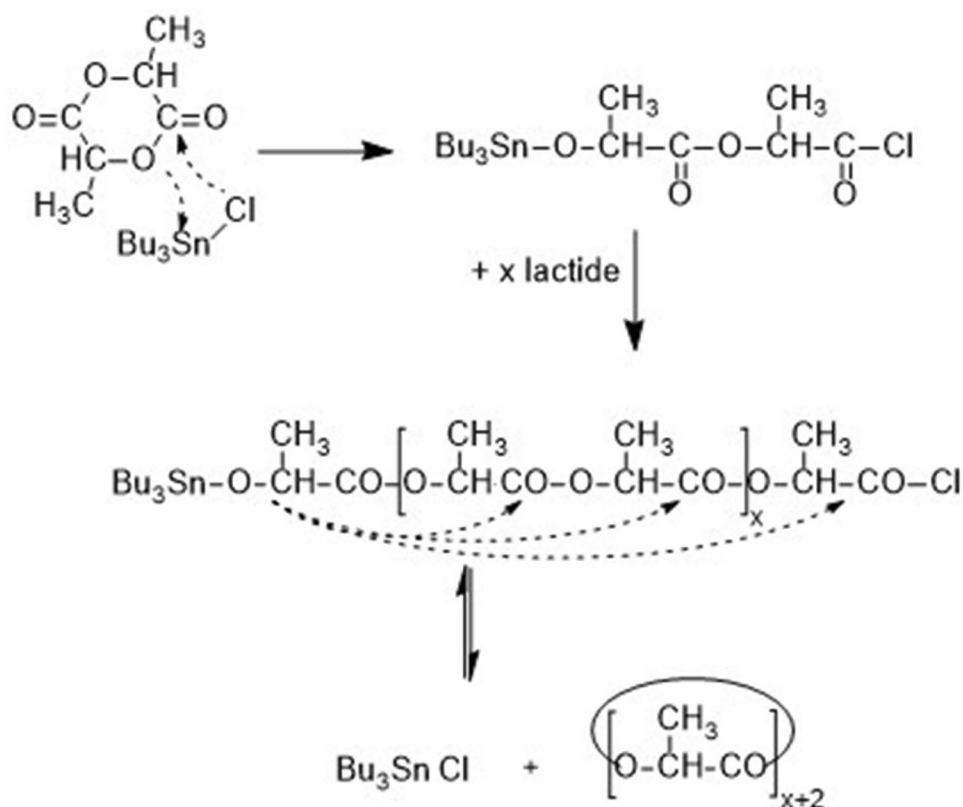
The second trend observed for  $\text{SnCl}_2$  is a predominance of even numbered chains (Fig. 1a), which indicates that equilibration by transesterification was not complete after a reaction time of 1 h. This phenomenon was not observed for  $\text{SnOct}_2$ -catalyzed ROPs under identical conditions and suggests that the transesterification activity of  $\text{SnOct}_2$  is higher than that of  $\text{SnCl}_2$ . Prolonged heating favors increasing equilibration and after 8 h complete leveling of even and odd-numbered species was achieved (Fig. 1b).

For several tin chlorides, such as  $\text{Bu}_3\text{SnCl}$  and  $\text{Ph}_2\text{SnCl}_2$  it was previously demonstrated [25] that the poly(L-lactide)s prepared in bulk at  $160\text{ }^\circ\text{C}$  almost exclusively consist of cycles when relatively low Lac/Cat ratios ( $< 600/1$ ) were used, and the polymerization mechanism outlined in Scheme 1 was proposed. Such a ROPPOC mechanism (ring-opening polymerization combined with simultaneous polycondensation, for definition and review see ref. [26]) was also proposed for polymerizations catalyzed by neat  $\text{SnOct}_2$ .



**Fig. 1** MALDI TOF mass spectra of poly(L-lactide)s prepared with  $\text{SnCl}_2$  (Lac/Cat = 1 000/1) at  $160\text{ }^\circ\text{C}$ : **a** after 1 h (No. 4A, Table 1), **b** after 8 h (No. 4D, Table 1)

**Scheme 1** Simplified reaction mechanism of  $\text{Bu}_3\text{SnCl}$  catalyzed polymerization of L-lactide



The mass spectra of the  $\text{SnCl}_2$ -catalyzed polymerizations obtained in this study suggest that the polymerization catalyzed by  $\text{SnCl}_2$  also follows this ROPPOC mechanism but involves more side reactions so that a nearly complete formation of cyclic poly lactides cannot be achieved.

With regard to discoloration the following trend was found. At a reaction time of 1 h the poly lactides were colorless regardless of the catalyst concentration. Slight discoloration became observable at a reaction time of 2 h, but this discoloration was so weak that the samples still looked white after crystallization. As expected, discoloration intensified with longer reaction times.

For two reasons several polymerizations were performed at  $180^\circ\text{C}$  (Table 2). First, this temperature is needed at the end of a technical polymerization to avoid crystallization and to enable extrusion of the melt from the reactor (whereupon the temperature may even be raised to  $200^\circ\text{C}$ ). Second, it should be found out, if the short time needed for complete conversion at this temperature involves partial racemization and/or discoloration. The high reactivity of  $\text{SnCl}_2$  in combination with the higher temperature had the consequence, that a reaction time of 0.5 h sufficed for complete conversion, meaning 97% according to the thermodynamic equilibrium concentration of L-lactide. At this short time the resulting poly lactides were still colorless, whereas a slight brownish discoloration was observable for the amorphous product

after 1 h. After crystallization this product was white. However, the molecular weights achieved at  $180^\circ\text{C}$  were all lower than those obtained at  $160^\circ\text{C}$  and thus, polymerization at  $180^\circ\text{C}$  proved not attractive.

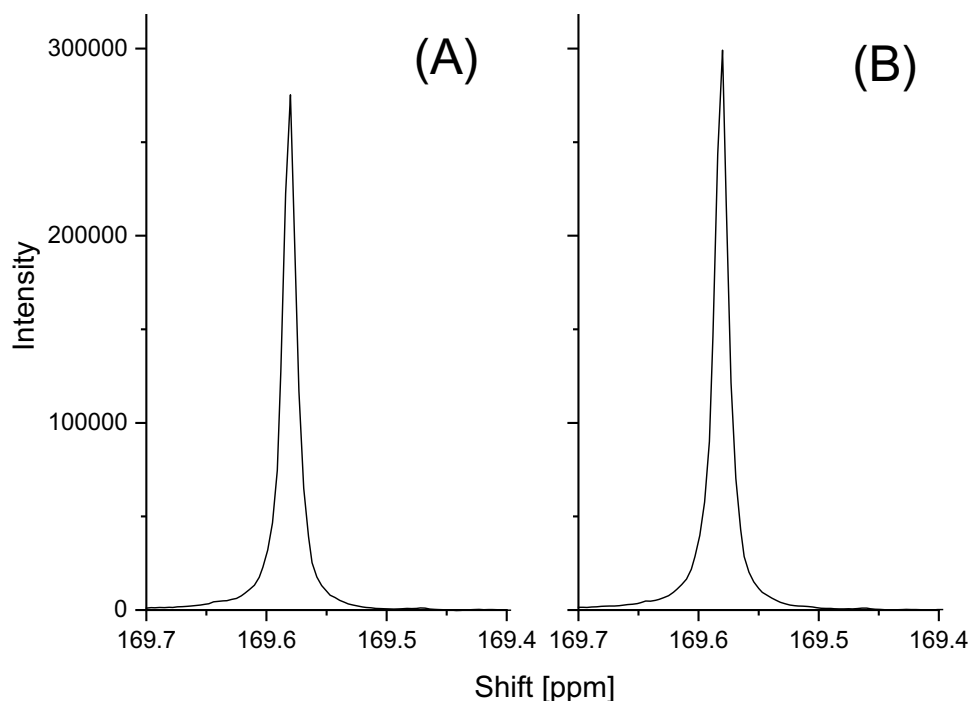
Concerning the optical purity of the poly(L-lactide)s prepared at  $160$  or  $180^\circ\text{C}$  it should be mentioned, that the technical production of poly(L-lactide)s and numerous publications showed that tin salts and compounds are less prone to cause racemization than salts of all other metal with exception of bismuth. However, when chloride ions are not solvated by hydrogen bonds or small cations (e. g. Li or Na), they are rather strong bases above all at high temperatures. Therefore, the samples Nos. 4B and 5B of Table 1 and Nos. 2–4 of Table 2 were subject to high-resolution  $^{13}\text{C}$  NMR measurements (150 MHz) with a s/n ratio  $> 200/1$ . All spectra were identical, and the CO or CH signals, which are particularly sensitive to the presence of different stereosequences were perfectly symmetrical and did not display a presence of L-D/D-L tetrads. Two CO signals are shown in Fig. 2.

### Polymerizations at $140^\circ\text{C}$

Polymerizations at  $140^\circ\text{C}$  were conducted for two reasons. Firstly, it should be found out, if Mw values around  $150,000\text{ g mol}^{-1}$  can also be achieved at this lower temperature which further reduces the risk of discoloration. Secondly,

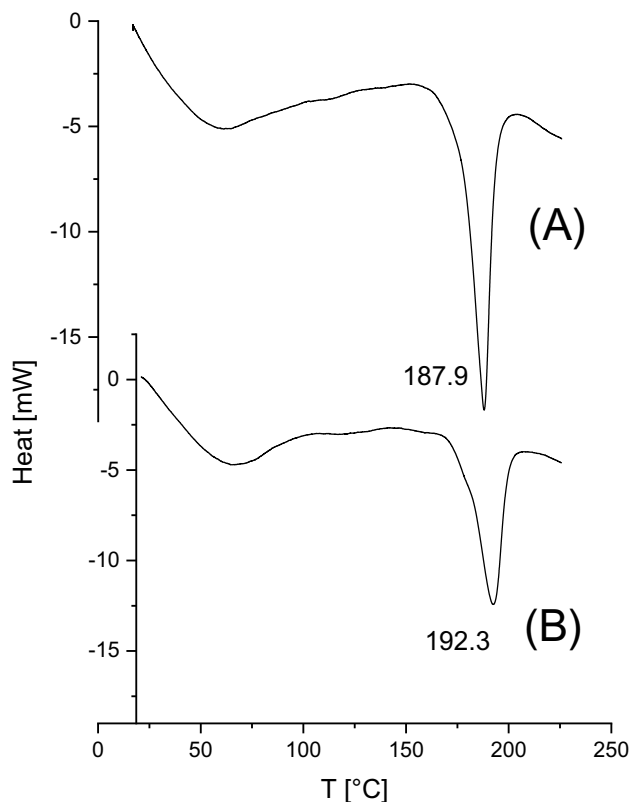


**Fig. 2** CO signals of the  $^{13}\text{C}$  NMR spectra of poly(L-lactide)s prepared with  $\text{SnCl}_2$  **a** at  $160\text{ }^\circ\text{C}/2\text{ h}$  (No. 4B, Table 1) and **b** at  $190\text{ }^\circ\text{C}/1.5\text{ h}$  (No.3, Table 2)



at this temperature poly(L-lactide) crystallizes within a few hours, and for the following reason, the melting temperature ( $T_m$ ) of the resulting crystallites was of interest. The standard  $T_m$  of optically pure poly(L-lactide) falls into the range of  $172\text{--}176\text{ }^\circ\text{C}$  with little annealing (e.g. at  $120\text{ }^\circ\text{C}$  for 1 h) and rises to  $176\text{--}180\text{ }^\circ\text{C}$  after intensive annealing [27–31]. However, quite recently the authors have shown that these  $T_m$  values only represent the kinetically controlled type of crystallites, whereas the thermodynamically controlled counterparts have a  $T_m$  in the range of  $193\text{--}196\text{ }^\circ\text{C}$  [32, 33]. The crystal modification ( $\alpha$ -modification) is the same, but the high  $T_m$  crystallites possess a smooth homogeneous surface resulting from thermodynamically controlled transesterification reaction across the flat surfaces of the crystallites typically combined with thickness growth. Formation of such high  $T_m$  crystallites was preferentially observed for catalysts and reaction conditions yielding cyclic poly lactides [33]. Therefore, it was of interest to see if and to what extent  $\text{SnCl}_2$  is capable of yielding poly(L-lactide)s having a  $T_m$  above  $180\text{ }^\circ\text{C}$ .

The results summarized in Table 3 indicate, firstly, that molecular weights (uncorrected  $M_w$ 's) close to  $150\,000\text{ g mol}^{-1}$  can indeed be achieved, and up to a polymerization time of 4 h the polylactides were colorless. Secondly, at 4 h the beginning of crystallization was observed and after 16 h a polylactide having a  $T_m$  of  $188\text{ }^\circ\text{C}$  was obtained. Further annealing at  $140\text{ }^\circ\text{C}$  finally yielded a polylactide with a  $T_m$  of  $190\text{ }^\circ\text{C}$  and 76% crystallinity (Fig. 3a). These results prove that  $\text{SnCl}_2$  is capable to produce high  $T_m$  poly(L-lactide) in analogy to the previously

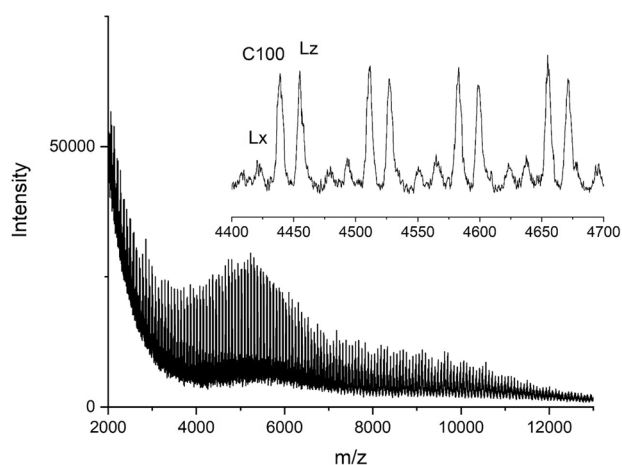


**Fig. 3** DSC heating traces of polylactides prepared with **a**  $\text{SnCl}_2$  + ethyl lactate at  $140\text{ }^\circ\text{C}/16\text{ h}$  (No. 5, Table 3), **b** neat  $\text{SnCl}_2$  at  $140\text{ }^\circ\text{C}/48\text{ h}$  (No. 4, Table 3)

studied tin(II) or dibutyltin(IV) catalysts. Comparable experiments with  $\text{SnOct}_2$  have not been published yet, but a pertinent study is in progress. Finally, an experiment with addition of ethyl L-lactate as initiator was conducted (No. 5, Table 3) which gave the unexpected result that even an alcohol-initiated polymerization catalyzed by  $\text{SnCl}_2$  yields a  $T_m > 180^\circ\text{C}$  (Fig. 3b), although similar experiments with  $\text{SnOct}_2$  as catalyst had failed to succeed in this regard [34].

### Attempts to Prepare Cyclic Poly lactides

Since a predominant formation of cyclic poly lactides was not observed, when neat  $\text{SnCl}_2$  was used as catalyst, further experiments were conducted with certain diphenols as cocatalysts. It has been previously reported that addition of salicylic acid or catechols or 2,2'-dihydroxybiphenyl to solutions of  $\text{SnOct}_2$  yields cyclic tin(II) compounds (illustrated in Scheme 2) [24, 35, 36]. These cyclic tin compounds catalyzed ring-expansion polymerizations (REPs) and yielded cyclic poly(L-lactide)s. Those results prompted the authors to study in the present work, if combinations of  $\text{SnCl}_2$  with afore mentioned difunctional cocatalysts also yield cyclic poly lactides (Table 4). The MALDI TOF mass spectra displayed a significant increase of the molar fraction of cyclics as compared with poly lactides prepared with neat  $\text{SnCl}_2$  (Fig. 4). However, none of these experiments yielded a product with total absence of linear chains. Hence, it may be concluded that

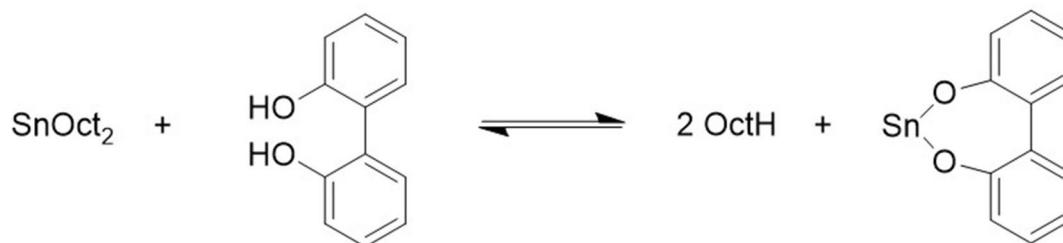
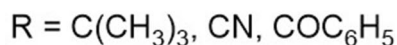
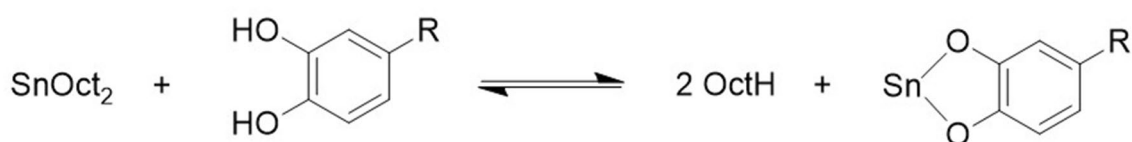


**Fig. 4** MALDI TOF mass spectra of the poly(L-lactide) prepared with  $\text{SnCl}_2$  (Lac/Cat = 1 000/1) at  $140^\circ\text{C}/48\text{ h}$ , (No. 4, Table 2)

$\text{SnCl}_2$  is inferior to  $\text{SnOct}_2$ , when a homogeneous cyclic topology is the goal of the experiments.

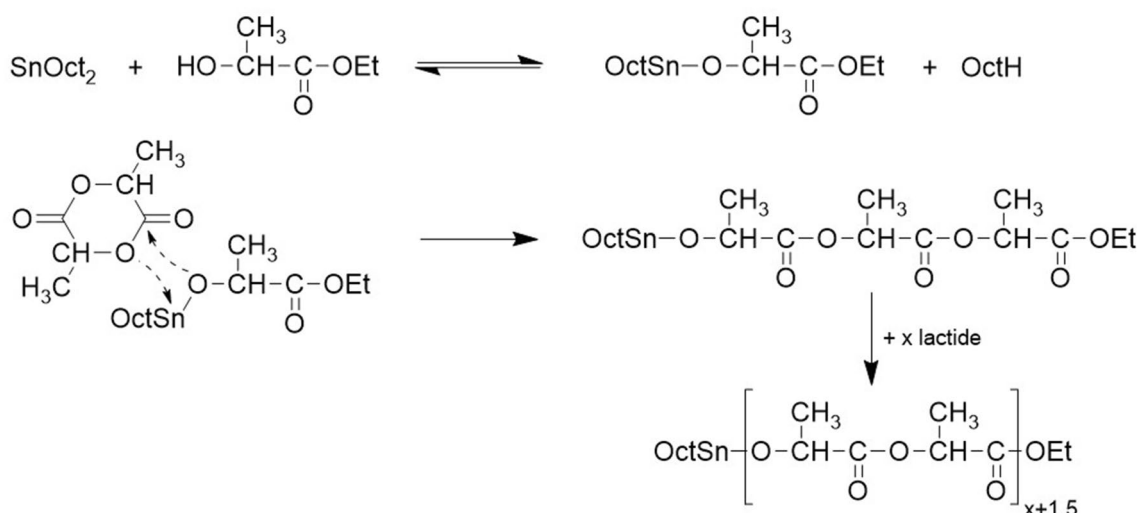
### Polymerizations with Addition of Ethyl L-Lactate as Initiator

If no maximum molecular weights are needed, as it is desirable for fiber spinning, alcohols are used as initiators (cocatalysts) in the technical production of poly lactide. Addition of alcohols accelerates the polymerization and allows for a rough control of the average molecular weights via the Lac/alcohol (Lac/In) ratio, because the alcohol is



**Scheme 2** Formation of cyclic Sn(II)bispheoxide from  $\text{SnOct}_2$



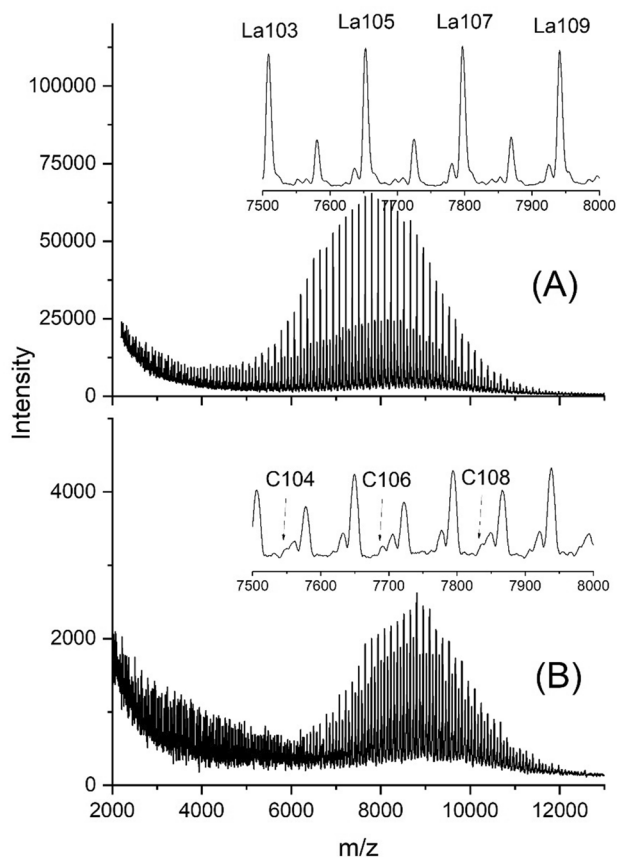


**Scheme 3** Ethylactate initiated ROP of L-lactide catalyzed by  $\text{SnOct}_2$

quantitatively incorporated as dead chain end (Scheme 3). When such ROPs are performed at relatively low temperatures (e.g. 80 °C) in solution, the alcohol-initiated ROPs catalyzed by  $\text{SnOct}_2$  even have the character of living polymerizations [37–39]. However, at temperatures around 130 °C (and higher [40]) transesterification reactions occur, which modify the initially kinetically controlled polymerization pathway.

A first series of alcohol-initiated polymerizations was performed with  $\text{SnOct}_2$  at 120 °C for comparison. These experiments were not listed in detail, because such polymerizations have already been reported by several other research groups [37–39, 41–43]. This temperature was selected for two reasons. First, formation of cycles by back-biting is negligible under these conditions. Second at 120 °C (and slightly above) a relatively rapid crystallization of poly(lactides) occurs with formation of the orthorhombic  $\alpha$ -modification which is the thermodynamically most stable crystal modification of poly(L-lactide)) [34]. As expected, the  $M_n$ 's parallel the Lac/Cat ratios and after correction with a factor of 0.68 [22] the agreement with the theoretical values is satisfactory. The MALDI-TOF mass spectra display a considerable predominance of even-numbered chains, a result which has already been reported by several groups over the past twenty years for polymerizations at temperatures < 130 °C (Fig. 5a). [37–43]

When  $\text{SnCl}_2$  was used as catalyst (Table 5) under identical conditions the ROPs initiated with L-ethyl lactate proved to be slower by a factor of 2–3 influenced by the fact that dissolution of the solid catalyst required up to 30 min. After 1.5 h, when all the  $\text{SnOct}_2$ -catalyzed poly(lactides) had almost completely crystallized, all the reaction mixtures containing  $\text{SnCl}_2$  were still liquid, and times of 3–5 h were required



**Fig. 5** MALDI-TOF mass spectra of poly(lactides) prepared at 120 °C with ethyl L-lactate as initiator (Lac/In = 100/1): **a**  $\text{SnOct}_2$  as catalyst (Lac/Cat = 1 000/1); **b**  $\text{SnCl}_2$  as catalyst (No. 3, Table 6)

to achieve crystallization (Table 5). The  $M_n$ 's were almost identical with those obtained from  $\text{SnOct}_2$ -catalyzed ROPs up to a Lac/In ratio of 100/1 but fell below the theoretical values at higher Lac/In ratios, partially due to side reactions including cyclization as indicated by the MALDI TOF mass spectra (Fig. 5b). Nonetheless the mass spectra suggest that the mechanism catalyzed by  $\text{SnCl}_2$  is the same as that discussed for  $\text{SnOct}_2$  and a rough control of the molecular weight can be achieved with addition of an alcohol as initiator. Furthermore, the dispersities are considerably lower than those obtained in the absence of an initiator Scheme 4.

DSC measurements of the poly lactides prepared with  $\text{SnCl}_2$  were recorded for comparison with sample No.5, Table 3, the DSC heating trace of which is presented in Fig. 3b. The DSC heating traces of the samples listed in Table 6 display melting endotherms ( $T_m$ 's) far below the  $T_m$  measured for sample No. 3, Table 5 (Fig. 6). This is a result that underlines the effect of long annealing at 140 °C in the presence of the catalyst on the properties of sample No. 5. Table 3.

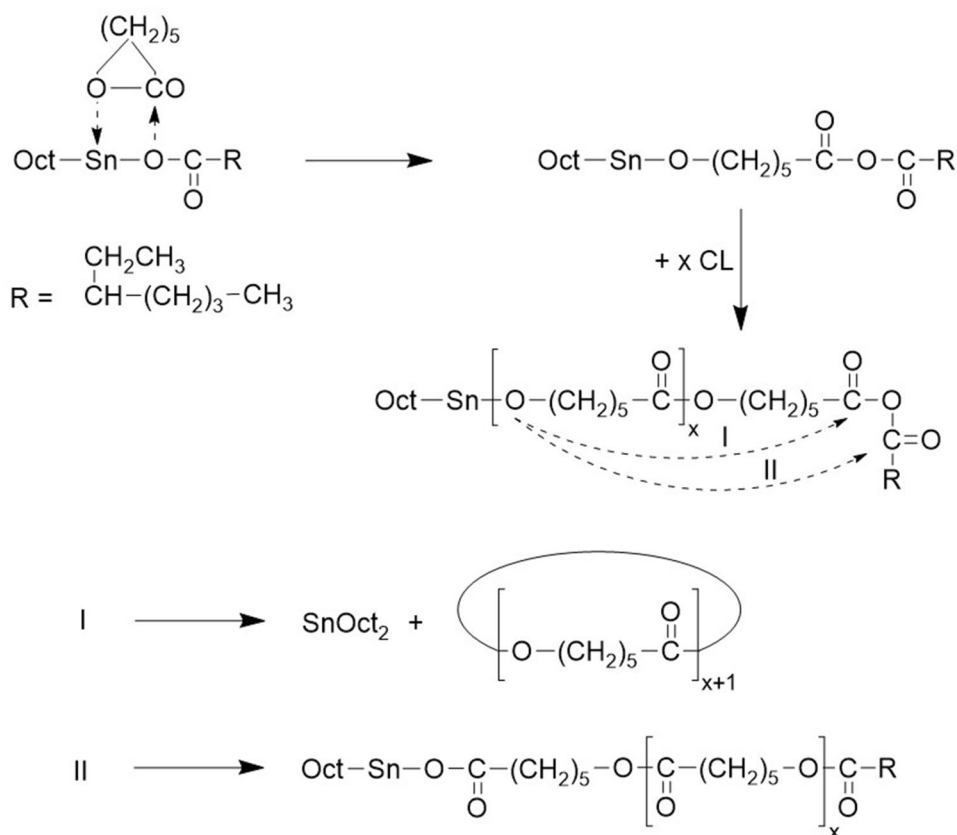
### Comparison with Various Metal Chlorides

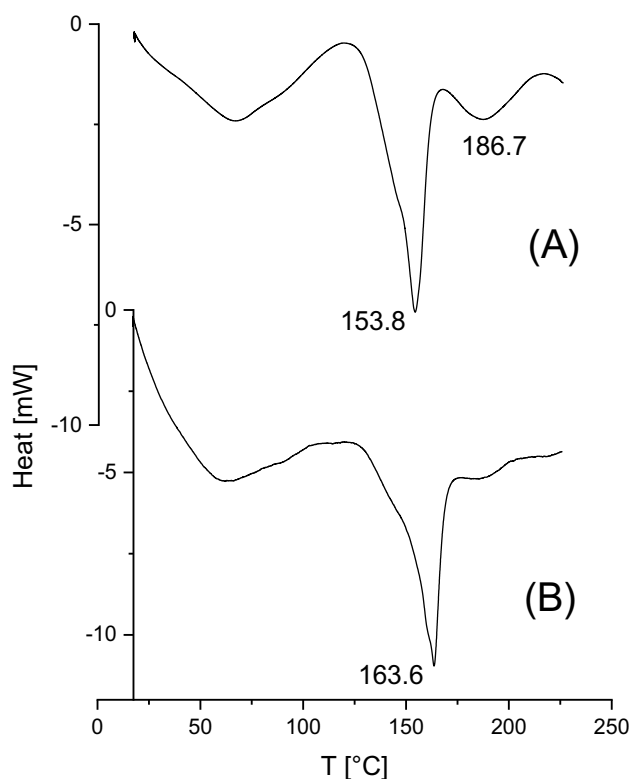
In order to see how  $\text{SnCl}_2$  compares to other metal chlorides two series of polymerizations were conducted. At first, a comparison of  $\text{SnCl}_2$  and  $\text{Bu}_2\text{SnCl}_2$  was studied. From a

couple of previously published polymerization conducted with  $\text{Bu}_2\text{SnCl}_2$  (and other butyltin(IV) chlorides) at 160 °C [25] it was expected that the  $\text{SnCl}_2$ -catalyzed polymerizations will be faster, and identical reaction conditions without interference of crystallization or thermal degradation would be difficult to find. After preliminary experiments, not described here in detail, low Lac/Cat ratios, at a temperature of 160 °C and a reaction time of 4 h were selected as reaction conditions for both catalysts (Table 6). Under these conditions the  $\text{SnCl}_2$ -catalyzed reaction mixtures turned viscous within a few minutes, although the  $\text{SnCl}_2$  did not dissolve completely at a Lac/Cat ratio of 100/1, whereas the  $\text{Bu}_2\text{SnCl}_2$  containing mixtures required 2–3.5 h to reach a high viscosity. The consequences of these different catalytic activities were considerably lower  $M_n$  and  $M_w$  values of  $\text{Bu}_2\text{SnCl}_2$  catalyzed poly lactides. The MALDI mass spectra proved to be rather complex with a pattern of five peaks, four peaks of different kinds of linear chains and the peak of cycles. In other words,  $\text{Bu}_2\text{SnCl}_2$  is even worse than  $\text{SnCl}_2$ , when a homogeneous topology is desired.

The second series of polymerizations was performed with the purpose to compare  $\text{SnCl}_2$  with the chlorides of other metals such as Mg, Zn, Fe(III), Bi or Hf. These chlorides were selected, because the toxicity of Mg(II), Zn(II) and Bi(III) is certainly lower than that of Sn(II). Since preliminary experiments had shown that  $\text{BiCl}_3$  is a sluggish catalyst,

**Scheme 4** Alternative mechanism of  $\text{SnOct}_2$  catalyzed-initiated ROPs of caprolactone



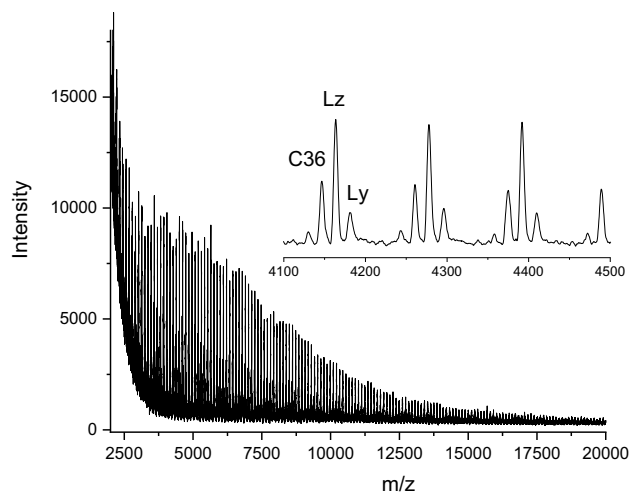


**Fig. 6** DSC heating traces of poly(lactides) prepared at 120 °C with  $\text{SnCl}_2$  and ethyl L-lactate as initiator: **(a)** Lac/In=100/1 (No. 3, Table 6); **(b)** Lac/Cat=200/1 (No. 4, Table 6)

the temperature was raised to 160 °C and the Lac/Cat ratio was lowered to 400/1. As expected on the basis of experiment No. 3, Table 1, the  $\text{SnCl}_2$ -catalyzed poly(lactide) melt turned viscous within 15 min, and when the product was isolated after 1 h a  $M_n$  of 102 000  $\text{g mol}^{-1}$  and a  $M_w$  of 161 000  $\text{g mol}^{-1}$  were found in good agreement with the results of No. 3, Table 1. However, the reaction mixtures of all other five experiments did not show a significant increase of the viscosity within 4 h and therefore, these experiments were stopped at that time. Hence, these experiments document that the effectiveness of  $\text{SnCl}_2$  as catalyst for ROPs of lactide is far superior to any other metal chlorides studied in this work.

### Polymerizations of $\epsilon$ -Caprolactone

CL is more basic and less electrophilic than lactide as demonstrated by the fact that 4-tolylene sulfonic acid catalyzes a cationic polymerization of CL, whereas in the case of lactide trifluoromethane sulfonic acid or fluorosulfonic acid are needed as catalysts. Furthermore, it was found that  $\text{BiCl}_3$  (and  $\text{BiBr}_3$  and  $\text{BiI}_3$ ) catalyze polymerizations of CL at 140 °C in bulk [44], whereas the experiments



**Fig. 7** MALDI TOF mass spectrum of the poly-CL prepared at 160 °C with  $\text{SnCl}_2$  (No. 2B, Table 7)

listed in Table 4 demonstrate that  $\text{BiCl}_3$  is an extremely poor catalyst for lactide. Since  $\text{SnCl}_2$  is a stronger Lewis acid than  $\text{SnOct}_2$ , it may be hypothesized that the negative reactivity ratio of the pair  $\text{SnCl}_2/\text{SnOct}_2$  found for ROPs of lactide might turn into a positive ratio when CL is used as monomer. To test this hypothesis several polymerizations were conducted at 160 °C in bulk, (i.e. under the conditions of Table 1) with variation of the CL/Cat ratio (Table 7). Since the solid  $\text{SnCl}_2$  needs more time for dissolution in CL than  $\text{SnOct}_2$ , which dissolves immediately, an exact kinetic comparison did not make sense. Therefore, the time when the increasing viscosity of the reaction mixture stopped stirring of the magnetic bar was used for a rough comparison of both catalysts. This comparison indicated that  $\text{SnCl}_2$  is more reactive by a factor of 1.5–2.0 than  $\text{SnOct}_2$ . However, the SEC measurements revealed that the molecular weights produced by  $\text{SnCl}_2$  are significantly lower than those obtained with  $\text{SnOct}_2$ , in close analogy to the results obtained from ROPs of lactide. The MALDI-TOF mass spectra (exemplarily illustrated in Fig. 7) showed that in addition to peaks of cycles two peaks of two kinds of linear chains were present, one of which was identified, namely the Ly peaks. These peaks represent polylactone chains having one  $\text{ClCH}_2$ - and one  $\text{COOH}$  end group. In other words, a Cl transfer from the catalyst to the  $\text{CH}_2\text{-O}$  group of monomeric or polymeric CL units has occurred. The formation of a  $\text{ClCH}_2$  end group was also confirmed by a triplet signal at 3.6 ppm in the  $^1\text{H}$  NMR spectra (not shown here). Such halogen transfer reaction was already reported for polymerizations of CL with other metal halides and their mechanisms were discussed, so that a more detailed discussion in this work is not necessary [45, 46]. This Cl transfer, which does not occur in ROPs of lactide, is the main reason why the

molecular weights obtained from the monomer/catalyst combination CL/SnCl<sub>2</sub> are lower than those obtained from the combinations CL/SnOct<sub>2</sub> or Lac/SnCl<sub>2</sub>.

## Conclusion

The results obtained in this work and previous publications allow for the following conclusions. SnCl<sub>2</sub> is inferior to SnOct<sub>2</sub> with regard to polymerization rates and maximum molecular weights that can be achieved in ROPs of L-lactide. However, uncorrected Mw values above 150 000 g mol<sup>-1</sup> can be obtained which suffice for applications of polylactides as engineering plastics for injection molding, because commercial polylactides designed for this purpose typically have Mw's in the range of 100 000–150 000 g mol<sup>-1</sup>. Furthermore, SnCl<sub>2</sub> is far more reactive than all other metal chlorides studied in this work, above all more reactive than the less toxic chlorides MgCl<sub>2</sub>, ZnCl<sub>2</sub> and BiCl<sub>3</sub>, which proved to be useless. Moreover, due to its higher Lewis acidity relative to SnOct<sub>2</sub>, SnCl<sub>2</sub> is useful as catalyst for polycondensations and can be used to catalyze ROPs and polycondensation in an “one-pot” procedure.

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**Data Availability** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

## Compliance with Ethical Standards

**Conflict of interest** The authors have no relevant financial or non-financial interests to disclose.

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