


Cite this: *RSC Adv.*, 2021, 11, 2872

# About the transformation of low $T_m$ into high $T_m$ poly(L-lactide)s by annealing under the influence of transesterification catalysts†

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Cyclic polylactides were prepared in bulk at 170 °C, crystallized at 120 °C and then annealed at temperatures between 130 and 170 °C with variation of catalyst, catalyst concentration and annealing time. The transformation of the initially formed low melting ( $LT_m$ ) crystallites, having melting temperatures ( $T_m$ ) < 180 °C into high melting ( $HT_m$ ) crystallites having  $T_m$  values > 189 °C was monitored by means of DSC measurements and characterized in selected cases by SAXS measurements. It was confirmed that the formation of  $HT_m$  crystallites involves a significant growth of the thickness of the lamellar crystallites along with smoothing of their surface. Annealing at 170 °C for 1 d or longer causes thermal degradation with lowering of the molecular weights, a gradual transition of cyclic into linear chains and a moderate decrease of lamellar thickness. An unexpected result revealed by MALDI TOF mass spectrometry is a partial reorganization of the molecular weight distribution driven by a gain of crystallization enthalpy.

Received 26th November 2020

Accepted 3rd January 2021

DOI: 10.1039/d0ra10012a

rsc.li/rsc-advances

## Introduction

Poly(L-lactide) is an important biodegradable and biosourced engineering plastic, which is produced by several chemical companies. Due to the higher costs compared to oil-based polymers, its application today is still severely limited. However, due to the rapidly increasing pollution of oceans, lakes and rivers with plastic and microplastic, polylactides might have a bright future. The first reports of the synthesis of poly(D,L-lactide) based on the polycondensation of *rac*-D,L-lactic acid were published in 1833 and 1845.<sup>1,2</sup> A first patent concerning the polymerization of L-lactide followed more than 100 years later.<sup>3</sup> Greater interest in the properties and commercial application of polylactide or copolymers of L-lactic acid arose after 1967, when Union Carbide patented strong biodegradable fibres based on polyglycolide.<sup>4</sup> In 1972 Ethicon Inc. followed with patenting of medical structures containing L-lactic acid.<sup>5,6</sup> Since then, the interest in polylactic acid and polylactide has risen dramatically.

Like almost all applications of poly(L-lactide), this and other medical applications (e.g. for implants) are based on its semi-

crystalline character with a glass transition around 62–64 °C and a melting temperature in the range of 174–177 °C with short annealing, or in the range of 176–180 °C after long annealing, when catalysts are absent or poisoned (typical for commercial polylactides).<sup>6–11</sup> The orthorhombic crystal lattice ( $\alpha$ -modification), first identified by DeSantis and Kovacs,<sup>12</sup> is the basis of this consideration, because it is the normal result of a stress-free annealing or slow cooling of molten poly(L-lactide) above 120 °C.<sup>13</sup> These values are typical for linear poly(L-lactide)s. Interestingly, during the past decade quite different  $T_m$  and  $\Delta H_m$  values were reported by several research groups for cyclic poly(L-lactide)s. At first (2011) Prasad *et al.* listed  $T_m$  values in the range of 140–147 °C recorded from virgin samples and a  $T_m$  of 159 °C for a sample annealed at 65 °C.<sup>14</sup> These samples were prepared *via* zwitterionic polymerization with an *in situ* generated carbene, a method with a high potential for racemization due to the anionic chain end, but information about optical purity was not disclosed. In 2012 the Waymouth group reported a  $T_m$  of 135 °C and  $\Delta H_m$  of 18 J g<sup>−1</sup> for a sample also prepared *via* carbene-catalyzed zwitterionic polymerization.<sup>15</sup> However, those authors also found a considerable extent of racemization. Again, a carbene-catalyzed zwitterionic polymerization was used by Si *et al.*,<sup>16</sup> but at −70 °C a highly stereoselective polymerization of racemic D,L-lactide was found yielding cyclic low molar mass poly(L-lactide)s ( $M_w$  < 9000 g mol<sup>−1</sup>) with up to 91% optical purity. For these samples  $T_m$  values in the range of 165–193 °C were measured.

In 2015 the Tezuka group described the synthesis of low molar mass cyclic poly(L- and D-lactide)s by a photochemical end-to-end cyclization of linear precursors.<sup>17</sup> This synthetic method avoids significant racemization but leaves a guest

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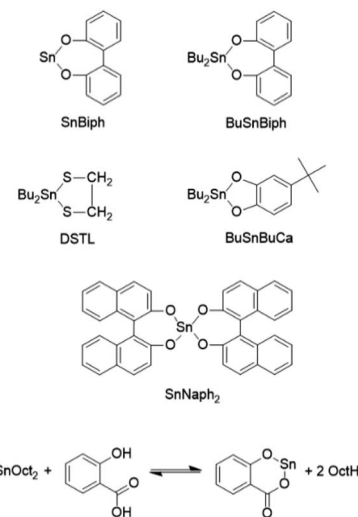
† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0ra10012a



comonomer in the cycles. The low  $T_m$  values (128 °C for L and 125 °C for D-poly(lactide)) along with the low melting enthalpies (26 J g<sup>-1</sup> for L and 25 J g<sup>-1</sup> for D-poly(lactide)) demonstrate the enormous influence of the guest comonomer on the physical properties. Nonetheless, those authors extrapolated a  $\Delta H_{m0}$  value of 44 J g<sup>-1</sup> for a perfect crystal with 100% crystallinity. Again, a guest–host copolymer was prepared by the Müller group *via* an end-to-end cycloaddition reaction of a linear precursor.<sup>18</sup> A  $T_m$  of 148.6 °C and  $\Delta H_m$  of -24.3 J g<sup>-1</sup> were found, similar to the values reported by the Tezuka group. An equilibrium  $T_{m0}$  of 164 °C was calculated for a perfect crystal of cyclic poly(L-lactide) and a  $T_{m0}$  of 159 °C for a linear polymer of similar low molecular weight ( $M_w < 17\,000$  g mol<sup>-1</sup>). The much higher experimental  $T_m$  values of linear poly(L-lactide)s reported by other research groups were ignored.<sup>7–11</sup> Particular noteworthy in this connection are the isothermal crystallization experiments of Kalb and Pennings, who extrapolated a  $T_{m0}$  of 215 °C.<sup>19</sup> Interestingly, the Pennings group had synthesized their poly(L-lactide)s themselves by polymerization of L-lactide in bulk using neat tin(II) 2-ethylhexanoate as catalyst (SnOct<sub>2</sub>). This catalyst was not removed nor poisoned. For almost five decades it was believed that polymerization of lactides by means of SnOct<sub>2</sub> yields linear polylactides regardless, if an initiator was added or not. Yet, quite recently it was demonstrated by the authors that neat SnOct<sub>2</sub> yields in fact cyclic polylactides.<sup>20</sup> Hence, it is probable, that the Pennings group observed cyclic poly(L-lactide) by microscope, and that their results were influenced by the presence of the catalyst. Finally, a recent study (2020) of Louisy *et al.* should be mentioned,<sup>21</sup> which describes a comparison of cyclic and linear poly(L-lactides) having identical molar masses ( $M_w < 50\,000$  g mol<sup>-1</sup>, respectively <30 000 g mol<sup>-1</sup> with a correction for THF as SEC solvent). Lanthanum borohydride was used as catalyst, but despite its basicity no information about optical purity was given. For the cyclic polylactide a  $T_m$  of 165 °C and  $\Delta H_m$  of 42 J g<sup>-1</sup> was reported, whereas a  $T_m$  of 171 °C with a  $\Delta H_m$  of 50 J g<sup>-1</sup> was found for the linear species. These data were determined from the 2nd heating trace of DSC measurements with a rate of 10 K min<sup>-1</sup>, a method which underrates the thermal properties of annealed samples.

Quite recently the authors also have reported<sup>22</sup> that syntheses of cyclic poly(L-lactide) by means of ring-expansion polymerization (REP) or by ring-opening polymerization with simultaneous polycondensation (ROPPOC, for definition see ref. 23) may yield high-melting poly(L-lactide) with  $T_m$  values up to 196 °C. The formation of this HT<sub>m</sub> poly(L-lactide)s by isothermal polymerization and crystallization at temperatures between 120 and 160 °C required long reaction times (20–70 h depending on the catalyst). By isothermal crystallization in the same temperature range Pennings *et al.*<sup>19</sup> found  $T_m$  values that were 10–15 °C lower than those of the authors.<sup>22</sup> In summary, the afore-mentioned data demonstrate that the fundamental physical data of cyclic and linear poly(L-lactide)s published so far do not give a consistent picture yet.

In this context the present work served three purposes. Firstly, it should be found out, if it is possible to transform the normal LT<sub>m</sub> crystallites into the HT<sub>m</sub> counterparts by annealing



Scheme 1 Tin catalysts and their acronyms used or discussed in this work.

in the solid state when reactive transesterification catalysts are present. Secondly (and more important), it should be confirmed, that the HT<sub>m</sub> polylactides with  $T_m$  values > 190 °C, represent the thermodynamically most stable combination of modification and morphology, regardless if cyclic or linear polylactides are concerned, the combination of the results presented in this work with our recently published results will, in turn demonstrate, that all lower  $T_m$  values published in the past do not represent the thermodynamically controlled maximum. Finally, it should be found out, which catalyst is best suited for such a transformation. The formulas and abbreviations of the catalysts used or discussed in this work were summarized in Scheme 1.

## Experimental

### Materials

L-Lactide, a product of PURAC was kindly supplied by Thyssen-Uhde (Berlin, Germany) and recrystallized from toluene (99.89% extra dry, ACROS Chemicals, Geel, Belgium). Ethyl L-lactate was purchased from Sigma-Aldrich (Taufkirchen, Germany) and used as received, tin(II) 2-ethylhexanoate (>96% purity) was purchased from Alfa Aesar (Karlsruhe, Germany) and used as received. DSTL,<sup>24</sup> BuSnBuCa,<sup>25</sup> BuSnBiph<sup>26</sup> and SnBiph<sup>27</sup> were synthesized as described in previous publications dealing with syntheses of cyclic poly(L-lactide)s by means of these catalysts. Those publications also contain the experimental evidence for the cyclic topology of the resulting polylactides.

### Polymerization and annealing

**A – with SnBiph as catalyst.** The catalyst (0.04 mmol) was weighed into a 50 mL flame-dried Erlenmeyer flask, L-lactide (40 mmol) and a magnetic bar were added under a blanket of argon. The catalysts were completely dissolved before the reaction mixtures became too viscous. The reaction vessel was immersed



into an oil bath thermostated at 170 °C. The reaction mixture became viscous within 5 min. After 1.5 h the reaction vessel was cooled with water and transferred to an oil bath thermostated at 120 °C. After 2 h the solid polylactide was isolated (usually by destruction of the Erlenmeyer flask) and the crystalline polylactide cake was subdivided into 2–4 pieces with a hammer. One piece was characterized without additional annealing, and other pieces after annealing for several hours at higher temperatures (see Tables 1–3). The annealing temperature was varied as described in Table 1. It was performed in a static atmosphere of argon in a closed vessel.

**B – with various catalysts.** These experiments were conducted as described before, but the time required for the polymerization of the L-lactide at 170 °C was varied according to the reactivity of the catalyst. For BuSnBuCa, BuSnBiph and SnOct<sub>2</sub> a reaction time of 1.5 h sufficed in analogy to SnBiph, whereas for DSTL the time was extended to 2.5 h.

The MALDI TOF mass spectra were measured with Bruker Autoflex III mass spectrometer equipped with a Smartbeam laser ( $\lambda = 355$  nm). All spectra were recorded in the positive ion linear mode. The MALDI stainless steel targets were prepared from chloroform solutions of poly(L-lactide) and 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 *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. 1  $\mu$ L of the corresponding solution was deposited on the MALDI target.

The GPC measurements were performed in a modular system kept at 40 °C consisting of an isocratic pump, 1 mL min<sup>-1</sup> and a refractive index detector (RI-501-Shodex). Samples were manually injected (100  $\mu$ L, 2–4 mg mL<sup>-1</sup>). 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) covering the mass range of 500–1 200 000 g mol<sup>-1</sup>.

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>. Only the

first heating traces were evaluated. The crystallinities were calculated with a  $\Delta H_m$  max of  $-106$  J g<sup>-1</sup>.

The WAXS and SAXS measurements were performed using our 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. For the WAXS measurements the sample-detector distance was 0.1 m, allowing to detect an angular range of  $2\theta = 5^\circ$ – $33^\circ$ . The recording time for each WAXS pattern was 300 s. 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>28</sup> For the evaluation of the crystallinity of the samples the data were imported 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.

## Results and discussion

### Annealing experiments with the SnBiph catalyst

Since it was expected that a transformation of crystallites from LT<sub>m</sub> into HT<sub>m</sub> form will be a slow process, the first series of experiments was performed with the most reactive polymerization catalyst, namely SnBiph (see Scheme 1). Furthermore, the highest possible temperature (170 °C) was used for the first experiments, together with a long reaction time of 2 d and a relatively high catalyst concentration corresponding to a Lac/Cat ratio of 1000/1 (No. 5, Table 1). When almost complete transformation (meaning  $T_m$  values > 190 °C) was indicated by the DSC measurements, the time was shortened (No. 2–4, Table 1), the catalyst concentration was lowered (No. 6–11, Table 1),

**Table 1** Annealing of cyclic poly(L-lactide)s with SnBiph as catalyst<sup>a</sup> at 170 °C

Exp. no.	Lac/Cat	$T$ (°C)	$t$ (h)	$M_n$	$M_w$	$T_m$ (°C)	$\Delta H_m$ (–J g <sup>-1</sup> )	Cryst. (%)
1	1000/1	120	2	73 000	191 000	176.4	45.0	42
2	1000/1	170	4	69 000	181 000	182.0	65.0	62
3	1000/1	170	8	64 500	174 000	194.5	88.5	83
4	1000/1	170	24	60 500	163 000	192.7	87.7	82
5	1000/1	170	48	48 500	126 000	193.8	91.1	86
6	2000/1	120	2	66 000	168 000	175.0	43.5	41
7	2000/1	170	24	65 000	158 000	192.8	93.7	88
8	2000/1	170	48	59 500	127 500	192.7	93.1	88
9	4000/1	120	2	35 000	101 000	175.5	42.5	40
10	4000/1	170	24	27 000	73 500	192.7	102.2	96
11	4000/1	170	48	26 000	67 000	194.0	101.5	95

<sup>a</sup> L-Lactide was polymerized at 170 °C for 1.5 h, crystallized at 120 °C for 2 h and then annealed under the conditions listed in the table.



Table 2 Annealing of cyclic poly(L-lactide)s with SnBiph at 160 °C (Lac/Cat = 1000/1)

Exp. no.	<i>T</i> (°C)	<i>t</i> (h)	<i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub>	<i>T</i> <sub>m</sub> (°C)	Δ <i>H</i> <sub>m</sub> (−J g <sup>−1</sup> )	Cryst. (%)
1	120	2	61 000	174 000	175.5	44.0	41
2	160	4	52 000	162 000	181.3	64.5	61
3	160	8	51 000	156 000	183.0	73.5	69
4	160	24	58 000	128 000	188.5	88.2	82
5	160	48	46 000	110 000	187.0	82.0	78

Table 3 Annealing of cyclic poly(L-lactide)s at 140 °C with SnBiph as catalyst

Exp. Nn.	<i>T</i> (°C)	<i>t</i> (h)	<i>M</i> <sub>n</sub>	<i>M</i> <sub>w</sub>	<i>T</i> <sub>m</sub> (°C)	Δ <i>H</i> <sub>m</sub> (−J g <sup>−1</sup> )	Cryst. (%)
1	120	2	63 000	187 000	176.0 <sup>a</sup>	42.5	40
2	140	8	35 000	162 500	179.0	57.0	54
3A	140	24	61 000	172 000	181.5	58.5	55
3B <sup>b</sup>	140	24	67 000	170 000	189.5	68.5	64
4	140	48	64 000	173 000	183.0	68.0	64
5	140	96	70 000	161 000	184.5	71.5	67
6A	140	192	34 000	88 000	184.5	76.0	72
6B <sup>b</sup>	140	192	27 000	68 000	190.0	79.5	85

<sup>a</sup> Repetition with another batch of L-lactide gave *T*<sub>m</sub>: 177.5 and Δ*H*<sub>m</sub> −41.0 J g<sup>−1</sup>. <sup>b</sup> Direct polymerization of L-lactide in bulk at 140 °C.

and finally the temperature was lowered (see Tables 2 and 3). Shortening of the time at 170 °C revealed that 8 h suffice to achieve nearly complete transformation. The experiments with higher Lac/Cat ratios demonstrated that even at 4000/1 the catalyst is still reactive enough to enable a nearly complete transformation within 1 d (Table 1, No. 10).

All DSC traces recorded in the course of this study have in common, that they display a simple monomodal endotherm, as exemplarily illustrated in Fig. 1 and S1 (ESI†). After annealing at 120 °C/2 h the DSC traces still display a glass-transition step and the melting endotherm has a broad “foot” beginning around 130 °C (Fig. 1A and S1A†) indicating that small rather imperfect crystallites are still present. Annealing at 170 °C results in narrowing of the endotherm, and the upper end of the “foot” shifts to temperatures around 210 °C (Fig. 1B and S1B†). This means that a few large and rather perfect crystallites are present melting in the range of 200–206 °C. Interestingly, these high melting points (>200 °C) come relatively close to the maximum *T*<sub>m</sub> of perfect single crystal with infinite layer thickness (*T*<sub>m0</sub> = 215 °C), calculated by Kalb and Pennings.<sup>19</sup> Therefore, these DSC data suggest that the *T*<sub>m0</sub> calculated by Kalb and Pennings was realistic, and indicate that the guest–host copolymers described by groups of Tezuka [b] and Müller [c] cannot serve as reasonable models of cyclic or linear optically pure poly(L-lactide)s, since their *T*<sub>m</sub> values (and Δ*H*<sub>m</sub> values, see below) are much too low.

One noteworthy result of these experiments was the steadily decrease of the molecular weights with increasing annealing time indicating steady thermal degradation. Nonetheless, the weight average molecular weights (*M*<sub>w</sub>) remained above 120 000 g mol<sup>−1</sup>. More information about this aspect was

obtained from the MALDI TOF mass spectra discussed below. A second noteworthy result was the increase of crystallinity accompanying thermal degradation. Extremely high values (up to 95%) were achieved, even when calculated with a maximum Δ*H*<sub>m</sub> of −106 J g<sup>−1</sup>, which seems to be the most widely accepted Δ*H*<sub>m max</sub> value today.<sup>29,30</sup> For a long period of time a Δ*H*<sub>m max</sub> of −93.5 J g<sup>−1</sup>, firstly published by Fischer and co-workers,<sup>31</sup> was used by several research groups.<sup>32</sup> Later Wunderlich and co-workers<sup>33</sup> even published a somewhat lower value (91 J g<sup>−1</sup>), which was also advocated by DiLorenzo.<sup>8</sup> The Colombier/Müller group used a Δ*H*<sub>m0</sub> as low as 44 J g<sup>−1</sup> for the calculation of crystallinities.<sup>18</sup> However, those values are certainly too low, because several samples obtained in this work and reported in a previous publication<sup>22</sup> would have crystallinities around or above 100%, even when calculated with the “Fischer or

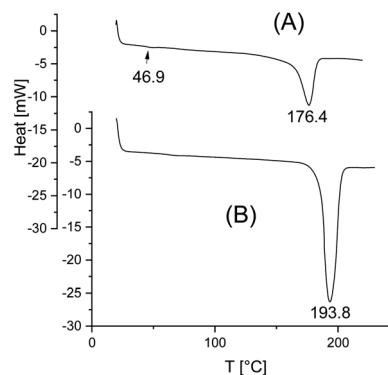
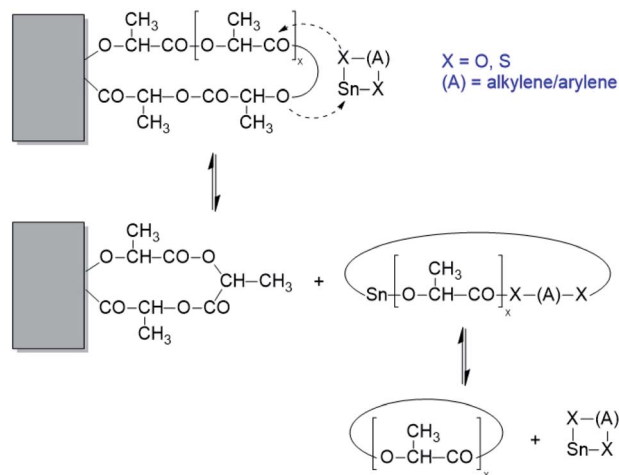


Fig. 1 DSC heating traces of (A) 120 °C/2 h (No. 1, Table 1), (B) 170 °C/2 h (No. 5, Table 1).







**Scheme 2** Example of a transesterification reaction shortening (or expanding) a loop on the surface of a crystallite.

Wunderlich values". Increasing crystallinity during thermal degradation may have two reasons. Firstly, shorter chains have higher kinetic and thermodynamic tendency to crystallize, and secondly, the transformation of cyclic into linear chains may also contribute to this phenomenon (see below).

Finally, it should be added that the DSC traces of samples annealed at 120 °C/2 h still display a weak glass-transition step around 50–55 °C in agreement with a relatively low crystallinity (<50%). This glass-transition step was no longer visible in the DSC traces at annealing at 170 °C (or 160 °C and 140 °C see below) in agreement with increasing crystallinity.

When the temperature was lowered to 160 °C (Table 2), one might not expect this small temperature difference to have a significant effect. But, in fact two noteworthy results were obtained. Firstly, even an annealing time of 2 d did not suffice to achieve a complete transformation of  $LT_m$  into  $HT_m$  crystallites having a  $T_m$  above 190 °C, although the  $T_m$ 's achieved after 1 d came close to this threshold. This failure is remarkable, because in the previously reported direct polymerization

experiments a reaction time of 1 d at 160 °C sufficed to obtain a polylactide having a  $T_m > 190$  °C. Secondly, the SEC measurements indicated that despite the lower temperature thermal degradation was nearly as effective as at 170 °C.

It is interesting to compare these observations with results obtained from annealing experiments with the catalyst  $SnNaph_2$  (Scheme 1).<sup>34</sup> These experiments were again performed at 160 °C and extended up to 4 d. Using even-numbered species (cycles and/or linear chains) as substrate allowed for monitoring the formation of odd-numbered species. Their detection proved, that the equilibration process involved all chains proceed in solid poly(L-lactide)s. As illustrated in Scheme 2, these transesterification reactions mainly involve the loops on the surface of the crystallites, because of their higher reactivity resulting from energetically unfavourable conformations. It was clearly demonstrated that the chain segments embedded in crystallites were not involved in transesterification reactions. Characteristic for these experiments with the sluggish  $SnNaph_2$  catalyst is the finding that despite long annealing times of 4 d, the  $T_m$  did not increase beyond 180 °C. Therefore, this comparison of  $SnBiph$  and  $SnNaph_2$  reveals firstly, that the reactivity of the catalyst is decisive for the transformation of  $LT_m$  into  $HT_m$  crystals and, secondly, that transesterification reactions involving all chains are restricted to the disordered phase on the surface of the crystallites and do not involve the interior of the crystallites or a melting of crystallites.

Further annealing experiments were performed at 140 °C (Table 3) and 130 °C (see Table S1, ESI†). Since both temperatures gave quite similar results, a separate discussion is not necessary. In both series a  $T_m > 185$  °C was not achieved, despite annealing times up to 8 d (No. 5, Tables 3 and S1†). These results confirmed that an annealing temperature > 160 °C is needed to reach an almost complete transformation of  $LT_m$  into  $HT_m$  crystallites with a  $T_m$  above 190 °C. The positive effect of the lower temperatures is significantly slower rate of thermal degradation. Up to an annealing time of 4 d (92 h) the  $M_w$  values remained above 160 000 g mol<sup>-1</sup> (from an initial value of 187 000 g mol<sup>-1</sup>) and the MALDI TOF mass spectra confirmed

**Table 4** Annealing of cyclic poly(L-lactide) with DSTL as catalyst

Exp. no.	Lac/Cat	<i>T</i> (°C)	<i>t</i> (h)	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	<i>T<sub>m</sub></i> (°C)	$\Delta H_m$ (–J g <sup>-1</sup> )	Cryst (%)
1A	1000/1	120	2	83 000	157 000	177.5	50.5	48
1B <sup>a</sup>	1000/1	120	2	87 000	162 000	176.5	48.5	46
2	1000/1	170	4	63 000	137 000	182.5	74.0	70
3	1000/1	170	8	33 000	91 000	185.0	75.0	71
4A	1000/1	170	24	26 000	63 500	187.0	59.0	56
4B <sup>a</sup>	1000/1	170	24	28 000	69 000	187.5	58.0	54
5A	1000/1	170	48	23 500	55 000	187.7	58.5	54
5B <sup>a</sup>	1000/1	170	48	22 000	57 000	187.0	59.0	55
6A	2000/1	170	2	91 000	157 000	178.0	64.5	61
6B <sup>a</sup>	2000/1	170	2	99 000	169 000	178.5	61.0	58
7	2000/1	170	24	33 000	81 000	189.0	86.5	81
8	2000/1	170	48	30 000	65 000	189.5	91.5	86

<sup>a</sup> Repetition with another batch of L-lactide.



that the cyclic species remained the predominant component of the entire sample. Somewhat surprising was the enormous difference between direct polymerization (B experiments) and annealing (A experiments) performed at identical temperature and time. Regardless, if a temperature of 130 °C or 140 °C was chosen, a polymerization time of 1 d sufficed to obtain a  $T_m$  of 189.5–190.5 °C. This enormous discrepancy raises the question, why the crystallization from the reaction mixture is far more effective in creating  $HT_m$  polylactides. A first-hand hypothesis suggests that the mobility of the catalyst along the surfaces of the crystallites is considerably higher, when the crystallites grow from the melt and are surrounded by a larger mobile amorphous phase. At 170 °C the situation is quite different, because no crystallization occurs during polymerization at this temperature.

### Annealing with various cyclic tin catalysts

This part of the work had the purpose to find out to what extent the results obtained with SnBiph can be achieved with the dibutyltin(IV) catalysts DSTL, BuSnBuCa and BuSnBiph, which showed a lower reactivity in polymerization experiments (Tables 4 and 5). Furthermore, the combination of SnOct<sub>2</sub> and salicylic acid was studied (Table 6). Considering the lower reactivity of the dibutyltin catalysts, and taking into account the results of SnBiph (Tables 1 and 2), all experiments listed in Tables 4–6 were performed at a temperature of 170 °C. A first series of annealing experiments was conducted with DSTL (Table 4), which gave excellent results in direct polymerization experiments despite its lower reactivity (in terms of polymerization rate). When a Lac/Cat ratio of 1000/1 was used (No. 1–5, Table 4), a time of 48 h did not suffice to achieve a  $T_m$  around 190 °C. Two more experiments were conducted with a Lac/Cat ratio of

2000/1, and despite the lower catalyst concentration, a  $T_m$  of 189.5 °C was reached.

The same Lac/Cat ratio was used for BuSnBuCa and BuSnBiph (Table 5), so that the performance of all three catalysts was comparable with each other and with the SnBiph experiments (Table 1.) at a Lac/Cat ratio of 2000/1. This comparison revealed that these dibutyltin catalyst were also reactive enough for complete transformation of  $LT_m$  into  $HT_m$  crystallites. Furthermore, they caused considerable reduction of the molecular weights, when the samples were annealed at 170 °C. An explanation of this phenomenon is provided in the discussion of the MALDI TOF mass spectra below.

SnOct<sub>2</sub> plays an extraordinary role in the chemistry of polylactides, since its technical production and most academic research concerning synthesis and properties of polylactides is based on this catalyst.<sup>35,36</sup> In a recent study it was shown by three experiments that alcohol-initiated and SnOct<sub>2</sub>-catalyzed ROPs of L-lactide failed to yield  $HT_m$  crystallites.<sup>13</sup> In this work, four annealing experiments were performed with the equimolar combination of SnOct<sub>2</sub> and salicylic acid (Table 6). Salicylic acid is a low toxic cocatalyst, which has been shown in a recent study to form a cyclic tin(II) salicylate which catalyzed a REP of L-lactide.<sup>37</sup> The standard procedure was applied, namely polymerization of L-lactide at 170 °C followed by annealing and crystallization at 120 °C for 2 h, whereupon crystallites with  $T_m$ 's below 175 °C were obtained (No. 1, Table 6). These samples were annealed at 170 °C for 4, 8, and 24 h in analogy to the experiments described for SnBiph in Table 1. Surprisingly, the SnOct<sub>2</sub>-salicylic acid system yielded a nearly complete transformation of the  $LT_m$  crystallites into the  $HT_m$ -crystallites within 8 h in close analogy to SnBiph. Although the  $T_m$ 's remained below 189 °C this transformation involved a considerable thickness growth of the lamellar crystallites as discussed below.

Table 5 Annealing of cyclic poly(L-lactide)s at 120 and 170 °C with BuSnBuCa and BuSnBuBiph at a Lac/Cat ratio of 2000/1

Exp. no.	Catalyst	$T$ (°C)	$t$ (h)	$M_n$	$M_w$	$T_m$ (°C)	$\Delta H_m$ (–J g <sup>–1</sup> )	Cryst. (%)
1	BuSnBuCa	120	2	98 000	197 000	176.0	52.5	49
2	BuSnBuCa	170	24	28 000	77 000	188.0	98.0	92
3	BuSnBuCa	170	48	31 000	65 000	190.5	98.0	92
4	BuSnBiph	120	2	47 500	107 000	155.5	56.5	53
5	BuSnBiph	170	24	22 000	67 000	191.0	94.0	88
6	BuSnBiph	170	48	24 000	62 000	189.0	101.0	95

Table 6 Annealing of cyclic poly(L-lactide)s at 120 and 170 °C prepared with the equimolar combination of SnOct<sub>2</sub> + salicylic acid as catalyst (Lac/Cat = 2000/1)

Exp. no.	$T$ (°C)	$t$ (h)	$M_n$	$M_w$	$T_m$ (°C)	$\Delta H_m$ (–J g <sup>–1</sup> )	Cryst. (%)
1	120	2	143 000	245 000	167.0	58.5	55
2	170	4	80 000	175 000	187.0	68.0	64
3	170	8	54 000	125 000	187.5	80.0	75
4	170	24	32 000	85 500	187.0	95.5	90



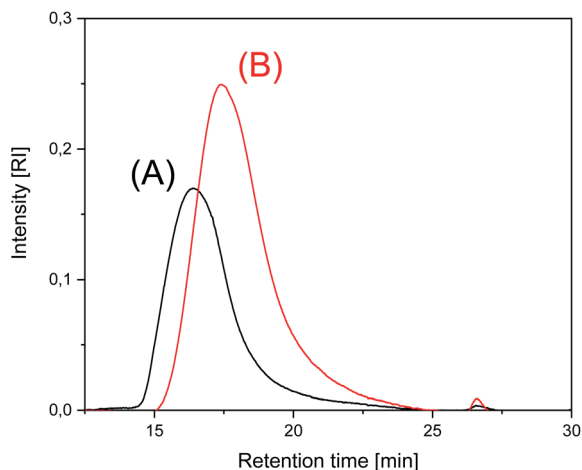


Fig. 2 SEC of poly(lactides) prepared and annealed with  $\text{SnOct}_2$  + salicylic acid: (A) No. 1, Table 6, (B) No. 3, Table 6.

These experiments allow for two conclusions. First, all catalysts enable transformation of  $\text{LT}_m$  into  $\text{HT}_m$  crystallites at  $170^\circ\text{C}$ . Second, annealing at  $170^\circ\text{C}$  for 24 h or longer results in decreasing molecular weights. This decrease is combined with an increase of crystallinity, but it is somewhat surprising that it occurred in solid poly(lactides) and proceeds without significant loss of mass ( $\Delta m < 5\%$ ). The SEC elution curves of  $\text{SnOct}_2$  +

salicylic acid-catalyzed poly(lactides) displayed in Fig. 2 and the elution curves of  $\text{BuSnBuCa}$ -catalyzed samples presented in Fig. S2 (ESI†) illustrate this process. All the curves obtained from poly(lactides) have in common that the dispersity increases upon annealing at  $170^\circ\text{C}$  partially due to formation of a larger fraction of oligomers as demonstrated by small maximum at long elution times. A partial alteration of the molecular weight distribution found by MALDI TOF mass spectrometry seems to play a role in the conspicuous decrease of the average molecular weights. Yet another contribution may result from chain scission.

## WAXS and SAXS measurements

In the first publication dealing with the preparation of  $\text{HT}_m$  crystallites by direct polymerization of  $\text{l-lactide}$  it was found, that the WAXS patterns do not allow for differentiation between  $\text{LT}_m$  and  $\text{HT}_m$  crystallites.<sup>22</sup> Both kinds of crystallites possess the orthorhombic  $\alpha$ -modification first described by DeSantis and Kovacs.<sup>12</sup> The  $\alpha$ -modification is known to be the thermodynamically most stable crystal modification of poly( $\text{l-lactide}$ ), which is usually formed at temperatures around and above  $120^\circ\text{C}$  in the absence of mechanical stress. The WAXS patterns of samples No. 1–4, Table 1, presented as Fig. S3(A–D)† in the supplemental part demonstrate that this modification is also formed by the poly( $\text{l-lactide}$ )s studied in this work, regardless of annealing temperature and time. Therefore, the WAXS powder

Table 7 Long periods of selected poly( $\text{l-lactide}$ )s from SAXS measurements grouped according to table numbers

Exp. no.	Table	Cat.	Temp./time ( $^\circ\text{C}$ )/(h)	$T_m$ ( $^\circ\text{C}$ )	$L$ (nm)	Cryst. (%)	$l_c$ (nm)	$\sigma_c$ ( $\text{J m}^{-2}$ )
1	1	SnBiph	120/2	176.0	— <sup>a</sup>	40	—	—
3	1	SnBiph	170/3	194.5	37	83	31	24
5	1	SnBiph	170/48	192.5	36	96	35	25
9	1	SnBiph	120/2	176.5	22	40	9	—
11	1	SnBiph	170/48	194.0	29	95	28	19
2	2	SnBiph	160/4	181.3	23	61	14	—
3	2	SnBiph	160/8	183.0	24	69	17	—
4	2	SnBiph	160/24	188.5	25	82	21	—
5	2	SnBiph	160/48	187.0	25	78	20	—
1	3	SnBiph	120/2	176.0	21	40	9	—
2	3	SnBiph	140/8	179.0	28	54	15	—
3A	3	SnBiph	140/24	181.5	26	55	15	—
4	3	SnBiph	140/48	183.0	26	64	17	—
6B	3	SnBiph	140/192	190.0	28	85	24	22
1A	4	DSTL	120/2	177.5	21	48	10	—
2	4	DSTL	170/4	182.5	25	70	18	25
4A	4	DSTL	170/24	187.0	24	56	13	—
5A	4	DSTL	170/48	187.7	23	54	12	—
2	5	BuSnBuCa	170/24	188.0	29	92	26	25
3	5	BuSnBuCa	170/48	190.5	28	92	26	22
5	5	BuSnBiph	170/24	191.0	39	88	34	30
6	5	BuSnBiph	170/48	189.0	33	96	32	27
1	6	$\text{SnOct}_2$ + Sal	120/2	167.0	21	55	12	—
2	6	$\text{SnOct}_2$ + Sal	170/4	187.0	40	64	26	35
3	6	$\text{SnOct}_2$ + Sal	170/8	187.5	38	75	28	33
4	6	$\text{SnOct}_2$ + Sal	170/24	187.0	32	90	29	28
2B	S1 (ESI)	SnBiph	130/24	190.5	29	66	20	22

<sup>a</sup> No SAXS reflex was detectable.

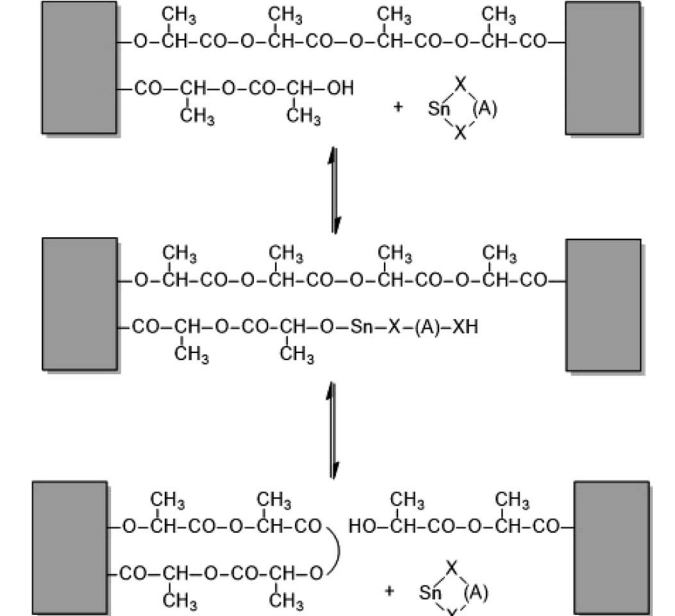


patterns do not contribute anything to a differentiation between  $LT_m$  and  $HT_m$  crystallites. As usual, they are sensitive to the degree of crystallization, and the WAXS patterns of Fig. S3(B)–(D)<sup>†</sup> confirmed, that by annealing at 170 °C crystallinities in the range of 80–90% can be reached.

It was also previously reported that samples with  $LT_m$  crystallites show SAXS reflections in the narrow range between 16–22 nm regardless of the molecular weights and if the samples were annealed at 120 °C or 160 °C.<sup>13</sup> For poly(L-lactide)s prepared by cyclic tin catalysts  $L$ -values (long distance periodicity) in the range of 28–34 nm were found. The  $L$ -values listed in Table 7 indicate, that the same correlation also exists for the samples studied in this work, as exemplarily illustrated in Fig. 3 (and Fig. S4 and S5, ESI<sup>†</sup>). For several samples even  $L$ -values in the range of 37–40 nm were found. To get a more accurate insight into the extent of thickness growth the average lamellar thickness ( $l_c$ ) was calculated from  $L$ -values by multiplication with the fraction of crystalline phase (see Table 7). These  $l_c$  values demonstrate that the thickness growth is indeed enormous and corresponds to a factor of 2.5–3.5. In the case of the SnBi and SnSal catalysts most of the thickness growth occurs during the first 8 hours. When the transformation was less complete, as it was characteristic for polylactides prepared with DSTL (Table 4), smaller  $l_c$ -values were found in combination with  $T_m$ 's around 184–187 °C. Hence, it may be concluded that an enhanced thickness of the lamellae is one important reason for the higher  $T_m$  values. However, a simple proportionality of  $T_m$  and  $L$  or  $l_c$  values does not exist, as already observed for the previous polymerization experiments. For example, the  $T_m$  values of the samples No. 6, Table 3, No. 3, Table 5, No. 5, Table 5 and No. 3B, Table S1,<sup>†</sup> all fall into narrow the range of 190–191 °C, whereas the  $l_c$  values vary between 20 and 34 nm. Therefore, it is unavoidable to assume that homogenization and “smoothing” of the surface is another factor, which contributes to the formation of  $HT_m$  crystallites. This “smoothing” of the lamellar surfaces reduces the free surface energy ( $\sigma_e$ ) with the consequence that  $T_m$  increases. The Gibbs–Thomson eqn (1)

$$T_m = T_{m0}[1 - (2\sigma_e/\rho\Delta H_m l_c)] \quad (1)$$

presents the correlation of the  $T_m$  with the free surface energy ( $\sigma_e$ ), the crystal density ( $\rho$ ), the melting enthalpy  $\Delta H_m$  and with the average thickness of the crystallites ( $l_c$ ).



Scheme 4 Example of a transesterification reaction cleaving (or generating) a tie molecule.

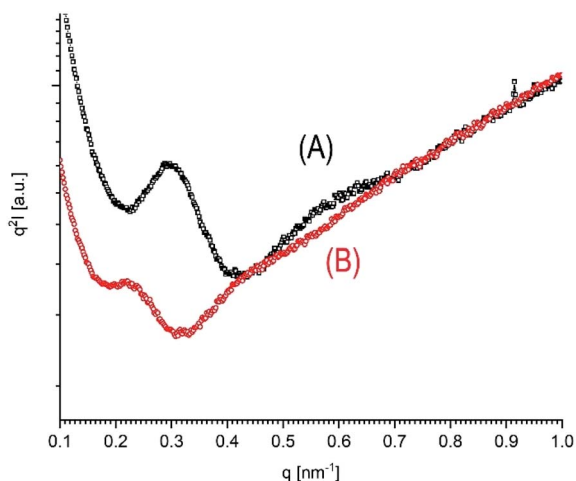


Fig. 3 SAXS Kratky plot of polylactides prepared and annealed with SnBiph at 140 °C: (A) 2 d (No. 4, Table 3), (B) directly polymerized for 8 d (No. 6B, Table 3).





polylactides (No. 6, Table 3, No. 3 and 5, Table 5, No. 3B, Table S1†) it can indeed be seen that a lower lamellar thickness is combined with lower  $\sigma_e$  values, meaning a more perfect smooth surface. The  $\sigma_e$  values of this work have the same order of magnitude as reported by Tezuka and coworkers for their cyclic guest–host copolylactides ( $24\text{--}28\text{ mJ m}^{-2}$ ).<sup>17</sup> They interpreted the low  $\sigma_e$  values of their cycles (relative to higher values of the linear counterparts) by a smooth surface mainly resulting from nearly identical loops containing the guest building blocks. This interpretation fits in with the afore-mentioned hypothesis of the authors that the formation of  $HT_m$  crystals is partially due to smoothing of the surfaces by transesterification.

Thickness growth and “smoothing” can be explained by at least three types of transesterification reactions, which are catalyzed by the presence of a reactive catalyst:

- (1) depolymerization (and polymerization) of large loops or chains sticking out from the surface of the crystallites,
- (2) depolymerization (and chain growth) of linear chain ends, and
- (3) cleavage of tie chains connecting neighbouring crystallites.

Schemes 2–4 and Fig. 4 present a simplified illustration of these transesterification processes. The driving force behind all these transesterification reactions is a gain in crystallization enthalpy. The “smoothing” of the surfaces and a removal of tie molecules enable, in turn, a more perfect 3-dimensional arrangement of the crystallites. This conclusion is confirmed by the 2<sup>nd</sup> order reflex in the SAXS measurements of samples annealed at 170 °C. Hence, the SAXS data and the extremely high degrees of crystallinity clearly support the hypothesis that “smoothing” of the crystallite surfaces plays an important role for the formation of  $HT_m$  poly(l-lactide)s.

### Optical microscopy

Numerous samples listed in Tables 1–3 and S1† were examined by optical microscopy regarding formation and size of spherulites. Samples annealed at 120 °C for 2 h did not display spherulites. The same negative result was obtained, when samples were annealed at 130 or 140 °C up to 4 d. However,

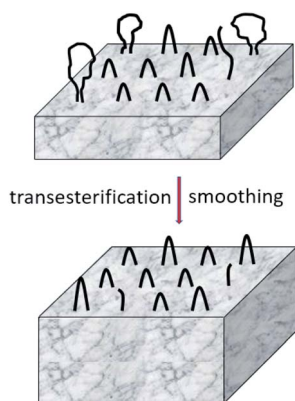


Fig. 4 Simplified model of “smoothing” of lamellar surfaces combined with thickness growth.

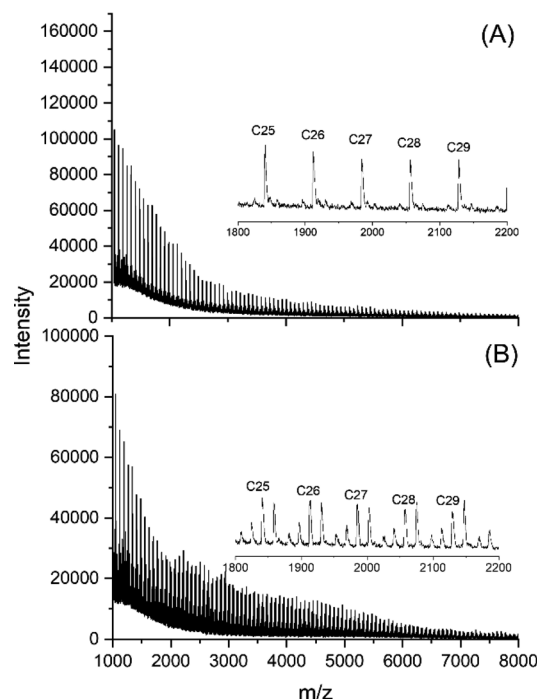


Fig. 5 MALDI-TOF mass spectra of polylactides prepared and annealed with SnBiph: (A) at 140 °C/24 h (No. 3A, Table 3), (B) 140 °C/192 h (No. 6A, Table 3.).

when the annealing at 130 or 140 °C was extended, spherulites with a diameter in the range of 0.7–1.0 mm became detectable. After annealing at 170 °C for 1 or 2 d no spherulites were visible regardless of the Lac/Cat ratio. Yet when the annealing temperature was lowered to 160 °C, nice spherulites appeared having diameters of 1.5–2.0 mm. Unfortunately, these observations do not contribute much to a better understanding of the transformation of  $LT_m$  into  $HT_m$  crystallites.

### MALDI-TOF mass spectrometry

MALDI TOF mass spectrometry enables differentiation between cyclic and linear species, and between even and odd-numbered linear or cyclic polylactides. Hence, mass spectrometry is a powerful tool to detect and identify transesterification reactions in solid polylactides. Two examples for such an application have recently been published by the authors.<sup>39,40</sup> The mass spectra of the SnBiph-catalyzed polylactides revealed the following trends. At relatively low temperatures of 130 °C and 140 °C the mass spectra remain unchanged up to 48 h but display a considerable transformation of cyclic into linear chains after annealing for 8 d (Fig. 5). At 160 and even more at 170 °C the transformation based on thermal side reactions is, of course faster as exemplarily illustrated in Fig. 6. After 1 d at 170 °C the peak pattern is similar to that obtained after 8 d at 140 °C (Fig. 6A) and after 2 d at 170 °C the peaks of cycles have almost completely disappeared (Fig. 6B) despite a low catalysts concentration (Lac/Cat ratio 4000/1).

Taking into account the previous data of cyclic poly(l-lactide) s these observations indicate that high molar mass cyclic and



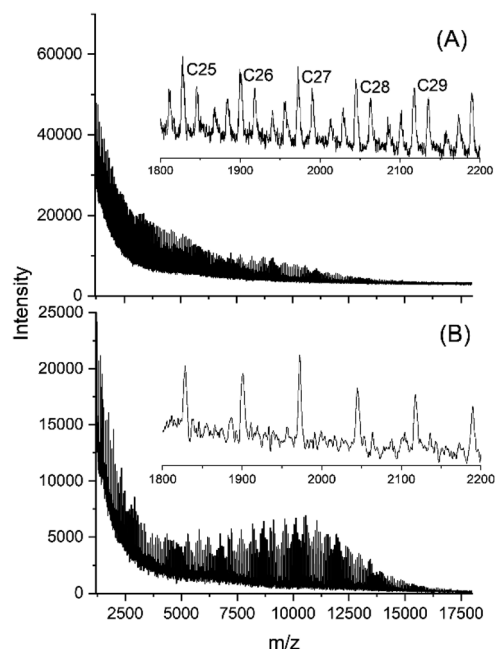


Fig. 6 MALDI-TOF mass spectra of poly(lactides) prepared and annealed with SnBiph: (A) 170 °C/24 h (No. 10, Table 1), (B) 170 °C/48 h (No. 11, Table 1).

linear chains can adopt the same high melting morphology with  $T_m$  values in the range of 193–196 °C in contrast to reports of other research groups.<sup>17,18,21</sup> Yet another consequence of this finding concerns the calculation of the equilibrium  $T_{m0}$  of

perfect crystals (215 °C) as described by Kalb and Pennings.<sup>19</sup> The present and previous<sup>20</sup> experimental  $T_m$  values suggest that the extrapolated 215 °C are close to reality, whereas  $T_{m0}$  values below 205 °C are certainly too low. For this conclusion it does not matter, whether cyclic or linear polylactides were investigated by Kalb *et al.*,<sup>19</sup> as indicated by the above results and by the following consideration. Real crystallites of cycles and linear chains differ in the number of loops on the “flat” surface of the crystallites. Yet, for crystallites of infinite thickness this difference and its influence on  $T_m$  vanishes.

A second, quite unexpected trend resulted from the variation of the Lac/Cat ratio of the SnBiph catalyst (No. 5–11, Table 1). At a Lac/Cat ratio of 4000/1 (but not at 1000/1) a flat maximum of the peak intensities with characteristic fine structure appeared around  $m/z$  11 000 (Fig. 6A). This maximum and its fine structure became more pronounced after 48 h (Fig. 6B). The third trend was again formation of a new maximum in the distribution of peak intensities, when the three dibutyltin(IV) catalysts were used (Fig. 7 and S6, ESI†). Yet, in contrast to the SnBiph experiments, the new maximum appeared around  $m/z$  5000–5500, the moiety of the maximum found for the SnBiph-catalyzed samples (Fig. 6). A new maximum around  $m/z$  5500 was also found when SnOct<sub>2</sub> + salicylic acid was used as catalyst (Fig. 8B).

In other words, the mass spectra indicate the beginning of a total reorganization of molecular weight distribution. It is well known and quite logic that transesterification causes broadening of the molecular weight distribution (MWD) when the virgin polyester has narrow MWD (*e.g.* <1.5). In such cases the

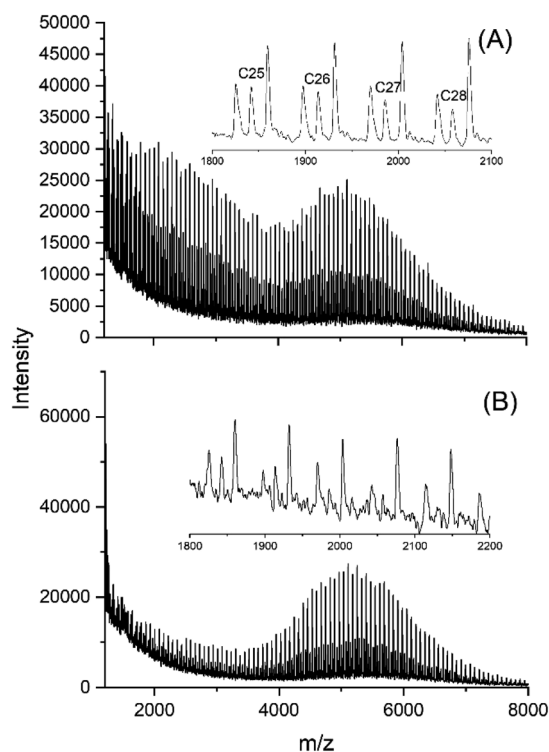


Fig. 7 MALDI-TOF mass spectra of poly(lactides) prepared and annealed with DSTL: (A) 170 °C/24 h (No. 4, Table 4), (B) 170 °C/48 h (No. 5, Table 4).

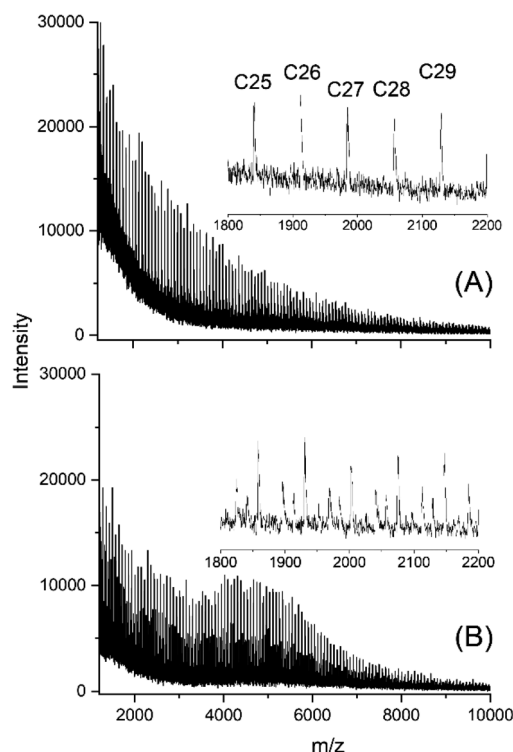


Fig. 8 MALDI-TOF mass spectra of poly(lactides) prepared and annealed with SnOct<sub>2</sub> + salicylic acid: (A) 120 °C/2 h (No. 1, Table 6), (B) 170 °C/24 h (No. 4, Table 6).

MWD tends to approach the “most probable distribution” known from Flory's analyses of polycondensates.<sup>41</sup> Characteristic for his MWD is a maximum of the number distribution of cyclic or linear polymers at the first reaction product, usually a dimer or rarely a tetramer. A segment of such a distribution is illustrated in the mass spectrum of Fig. 8A. The formation of such a broader distribution is driven by a gain in entropy. Yet, the mass spectra displayed in Fig. 5–8 demonstrate formation of maxima in the MWD around  $m/z$  5500 or 11 000. Since equilibration (transesterification) reactions between polyester chains have a thermal character, a gain in crystallization enthalpy is the most likely explanation for this change. Since the fraction of molecules involved in the formation of a new maximum in the mass spectrum is small, an influence on the SEC elution curves may not be expected.

## Conclusion

The results elaborated in this work allow for the following conclusions. First, transformation of  $LT_m$  crystallites into  $HT_m$  crystallites with  $T_m$  values > 190 °C is feasible, but requires an annealing temperature > 160 °C. Second, this transformation performed by annealing in absence of mechanical stress confirms that the  $HT_m$  crystals represent the thermodynamically most stable crystalline phase of poly(L-lactide). Third, the most effective polymerization catalysts SnBi and BuSnBi gave the best results in terms of high  $T_m$  values and high degrees of crystallinity. Fourth, direct polymerization is the more efficient method for the preparation of  $HT_m$  crystallites at reaction temperatures < 160 °C, whereas at 170 °C crystallization of the freshly prepared poly(L-lactide)s was not achieved. Therefore, the annealing method is superior at 170 °C. Fifth, the formation of  $HT_m$  crystallites involves growth of the lamellar thickness by 250–350% during the first 24 h combined with more perfect 3d-order of the crystallites. Sixth, annealing at 170 °C is accompanied by degradation of the molecular weights, by transformation of cycles into linear chains, whereas the degree of crystallinity increases. Seventh, high molar mass linear and cyclic poly(L-lactide)s can reach the same high  $T_m$  values in the range of 130–196 °C. Eighth, the  $T_{m0}$  (215 °C) and  $\Delta H_{m0}$  (106 J g<sup>-1</sup>) of perfect crystallites reported by Kalb *et al.*,<sup>19</sup> Tsuji *et al.*<sup>30</sup> and Sarasua *et al.*<sup>29</sup> are almost correct, whereas lower values reported by several research groups are too low. Finally, the decrease of molecular weights and lamellar thickness is to some extent the result of a reorganization of the molecular weight distribution with a predominant formation of crystallites consisting of low molar mass rings and/or linear chains. In summary, in the presence of reactive transesterification catalysts, solid poly(L-lactide)s may be considered as a ‘living system’ with a slow but permanent progress of transesterification reaction entailing a change of various properties.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors wish to thank Dr U. Mühlbauer (Thyssen-Uhde, Berlin) for kindly supplying the L-lactide and Mrs A. Myxa (BAM, Berlin) for all SEC measurements.

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