

RESEARCH ARTICLE

Polycondensation of poly(L-lactide) alkyl esters combined with disproportionation and symproportionation of the chain lengths

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Abstract

Ring-opening polymerizations (ROPs) of L-lactide (LA) were performed with ethyl L-lactate or 11-bromoundecanol as initiators (In) and tin(II) ethyl hexanoate (SnOct₂) as catalyst (Cat) using four different LA/In ratios (20/1, 40/1, 60/1, and 100/1). One series of ROPs was conducted in bulk at 120 °C, yielding PLAs with low dispersities ($\mathcal{D} \sim 1.2\text{--}1.4$), and a second series was conducted in bulk at 160 °C, yielding higher dispersities ($\mathcal{D} \sim 1.3\text{--}1.9$). Samples from both series were annealed for 1 or 14 days at 140 °C in the presence of SnOct₂. Both polycondensation and disproportionation reactions occurred, so that all four samples tended to form the same type of molar mass distribution below 10,000 Da, regardless of their initially different number average molar masses (M_n). Both initiators gave nearly identical results. The thermodynamic control of all reversible transesterification processes favored the formation of crystallites composed of chains with a M_n around 3500–3700, corresponding to a crystal thickness of 10–13 nm.

KEYWORDS

crystallization, disproportionation, lactide, polycondensation, ring-opening polymerization, transesterification

1 | INTRODUCTION

Over the past 50 years poly(L-lactide), PLA, has made a steep career as a biodegradable and resorbable material and has found numerous applications.^{1–5} Starting with a production of a few tons p.a. for medical applications, the technical production of PLA has meanwhile increased to more than 700,000 tons p.a. This career has entailed numerous research activities in all directions concerning synthetic methods, characterization, and potential applications. The technical production is based on an alcohol-initiated ring-opening polymerization (ROP) catalyzed by

tin(II) 2-ethylhexanoate (abbreviated as SnOct₂ or Cat). The main purpose of alcohol addition is the control of the molar masses via the LA/alcohol ratio. Therefore, alcohol-initiated ROPs have attracted much interest and have been studied by numerous research groups. The structure of monofunctional alcohols has been varied, di- and multifunctional alcohols have been used as initiators, the nature of catalysts has been varied over a broad range and the influence of their concentration, time, and temperature has been studied.^{6,7}

It has been speculated by numerous research groups^{8–18} that tin-containing catalysts possess a rather

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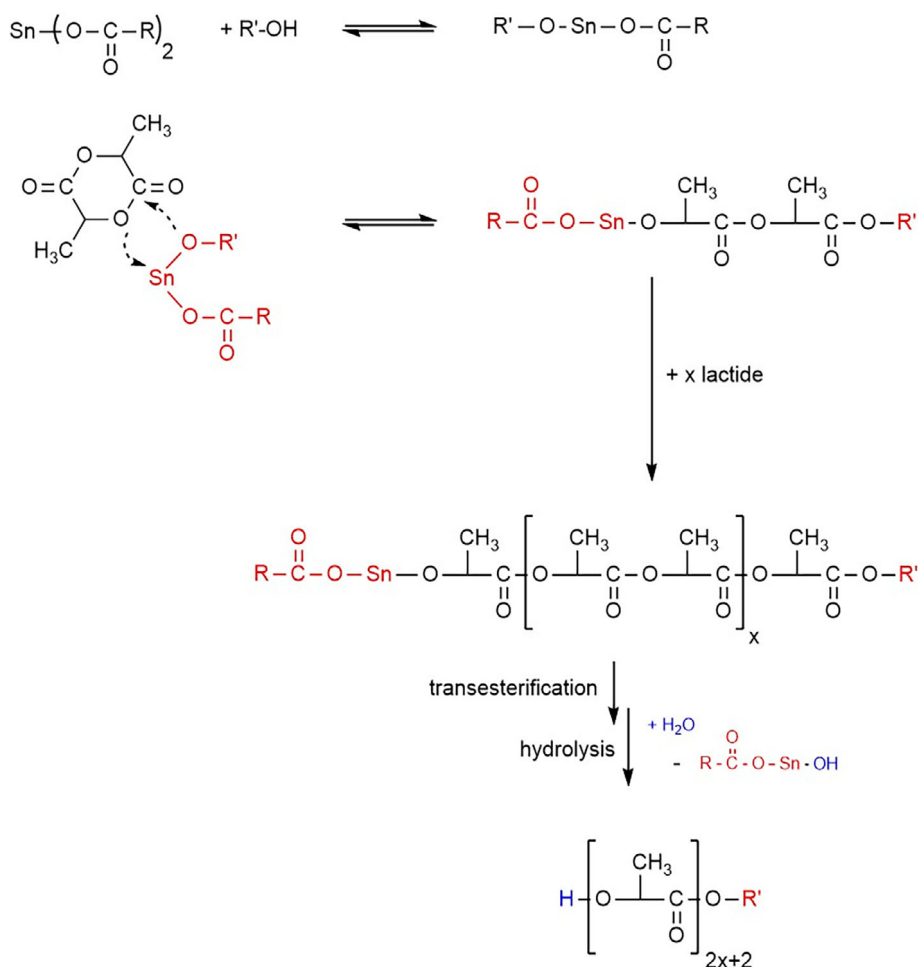
high human toxicity and should be replaced by metal-free^{8–17} or by zinc-containing catalysts.¹⁸ However, the data available from literature^{6,19,20} and the vote of the toxicity experts of the American FDA²¹ clearly show that the human toxicity of tin(II) salts is quite low, despite a high toxicity against certain microbes. For all these reasons, the authors believe that it is still justified to study SnOct₂-catalyzed polymerizations of lactide, as even the frequently studied alcohol-initiated ROPs catalyzed by SnOct₂ are far from being well understood.

The mechanism of alcohol-initiated and SnOct₂-catalyzed ROPs of LA has been elucidated by three research groups and was found to proceed according to Scheme 1. The research groups of Penczek²² and Prud-Homme²³ studied ROPs initiated by primary amines or primary alcohols at 70 °C or 80 °C in solution and found that these ROPs proceed as living polymerizations so that the dispersities were low (<1.2) and the average degrees of polymerization (DPs) parallel the LA/In ratio. However, it was shown by the authors, that ROPs conducted at high temperatures (>140 °C) yield cyclic PLAs as by-products in addition to higher dispersities, so that the DP no longer parallels the LA/In ratio when the In/Cat ratio

decreases below a value of 20. The formation of cycles results from the competition of the ROPPOC mechanism (ring-opening polymerization with simultaneous polycondensation) which is initiated by neat SnOct₂ (Scheme 2).^{24,25}

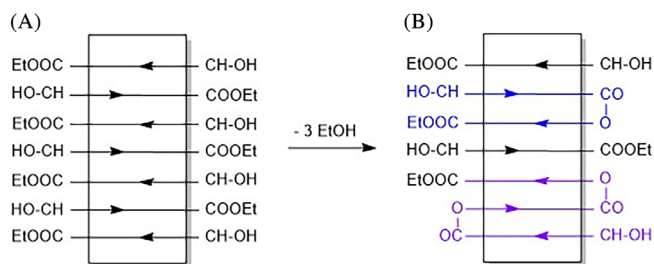
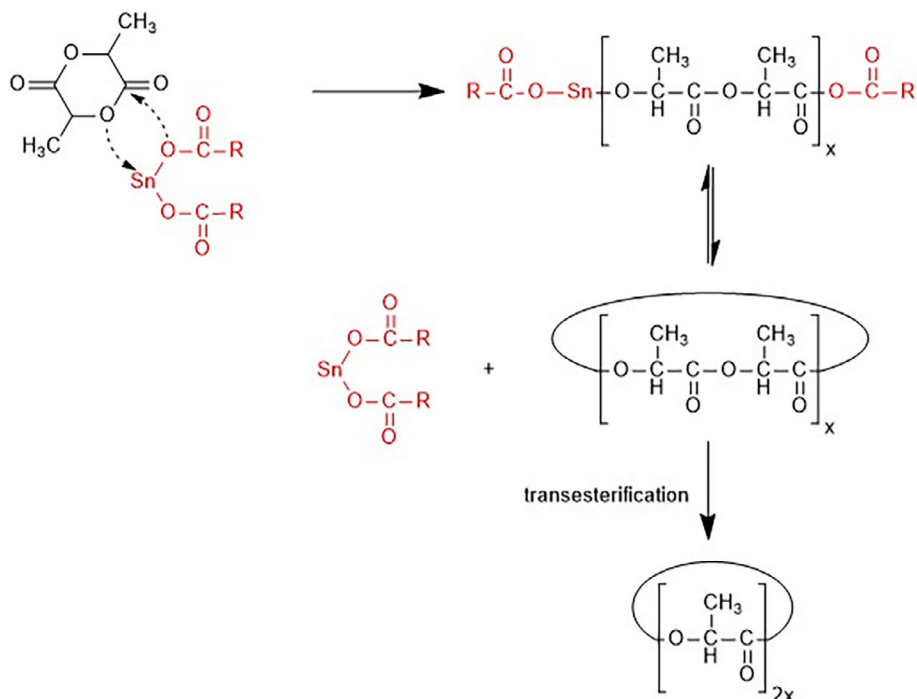
A second complication arises from the fact that the nature of the alcohol influences the rate of polymerization and the extent of transesterification (e.g., equilibration of even- and odd-numbered chains). The third complication arises from the fact that the alkyl ester end groups can undergo (poly)condensation reactions when heated above 120 °C in the presence of SnOct₂ or other active catalysts, and these (poly)condensation reactions continue even in the solid state (Scheme 3).²⁶

While studying these (poly)condensation reactions, the authors became aware of a fourth complication called here “disproportionation” of the chain lengths. This new phenomenon was discovered when PLAs prepared with varying LA/In ratios were characterized by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. A disproportionation of chain lengths due to transesterification reactions (as formulated in Scheme 3) was observed during and



SCHEME 1 Mechanism of the alcohol-initiated ROP of La catalyzed by SnOct₂.

SCHEME 2 SnOct₂-catalyzed ROPPOC mechanism yielding cyclic PLAs.



SCHEME 3 Polycondensation in solid PLAs via the formation of loops on the surface of crystallites.

after crystallization. Therefore, the aim of the present work was to document and study this new phenomenon using two different alcohols as initiators and SnOct₂ as catalysts.

2 | EXPERIMENTAL

2.1 | Materials

L-Lactide, a product of Corbion-Purac, was kindly supplied by Thyssen-Uhde SE (Berlin) and recrystallized from toluene (99.98%, extra dry, Thermo-Scientific Fisher, Schwerte, Germany). Anhydrous dichloromethane and SnOct₂ (>96%) were also purchased from Thermo-Scientific Fisher. Ethyl L-lactate (ELA) and 11-bromoundecanol (BrUnd) were purchased from Sigma Aldrich (Taufkirchen, Germany) and used as received.

2.2 | ELA-initiated polymerization at 120 °C in bulk

Ethyl L-lactate (ELA) (2.0 mmol) and L-lactide (40 mmol) were weighed into a 50 mL Erlenmeyer flask, a magnetic bar was added, and SnOct₂ (0.04 mmol) was injected as a 0.4 M solution in toluene (Table 1). The reaction vessel was immersed in an oil bath thermostated at 120 °C. After 40 min, the reaction mixture crystallized and after 1 h, the polymerization was stopped and part of the product (approximately 1 g) was isolated using a spatula and pincer. The remaining PLA was thermostated at 140 °C and after 1 day another part of the product was isolated for characterization. The remainder was annealed at 140 °C for another 13 days. The experiments were performed with smaller amounts of ELA corresponding to LA/ELA ratios of 40/1, 60/1, and 100/1. In all experiments, the reaction mixtures crystallized within 30–45 min. Conversions around or above 99% were confirmed by ¹H (nuclear magnetic resonance) NMR spectroscopy.

2.3 | ELA-initiated polymerizations at 160 °C in bulk

ELA (2.0 mmol) and L-lactide (40 mmol) were weighed into a 550 mL Erlenmeyer flask under an argon blanket and a magnetic bar was added (Table 2). The reaction vessel was immersed in an oil bath thermostated at 160 °C. After 1 h, all reaction mixtures were turned

TABLE 1 Ethyl lactate-initiated ROP of LA at 120 °C in bulk followed by annealing at 140 °C (LA/Cat = 1000/1).

Exp. No.	LA/ELA	Temperature (°C)	Time	M_n (NMR)	M_n (GPC)	M_w (GPC)	\bar{D}	T_m (°C)	ΔH_m (Jg ⁻¹)	Cryst (%)	L (nm)	l_c
1A	20/1	120	1 h	2900	5200	7000	1.3	153.8	57.6	49	13.4	~7
1B	20/1	140	1 d	3000	6500	9200	1.4	162.0	71.3	61	–	–
1C	20/1	140	14 d	3400	11,000	16,500	1.5	173.9	85.3	74	16.2	10
2A	40/1	120	1 h	5900	8800	14,400	1.6	166.3	68.8	60	18.5	10
2B	40/1	140	1 d	7200	12,900	19,100	1.5	175.4	84.3	74	14.7	9
2C	40/1	140	14 d	7700	15,000	23,700	1.6	177.7	90.8	80	15.5	11
3A	60/1	120	1 h	7500	12,500	21,800	1.7	172.2	70.3	61	16.7	10
3B	60/1	140	1 d	8300	13,300	25,100	1.8	178.8	92.6	81	17.6	9
3C	60/1	140	14 d	9700	17,300	29,000	1.7	183.8	97.7	86	19.2	14
4A	100/1	120	1 h	10,500	19,600	32,000	1.7	174.7	63.8	56	16.2	13
4B	100/1	140	1 d	13,000	21,000	33,500	1.7	181.3	90.3	89	14.5	13
4C	100/1	140	14 d	14,500	22,200	36,500	1.7	184.7	97.7	86	16.2	14

TABLE 2 Ethyl lactate-initiated ROP of LA at 160 °C in bulk followed by annealing at 140 °C (LA/Cat = 1000/1).

Exp. No.	LA/BrUND	Temperature (°C)	Time	M_n (meas.)	M_w (meas.)	\bar{D}	T_m (°C)	ΔH_m (Jg ⁻¹)	Cryst (%)
1A	20/1	160	1 h	5200	7000	1.3	–	–	–
1B	20/1	140	1 d	6700	9000	1.3	161.3	48.6	31
1C	20/1	140	14 d	8700	14,000	1.6	169.5	65.0	57
2A	40/1	160	1 h	8900	14,200	1.5	–	–	–
2B	40/1	140	1 d	11,700	17,700	1.5	170.5	76.1	66
2C	40/1	140	14 d	12,300	22,000	1.8	178.8	88.4	76
3A	60/1	160	1 h	12,000	20,700	1.7	–	–	–
3B	60/1	140	1 d	15,500	24,000	1.5	172.5	79.8	69
3C	60/1	140	14 d	15,900	28,000	1.8	179.0	88.6	78
4A	100/1	160	1 h	19,200	36,600	1.9	–	–	–
4B	100/1	140	1 d	21,500	36,500	1.9	176.4	85.0	74
4C	100/1	140	14 d	22,000	36,000	2.0	180.2	89.8	79

TABLE 3 11-Bromoundecanol-initiated ROPs of LA in bulk at 120 °C.

Exp. No.	LA/ELA	Temperature (°C)	Time	M_n	M_w	T_m (°C)	ΔH_m (Jg ⁻¹)	Cryst (%)
1A	20/1	120	1 h	5300	6200	143.3	56.5	49
1B	20/1	140	1 d	5500	6400	151.3	42.7	38
1C	20/1	140	14 d	10,500	15,900	165.3	73.4	64
2A	60/1	120	1 h	13,500	17,000	164.8	64.1	56
2B	60/1	140	1 d	15,000	17,600	170.4	81.3	71
2C	60/1	140	14 d	16,900	28,000	173.0	92.0	80
3A	100/1	120	1 h	16,400	23,500	166.0	64.4	56
3B	100/1	140	1 d	17,000	24,500	175.5	81.1	71
3C	100/1	140	14 d	28,000	48,000	181.8	92.8	81

viscous, and after 2 h, a sample of approximately 500 mg was removed using a spatula or pincer. The reaction vessel was again filled with argon and the remaining PLA was annealed at 140 °C for 1 day or 14 (see Table 2).

2.4 | BrUnd-initiated polymerizations

Three BrUnd-initiated polymerizations (LA/In = 20/1, 60/1, and 100/1) were performed at 120 °C, analogous to those described above for ELA. All annealing experiments were conducted in an argon atmosphere (Table 3).

2.5 | Measurements

The ^1H NMR measurements were performed with a Bruker Advance 400 III in 5 mm o.d. sample tubes, using CDCl_3 containing TMS as a solvent and shift reference. The ethyl ester end group shows four signals of equal intensity between 3.5 and 3.8 ppm and a triplet at 1.4 ppm.

The MALDI TOF mass spectra were measured on an Autoflex Max mass spectrometer (Bruker Daltonik, Bremen, Germany). All spectra were recorded in the positive ion linear mode. The MALDI stainless steel targets were prepared from chloroform solutions of poly(L-lactide) (3–5 mg mL $^{-1}$) doped with potassium trifluoroacetate (2 mg mL $^{-1}$ in THF). Typically, 20 μL of the sample solution, 2 μL of the potassium salt solution, and 50 μL of the matrix solution (DCTB – trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile, 20 mg mL $^{-1}$ in CHCl_3) were premixed in an Eppendorf vial. A droplet (1 μL) of this solution was deposited on the MALDI target and, after evaporation of the solvent, inserted into the mass spectrometer. Eight thousand individual spectra were recorded and accumulated from four different locations of each spot.

The gel permeation chromatography (GPC) measurements were performed in chloroform in an LC 1200 instrument (Agilent, USA) kept at 40 °C. The flow rate was 1 mL min $^{-1}$ and a refractive index detector was used. Samples were injected automatically (100 μL , 2–4 mg mL $^{-1}$ in chloroform). Win GPC software (Polymer Standards Service—PSS, Mainz, Germany) was used for instrument control and data calculation. Calibration was performed using polystyrene standard sets (Polymer Standards Service—PSS, Mainz, Germany). The number of average (M_n) and weight average (M_w) masses listed in Tables 1–3 are uncorrected. Fractionation experiments were performed manually by collecting the eluent at the end of the capillary.

The differential scanning calorimetry (DSC) heating traces were recorded on a Mettler-Toledo DSC-1 (freshly calibrated with indium and zinc) equipped with Stare Software-11 at a heating rate of 10 K min $^{-1}$. Only the first heating curves were evaluated.

3 | RESULTS AND DISCUSSION

3.1 | ELA-initiated polymerizations at 120 °C

A first series of ELA-initiated ROPs was conducted at 120 °C in bulk with a reaction time of 1 h (Table 1). These conditions were chosen to obtain PLAs with a narrow molar mass distribution, that is, dispersities (\bar{M}_w/\bar{M}_n) around or below 1.2, and to avoid the influence of transesterification and condensation reactions. The reaction mixtures started to crystallize after 30 min and the PLAs were isolated after 1 h, when the reaction volume of all samples was filled with spherulites. The ^1H NMR spectra confirmed >99% conversion and complete incorporation of the initiator. The MALDI TOF mass spectra presented in Figure 1 show that the maxima of the distribution curves shifted to higher masses but did not exactly parallel the LA/In ratios. The main reason for this deviation is also evident from the mass spectra, namely transesterification reactions yielding low molar mass poly(lactides). Consistent with similar ROPs conducted at 130 °C²⁷ the even-odd equilibration was not complete under these conditions, and since the initiator contained one lactyl unit, the predominant peaks resulted from odd-numbered chains. Remarkably, the ROP was found to be accompanied by random transesterification, yielding linear PLAs in the mass range of m/z 1000–8000 with a broad mass peak distribution (MPD). This side reaction increased with higher LA/In ratios (Figure 1). Since the sum of ethyl ester end groups cannot have increased, the formation of these low molar mass species must be accompanied by either cyclic or high molar mass chains.

Yet, in the mass spectra of all PLAs prepared at 120 °C, cycles were not detectable. The assumption that the formation of longer chains significantly exceeds the average defined by the LA/In ratio, has been proven by fractionation combined with mass spectrometry of the individual fractions. Weak maxima of the MPD were indeed detectable above m/z 15,000 (Figure S1). To what extent these polycondensates were formed in the melt or the solid state is difficult to elucidate. This interpretation is supported by the GPC data and by the shapes of the elution curves (Figure 2A).

The following four trends were observed. At first glance, the number of average molar masses (M_n) was

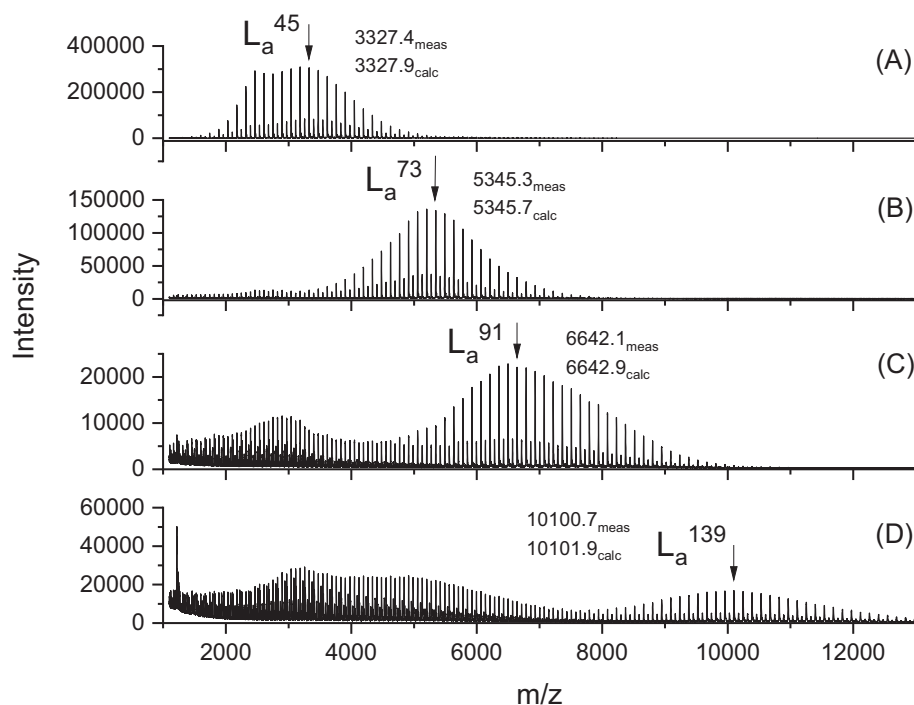


FIGURE 1 MALDI TOF mass spectra of ELA-initiated PLAs prepared at 120 °C/1 h (Table 1): (A) LA/In = 20/1, (B) LA/In = 40/1, (C) LA/In = 60/1, and (D) LA/In = 100/1; L_a = ethyl ester terminated linear chains (potassium adduct ions).

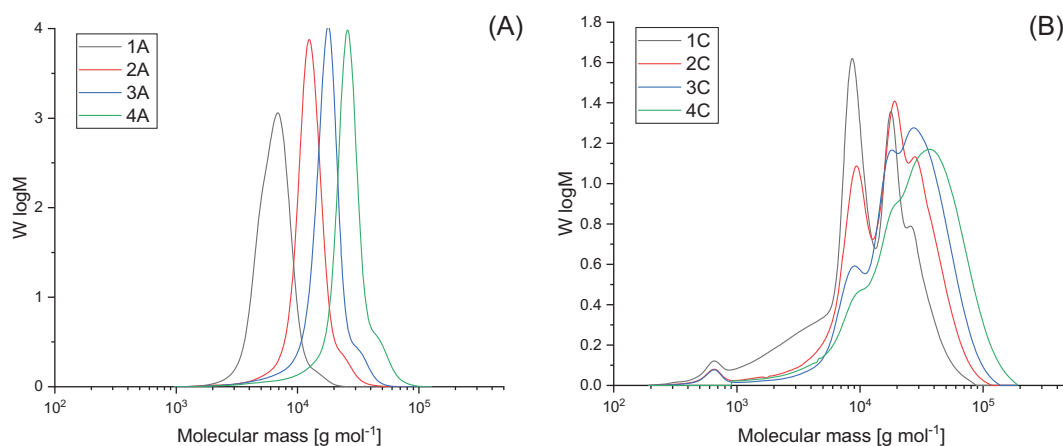


FIGURE 2 GPC curves of PLAs initiated with ELA: after 1 h at 120 °C: (A) (A-experiments in Table 1) and (B) after 14 days at 140 °C (C-experiments in Table 1).

considerably higher than expected from the LA/In ratios. This difference mainly results from the long-known fact that calibration of GPC measurements of aliphatic polyesters with polystyrene overestimates the real M_n 's by about 50%–70% (see the discussion in the following text). In the case of PLAs, a correction factor of 0.68 is required to transform the measured M_n values. A slight overestimation of M_n also results from the fact that they were calculated from 800 Da upwards so the lowest oligomers were not included. The ^1H NMR spectroscopic quantification of the ethyl ester end groups (for chemical shifts, see Experimental) yielded M_n 's of the starting materials in satisfactory agreement with the LA/In ratios and

confirmed that polycondensation steps occurred during annealing primarily in the case of the shortest PLAs (Table 1).

Second, the dispersity was rather low ($\bar{D} = 1.3$) for the PLA prepared with an LA/In = 20/1, but increased to 1.7 at higher LA/In ratios in agreement with the broadening of the MPD observed in the MALDI mass spectra (Figure 1). The third trend became apparent after annealing at 140 °C (Figure 2B experiments in Table 1). One day was sufficient to cause an increase in number-average (M_n) and weight-average (M_w) molar masses, accompanied by a further increase in dispersity due to condensation steps of the ethyl ester end groups.

At first glance, these GPC results were in contradiction to the corresponding MALDI mass spectra (Figure 3), which showed the surprising fact that the MPDs of all four samples were nearly identical. A rather narrow MPD with a maximum around m/z 3400–3700 was formed which did not reflect the large differences in the molar masses. A shift of the MPD to somewhat higher values, from m/z below 3000 (see Figure 1) to m/z above 3000, can easily be explained by polycondensation reactions. In a recent publication, the authors have demonstrated that PLA ethyl esters undergo polycondensation in the solid state when SnOct_2 or another reactive catalyst is present (Scheme 3).²⁶ However, condensation reactions cannot explain how and why the samples prepared with higher LA/In ratios yield an MPD around m/z 3500–3700. This new phenomenon requires us to assume that cycles or high molar mass linear chains were formed in addition to the shorter chains. Cycles were again not detectable. However, fractionation with mass spectrometric characterization of the individual fractions clearly revealed that more and larger quantities of PLA chains having masses above m/z 15,000 were formed. The mass spectra presented in Figure 4A,B illustrate this interpretation. After 14 days at 140 °C the mass spectra of all four samples were almost identical (Figure S2) and displayed a strong maximum around m/z 3500–3700 and a broader weak maximum around m/z 7500. The formation of polycondensation products, most of which were multiples of the starting material, resulted in a dramatic change of the GPC curves from monomodal to a tri- or tetra-modal character as shown in Figure 2B.

A second interesting aspect of the mass spectra obtained after annealing at 140 °C is the disappearance of the broad MPD of low molar mass chains between m/z 1000 and 2000. Obviously, some kind of “symproportionation” has taken place in the solid state. To understand that both disproportionation and “symproportionation” occurred in the solid state, it is necessary to mention that the narrow molar mass distribution (MWD) around m/z 3500–3700 did not change significantly upon prolonged annealing at 140 °C (up to 14 days). Considering that all transesterification reactions are reversible, this finding clearly proves that the narrow MPD around m/z 3500–3700 is a thermodynamically favored property of solid PLAs. This conclusion also holds for the second maximum around m/z 7500. The results discussed below for samples prepared at 160 °C confirm this conclusion.

At this point, it may be useful to explain that the terms “disproportionation” and “symproportionation” as used in this work, have nothing in common with their use in the radical polymerization of vinyl monomers. They simply express certain changes in the lengths of the linear chains via transesterification reactions as shown in Scheme 4.

These transesterification reactions do not change the number or the structure of the end groups. Such chain equilibration reactions have been studied by the Penczek group for polylactides and other polyesters in solution.^{28–30} It was found that these exchange reactions do not change M_n and tend to increase the dispersity

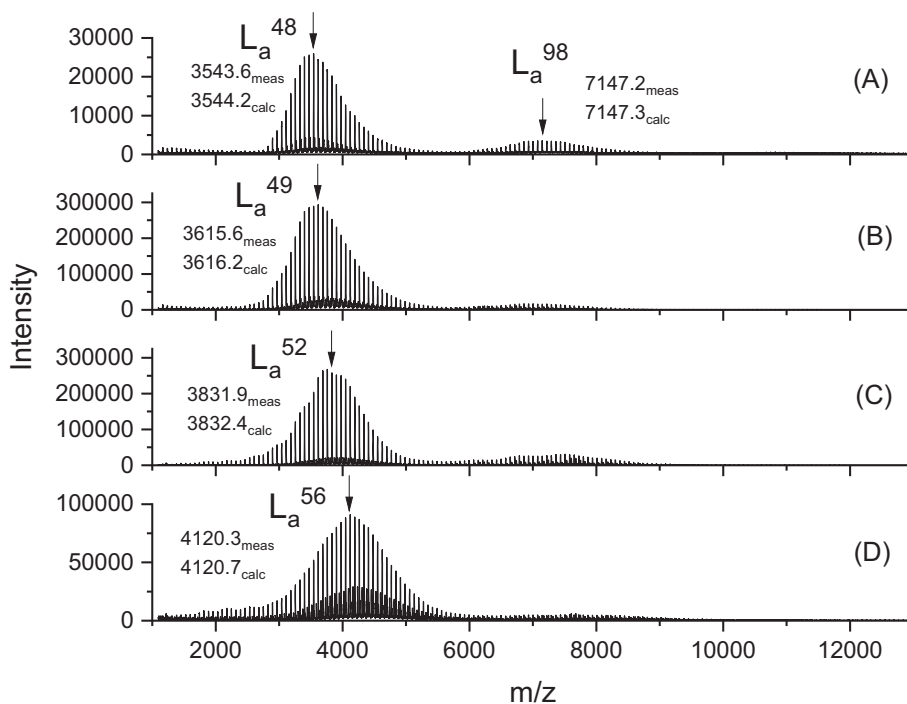


FIGURE 3 MALDI TOF mass spectra of ELA-initiated PLAs annealed at 140 °C/14 days (Table 1): (A) LA/In = 20/1, (B) LA/In = 40/1, (C) LA/In = 60/1, and (D) LA/In = 100/1; L_a = ethyl ester terminated linear chains (potassium adduct ions).

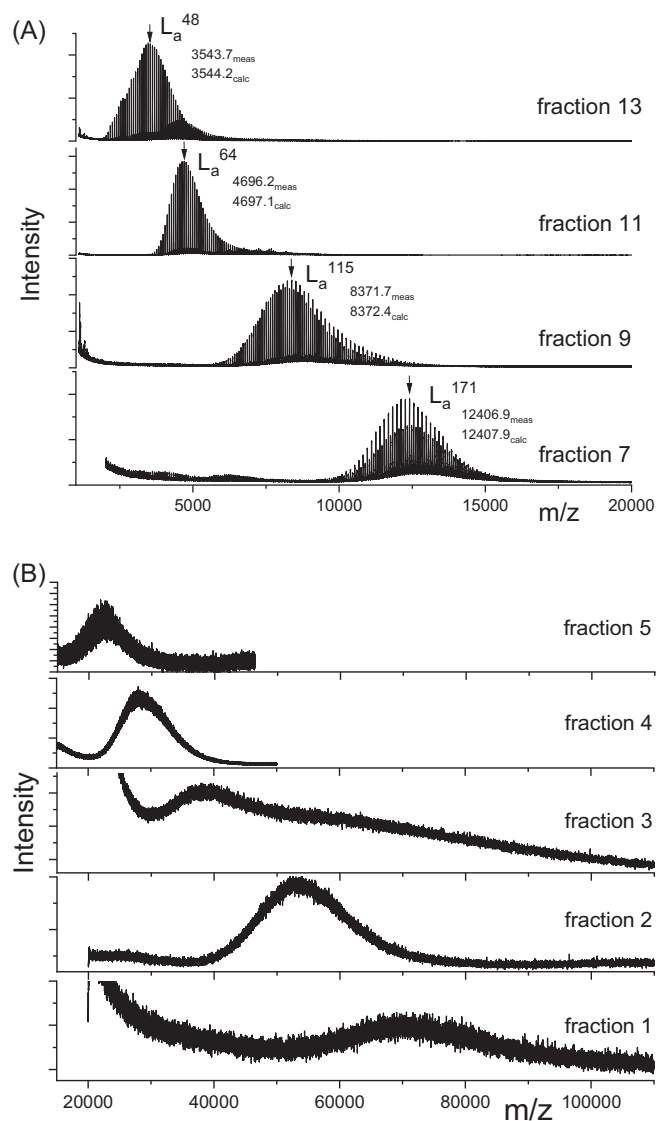
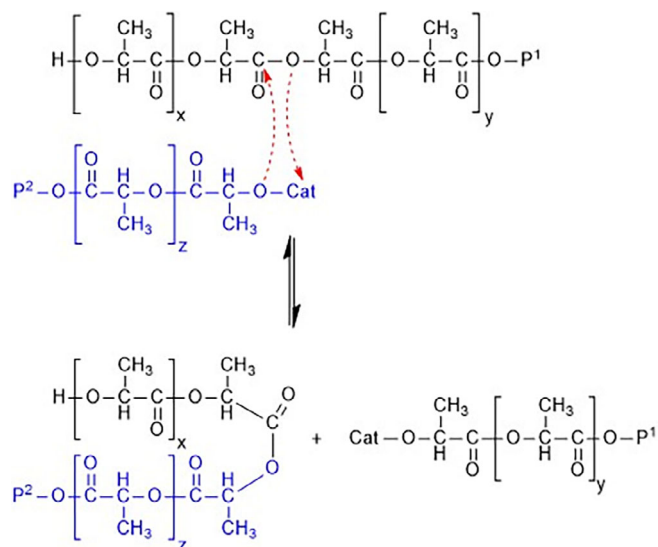


FIGURE 4 (A) MALDI TOF mass spectra of GPC fractions of a PLA prepared with LA/In = 100/1 at 120 °C after annealing at 140 °C/1 day (4B, Table 1); lower mass fractions L_a = ethyl ester terminated linear chains (potassium adduct ions). (B) MALDI TOF mass spectra of GPC fractions of a PLA prepared with LA/In = 100/1 at 120 °C after annealing at 140 °C/1 day (4B, Table 1), higher mass fractions.

when the starting material had a low dispersity (e.g., 1.2) in the direction of the “most-probable distribution” calculated by Flory.³¹ The driving force for these equilibration reactions in solution (or in the melt) is again entropy. The results of this work demonstrate that upon crystallization the thermodynamic situation changes completely, and the driving force is now a gain in crystallization enthalpy favoring a certain type of crystallites. The overall increase in crystallinity discussed in the last section supports this view.



SCHEME 4 Transesterification of linear chains resulting in equilibration of chain lengths.

3.2 | ELA-initiated polymerizations at 160 °C

A second series of ROPs was performed in bulk at 160 °C using the same LA/ELA ratios as described for the ROPs at 120 °C, and the molar LA/Cat ratio was fixed at 1000/1 (Table 2). Since the melt viscosity had significantly increased after 1 h, small samples were taken from the reaction mixtures after 1 h for characterization (Table 2). The remaining products were annealed at 140 °C, whereupon crystallization occurred within 2 h. The MALDI mass spectra of the freshly prepared 1 h samples displayed broad MWDs resembling the “most probable distribution” described by Flory for polycondensates.³¹ In addition, the even-odd equilibration was now almost complete, as illustrated in Figure 5.

These results perfectly agree with previous studies of the authors dedicated to alcohol-initiated ROPs of LA at high temperatures performed with high LA/In and high LA/Cat ratios. The GPC measurements proved that the M_n and M_w (weight average) values increased with the LA/In ratios, but the dispersities were now around 2.0 in agreement with the message of the mass spectra. Fractionation of sample 4A (Table 2) revealed that polycondensation products up to 10,000 Da were formed despite the short reaction time (Figure S3). The remaining PLAs were annealed at 140 °C (B + C experiments in Table 2) for comparison with the annealing products based on the PLAs prepared at 120 °C. As shown in Figure S4, the mass spectra after 1 day showed the formation of a narrow MPD

FIGURE 5 MALDI TOF mass spectra of ELA-initiated PLAs prepared at 160 °C/1 h (A-experiments, Table 2): (A) LA/In = 20/1, (B) LA/In = 40/1, (C) LA/In = 60/1, and (D) LA/In = 100/1; L_a = ethyl ester terminated linear chains (potassium adduct ions), C = cyclic polymers.

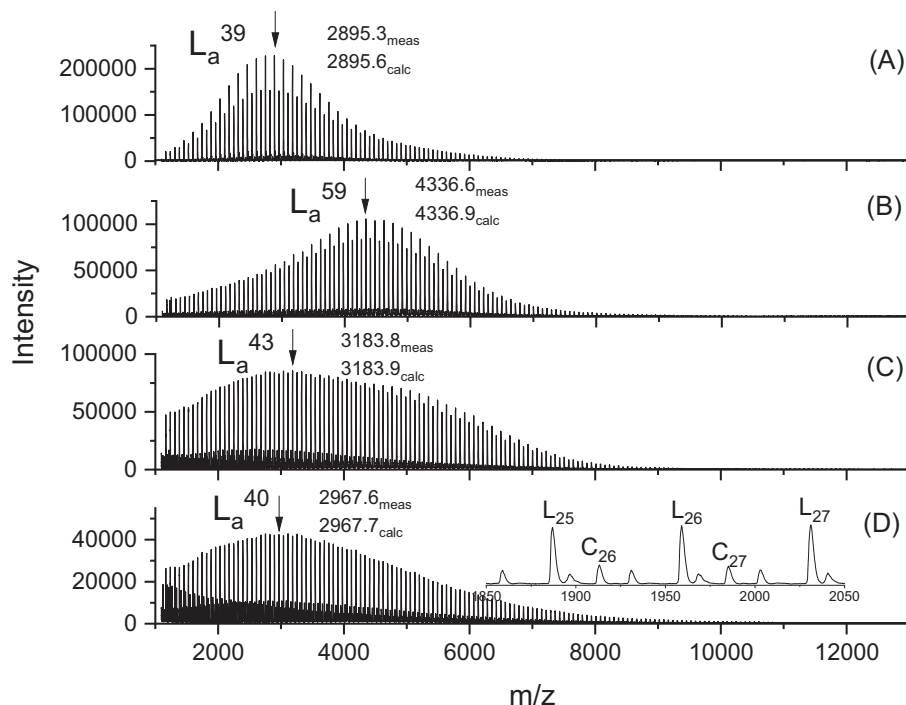
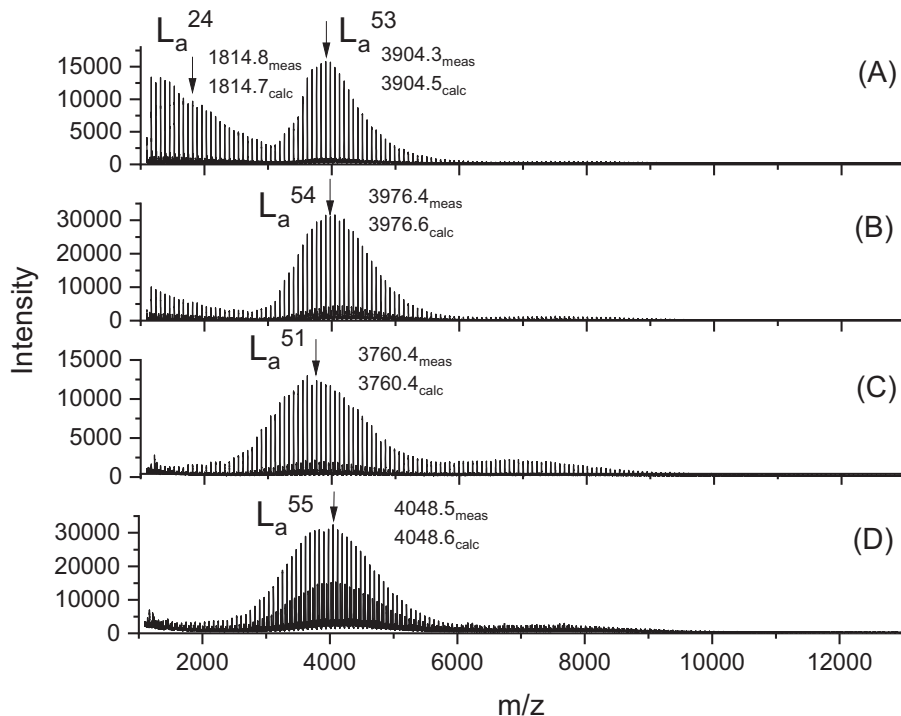


FIGURE 6 MALDI TOF mass spectra of ELA-initiated PLAs prepared at 160 °C and annealed at 140 °C for 14 days (C experiments, Table 2); L_a = ethyl ester terminated linear chains (potassium adduct ions).



around m/z 3700 for all four samples, and the intensity of this MPD was enhanced by annealing for 14 days as shown in Figure 6. Therefore, the results obtained with PLAs prepared at 160 °C confirm those obtained with the 120 °C samples. The formation of a narrow MPD around m/z 3700 is a thermodynamically controlled feature of solid PLAs.

3.3 | BrUnd-initiated polymerizations at 120 °C

A third series of polymerizations was conducted using 11-bromoundecanol (BrUnd) as the initiator for the following reasons. First, in contrast to ELA, BrUnd is a primary alcohol and thus, the rate of initiation should be

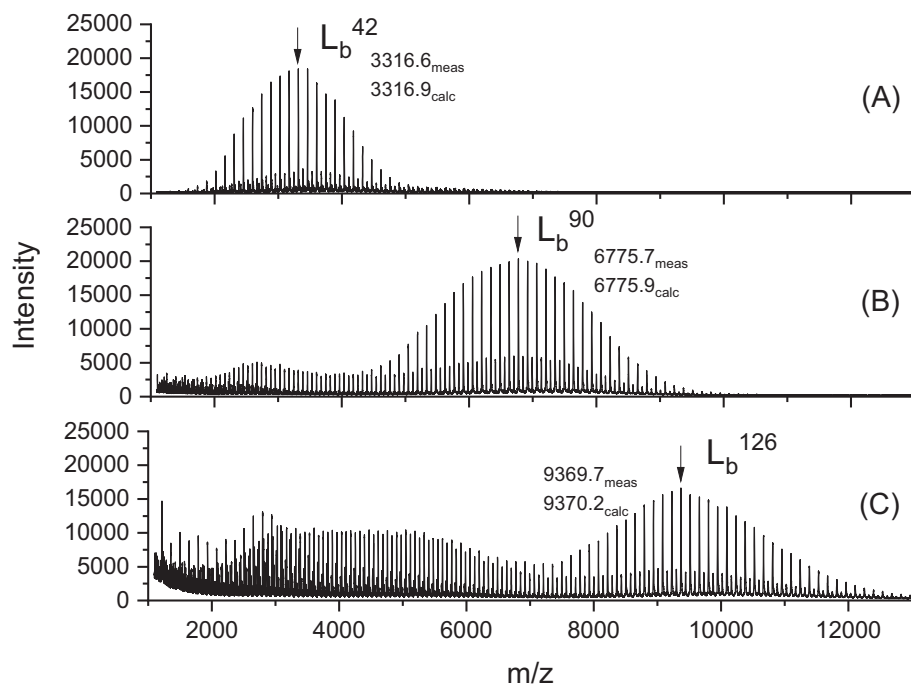


FIGURE 7 MALDI TOF mass spectra of BrUnd-initiated PLAs prepared at 120 °C/1 h (A-experiments in Table 3): (A) LA/IN = 20/1, (B) LA/In = 60/1, and (C) LA/In = 100/1; L_b = BrUnd ester terminated linear chains (potassium adduct ions).

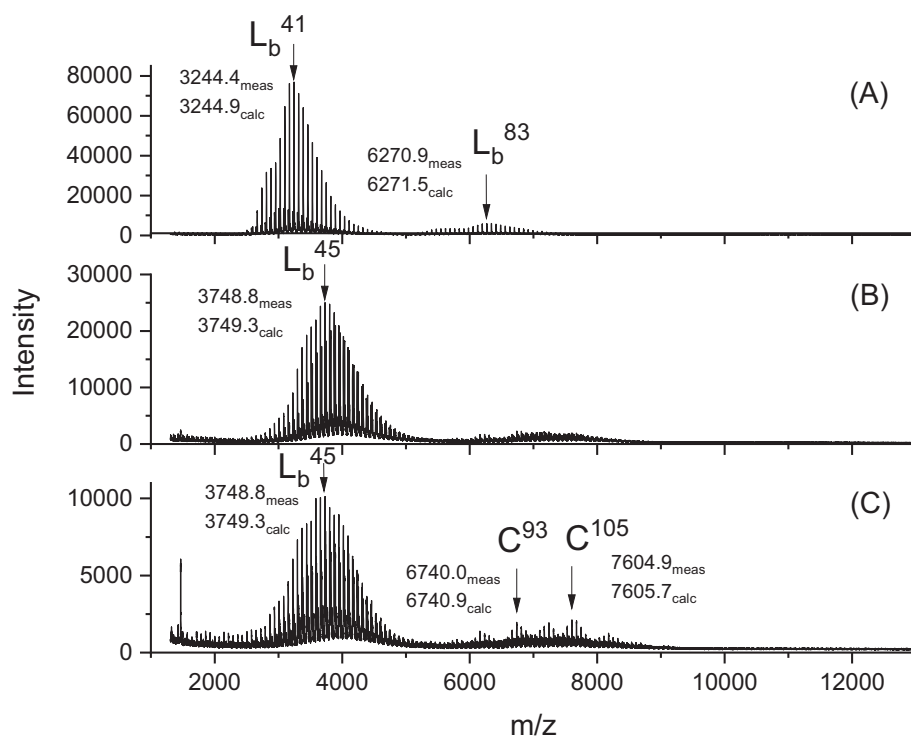


FIGURE 8 MALDI TOF mass spectra of the BrUnd-initiated PLAs after 14 days at 140 °C, (A) LA/IN = 20/1, (B) LA/In = 60/1, and (C) LA/In = 100/1; L_b = BrUnd ester terminated linear chains (potassium adduct ions), C = cyclic polymers.

higher than the propagation rate, so that a lower dispersity should result unless polycondensation reactions occur. Second, BrUnd is less volatile than ethanol and its dwelling time on the surface of the crystallites should be much longer. Third, due to its higher steric demands, it might reduce the efficiency of any type of transesterification reaction. The ROPs with BrUnd were performed at 120 °C and, analogous to the ELA-initiated ROPs, all

samples crystallized within 1 h. The mass spectra displayed in Figure 7 were quite similar to those of the ELA-initiated PLAs (Figure 1). Furthermore, the GPC data indicate that the dispersities were similar but slightly lower than those obtained with ELA. Annealing at 140 °C for 1 day modified the MPD in the direction already found for ELA-initiated PLAs because all three samples formed a maximum around m/z 3500–3700.

After 14 days, the MALDI mass spectra of all three samples were nearly identical as demonstrated in Figure 8. Fractionation of the 100/1 sample 3C, Table 3, yielded mass spectra which again showed that further maxima of the MPD were formed up to m/z 70,000 resulting from polycondensation and disproportionation in the solid state. In other words, the end groups formed by BrUnd did not hinder or alter the course of the transesterification reactions taking place in solid PLA, despite the greater steric demands. However, one small difference with respect to the ELA-initiated samples should be noted, namely the formation of small amounts of cyclic PLAs with masses in the range of m/z 6000–8500. These cycles were absent in the mass spectrum of the 20/1 sample (Figure 8A), appeared in the spectrum of the 60/1 sample together with linear chains in the same mass range (Figure 8B), and predominated in the spectrum of the 100/1 sample (Figure 8C).

In a recent study dealing with the polycondensation of ELA-initiated PLAs in the presence of four different catalysts, no cycles were found after annealing at 140 °C even after 28 days.²⁶ Thus, the mass spectra of Figure 8 prove that the BrUnd end groups favor the formation of cycles more than the ELA end groups. A satisfactory explanation for this phenomenon cannot be given at this time. The origin of the “saw-tooth pattern” of the cyclic PLAs has been recently discussed.³² Finally, it should be mentioned that the shapes of the GPC elution curves displayed the same structure and structural changes already discussed for the ELA-initiated samples at 120 °C (Figures S5 and S6).

From these results, it can be concluded that the thermodynamic control favors two types of crystallites for linear chains in the mass range below 10,000 Da. The predominant type of crystallites consists of extended linear chains with a degree of polymerization in the range of 40–60 lactyl units. Considering the results of Wasanasuk and Tashiro,³³ who found a length of 2.9 nm for a helical chain segment of 10 lactyl units in the α -modification, one can calculate a crystallite thickness of 10–14 nm, taking into account that at least one or two lactyl units will stick out from the surface of the crystalline lamellae. The L-values measured by SAXS for the samples listed in Table 1 allow a rough estimation of the lamellar thickness (l_c) which is in good agreement with this interpretation. For the chains having masses around 7500 Da two alternatives may, in principle, be considered. Either, they form crystallites with a thickness of about 20–28 nm or they form crystallites with the same thickness as the shorter chains by folding. The first alternative is unlikely because such large crystal thicknesses have only been found for cyclic PLAs annealed at high temperatures (160 °C or above).³⁴ Therefore, the more likely alternative is the hypothesis that the longer chains

fold at least once to form crystallites with thicknesses around 10–14 nm. In summary, the results of this work indicate that a lamellar thickness in the range of 10–14 nm is thermodynamically favored.

3.4 | DSC measurements

The DSC measurements revealed the following trends for all three series of PLA alkyl esters. First, both, T_m and ΔH_m increase with the chain length. Second, annealing at 140 °C significantly increases T_m and ΔH_m even after 1 day only. Third, further annealing at 140 °C (up to 14 days) increases both T_m and ΔH_m , even more, and for two samples (4B and C, Table 3) T_m 's above 180 °C were achieved. Regarding the crystallinities, it should be emphasized that the authors used the highest ΔH_m^0 value reported in the literature so far (for reasons discussed in Ref. [32]), which means that the crystallinities calculated by all other research groups overestimated the real crystallinity by 10%–20%. Despite this high ΔH_m^0 values and crystallinities of up to 80% were achieved. The higher T_m values and the increasing crystallinity with increasing annealing time indicate that all transesterification reactions support a thermodynamic optimization of crystals and morphology. Some DSC curves illustrating the absence of glass transition steps in the case of annealed samples and showing monomodal endotherms are presented in the Supporting Information. Only in the case of one BrUND-initiated sample a weak shoulder of the main endotherm was found (Figure S10).

4 | CONCLUSIONS

The results obtained in the present study indicate that SnOct₂-catalyzed transesterification reactions promote “disproportionation” and “symproportionation” reactions of linear chains in solid poly(L-lactide)s, which modify the molar mass distribution formed during the ROP in the melt. All transesterification reactions together, including (poly)condensation, proceed under thermodynamic control. It can be concluded that the formation of crystallites consisting of extended linear chains with DPs between 40 and 60 lactyl units is thermodynamically favored, regardless of the initial MWD. Such crystallites have a lamellar thickness of around 10–13 nm, which is surprisingly identical to the lamellar thickness of extended-ring crystals described in recent publications. The mass spectra obtained after 14 days at 140 °C also suggest that a weak maximum around m/z 7500, which is formed by all samples represents another thermodynamically favored species of crystallites. Since the lengths of the PLAs double those of the main maximum around m/z 3700, it can be

hypothesized that the second maximum in the MPD represents crystallites composed mainly of single-folded chains. Since the trends and facts found in this study are identical for two quite different types of alkyl ester end groups, it can also be concluded that they are characteristic of the vast majority of alkyl ester end groups.

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REFERENCES

- [1] L.-T. Lim, R. Auras, M. Rubino, *Prog. Polym. Sci.* **2008**, *33*, 820.
- [2] I. Armentano, N. Bitinis, E. Fortunati, S. Mattioli, N. Rescignano, R. Verdejo, M. A. López-Manchado, J. M. Kenny, *Prog. Polym. Sci.* **2013**, *38*, 1720.
- [3] R. A. Auras, L.-T. Lim, S. E. Selke, H. Tsuji, *Poly (lactic acid): synthesis, structures, properties, processing, and applications*, John Wiley & Sons, Hoboken **2011**.
- [4] R. P. Pawar, S. U. Tekale, S. U. Shisodia, J. T. Totre, A. J. Domb, *Recent Patents Regener. Med.* **2014**, *4*, 40.
- [5] M. L. di Lorenzo, R. Androsch, in *Advances in Polymer Science* (Eds: M. L. di Lorenzo, R. Androsch), Springer International Publishing, Cham **2017**.
- [6] H. R. Kricheldorf, S. M. Weidner, *Polym. Chem. UK* **2022**, *13*, 1618.
- [7] S. Corneillie, M. Smet, *Polym. Chem. UK* **2015**, *6*, 850.
- [8] F. Nederberg, E. F. Connor, M. Möller, T. Glauser, J. L. Hedrick, *Angew. Chem. Int. Ed.* **2001**, *40*, 2712.
- [9] E. F. Connor, G. W. Nyce, M. Myers, A. Möck, J. L. Hedrick, *J. Am. Chem. Soc.* **2002**, *124*, 914.
- [10] B. G. Lohmeijer, R. C. Pratt, F. Leibfarth, J. W. Logan, D. A. Long, A. P. Dove, F. Nederberg, J. Choi, C. Wade, R. M. Waymouth, *Macromolecules* **2006**, *39*, 8574.
- [11] L. Zhang, F. Nederberg, R. C. Pratt, R. M. Waymouth, J. L. Hedrick, C. G. Wade, *Macromolecules* **2007**, *40*, 4154.
- [12] L. Zhang, R. C. Pratt, F. Nederberg, H. W. Horn, J. E. Rice, R. M. Waymouth, C. G. Wade, J. L. Hedrick, *Macromolecules* **2010**, *43*, 1660.
- [13] Y. Wang, W. Zhao, X. Liu, D. Cui, E. Y.-X. Chen, *Macromolecules* **2012**, *45*, 6957.
- [14] A. P. Dove, *ACS Macro Lett.* **2012**, *1*, 1409.
- [15] C. Thomas, B. Bibal, *Green Chem.* **2014**, *16*, 1687.
- [16] L. Mezzasalma, A. P. Dove, O. Coulembier, *Eur. Polym. J.* **2017**, *95*, 628.
- [17] Y. Shen, J. Zhang, N. Zhao, F. Liu, Z. Li, *Polym. Chem. UK* **2018**, *9*, 2936.
- [18] A. Nachtergaele, O. Coulembier, P. Dubois, M. Helvenstein, P. Duez, B. Blankert, L. Mespouille, *Biomacromolecules* **2015**, *16*, 507.
- [19] P. M. Schäfer, K. Dankhoff, M. Rothmund, A. N. Ksiazkiewicz, A. Pich, R. Schobert, B. Weber, S. Herres-Pawlis, *ChemistryOpen* **2019**, *8*, 1020.
- [20] G. G. Briand, N. Burford, *Chem. Rev.* **1999**, *99*, 2601.
- [21] D. A. Kessler, W. L. Pines, *JAMA* **1990**, *264*, 2409.
- [22] A. Kowalski, J. Libiszowski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 1964.
- [23] M. Jalabert, C. Frascini, R. E. Prud'Homme, *J. Polym. Sci. A Polym. Chem.* **2007**, *45*, 1944.
- [24] H. R. Kricheldorf, S. M. Weidner, *Polym. Chem. UK* **2020**, *11*, 5249.
- [25] H. R. Kricheldorf, S. M. Weidner, *J. Polym. Sci.* **2021**, *59*, 439.
- [26] S. M. Weidner, A. Meyer, J. Falkenhagen, H. R. Kricheldorf, *Polym. Chem. UK* **2024**, *15*, 71.
- [27] S. M. Weidner, A. Meyer, J. Falkenhagen, H. R. Kricheldorf, *Eur. Polym. J.* **2021**, *153*, 110508.
- [28] J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol. Rapid Commun.* **1997**, *18*, 325.
- [29] S. Penczek, A. Duda, R. Szymanski, *Macromol. Symp.* **1998**, *132*, 441.
- [30] S. Penczek, R. Szymanski, A. Duda, J. Baran, *Macromol. Symp.* **2003**, *201*, 261.
- [31] P. J. Flory, *Chem. Rev.* **1946**, *39*, 137.
- [32] H. R. Kricheldorf, S. M. Weidner, A. Meyer, *Polymer* **2022**, *263*, 125516.
- [33] K. Wasanasuk, K. Tashiro, M. Hanesaka, T. Ohhara, K. Kurihara, R. Kuroki, T. Tamada, T. Ozeki, T. Kanamoto, *Macromolecules* **2011**, *44*, 6441.
- [34] H. Kricheldorf, S. Chatti, A. Meyer, S. Weidner, *RSC Adv.* **2021**, *11*, 2872.

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