



Verfahrenstechnik
auf einem neuen Level?
It takes
#HumanChemistry

Wir suchen kreative Ingenieurinnen und Ingenieure, die mit uns gemeinsam neue Wege gehen wollen – mit Fachwissen, Unternehmertum und Kreativität für innovative Lösungen. Informieren Sie sich unter:

[evonik.de/karriere](https://www.evonik.de/karriere)

RESEARCH ARTICLE

SnOct₂-catalyzed ROPs of L-lactide initiated by acidic OH- compounds: Switching from ROP to polycondensation and cyclization

Steffen M. Weidner¹ | Hans R. Kricheldorf² 

¹Bundesanstalt für Materialforschung und -prüfung – BAM, 6.3, Richard-Willstätter-Str. 11, Berlin, 12489, Germany

²Universität Hamburg, Institut für Technische und Makromolekulare Chemie, Bundesstr. 45, Hamburg, 20146, Germany

Correspondence

Hans R. Kricheldorf, Institut für Technische und Makromolekulare Chemie der Universität, Bundesstr. 45, D-20146, Hamburg, Germany.
Email: hrkricheldorf@aol.de

Abstract

Ring-opening polymerizations (ROPs) of L-lactide are performed in bulk at 130°C with tin(II) 2-ethylhexanoate as catalyst and various phenols of different acidity as initiators. Crystalline polylactides having phenyl ester end groups are isolated, which are almost free of cyclics. The dispersities and molecular weights are higher than those obtained from alcohol-initiated ROPs under identical conditions. Polymerizations at 160°C yield higher molecular weights than expected from the monomer/initiator ratio and a considerable fraction of cycles. The fraction of cycles increases with higher reactivity of the ester end group indicating that the cycles are formed by end-to-end cyclization.

KEYWORDS

cyclization, lactide, MALDI TOF mass spectrometry, ring-opening polymerization, tin catalysts

1 | INTRODUCTION

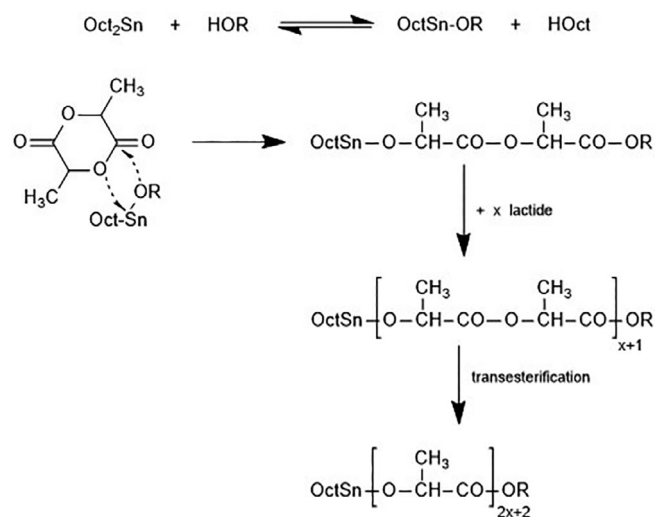
The technical production of poly(L-lactide) is based on the ring-opening polymerization (ROP) of L-lactide (LA) catalyzed by Sn(II) 2-ethylhexanoate (SnOct₂) in combination with an aliphatic alcohol as initiator (In).^{1–4} The addition of an alcohol serves two purposes. First, it accelerates the polymerization by formation of a more nucleophilic Sn-O-alkyl group (Scheme 1), and second, it allows for a rough control of the molecular weight via the LA/In ratio. For polymerizations in solution at temperatures <100°C several research groups have demonstrated that the alcohol-initiated ROP of lactide proceeds like a living polymerization with narrow molecular weight distribution and a degree of polymerization proportional to the LA/in ratio and to the conversion.^{5–7} For ROPs in bulk the polymerization process is more complex due to

transesterification reactions and formation of cycles which cause broadening of the molecular weight distribution and reduction of the DP below the theoretical value calculated for a living polymerization.^{7–10} Therefore, commercial polylactides contain at least low molar mass cycles and have dispersities above 2.0.

These properties are unavoidable, when ROPs of L-lactide are performed in bulk at temperatures >130°C, and they are advantageous for any application which requires thermal processing, such as injection molding, extrusion, or bottle blowing. The reasons are twofold. Cyclic oligomers reduce the melt viscosity and thus, ease thermal processing and they tend to raise the glass transition temperature, because highly mobile loose chain ends are missing. A broad MWD gives a better balance of moderate melt viscosity and good mechanical properties than polymers having a similar molar mass with narrow MWD.

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2021 The Authors. *Journal of Polymer Science* published by Wiley Periodicals LLC.



SCHEME 1 Simplified mechanism of SnOct_2 -catalyzed ROP of lactides initiated by OH-compounds

Whereas the role of alcohols in ROPs performed in solution has intensively been studied, because the reaction conditions are favorable for kinetic measurements, much less is known about their role in ROPs conducted in bulk. The authors have recently shown that unexpectedly alcohols of different structure have a significant influence on rate and extent of transesterification reaction when SnOct_2 -catalyzed ROPs are conducted in bulk at 130°C .¹¹ Yet, to the best knowledge of the authors the influence of more acidic initiators such as oximes or phenols has never been studied yet. Phenols may be poisonous and aggressive towards skin, but they may also play the role of vitamins (e.g., tocopherols), they belong to the metabolism of numerous plants (e.g., catechol, tannin, salicylic acid) or they are used as food and drink preservatives, such as esters of 4-hydroxybenzoic acid. Hence, there is no reason to exclude phenols from studies of R-OH-initiated ROPs of lactide. The present work had the purpose to elaborate first hand information on the fundamental aspects of SnOct_2 -catalyzed ROPs of L-lactide initiated with acidic R-OH compounds. Higher acidity of the OH group results in higher electrophilicity of the ester end group formed by incorporation of the initiator. A higher electrophilicity of the CO-chain end favors, in turn, end-to-end (ete) cyclization and chain growth via intermolecular condensation ([a] in Scheme 2). When such transesterification reactions occur, a simple ROP turns into a ROPPC mechanism (ROP combined with simultaneous polycondensation) as defined and discussed in a recent review article.¹² Therefore, the formation of cycles and its dependence on the structure of the initiator was in the focus of the present study.

The question, how the reaction conditions influence the formation of cycles and their origin is not only of interest for the chemistry of polyLAs, but also for the proper understanding of reversible polycondensations. In his first theory of step-growth polymerizations 1946 (the basis of all later theories and textbooks) Flory had excluded that ete-cyclizations may occur.¹³ Jacobson and Stockmayer describing a new theory of reversible polycondensations a few years later, accepted Flory's dogma and attributed formation of cyclic oligomers exclusively to ring-chain equilibration via "back-biting" ([b] in Scheme 2).^{14,15} In the following decades, numerous researchers have studied the formation of cyclic oligomers via ring-chain equilibration.^{16–22} Szymanski has adapted the Jacobson-Stockmayer theory to various ROPs.²³ The potential existence and role of ete-cyclization was completely ignored. Quite recently the authors have demonstrated that ete-cyclizations are a theoretical necessity and occur in ROPPCs of LA and ϵ -caprolactone catalyzed by dibutyltin compounds.²⁴ In this context the present work had the purpose to shed more light on question if and how the formation of cycles is influenced by the variation of the experimental conditions including the nature of initiator.

2 | EXPERIMENTAL

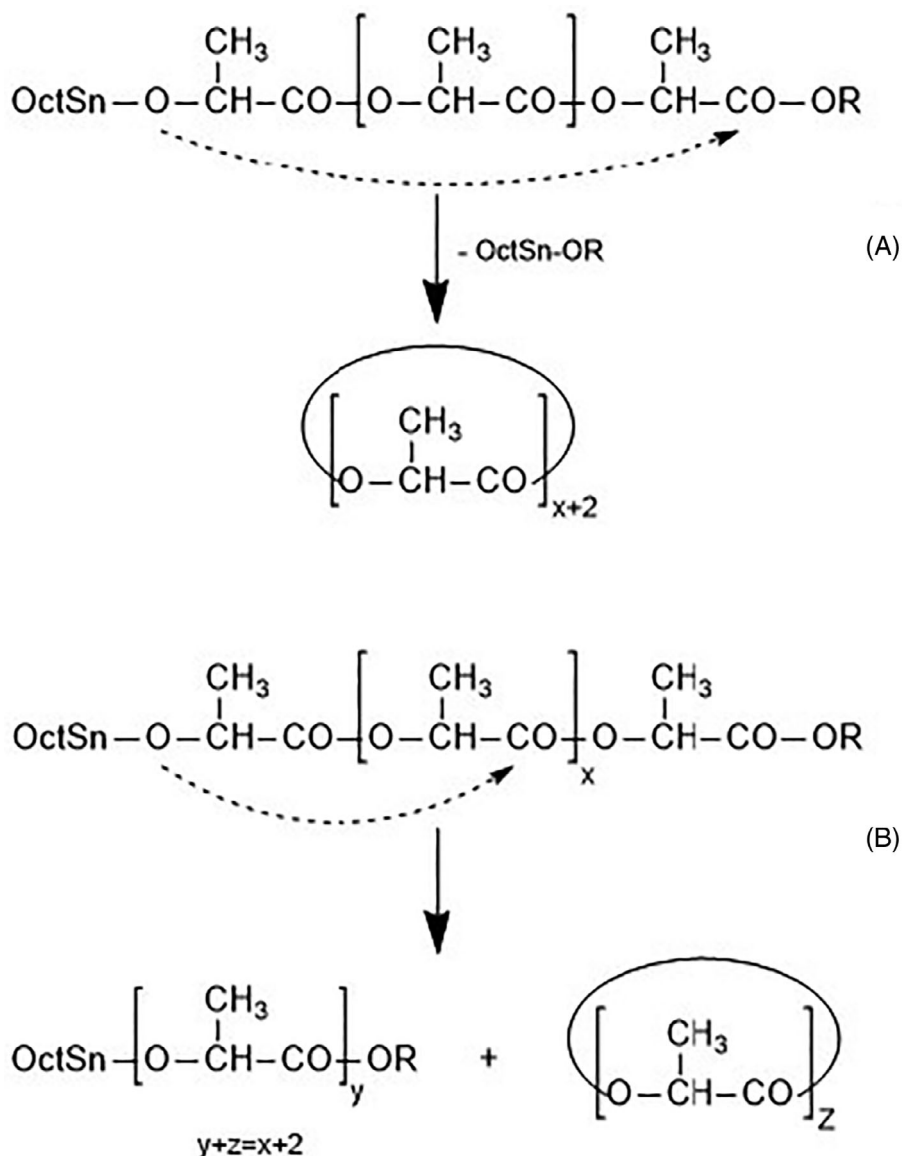
2.1 | Materials

L-lactide, a product of Corbion Purac, was kindly supplied by Thyssen-Uhde AG (berlin, Germany). It was recrystallized from "Toluene 99.98% extra dry" (ACROS Chemicals, Belgium). 11-undecenol (UND), hydroxy acetone, cyclohexanone oxime, N-hydroxy succinimide, 4-chlorophenol, 4-cyanophenol, 4-nitrophenol, pentafluorophenol, pentafluorothiophenol, and tin(II) 2-ethylhexanoate (purity >96%) were all purchased from Alfa Aesar (Kandel, Germany) and used as received.

2.2 | Polymerizations and annealing at 130°C

The initiator (0.8 mmol) was weighed into a 50 ml Erlenmeyer flask and L-lactide (40 mmol) plus a magnetic bar were added under a blanket of argon. Finally, 0.1 ml of a 0.4 M solution of SnOct_2 in toluene was injected. The reaction vessel was immersed into an oil bath thermostated at 130°C . After 1 h the reaction vessel was rapidly cooled to 20°C and the crystalline reaction product was crushed into pieces by means of a spatula. Part of the product was used for characterization, whereas

SCHEME 2 Formation of cycles in polymerizations of lactides: (A) via end-to-end cyclization, (B) via “back-biting”



another part was annealed in an Erlenmeyer flask under argon at 130°C for 21 h. Due to the slower polymerization, an additional experiment with a duration of 2 h was conducted in the case of 4-nitrophenol and in the case of pentafluorophenol the first sample was taken after 1.5 h.

2.3 | Polymerizations at 160°C

The reaction mixtures were prepared and polymerized as described above. However, three parallel experiments were performed for each initiator. The samples isolated after 0.5 and 1.0 h were taken from the first experiment, the 2 and 4 h samples from the second experiment, whereas the third experiment was stopped after 24 h.

2.4 | Measurements

The 400 MHz ^1H NMR spectra were recorded with a Bruker Avance 400 in 5 mm sample tubes. CDCl_3 containing TMS served as solvent and shift reference.

MALDI TOF mass spectrometry was performed using an Autoflex max (Bruker Daltonik GmbH, Bremen) in the linear positive mode. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) dissolved in chloroform (20 mg/ml) was chosen as matrix. Matrix solutions were doped with potassium trifluoroacetate to promote selective adduct ion formation. This solution was premixed with the analyte solution (chloroform, 4 mg/ml) in a ratio of 5/2 (vol/vol). A 1 μl of the resulting solution was deposited on the sample target. Typically, 8000 single spectra recorded at four different positions within one spot

were accumulated. The instrument was previously calibrated with PEO standards.

For the GPC experiments a modular system kept at 40°C (isocratic pump, 1 ml/min, refractive index detector, Optilab rEX, Wyatt Technology) was applied. Samples were manually injected (100 µl, 2–4 mg/ml). For instrument control Clarity software (GPC extension, DataApex) was used. The calculation of the molecular masses was performed using Astra 6.1 software (Wyatt Technology). The calibration was performed using polystyrene standard sets (Polymer Standards Service – PSS, Mainz, Germany).

3 | RESULTS AND DISCUSSION

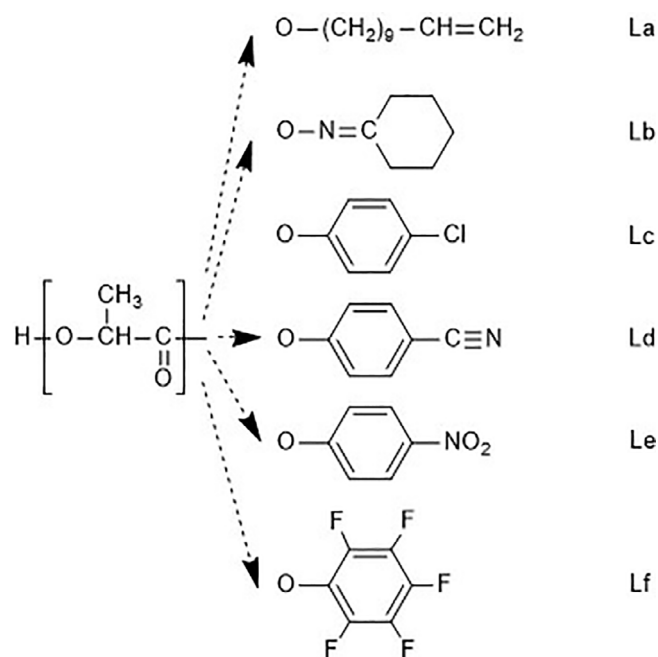
3.1 | Polymerizations at 130°C

A temperature of 130°C is the lowest temperature used for technical polymerizations of L-lactide.^{4,9,25} It has the advantage of little side reactions (incl. cyclization), but the kinetic course of the entire polymerization process is complicated by crystallization of the polylactide. In this work a first series of polymerizations was conducted at 130°C with eight different initiators. 11-undecenol (UND) as example of an aliphatic primary alcohol of low volatility was used for comparison with the seven acidic initiators hydroxy acetone, cyclohexanone oxime, N-hydroxy succinimide, 4-chloro-, 4-cyano- and 4-nitrophenol, pentafluoro phenol and pentafluoro thiophenol.

The first result of these experiments was the observation that with hydroxy acetone, N-hydroxy succinimide and pentafluorothiophenol no polymerization was detectable within the first 4 h. Thus, further studies with these three initiators were abandoned. In contrast, the other acidic initiators yielded crystalline polyLAs quite analogous to UND. Their characterization by GPC was given in Table 1. The structures of the isolated polyLAs and

their symbols used for peak assignments in the MALDI TOF mass spectra are summarized in Scheme 3.

The second result was GPC data indicating a slight broadening of the molecular weight distribution (MWD) with dispersities increasing from 1.2 to 1.5 for increasing acidity of the initiator. This trend is also observable in the MALDI TOF mass spectra as illustrated in Figures S1A and S2A and in Figures 1A, 2A,B, and 3A. The GPC data also demonstrate that the number average molecular weights (M_n) of the polyLAs initiated with phenols are higher than expected from the LA/In ratio, in contrast to the UND and cyclohexanone oxime-initiated polyLAs, where a satisfactory agreement between experimental and theoretical M_n was found (No. 1 and 2, Table 1).



SCHEME 3 Linear polyLAs and their abbreviations used in the MALDI

TABLE 1 SnOct₂-catalyzed syntheses of poly(L-lactides)s having activated ester end groups in bulk at 130°C, LA/in = 50/1; LA/cat = 1000/1

Exp. no.	Initiator	LA/in	Time (h)	$M_n^{a,b}$ (corr)	M_n	M_w	\bar{D}
1	11-Undecenol	50/1	1	8100	11,700	13,000	1.1
2	Cyclohexanone oxime	50/1	1	7300	10,300	13,800	1.3
3	4-Chlorophenol	50/1	1	11,500	16,900	22,300	1.3
4	4-Cyanophenol	50/1	1	17,700	26,200	40,000	1.5
5A	4-Nitrophenol	50/1	1	16,300	23,600	33,400	1.4
5B	4-Nitrophenol	50/1	2	22,600	33,000	48,000	1.4
6	Pentafluorophenol	50/1	1.5	27,300	40,000	57,000	1.4

^aMeasured M_n values multiplied with a correction factor of 0.68 (Ref. 5).

^bThe theoretical M_n amounts to 7300 calculated for a conversion of 99% plus end group.

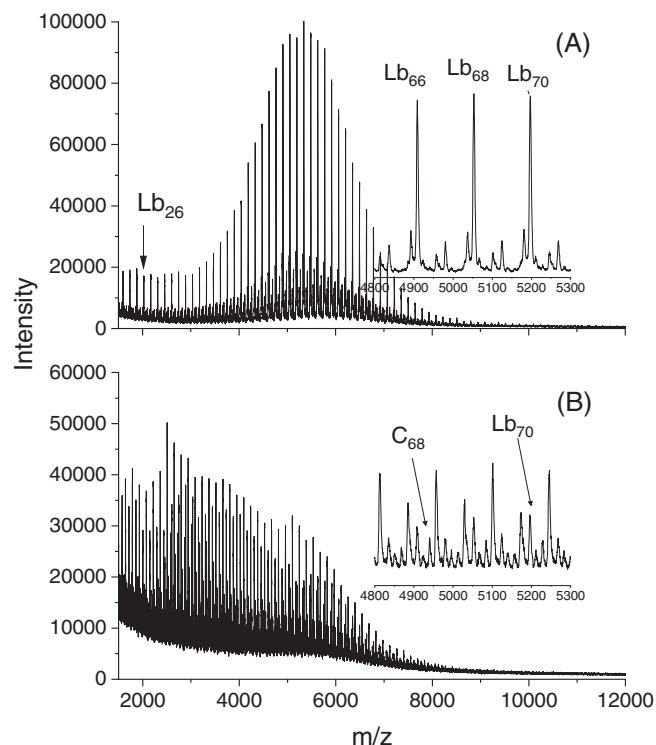


FIGURE 1 MALDI TOF mass spectra of SnOct_2 -catalyzed ROP of LA at 130°C initiated by cyclohexanone oxime: (A) after 1 h, (B) after 24 h

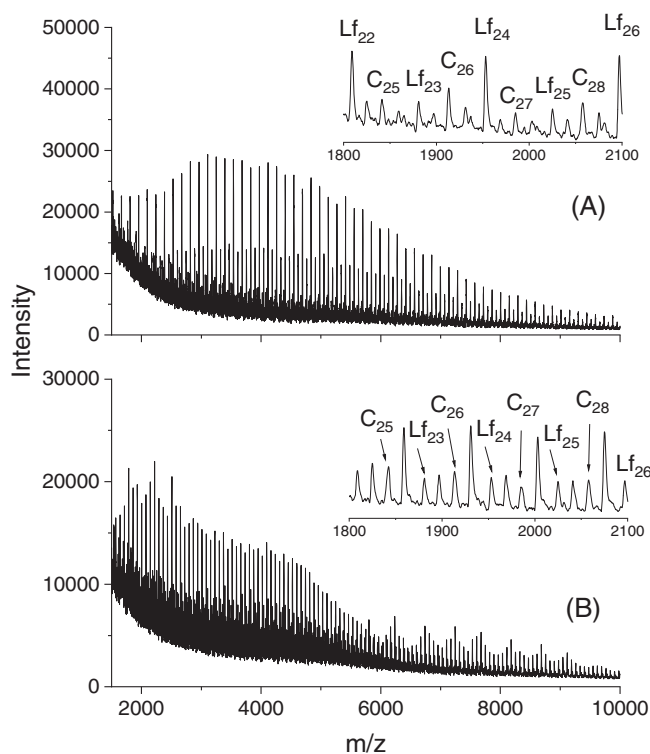


FIGURE 3 MALDI TOF mass spectra of SnOct_2 -catalyzed ROP of LA at 130°C initiated by pentafluorophenol: (A) after 1 h, (B) after 24 h

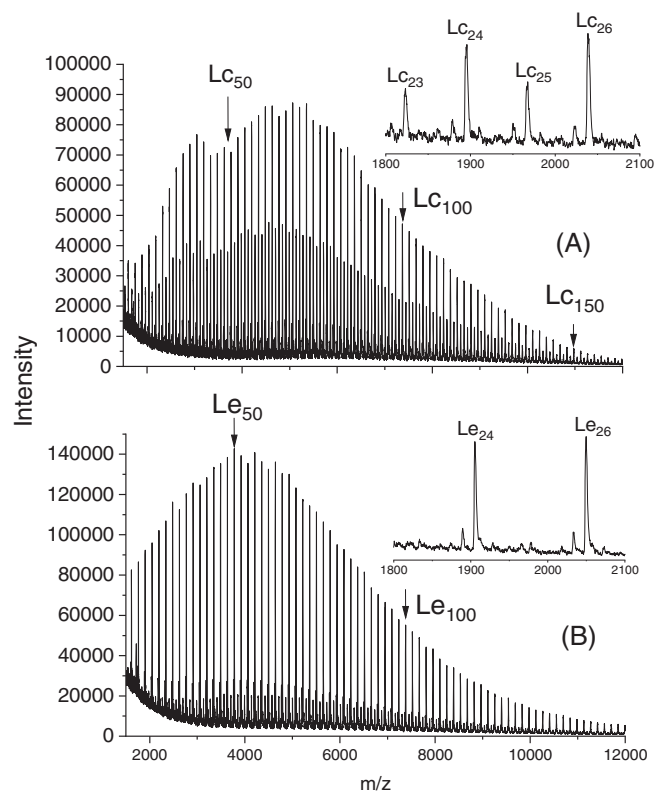


FIGURE 2 MALDI TOF mass spectra of SnOct_2 -catalyzed ROPs of LA at $130^\circ\text{C}/1\text{ h}$: (A) initiated by 4-chlorophenol, (B) initiated by 4-nitrophenol

This trend can be interpreted as consequence of different rate constants of the initiation reactions. Whereas the rate constant of the propagation (k_p) is independent of the initiator, the rate constant of initiation (k_i) decreases with lower nucleophilicity of the OH compound, and its nucleophilicity decreases with increasing acidity (in absence of steric hindrance). In other words, k_p/k_i increases with increasing acidity of the initiator with the consequence that complete conversion of the monomer can be reached, before all initiator molecules have reacted.

The third result concerns the intensity of transesterification reactions, above all, the even-odd equilibration. A clean ROP of LA yields even-numbered chains and thus, the formation of odd-numbered ones indicates the existence of transesterification reactions (Scheme 1). A comparison of Figures S1A and S2A and Figures 1A, 2A,B, and 3A demonstrates that the extent of the even-odd equilibration depends largely on the nature of the initiator but does not parallel its acidity. The highest degree of even-odd equilibration was found for 11-undecanol and the lowest for 4-nitrophenol. This finding agrees with the previous study of several alcohols where n-butanol gave the highest extent of equilibration and 4-nitrobenzylalcohol the lowest one.²⁴ Apparently, the nitro group can form a donor-acceptor interaction

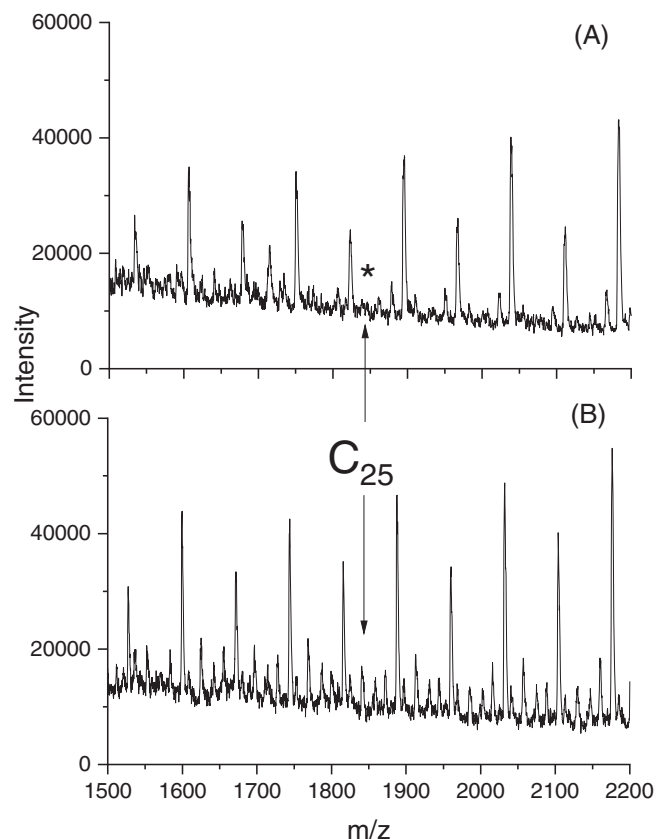


FIGURE 4 MALDI TOF mass spectra (segments) of polyLAs prepared with SnOct₂ at 130°C/1 h: (A) initiated with 4-chlorophenol, (B) initiated with 4-cyanophenol

with the Sn²⁺ ion which reduces its activity as transesterification catalyst.

The fourth result concerns formation of cycles. In the mass spectra of the UND-initiated polyLA no peaks of cycles were detectable in agreement with previous results obtained from other alcohols. Again, no cycles were found in the MALDI TOF mass spectra of the poly lactides initiated with cyclohexanone oxime or 4-chlorophenol, as demonstrated for the latter case in Figure 4A. However, weak peaks of cycles were observable in the mass spectra of the polyLAs initiated with the more acidic phenols, exemplarily illustrated by Figure 4B. This observation suggests that formation of cycles is favored, when the CO end groups are highly electrophilic, a correlation which also indicates that the cycles are formed by end-to-end cyclization and not by “back-biting”. Compelling evidence for the correctness of this interpretation is provided by the 160°C experiments discussed below.

3.2 | Annealing at 130°C

In a previous work of the authors, based on the variation of alcohols, it was found transesterification

TABLE 2 Annealing of polyLAs having activated ester end groups at 130°C/22 h. the polyLAs listed in Table 1 served as starting materials

Exp. no.	Initiator	M_n	M_w	\mathcal{D}
1	11-Undecenol	13,300	18,200	1.4
1	Cyclohexanone oxime	10,500	16,600	1.6
2	4-Chlorophenol	15,500	31,000	2.0
3	4-Hydroxybenzoxime	18,200	42,000	2.3
4	4-Nitrophenol ^a	31,000	77,000	2.4
5	Pentafluorophenol	39,000	90,000	2.3

^aThe polyLA isolated after 2 h was used.

reactions incl. The even-odd equilibration continues after solidification.¹¹ Not only the amorphous phase, but all chains were involved, even those forming crystallites. The chain segments forming the crystal lattice were not involved, but the loops and loose chain ends on the surface of the crystallites were included in the transesterification reactions. To elucidate the influence of acidic initiators on the solid phase chemistry, the ROPs performed at 130°C were continued up to 22 h. The GPC measurements signaled a substantial broadening of the MWD resulting from a slight lowering of M_n and a significant increase of the weight average molecular weight (M_w) (Table 2).

The MALDI TOF mass spectra after initiation with UND revealed a nearly complete equilibration of even and odd species along with a broadening of the MWD (Figure S1B). The cyclohexanone oxime and phenol initiated polyLAs follow, in principle, this trend (Figures 1B, 3B, and S2B), but with a conspicuous difference. New peaks of (yet unidentified) byproducts appeared, which indicate a complex chemistry with unexpected and undesirable side reactions. A deeper look into this complex solid-state chemistry was outside the scope of the present work.

3.3 | Polymerization at 160°C

A polymerization temperature of 160°C was frequently used by the authors, as well as by other research groups for the following reasons. It accelerates, of course any kind of transesterification reactions including propagation and condensation steps. Furthermore, it hinders crystallization for several hours, usually up to 10 h, provided nucleation is not purposely introduced. Moreover, side reactions such as racemization or cleavage of single bonds in the polyLA backbone are negligible at this temperature (up to 48 h at least) in contrast to temperatures around or above 180°C. The experiments summarized in Table 3 were conducted with variation of time from 0.5

TABLE 3 SnOct₂-catalyzed ROPs of L-lactide in bulk at 160°C initiated with undecenol or acidic phenols LA/cat 1000/1, LA/in = 50/1)

Exp. no.	Initiator	Time (h)	Conv. ^a (%)	M_n^b (corr)	M_n (meas.)	M_w (meas.)	\bar{D}
1A	11-Undecenol	0.5	95	—	—	—	—
1B	11-Undecenol	1	96	8400	12,300	20,300	1.7
1C	11-Undecanol	2	96	7300	10,700	22,600	2.1
1D	11-Undecanol	4	96	6900	10,100	22,200	2.2
1E	11-Undecanol	24	>99	6500	9500	20,500	2.2
2A	4-Cyanophenol	0.5	95	—	—	—	—
2B	4-Cyanophenol	1	96	13,500	20,000	47,000	1.6
2C	4-Cyanophenol	2	96	23,000	34,500	77,000	2.2
2D	4-Cyanophenol	4	96	20,100	29,500	62,000	2.1
2E	4-Cyanophenol	24	>99	19,000	28,000	60,000	2.1
3A	Pentafluorophenol	0.5	81	—	—	—	—
3B	Pentafluorophenol	1	87	21,000	30,500	62,000	2.0
3C	Pentafluorophenol	2	92	21,200	29,000	73,500	2.4
3D	Pentafluorophenol	4	96	16,500	24,000	60,000	2.5
3E	Pentafluorophenol	24	>99	14,200	21,000	57,500	2.7
3F	Pentafluorophenol	+4 (V) ^c	>99	14,400	21,300	58,000	2.7

^aDetermined by ¹H NMR spectroscopy.

^bMeasured M_n multiplied with the factor 0.68.

^cAfter 24 h under normal pressure a vacuum of 15 mbar was applied for 3 h.

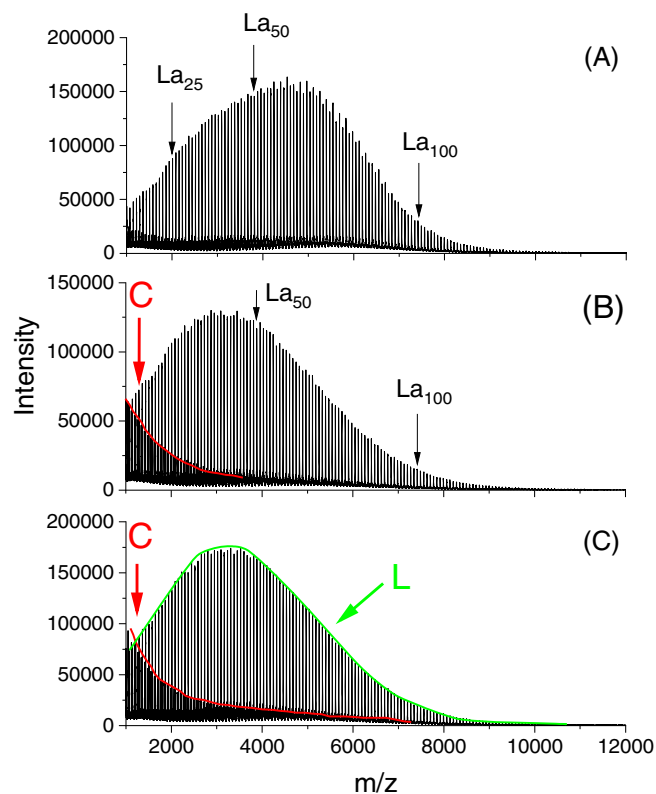


FIGURE 5 MALDI TOF mass spectra of polyLAs prepared with SnOct₂ and UND as initiator at 160°C: (A) after 0.5 h, (B) after 4 h, (C) after 24 h

to 24 h. Three different initiators were compared. UND served as standard and basis for the comparison.

A result derived from the GPC measurements of UND-initiated samples was an acceptable agreement of the corrected M_n values with the theoretical value of 7200 g/mol calculated for 96% conversion including the end group, when a time range of 1–4 h is considered. The MALDI TOF mass spectra (Figure 5) gave three more results. First, a comparison of Figure 5A with S1A indicates a slight broadening of the MWD. Second, this comparison also indicates completion of the even-odd equilibration and third, the 160°C experiment yielded a small fraction of cycles below m/z 2000. The comparison of Figure 5A-C revealed the influence of the polymerization time which caused an increase of the cyclic fraction by factor of four roughly estimated from the peak intensities.

In the case of 4-cyanophenol or pentafluorophenol-initiated polyLA the GPC data indicated M_n values far above the theoretical value in contrast to the UND-initiated samples, but close in analogy to the experiments at 130°C (Table 1). Yet, compared to the 130°C experiments, the dispersities were significantly higher indicating a strong influence of transesterification reactions. The MALDI TOF mass spectra of the 4-cyanophenol and pentafluorophenol-initiated ROPs illustrated in Figures 6A-C and 7A-C allowed for the following conclusions.

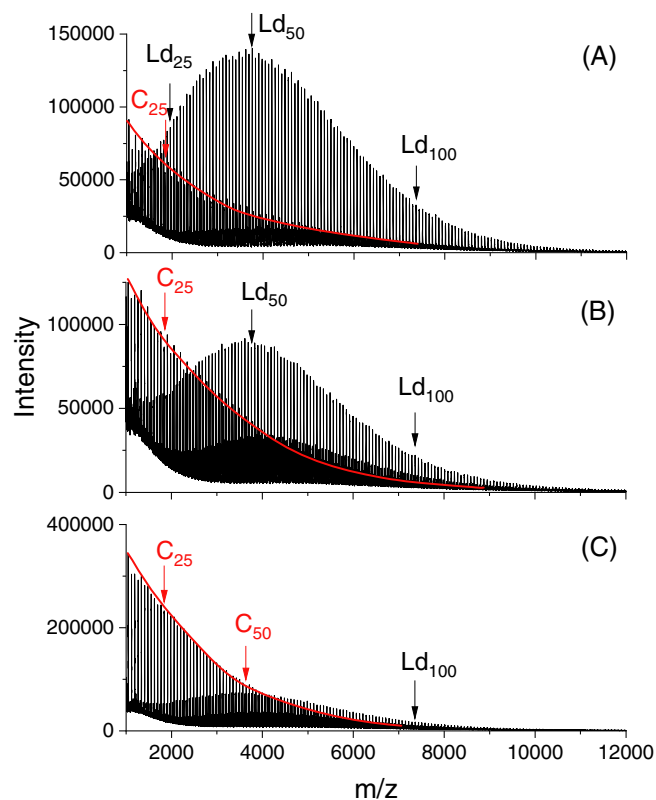


FIGURE 6 MALDI TOF mass spectra of polyLAs prepared with SnOct₂ and 4-cyanophenol as initiator at 160°C: (A) after 0.5 h, (B) after 4 h, (C) after 24 h

A considerable fraction of cycles was formed even at the shortest reaction time (0.5 h). This fraction was higher than that of the UND experiment after 24 h. The fraction of cycles increased substantially upon further heating in analogy to the results obtained for initiation with UND. With pentafluorophenol the fraction of cycles is higher than with 4-cyanophenol. Therefore, the experiments conducted at 160°C clearly prove that at least the vast majority of cycles formed in these ROPs result from ete-cyclization and not from “back-biting”. Since nature and reactivity of the nucleophilic chain ends (SnO-CH-) is independent of the initiator and thus, identical for all experiments of Table 3, the fraction of cycles should be almost identical for all three series of ROPs, if the cycles are formed by back-biting.

These results therefore support the above given interpretation of the 130°C experiments (Table 1) and they agree with previous ROPPOC experiments²⁶ based on other catalysts in that ete-cyclization plays an important role in ROPs of cyclic esters and in reversible polycondensations. The work of Flory and of Jacobson and Stockmayer has caused for decades a misleading overestimation of “back-biting” combined with a corresponding underrating of ete-cyclization. Even in the case of UND-initiated ROPs, it is not a priori clear that the small fraction of cycles is a result of

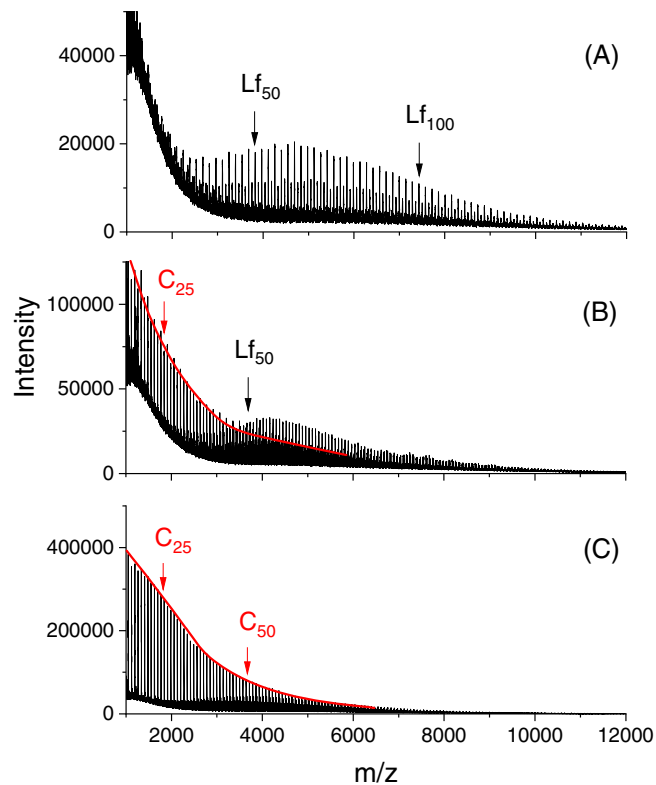


FIGURE 7 MALDI TOF mass spectra of polyLAs prepared with SnOct₂ and pentafluorophenol as initiator at 160°C: (A) after 0.5 h, (B) after 4 h, (C) after 24 h

“back-biting”, because the authors have recently demonstrated that the ethyl ester end group of lactic acid or oligolactides undergoes condensation steps when heated in the presence of SnOct₂ or tin(IV) catalysts at temperatures around or above 130°C.²⁷

4 | CONCLUSION

From the results presented in this work two conclusions should be highlighted. First, certain acidic OH-compounds such as cyclohexanone oxime and various phenols may be used as initiators in SnOct₂-catalyzed ROPs in analogy to alcohols. However, the molecular weights of the resulting polyLAs and the dispersities are higher than expected from the LA/In ratio due to slow initiation steps. Second, the activated ester end groups favor formation of cycles via ete-cyclization, an effect which increases with higher temperatures and higher electrophilicity of the activated end groups. Together with recently published results based on other tin catalysts the findings of this work provide a new insight into the course of ROPs and reversible polycondensations in that they demonstrate that formation of cycles may be predominantly or even exclusively a consequence of ete-

cyclization and not of “back-biting” in contrast to the theory of Jacobson and Stockmayer.

ACKNOWLEDGMENTS

We wish to thank BAM for technical support and especially Ing. A. Myxa for the GPC measurements and Dr. U. Mühlbauer (Thyssen-Uhde, Berlin) for having kindly supplied all lactides. Open Access funding enabled and organized by Projekt DEAL.

ORCID

Hans R. Kricheldorf  <https://orcid.org/0000-0002-8634-6648>

REFERENCES

- [1] G. Kharas, F. Sanchez-Riera, D. Severson, Polymers of lactic acid. in *Plastics from Microbes* (Ed: D. P. Mobley), Munich, Hanser Gardner Publications, Inc. **1994**.
- [2] G. Schwach, J. Coudane, R. Engel, M. Vert, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, 35, 3431.
- [3] R. A. Auras, L.-T. Lim, S. E. Selke, H. Tsuji, *Poly(lactic acid): Synthesis, Structures, Properties, Processing, and Applications*, Hoboken, New Jersey, John Wiley & Sons **2011**.
- [4] J. A. Byers, A. B. Biernesser, K. R. D. Chiaie, A. Kaur, J. A. Kehl, in *Advances in Polymer Science* (Eds: M. L. Di Lorenzo, R. Androsch), Springer, Cham **2017**, p. 67.
- [5] A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **2000**, 33, 7359.
- [6] S. Penczek, A. Duda, A. Kowalski, J. Libiszowski, K. Majerska, T. Biela, *Macromol. Symp.* **2000**, 157, 61.
- [7] M. Jalabert, C. Fraschini, R. E. Prud'Homme, *J. Polym. Sci. Pol. Chem.* **2007**, 45, 1944.
- [8] K. Jamshidi, S.-H. Hyon, Y. Ikada, *Polymer* **1988**, 29, 2229.
- [9] Y. C. Yu, G. Storti, M. Morbidelli, *Ind. Eng. Chem. Res.* **2011**, 50, 7927.
- [10] S. M. Weidner, H. R. Kricheldorf, *Macromol. Chem. Phys.* **2017**, 218, 331.
- [11] H. R. Kricheldorf, S. M. Weidner, *J. Polym. Sci.* **2021**, 59, 439.
- [12] H. R. Kricheldorf, S. M. Weidner, *Macromol. Rapid Commun.* **2020**, 41, 152.
- [13] P. J. Flory, *Chem. Rev.* **1946**, 39, 137.
- [14] H. Jacobson, W. H. Stockmayer, *J. Chem. Phys.* **1950**, 18, 1600.
- [15] H. Jacobson, C. O. Beckmann, W. H. Stockmayer, *J. Chem. Phys.* **1950**, 18, 1607.
- [16] J. F. Brown, G. Slusarcz, *J. Am. Chem. Soc.* **1965**, 87, 931.
- [17] J. B. Carmichael, D. J. Gordon, F. J. Isackson, *J. Phys. Chem.* **1967**, 71, 2011.
- [18] J. Carmichael, J. Kinsinger, *Can. J. Chem.* **1964**, 42, 1996.
- [19] S. J. Clarson, *Cyclic Polymers; Semlyen*, Kluwer Academic Publisher, Dordrecht **2000**.
- [20] J. Roovers, *Macromolecules* **1988**, 21, 1517.
- [21] J. A. Semlyen, *Large Ring Molecules; Semlyen*, John Wiley & Sons, Chichester **1996**.
- [22] J. A. Semlyen, *Cyclic Polymers*, Dordrecht, Springer **2000**, p. 1.
- [23] R. Szymanski, in *Comprehensive Polymer Science* (Eds: K. Matyjaszewski, M. Möller), Elsevier BV, Amsterdam **2012**, p. 31.
- [24] S. M. Weidner, A. Meyer, J. Falkenhagen, H. R. Kricheldorf, *Eur. Polym. J.* **2021**, 153, 110508.
- [25] J. R. Dorgan, J. Janzen, M. P. Clayton, S. B. Hait, D. M. Knauss, *J. Rheol.* **2005**, 49, 607.
- [26] H. R. Kricheldorf, S. M. Weidner, F. Scheliga, *Polym. Chem.* **2020**, 11, 2595.
- [27] H. R. Kricheldorf, S. M. Weidner, J. Falkenhagen, *Polym. Chem.* **2021**, 12, 5003.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

How to cite this article: S. M. Weidner, H. R. Kricheldorf, *J. Polym. Sci.* **2021**, 1. <https://doi.org/10.1002/pol.20210823>