



Ring-ring equilibration (RRE) of cyclic poly(L-lactide)s by means of cyclic tin catalysts

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ABSTRACT

With 2,2-dibutyl-2-stanna-1,3-dithiolane (DSTL) and 2-stanna-1,3-dioxo-4,5,6,7-dibenzoxepane (SnBiPh) as catalysts ring-expansion polymerizations (REP) were performed either in 2 M solution using three different solvents and two different temperatures or in bulk at 140 and 120 °C. A kinetically controlled rapid REP up to weight average molecular masses (M_w s) above 300 000 was followed by a slower degradation of the molecular masses at 140 °C, but not at 120 °C. Furthermore, a low molecular mass cyclic poly(L-lactide) (cPLA) with a M_n around 16 000 was prepared by polymerization in dilute solution and used as starting material for ring-ring equilibration at 140 °C in 2 M solutions. Again, a decrease of the molecular mass was detectable, suggesting that the equilibrium M_n is below 5 000. The degradation of the molecular masses via RRE was surprisingly more effective in solid cyclic PLA than in solution, and a specific transesterification mechanism involving loops on the surface of crystallites is proposed. This degradation favored the formation of extended-ring crystallites, which were detectable by a “saw-tooth pattern” in their MALDI mass spectra.

1. Introduction

Ring-Ring equilibration (RRE) is a kind of reaction that *a priori* cannot be classified either as polymerization process or a degradation reaction, because it may belong to both groups of reactions depending on the starting material. If the starting materials are cyclic monomers or dimers, the equilibration will necessarily yield higher molecular masses and thus, merit the classification as polymerization. However, if the starting material is a high molecular mass cyclic polymer (e. g. with $M_n > 100\ 000$ and $M_w > 200\ 000$), ring-ring equilibration will most likely result in a reduction of the average molecular masses due to the formation of small cycles. Therefore, RREs require a new definition of conversion, because 100 % conversion can neither be defined by 100 % conversion of a monomer (typical for chain growth polymerization), nor by 100 % conversion of functional groups (typical for step-growth polymerization). Regardless of whether low or high molecular mass cycles serve as starting materials the final goal of the equilibration is the equilibrium concentration of each cycle. Thus, the equilibrium concentration represents 100 % conversion, and based on this consideration a new definition of conversion was formulated in a recent review article on the meaning of conversion in polymer science.[1] It is therefore

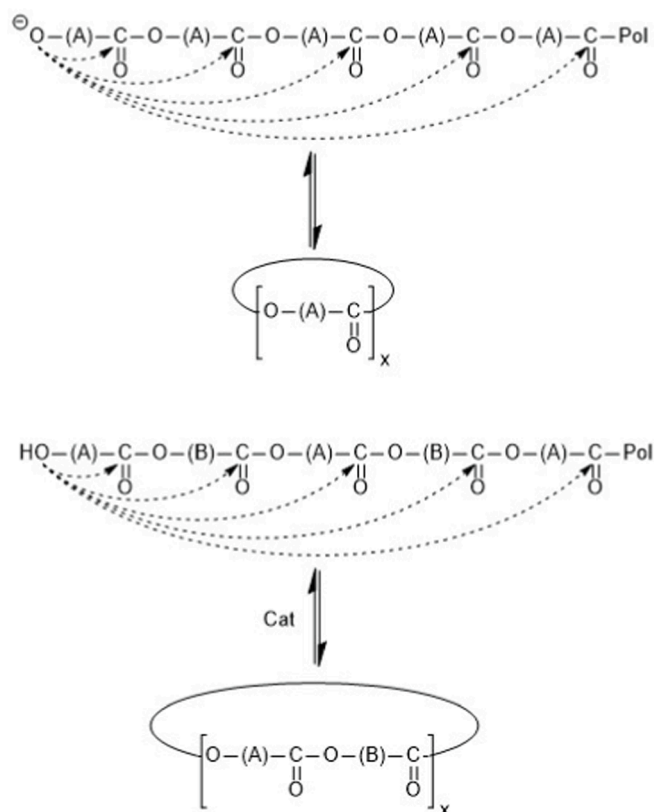
impossible to determine the conversion if the equilibrium concentration is unknown. Therefore, it is of great interest to determine the equilibrium concentration for a given system.

From the point of view of reaction mechanisms, RREs can be divided into two categories, namely reaction pathways involving linear chains (I), or reaction pathways based exclusively on reactions between cycles (II). In the first category an active chain end of the linear species plays the role of catalyst (Scheme 1), whereas in the second category at least one type of cycles must be present, which acts as catalyst (Schemes 2 and 3).

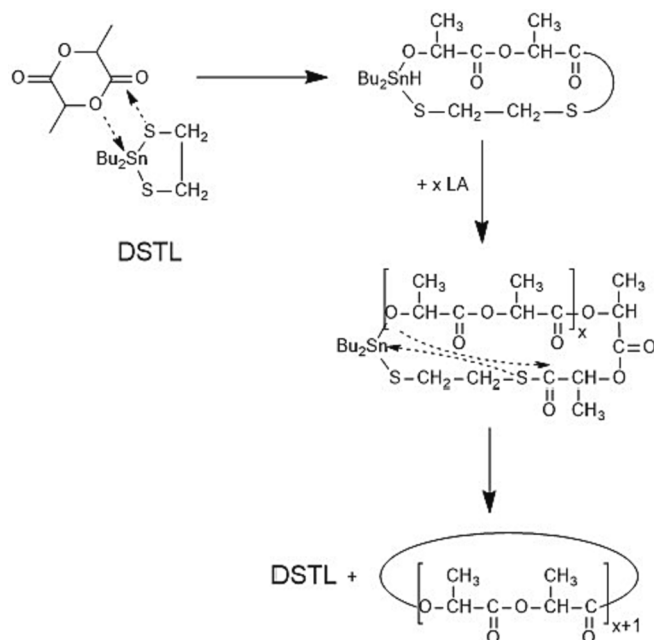
A first experimental and theoretical study of category (I) was the work of Jacobson and Stockmayer, who postulated that reversible polycondensations involve reversible formation of cycles from active chain ends.[2,3] In the following decades numerous experimental studies dealing with this concept were published. [4–9] The second category (II) is a relatively new approach mainly involving covalent cyclic tin catalysts. First steps in this direction were published by the first author after 1994.[10–14] In this context the present work had the purpose to study the consequences of RRE for L-lactide and cyclic poly(L-lactide)s. 2,2-Dibutyltin-2-stanna-1,3-dithiolane (DSTL) was used for most of the experiments, because the Sn-S bond is less basic than the Sn-

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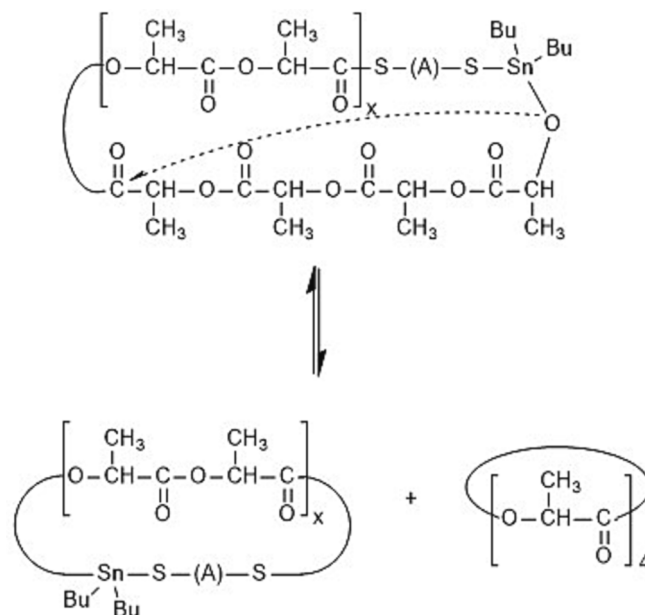


Scheme 1. Reversible formation of cyclic esters from a ring-opening polymerization of lactones or from a polycondensation of diols and dicarboxylic acid esters.



Scheme 2. Ring-expansion polymerization of lactide catalyzed by DSTL.

O bond and thus, less prone to cause side reactions when the reaction mixtures were heated for several weeks at temperatures in the range of 120–140 °C. [12] Additional experiments were conducted with SnBiph which is about ten times more reactive as polymerization catalyst than DSTL. [12] Ring-expansion polymerization (REP) and RRE of LA were



Scheme 3. Equilibration of cyclic PLA catalyzed by DSTL.

compared with RRE of preformed cyclic poly lactides (cPLA), and RRE in solution was compared with RRE in solid PLA.

2. Experimental

2.1. Materials

L-Lactide (LA) was kindly supplied by Thyssen-Uhde (Berlin, Germany) and recrystallized from Toluene (99.89 % extra dry, Acros Organics now Thermo Scientific Chemicals, Germany). Anisole (99.7 % anhydrous) and anhydrous *o*-dichlorobenzene were purchased from Sigma-Aldrich (Taufkirchen, Germany). The catalysts 2,2-dibutyl-2-stanna-1,3-dithiolane (DSTL)13 and 2-stanna-1,3-dioxa-4,5,6,7-dibenzoxepane (SnBiph) were prepared as described previously. [15] The catalyst 2-dibutyltin bis(pentafluorophenoxide) was prepared from Bu_2SnO and pentafluoro-phenol as described previously. [16] *o*-Dichlorobenzene and anisole anhydrous were purchased from Thermo-Fisher Scientific (Schwerte, Germany) and stored over mol sieves.

2.2. Syntheses of cyclic PLA

A) Low molecular mass cyclic PLA (low cPLA)

Dibutyltin bis(pentafluorophenoxide) (0.5 mmol) and LA were weighed into a flame-dried 250 mL round-bottom, flask under a blanket or argon and a magnetic bar was added. The reaction vessel was immersed into an oil bath thermostated at 115 °C, and after 6 d the reaction mixture was concentrated in vacuo at a bath temperature of 40 °C until the PLA began to crystallize. The resulting suspension was then precipitated into ligroin (1.2 L) with stirring. The precipitated PLA was isolated by filtration and dried in vacuo at 60 °C.

B) High molecular mass PLA (high cPLA) via equilibration of LA

DSTL (0.2 mmol) and LA (40 mmol) were weighed into a 50 mL Erlenmeyer flask under an argon blanket and a magnetic bar was added. The reaction vessel was immersed into an oil bath thermostated at 140 °C. The polymerization was followed by crystallization within 1 d. Finally, the virgin reaction product was characterized. The cPLA isolated after 1 d was divided into two parts, one of which was used for characterization, while the second part was annealed for two more days. In

an analogous experiment the cPLA was isolated after 7 and 10 d and in a third parallel experiment the reaction product was characterized after 21 d.

2.3. Equilibration of low molecular mass cPLA

a) In solution

DSTL (0.6 mmol) and a low molecular mass cPLA (30 mmol) were weighed into a flame-dried round bottom flask and a magnetic bar was added. Chlorobenzene (12 mL) (10 % excess to compensate for a loss by evaporation) and dichloromethane (15 mL) were added, and the reaction vessel was gently shaken until a clear solution was obtained. The reaction vessel was sealed with a one-way valve and immersed into an oil bath thermostated at 140 °C. After annealing the resulting PLA was characterized in the virgin state.

The experiments in o-dichlorobenzene and anisole were performed analogously.

b) In the solid state

DSTL (0.6 mmol) and low cPLA (30 mmol) were weighed into a flame-dried 50 mL round-bottom flask and a magnetic bar was added. The contents of the reaction vessel were dissolved in dichloromethane (20 mL), the reaction vessel was equipped with a one-way valve and slowly immersed into an oil bath thermostated at 140 °C. After evaporation of the solvent the round bottom flask was sealed with a glass stopper (held in place by a steel spring) and the reaction mixture was annealed for several days (see Table 1). Finally, the crude reaction product was characterized.

2.4. Measurements

The MALDI TOF mass spectra were recorded with an Autoflex Max MALDI TOF mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) in the linear positive ion mode. Typically, 8000 individual spectra recorded at 4 different, randomly selected positions of the sample spot were accumulated for one spectrum. The MALDI targets were prepared from chloroform solutions of PLA (3–5 mg mL⁻¹) doped with potassium trifluoroacetate (2 mg mL⁻¹). Typically, 20 µL of the sample solution, 2 µL of the potassium salt solution (0,01 M in tetrahydrofuran) and 50 µL of a solution of 2-[(2E)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB, 20 mg mL⁻¹ in chloroform (CHCl₃)) were pre-mixed in an Eppendorf vial. 1 µL of this solution was dropped in the stainless steel MALDI target. FlexControl software (Bruker) was used for data acquisition and Origin 2021 (OriginLab Corporation, USA) for data evaluation and drawings.

The GPC measurements were performed an Agilent 1200 series instrument (Agilent, USA) at 40 °C with a flow rate of 1 mL min⁻¹. A refractive index detector was used. Samples were dissolved in chloroform (2–4 mg mL⁻¹). WINGPC (Polymer Standards Service - PSS, Mainz, Germany) was used for instrument control and data calculation.

Table 1

REP and Equilibration of LA with DSTL in o-dichlorobenzene at 140 and 120 °C.

Exp. No.	Temp. (°C)	Time (h)	Yield (%)	M _n	M _w	Disp. D
1A	140	1	92	87 000	170 500	1.96
1B	140	4	93	81 000	146 000	1.80
1C	140	7	92	61 000	107 000	1.75
1D	140	11	93	47 500	87 000	1.83
1E	140	21	94	26 000	59 000	2.27
2A	120	1	91	17 000	33 000	1.94
2B	120	7	93	34 500	100 000	2.90
2C	120	14	93	41 000	327 000	7.98
2D	120	21	93	42 000	351 000	8.36
2E	120	28	91	39 000	320 000	8.21

Calibration was performed using polystyrene standard sets (PSS, Mainz). The number average (M_n) and weight average molecular masses (M_w) listed in the tables are not corrected because the hydrodynamic volume of cyclic PLA is nearly identical with that of polystyrene, in contrast to the hydrodynamic volume of linear PLA.

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⁻¹. Only the first heating traces were considered.

3. Results and discussion

3.1. REP and equilibration of LA in solution

For three reasons, most equilibration experiments of this study were performed with DSTL as the catalyst. First, the Sn-S group is less basic than the Sn-O group and thus less prone to catalyze side reactions, such as racemization or β-elimination. This aspect was important because of the long reaction times at temperatures above 120 °C. Second, DSTL is soluble in all non-polar solvents used in this work, even at high concentrations. Third, high molecular masses (M_n > 100 000 and M_w > 300 000) can be obtained with this catalyst as shown in a recent publication and confirmed by the results presented below. A rather high catalyst concentration corresponding to an LA/Cat ratio of 50/1 was used in most experiments to accelerate the equilibration, taking into account that this concentration did not hinder the formation of high molecular masses, because in a ring expansion polymerization (REP) and in ring-ring equilibration the molecular mass is not parallel to the monomer/catalyst ratio.

Two parallel series of experiments were performed in o-dichlorobenzene (Table 1) and in chlorobenzene (Table 2) at a reaction temperature of 140 °C (higher temperatures were avoided to prevent side reactions and to avoid a high vapor pressure of chlorobenzene). Both series had in common that the reaction mixtures remained clear over the entire reaction time of 3 weeks. Furthermore, the MALDI TOF spectra, exclusively displaying peaks of cycles (see Figure S1, Supplementary Information), did not change during the reaction time of 3 weeks. Moreover, a considerable decrease of the molecular masses to about one third of the initial maximum was found. In chlorobenzene at 140 °C (No. 1A-1E, Table 2) the molecular masses were higher, possibly due to a higher purity of the solvent, but the trends were the same as those found in o-dichlorobenzene. The mass spectra were identical to those displayed in Figure S1 and the molecular masses decreased by about 2/3 within 21 days. At 120 °C, quite different results were found. The solution in o-dichlorobenzene was still clear after 7 d, and a MALDI mass spectrum almost identical to that obtained at 140 °C was recorded (Fig. 1A), but after 14 d gelation had occurred. Upon heating to 140 °C, the gelation disappeared and reappeared upon cooling to 20 °C. This observation proves that the gelation was based on aggregation and not on crystallization. A similar phenomenon was recently observed for low molecular mass PLA in toluene.[17] Heating after 21 or 28 d removed part of the gelation but left a turbid solution suggesting that a small fraction of crystallites had formed. This suggestion was confirmed by the

Table 2

REP and equilibration of LA with DSTL (50/1) in chlorobenzene at 140 and 120 °C.

Exp. No.	Temp. (°C)	Time (d)	Yield (%)	M _n	M _w	Disp. D
1A	140	1	94	127 000	327 000	2.57
1A	140	7	94	99 000	245 000	2.47
1B	140	14	93	56 000	158 000	2.82
1C	140	21	92	47 000	102 000	2.17
2A	120	7	89	149 000	362 000	2.43
2B	120	14	94	155 000	371 000	2.39
2C	120	21	92	161 000	377 000	2.34
2D	120	28	91	131 000	412 000	3.15

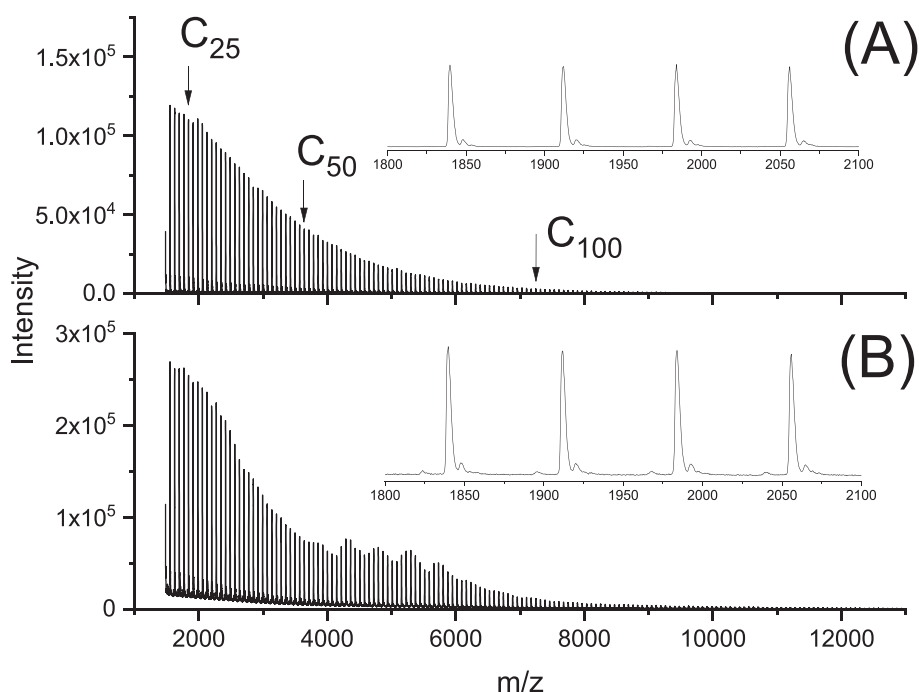


Fig. 1. MALDI TOF mass spectra of cyclic PLA equilibrated with DSTL in o-dichlorobenzene at 120 °C: (A) after 7 d (2C, Table 1), (B) after 28 d (2E, Table 1).

MALDI mass spectrum (Fig. 1B), which displayed a weak “saw-tooth pattern” (STP). The spectra obtained after 21 d and after 28 d were almost identical. To improve the mass spectrometric evidence for the STP and its lateral dimension, the 28 d sample (2D, Table 1) was fractionated by GPC and the fractions subjected to MALDI-TOF mass spectrometry. Fig. 2 displays a fraction between m/z 6 000 and 12 000 which shows a clear STP. In contrast, the fractions of lower or higher masses did not show such an STP (Figure S2).

As mentioned above, the STP results from a thermodynamically controlled modification of the surfaces of extended-ring crystals. Crystallites composed of cycles having a similar ring size are formed, with the consequence of a smooth surface as schematically illustrated in Fig. 3A (compared to a less perfect crystallite composed by linear chains, Fig. 3B). At 120 °C in chlorobenzene the reaction mixture remained clear up to 14 d and showed a MALDI mass spectrum (Figure S3A)

analogous to that of Fig. 1A, but after 21 d gelation occurred. After 28 d, the mass spectrum (Figure S3B) displayed again a weak STP analogous to the spectrum shown in Fig. 1B. For a better understanding of this phenomenon, it may be useful to mention at this point, that several research groups have found that both, nucleation and crystal growth of cyclic PLAs and other cyclic polymers, are faster than those of their linear counterparts.[18–21] Hence, formation and crystallization of extended-ring crystals is kinetically and thermodynamically favored.

Another unexpected result was the finding that no degradation of the molecular masses was observed at 120 °C. In o-dichlorobenzene a slow polymerization was followed by a constant molecular mass. In chlorobenzene even a slight increase of the weight average molecular mass (M_w) was found combined with a higher dispersity after 28 d. At first glance, these results suggest that RRE has almost disappeared, but the RRE reactions yielding the STP can only have proceeded within the few days after crystallization of extended rings. However, the RRE reactions on the surface of the crystallites may be favored by the proximity of loops (see discussion below), and thus do not prove that the RRE reactions in solution are fast.

Further experiments were conducted with the more reactive polymerization catalyst SnBiph in o-dichlorobenzene and anisole at 140 °C (Table 3). The time was extended to 42 d, the reaction mixtures remained clear, and the mass spectra showed no unusual feature (Figure S4).

GPC measurements revealed that the molecular masses were reduced by a factor of 2.5–3.0 within 42 d, but as discussed in the next section, they still remained far above the equilibrium M_n or M_w value, which is in agreement with the results obtained with the DSTL catalyst.

3.2. Equilibration of preformed cyclic PLA in solution

To clarify whether the molecular masses obtained at 140 °C after 21, 28 or 42 d were close to the equilibrium values, two low molecular mass cyclic PLA were prepared and subjected to RRE with DSTL (Table 4). These cPLAs were prepared using dibutyltin bisphenoxide in dilute toluene solution as previously described.[16] As listed in Table 4, M_n values of 16 000 Da (cPLA-I) and 16 500 Da (cPLA-II) were obtained. The M_n values were significantly lower than the those obtained from

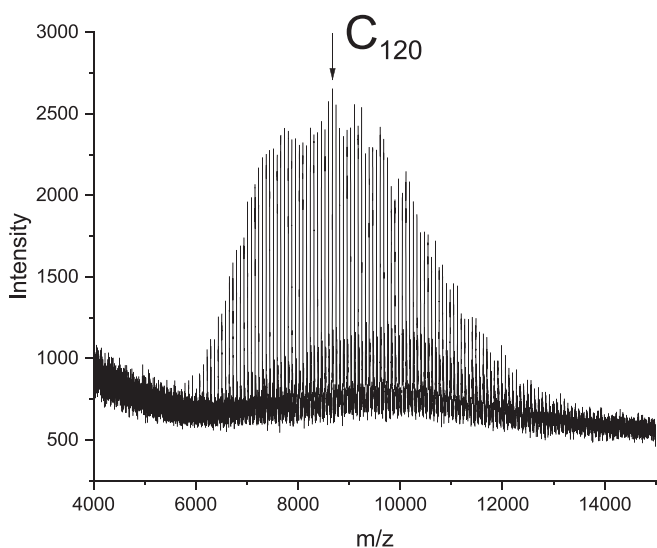


Fig. 2. MALDI TOF mass spectrum of a fractionated PLA equilibrated with DSTL in o-dichlorobenzene at 120 °C after 28 d (2E, Table 1).

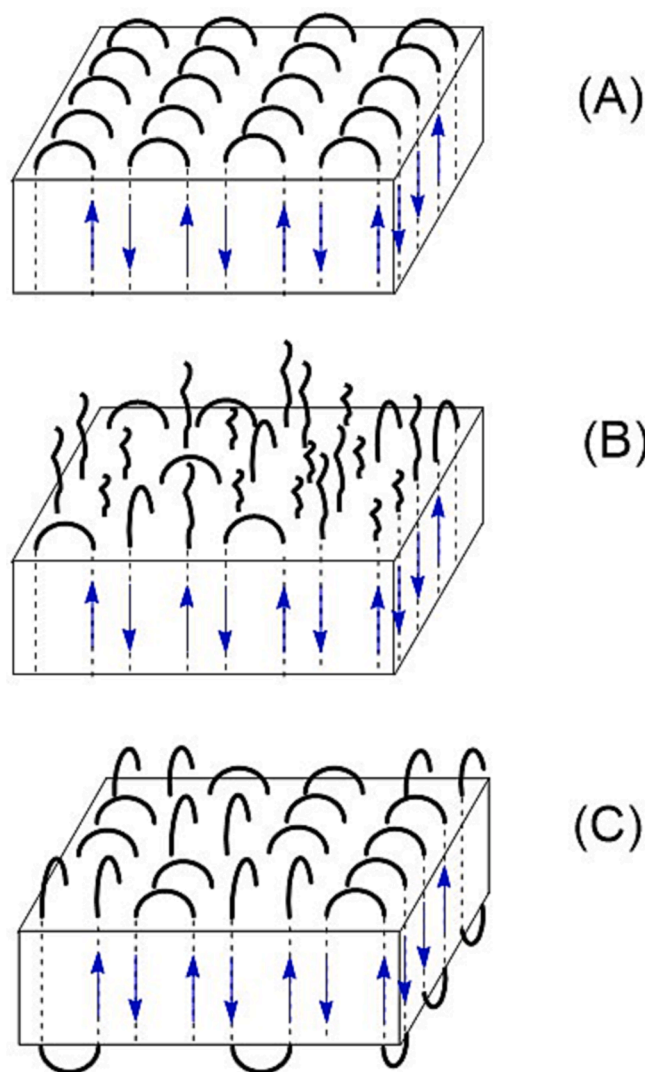


Fig. 3. Models of PLA crystallites formed: (A) by extended-rings, (B) by linear chains, (C) by once-folded rings.

Table 3

REP and equilibration of LA with SnBiph (LA/Cat = 500/1) in two different solvents at 140 °C, with a 2 M monomer concentration.

Exp. No.	Solvent	Time (d)	Yield (%)	M_n	M_w	Disp. \bar{D}
1A	o-Dichlorobenzene	2	93	81 000	201 000	2.5
2.51B	o-Dichlorobenzene	11	93	49 000	110 500	2.2
1C	o-Dichlorobenzene	42	91	32 000	77 000	2.3
2A	Anisole	2	93	113 000	330 000	2.4
2B	Anisole	28	91	57 000	150 000	2.6
2C	Anisole	42	89	43 000	101 000	2.3

RRE of LA in Tables 1-3. Heating of cPLA-I in 2 M solution in chlorobenzene with DSTL at the same concentrations used in the LA equilibration experiments clearly demonstrated that a degradation of the molecular masses, rather than a ring-expansion polymerization, occurred. MALDI mass spectra recorded after 7 and 28 d did not display any change resulting from chain scission. Therefore, this experiment

Table 4

Equilibration of cPLA with DSTL (50/1) in chlorobenzene (2 M) at 140 °C.

Exp. No.	Solvent	Time (h)	Yield (%)	M_n	M_w	Disp. \bar{D}
1A	Toluene ^{a)}	0	–	16 000	36 000	2.3
1B	Chlorobenzene	7	85	13 700	29 000	2.2
1C	Chlorobenzene	11	91	10 100	21 000	2.1
1D	Chlorobenzene	21	90	7 500	15 000	2.0
1E	Chlorobenzene	28	89	5 500	1 200	2.2
2	o-Dichlorobenzene	11	91	3 450	9200	2.6
3	Anisole	10	93	3 150	7 900	2.5

a. Starting materials prepared with $\text{Bu}_2\text{Sn}(\text{OC}_6\text{F}_5)_2$ in 0.5 M toluene solution at 115 °C/7 d.

with a preformed low cPLA proves that the equilibrium M_n must be below 5 000 Da. The degradation of preformed cPLA with DSTL was confirmed by two more experiments with cPLA-II in o-dichlorobenzene and anisole (Table 4). Such low equilibrium M_n values may be surprising at first glance when compared to the high M_n values found after 21 or 28 d in the experiments of Tables 1-3, but they are consistent with the Jacobson-Stockmayer theory of ring-ring equilibria.[2,3] According to this theory (experimentally proven for several cyclic polymers [5–8,22]) the degree of polymerization (DP) of individual cycles decreases with the exponent $-(5/2)$. This steep decrease (illustrated in Figure S5. of Flory's famous book [23]) means that cyclic oligomers with $\text{DP} < 20$ represent the majority of the reaction mixture, and since M_n depends on the number fraction of the cycles, it is a corollary that the equilibrium M_n values of cyclic PLA and other cycles with low molecular mass repeat units are below 5 000 Da.

Hence, the most surprising result of these equilibration experiments is not the low M_n data in Table 4, but the high M_n data in Tables 1-3 and the almost complete absence of degradation at 120 °C, although equilibration reactions take place. The large amounts of DSTL purposely used in those experiments and the high M_n and M_w values obtained upon REP of LA exclude that the catalyst was poisoned by impurities in the solvent.

3.3. REP of LA in bulk and equilibration in the solid state

First, a series of RREs were conducted at 140 °C in bulk with an LA/DSTL ratio of 50/1, reaction conditions selected for comparison with the experiments performed in 2 M solution. As demonstrated by the M_n and M_w data listed in Table 5A, a dramatic decrease of the molecular masses down to 20–25 % of the initial values was found. Therefore, this degradation went further down than the degradation in solution. Considering that the PLA of these experiments began to crystallize within a few hours after the start of the polymerization, the entire degradation process must have taken place in the solid state, i.e. in the amorphous phase and across the surface of the crystallites. To make sure that this surprising trend was reproducible, an analogous series of experiments was performed with a LA/Cat ratio of 200/1. As demonstrated by the data compiled in Table 5B, the conspicuous decrease of the molecular masses was confirmed despite the lower concentration of DSTL.

To explain this phenomenon the crystallinity of the cyclic PLA listed in Tables 5A and 5B requires discussion. Previously, other research groups have used a ΔH_m^0 value of 106 J g^{-1} as maximum melting enthalpy of a perfect crystal for calculating crystallinities from DSC measurements.[24,25] This value was also used in this work for comparison with literature data (see Table 5A and 5B). However, the authors have recently demonstrated that this ΔH_m^0 value is too low, and that 115 J g^{-1} is the minimum ΔH_m^0 required for the calculation of realistic crystallinities.[26] However, even using this new high ΔH_m^0 value, the crystallinities of the PLA listed in Tables 5A and 5B are very high,

Table 5A

REP and equilibration of LA with DSTL at 140 °C in bulk (LA/Cat = 50/1).

Exp. No.	Time (d)	M _n	M _w	T _m (°C)	ΔH _m (J/g)	Cryst. (%) ^{a)}
1A	1	129 000	321 000	191.5	90.4	78
1B	4	90 000	234 000	198.5	100.1	88
1C	7	65 000	151 000	199.5	101.7	88
1D	14	38 000	86 000	201.3/ 202.0/202.3	104.7/ 104.0/106.0	90–92
1E	21	28 000	69 000	195.1/195.4	102.9/102.5	89

a) calculated with ΔH_m⁰ = 115 J g⁻¹.**Table 5B**

REP and equilibration of LA with DSTL at 140 °C in bulk (LA/Cat = 200/1).

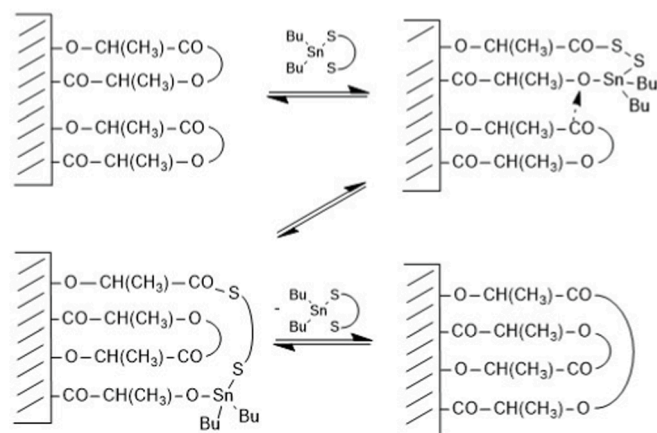
Exp. No.	Time (d)	M _n	M _w	T _m (°C)	ΔH _m (J/g)	Cryst. (%) ^{a)}
1A	2	112 000	305 000	192.5	93.6	81
1B	4	91 000	264 000	199.1	101.2	88
1C	7	65 000	156 000	–	–	–
1D	14	36 000	83 000	195.8	99.4	87
1E	21	27 000	64 500	194.6	106.6	92

a) calculated with ΔH_m⁰ = 115 J g⁻¹.

approaching values up to 90 %. Considering the high crystallinities, it is hard to believe that the extent of degradation can depend exclusively on RRE in the small fraction of the amorphous phase. It must be considered that only part of the difference between the measured crystallinity and 100 % may be attributed to a true amorphous phase. Perhaps up to 30 % of the non-crystalline phase be attributed to the rather immobile disordered phase on the flat surfaces of the crystallites, which mainly consists of loops of various lengths, so that the true amorphous phase of most samples does not exceed 10 wt%.

Therefore, the authors propose a special transesterification mechanism, which involves adjacent loops resulting from folding of long cycles (Fig. 4 and Scheme 4).

Since these loops belong to cyclic PLA, this transesterification may also be understood as a special type of RRE. When two loops resulting from folding of a large cycle (so-called “fold-loops”) are transformed into two loops representing “end loops” of two smaller cycles, the molecular mass of the longer cycles is (on the average) halved. Apparently, the close proximity of two “fold loops” favors their transesterification and this factor can explain the efficient degradation of large cycles in the solid state, even when other transesterification reactions are slow. Since this mechanism is reversible, it may, in principle, also explain the formation of longer cycles from smaller ones. In any case, the maxima of the mass distribution underlying the STP observed in all cases studied so far indicate that the formation of extended -ring crystals is thermodynamically favored. When the REP and RRE of LA was performed at

**Scheme 4.** Re-arrangement of neighboring loops via DSTL-catalyzed transesterification.

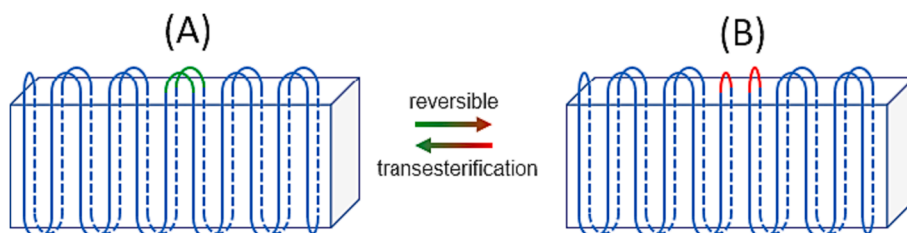
120 °C (Table 6), the first important result was the observation that no significant degradation of the molecular masses took place. In this respect the experiments conducted in bulk agree well with those performed in *o*-dichlorobenzene solution (Table 1) and in chlorobenzene (Table 2). Nevertheless, RRE reactions took place, as evidenced by the formation of mass distributions with STP, but these equilibration reactions were slow, and after 7 d no change in the mass distribution was detectable yet (No. 1B in Table 6 and Fig. 5A). However, after 28 d (No. 1D, Table 6), a new, broad maximum of the mass distribution has developed along with a well-defined STP (Fig. 5B) which extends up to approximately *m/z* 14 000.

When this sample was fractionated, the mass spectra of the fractions confirmed that the STP ended between *m/z* 14 000 and 15 000 (Fig. 6A). The next higher fraction did not display a STP (Fig. 6B). This finding is in good agreement with the fractionation illustrated in Fig. 2 and Fig. S2. To confirm the reproducibility of these experiments an analogous REP and RRE of lactide was conducted, but with the addition of 4 vol% of anisole (No. 2, Table 6). This modification was chosen, because in a recent study it was found that the addition of small amounts

Table 6

REP and equilibration of LA at 120 °C in bulk, (LA/Cat = 50/1).

Exp. No.	Solvent	Time (d)	M _n	M _w	T _m (°C)	ΔH _m (J/g)	Cryst. (%) ^{a)}
1A	–	3	50 000	95 000	189.0	85.0	74
1B	–	7	61 000	159 000	189.2	88.2	77
1C	–	14	55 000	152 000	190.6	90.2	78
1D	–	28	49 000	153 000	191.1	97.2	83
2	Anisole ^{b)}	28	42 000	115 000	192.3	99.9	87

a) calculated with ΔH_m⁰ = 115 J g⁻¹, c) addition of 4 vol% of anisole.**Fig. 4.** Schematic illustration of a transformation of “fold loops” (A) into “end-loops” (B) by ring-ring equilibration (RRE).

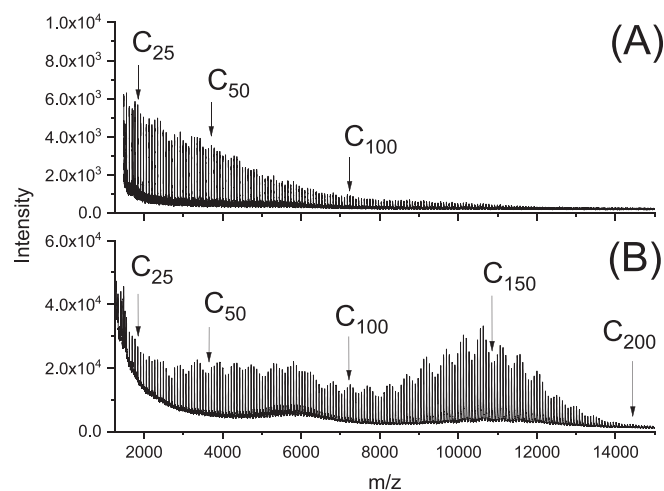


Fig. 5. MALDI TOF mass spectra of cyclic PLA prepared via REP in bulk at 120 °C (A) after 7d (1B, Table 6), (B) after 28 d (1D, Table 6).

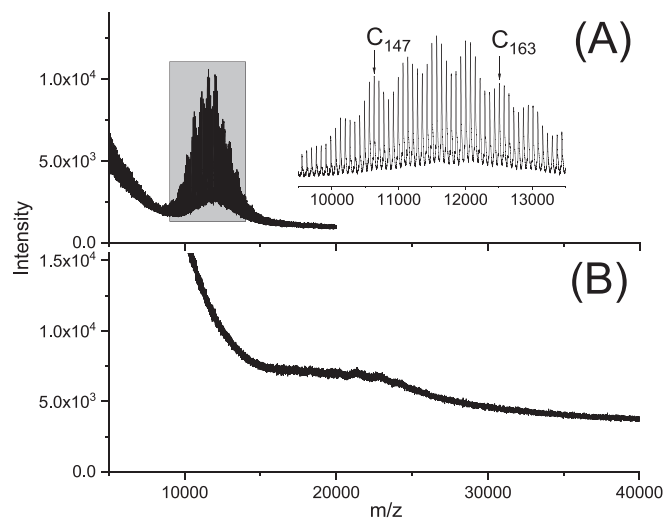


Fig. 6. MALDI TOF mass spectra of two SEC fractions of a PLA equilibrated with DSTL in bulk at 120 °C after 28 d (1D, Table 6).

of anisole (or, to a lesser extent, chlorobenzene) slightly enhances the efficiency of equilibration/transesterification reactions of DSTL in solid cyclic PLA. [27] Possibly, the addition of suitable solvents improves the mobility of DSTL in the non-crystalline phase of the solid PLA.

Experiment No. 2 with anisole yielded a mass spectrum very similar to that of Fig. 5B, but the mass range of the saw-tooth pattern extended beyond m/z 15 000. Fractionation proved that the STP indeed approached the mass of m/z 19 000 (Fig. 7). In analogy to the other fractionations discussed above, no STP was observable in the next higher fraction. An STP up to m/z 19 000 represents a record among the nearly 100 PLA samples with STP found by the authors in the last four years. It demonstrates, that under ideal conditions even cycles with masses above 15 000 and certainly about 19 000 do not yield a STP can be explained by the consequences of chain folding. Cycles with such high masses must fold at least once to fit in crystallites having a thickness in the range of 16–26 nm, as it was found for almost all annealed cyclic PLAs. This conclusion is based on the X-ray study of Wasanasuk and Tashiro [28] (as discussed recently [29]), who found a length of nearly 3.0 nm for 10 lactyl units in the 10^3 helix typical for the α -modification of PLA.

Folding of cyclic PLA generates a disordered surface (when

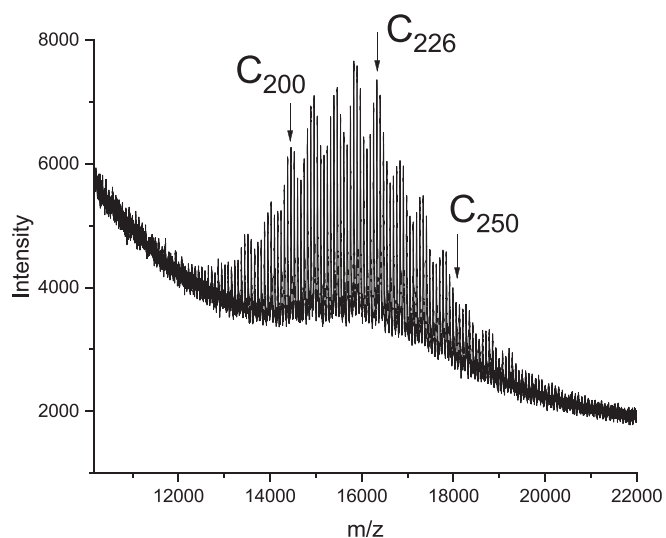
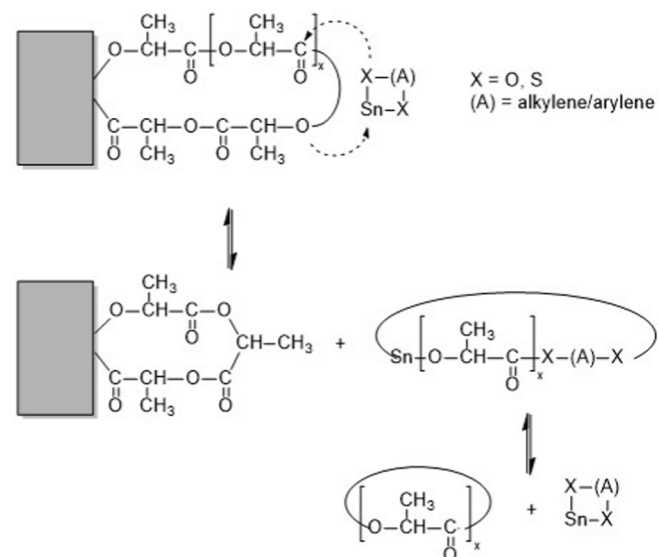


Fig. 7. MALDI-TOF mass spectrum of a SEC-fractionated PLA equilibrated with DSTL in bulk at 120 °C after 28 d with addition of 4 vol% of anisole (2, Table 6).

compared to extended-ring crystallites), because the “folding-lops” are necessarily in a perpendicular position relative to the “end loops” as illustrated by the crystal model of Fig. 3C. Obviously, the parallel arrangement of loops on the surface of extended-ring crystals and the absence of linear chain ends (Scheme 3B) are prerequisites for the formation of the STP via RRE. The loop extension and contraction mechanism outlined in Scheme 5 provides the chemical explanation, a mechanism that is also responsible for RRE in solution. Therefore, RRE in solution and in solid PLA share the same chemical basis.

4. Conclusions

The results of this work show in agreement with a recent study that ring-ring equilibration of LA and cyclic PLA may play three different roles. First, it could be considered as a polymerization process when the monomer is used as the starting material. Second, it may play the role of a degradation reaction when the molecular mass of cyclic PLA is significantly higher than the average at equilibrium. However, at 140 °C, the degradation is slow, and reaction times of one year or more



Scheme 5. Expansion or shortening of loops via transesterification catalyzed by DSTL.

are required to approach the equilibrium. Third, it can modify the surface of crystallites, when it occurs in solid cyclic PLA.

CRedit authorship contribution statement

Hans R. Kricheldorf: Writing – original draft, Supervision, Methodology, Investigation, Conceptualization. **Steffen M. Weidner:** Writing – review & editing, Visualization, Resources, Methodology, Investigation, Data curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hans R. Kricheldorf reports equipment, drugs, or supplies was provided by Thyssen Uhde SE. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2024.112765>.

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