

# About the Influence of (Non-)Solvents on the Ring Expansion Polymerization of L-Lactide and the Formation of Extended Ring Crystals

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Ring-expansion polymerizations (REPs) catalyzed by two cyclic tin catalysts (2-stanna-1,3-dioxa-4,5,6,7-dibenzazepine [SnBiph] and 2,2-dibutyl-2-stanna-1,3-dithiolane [DSTL]) are performed at 140 °C in bulk. Small amounts (4 vol%) of chlorobenzene or other solvents are added to facilitate transesterification reactions (ring–ring equilibration) in the solid poly(L-lactide)s. In the mass range up to  $m/z$  13 000 crystalline PLAs displaying a so-called saw-tooth pattern in the MALDI-TOF mass spectra are obtained indicating the formation of extended-ring crystals. The characteristics of extended-ring crystallites and folded-ring crystallites are discussed. Furthermore, extremely high melting temperatures ( $T_m$ 's up to 201.2 °C) and melting enthalpies ( $\Delta H_m$ 's up to 106 J g<sup>-1</sup>) are found confirming that  $\Delta H_m$  max, the  $\Delta H_m$  of a perfect crystal, is around or above 115 J g<sup>-1</sup> in contrast to literature data.

## 1. Introduction

Since the beginning of the technical production of small amounts of pol(L-lactide)s (PLAs) for medical applications like sutures about 50 years ago, the quantity of technically produced PLA and the number of applications has dramatically increased and include for example applications as medical implants, drug delivery

systems, films for agriculture and packaging or as engineering plastic for 3D printing.<sup>[1–6]</sup> The numerous research activities concerning PLAs may roughly be subdivided into three directions:

- I. preparative and mechanistic aspects of the polymerization processes,
- II. optimization of structure and properties for certain applications,
- III. research on the fundamental chemical and physical properties of PLA

The present work concerns the third direction and is focused on the correlation between polymerization conditions and the crystallization of cyclic PLAs (cPLA). Synthesis and characterization of cPLA have rapidly increased over the past 15 years.<sup>[7–40]</sup>


The polymerization methods may be subdivided into two categories, first, polymerizations obeying the ROPPOC definition, meaning ring-opening polymerization with simultaneous polycondensation (including cyclization),<sup>[41]</sup> and second, ring-expansion polymerization (REP) using covalent cyclic catalysts.<sup>[42]</sup> The present work is based on REPs catalyzed by two cyclic tin compounds, 2,2-dibutyl-2-stanna-1,3-dithiolane (DSTL) and 2-stanna-1,3-dioxa-4,5,6,7-dibenzazepine (SnBiph, see **Scheme 1**), because these catalysts have proven in recent REPs conducted in bulk, that they may yield medium and high molecular weight cPLA with average number molecular weights ( $M_n$ ) up to 200 000 and average weight molecular weights ( $M_w$ ) up to 400 000 along with extraordinarily high melting temperatures ( $T_m$ ) and melting enthalpies ( $\Delta H_m$ ).<sup>[35,43]</sup>

As demonstrated in recent publications,<sup>[35,43]</sup> tin catalysts, including the afore-mentioned cyclic compounds have not only the capability to polymerize L-lactide (LA) but also to cause transesterification reactions in solid PLAs. These transesterification reactions involve the amorphous phase and the disordered immobile phase on the surface of the crystallites. Such transesterification reactions may have the consequence a) that the thickness of crystallites continues to grow, b) that the surface of the crystallites becomes smoother and c) that the 3d-packing of the crystallites in the spherulites achieves a higher degree of order. SnBiph and DSTL have proven to be particularly effective in this regard. However, as polymerization catalyst SnBiph has shown to be approximately ten times more active than DSTL. This scenario raises the question, why is DSTL so effective as a catalyst in transesterification reactions in solid PLA. The authors

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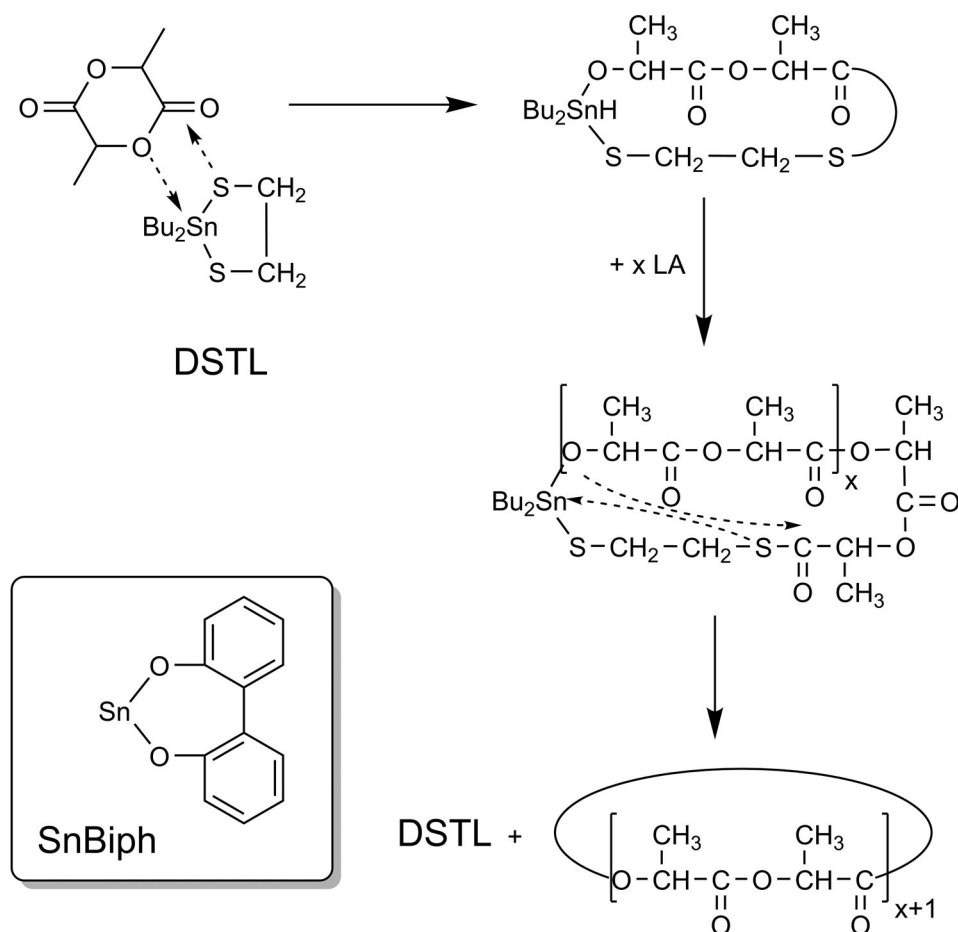
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**Scheme 1.** Mechanism of REP of L-lactide using DSTL or SnBiph as a catalyst.

have hypothesized that the mobility of DSTL in solid PLA is higher than that of SnBiph due its flexibility and lower bulkiness. To test this hypothesis, it was the first purpose of this work to perform REP and annealing processes in the presence of a small amount of a high-boiling liquid (e.g., 4 vol%) to improve the mobility of the catalysts in the amorphous and disordered immobile phase. The liquids used in this work are solvents for LA and amorphous low molar mass PLA but nonsolvents for crystalline PLA. The second purpose was to find out, to what extent  $T_m$  and  $\Delta H_m$  (and thus the crystallinity) of -PLA can be improved.

## 2. Experimental Section

### 2.1. Materials

L-Lactide (LA) a product of Corbion-Purac was kindly supplied by Thyssen-Uhde AG (Berlin, Germany) and recrystallized from "Toluene 99.89% extra dry" (ACROS Chemicals). The catalysts DSTL and SnBiph were prepared as described previously.<sup>[24,32]</sup> Chloronaphthalene, chlorobenzene (99.8% anhydrous), anisole (99.9%, anhydrous), and o-xylene (anhydrous) were purchased from Sigma-Aldrich (Taufkirchen, Germany).

**Table 1.** SnBiph-catalyzed REPs of L-lactide at 140 °C in bulk with the addition of 4 vol% of chlorobenzene (LA/Cat = 500/1a).

Exp. No.	Time [d]	$M_n$	$M_w$	$T_m$ [°C]	$\Delta H_m$ [J g <sup>-1</sup> ]	Cryst. <sup>a</sup> [%]	$L$ [nm]	$l_c$ [nm]
1A	1	172 000	445 000	191.6	68.2	51	-	-
1B	2	121 000	315 000	194.7	77.9	68	35	24
1C	4	129 000	313 000	196.9	83.2	73	34	25
1D	7	102 000	243 000	198.2	87.8	76	33	25

<sup>a</sup> Calculated with a  $\Delta H_{m,max}$  of 115 J g<sup>-1</sup>.

### 2.2. Polymerizations

#### 2.2.1. Catalyzed by SnBiph and with Addition of Chlorobenzene (Table 1)

SnBiph (0.08 mmol) and L-lactide (40 mmol) were weighed into a 50 mL flame-dried Erlenmeyer flask under a blanket of argon, chlorobenzene (0.2 mL) was injected, and a magnetic bar was added. The reaction vessel was immersed into an oil bath thermostated at 140 °C. After 1d the reaction vessel was destroyed

**Table 2.** DSTL catalyzed REPs of L-lactide at 140 °C in bulk with the addition of 4 vol% of chlorobenzene.

Exp. No.	LA/Cat	Time [d]	$M_n$	$M_w$	$T_m$ [°C]	$\Delta H_m$ [J g <sup>-1</sup> ]	Cryst <sup>a)</sup> [%]
1A	200/1	1	78 000	173 000	-	-	-
1A	200/1	2	86 000	221 000	194.8	102.5	89
1B	200/1	4	82 000	203 000	197.4	101.5	88
1CX	200/1	7	61 000	167 000	198.5	98.2	85
1CY	200/1	7	-	-	199.2	101.1	88
2A	500/1	2 <sup>b)</sup>	123 000	290 000	199.6	99.3	86 <sup>b)</sup>
2BX	500/1	4 <sup>c)</sup>	90 000	250 000	201.2	105.6	92 <sup>c)</sup>
2BY	500/1	4	83 000	231 000	200.5	102.5	89
3C	500/1	7 <sup>d)</sup>	102 000	280 000	200.9	105.4	92 <sup>d)</sup>
3A	1 000/1	4	83 000	222 000	199.4	101.9	89
3B	1 000/1	7	66 000	171 000	196.5	104.6	91

<sup>a)</sup> Calculated with a  $\Delta H_m$ , max of 115 J g<sup>-1</sup>; <sup>b)</sup>  $L = 31(+/-1)$  nm,  $l_c = 27$  nm; <sup>c)</sup>  $L = 30(+/-1)$  nm;  $l_c = 28$  nm<sup>1)</sup>; <sup>e)</sup>  $L = 35(+/-1)$  nm,  $l_c = 32$  nm.

to isolate the crystalline plaque of the cPLA. The virgin plaque was broken or sawn into four pieces, two of which were used of characterization, whereas the other two pieces were annealed for one more day in an argon atmosphere. In a parallel experiment, the polymerization was stopped after 4 d and part of the resulting crystalline cPLA was annealed for three more days.

### 2.2.2. Catalyzed by DSTL and with Addition of Chlorobenzene (Tables 2 and 3)

These REPs were performed analogously to the polymerizations described above. The REPs of Table 2 were conducted with 0.25 mmol, 0.08 mmol or 0.04 mmol of DSTL. In the case of Table 3 0.1, 0.2, 0.3, or 0.5 mL of chlorobenzene was added, whereas the amount of DSTL (0.08 mmol) was constant. After characterization of the virgin polymerization products, they were dried at 70 °C in vacuo for 3d and characterized again.

### 2.2.3. Catalyzed with DSTL and Variation of the Solvent

These polymerizations were performed as described above with 0.08 mmol of DSTL and the addition of various (non-)solvents (0.2 mL).

## 2.3. Measurements

The MALDI TOF mass spectra were recorded with an Autoflex Max mass spectrometer Bruker Daltonik, Bremen, Germany) in the linear positive ion mode. 8000 single spectra recorded at four different, randomly chosen positions of the sample spot were accumulated for one spectrum. The MALDI targets were prepared from chloroform solutions of PLA (3–5 mg mL<sup>-1</sup>) doped with potassium trifluoroacetate (2 mg mL<sup>-1</sup>). Typically, 20  $\mu$ L of sample the solution, 2  $\mu$ L of the potassium salt solution, and 50  $\mu$ L of a solution of 2-[(2E)-3-(4-tert-Butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB).

The GPC measurements were performed in an Agilent 1100 HPLC (Agilent, USA) system running with 1 mL min<sup>-1</sup> flow rate at 40 °C. The system was equipped with a refractive index detector. Samples dissolved in chloroform (2–4 mg mL<sup>-1</sup>) were automatically injected (100  $\mu$ L). For instrument control and data calculation WinGPC software (Polymer Standards Service – PSS, Mainz) was used. The calibration was performed using polystyrene standard sets (PSS, Mainz). The number average ( $M_n$ ) and weight average molecular weights ( $M_w$ ) listed in the table below are not corrected because the hydrodynamic volume of cyclic PLAs is nearly identical with that of polystyrene in contrast to the hydrodynamic volume of the linear PLAs.

The DSC heating traces were recorded on a (with indium and zinc freshly calibrated) Mettler–Toledo DSC-1 equipped with Stare Software-11 using a heating rate of 10 K min<sup>-1</sup>. Several samples listed in Table 4 were also measured at the Institute for Polymer Research in Dresden with a DSC 2500 TA instrument again with a rate of 10 K min<sup>-1</sup>. Only the first heating traces were evaluated.

The SAXS measurements were performed using the in-house SAXS/WAXS apparatus equipped with an Incoatec X-ray source I $\mu$ S and Quazar Montel optics. The wavelength of the X-ray beam was 0.154 nm and the focal spot size at the sample position was 0.6 mm<sup>2</sup>. The samples were measured in transmission geometry and were recorded with a Rayonix SX165 CCD-Detector. The SAXS measurements were performed at sample-detector distance of 1.6 m and the accumulation was 1200 s. DPDAK, a customizable software for reduction and analysis of X-ray scattering data sets was used for gathering 1D scattering curves.<sup>[44]</sup> For the evaluation of the crystallinity of the samples, the data were imparted in Origin and analyzed with the curve fitting module. After subtracting of the instrumental background, the integral intensity of the crystalline reflections was divided by the overall integral intensity to determine the crystallinity  $X_c$ . The SAXS curves were converted into Kratky plots. The long periods of the lamellar domains were determined by the  $q$  values of the reflection maxima. All reflections were weak, so that a margin of error of +/-1 nm must be taken into account.

## 3. Results and Discussion

### 3.1. SnBiph-Catalyzed REPs

All polymerizations of this work were performed at 140 °C for comparison with the experiments of a previous study, where the REPs with SnBiph and DSTL were conducted in bulk. This temperature has proven to be an optimum for transesterification in solid PLAs and low enough to avoid degradation reactions at long reaction times (>4d). For the first small series of REPs SnBiph was used as catalyst and chlorobenzene as (non-)solvent (Table 1), whereas a more detailed variation of the experimental conditions was performed with DSTL, because higher  $T_m$  and  $\Delta H_m$  values were obtainable with this second catalyst. The experiments with DSTL had shown that chlorobenzene gave better results (in terms of molecular weights and  $T_m$ 's) than the other aromatic solvents. Therefore, chlorobenzene was the only (non-)solvent used for the polymerizations conducted with SnBiph as a catalyst. For the REPs performed with SnBiph the time was varied between 1 d and 7 d and cPLA with  $M_n$ 's above 100 000 and  $M_w$ 's up to 315

**Table 3.** REPs of L-lactide in bulk at 140 °C catalyzed by DSTL (LA/Cat = 500/1) with variation of the added chlorobenzene volume.

Exp. No.	Volume [%]	Time [d]	$M_n$	$M_w$	$T_m^a$ [°C]	$\Delta H_m^a$ [J g <sup>-1</sup> ]	$T_m^b$ [°C]	$\Delta H_m^b$ [J g <sup>-1</sup> ]	Cryst. <sup>d</sup> [%]
1AX	2	4	90 000	214 000	198.0	101.1	197.9	103.5	90
1B	2	7	56 000	113 000	197.6	106.0/108.3 <sup>c</sup>	-	-	-
2A	4	4	80 000	195 000	199.8	101.0	200.0	102.6	89
2B	4	7	49 000	118 000	198.2	104.4/107.3 <sup>c</sup>	-	-	-
3AX	6	4	68 000	198 000	199.3	98.0	201.0	100.3	87
3B	6	7	48 000	125 000	197.7	104.1/(103.5) <sup>c</sup>	-	-	-
4AX	10	4	59 000	196 000	200.4	101.5	200.5	103.1	90
4B	10	7	47 000	128 000	196.3	104.9/108.5 <sup>c</sup>	-	-	-

<sup>a</sup> Virgin samples containing chlorobenzene; <sup>b</sup> After drying at 80 °C in vacuo; <sup>c</sup> Measured at the IPF in Dresden; <sup>d</sup> Calculated for the dry samples.

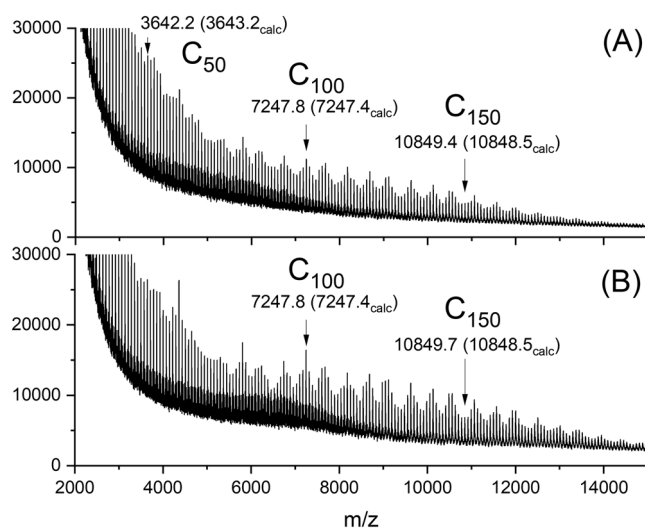
**Table 4.** DSTL-catalyzed REPs at 140 °C in bulk with addition of various non-solvents (vol fraction 4%; (LA/Cat = 500/1).

Exp. No.	Nonsolvent	Time [d]	$M_n$	$M_w$	$T_m$ [°C]	$\Delta H_m$ [J g <sup>-1</sup> ]	Cryst. [%] <sup>a</sup>
1A	1,2-Xylene	4	48 000	110 000	195.8	106.7	92
1B	1,2-Xylene	7	36 000	78 000	-	-	-
2A	Anisole	4	76 000	215 000	199.2	101.7	88
2B	Anisole	7	75 000	245 000	200.8	104.4	91
4A	1,2-Dichlorobenzene	4	65 000	167 000	197.2	96.3	83
4B	1,2-Dichlorobenzene	7	58 000	153 000	196.6	103.2	90
5A	2-Chloronaphthalene	4	71 500	241 000	197.5	94.5	82
5B	2-Chloronaphthalene	7	69 000	165 000	197.5	95.9	83
6A	Di-n-butyl ether	4	52 000	103 000	191.8	98.9	86
6B	Di-n-butyl ether	7	35 000	79 000	193.0	103.7	91

<sup>a</sup> Calculated with a  $\Delta H_m$  max of 115 °C.

000 were obtained in analogy to previous REPs conducted at 160 °C with short reaction times (<3 h). The MALDI TOF mass spectra showed that the “saw-tooth pattern” (STP) began to appear already after 1 d, it became clearly evident after 2 d (**Figure 1A**) and was more pronounced after 7 d (**Figure 1B**). When compared with previous experiments performed in bulk without addition of a (non-) solvent, the REPs listed in Table 1 indicate that at least chlorobenzene facilitated the formation of the STP.

It is important to emphasize, that in this work and in recent studies the STP is always formed in connection with the appearance of a new maximum in the molecular weight distribution between  $m/z$  5 000 and 12 000–15 000 (as demonstrated by the MALDI mass spectra). The formation of this maximum indicates that crystallites consisting of cycles having masses in that mass range are thermodynamically favored, so that smaller and larger cycles are gradually transformed into these cycles via transesterification reactions mainly via the ring-ring equilibration reaction outlined in **Scheme 2**. Considering the SAXS measurements discussed recently the formation of this maximum along with STP has been explained by the following hypothesis. The crystallites formed by cycles having masses between  $m/z$  5000 and 15 000 are formed by extended rings, so each crystallite consists of rings with narrow molecular weight distribution. Each tooth represents a class of crystallites defined by identical thickness.

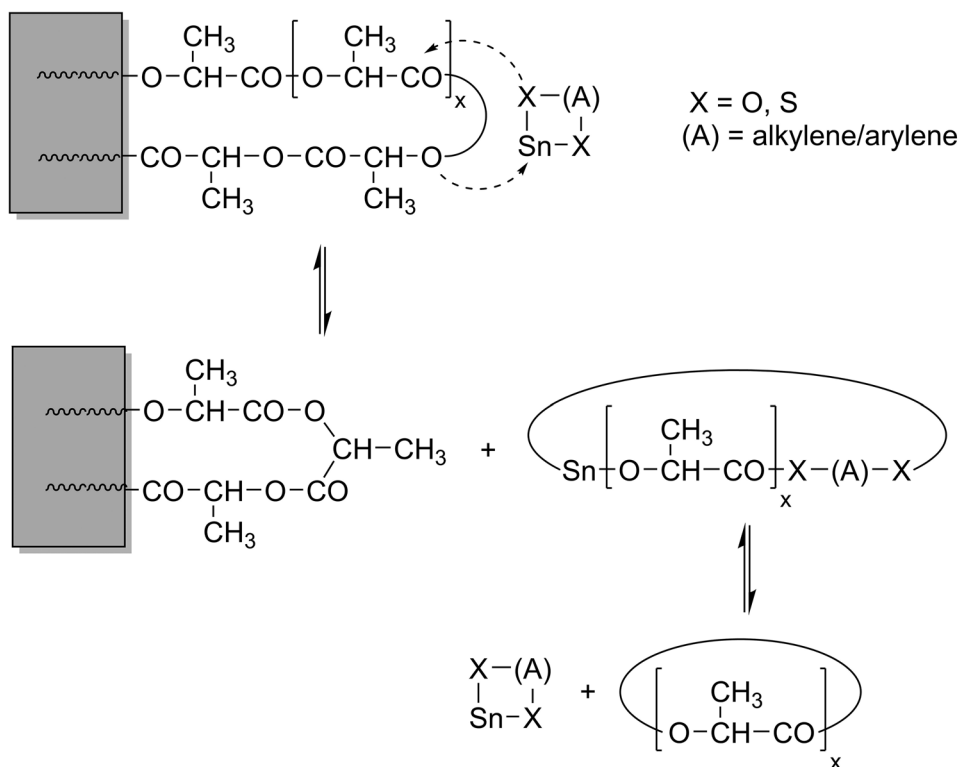


**Figure 1.** MALDI TOF mass spectra of cPLA prepared with SnBiph at a LA/Cat ratio of 500/1: A) isolated after 2 (No. 2B, Table 1); B) after 7 d (No. 1D, Table 1).

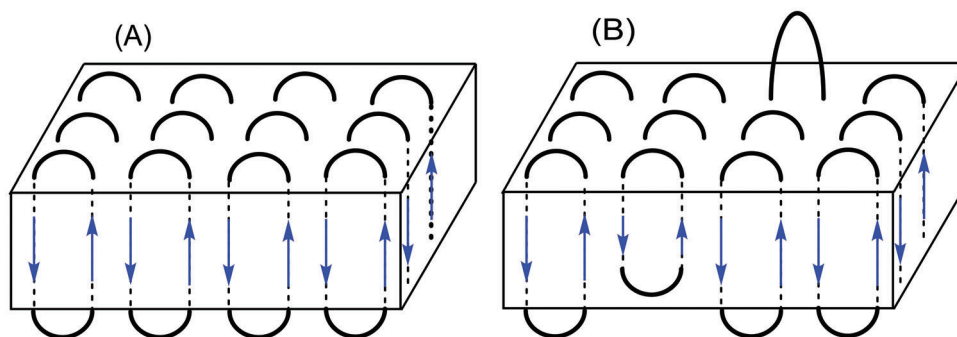
The highest peak of a tooth indicates the cycles with the greatest abundance in these crystallites, cycles having one or two repeat units more or less are somewhat less abundant.

For the following reasons, such crystallites represent a thermodynamic optimum. First, when the loops of neighboring cycles differ by only one or two repeat units, a relatively smooth energetically favorable surface is the result. Second, short cycles, which have the consequence that loops are buried inside the crystals (see **Figure 2B**), are not accepted and left to thinner crystallites. Third, in contrast to crystallized linear chains, crystallized cycles contain necessarily a perfect 1:1 ratio of antiparallel chain segments in the crystal lattice (indicated by the arrows in **Figure 2A**). Fourth, the loops of larger cycles that may stick out from the crystal surfaces immediately after crystallization (**Figure 2B**) are shortened by transesterification (**Scheme 2**).

The  $M_n$  and SAXS measurements (for typical examples see **Figure 3**) listed in Table 1 also shed light on the crystallization of larger cycles. Basis of this consideration is the X-ray studies of Wasanasuk et al. who determined that the length of 10 repeat units (lactyl units) in the 10<sub>3</sub>-helical conformation of the  $\alpha$ -modification of PLA amounts to 2.89 nm.<sup>[45]</sup> Annealed cPLA typ-



**Scheme 2.** Possible transesterification leading to a shortening or growing of loops on a crystal surface.

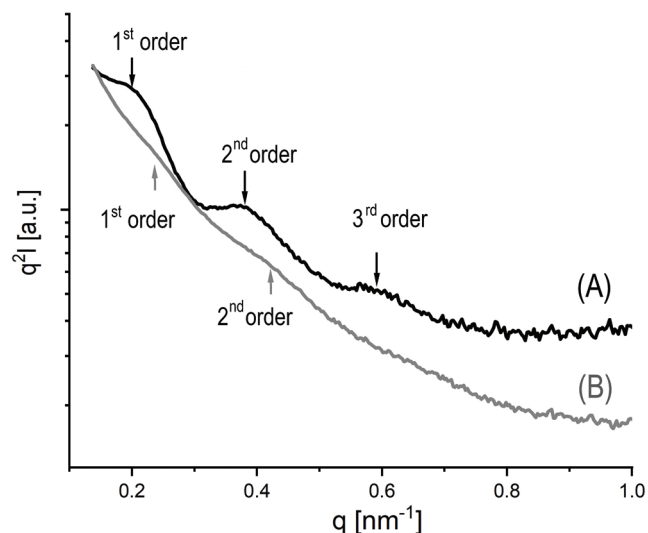


**Figure 2.** Schemes of crystallites: A) Composed of extended rings having a low dispersity, B) containing a smaller or larger ring than required for an optimum extended-ring crystal.

ically have crystal thicknesses ( $l_c$ ) in the range of 20–28 nm,<sup>[35,38]</sup> and the values recorded for the SnBiph catalyzed samples listed in Table 1 fall into this range. For example, a crystal thickness of 25 nm corresponds to chain segment of  $\approx 85$  repeat units, including two loops with together 8 units. This means that an extended cycle of such a crystallite consist of approximately 180 lactyl units corresponding to a mass of  $\approx 13\,000$  Da. The incorporation of larger cycles, such as those having masses in the range of 16 000–22 000 Da reduces the perfection of the crystallites in two ways. Either they do not fold, and large loops stick out from the surfaces of the crystallites (see Figure 2B) or they fold once, and at least one the loop of one “ring end” is buried inside the crystal lattice causing a significant defect. When the cycles have

a mass of  $\approx 26\,000$  Da they can accommodate to the thickness of the crystallite by folding once in the middle of the extended cycle. However, the loops resulting from folding and those representing the “ring ends” will adopt a perpendicular position on the surface of the crystallite (Figure 4A), whereupon the perfection of the surface is reduced relative to that of an extended-ring crystal. With increasing ring-size the number of folds will increase, and cycles having a  $M_n$  around 130 000 (corresponding to the  $M_n$  of No 1C, Table 1) can form rather perfect crystallites with a thickness of 25 nm, when folding nine times as illustrated by Figure 4B. The perfection of the surface increases with the number of folds, because all the loops of the folds will adopt a parallel arrangement. Hence, ring folding in combination with ring-ring





**Figure 3.** SAXS curves (Kratky plots) of PLAs isolated after 4d at 140 °C: A) No. 2BX, Table 2, B) No. 1C, Table 1

equilibration (Scheme 2) across the surface has the consequence that even samples having high molar masses and high dispersities can reach extraordinarily high  $T_m$ 's and crystallinities, although the weight fraction of the perfect extended-ring crystals will certainly be below 20% or even below 10%. This conclusion is supported by the results obtained with DSTL-catalyzed REPs.

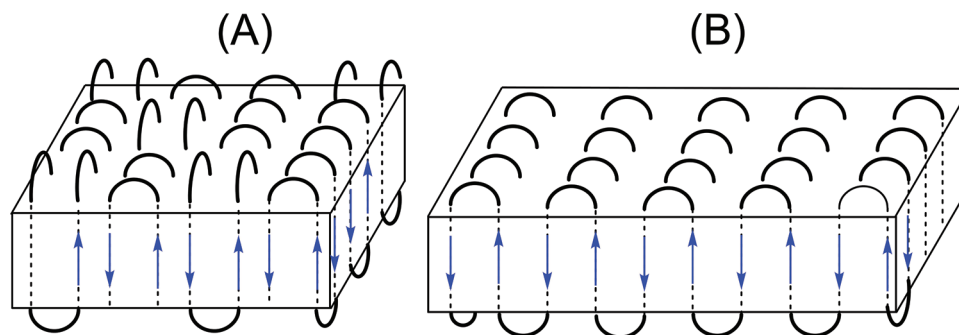
### 3.2. DSTL-catalyzed REPs

In the beginning of this work DSTL-catalyzed polymerizations were conducted in six different aromatic solvents and chlorobenzene was found to give the highest molecular weights, the highest  $T_m$ 's, and the "cleanest" MALDI TOF mass spectra. Hence, the role of chlorobenzene was studied in more detail (Tables 2 and 3). The experiments summarized in Table 2 had the purpose to study the influence of the LA/Cat ratio and the influence of the annealing time, whereas the volume of chlorobenzene was fixed at 4% in analogy to the experiments with SnBiph. The GPC data showed three trends. Again, in analogy to most SnBiph-catalyzed REPs  $M_w$ 's around 300 000 were obtained. The  $M_n$ 's and  $M_w$ 's slightly decreased with higher LA/Cat ratios and they

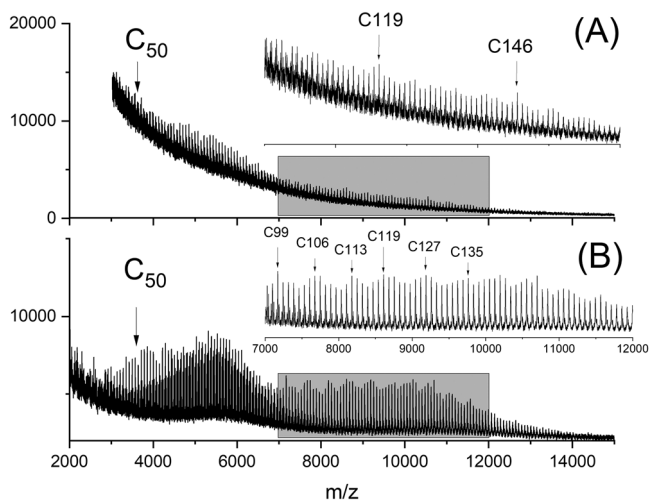
decreased considerably with longer annealing times. The DSC measurements, conducted as usual for PLAs, with a heating rate of 10 K min<sup>-1</sup> yielded the highest  $T_m$  and  $\Delta H_m$  values for the LA/Cat ratio of 500/1. These values were higher than those obtained with SnBiph. Three samples of Table 2 and one sample of Table 3 gave  $T_m$ 's even slightly above 200 °C. Two  $T_m$ 's between 200 and 201 °C had already been found for DSTL catalyzed REPs of LA in bulk, and thus, the  $T_m$  data listed in Tables 2 and 3 confirm that optimized crystallites of cyclic PLAs may indeed have  $T_m$ 's  $\approx$  200 °C. More important are the extremely high  $\Delta H_m$  values, which reached values up to 106 J g<sup>-1</sup> when measured on a Mettler Toledo instrument at the TMC institute in Hamburg or up to 108.5 J g<sup>-1</sup> when recorded with a TA 2500 instrument at the Institute for Polymer Research (IPF) in Dresden (see footnote c) of Table 3). The numerous  $\Delta H_m$  values above 100 J g<sup>-1</sup> found in this work confirm the few similarly high values found for DSTL-catalyzed REPs in bulk. These  $\Delta H_m$  values are remarkable not only as a record, but they also have the consequence that all the  $\Delta H_m$  max values previously reported by other groups as a characteristic property of an ideal PLA crystal are too low (93 J g<sup>-1</sup>,<sup>[46]</sup> 91 J g<sup>-1</sup>,<sup>[47]</sup> 106 J g<sup>-1</sup>,<sup>[48,49]</sup> 68 J g<sup>-1</sup><sup>[19]</sup>). This means, in turn, that all the crystallinities previously determined via DSC measurements using the lower  $\Delta H_m$  max values as reference are in fact too low. In our quite recent study of DSTL-catalyzed REPs in bulk it was concluded that a melting enthalpy of 115 J g<sup>-1</sup> is the minimum  $\Delta H_m$  max, and values up to 120 J g<sup>-1</sup> might even be more realistic. Based on these DSC results and their interpretation the crystallinities listed in Tables 1–4 were calculated with a  $\Delta H_m$  max of 115 J g<sup>-1</sup>.

The positive influence of a suitable (non)solvent such as chlorobenzene on the optimization of the cPLA crystallites is also indicated by the formation of the STP in the mass spectra of all samples listed in Tables 2 and 3 after annealing for more than 1 d. **Figure 5** illustrates exemplarily the influence of the time.

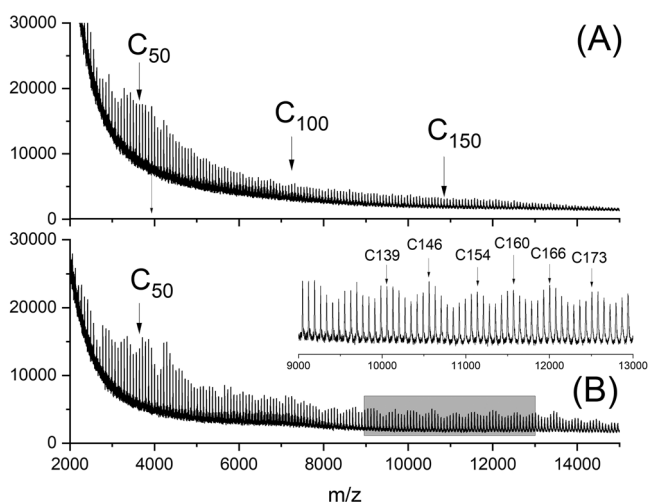
The experiments summarized in Table 3 had the purpose to find out, to what extent the volume fraction of the (non)solvent influences the properties of resulting PLAs. Somewhat unexpected for the authors it was found that variation of the volume fraction between 2% and 10% had little influence on molecular weights,  $T_m$  and  $\Delta H_m$ . When the DSC measurements were performed after drying in vacuo slightly higher  $T_m$ 's and  $\Delta H_m$ 's were recorded, what means that the DSC data of the virgin samples listed in Tables 2 and 3 rather underestimate than overrate the



**Figure 4.** Schemes of crystallites: A) Crystallite consisting of once-folded rings having twice the size required for an extended-ring crystal, B) formation of a crystallite with a thickness of 25 nm by folding of a ring with  $M_n = 130\ 000$  Da.



**Figure 5.** MALDI TOF mass spectra of cPLA prepared with DSTL at a LA/Cat ratio of 200/1: A) after 2 d (No. 1A, Table 2), B) after 7 d (No. 1CY, Table 2).



**Figure 6.** MALDI TOF mass spectra of cPLA prepared with DSTL at a LA/Cat ratio of 500/1: A) Addition of di-n-butyl ether after 4 d (No. 6A, Table 4), B) addition of anisole after 4 d (No. 2A, Table 4).

real values. The fact that all samples gave  $\Delta H_m$  values above  $100 \text{ J g}^{-1}$  underlines that the addition of small amounts of chlorobenzene has a beneficial influence on the optimization of the cPLA crystallites.

Table 4 summarizes the results of REPs conducted with the addition of various (non)solvents (with exclusion of chlorobenzene). Three points should be highlighted. First, the lowest molecular weights were obtained with di-n-butyl ether. Second, the highest  $T_m$  and  $\Delta H_m$  values were achieved with the addition of anisole. Third, di-n-butyl ether and anisole also differ with respect to their MALDI TOF mass spectra. As illustrated in **Figure 6**, the former (non-)solvent does not yield a STP, whereas the cPLA produced in anisole displays a clear STP, which covers the mass range from  $m/z$ . 3000 to 15 000, the highest mass range the authors have observed so far.

## 4. Conclusions

The results of this work allow for the following conclusions. First, for transesterification reactions in solid PLAs DSTL was superior to SnBiph whether (non-) solvents were added or not. Second, the addition of (non-)solvents facilitated a rapid formation of extended-ring crystallites including the formation of the saw-tooth-pattern (STP) in the MALDI mass spectra. However, (non-) solvents also favor side reactions at long reaction times (7 d). Chlorobenzene is superior to other aromatic solvents tested in this work by yielding higher molecular weights, and it also favors the modification of the surfaces of all crystallites, so that extremely high  $T_m$ 's and  $\Delta H_m$ 's can be achieved, which, together with other recently reported REPs conducted in bulk, require that all previously published  $\Delta H_m$  max values need to be replaced by a higher value, and a value of  $115 \text{ J g}^{-1}$  proposed quite recently, seems indeed to be a useful approach to the reality.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

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

## Keywords

crystallization, cyclization, poly(L-lactide), ring-expansion polymerization

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