

# Ring-Expansion Polymerization of $\epsilon$ -Caprolactone, Glycolide, and L-lactide with a Spirocyclic Tin(IV) Catalyst Derived from or 2,2'-Dihydroxy-1,1'-Binaphthyl – New Results and a Revision

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In contrast to other cyclic tin bisphenoxides, polymerizations of glycolide and L-lactide with the spirocyclic tin(IV) bis-1,1'-bisnapthoxide yield linear chains having a 1,1'-bisnapthol end group and no cycles. In the case of L-lactide, LA/Cat ratio and temperature are varied and at 160 °C or below, all polylactides mainly consist of even-numbered chains. A total predominance of even-numbered chains is also found for homopolymerization of glycolide, or the copolymerization of glycolide and L-lactide, when conducted <120 °C. Linear chains having a bisnaphthol end group are again the main reaction products of ring-expansion polymerizations (REP) of  $\epsilon$ -caprolactone, but above 150 °C cycles are also formed.

# 1. Introduction

Ring-expansion polymerization (REP) of cyclic monomers, in general, and cyclic esters, in particular, was first reported by Kricheldorf and Lee in 1994.<sup>[1,2]</sup> Cyclic dibutyltin bisalkoxides served as initiators/catalysts (**Scheme 1**). For this type of REP it is characteristic that the initiator remains in the cyclic polymer connected to the polyester chain via two reactive Sn–O bonds. Stabilization of this primary cyclic species requires a second

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step, for example incorporation of a (nonpolymerizable) five-membered thiolactone, which transforms the Sn–O into the hydrolytically stable Sn–S bonds (Scheme 1). Hydrolysis of the primary cyclic polyesters or their reactions with acid chlorides yields telechelic linear polyesters. Numerous REPs of this type have been reported.<sup>[3,4]</sup>

A first REP involving spontaneous elimination of the initiator/catalyst and yielding a catalyst-free cyclic polymer was described by the Grubbs group based on a metathesis catalyst and cyclooctene or cyclooctadiene as monomers.<sup>[5,6]</sup> Further examples of REPs based on metathesis catalysts

and substituted acetylenes were later published by the research group of Veige.<sup>[7–9]</sup> Moreover, cyclic polyalkylene sulfides via REP of thiiranes have been reported.<sup>[10]</sup>

REPs of cyclic esters, in particular polylactides, involving elimination of the catalyst were reported by the authors since 2017.<sup>[11–15]</sup> The first examples were based on the cyclic dibutyltin bismercaptides DSTL and DSTD (Scheme 2).<sup>[11,12]</sup> Eventually, seven membered cyclic bisphenoxides, such as BuSnBiph,<sup>[13]</sup> BuSnNaph,<sup>[13]</sup> SnBiph,<sup>[14]</sup> and SnNaph<sup>[14]</sup> (Scheme 2) were found to be more reactive. A simplified scheme of this second type of REP is presented in Scheme 3. In this connection the spirocyclic catalyst SnNaph2 was synthesized (and analogous Ge and Zr bisnaphthoxides) and its usefulness for the REP of Llactide was explored.<sup>[15]</sup> The reaction products which showed an anomalous strong predominance of even-numbered species were interpreted as cyclic polylactides in analogy to the experiments with SnNaph and BuSnNaph. This interpretation was, of course, also based on matrixassisted laser desorption/ionisation time-of-flight (MALDI TOF) mass spectra, but the authors made the mistake to overlook that the masses of linear polylactides having a 1,1'-bisnaphthol end group (see Scheme 4,  $R = CH_3$ ) have nearly the same mass as cyclic polylactides ( $\Delta m \approx 1.8$  Da), which can be hardly differentiated in the linear instrument mode having no isotope peak resolution. Comparison of the intrinsic viscosities with commercial linear polylactides performed after publication, however, suggested that the SnNaph<sub>2</sub> catalyzed polylactides have a linear topology.

This finding prompted now the authors to reinvestigate  $SnNaph_2$ -catalyzed polymerizations of I-lactide and to include glycolide and  $\epsilon$ -caprolactone, because the masses of their cyclic and linear polymers having a bisnaphthol end group are quite





**Scheme 1.** REP of  $\epsilon$ -CL initiated with 2,2-dibutyl-2-stanna-1,3-dioxacycloalkanes.



Scheme 2. Structures and acronyms of catalysts used or discussed in this work.

different, so that an unambiguous interpretation of mass spectra is easy to achieve. Furthermore, it was of interest to find out, if also in the case of glycolide (GL) a largely predominant formation of even-numbered chains will occur. Such a result is not predictable on the basis of REPs of L-lactide because the ester bonds of polyGL are more reactive, and thus, more prone to transesterification than LA–LA bonds.

# 2. Experimental Section

## 2.1. Materials

L-Lactide (LA), a product of Corbion Purac, was kindly supplied by Thyssen-Uhde AG (berlin) and recrystallized from "Toluene 99.89%, extra dry" (ACROS Organics). Glycolide (GL), (kindly supplied by Thyssen-Uhde AG) was recrystallized from a 1:1 (v/v) mixture of tetrahydrofuran (THF) and toluene.  $\epsilon$ -Caprolactone ( $\epsilon$ CL), (Alpha Aesar, Karlsruhe, Germany) was stirred with P<sub>4</sub>O<sub>10</sub> for 10 min, decanted stirred again with P<sub>4</sub>O<sub>10</sub> and then distilled over CaH<sub>2</sub> powder in vacuo at a bath temperature of 95 °C. The catalyst SnNaph<sub>2</sub> was synthesized as described previously.

## 2.2. Polymerizations

## 2.2.1. Polymerization of Glycolide

 $SnNaph_2$  (0.5 mmol) was weighed into a 50 mL Erlenmeyer flask and glycolide (50 mmol) was added under a blanket or







Scheme 3. REP of lactide catalyzed by SnBiph.

argon together with a magnetic bar. The reaction vessel was immersed into an oil bath preheated to 105 °C. After 20 h, part of the crystalline reaction product was isolated and extracted with hexafluoro-iso-propanol (HFiP) by stirring at 20–22 °C overnight. The extract was subject to MALDI TOF mass spectrometry.

#### 2.2.2. Copolymerization of Glycolide and L-Lactide

SnNaph<sub>2</sub> (0.5 mmol) was weighed into a 50 mL Erlenmeyer flask, GL (25 mmol) LA (25 mmol) and a magnetic bar were added under a blanket of argon. The reaction vessel was the immersed into an oil bath thermostated at 105 °C. After 8 h the virgin copolymer was characterized.

#### 2.2.3. Polymerization of L-Lactide

SnNaph<sub>2</sub> (0.4 mmol) was weighed into a flame-dried 50 mL Erlenmeyer flask ad L-lactide (40 mmol) and a magnetic bar were added under a blanket of argon. The reaction vessel was immersed into an oil bath. Finally, the crystallized polyLA was crashed with a spatula, so that it pieces of the product could be removed from the reaction vessel, and the crude polyLAs were characterized.

#### 2.2.4. Polymerization of $\epsilon$ -Caprolactone

SnNaph<sub>2</sub> (0.5 or 0.25 mmol) was weighed into a 50 mL Erlenmeyer flask,  $\epsilon$ -CL (50 mmol) and a magnetic bar was added. The reaction vessel was immersed into an oil bath thermostated at 120, 150, or 180 °C (see Table 4). The viscous product was removed from the reaction vessel by means of a spatula and characterized in the virgin state.

#### 2.3. Acetylation of 1,1'-Bisnaphthol

1,1'-Bisnahthol (10 mmol) was weighed into a 100 mL roundbottom flask, acetic anhydride (40 mmol), pyridine (10 mmol), and a magnetic were added. After addition of chloroform (50 mL) the reaction mixture was refluxed for 4 h and then concentrated in vacuo. Toluene (50 mL) was added to the remainder and the resulting solution was again concentrated in vacuo at 60 °C until all volatile components had seemingly evaporated. The <sup>1</sup>H NMR spectrum of the viscous colorless remainder displayed a sharp singlet signal of the acetate protons at 1.74 ppm with the expected intensity ratio relative to the aromatic protons.

#### 2.4. Measurements

The <sup>1</sup>H NMR measurements were performed with a Bruker Advance 400 III in 5 mm o.d. sample tubes, using CDCl<sub>3</sub> containing TMS as solvent and shift reference.

The MALDI TOF mass spectra were recorded with an Autoflex-Max mass spectrometer (Bruker Daltonik, Bremen, Germany). All spectra were recorded in the positive ion linear mode. The MALDI stainless steel targets were prepared from chloroform solutions of poly(I-lactide) ( $3-5 \text{ mg mL}^{-1}$ ) doped with potassium trifluoroacetate (THF, 2 mg mL<sup>-1</sup>). Typically, 20 µL of sample the solution, 2 µL of the potassium salt solution, and 50 µL of a solution of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 20 mg mL<sup>-1</sup>, CHCl<sub>3</sub>) serving as matrix were mixed in an Eppendorf vial. A droplet (1 µL) of this solution was deposited on the MALDI target.

The gel permeation chromatography (GPC) measurements were performed with chloroform solutions in a modular system kept at 40 °C consisting of an isocratic pump, 1 mL min<sup>-1</sup> and a refractive index detector (Wyatt, Optilab reX). Samples were manually injected (100  $\mu$ L, 2–4 mg mL<sup>-1</sup>). For instrument control Clarity software (GPC extension, DataApex) and for mass

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Scheme 4. ROP of glycolide or lactide initiated with SnNaph<sub>2</sub>.

calculation Wyatt Astra 6.1 (Wyatt corporation, USA) were used. The calibration was performed using polystyrene standard sets (Polymer Standards Service – PSS, Mainz). The number average  $(M_n)$  and weight average  $(M_w)$  data listed in **Tables 1–3** are uncorrected.

# 3. Results and Discussion

## 3.1. Preparative Aspects

Since in the case of GL or  $\epsilon$ CL the masses of cycles are different from those of linear chains having a 1,1-bisnapthol end group,

**Table 1.** Correlation between mass numbers of peaks observed in Figure 2(B) and composition of linear GL/LA copolymers having a 1,1'bis-naphthol ester end group (incl. K-doping).

LA→GL↓	6	8	10	12	14	16
8	-	-	-	1654.2	1798.2	1942.4
10	-	-	1626.1	1770.4	1913.9	2058.5
12	-	1598.1	1742.2	1886.4	2030.5	_
14	1570.1	1714.2	1858.3	2002.5	-	_
16	1686.2	1830.4	1974.4	-	-	_
18	1802.3	1946.7	-	-	-	_
20	1918.5	2062.6	-	-	-	-
22	2044.5	-	-	-	-	-

Table 2. SnNaph<sub>2</sub>-catalyzed ROPs of L-lactide in bulk at 120  $^\circ\text{C}$  with variation of LA/Cat ratio and time.

Exp. No	. LA/ Cat	Time [h]	$M_n^{(a)}$ (theor.)	$M_n^{(b)}$ (corr.)	M <sub>n</sub> (meas.)	M <sub>w</sub> (meas.)	Disp.Ð
1	50/1	24	3800	3 100	4500	6500	1.5
2	100/1	2	7400	4000	6100	11 100	1.8
3	100/1	4	7400	5000	7300	12 400	1.7
4X	100/1	22	7400	6000	8700	13 200	1.5
4Y	100/1	22	-	-	8600	13 000	1.5
5X	100/1	192	14 600	-	6000	11 200	1.8
5Y	100/1	192	-	-	6100	11 400	1.8
6	200/1	192	14 600	-	10 200	16 000	1.6
7	400/1	192	29 200	-	17 500	27 000	1.7
8	600/1	192	44 000	-	27 000	43 500	1.6

 $^{a)}$  calculated from LA/Cat ratio and 100% conversion assuming that 2 chains were initiated by one SnNaph\_2 molecule. (real conversions were between 95 and 97%);  $^{b)}$  measured  $M_n$  values multiplied with a correction factor of 0.68.

the first experiments were performed with glycolide . In the case of GL a low GL/Cat ratio of 100/1 was used and a low temperature (105 °C) to obtain a low molecular polyester, because high molar mass polyGL is insoluble in all inert solvents. In contrast to condensation products of glycolic acid which may be completely or largely soluble in hexafluoro-isopropanol (HFiP) the

Table 3.  $\mathsf{SnNaph}_2\text{-catalyzed ROPs}$  od L-lactide at 160 °C with variation of LA/Cat and time.

Exp.No.	LA/Cat	Time[h]	$M_n^{a)}$ (theor.)	$M_{n}^{b)}$ (corr.)	M <sub>n</sub> (meas.)	M <sub>w</sub> (meas.)	Disp.Ð
1	50/1	1.5	3800	2100	3200	5700	1.7
2	50/1	3.0	3800	2300	3400	5900	1.7
3	100/1	1.5	7400	4300	6400	9200	1.5
4	100/1	6.0	7400	4500	6700	11 200	1.55
5	100/1	22.0	7400	5800	8400	13 700	1.70
6	200/1	2.0	14 800	9000	13 000	16 500	1.30
7	200/1	22.0	14 800	1100	16 200	24 400	1.55
8	400/1	3.0	29 600	13 200	19 500	27 500	1.40
9	400/1	22.0	29 600	17 000	25 000	40 000	1.60

<sup>a)</sup> calculated from LA/In ratios and 100% conversion assuming that 2 chains were initiated by one SnNaph<sub>2</sub> and including the end group (real conversions were between 95% and 97%); <sup>b)</sup> measured  $M_n$  values multiplied with a correction factor of 0.68.





Figure 1. MALDI TOF mass spectrum of a polyGL polymerized at 105 °C/12 h with a GL/SnNaph<sub>2</sub> ratio of 100/1. L = linear chains having a bisnaphthol ester end group (see Scheme 4).

polyglycolide prepared by ROP of glycolide is insoluble even in this solvent. The ROP performed in this work with SnNaph, at 105° yielded a polyGL which was partly soluble in HFiP, so that a MALDI TOF mass spectrum could be recorded. This mass spectrum is presented in Figure 1 and demonstrates that polymerization product mainly consists of linear chains having a bisnaphthol end group and an even number of glycolyl units as expected from a simple REP without elimination of the catalyst (Scheme 4). The next step was a 1:1 copolymerization of GL and LA under the same conditions. A copolyester, which was completely soluble in chloroform, was obtained and the mass spectrum of this copolyester (Figure 2A) displayed a characteristic pattern as illustrated by expanded segment of Figure 2B. The correlation of mass peaks and GL/LA ratios presented in Table 1 allowed for an unambiguous assignment of all peaks to copolyester chains of GL and LA units having a bisnaphthol end group.



Figure 3. MALDI TOF mass spectra of polyLAs polymerized in bulk at 120 °C with a LA/Snaph<sub>2</sub> ratio of 100/1: A) after 2 h, B) after 192 h (Table 1).

Compositions containing an odd-number of GL or LA units were not detectable, what indicates that back-biting or other transesterification reactions were absent at the relatively low temperature of 105 °C. These results also prove that SnNaph<sub>2</sub>intiated polymerizations of LA will results in linear chains and



Figure 2. MALDI TOF mass spectrum of a 1:1 GL/LA copolyester polymerized at 105 °C with a monomer/SnNaph<sub>2</sub> ratio of 100/1.









Scheme 5. Alternative intermediates in the ROP of lactide initiated by SnNaph<sub>2</sub>.

not in cycles. This interpretation also means that SnNaph<sub>2</sub> plays the role of an initiator and not the role of a catalyst in contrast to the other tin catalysts based on 1,1'-bisnaphthol (SnNaph and Bu<sub>2</sub>SnNaph in Scheme 2). On the basis of these results two series of homopolymerizations of LA were performed, one series at 120 °C (Table 2) and the second series at 160 °C (Table 3).

At 120 °C the LA/In ratio was varied to find out if the  $M_n$  increases with the LA/In ratio, as expected for an initiator. The  $M_n$  data listed in Tables 2 and 3 carry two important messages. First,  $M_n$  increases indeed with the LA/In ratio but a perfect proportionality was not achieved. The problem behind the deviation of experimental  $M_n$  from the theoretical  $M_n$  mainly consists in the sluggishness of the catalyst. It proved to be difficult to find the optimum time for a maximum  $M_n$ . Long times (22 h, No. 4, Table 2) are needed to achieve >95% conversion (measured by <sup>1</sup>H NMR spectroscopy), but when the time is too long (192 h) degradation affects the results (e.g., No. 5, Table 2). Second, the even-numbered chains were largely prevalent, and even a polymeriza-

tion time as long as 192 h did not suffice to achieve full equilibration. The MALDI TOF mass spectra presented in **Figure** 3A,B) illustrate this aspect. In SnOct<sub>2</sub>-catalyzed, alcohol-initiated ROPs of LA at 130 °C nearly complete equilibration is reached after 24 h as reported previously.<sup>[16]</sup> Therefore, the low reactivity of the SnNaph<sub>2</sub>-initiator is indicated by two observations: slow polymerization, and slow odd–even equilibration.

The polymerizations performed at 160 °C confirmed the above observations and conclusions. Extension to the polymerization time to 22 h enhanced the  $M_n$  and  $M_w$ , but also enhanced the dispersity. Despite such long reaction times and conversions >95% the Mn´s were significantly lower than those calculated for the reaction of both naphthol units (s. Formula II, **Scheme 5**). Interestingly, higher molecular weights were achieved than at 130 °C, when LA/In ratios of 200/1 and 400/1 were used. The MALDI TOF mass spectra revealed the following difference. At a LA/In of 100/1, the fraction of odd chains was still low (<10%) after 1.5 h, but slightly increased with time and was still far from

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**Figure 4.** MALDI TOF mass spectra of polyLAs polymerized in bulk at 160 °C with a LA/SnNaph<sub>2</sub> ratio of 100/1: A) after 6 h, B) after 22 h (Table 2).

full equilibrium after 22 h. The same trend was observed for the polyLAs prepared with a LA/In ratios of 200/1 and 400/1 as demonstrated in **Figure 4**. At a ratio of 400/1 small peaks of unidentified by products appeared and a broadening of the molecular weight distribution was detectable (Figure 4B).

Polymerizations with  $\epsilon$ -caprolactone (**Table 4**) gave similar results as lactide. No cycles, but linear chains having a bisnaphthol end group were formed at 120 °C. At 150 °C tiny peaks of cycles became detectable below m/z 1 500 (**Figure 5**A) and these peaks became intensive at 180 °C along with peaks of unidentified byproducts (Figure 5B). Remarkable are the higher molecu-



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Figure 5. MALDI TOF mass spectrum of a polyCL polymerized in bulk at 180  $^\circ\text{C}$  with a CL/SnNaph2 ratio of 100/1.

lar weights with a good agreement between theoretical and (corrected) experimental values at 120 °C. A correction factor of 0.68 was used which based on previous experiments with other catalysts. At higher temperatures the experimental data are slightly lower than the theoretical ones in agreement with the observation of cycles and other degradation products in the MALDI TOF mass spectra.

#### 3.2. Mechanistic Aspects

In the above comments the MALDI TOF mass spectra were interpreted as linear chains having a 1,1'-bisnaphthol end group (Lx) according to the formula at the bottom of Scheme 4. Yet,

Table 4. SnNaph<sub>2</sub>-catalyzed ROP of CL in bulk with variation of LA/Cat ratio, temperature, and time.

Exp. No.	La/Cat	Temp. [°C]	Time [h]	$M_{\rm n}^{~\rm a)}$ (theor)	$M_{\rm n}^{\rm b)}$ (corr.)	M <sub>n</sub> (meas.)	M <sub>w</sub> (meas.)	Disp.Đ
1	100/1	120	24	11 400	11500	15 300	29 000	1.9
2	100/1	150	1.5	11 400	11 100	14 700	28 000	1.0
3	100/1	150	3.0	11 400	11 200	15 000	30 000	2.0
4	200/1	120	24	22 800	24 000	35 500	74 000	2.1
5	200/1	150	2	22 800	21 000	31 000	60 000	1.9
6	200/1	150	4	22 800	23 500	34 500	76 000	2.2
7	200/1	180	1	22 800	20 000	30 700	70 000	2.3
8	200/1	180	4	22 800	21 200	31 000	68 000	2.2

<sup>a)</sup> calculated from LA/In ratios and 100% conversion assuming that 2 chains were initiated by one SnNaph<sub>2</sub> and including the end group (real conversions were between 95% and 97%); <sup>b)</sup> measured *M*<sub>n</sub> values multiplied with a correction factor of 0.68.





**Figure 6.** 400 MHz <sup>1</sup>H NMR spectra (segments) of: A) O bisacetylated 1,1'-bisnaphthol, B) 1,1'-bisnaphthol end group in a polyLA polymerized with a LA/SnNaph<sub>2</sub> ratio of 50/1 (No.1, Tables 2 and 3).

when both Sn-O bonds of the same bisnaphthol unit react with monomers, the primary spirocyclic reaction products may have the formulas III or IV and the polyester chains isolated after hydrolysis of the Sn-O bonds contain the bisnaphthol unit somewhere in the middle of the chains (Ly chains). Since such polyesters are isomers of the chains having a bisnaphthol end group MALDI TOF mass spectroscopy cannot differentiate between both structures. However, an unambiguous distinction between both alternatives may be expected from NMR spectroscopy, because the end group represents a non-symmetrical substitution of the bisnaphthol unit, so that the number of NMR signals should be twice as high as in the case of a symmetrical substitution. In order to obtain a model of a symmetrical substitution 1,1'-bisnaphthol was acetylated with an excess of acetic anhydride and the <sup>1</sup>H NMR spectrum of this model was compared with that of end groups in the polyLAs No. 1, Table 2, and No. 1+2, Table 3. Figure 6 displays a segment of the <sup>1</sup>H NMR spectra which provides the desired information. Whereas in the case of the symmetrical model compound only two signals appear in the range of 7.7–8.0 ppm, four signals of identical intensity are detectable in the case of the polyLA samples. Hence, the <sup>1</sup>H NMR spectra definitely demonstrate that the reaction mechanism of Scheme 4 with formation of Lx-chains is the correct interpretation of the reaction pathway. The low molecular weights found for all poly-LAs also suggest that both cycles of the same catalyst are involved (Formula IV, Scheme 5).

As already mentioned above, SnNaph<sub>2</sub> differs from SnNaph and Bu<sub>2</sub>SnNaph by a considerably lower rate of polymerization, by a considerably lower rate of odd-/even equilibration and by a considerably lower tendency to form cyclic polyGL and polyLA. The experiments of this work do not allow for complete elucidation and explanation of these properties, but a consistent hypothesis can be forwarded. Spectroscopic data and computer modelling of od-/even equilibration of alcohol-initiated ROPs of LA suggest that the last LA (or GL) unit attached to a Sn atom via a O-CHR group forms a five-membered cyclic ring via coordination of the next carbonyl oxygen with the Sn atom (Scheme 6).<sup>[17,18]</sup> If this happens twice in the case of the spirocyclic structure II





**Scheme 6.** Illustration of intramolecular donor-acceptor (DA) interaction of the lactide CO group directly neighboring the Sn atom.

(Scheme 5) the complex X in Scheme 6 is formed, where all six sp<sup>3</sup>d<sup>2</sup> orbitals are occupied. Since any kind of transesterification, regardless of intra or intermolecular requires coordination of the reaction partner prior to the rearrangement of  $\sigma$ -bonds, all transesterification reactions are hampered relative to analogous reactions of SnNaph or Bu<sub>2</sub>SnNaph.

Formula Y in Scheme 6 illustrates that the internal coordination of the last LA unit leads to occupation of five  $sp^3d^2$  orbitals, so that one orbital remains free. **Scheme 7** explains on the basis of the spirocyclic structure I (Scheme 4) how odd-/even equilibration may proceed as an intramolecular exchange of one repeat unit. If this hypothesis is correct it is again evident that in the case of structure II/X (Scheme 6) such a rearrangement is impeded by the occupation of all  $sp^3d^2$  orbitals. The same line of argumentation can be used for the formation of cyclic poly-LAs (and polyGLs). **Scheme 8** illustrates how intracircular backbiting results in formation of low molar mass cyclics. Such a mechanism has already been formulated to explain the easy formation of cyclics in REPs of  $\epsilon$ CL catalyzed by cyclic dibutyltin bisalkoxides the basic polymerization pathway of which has been outlined in Scheme 1.

2100308 (8 of 10)





**Scheme 7.** Hypothetical mechanism of an intramolecular single lactyl unit exchange.

In the case of cyclic dibutyl tin catalysts there are enough free orbitals to enable such an intramolecular cyclization at moderate temperatures, whereas the electronic structure of II/X is unfavorable. In summary, the assumption that an intramolecular coordination (by DA interaction) of the last CO group with the Sn-atom provides a consistent explanation of all experimental observations. This hypothetical explanation is strongly supported by the work of Gibson and co-workers and Carpentier and coworkers.<sup>[19,20]</sup> The existence of DA-interactions between Sn(II) and the attached lactyl unit has been proven for several Sn(II) complexes on the basis of X-ray structure analyses, NMR spectroscopy and computer modelling of the initiation reaction.

# 4. Conclusions

The ROPs of cyclic esters initiated by spirocyclic  $SnNaph_2$  include several unusual features. At temperatures  $<120^{\circ}$  linear chains having a 1,1'-bisnaphthol ester end group are formed, whereas other tin catalysts containing the 1,1'-bisnaphthol unit yield cyclic polyesters. At such low temperatures polyglycolide or polylactide almost exclusively consist of even-numbered chains. The transesterification process yielding odd-numbered chains does not broaden the molecular weight distribution and seems to involve an exchange of one single monomeric unit. Whether



**Scheme 8.** Hypothetical mechanism of intracircular cyclization with loss of a single lactyl unit.

other spirocyclic tin catalysts also show a similar unusual activity is under investigation.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Data Availability Statement**

Research data are not shared.

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