



Ring–Ring Equilibration in Solid, Even-Numbered Cyclic Poly(L-lactide)s and their Stereocomplexes

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Even-numbered cyclic poly(D-lactide) and poly(L-lactide) are prepared by ring-expansion polymerization. The cyclic poly(L-lactide) is annealed either at 120 or at 160 °C for several days. The progress of transesterification in the solid state is monitored by the formation of odd-numbered cycles via matrix-assisted laser desorption/ionization-time of flight mass spectrometry. The changes of the crystallinity are monitored by differential scanning calorimetry, wide- and small-angle x-ray scattering (WAXS and SAXS) measurements. Despite total even-odd equilibration at 160 °C, the crystallinity of poly(L-lactide) is not reduced. Furthermore, the crystallinity of the stereocomplexes of both cyclic poly(lactides) do not decrease or vanish, as expected, when a blocky or random stereosequence is formed by transesterification. This conclusion is confirmed by ¹³C NMR spectroscopy. These measurements demonstrate that transesterification is a ring–ring equilibration involving the loops on the surfaces of the lamellar crystallites thereby improving crystallinity and 3D packing of crystallites without significant broadening of the molecular weight distribution.

transesterification with a random attack of active chain ends on ester groups in the polymer backbone. Experimental evidence for the existence of such a mechanism in the melt at 120 or 160 °C has previously been published.^[2,3] For cyclic poly(L-lactide)s existence of ring–ring equilibration in the solid state has also been found in one case.^[1] Ring–ring equilibration is a normal consequence of ring-chain equilibration based on “back-biting” reactions as already pointed out by Jacobson and Stockmayer in 1950.^[4] Identification of ring–ring equilibration in the absence of ring-chain equilibration is a relatively new phenomenon which requires covalent cyclic catalysts, such as those recently elaborated by the authors for ring-expansion polymerizations (REPs) of lactides.^[5–8] Syntheses of cyclic poly(lactides) were reported by several groups.^[5–18] When a zwitterionic mechanism was involved,

1. Introduction

Transesterification reactions may not only occur in solution or in the melt of polyesters, but also in the solid state, at least in the amorphous phase above the glass-transition. Recently it has been demonstrated for poly(L-lactide) that at least two kinds of transesterification reactions proceed in the solid state at 120 °C.^[1] For linear poly(L-lactide)s a broadening of the mass peak distribution was observed by matrix-assisted laser desorption/ionization-time of flight (MALDI TOF) mass spectrometry suggesting

ring–ring equilibration was also observed, but only in solution or in the melt.^[11–13,16] However, it is unlikely and unproven that the zwitterionic rings are permanently closed via contact ion pairs, in as much as the steric demands of the carbene used as catalyst for the stabilization of the cationic chain end is unfavorable for the formation of contact ion pairs. Hence, the ring-equilibration is just a consequence of ring-chain equilibration.

Ring–ring equilibration in the solid state is a particularly interesting aspect of chemical reactions in the solid state, because it raises the question, which part of the solid is involved. REP of lactides is particularly suited for studies of ring–ring equilibration, because a clean REP free of transesterification reactions must yield even-numbered cycles or in rare cases odd-numbered rings.

In the case of linear poly(L-lactide)s it was observed that complete equilibration of even and odd-numbered chains may be achieved in the solid state upon prolonged heating at 120 °C, when the catalyst 2-stanna-1,3-dithiolane was present.^[1] This observation proves that not only the amorphous phase, but also all crystallites are somehow involved in transesterification reactions. This result raises the question, if the transesterification reactions underlying the even-odd equilibration exclusively concerns the surface of the crystallites or if a complete rearrangement of the crystallites occurs. In this context, the present work served three purposes. First, it should be found out if it is possible to find a catalyst and reaction conditions favoring ring–ring equilibration without ring chain equilibration in the solid state. Second, it should be elucidated, if ring–ring equilibration of all cyclic species can be achieved and how the chains inside the crystallites are involved. The third purpose was to elucidate,

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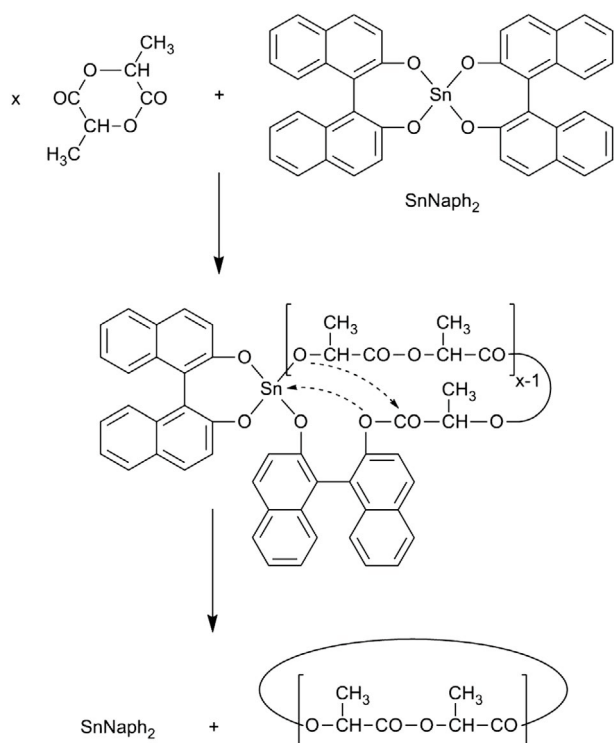
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Scheme 1. Simplified illustration of the ring-expansion mechanism catalyzed by SnNaph₂.

to what extent the ring–ring equilibration influences crystallinity, crystal size and morphology of the poly(L-lactide)s.

In previous decades several research groups have intensively studied crystallization processes of poly(L-lactide)s^[19–29] and properties of their stereocomplexes,^[30–33] but to the best of our knowledge no research group has monitored transesterification reactions in the solid state by MALDI TOF mass spectrometry, and no other research group has studied the existence of ring–ring equilibration in solid cyclic poly(L-lactide)s.

2. Experimental Section

2.1. Materials

L-lactide was purchased from TCI Chemicals Deutschland GmbH (Eschborn, Germany) and twice recrystallized from

toluene. “Toluene 99.89%, extra dry” of ACROS Organics (Geel, Belgium) was used for this purpose. The tin(IV) compound of 2,2'-dihydroxy-1,1'-binaphthyl (SnNaph₂, see **Scheme 1**) was prepared from tin tetra-*t*-butoxide and the double molar amount of the diphenol as described recently.^[6] D-lactide was kindly supplied by Uhde Inventa-Fischer (Berlin, Germany) and was twice recrystallized from dry toluene. Dichloromethane was distilled over P₄O₁₀.

2.2. Synthesis and Annealing of Neat Cyclic Poly(L-lactide)

L-lactide (100 mmol) and SnNaph₂ (0.5 mmol) were weighed under dry argon into a 100 mL Erlenmeyer flask which was pretreated with a solution of dichlorodimethylsilane and dried with a stream of hot air (300 °C). After addition of a magnetic stirring bar, the reaction vessel was immersed into an oil bath at 120 °C. The lactide polymerized and crystallized within 8 h. After 24 h the reaction vessel was destroyed and the polylactide was broken into pieces. Samples of ≈1 g were used for the annealing experiments. The sample isolated after polymerization for 24 h at 120 °C (No. 1, **Table 1**) served as starting material for all annealing experiments. One sample was annealed for additional 7 d at 120 °C and a second sample for additional 14 d. A third sample was annealed for 1 d at 160 °C, the fourth sample for 2 d and the fifth sample for 4 d (see **Table 1**).

2.3. Preparation and Annealing of the Stereocomplex of Cyclic Poly(L- and D-lactide)

Cyclic poly(L-lactide) and poly(D-lactide) were prepared from 50 mmol of D- or L-lactide at 120 °C as described above, but the time was limited to 12 h. The virgin polylactides having *M_w* values around 17 000 were dissolved in dry dichloromethane (60 mL portions for each enantiomer) and, finally, these solutions were unified. Approximately 30 mL of dichloromethane were distilled off under normal pressure and the remaining solution was thermostated (in a closed 100 mL round bottom flask) at 50 °C for 4 d, whereupon the stereocomplex began to crystallize. The dichloromethane was then slowly evaporated at a bath temperature of 60 °C and the remaining stereocomplex was annealed at 120 °C for 1 d. The resulting product was broken into small pieces, and three 2 g samples were annealed as described above (see also **Table 2**).

Table 1. Influence of the annealing time at 120 or 160 °C on the physical properties of crystalline, catalyst containing poly(L-lactide)s.

Exp No.	Temp. [°C]	Time [d]	<i>M_n</i>	<i>M_w</i>	<i>D</i>	<i>T_m</i> ^{b)} [°C]	Δ <i>H_m</i> ^{b)} [J g ⁻¹]	Cryst. ^{b,c)} [%]	Cryst. ^{d)} [%]
1	120	1	9800	17300	1.8	172.0	-60.0	58	40
2	120	8	8100	17000	2.1	175.0	-84.5	79	84
3	120	15	7400	16200	2.2	179.5	-85.0	80	86
4	160	1 ^{a)}	11500	22700	2.0	177.0	-87.0	82	81
5	160	2 ^{a)}	11200	24000	2.1	178.0	-88.0	83	84
6	160	4 ^{a)}	12000	27000	2.2	179.0	-89.0	84	86

^{a)}After synthesis and annealing for 1 d at 120 °C; ^{b)}From DSC measurements with a heating rate of 10 K min⁻¹; ^{c)}From DSC measurements with a Δ*H_m* of -106 J g⁻¹ for 100% crystallinity^[34,35]; ^{d)}Estimated from the WAXS powder patterns (margin of error +/-5%).

Table 2. Influence of the annealing time at 160 °C on physical properties of the catalyst containing stereocomplex prepared from even-numbered cyclic poly(D-lactide) and poly(L-lactide) used as starting material for the experiments of Table 1

Exp. No.	Time [d]	T_m^a [°C]	ΔH_m^b [J g ⁻¹]	Cryst. ^b [%]
1	0	226.5	-74.0	52
2	2	228.5	-82.5	57
3	4	227.5	-88.0	62
4	6	224.5	-92.5	66

^a)From DSC measurements with a heating rate of 10 K min⁻¹; ^b)Calculated with a ΔH_m of -142 J g⁻¹.^[29,30]

2.4. Measurements

The 600 MHz ¹H NMR spectra and the 150 MHz ¹³C NMR spectra were recorded with a Bruker Avance III 600 FT NMR Spectrometer in 5 mm sample tubes. Hexafluoroisopropanol-d₂ served as solvent and TMS for shift referencing.

The MALDI TOF mass spectra were measured with Bruker Autoflex III mass spectrometer equipped with a smartbeam™ laser ($\lambda = 355$ nm). All spectra were recorded in the positive ion linear mode. The MALDI stainless steel targets were prepared from chloroform solutions of poly(L-lactide) or solutions of the stereocomplex in hexafluoroisopropanol (3–5 mg mL⁻¹) doped with potassium trifluoroacetate (2 mg mL⁻¹). Typically, 20 μ L of sample the solution, 2 μ L of the potassium salt solution and 50 μ L of a solution of trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 20 mg mL⁻¹, THF) serving as matrix were mixed in an Eppendorf vial. 1 μ L of the corresponding solution was deposited on the MALDI target.

The GPC measurements were performed in a modular system running in chloroform at 40 °C consisting of an isocratic pump (1 mL min⁻¹) and a refractive index detector (RI-501-Shodex). Samples were manually injected (100 μ L, 2–4 mg mL⁻¹ in chloroform). For instrument control and data calculation Clarity software (GPC extension, DataApex) was used. The calibration was performed using polystyrene standard sets (Polymer Standards Service–PSS, Mainz).

The differential scanning calorimetry (DSC) heating traces were recorded on a (freshly with indium and zinc calibrated) Mettler-Toledo DSC-1 equipped with Stare Software-11 using a heating rate of 10 K min⁻¹. Only the first heating traces were considered.

The wide-angle x-ray scattering (WAXS) measurements were performed using our in-house small-angle x-ray scattering (SAXS)/WAXS apparatus equipped with an Incoatec X ray source I μ S and Quazar Montel optics. The wavelength of the X-ray beam was 0.154 nm and the focal spot size at the sample position was 0.6 mm². The samples were measured in transmission geometry. The sample-detector distance was 0.1 m, allowing us to detect an angular range of $2\Theta = 5^\circ$ – 33° . The patterns were recorded with a Rayonix SX165 CCD-Detector and the accumulation time per WAXS measurement was 600 s. 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 analyzed with the curve fitting module.

After subtracting of the instrumental background, the integral intensity of the crystalline reflections was divided by the overall integral intensity to determine the crystallinity x_c .

3. Results and Discussion

3.1. Transesterification of Cyclic Poly(L-lactide) at 120 or 160 °C

A cyclic poly(L-lactide) was prepared via ring-expansion polymerization in bulk at 120 °C with Sn(IV) bi(1,1'-dinaphthoxide), (SnNaph₂) as catalyst (see Scheme 1) according to a recently published procedure.^[6] The resulting poly(L-lactide) mainly consisted of even-numbered cycles as demonstrated by the MALDI TOF mass spectrum of Figure 1A. This cyclic poly(L-lactide) was used for the annealing experiments in the virgin state, so that all the catalyst used for the ROP remained in the sample. This sample was subdivided into six parts. One part was used for characterization and the other five parts for the annealing experiments listed in Table 1. The starting material (No. 1, Table 1) was characterized by MALDI TOF mass spectrometry (Figure 1A) and by DSC measurements, conducted as usual for polylactides with a heating rate of 10 °C/min. (Figure S1, Supporting Information). Furthermore, SEC measurements were performed, which yielded the elution curve “1 d” in Figure S2 (Supporting Information). A weight average molecular weight of 17000 with a dispersity of 1.8 was obtained. The WAXS and SAXS measurements are discussed below.

After annealing for additional 7 days at 120 °C, the MALDI-TOF mass spectrum revealed that partial even-odd equilibration had indeed occurred in the solid state, so that ≈ 30 – 40% of the sample consisted of odd-numbered cycles (Figure 1B). After one more week of annealing, only a slight additional increase of odd-numbered cycles was detectable ($\approx 5\%$, Figure S3, Supporting Information). The observation, that $\approx 40\%$ equilibration was achieved despite a degree of crystallinity around 80% (see Table 1) suggested that not only the amorphous phase, but also part of the crystallites was involved in the transesterification process.

The DSC measurements were conducted as usual for polylactides with a heating rate of 10 K min⁻¹ and only the first heating trace was evaluated with regard to T_m and melting enthalpy (ΔH_m). Crystallinities were calculated from these ΔH_m values on the basis of a ΔH_m max of -106 J g⁻¹.^[33,35] Both T_m and ΔH_m shifted to higher values with increasing annealing time and the crystallinity reached a level of 80% after 15 d. The WAXS measurements of all six samples proved that the orthorhombic α -modification, first described by DeSantis and Kovacs,^[19] was formed in all cases (Figure S4, Supporting Information). Since it is well known that this modification is the thermodynamically most stable modification of poly(L-lactide)s, it is not surprising that the modification was not affected by the annealing experiments. From the “sharpening” of the WAXS reflections, illustrated by the superposition of three WAXS patterns in Figure 2, it may be deduced that the annealing resulted in greater perfection and lamellar thickness of the crystallites. When crystallinities were calculated from these WAXS patterns, a satisfactory agreement with the DSC measurements was found considering a margin of error of $\pm 3\%$ or more

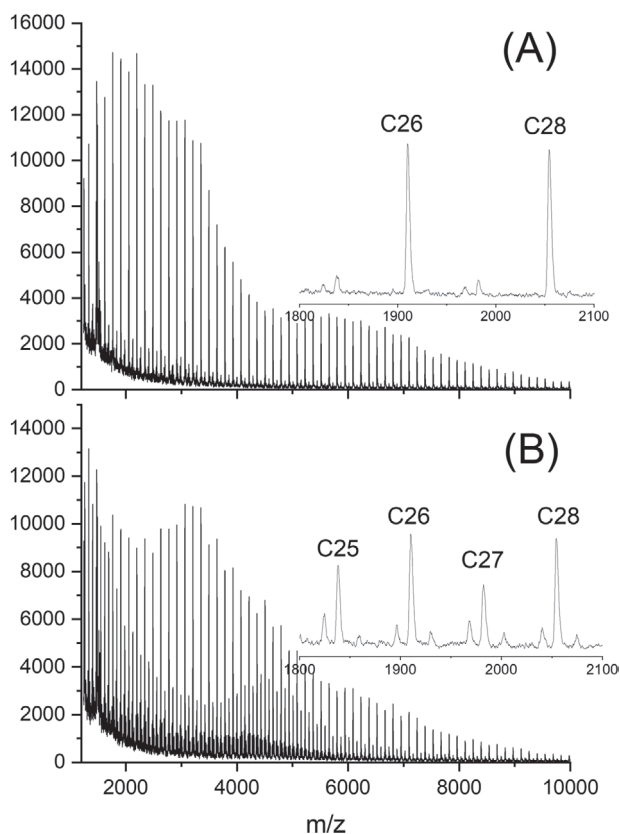


Figure 1. MALDI TOF mass spectra of cyclic poly(L-lactide) A) after polymerization for 1 d at 120 °C, B) after annealing at 120 °C for 7 d (after annealing for 15 d, see Figure S3, Supporting Information)

cautiously $\pm 5\%$. An exception was No. 1, Table 1, where for unknown reasons the crystallinity determined by DSC was higher. This higher value seems to be more realistic because no glass-transition step was observable in the DSC heating trace.

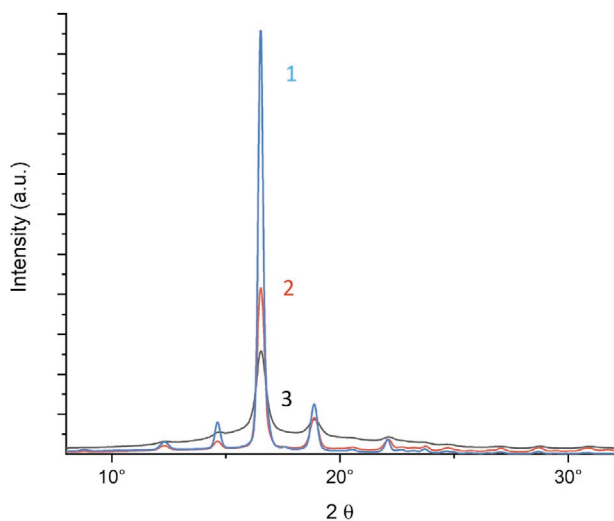


Figure 2. WAXS powder pattern of poly(L-lactide)s: 1-sample No. 1, 3-sample No. 3, and 6-sample No. 6 (all Table 1).

Unexpectedly, the SAXS measurements did not provide a satisfactory contribution to the characterization of these poly-lactides. None of the six samples displayed a reflection in the range of scattering angles relevant for the calculation of lamella thicknesses as illustrated by Figure S5 (Supporting Information). From literature^[37] and from a recent publication of the authors^[38] it is known that poly(L-lactide)s having $T_m < 180$ °C show L-spacings in the range of 15–23 nm. However, the SAXS curves obtained from the samples listed in Table 1 did not show any reflection corresponding to L-spacings in the range of 10–40 nm (a reflection representing a spacing of 4 nm found in the SAXS pattern of No. (Figure S5A, Supporting Information) is not relevant in this regard).

The reproducibility of these featureless SAXS curves was checked by Dr. K. Jähnichen at the Institute for Polymer Research (IPF) at Dresden (Germany). The absence of reflections suggests that the interface between the crystallites mainly consists of a partially oriented phase, which has a higher density than an isotropic mobile amorphous phase. Furthermore, it must be considered that these samples contain ≈ 2.6 wt% of the compact catalyst which is concentrated the small fraction of disordered and amorphous phase and contributes to their density.

A second series of annealing experiments was performed at 160 °C (Nos. 4–6, Table 1). These experiments resulted in a slight broadening of the molecular weight distribution as illustrated by the dispersities listed in Table 1 and by the SEC elution curves displayed in Figure S6 (Supporting Information). Furthermore, the MALDI TOF mass spectra indicated beginning thermal degradation by appearance of a mass peak with +16 Da relative to the mass of cycles, whenever long reaction times (8 d or 15 d at 120 °C) or higher temperatures (160 °C, 4 d, see Figure 3B) were involved. Yet, the most conspicuous result was the observation that formation of odd-numbered cycles reached the maximum after 4 d, meaning equimolarity with the even-numbered cycles as demonstrated by Figure 3B. Completion of this ring–ring equilibration definitely proves that not only the amorphous and disordered phase, but also all cycles embedded in the crystallites were involved.

These results are best explained by the following hypothesis. In the presence of a catalyst, transesterification reactions are not limited to the mobile amorphous phase, but also involve the disordered phase on the surface of all crystallites. As outlined in Scheme 2 the catalyst can react with loops by extrusion of even and odd-numbered small cyclics. This process is reversible as long as the catalyst is sufficiently mobile in the disordered phase and yields at higher temperatures and after long enough time a perfect even/odd equilibrium. This process, which may also be understood as special kind of ring–ring equilibration, causes homogenization of the loops along the lamellar surface as illustrated in Figure 4. Due to the reversibility of these transesterification reactions a significant change of the molecular weight might not be expected. Annealing at 120 °C leaves M_w and the shape of the elution curves almost unchanged (see Figure S2, Supporting Information), whereas at 160 °C a moderate increase of M_w and a slight broadening of the molecular weight distribution occurs (see Figure S6, Supporting Information).

Considering Figure 4 it must be taken into account, that it does not illustrate all details of the entire transesterification

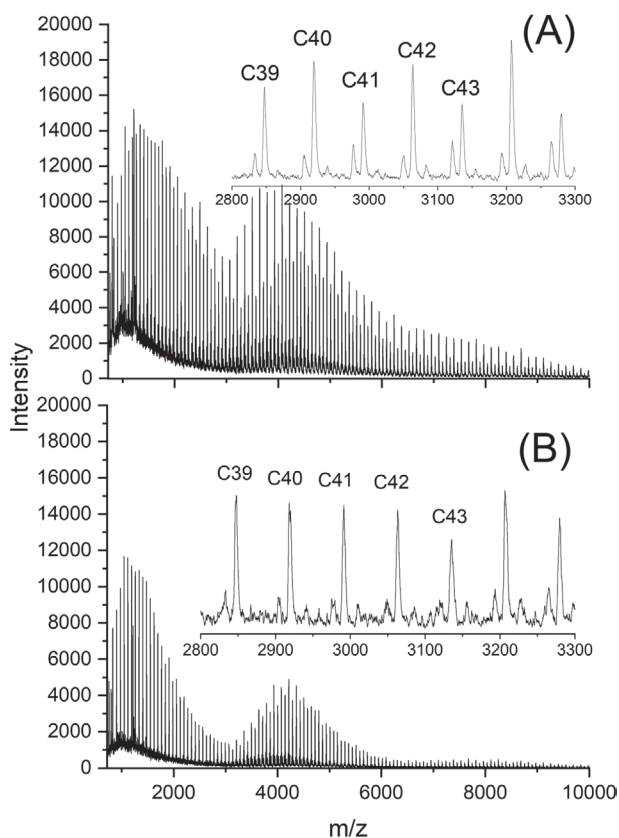
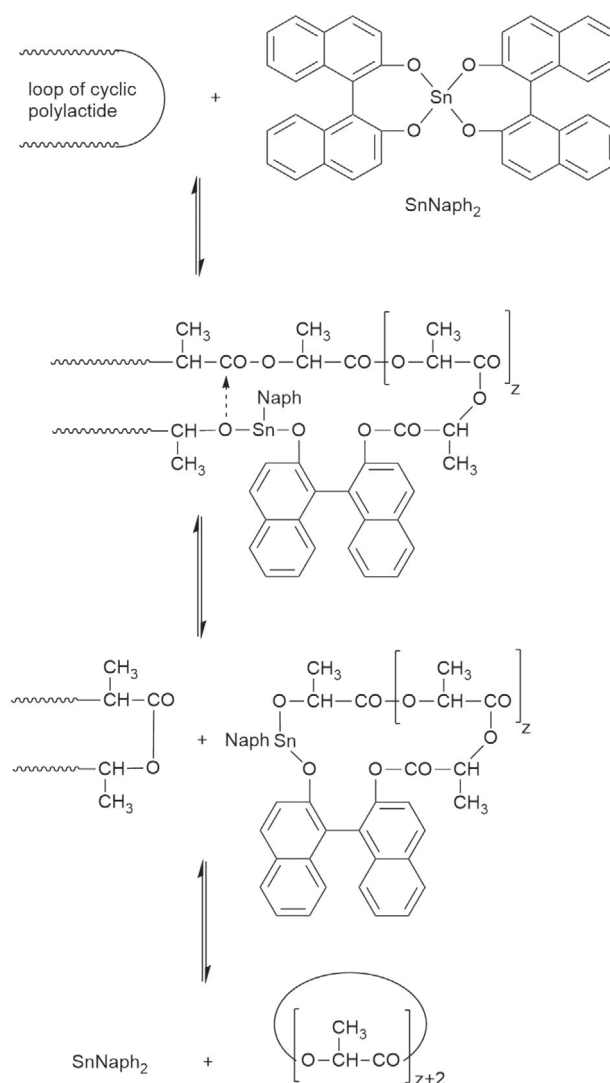


Figure 3. MALDI-TOF mass spectra of cyclic poly(L-lactide)s: A) after annealing at 160 °C for 1 d, B) after 4 d at 160 °C.

process. Lactide and cyclic oligomers will also be formed by transesterification reactions in the amorphous phase. They will mostly be consumed by slight thickening of the lamellae (Figure 4). Therefore, their formation does not significantly enhance their quantity and does not cause a significant broadening of the molecular weight distribution. The size of cycles is correlated with the thickness of the crystallites. Since even and odd-numbered cycles grow on the crystallite surfaces at the same rate the molecular weight distribution of the odd cycles must be almost identical with that of the even cycles. Thickening of the lamellae, smoothing of their surface and reduction of the amorphous phase have the consequence of denser crystal packing and higher crystallinity, a process which is driven by a gain in crystallization enthalpy. An interesting aspect of the high selectivity of this ring–ring equilibration is the finding that the T_m does not increase beyond 180 °C, despite long annealing at 160 °C. In contrast, poly(L-lactide)s having T_m 's between 190 and 196 °C are formed when L-lactide is polymerized at 160 °C with cyclic tin catalysts which are several orders of magnitude more reactive than SnNaph₂.^[38] Those catalysts cause a more perfect “smoothing” of the crystal surfaces and a considerable thickness growth of the lamellae as indicated by SAXS measurements of the L-spacings. Therefore, the present work and the previous study illustrate two extreme scenarios of transesterification processes that may exist in solid poly lactides, when the polymerization catalysts are not poisoned and remain in the reaction products.



Scheme 2. Ring–ring equilibration via transesterification of loops on the surface of crystallites.

3.2. Annealing Experiments with a Stereocomplex of Even-Numbered Cycles

Annealing experiments with a so-called stereocomplex (racemate) of the low molar mass cyclic poly(lactides) were performed with the purpose to get additional evidence for the transesterification hypothesis outlined in Scheme 2 and Figure 4. Nearly random stereosequences of D- and L-units or sequences containing only short blocks of each enantiomeric unit (e.g., <5 lactic acid units) cannot form a stereocomplex and cannot crystallize. When several longer blocks are present. These blocks may form stereocomplexes and partial crystallization may occur. The degree of crystallinity is then, of course, reduced relative to a stereocomplex sample formed from perfect stereohomopolymers. Hence, transesterification between the closely neighboring D- and L-chains in a stereocomplex should result in reduced or completely vanishing crystallinity.

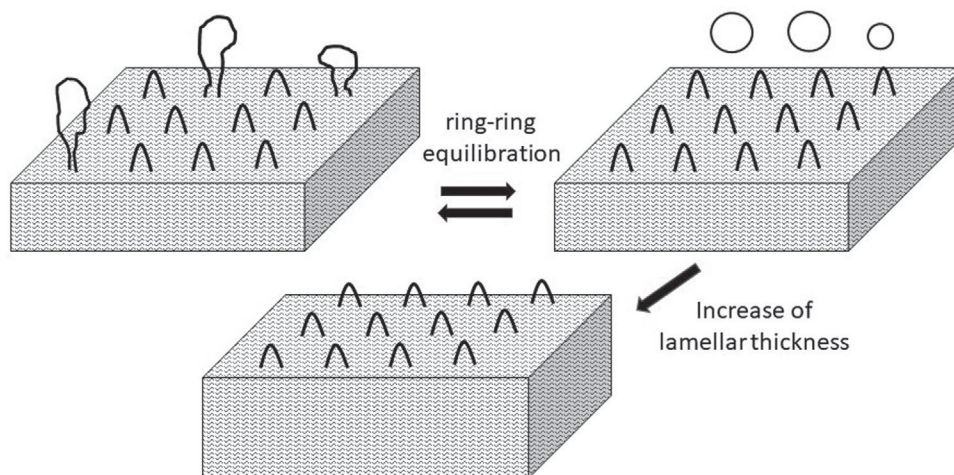


Figure 4. Schematic illustration of ring–ring equilibration and homogenization of loops on the lamellar surfaces possibly followed by slight thickening of the lamellae with consumption of cyclic oligomers (depending on temperature and time).

For the preparation of the stereocomplex of cyclic poly(lactides), D-lactide and L-lactide were polymerized with SnNaph_2 as catalyst at 120 °C, but the reaction time was limited to 12 h, because it was learned from the polymerization of L-lactide described above that this shorter time suffices for a conversion around 99% and the predominance of even-numbered cycles is more pronounced at shorter reaction times. Solutions of both enantiomeric cyclic poly(lactides) in dichloromethane were mixed and thermostated at 50 °C for several days, whereupon a gel was formed because part of the enantiomeric poly(lactides) formed a stereocomplex, which forms crystallites that are insoluble in dichloromethane. The stereocomplex containing all the catalyst used for the preparation of the enantiomeric cycles was included in the mass remaining after evaporation of the solvent, so that neither any fractionation nor an extraction of the catalyst occurred. This “master batch” was subdivided into three samples that were annealed at 160 °C for 2, 4, or 6 d (Table 2). Temperature and time matched the experiments with neat poly(L-lactide) listed in Table 1 to enable a comparison of the results.

The DSC measurement yielded T_m values in the range of 224.5–228.5 °C regardless of the annealing time. A T_m of 230 ± 2 °C is the maximum value of perfect stereocomplexes of linear poly(lactides) reported in the literature.^[29–33] Therefore, the T_m values measured in this work confirm that low molar mass cyclic poly(lactides) were capable of forming nearly perfect stereocomplexes a result already presented in a quite recent publication.^[36] Absence of a glass transition steps in the DSC traces indicated a high degree of crystallinity.

When compared with the stereohomopolymers listed in Table 1, the degrees of crystallinity were somewhat lower, but this is a characteristic property of stereocomplexes as demonstrated by Sarasua et al.^[35] and by the authors.^[36]

As indicated by the melting enthalpies (ΔH_m) and thus, the degree of crystallinity slightly increased with the annealing time. Hence, the DSC measurements clearly indicated that no significant transesterification yielding L-D and D-L sequences inside the crystallites had occurred. This interpretation was confirmed by the ^{13}C NMR spectrum of the stereocomplex

annealed for 4 d at 160 °C. The ^{13}C NMR signal of the CO group is perfectly symmetrical and did not differ from the signal of the stereocomplex prior to annealing (Figure 5). Two weak signals on the left and on the right side of the main signal were detectable with an intensity <3% of the main signal. These weak signals might result from stereosequences containing D-L/L-D dyads, resulting from transesterification in the amorphous phase. For comparison the ^{13}C NMR CO signal of a 1:1 stereocopolymer prepared from L- and meso-lactide is presented in the Supporting Information (Figure S7, Supporting Information). Seven of eight possible tetrads were observable. The enormous difference between this signal and that presented in Figure 5 is evident. Hence, it may safely be concluded that the even/odd transesterification and other side reactions yielding linear chains, which were observable in the mass spectra (see Figure 6), must be limited to the interface between the crystallites and to the surface of the crystallites. Therefore, these results clearly support the hypothesis outlined in Scheme 2 and Figure 4.

This ring–ring equilibration mechanism also explains a previously published result obtained from annealing of a cyclic stereocomplex at 205 °C for 1 h.^[36] Although the catalyst concentration was low, ring–ring equilibration was observed, so that the fraction of odd-numbered cycles increased from $\approx 5\%$ to 30% (see Figure S8, Supporting Information). The peak intensity (molecular weight) distribution paralleled that of the even-numbered cycles. No broadening of the distribution was observed as expected for an intermolecular transesterification and absence of intermolecular transesterification was also confirmed by ^1H and ^{13}C NMR spectroscopy.

4. Conclusions

MALDI TOF mass spectrometry proved to be a useful tool to monitor ring–ring equilibration in solid cyclic poly(L-lactide)s and their stereocomplexes, provided that the cyclic substrate contains a large excess of even-numbered cycles. The results demonstrate that complete ring–ring

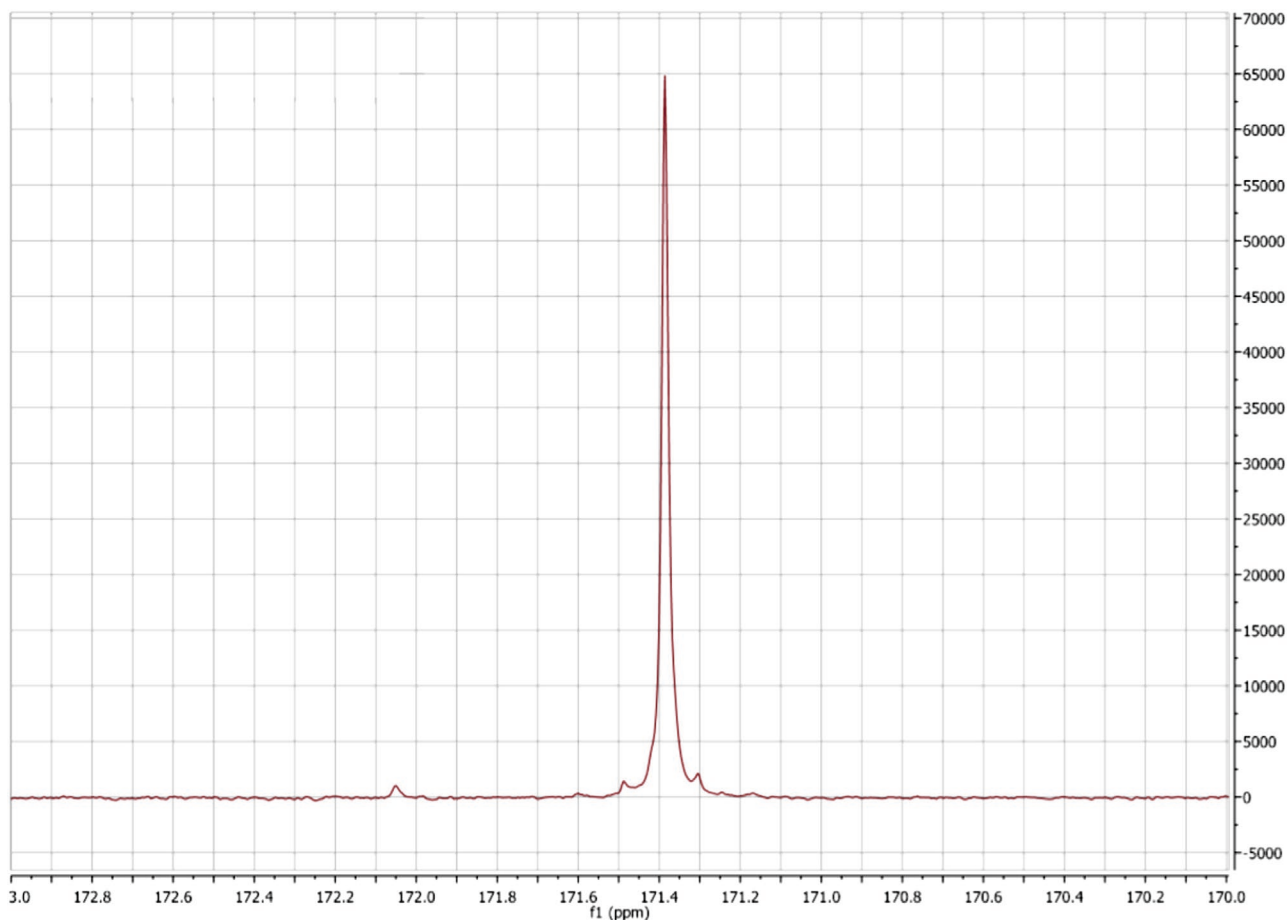


Figure 5. ^{13}C NMR CO signal of the stereocomplex after annealing at 160 °C for 4 d (No. 3, Table 2).

equilibration involving all chains, even those of crystallites, may be achieved upon annealing at 160 °C. However, no evidence for intermolecular transesterification between the enantiomeric stereo-homopolymers in stereocomplexes was found. Hence it may be concluded that the ring–ring equilibration and side

reactions due to thermal degradation exclusively involve the surface of the crystallites and the amorphous phase. Since $\approx 95\%$ of the repeat units of the cycles is embedded in the lamellar crystals, and thus, protected against transesterification, the ring–ring equilibration does neither significantly change the average ring size, nor does it significantly change the molecular weight distribution. The cyclic oligomers formed via the ring–ring equilibration are mostly consumed by a slight thickening of the lamellar crystal. This process and a denser packing of the crystallites enhances, in turn, the degree of crystallinity. It is conceded that this hypothesis is not definitely proven in all details, but it explains all experimental results obtained from MALDI TOF mass spectrometry, GPC and DSC measurements and WAXS and SAXS patterns.

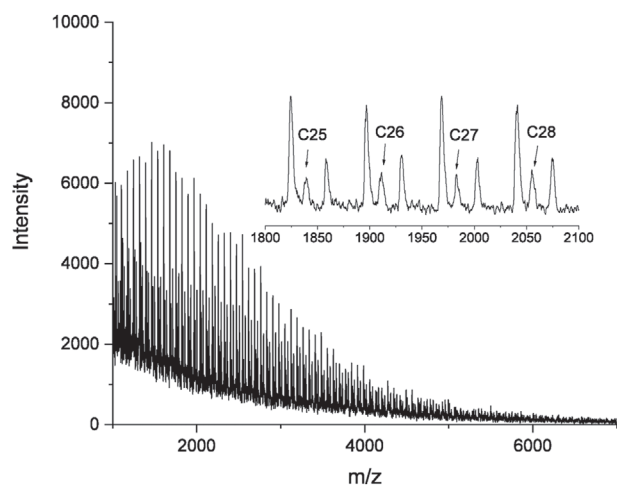


Figure 6. MALDI-TOF mass spectrum of the stereocomplex of cyclic poly-lactides after annealing at 160 °C for 4 d (No. 3, Table 2).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

poly lactides, ring-expansion-polymerization (REP), ring–ring equilibration, stereocomplexes, transesterification

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