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Poly(L-lactide): optimization of melting temperature and melting enthalpy and a comparison of linear and cyclic species

Hans R. Kricheldorf,*[a] Steffen M. Weidner[b] and Andreas Meyer[c]

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Twice recrystallized L-lactide was polymerized with a dozen different tin or bismuth catalysts in bulk at 160 °C for 24 h and was annealed at 150 °C afterwards. In two cases T_m values above 197.0 °C were obtained. The parameters causing a scattering of the DSC data were studied and discussed. The samples prepared with $SnCl_2$, 2,2-dibutyl-2-stanna-1,3-ditholane (DSTL) or cyclic tin(II) bisphenyldioxide (SnBiph) were subject to annealing programs with variation of time and temperatures, revealing that the T_ms did not increase. Hower, an increase of ΔH_m was achieved with maximum values in the range of 93–96 J g^{-1} corresponding to crystallinities of around 90%. Further studies were performed with once recrystallized L-lactide. Again, those samples directly crystallized from the polymerization process showed the highest T_m values. These data were compared with the equilibrium T_{m0} and ΔH_{m0} data calculated by several research groups for perfect crystallites. A T_{m0} of 213 +/−2 °C and a ΔH_{m0} of 106 J g^{-1} show the best agreement with the experimental data. The consequences of annealing for the thickness growth of crystalites are discussed on the basis of SAXS measurements. Finally, a comparison of cyclic and linear poly(L-lactide)s is discussed.

Introduction

Since the beginning of the technical production of polylactide in the 70s of the last century research activities concerning chemical and physical properties of polylactides have dramatically increased.[1–5] The most fundamental physical properties, glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m), a measure of crystallinity, are the most fundamental physical properties. They are responsible for mechanical properties and are thus, decisive for most potential applications. In contrast to many other polymers T_m and ΔH_m of polylactides can vary over a broad range, for example 120–200 °C in the case of T_m and 20–100 J g^{-1} in the case of ΔH_m. They are influenced by three parameters.

1. Optical purity – Since lactic acid is chiral compound polylactides may, in principle, contain various ratios of D- and L-units which sequences may vary over a broad range from random to optically pure poly(L-lactide) PLLA, or poly(D-lactide) PDLA. Stereocopolymers containing more the 20% of the enantiomer are amorphous. The influence of D-units on the physical properties of PLLA has been intensively studied by several research groups.[6–11]

2. Thermal history – It is, in principle trivial, that experimental parameters such as crystallization temperature, heating rate, annealing time and mechanical stress have a significant influence on the physical and mechanical properties of polylactides. A first intensive study in this direction was performed by the group of Pennings[12–15] followed by numerous other research groups.[16–27] Studies above 120 °C are simplified by the fact that the α-modification is the thermodynamically most stable crystal modification.[28]

3. Chemical reactions in the solid state – Recently, it was found by the authors that in the presence of a reactive transesterification (polymerization) catalyst several kinds of transesterification reaction may proceed in the solid state, which modify the fraction of the mobile amorphous phase, structure and fraction of the immobile amorphous phase on the surface of the crystallites and the thickness of the crystallites. Hence these transesterification reactions have a strong influence on the morphology and thus, on T_m and ΔH_m. In addition of the experimental parameters mentioned above, nature and activity of the catalyst and its concentration play a role for extent and consequences of the transesterification reactions. This aspect was recently discovered by the authors and needs further studies.[29–32]

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[a] *Institut für Technische und Makromolekulare Chemie, Universität Hamburg, Bundesstr. 45, D 20146 Hamburg, Germany. E-mail: hrkricheldorf@aol.de*

[b] *BAM – Bundesanstalt für Materialforschung und-Prüfung, Richard Willstätter Str. 11, D 12489 Berlin, Germany*

[c] *Institut für Physikalische Chemie, Universität Hamburg, Grindelallee 117 D-20147 Hamburg, Germany*

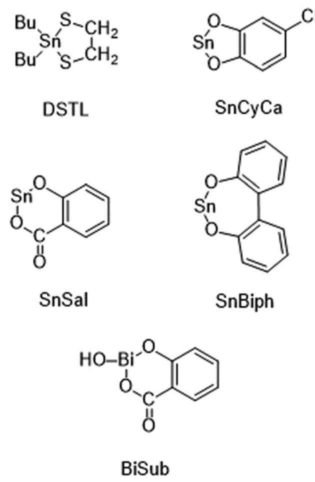
Table 1 Thermal properties of polyLAs polymerized with various tin catalysts at 160 °C (22 h) in bulk at LA/Cat = 1000/1 ratio followed by annealing at 150 °C/22 h

Exp. no.	Catalyst	M_n	M_w	$T_m{}^a$ (°C)	$\Delta H_m{}^a$ (J g^{-1})	$T_m{}^a$ (°C)	$\Delta H_m{}^a$ (J g^{-1})	$T_m{}^b$ (°C)	L (nm)	Cryst^c (%)	l_c (nm)
1	$SnCl_2$	38 500	101 000	196.3	93.3	196.7	88.7	195.5	35	90	30
2	$SnAc_2$	45 000	100 000	193.6	84.7	193.3	80.5	191.6	35	80	28
3	$SnOct_2$	41 000	109 000	189.7	85.6	191.0	77.0	—	28	80	23
4	SnCyca	68 000	153 000	184.0	74.6	187.7	88.2	—	23	81	19
5	SnSal	24 000	61 000	186.1	82.3	185.2	75.2	—	23	83	20
6	SnBiph	111 000	235 000	198.0	78.6	197.6	83.6	197.2	34	79	27
7	Me_2SnCl_2	Slow pol.	—	—	—	—	—	—	—	—	—
8	Me_2SnO	22 500	46 000	185.2	79.2	183.8	79.4	—	21	79	17
9	Bu_2SnO	31 000	81 000	190.4	87.2	189.3	76.9	—	23	82	19
10	Ph_2SnO	25 000	68 000	190.7	85.4	189.2	79.2	189.0	26	81	21
11	DSTL	68 000	167 000	197.7	93.0	197.3	87.4	196.5	32	90	27
12	BiSub	20 500	54 000	187.0	80.6	187.6	82.0	—	20	77	16

[a] Measured with a Mettler-Toledo DSC 1 on two sites of the same product. [b] Measured with a Setaram TGA 24. [c] Highest ΔH_m value was used for the calculation.

In this context it was the purpose of this work to find reaction conditions allowing for an optimization of T_m and ΔH_m. Variation of structure and activity of catalysts of primary interest. Eleven tin catalysts and one Bi-based catalysts were tested in this work (Table 1).

In this connection it should be mentioned that several research groups have attempted to calculate the maximum T_m of perfect PLLA crystals, the s. c. equilibrium melting temperature T_{m0} and, the maximum melting enthalpy ΔH_{m0}. ΔH_{m0} is of particular interest for analytical purposes because its knowledge allows the calculation of crystallinities from DSC measurements. Unfortunately, there is no satisfactory agreement about T_{m0} and ΔH_{m0} in the literature, and the knowledge of the highest experimentally accessible T_m's and ΔH_m's allows for sorting out those T_{m0} and ΔH_{m0} values that are too low and thus, allows identification of the most reasonable and trustworthy T_{m0} and ΔH_{m0} values.



Scheme 1 Catalysts and their acronyms used in this work.

Experimental

Materials

L-Lactide, a product of Corbion Purac, was kindly supplied by Thyssen-Uhde AG (Berlin). It was once or twice recrystallized from toluene (99.89% extra dry, ACROS Organics). Tin(II) 2-ethylhexanotae ($SnOct_2$) with >96% purity was purchased from Alfa Aesar (Kandel, Germany) and used as received. $SnCl_2$, Me_2SnCl_2 Me_2SnO, Bu_2SnO, Ph_2SnO and Bi(III)subsalicylate (BiSub) were all purchased from Alfa Aesar and used as received, $SnAc_2$ (Alfa Aesar) was dried at 40 °C *in vacuo* in the presence of solid NaOH for 4 d to remove traces of acetic acid. The following cyclic catalysts prepared in previous studies were used: DSTL,[33] SnSal,[34] SnCyca[35] and SnBiph[35] (for acronyms see Scheme 1).

Polymerizations

Tables 1–5. The catalyst (0.06 mmol) was weighed into a 100 mL flame-dried Erlenmeyer flask, L-lactide (60 mmol) and a magnetic bar were added under a blanket of argon. The reaction vessel was immersed into an oil bath thermostated at 160 °C. After 24 h the temperature was lowered to 150 °C. After 22 the Erlenmeyer flask was destroyed and the crystalline disk of PLLA was cut into 8 pieces which were used for separate DSC measurements (Table 1 and 2) of for annealing experiments (Tables 3–5).

Table 6 and 7. These ROPs were performed as described above, but the experiments were stopped after 24 h. The resulting crystalline disks were characterized in the virgin state and were cut into 6 pieces for annealing experiments.

Measurements

The MALDI TOF mass spectra were measured with an Autoflex-Max mass spectrometer Bruker Daltonik, Bremen, Germany) in the positive ion linear mode. For sample spot preparation chloroform solutions of poly(L-lactide) (3–5 mg mL^{-1}) doped with potassium trifluoroacetate (2 mg mL^{-1}) were premixed in an Eppendorf vial with a solution of trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 20 mg mL^{-1}, $CHCl_3$) in a ratio of 20/2/50 (sample/salt/matrix). 1 μL of this solution was deposited on the MALDI stainless steel target.

Table 2 Influence of local inhomogeneity on T_m and ΔH_m in crystalline disks of polyLA

	Site A, 1st meas.		Site A, 2nd meas.		Site B		Site C		Powder	
Catalyst	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})	T_m (°C	ΔH_m (J g^{-1})	T_m (°C)	ΔH_m (J g^{-1})
$SnOct_2$	187.4	80.1	187.8	86.4	190.4	86.0	189.2	81.7	189.4	79.0
Ph_2SnO	188.6	90.0	189.9	88.2	190.2	85.6	187.1	84.4	187.9	81.6

Table 3 Annealing experiments with PLLA catalyzed by $SnCl_2$

Exp. no.	Temp. (°C)	Time (h)	M_n	M_w	T_m (°C)	ΔH_m (J g^{-1})	Cryst. (%)
1	—[a]	—	38 500	101 000	196.7	96.0	91
2	170	10	24 000	62 000	195.6	92.7	87
3	180	2	27 000	66 000	196.4	93.8	88
4	180	4	19 000	52 000	195.6	84.9	80
5	180	10	33 000	85 000	196.5	91.1	86
6	170 + 187	10 + 1.5	26 000	72 000	196.0	88.0	83
7	170 + 187	10 + 3.0	20 000	51 000	195.7	88.5	84

[a] Starting material no. 1 Table 1.

Table 4 Annealing experiments with PLLA catalyzed by DSTL

Exp. no.	Temp. (°C)	Time (h)	M_n	M_w	T_m (°C)	ΔH_m (J g^{-1})	Cryst. (%)
1	—[a]	—	60 000	167 000	197.7	93.0	88
2	170	10	45 000	101 000	197.6	92.0	87
3	180	2	36 000	75 000	194.2	83.8	79
4	180	4	22 000	69 000	192.8	83.5	79
5	180	10	30 000	85 000	196.5	85.4	80
6	170 + 187	10 + 1.5	41 000	113 000	197.6	81.8	77
7	170 + 187	10 + 3.0	23 000	80 000	195.0	74.0	70

[a] Starting material no. 11 Table 1.

Table 5 Annealing experiments with PLLA catalyzed by SnBiph

Exp. no.	Temp. (°C)	Time (h)	M_n	M_w	T_m (°C)	ΔH_m (J g^{-1})	Cryst. (%)
1	—[a]	—	111 000	235 000	198.0	78.6	74
2	170	10	45 000	112 000	196.2	95.7	90
3	180	2	67 000	173 000	195.3	94.4	89
4	180	4	52 000	136 000	198.0	90.1	85
5	180	10	47 000	132 000	196.6	87.0	83
6	170 + 187	10 + 1.5	36 000	104 000	195.4	87.5	84
7	170 + 187	10 + 3.0	34 000	77 000	195.5	96.2	91

[a] Starting material no. 6 Table 1.

Table 6 Annealing experiments of PLLA prepared from once (no. 1–4) or twice (no. 5–8) recrystallized L-lactide with DSTL at 160 °C (LA/Cat = 1 000/1)

Exp. no.	Temp. (°C)	Time (h)	M_n	M_w	T_m (°C)	ΔH_m (J g^{-1})	Cryst. (%)	L (nm)	l_c (nm)
1	160	24	71 000	153 000	191.6	57.0	55	36.0	20
2	+170	4	26 500	64 500	188.6	73.5	69	33.5	23
3	+170	22	35 500	76 000	192.4	82.5	78	33	26
4	+180	4	21 000	59 500	186.7	72.0	68	32	22
5	160	24	63 000	141 000	194.0	79.3	75	29	22
6	+170	4	27 000	61 000	189.5	78.8	74	30	22
7	+170	22	29 000	68 000	193.3	91.0	86	29.5	25
8	+180	4	23 000	56 000	187.5	73.0	69	31	22

Table 7 Annealing experiments of PLLA prepared from once (no. 1–4)or twice (no. 5–8) recrystallized L-lactide with SnBiph at 160 °C (LA/Cat = 1 000/1)

Exp. no.	Temp. (°C)	Time (h)	M_n	M_w	T_m (°C)	ΔH_m (J g^{-1})	Cryst. (%)	L (nm)	l_c (nm)
1	160	24	98 000	248 000	197.7	73.3	69	40.0	28
2	+170	4	46 500	154 000	194.5	79.3	75	36.5	27/28
3	+170	22	40 500	131 000	194.0	84.7	80	35.0	28
4	+180	4	45 000	127 000	194.2	82.4	78	38.0	29/30
5	160	24	93 000	231 000	196.2	82.3	78	36.0	28
6	+170	4	55 000	138 000	193.6	81.0	77	33.0	26/27
7	+170	22	35 500	96 000	193.7	89.0	84	31.5	27
8	+180	4	45 000	117 000	193.8	82.0	78	33.0	26/27

Spectra were recorded from at least 4 different positions of the spot and accumulated.

The GPC measurements were performed in a modular system kept at 40 °C consisting of an isocratic pump, 1 mL min^{-1} and a refractive index detector (Optilab rex, Wyatt). Samples were manually injected (100 μL, 2–4 mg mL^{-1}). For instrument control and data calculation Astra software (Wyatt) was used. The calibration was performed using polystyrene standard sets (Polymer Standards Service – PSS, Mainz). The number average (M_n) and weight average (M_w) molecular weights reported in the Tables below are uncorrected for convenient comparison with the uncorrected GPC data of other research groups. For a correlation of intrinsic viscosities with molecular weights, Mark–Houwink–Sakurada (MHS) measurements were performed (Astra, Wyatt).

The DSC heating traces were recorded on a freshly (with indium and zinc) calibrated Mettler–Toledo DSC-1 equipped with Stare Software-11. Quantities of 8–10 mg were used for these measurements. Only the first heating traces were considered. A heating rate of 10 K min^{-1} described by almost all other research groups was also used in this work. The influence of the heating rate on T_m was studied by Kishore *et al.*[13] The crystallinities listed in the Tables were calculated with a $\Delta H_{m\,max}$ of 106 J g^{-1}.

The SAXS measurements were performed using our in-house SAXS/WAXS apparatus equipped with an Incoatec™ X-ray source IμS 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^2. 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 $2\Theta = 5$–33°. 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 20 minutes. DPDAK, a customizable software for reduction and analysis of X-ray scattering data sets was used for gathering 1D scattering curves.[36] For the evaluation of the crystallinity of the samples the data were imported in Origin™ and analysed 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

Evaluation of catalysts

Eleven tin catalysts were selected for this study considering the following aspects. A high efficiency as polymerization catalyst was desirable, because high rates of polymerization may also indicate high rates of transesterification. From this point of view $SnAc_2$, $SnOct_2$, SnSal and above all SnBiph were included as the most promising candidates. However, a small size of the catalyst might also be beneficial for efficient transesterification in the immobile amorphous fraction (IMF), because of a higher mobility in this extremely viscous phase. Under this aspect $SnAc_2$ and $SnCl_2$ should be most favourable for efficient transesterification among the tin(II) catalysts and Me_2SnCl_2 and Me_2SnO among the tin(IV) catalysts. Considering previous experiments with cyclic tin catalysts, polymerizations conducted at 160 °C/24 h with a LA/Cat ratio of 1000/1 seemed to be favourable for the spontaneous crystallization of PLLA from the melt. However, Me_2SnCl_2 failed to give a high conversion under these conditions and in the cases of Me_2SnO and BiSub crystallization was still far from complete. Therefore, the temperature was lowered to 150 °C for 22 h, whereupon complete crystallization was achieved for all PLLAs with exception of the Me_2SnCl_2-catalyzed oligomers.

The results summarized in Table 1 show a broad variation of T_m (between 184 and 198 °C) and also a broad variation of ΔH_m (between 74 and 93 J g^{-1}). A straightforward correlation of T_m's with the afore-mentioned properties of the catalyst was not detectable. Whereas the success of $SnCl_2$ and SnBiph in terms of high T_m's was understandable based on the above arguments, the failure of $MeSnCl_2$ and the sluggishness of Me_2SnO were not. The extraordinarily high T_m obtained with DSTL was not unexpected considering previous results,[33] but it does not correlate with the observation that the activity of DSTL as polymerization catalyst is rather low. The three samples with the highest T_m's were then subject to several annealing experiments which were discussed in the next section. Yet, prior to this discussion accuracy and reproducibility of the DSC measurements deserve a comment.

DSC data are usually presented without margin of error and without information on a scattering of the measurements. However, such a presentation of T_m and ΔH_m data is only justified for measurements of a single crystal, but not for measurements of larger specimens of crystalline PLLA as they were prepared in this work. A scattering of thermal data has mainly two sources. First, the inhomogeneity of the sample and second, different DSC apparatus. The samples listed in Table 1 were prepared in quantities of 8.5 g in Erlenmeyer flasks and thus formed disks with a diameter of c. 5 cm and a thickness of *ca.* 4 mm. It was observed that in several cases the nuclei of the crystallization process were not homogeneously distributed but began to form in the neighbourhood of the stirring bar, because its motion immediately before it was stopped by the increasing melt viscosity caused weak mechanical stress in its direct neighbourhood, and the parallel alignment of chain segments induced nucleation.

The disks were cut into eight pieces for annealing experiments and when a piece from the interior of the disk was compared with a piece from the outer sphere, the scattering of the DSC data listed in two columns of Table 1 was found. Whereas this scattering was weak for T_m considerable differences were found for ΔH_m. A more detailed examination of the inhomogeneity was conducted with PLLAs prepared with $SnOct_2$ and Ph_2SnO. At first two probes were taken from the same site of the same piece, but nonetheless a slight scattering of the results was found as demonstrated by the columns "Site A, 1. and 2. measurement" in Table 2. Furthermore, probes were taken from two other pieces (sites B and C) and a somewhat broader scattering of T_m and ΔH_m was found. Finally, a piece of each sample was pulverized in a mortar after cooling with liquid air (last column). The powder data were somewhere in between the extremes of the individual sites. Pulverization has, of course, the advantage of homogenization of larger samples, but also has two disadvantages. First, the large surface attracts moisture and thus, powders of PLLA are unfavourable for storage and later measurements. Second, the chance to find spherulites with a higher perfection than the average of the sample does not exist anymore.

When five samples were subject to DSC measurements with SEATRAM apparatus (BAM, Berlin), the T_m, data were about 1 °C lower than those recorded with the Mettler Toledo apparatus (TMC, Hamburg) (last column Table 1). Furthermore, it should be mentioned that quite recently the authors compared numerous PLLA samples prepared (and annealed) with $SnOct_2$ with DSC data of the Pennings group[12–14] crystallized and annealed under comparable conditions. A good agreement of all data was found, for example, the maximum T_m observed by both groups (194.5 °C) was identical.[37] For these reasons the authors consider the DSC data reported in this work to be reliable and representative for PLLA in its optimum morphology. This conclusion means that T_m's in the range of 197–198 °C as they were observed in 7 experiments (incl. Tables 3–5) are the highest experimental T_m's reported so far.

The highest ΔH_m values fall into the range of 90–96 J g^{-1}, identical with or slightly higher than the maximum values reported by other research groups[13,19] (90–92 J g^{-1}).

The consequence of this results for the calculation of crystallinities is discussed below.

Annealing experiments

The PLLA samples prepared with $SnCl_2$, DSTL and SnBiph were subject to an annealing program with variation of temperature and time as indicated by the 2 and 3 columns in Tables 3–5. Due to the high T_m's of the starting materials annealing was feasible at 180 and even at 187 °C. However, no increase of T_m was found regardless of the catalyst and the annealing conditions Here and in previous experiments with SnBiph at lower temperatures (130 or 140 °C) and in annealing experiments with $SnOct_2$, the PLLA obtained by direct crystallization from the polymerization process had the highest T_m values. An overriding trend across all three series of annealing experiments is the considerable degradation of the molecular weights. It is in general accepted that the T_m of PLLA slightly increases with the molecular weight, because a lower concentration of end groups results in a lower number of defects in the crystal lattices. Hence, the slightly lower T_m's observed in this work after annealing may to be ascribed to the lower molecular weights, and this interpretation is certainly reasonable as an overriding trend but does not suffice for a satisfactory explanation of all results. For example, in the case of the $SnCl_2$-catalyzed PLLAs, the T_m values obtained after annealing at 180 or 187 °C (no. 1, 3, 6, Table 3) are as high as those of the starting material, despite lower M_w's. The same is true for the DSTL-catalyzed samples annealed at 170 or 187 °C (no. 2, 6, Table 4) Since the T_m also depends on the thickness of the lamellar crystal (l_c) and on the surface free energy (σ_e) according to the Gibbs–Thomson equation (eqn (1)), nature and extent of transesterification catalyst across the surface of the crystallites play an important role for the morphology and thus, for the T_m. Evidence for such transesterification reactions in solid PLLA has been presented and discussed in several previous publications[29–32] and thus, should not be repeated here again.

$$T_m = T_m^0\left[1 - \left(2\sigma_e/\rho\Delta H_m^0 l_c\right)\right] \qquad (1)$$

Four more series of annealing experiments were performed with PLLA samples prepared with DSTL and SnBiph (Tables 6 and 7). The starting materials were prepared at 160 °C/24 h from once or twice recrystallized L-lactide for the following reasons. Firstly, the effect of repeated recrystallization should be elucidated. Secondly, the total polymerization time should be shortened relative to the experiments of Table 1 to obtain higher molecular weights. This second goal was in fact not realized as demonstrated by the M_w's of 153 000 and 141 000 for the DSDTL-catalyzed PLLAs (no. 1 and 5, Table 6) and 248 000 plus 239 000 for the SnBiph-catalyzed starting material (no. 1 and 5, Table 7). Unexpectedly, the M_w's obtained from the PLLAs derived from once recrystallized lactide were slightly higher than those of PLLAs derived from twice recrystallized lactide. A similar result was found by the authors in a previous study based on L-lactide of the same origin.[35] Concerning the T_m's and ΔH_m's, a systematic difference between PLLAs derived from once or twice recrystallized lactide was not detected considering the scattering of the measurements taken from different pieces of the same sample. In fact, the cautiousness to recrystallize L-lactide twice for the screening of the catalysts (Table 1) was not necessary.

Nonetheless, the experiments compiled in Tables 6 and 7 confirmed two trends already revealed by the data of Tables 4 and 5. Firstly, the highest T_ms were obtained from the starting materials directly crystallized from the polymerization. Secondly, annealing at temperatures >160 °C causes degradation of the molecular weights. This degradation has certainly two sources, namely formation of a larger fraction of low molar mass cycles, and second, cleavage of σ-bonds in the PLLA backbone. The cleavage of one single σ-bond suffices to transform a cycle into a linear chain.

In this connection the MALDI TOF mass spectra were of interest. Characterization by this method was focused on the PLLAs prepared by $SnCl_2$, DSTL and SnBiph which were preferentially studied in this work. As illustrated by Fig. 1, the mass spectra of $SnCl_2$-catalyzed PLLAs displayed cycles only in the low molar mass range ($<m/z$ 4000) and seral peaks of linear species at higher masses indicating side reactions in agreement with the relatively low molecular weights. In contrast the mass spectra of the PLLAs prepared with DSTL or SnBiph under relatively moderate annealing conditions (no. 1, Tables 5–7) exclusively display peaks of cycles (Fig. 2A, B and 3A). The MHS measurements confirmed that the high molar mass fraction was also cyclic (see (C), Fig. 4). The formation of cyclic PLLA by cyclic tin catalysts *via* ring-expansion polymerization (see (a) + (b) in Fig. 2) has been published previously.[33–35,37] In contrast

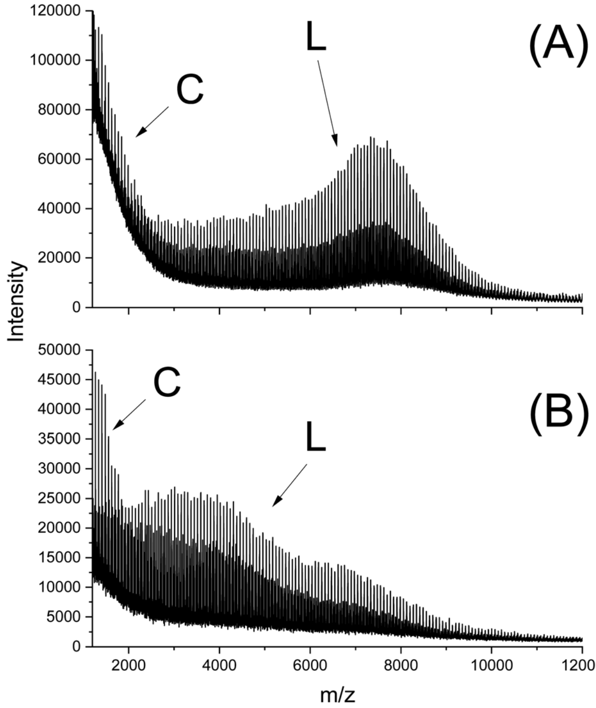


Fig. 1 MALDI TOF mass spectra of PLLA prepared with $SnCl_2$: (A) after annealing at 180 °C/4 h (no. 4, Table 3), (B) after annealing at 187 °C/1.5 h (no. 6, Table 3).

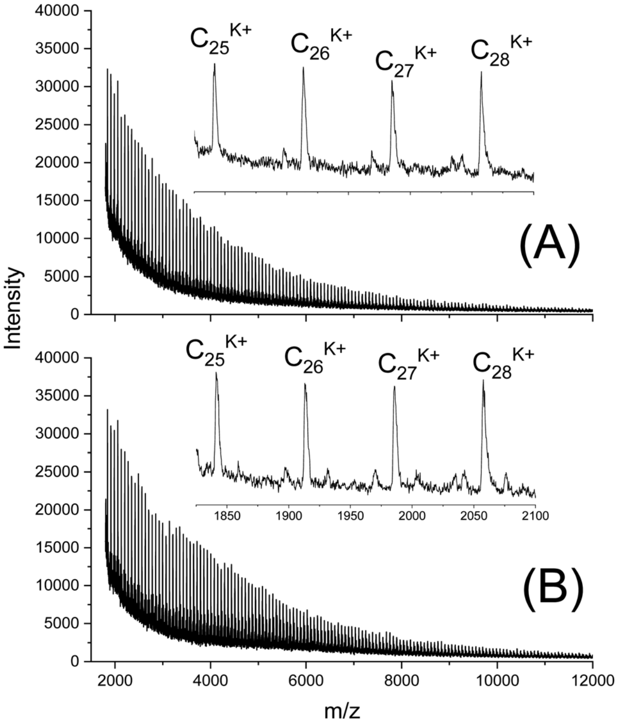


Fig. 2 MALDI TOF mass spectra of PLLAs prepared with DSTL at 160 °C/22 h: (A) LLA 1× recrystallized (no. 1, Table 6), (B) LLA 2× recrystallized (no. 5, Table 6).

to these previous measurements, where the samples were isolated after 1–3 h in this study a more extensive annealing of 22 h was performed. The mass spectra displayed in Fig. 3B and C demonstrate that annealing at 170 or 180 °C entails appearance of a linear species in the low molar mass range, but the intrinsic viscosity measurements prove that the cyclic topology was not seriously damaged (curve (D), Fig. 4). However, with DSTL as catalyst partial degradation of the cycles was more pronounced.

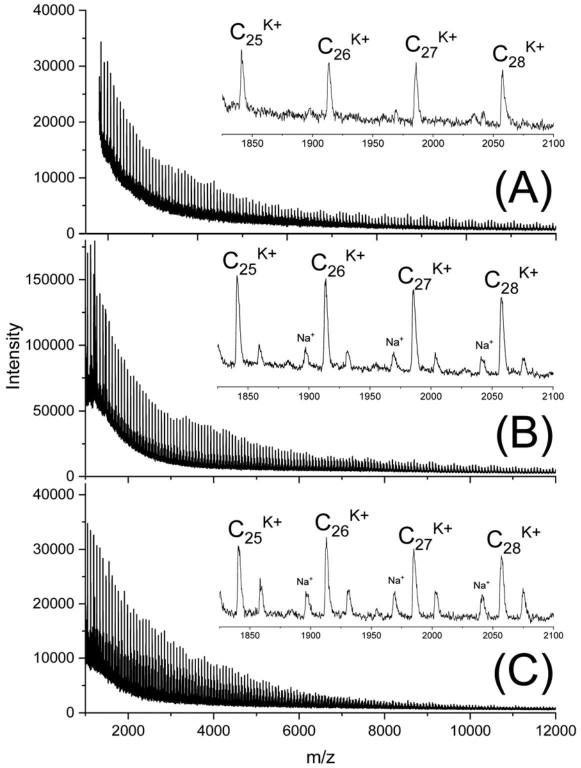


Fig. 3 MALDI TOF mass spectra of PLLAs prepared with SnBiph at 160 °C/22 h (A) LLA 2× recrystallized (no. 1, Table 7), (B) after annealing at 170 °C/22 h (no. 7, Table 7), (C) after annealing at 180 °C/4 h (no. 8, Table 8).

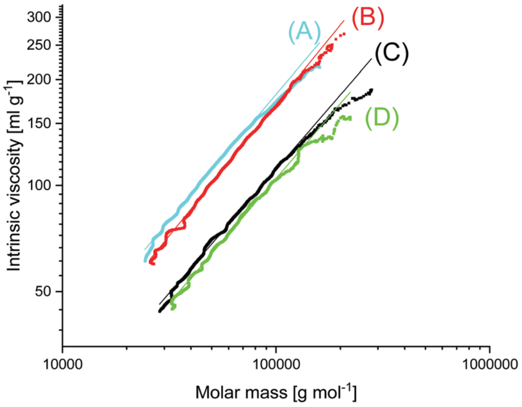


Fig. 4 MHS plots of (A) Purapol L 105, (B) PLLA initiated with ethyl L-lactate (no. 4, Table 10), (C) PLLA catalyzed with SnBiph (no. 5, Table 7), (D) after annealing at 170 °C/22 h (no. 7, Table 7).

Evaluation of SAXS measurements

It has recently been demonstrated by the authors[30] that cyclic PLLAs prepared at 160 or 170 °C with short times (1–3 h) quenched to *ca.* 50 °C and annealed at 120 °C crystallize in the low melting morphology (LT_m) with T_m's below 176 °C. For this kinetically controlled standard morphology crystal thicknesses (l_c) in the range of 8–12 nm are characteristic. For the high melting (HT_m) morphology (T_m's >190 °C) l_c values in the range of 20–34 nm were found.[29–31] Samples having intermediate T_m's show intermediate l_c values. The SAXS measurements of the 11 PLLAs listed in Table 1 fit well into this picture. Samples having T_m's in the range of 184–189 °C gave l_c values in the range of 16–20 nm, whereas samples with T_m's >190 °C showed l_c values above 20 nm.

Furthermore, the PLLAs listed in Tables 6 and 7 were characterized by SAXS measurements. Interestingly, the data recorded from DSTL catalyzed PLLAs displayed a systematic difference. On the average, the DSTL samples had lower l_c values in combination with lower T_m's and lower molecular weights. The samples having the highest T_m's (no. 1 and 5, Table 7) also gave the highest l_c values. A correlation between higher M_w's and higher T_m's has already been tentatively assumed for the results of Tables 4 and 5. The data summarized in Tales 6 and 7 support this assumption and extend it to l_c values. An exemplary illustration of the SAXS curves recorded in this work is given in Fig. 5 and 6. The existence of a second order reflex in most SAXS curves indicates a high degree of 3-dimensional order inside the spherulites.

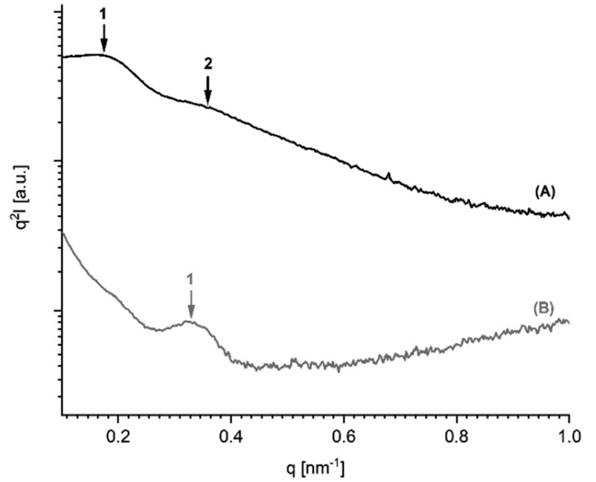


Fig. 5 SAXS curves (Kratky plots) of PLLAs polymerized with DSTL: (A) polymerized at 160 °C/22 h (no. 1, Table 6), (B) annealed at 187 °C/1.5 h (no. 6, Table 4).

About the equilibrium melting temperature (T_{m0}) and melting enthalpy, ΔH_{m0}

Beginning with Penning and coworkers[12,13] several research groups have extrapolated the equilibrium melting temperature (T_{m0}) of ideal PLLA crystals from the T_m's of their real samples (Hoffmann–Weeks method). Table 8 summarizes the published data. The DSC measurements of this work yield T_m's up to 198 °C defined as maximum of the endotherm at a heating rate of 10 K min^{-1} (as usual). The high temperature end of the endotherm hits the base line around 204–205 °C suggesting that a small fraction (~1%) of crystallites is present melting in the range of 200–203 °C from these results it may be concluded that all T_{m0} values below 210 °C are too low, whereas T_{m0}'s in the range of 211–215 °C (calculated by four groups) seem to be realistic.

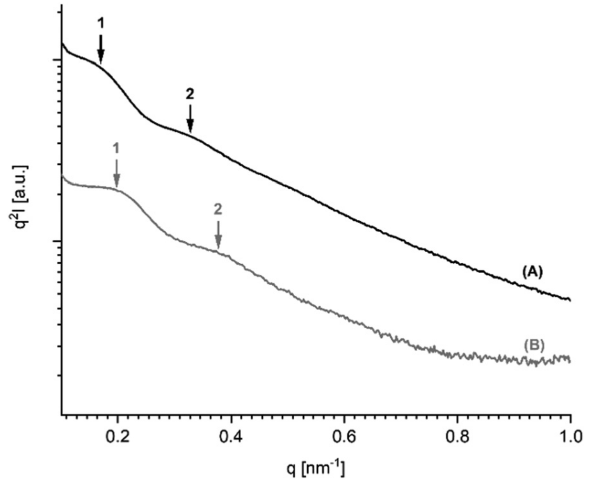


Fig. 6 SAXS curves (Kratky plots) of PLLAS prepared with SnBiph: (A) from 1× recrystallized LA (no. 1, Table 7), (B) from 2× recrystallized LA (no. 5, Table 7).

Table 8 Equilibrium melting temperatures, T_{m0}, of linear poly(L-lactide), L-PLLA, linear poly(D-lactide), L-PDLA, cyclic poly(L-lactide), c-PLLA, and cyclic poly(D-lactide), c-PDLA, reported by various research groups

Authors	Ref.	Species	M_w or M_v	T_{m0}
Kalb, Penning	12	L-PLLA	350 000[b]	215
Vasanthakumari	14	L-PLLA	350 000[b]	207
Tsuji, Ikada	18	L-PLLA	1 330 000[a]	211
Tsuji, Ikada	42	L-PLLA	1 330 000[a]	205
Tsuji, Ikada	11	L-PLLA	50 000–60 000[a]	200
Tsuji, Ikada	43	L-PLLA	400 000–500 000[a]	215
Huang *et al.*	44	L-PLLA	127 000[a]	214/215
Iannace, Nicolas	45	L-PLLA	No inform.	206
Abe *et al.*	46	L-PLLA	152 000[a]	199/227[c]
Abe *et al.*	47	L-PLLA	152 000[a]	215
Zaldua *et al.*	38	L-PLLA	18 300[a]	159
Zaldua *et al.*	38	L-PDLA	18 000[a]	159
Zaldua *et al.*	38	c-PLLA	16 800[a]	164
Zaldua *et al.*	38	c-PDLA	16 900[a]	164

[a] M_w. [b] M_v. [c] Two different methods were used.

Particularly low are the T_{m0} data of Zaldua *et al.*[38] Those authors studied rather low molar mass PLLAs having end groups that don't fit into the crystal lattice (designed for ''Click cyclization''), and obviously these end groups disturb the crystal lattices to such an extent that experimental T_m's below were recorded.

Several research groups also calculated the ΔH_{m0} value of ideal crystals (Table 9). The experimental data of this work and a couple of previous publications demonstrate that all ΔH_{m0} values below 100 J g^{-1} cannot be correct. The 93 J g^{-1} value published by Fischer *et al.*[6] nearly 50 years ago was widely used by numerous research groups to determine crystallinities *via* DSC. The results of this work suggest that a ΔH_{m0} of 106 J g^{-1} first used by Sarasua[22] and Tsuji[23] is reasonable, although its origin is not clear, because the reference cited by those authors (ref. 39 in this work) does not mention the origin of this ΔH_{m0} value. Taking the 106 J g^{-1} value serious means, in turn, that the crystallinities calculated *via* the ''Fischer value'' overestimate the true crystallinities by 10–15%.

Comparison of cyclic and linear polylactides

Finally, a comparison of cyclic and linear polylactides with regard to T_m, T_{m0}, ΔH_m and ΔH_{m0} should be discussed. Sugai *et al.*[40] also determined ΔH_{m0} values for cyclic PPLLAs and PDLLAs and compared them with the ΔH_{m0} values of linear chains having identical molecular weights and dispersities,

Table 9 Various ΔH_{m0} data reported in the literature

Authors	Ref.	Species	M_w or M_v	ΔH_{m0} (J g^{-1})
Fischer *et al.*	6	L-PLLA	~100 000[b]	93
Miyake, Masuko	48	L-PLLA	50 000–200 000[a]	135
Pyda *et al.*	21	L-PLLA	—	91
Sarasua *et al.*	22	L-PLLA	~30 000[a]	106
Sugai *et al.*	40	L-PLLA	<4000[a]	60
Sugai *et al.*	40	L-PDLA	<4000[a]	68
Sugai *et al.*	40	c-PLLA	<4000[a]	44
Sugai *et al.*	40	c-PDLA	<4000[a]	44

[a] M_w. [b] M_v.

because the cycles were prepared by photochemical end-to-end cyclization of the linear precursors. Due to this synthetic strategy the molecular weights were extremely low (M's ~ 4000) Hence, the functional end groups of the linear chains and the guest units in the cycles had a strong influence on the physical properties, so that extremely low T_m and ΔH_m values were found (Table 9). A similar strategy was used by Zaldua *et al.*[38] using a ''Click Reaction'' for cyclization of a linear precursor. The molecular weights were higher (Table 8) but still much lower than those of the polylactides studied in this work. Therefore, end groups and guest units still depressed T_m and ΔH_m values far below the values listed in this work. Whereas Sugai found higher T_m's and ΔH_m's for the linear species, Zaldua reported the opposite trend. In other words, these so-called. Model compounds are in fact not suited as models of high molar mass homo-PLLAs. A comparison of cyclic and linear PLLAs was also reported by Louisy *et al.*[41] with higher T_m and ΔH_m values for the linear chains. However, those authors did prove that their cyclic PLLA mainly consists of cycles because a MALDI TOF mass spectrum up to a mass of *m/z* 2500 was presented as the only evidence for a cyclic topology. However, such a characterization does not suffice as demonstrated by Fig. 4 (curves A and B) and Fig. 7 of this work. Furthermore, no information about the optical purity of their polylactides was provided, although a slightly basic catalyst was used, which might have partially racemized the monomer.

In this work, the highest T_m and ΔH_m values were obtained for cyclic PLLAs resulting from REP catalyzed by DSTL and SnBiPh (Tables 1, 4, 5 and 6), In order to obtain a reasonable basis for a comparison of cyclic and linear chains having at least M_w's around 100 000, two series of ROPs initiated with ethyl L-lactate and catalyzed by SnBiph were performed (Scheme 2(c) and Table 10). These conditions were used, because the ethyl end group does not cause a significant defect inside the crystal lattice of PLLA and because SnBiph proved to be the optimum catalyst for the preparation of alcohol-initiated PLLAs that crystallize spontaneously from the reaction mixture at 160 °C, a goal which cannot be achieved with $SnOct_2$.[31] In the first series of ROPs (no. 1–4, Table 10) the catalyst concentration was kept constant, and the LA/In ratio was varied. It was found that T_m increases substantially with higher molecular weights, *i.e.*, values up to 196.5 °C were recorded for the PLLA with the highest M_w (no. 4, Table 10).

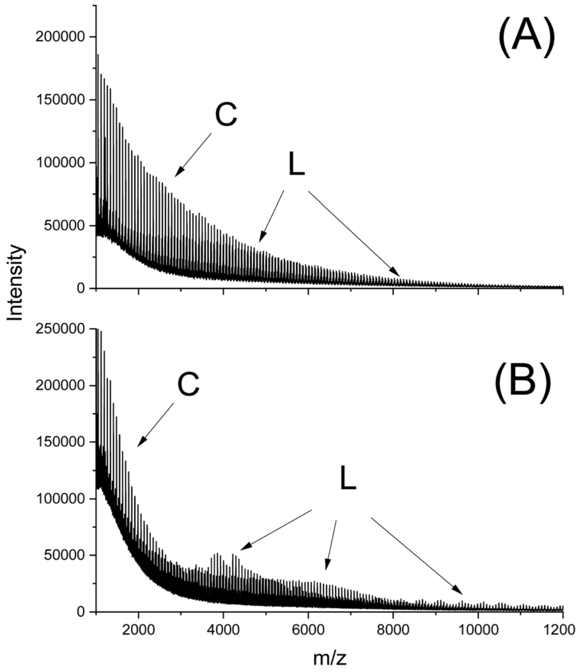
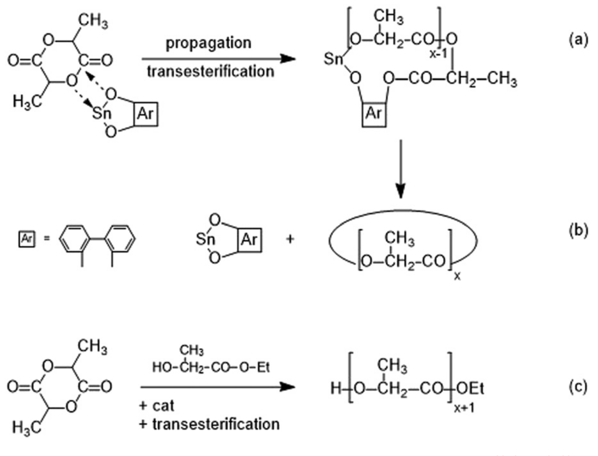


Fig. 7 MALDI TOF mass spectra of alcohol-initiated PLLAs: (A) purapol L105 initiated with propanol, (B) PLLA initiated with ELA and catalyzed with SnBiph (no. 4, Table 10).

The MALDI TOF mass spectra revealed formation of cycles (Fig. 7B), the fraction of which increased with decreasing initiator concentration (higher LA/In ratios). Nonetheless, measurements of the intrinsic viscosity proved the predominance of linear chains in all samples (curve B in Fig. 4). The existence of a considerable molar (but low weight) fraction of cycles in the low molar mass range of alcohol-initiated high molar mass PLLAs is quite normal as demonstrated for the commercial sample PURAPOL L105 (curve A, Fig. 4). Similar results were obtained from other commercial PLLAs such as NW 3251 D or NW 3001 D.

The second series illustrates the influence of annealing at higher temperatures in analogy to the experiments listed in Tables 3–7. In analogy to the results found for cyclic PLLAs annealing did not enhance the T_m values. Once again, the highest T_m's were obtained by direct crystallization from the polymerization. The ΔH_m values of the ethyl lactate-initiated ROPS were comparable with those found for the cyclic PLLAs. One may interpret these results, so that the T_m's of the cyclic PLLAs are 1.0–2.0 °C higher than those of their linear counterparts with similar molecular weights (M_w's 100 000–170 000), but even when this interpretation is correct, one has to consider that this small difference will vanish at higher molecular weights (M_w > 500 000). The crystallites formed by extremely high molar mass cyclic and linear PLLAs will become identical, because the long linear chains have to fold many times, so that



Scheme 2 Simplified illustration of a SnBiph-catalyzed REP ((a) + (b)) and an alcohol-initiated ROP ((c)).

Table 10 Properties of PLLA prepared with SnBiph as catalyst and ethyl L-lactate as initiator

Exp. no.	LA/Cat	LA/In	Temp. (°C)	Time (h)	M_n	M_w	T_m (°C)	ΔH_m (J g^{-1})	Crystallinity (%)
1	1000/1	100/1	160	22	20 500	33 500	183.2	81.8	78
2	1000/1	200/1	160	22	33 000	62 500	190.4	89.0	84
3[a]	1000/1	300/1	160	22	41 500	91 000	192.6	91.0	86
							193.0	91.7	87
							193.8	91.1	86
4[a]	1000/1	400/1	160	22	67 000	136 000	195.0	84.6	80
							195.3	87.1	83
							196.5	92.2	87
5A	2000/1	300/1	160	22	40 000	99 500	192.8	84.7	80
5B	2000/1	300/1	+160	22	—	—	194.0	95.0	90
5C	2000/1	300/1	+170	4	—	—	190.4	92.3	87
5C	2000/1	300/1	+170	22	—	—	191.2	84.7	80
5D	2000/1	300/1	+180	+4	—	—	193.3	82.0	78

[a] For the DSC measurements three pieces from different places of the same sample (disk) were taken.

the surface of the crystallites will be covered by loops quite analogous to crystallites based on cyclic PLLAs, and the number of defects inside the crystallites will tend towards zero.

Conclusions

The results of this work allow for the following conclusions. First, variation of the catalyst revealed that $SnCl_2$, DSTL and SnBiph are best suited to yield high T_m PLLA. Second, direct crystallization from the polymerization process is particularly favourable to achieve high T_ms, and in this way T_ms around 197–198 °C were obtained Third, high ΔH_m values are best obtained by annealing at 170 or 180 °C, whereupon ΔH_ms in the range of 92–97 J g^{-1} were achieved corresponding to crystallinities of around 90%. Fourth, decisive for optimum results is the presence of a reactive polymerization/transesterification catalyst which enhances crystal thickness, reduces the surface free energy by smoothing of the crystal surface and improves the 3d-order of crystallites in the spherulites. Fifth comparison with equilibrium melting temperatures of ideal crystals (T_{m0}) reported in the literature indicates that T_{m0} values below 210 °C are too low and a value of 213+/−2 °C shows the best agreement with the experimental T_ms. Sixth, comparison of the experimental melting enthalpies with ΔH_{m0} values calculated by several research groups indicates that all ΔH_{m0}s below 100 J g^{-1} are too low, whereas 106 J g^{-1} advocated by two research groups gives a reasonable fit. Seventh, cyclic and linear poly(L-lactide)s possess nearly identical T_m and ΔH_m values for M_w's $> 100\,000$.

Author contributions

HRK – conceptualization, project administration, investigation, writing original draft, SMW – investigation, data curation, resources, visualization, writing – review & editing, AM – investigation, data curation, resources, visualization.

Conflicts of interest

There are no conflicts to declare.

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