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Reversible Polycondensations outside the Jacobson-Stockmayer Theory and a New Concept of Reversible Polycondensations

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L-lactide was polymerized with tin(II)acetate, tin(II)2-ethyl hexanoate, diphenyltin dichloride and dibutyltin bis(pentafluorophenoxide) at 130°C in bulk. When an alcohol was added as initiator linear chains free of cycles were formed having a degree of polymerization (DP) according to the lactide/initiator (LA/In) ratio. Analogous polymerizations in the absence of an initiator yielded high molar mass cyclic polylactides. Quite similar results were obtained, when \(\varepsilon\)-caprolactone was polymerized with or without initiator. Several transesterification experiments were conducted at 130°C, either with polylactide or poly(\(\varepsilon\)-caprolactone) indicating that several transesterification mechanisms are operating under conditions that do not include formation of cycles by back-biting. Furthermore, reversible polycondensations (revPOCs) with low or moderate conversions were found that did not involve any kind of cyclization. Therefore, these results demonstrate the existence of revPOCs, which do neither obey the theory of irreversible polycondensation as defined by Flory nor the hypothesis of revPOCs as defined by Jacobson and Stockmayer. A new concept encompassing any kind of revPOCs is formulated in the form of a “polycondensation triangle”.

Introduction

When Flory elaborated the first theory of polycondensations he formulated a theory of irreversible polycondensations, although his experimental experience was based on syntheses of polyesters and polyamides under conditions typical for a reversible polycondensation (revPOC).\textsuperscript{1, 2} The differentiation between irreversible and reversible step-growth polymerizations was defined and established in 1950 by two papers of Jacobson and Stockmayer (J+S).\textsuperscript{3, 4} An irreversible polymerization is defined by a kinetically controlled course, where every growing and cyclization step is irreversible. In the reversible case every growing and cyclization reaction is reversible and thus part of an equilibrium, so that the reaction mixture presents sooner or later the thermodynamically most favourable scenario. The experimental work of J+S was based on proton-catalyzed polycondensations of 1,10-decane diol with adipic acid, and the permanent equilibration of the reaction products occurs.\textsuperscript{4} Other equilibration reactions, such as the attack of an activated end group on bonds in the polymer backbone (so-called random transesterification - RT), were not taken into account. At the time, when J+S performed their work, analytical methods allowing for the detection of such reactions (e.g. transesterification or transamidation) did not yet exist.

\[
\text{HOOC-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)}_n\rightarrow \text{HOOC-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)-(CH}_2\text{COO)}_n + n\text{HO}_2
\]

Scheme 1 Synthesis of poly(decamethylene adipiate) and reversible formation of cyclic polymers

Critique of part of the JS-theory was recently published by the authors\textsuperscript{5, 6} who demonstrated that formation of cyclic oligomers and polymers does not only result from “back-biting” but also from end-to-end (ete) cyclization, which is in contrast to the assumption of J+S. However, previous results and the results presented below demonstrate that ete-cyclization is a very efficient process. Moreover, it is unproven that the cycles...
indirectly detected by J+S (mass spectrometry and NMR spectroscopy did not exist at that time) mainly or exclusively result from back-biting. A consequence of ete-cyclization is that the JS theory does not provide a correct description of all revPOCs. Furthermore, it is necessary to emphasize that J+S did never study a stoichiometric polycondensation up to high conversions (>99.5%). Nonetheless, the widely accepted view and understanding of revPOCs is still such that the reversibility and thermodynamic control is mainly or exclusively the result of ring chain equilibration via “back-biting”. Recently the authors have detected and defined a special kind of polymerization which combines ring-opening polymerization (ROP) with simultaneous polycondensation (ROPPOC). 7, 8 Such ROPPOC polymerizations arise from ROPs initiated with a compound that introduces a reactive end group, so that linear chains having two reactive chains will be formed. ROPPOC polymerization may be equivalent to a normal revPOC of a non-cyclic monomer as illustrated by syntheses of nylons from ω-amino acids alone or in combination with the corresponding lactams (Scheme 2). 8

From a preparative and theoretical point of view, ROPPOCs have the advantage that they allow for simulation of polycondensations with conversions >99.9%. Consider a monomer/Cat ratio of 1 000/1 as used in this work, the ROP of the monomer corresponds to a polycondensation with 99.9% conversion. Any inter or intramolecular condensation following or accompanying the ROP will then raise the conversion above 99.9% and conversions of 99.99% or higher may be achieved, which can hardly be realized by a normal polycondensation starting out from linear monomers. Such extreme conversions are interesting, because the modern theories of reversible and irreversible polycondensations predict that the fraction of cycles increases with the conversion until all reaction products have a cyclic topology at 100% conversion. For ROPPOC syntheses of cyclic polyesters two classes of catalysts have been found, namely strong nucleophiles, such as pyridines 10-14 heterocyclic carbenes 15-22 on the one hand, and covalent tin(II) or tin(IV) compounds 23-26 on the other. A simplified polymerization mechanism involving covalent end groups catalyzed by dibutyltin bis(pentafluorophenoxide) BuSnOPF is outlined in Scheme 3. 24 These ROPPOCs of lactide or CL play an important role in the present work.

The present study was stimulated by an observation mentioned by several research groups 27-30, which reported that alcohol-initiated ROPs of lactide catalyzed by tin(II)2-ethylhexanoate (SnOct2) proceed without back-biting at temperatures around 130°C or below. Yet, despite absence of back-biting a smaller or larger fraction of odd-numbered chains was detectable (depending on temperature) indicating occurrence of a transesterification reaction. In the absence of transesterification reactions, a clean polymerization of lactide must yield even-numbered species regardless if linear or cyclic (if the initiator does not incorporate an additional unit). Hereinafter, this type of transesterification will be called “single unit exchange mechanism” (SUE).

As a typical example, Figure 1A presents a MALDI mass spectrum of an ethyl L-lactate-initiated polymerization of L-lactide catalyzed by SnOct2 at 130°C with a lactide/initiator ratio of 40/1.

Scheme 2 Synthesis of nylon-6 by polycondensation of aminocaproic acid or equilibration of caprolactam with aminocaproic acid

This spectrum shows a predominance of odd-numbered chains (due to incorporation of an ethyl lactate end group) along with a considerable fraction of even-numbered species. These findings raise the question, if it is possible to perform ROPPOC syntheses of cyclic polyesters in the absence of back-biting, but in the presence of other transesterification/equilibration reactions. Since in this case the formation of cyclic polyesters will exclusively result from ete-cyclization, such a ROPPOC synthesis of cyclic polyesters will be outside the JS-hypothesis of revPOCs. To avoid misunderstanding, it should be clarified that the authors differentiate between two aspects of the JS-theory. On the one hand, the work of J+S is a theory of ring-chain equilibration, which allows for the calculation of equilibrium constants and their correlation with the conformational properties of the polyester chains under investigation. On the other hand, J+S have developed a hypothesis of revPOCs on the basis of ring chain equilibration with a mathematical approach predicting the composition of the reaction mixture with increasing conversion. Both aspects of the JS theory overlap, of course, but are not identical. The critique of the authors in their previous publications 5, 6 and in the present work is exclusively directed against the JS-hypothesis of revPOCs.
In this context, the present work was aimed at finding catalysts and reaction conditions allowing for the realization of revPOCs proceeding without equilibration via back-biting, which is the chemical basis of the JS concept.

Figure 1 MALDI TOF mass spectra of polyLA polymerized at 130°C with SnOct2 as catalyst: (A) initiated with ELA (No.1A, Table 1), (B) initiated with pentaerythritol (No.6, Table 1)

Experimental

Materials

L-Lactide (Lac), a product of Corbion Purac, was kindly supplied by Thyssen-Uhde AG (Berlin) and purified by crystallization from “Toluene 99.89% extra dry” (ACROS Organics, Geel, Belgium). ε-caprolactone (CL) was purchased from Alfa Aesar (Karlsruhe, Germany) and distilled over P2O5 in a vacuum <1 mbar. For this purpose, CL was shaken with a small amount of P2O5 for approx. 1 min, and decanted. Again, a small amount of P2O5 was added, followed immediately by distillation at a bath temperature of 95-97°C, which was raised to 107°C in the course of 1 h. Yield 60-70%. Tin(II)2-ethylhexanoate (SnOct2), diphenyltin dichloride (Ph2SnCl2), dibutyltin oxide, pentafluorophenol and ethyl L-lactate were all purchased from Alfa Aesar and used as received. Tin(II) acetate (SnAc2), 2-hydroxyethyl 3,4 benzo-1,4-dioxane (HMBD) and pentaerythritol (PENT) were also purchased from Alfa Aesar and used in the presence of solid NaOH. Dibutyltin bis(pentafluorophenoxy), (BuSnOPF) was prepared as described previously.24

Polymerizations

at 130°C with initiator

A solid catalyst (0.2 or 0.1mmol), ethyl L-lactate (1mmol) and L-lactide or ε-caprolactone (40 mmol) were weighed into a flame-dried 50mL Erlenmeyer flask under a blanket of argon and a magnetic bar was added. SnOct2 was injected in the form of a 0.4M solution in toluene (0.1mL). The reaction vessel was immersed into an oil bath thermostated at 130°C. In certain time intervals (see Tables) a sample of approx. 1 g was taken with a spatula under a blanket of argon. All samples were characterized in the virgin state.

without initiator

These polymerizations were performed as described above, but without addition of an alcohol.

at 160°C

These polymerizations were performed as described above but the oil bath was thermostated at 160°C.

Synthesis of Ac-PLA-Et

Ethyl lactate (4 mmol) was weighed into a flame-dried 100mL Erlenmeyer flask; a magnetic bar and L-lactide (160 mmol) were added under blanket of argon. SnOct2 (0.4mLof a 0.4M solution in toluene) was injected. The reaction vessel was immersed into an oil bath thermostated at 130°C. After 1.5 h the crystallized product was dissolved in 100 mL of dichloromethane and acetic anhydride (3 mL) and pyridine (0.5mL) were added. After 3d at 22°C the reaction mixture was refluxed for 1 h and precipitated into ligroin (1 l). The crystalline precipitate was isolated by filtration and dried at 60°C in vacuo. In the 1H NMR spectrum the triplet signal of the ethyl ester end group at 1.28 ppm and the singlet signal of the acetyl end group at 2.15 ppm had equal intensities.

Synthesis of Ac-PCL-Et

This synthesis was performed with ε-caprolactone (160 mmol) as described above. The crystalline polyester was dried at 40°C in vacuo. In the 1H NMR spectrum the CH3 triplet signal of the ethyl ester end group at 1.28 ppm and the singlet signal of the acetyl end group at 2.04 ppm had equal intensities.

Transesterification experiments:

Polylactide and diethyl succinate

The Ph2SnAc2 or Bu4Sn(OcF5)2 (0.1 mmol) and L-Lactide (50 mmol) were weighed into a 50 mL flame-dried Erlenmeyer flask under a blanket of argon and a magnetic bar was added. The reaction vessel was immersed into an oil bath thermostated at 160°C. After 1h the reaction product was cooled to approx. 22°C and dry dichloromethane (20 mL) was added. After one day dimethyl succinate (40 mmol) was added to the viscous solution, which was the stirred with a spatula and stored at 22°C for 24 h. Afterwards the dichloromethane was evaporated at a bath temperature of 80°C. Finally, the remaining reaction mixture was thermostated at 130°C and a sample was taken after 1 h, 2h and 4h.

When SnOct2 was used as catalyst, 0.1 mL of a 0.4 M solution in toluene was added to the lactide by means of a syringe.

Polycondensation of ethyl L-lactate

The catalyst (0.25 mmol) was weighed into a 50 mL Erlenmeyer flask a magnetic bar and ethyl L-lactate (100 mmol) were added. The reaction vessel was closed with a kind of stopper having a gas inlet and outlet tube, and argon was slowly bubbled over the ethyl L-lactate. The reaction vessel was immersed into an oil bath thermostated at 130 or 160°C. After 4 h, the reaction mixture was subject to Electrospray ionization (ESI) and Matrix-
assisted laser desorption/ionization time-of-flight (MALDI TOF) measurements.

An analogous experiment was performed with 0.1 mmol of SnOct$_2$ and a duration of 24 h.

**Ac-PLA-ET + ROP of ε-caprolactone**

Diethylene glycol monomethyl ether (1.25 mmol), ε-caprolactone (50 mmol) and Ac-PLA-ET (5.8 g ~ 50 mmol CL units) were weighed into a flame-dried 50 mL Erlenmeyer flask under a blanket of argon and a magnetic bar was added. The reaction vessel was placed into an oil bath thermostated at 130°C for 1 h to obtain a homogeneous melt. The catalyst was then added either as solid (BuSnOPF$_3$, PhSnAc) or as 0.1 mL of a 0.4 M solution in toluene (SnOct$_2$). At certain time intervals a sample of approx. 1 g was removed with a spatula under a blanket of argon and characterized in the virgin state.

**Measurements**

The 400 MHz $^1$H NMR spectra were recorded with a Bruker Avance 400 in 5 mm sample tubes. CDC$_3$ containing TMS served as solvent and shift reference. MALDI TOF mass spectrometry was performed using an AutoflexMax mass spectrometer (Bruker Daltonik GmbH, Bremen). Trans-2-[3-[4-tert-butylyphenyl]-2-methyl-2-propenylidene] malononitrile (DCTB) dissolved in tetrahydrofuran (10 mg mL$^{-1}$) was doped with potassium trifluoroacetate and served as matrix. 1 µL of premixed solutions of matrix and analyte (chloroform, 4 mg mL$^{-1}$) in a ratio of 5/1(v/v) were prepared and deposited on the sample target. 8000 single spectra recorded at four different positions within the spots were accumulated in the linear positive mode. The instrument was previously calibrated with PEO standards.

For the GPC experiments a modular system kept at 40°C (isocratic pump, 1 mL min$^{-1}$, refractive index detector, RI-S01 - Shodex) was applied. Samples were manually injected (100 µL, 2-4 mg mL$^{-1}$). 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, Germany). For the determination of the Mark-Houwink-Sakurada (MHS) relationship a viscometer (Viscotar, Wyatt, Germany) and a multiangle laser light scattering (MALS) detector (Dawn EOS, Wyatt, Germany) were used. Astra 6.1 software (Wyatt) served for calculating the MHS curves.

**Results and Discussion**

**General considerations**

The polymerization experiments conducted in this work are subdivided into two groups. The first group is characterized by the use of an alcohol as initiator (mainly ethyl L-lactate, ELA), whereas neat catalysts were used for the second group of polymerizations under identical or similar conditions as the alcohol-initiated ROPs. The alcohol-initiated experiments had the purpose to find out, if cycles are formed by back-biting (intra molecular transesterification). The second series had the purpose to find out, if intermolecular transesterification occurs and if cycles are formed by end-to-end (ete) cyclization via the ROPOC mechanism (e.g. Scheme 3). Most polymerizations were performed with L-lactide because the dimeric character of this monomer includes an important analytical advantage. Any clean polycondensation and polymerization initiated by an alcohol will yield even-numbered polylactides and the appearance of odd-numbered species evidences the occurrence of transesterification reactions. ELA as initiator will, of course, result in the inverse pattern. Since MALDI TOF mass spectrometry enables a sensitive and unambiguous differentiation between odd- and even-numbered chains or cycles in the mass range up to m/z 10 000, this type of mass spectrometry was used for the characterization of all reaction products. The MALDI-TOF mass spectra of the alcohol-initiated polylactides typically displayed a pattern of four signals: two strong signals of even and odd-numbered linear chains doped with K ions ad two accompanying weak signals resulting from unintended Na doping.

The LA/In ratio was fixed at the low value of 40/1 for all experiments of this work, for the following reason. It was found in a previous study of SnOct$_2$-catalyzed ROPs that a high initiator/catalyst ratio (typically > 10/1) is beneficial for the suppression of back-biting. Presumably, a high catalyst concentration has the consequence that the ROPOC mechanism can compete with the alcohol-initiated ROP, so that cycles are formed by ete cyclization and appear to result from back-biting. Therefore, a LA/Cat ratio of 1000/1 was preferentially used, when SnOct$_2$ served as catalyst (Table 1). However, for other catalysts, such as Ph$_3$SnCl$_2$ or BuSnOPF$_3$ it was found that higher catalyst concentrations (LA/Cat = 100/1 up to 400/1) are beneficial to avoid side reactions including cyclization. Finally, it should be mentioned that most experiments were performed at 130°C, because it was learned from ROPs catalyzed with SnOct$_2$ that at this temperature and short reaction times (<3 h) formation of cycles by back-biting is avoidable. The following description of results is subdivided into sections according to the catalysts used for the polymerizations.

**ROPs and ROPPOCs of L-lactide catalyzed by SnOct$_2$**

A first series of polymerizations was performed with SnOct$_2$ as catalyst for three reasons. First, this tin(II) salt is the standard catalyst for the technical production of polylactide, via an alcohol-initiated polymerization process outlined in Scheme 4. Second, it is the most widely studied catalyst for polymerizations of lactide and third, the authors have recently found that neat SnOct$_2$ catalyses a ROPOC mechanism yielding high molecular weight cyclic poly(L-lactide) (Scheme 5). Most ROPs summarized in Tables 1, were conducted in bulk at 130°C and a few experiments were performed at 160°C. These reaction conditions were selected for the following reasons. A temperature of 130°C was the highest temperature reported in literature where alcohol-initiated ROPs (catalyzed by SnOct$_2$) were shown to proceed without formation of cycles, meaning without back-biting. Previous studies of the authors have confirmed that at 120°C and polymerization times of several hours may result in formation of cycles. The authors have also shown for ROPs at 160°C, that formation of cycles is favoured
Table 1  SnOct$_2$-catalyzed ROPs of L-lactide in bulk with or without addition of an initiator

| Exp. No. | Initiator | LA/Cat | Temp. (°C) | Time (h) | Mn  | Mw  | D.  | Cycles |
|----------|-----------|--------|------------|----------|-----|-----|-----|--------|
| 1        | ELA       | 400/1  | 130        | 1        | 11  | 100 | 1.1 | -      |
| 1B       | ELA       | 400/1  | 130        | 3        | 11  | 000 | 1.1 | -      |
| 2A       | ELA       | 1000/1 | 130        | 1        | 10  | 600 | 1170| 1.1    |
| 2B       | ELA       | 1000/1 | 130        | 3        | 10  | 800 | 1190| 1.1    |
| 3        | ELA       | 1000/1 | 160        | 1        | 10  | 900 | 1500| 1.4 traces |
| 4A       | HMBBD     | 1000/1 | 130        | 1        | 10  | 700 | 1230| 1.2    |
| 4B       | HMBBD     | 1000/1 | 130        | 3        | 11  | 000 | 1230| 1.1    |
| 5        | PENT      | 1000/1 | 130        | 1        | 8   | 900 | 1040| 1.2    |
| 6A       | -         | 400/1  | 130        | 1        | 44  | 000 | 7600| 1.7 +   |
| 6B       | -         | 400/1  | 130        | 3        | 48  | 000 | 8400| 1.7 +   |
| 7A       | -         | 1000/1 | 130        | 1        | 118 | 500 | 1880| 1.6 +   |
| 7B       | -         | 1000/1 | 130        | 3        | 121 | 500 | 2170| 1.8 +   |
| 8        | -         | 1000/1 | 160        | 1        | 91  | 000 | 2400| 2.6 ++  |

by lower initiator/ catalyst ratios. Alcohol/SnOct$_2$ ratios above 5, better above 10, are needed to avoid formation of cycles. The ROPs initiated by ELA yielded polyLAs having a low dispersities (1.1-1.2) and a kind of broadened Poisson distribution of peak intensities in the MALDI TOF mass spectra (Figure 1A and Figure 2A). The even/odd equilibration was above 50% for the ELA experiments (No. 1-5 Table 1). It increased with the catalyst concentration (No. 1 versus No. 2A), with time (No. 2A versus No. 2B) and with temperature (No. 2A versus No. 3 and Figures 1A versus S2A).

These three trends were also valid for all alcohol initiated ROPs based on other catalysts (Tables 2-6). An even/odd equilibration around 50% (Figure S1), which increased with time, was also found for the ROPs initiated with the primary alcohol HMBD (Nos. 4A and 4B).

Scheme 4 Alcohol-initiated ROP of L-lactide catalyzed by SnOct$_2$ at low temperature and high In/lac ratio

Scheme 5 Formation of cyclic polylactides via the SnOct$_2$ catalysed ROPPOC mechanism
Their mass spectra were quite similar to those of Figures 1A. For a project dealing with biodegradable coatings, a ROP initiated with pentaerythritol was performed at 130°C and in this case the odd-/even equilibrium was even complete as displayed in Figure 1B. All these mass spectra have in common, that no cycles were detectable (s. Figure S1B). In the case of experiments 2B and 3, the low molar mass fraction was subject to ESI mass spectroscopy and again no cycles were found for No. 2B (130°C) and only a trace for No. 3 (160°C). The 160°C experiment also revealed almost complete odd-/even equilibration along with broadening of the molecular weight distribution indicating random intermolecular transesterification. (Figure S2A). Hence these experiments demonstrate that under the given reaction conditions ROPs including intermolecular transesterification exist without contribution of back-biting.

With neat SnOct₂ completely different results were obtained. The polymerizations were slower without addition of alcohol (a well-known phenomenon), and with a LA/Cat ratio of 1000/1 only a conversion of 91 % was reached after 1h, but after 3 h the conversion had reached the equilibrium level of 97%. With a LA/Cat ratio of 400/1, a conversion of 97% was reached within 1 h. Regardless of the LA/Cat ratio, high molecular weights were achieved, and quite similar mass spectra were obtained which displayed strong peaks of cycles (Figure 2B) along with a peak of an unidentified linear species.

Complete odd/even equilibration was not achieved, what indicates that the cycles were formed by ete-cyclization and not by back-biting. At 160°C complete conversion, complete equilibration and a high molecular weight was already obtained after 1 h. MALDI TOF mass spectra exclusively displaying peaks of cycles (Figure S2B) and intrinsic viscosity measurements confirming a cyclic topology also for the high molar mass fraction were found, results that were recently published and thus, do not need extensive discussion at this point. These properties were in agreement with the ROPPOC mechanism outlined in Scheme 3 as discussed in a recent publication.

ROPs and ROPPOCs of L-lactide catalyzed by SnAc₂ or Ph₂SnAc₂

The mass spectra of polyLAs prepared with SnOct₂ have the shortcoming that they cannot differentiate between cycles and linear chains terminated by a 2-ethyl hexanoate end group, because 2-ethyl hexanoic acid has the same mass as lactide. As outlined in Scheme 3, formation of linear chains having a COOH chain end may compete with the formation of cycles although to a low extent. This analytical problem does not exist for tin acetates. As published recently, the reactivity of SnAc₂ is quite similar to that of SnOct₂. At LA/In ratios <100/1 linear acetate terminated chains are predominantly formed, but at higher ratios formation of cycles is prevalent and at LA/In ratios >400 linear chains are not detectable in the mass spectra.
anymore. Furthermore, SnAc$_2$ can catalyse alcohol-initiated ROPs, so that the average degree of polymerization (DP) parallels the LA/In ratio and low dispersities are obtained. The results listed in Table 2 are in line with previous results.26

The MALDI TOF mass spectra of the ELA-initiated polyLAs (No. 1-4, Table 2) were quite similar to those obtained with SnOct$_2$, and Figure 3 also illustrates the dependence of the even/odd equilibration on the catalyst concentration. Particular important is again the absence of cycles. The results obtained with neat SnAc$_2$ were also analogous to those found with SnOct$_2$, because a considerable fraction of cycles was formed after 1h at 130°C (Figure 4A). At 160°C the predominance of cycles was more complete (Figure 4 B). Regardless of temperature, again high molecular weights and high dispersities were obtained along with full odd/even equilibration. Therefore, the SnAc$_2$ experiments were in full agreement with the SnOct$_2$-catalyzed polymerizations and their interpretation.

ROPs and ROPPOCs of L-lactide catalyzed by Ph$_2$SnCl$_2$

Again, two series of polymerizations were performed with Ph$_2$SnCl$_2$ as catalyst and compiled in Table 3. Relatively low LA/Cat ratios were used and varied, because it was found in a previous study where neat Ph$_2$SnCl$_2$ served as catalyst at 160°C that the highest molecular weights and the most uniform topology (i.e. cyclic polylactide)s were obtained when LA/Cat ratios <400/1 were used.25

The MALDI TOF spectrum presented in Figure 5 not only illustrates the relatively narrow MWDs, but also the absence of cycles.

In contrast, all polymerizations conducted with neat Ph$_2$SnCl$_2$ yielded considerably higher molecular weights and higher
differences. Furthermore, the mass spectra evidenced that mainly cyclic polylactides were formed as demonstrated in Figure 6. In summary, the results obtained with Ph$_2$SnCl$_2$ were similar to those obtained from SnOct$_2$ and SnAc$_2$, and the predominant formation of high molar mass cyclic polylactides is also in good agreement with the previously published experiments. The results of the neat catalyst are also in perfect agreement with the hypothesis of a ROPPOC mechanism involving the intermediate formation of CO-Cl end groups as discussed previously.

ROPs and ROPPOCs of L-lactide catalyzed by Bu$_3$Sn(OC$_6$F$_5$)$_2$

From a previous study ROPs catalyzed with neat BuSnOPF it was learned that the best results in terms of high molecular weights and homogeneous topology were obtained at relatively low LA/Cat ratios such as 100/ to 400/1, quite analogous to Ph$_2$SnCl$_2$. Therefore, the experiments of this work were performed with such low LA/Cat ratios. Two ROPS initiated with ELA were conducted at 130°C and two ROPs at 160°C (Table 4). The results were, in principle analogous to those described above for Ph$_2$SnAc$_2$ and Ph$_2$SnCl$_2$, but with two noteworthy differences. The odd/even equilibration was almost complete after 1 h at 130°C favoured by the high catalyst concentration (Figure 7A). A comparison of Figure 7A and S3A illustrates the role of the catalyst concentration. The absence of cycles underlines that here again transesterification reactions occur without contribution of back-biting. The second difference concerns the relatively high dispersities of 1.4 at 130°C and 1.7 at 160°C. The Mn values agree with the theoretical value (6 000) calculated from the LA/In ratio taking a correction factor of 0.68 (+/-0.01) into account. However, the Mw values were somewhat higher than in previous experiments (Tables 1-3), possibly due to more intensive transesterification reactions. Noteworthy is the absence of cycles in the 130°C samples, whereas traces of cycles were detected in the 160°C samples. The polymerizations catalyzed with neat BuSnOPF yielded polylactides with the four characteristics typical for a ROPPC process (see Scheme 4). First, the molecular weights were considerably higher, second the dispersities were higher, the odd/even equilibration was complete, and cycles were the predominant reaction products as demonstrated in Figures 7B and S3B.

| Exp. No. | Init. | Lac/Cat | Temp. (°C) | Time (h) | Mn (meas.) | Mw (meas.) | D | Cycles |
|---------|-------|---------|------------|----------|------------|------------|---|--------|
| 1       | ELA   | 200/1   | 130        | 1        | 9 200      | 10 600     | 1.2| --     |
| 2       | ELA   | 400/1   | 130        | 1        | 9 100      | 10 200     | 1.2| --     |
| 3       | ELA   | 400/1   | 160        | 1        | 9 100      | 14 000     | 1.5| --     |
| 4       | ELA   | 400/1   | 160        | 3        | 10 000     | 15 100     | 1.5| --     |
| 5       | -     | 200/1   | 130        | 1        | 47 000     | 105 000    | 2.2| +      |
| 6       | -     | 400/1   | 130        | 1        | 63 000     | 153 000    | 2.4| +      |
| 7       | -     | 400/1   | 160        | 1        | 79 500     | 205 000    | 2.6| ++     |

Table 2: SnAc$_2$-catalyzed ROPs of L-lactide in bulk at 130°C with or without addition of ethyl L-lactate as initiator corresponding to a Mn of 5 900
Table 4 BuSnOPF-catalyzed ROPs of L-lactide in bulk with or without addition of ethyl L-lactide as initiator (Lac/In = 40/1)

| Exp. No. | Init. | Lac/Cat | Temp. (°C) | Time (h) | Mn (meas.) | Mw (meas.) | Ð. | Cycles |
|----------|-------|----------|------------|----------|------------|------------|----|--------|
| 1        | ELA   | 200/1    | 130        | 1        | 8 500      | 12 000     | 1.4 | -      |
| 2        | ELA   | 400/1    | 130        | 1        | 8 300      | 11 500     | 1.4 | -      |
| 3        | ELA   | 400/1    | 160        | 1        | 8 800      | 15 000     | 1.7 | traces |
| 4        | ELA   | 400/1    | 160        | 3        | 8 500      | 14 700     | 1.7 | traces |
| 3A       | -     | 200/1    | 130        | 0.5      | 53 000     | 111 000    | 2.1 | ++     |
| 3B       | -     | 200/1    | 130        | 1        | 50 000     | 103 000    | 2.1 | ++     |
| 4        | -     | 400/1    | 130        | 1        | 55 000     | 139 000    | 2.5 | ++     |
| 3A       | -     | 600/1    | 130        | 1        | 75 000     | 181 000    | 2.4 | ++     |
| 3B       | -     | 600/1    | 130        | 2        | 68 000     | 157 000    | 2.3 | ++     |

Table 5 BuSnOPF-catalyzed ROPs of ε-caprolactone at 130°C in bulk with or without ethyl 6-hydroxyhexanoate (EHH) as initiator (CL/Init = 40/1)

| Exp. No. | Init. | CL/Cat | Time (h) | Mn     | Mw     | Ð.  | Cycles |
|----------|-------|--------|----------|--------|--------|-----|--------|
| 1        | EHH   | 200/1  | 1.0      | 8 100  | 16 000 | 2.0 | -      |
| 2        | EHH   | 400/1  | 1.0      | 8 300  | 17 000 | 2.0 | -      |
| 3        | EHH   | 1 000/1| 1.0      | 9 000  | 18 500 | 2.1 | -      |
| 4A       | HMBD  | 400/1  | 1.0      | 6 500  | 15 700 | 2.5 | -      |
| 4B       | HMBD  | 400/1  | 2.0      | 4 100  | 15 300 | 3.7 | -      |
| 5A       | HMBD  | 600/1  | 1.0      | 6 100  | 15 300 | 2.1 | -      |
| 5B       | HMBD  | 600/1  | 2.0      | 4 100  | 15 300 | 2.7 | -      |
| 6        | -     | 200/1  | 1.0      | 46 000 | 92 000 | 2.0 | ++     |
| 7        | -     | 400/1  | 1.0      | 61 000 | 127 000| 2.1 | ++     |
| 8        | -     | 600/1  | 1.0      | 70 500 | 143 000| 2.1 | ++     |
| 9        | -     | 1 000/1| 1.5     | 85 000 | 168 000| 2.0 | ++     |

ROP and ROPPOC of CL with and without initiator catalyzed by BuSnOPF

To demonstrate that the results described above were not a peculiarity of the lactide chemistry, two series of experiments was performed with CL. In the first series (No. 1-5B, Table 5) two primary alcohols were added as initiators at a LA/In ratio of 40/1. In agreement with analogous ROPs of lactide linear chains were the main polymerization products, but a small amount of a linear by-product of unknown structure was also formed below m/z 2 000. However, cycles were not detectable (Figure S6).

A remarkable difference relative to analogous ROPs of lactide is the higher dispersity which is immediately evident from the MALDI TOF mass spectra (Figures 8A and S4A). In absence of an initiator higher molecular weights were achieved and the mass spectra exclusively displayed peaks of cycles (Figure 8B).

Although information about transesterification yielding odd/even equilibration is, of course, lacking in the mass spectra of polylactones, the results obtained from the BuSnOPF catalyzed polymerizations listed in Table 6 clearly support the conclusions extracted from the polymerizations od L-lactide.

Model reactions of intermolecular transesterifications

The results described above demonstrate that ROPs conducted with addition and without addition of an alcohol take a quite different course. Without alcohol low and high molar mass cycles are the main reaction product as expected from a
polycondensation process with high conversion (>99.9%). However, formation of cycles via ete-cyclization also occurs in irreversible polycondensations as predicted by Gordon et al.\textsuperscript{32, 33} and Stepto et al.\textsuperscript{34} and experimentally confirmed by the first author.\textsuperscript{35}

Therefore, the results presented in this work would not be new, if equilibration reactions were absent. As mentioned in the Introduction reversible back-biting was considered by J+S to be the only source of ring-chain, ring-ring and chain-chain equilibration. Therefore, it was a particular important aspect of the present study to demonstrate that equilibration reactions occur in the absence of back-biting. As discussed above, the SUE mechanism, which is perhaps confined to the chemistry of lactide is a first example of a transesterification/equilibration mechanism which operates at temperature below which back-biting sets out. However, intermolecular transesterification reactions that broaden the MWD occur more frequently and at lower temperatures than back-biting, which was already reported previously.\textsuperscript{36}

That model reaction was performed at 120°C in such a way that L-lactide was polymerized by means of SnOct\textsubscript{2} + benzyl alcohol in the presence of preformed polylactide having blocked end groups (Ac-PLA-Et). Three series of additional experiments was performed in the present work.

In the first series L-lactide was polymerized at 160°C with neat SnOct\textsubscript{2}, SnAc\textsubscript{2} or BuSnOPF, so that cyclic polylactides were formed. After 1 h the reaction was stopped by cooling. The polyLA was dissolved in dry dichloromethane and combined with diethyl succinate.

After homogenization the dichloromethane was evaporated at 80°C and the remaining reaction mixture was thermostated at 130°C for 1 or 2 h (see Table 6). Diethylsuccinate was selected as reaction partner of polyLA for three reasons. First its boiling point is high enough to avoid premature vaporization. Second it seemed to be partially miscible with molten poly(L-lactide) and the masses of reaction products expected from transesterification (Lc and Ld chains, Scheme 6) allowed for easy identification by mass spectrometry (Lc and Ld are isomers and give identical mass peaks). The mass spectra proved that Lc and Ld chains were formed in the experiment with BuSnOPF after 2h (Figure S 6).

A second series of experiments was performed in such a way that the potential polycondensation of ethyl L-lactate was studied at 130°C with addition of SnOct\textsubscript{2} or BuSnOPF as catalysts (Table 7).

| Exp. No. | Catalyst | Lac/Cat | Time (h) | Lc + Ld chains |
|---------|----------|---------|----------|----------------|
| 1A      | SnOct\textsubscript{2} | 400/1   | 1        | -              |
| 1B      | SnOct\textsubscript{2} | 400/1   | 2        | -              |
| 2A      | BuSnOPF  | 400/1   | 1        | ++             |
| 2B      | BuSnOPF  | 400/1   | 2        | ++             |

a) time of transesterification

| Exp. No. | Catalyst | Lac/Cat | Temp (°C) | Time (h) | La Chains | Cyclics |
|---------|----------|---------|-----------|----------|-----------|---------|
| 1A      | SnOct\textsubscript{2} | 1000/1  | 130       | 4        | +         | -       |
| 1B      | SnOct\textsubscript{2} | 400/1   | 130       | 24       | ++        | -       |
| 2A      | SnOct\textsubscript{2} | 400/1   | 160       | 4        | ++        | -       |
| 3       | BuSnOPF  | 400/1   | 130       | 4        | +         | -       |
| 4A      | BuSnOPF  | 400/1   | 130       | 4        | ++        | traces  |
| 4B      | BuSnOPF  | 400/1   | 130       | 24       | ++        | -       |

| Exp. No. | Catalyst | Lac/Cat | Time (h) | Lc + Ld chains |
|---------|----------|---------|----------|----------------|
| 5       | BuSnOPF  | 400/1   | 130       | 4             | ++        | -       |

After homogenization the dichloromethane was evaporated at 80°C and the remaining reaction mixture was thermostated at 130°C for 1 or 2 h (see Table 6). Diethylsuccinate was selected as reaction partner of polyLA for three reasons. First its boiling point is high enough to avoid premature vaporization. Second it seemed to be partially miscible with molten poly(L-lactide) and the masses of reaction products expected from transesterification (Lc and Ld chains, Scheme 6) allowed for easy identification by mass spectrometry (Lc and Ld are isomers and give identical mass peaks). The mass spectra proved that Lc and Ld chains were formed in the experiment with BuSnOPF after 2h (Figure S 6).

A second series of experiments was performed in such a way that the potential polycondensation of ethyl L-lactate was studied at 130°C with addition of SnOct\textsubscript{2} or BuSnOPF as catalysts (Table 7).
Due to the low reactivity of the ethyl ester group a first experiment was performed with the relatively low LA/SnOct$_2$ ratio of 400/1 and La chains were indeed detectable after 4h (Figure 9A). Their concentration was higher after 4 h at 160°C (Figure 9B). Even with a LA/SnOct$_2$ ratio of 1 000/1 oligoLAs were formed, when the time was prolonged to 24 h and the La chains became detectable in the MALDI mass spectrum up to a DP of 25. In all three experiments peaks of cycles were absent. Similar results were obtained with BuSnOPF, which proved to be slightly more reactive than SnOct$_2$. Cycles were again absent in the 4 h experiments (Nos. 4A and 5, Table 7 and Figure S7), but traces of cycles were observable in the ESI spectrum after 24h at 130°C (Figure S8). In the MALDI mass spectra La chains were detectable up to DPs around 40 (No. 5, Figure S9A), and up to DPs around 140 (No. 4B, Figure S9B), whereas peaks of cycles were absent. These results include three remarkable aspects. First, they demonstrated the existence of an intermolecular transesterification of the ethyl ester end groups, which is reversible as long as the liberated alcohol is present in the reaction mixture. Second, they indirectly indicate that the active chain ends (Sn-O-CH) can also react with the lactyl-lactyl bonds in the polymer backbone, because those ester bonds are more reactive than the ethyl ester end groups. This conclusion is confirmed by previously published transesterification experiments. In other words, the polycondensations of ELA involve two types of intermolecular transesterification reactions. Third, the experiments of Table 7 present in this work the first examples of reversible polycondensations without back-biting outside the ROPPOC chemistry discussed before.

A third series of transesterification experiments was performed with Ac-PCL-Et (Scheme 7 and Table 8) as reaction partner of dimethyl succinate. Ac-PCL-Et having a DP of 40 was prepared by SnOct$_2$-catalyzed and ethyl 6-hexanoate-initiated polymerization of CL at 130°C followed by acylation of the OH-CH end group with acetic anhydride and pyridine. The MALDI TOF mass spectrum presented in Figure 10A proved the formation of the expected structure. This model polymer was dissolved in dimethyl succinate and thermostated at 130°C in the presence of BuSnOPF. The results listed in Table 8 and Figure 10 demonstrate that the Lf, Lg and Lh chains indicating transesterification were detectable after 1 h, when a LA/Cat ratio of 200/1 was used or after 2 h with a LA/Cat ratio of 400/1. Analogous results, although with different intensity ratios of the Lf, Lg and Lh peaks were obtained with SnOct$_2$ as catalyst. In summary, including previous results four different kinds of intermolecular transesterifications were performed at 120 or 130°C which all proceeded under conditions where back-biting was absent.

Table 8 Transesterification experiments with Ac-PCL-Et and dimethyl succinate catalyzed by BuSnOPF or SnOct$_2$ in bulk at 130°C

| Exp. No. | Catalyst    | CL/Cat | Time (h) | Lf, Lg, Lh-chains |
|----------|-------------|--------|----------|-------------------|
| 1A       | SnOPF       | 200/1  | 1        | +                 |
| 1B       | SnOPF       | 400/1  | 2        | ++                |
| 1C       | SnOPF       | 400/1  | 4        | ++                |
| 2A       | SnOct$_2$   | 200/1  | 1        | +                 |
| 2B       | SnOct$_2$   | 200/1  | 2        | ++                |

Figure 9 ESI mass spectra of oligoLA prepared by polycondensation of ELA with SnOct$_2$ (A) at 130°C/4 h in, (B) 160°C/4h
or does at least not play a significant role. Nonetheless, the demonstration that intermolecular transesterification reactions summarized in Tables 7-9 or reported previously lactide, the broadening of the MWD observed in the mass spectra and the results of the transesterification experiments presented in Tables 1-6 may be called reversible ROPPOC experiments include formation of large amounts of low polymerizations and polycondensations despite absence of back-biting. Therefore, it is justified to conclude that the ROPPOCs presented in Tables 1-6 may be called reversible polymerizations and polycondensations despite absence of back-biting.

Discussion
Identification of the SUE-type transteranfronation in the case of lactide, the broadening of the MWD observed in the mass spectra and the results of the transteranfration experiments summarized in Tables 7-9 or reported previously\textsuperscript{16} clearly demonstrate that intermolecular transteranfration reactions exist under conditions, where back-biting is either totally absent or does at least not play a significant role. Nonetheless, the ROPPOC experiments include formation of large amounts of low and high molar mass cycles which are exclusively formed by ete-cyclization. In most cases, the odd/even equilibration is complete indicating a nearly complete ring-ring equilibration. These ring-ring equilibria are, of course, the same as those resulting from the ring chain equilibration, when back-biting occurs. In a recently published comment on the JS-theory Szymanski\textsuperscript{17} has calculated that polymerizations of lactide may yield a nearly quantitative fractions of cycles even when conducted in bulk, a result which was not immediately evident from the papers of J+S. From this viewpoint, the ROPPOC experiments of this work may be understood to be part of the JS-theory. Yet, the authors of this work do not share this view.

First: As already mentioned in the Introduction, the work of J+S has two aspects. On the one hand, it is a theory of ring-chain equilibria, on the other hand, it has been presented as a general theory of revPOCs. It is this second aspect, which is criticized by the authors. Characteristic for the JS-hypothesis of revPOCs is the assumption that equilibration exclusively results from back-biting. In contrast, the experiments presented above prove that revPOCs may proceed without back-biting. Any evidence is lacking that polycondensations exist, where according to J+S the reversibility is exclusively based on back-biting. Second: J+S excluded that ete-cyclization plays a noteworthy role in the course of revPOCs. The ROPPOC experiments presented in this work (and previously\textsuperscript{9}) demonstrate that ete-cyclization plays an important role in revPOCs, even when back-biting takes place. The results presented above demonstrate, that efficient formation of cycles may also occur in absence of back-biting. Any experimental evidence is lacking that polycondensations exist, which involve formation of cycles exclusively on the basis of backbiting. Therefore, the results described above are in total contradiction to the J+S hypothesis of revPOCs and thus, are considered to be outside the JS concept of revPOC, even when a ring-chain equilibration takes place.

Third: Even when back-biting is the main or only source of equilibration, the JS hypothesis does not provide a correct description of the course of revPOCs up to 100% conversion. For polycondensations at high conversions the JS theory predicts that a group of monomers yields 100% cycles at 100% conversion whereas, for other groups of monomers only a few percent of cycles is predicted. This calculation is a total failure of chemical logic, because 100% conversion yields 100% of cycles for any kind of monomers and all reaction conditions. Furthermore, it should be considered that all the experiments presented above have in common that they are based on cyclic esters and thus, indirectly on polycondensations of hydroxy acids. However, the technical production of most polyesters and the Jacobson-Stockmayer-Beckmann experiments\textsuperscript{3} are based on polycondensations of α,ω-diols and dicarboxylic acids or their dimethyl esters. Hence, such polycondensations need to be considered (and (re)investigated) to find out, to what extent the results and conclusions achieved in this work agree with a2+b2 polycondensations. However, first pertinent experiments that shed light on this aspect have already been published by the first author in another context.\textsuperscript{38-40} For example, telechelic polyesters were prepared from dimethyl adipate or dimethyl sebacate and excess of ethane diol.\textsuperscript{38} With bismuth catalysts no cycles were formed up to temperatures of 240°C. A typical MALDI TOF mass spectrum is displayed in Figure S10. Furthermore, telechelic polyesters were prepared from dimethyl terephthalate and excess 1,4-butane diol and with bismuth catalysts no cycles were formed up to 240°C. Szymanski\textsuperscript{38} has published by the first author in another context.

Figure 10 MALDI TOF mass spectra of (A) Ac-PCL-Et (average DP = 40), (B) reaction product of Ac-PCL-Et and dimethyl succinate catalyzed by BuSnOPF (LA/Cat = 200/1) after 1 h at 130°C (No. 1A, Table 8) measured with Na doping.
by both reaction pathways remains an open question. Anyway, when those polycondensations are stopped because a sufficiently high molecular weight is achieved, they are certainly still far from complete equilibration, because perfect equilibration either requires extremely fast trans esterification reaction or long reaction times, which are usually not applied in preparative experiments.

In all those polycondensations, chain growth steps are reversible, because the liberated methanol in combination with catalyst can cleave any ester bond in the polymer chains. Hence, those experiments indicate that also in the field of a2+b2 polycondensations reaction conditions exist that allow for polyester syntheses involving intramolecular transesterification in the absence of back-biting or with a negligible contribution of back-biting. Hence, also those polycondensations are outside the JS-hypothesis. All these facts and arguments together clearly demonstrate that the JS concept cannot serve as a general theory of revPOCs.

As a consequence of this conclusion, the authors propose a new concept of revPOCs based on the definition of three classes of polycondensations:

**Class I:** Irreversible polycondensations that may also be labelled kinetically controlled polycondensations. This definition, in principle, agrees with Flory’s polycondensation theory with the exception that ete-cyclization occur, which was denied by Flory.

**Class II:** RevPOCs exclusively involving back-biting as the only source of reversibility and including such a high rate of equilibration that that thermodynamic control is given at any state of the polycondensation process.

**Class III:** RevPOCs involving rapid intermolecular trans-reactions in the absence of back-biting. Again, equilibration is so efficient that thermodynamic control is given at any stage of the polycondensation.

To avoid misunderstanding the term “thermodynamically controlled polycondensation” needs to be clarified. At long reaction times (i.e. weeks or months), all revPOC will end up with complete equilibration of all reaction products and thus, justify being called “thermodynamically controlled” polycondensations. Yet, as demonstrated by the ROPPOC experiments above and by the experiments in refs.38–41, in many real polycondensations the equilibration reactions will not be efficient enough to reach thermodynamic control at any stage of the process.

The three classes of polycondensations defined above should be considered as extreme cases which form the corner of a triangle. The vast majority of revPOCs will, in fact, be located somewhere inside this triangle. Consider, a series of class III-type polycondensations with decreasing rate constants of trans-reactions. When the rate constants approach zero the definition of Class I is reached and thus, this series of polycondensations is located on the line connecting Class III and Class I. An analogous thought experiment can be formulated for Class II polycondensations. The line connecting class I and II is formed by polycondensations that involve fast equilibration reactions, so that thermodynamic control is established at any time, but the contributions of back-biting and intermolecular equilibration reactions varies. If all the equilibration reactions are not fast enough to establish full thermodynamic control at any stage, this polycondensation will be positioned somewhere inside the triangle. In other words, revPOCs cover a wide area of kinetic and thermodynamic properties and exact knowledge of the effectiveness of all involved trans-reactions is required for a detailed description of an individual polycondensation process.

Finally, a publication of Montaudo et al. 41 should be cited which, as early as 1997, described MALDI TOF mass spectrometric analyses of polylactides prepared by means of an Al complex containing one Al-OCH3 group. This methoxide group played the role of initiator and yielded methyl ester terminated polylactides. Despite the low temperature of 70°C and short times complete odd/even equilibration was observed although cyclic oligomers were absent and only appeared after long polymerization times. Hence, these results demonstrate that a significant predominance of intramolecular transesterification reactions (entailing broadening of the Mw) over back-biting is not limited to the chemistry of tin catalysts. This conclusion and the results presented in refs.39-41 also suggests that catalyst of other elements (e.g. Zn, Ti and Bi) may be found, that enable ROPPOC of cyclic esters obeying to the principles of Class III polycondensations.

**Conclusions**

The numerous ROP and ROPPOC experiments performed in this work, based on two different monomers, three initiators and four different catalysts carry one message: revPOCs free of back-biting but involving intermolecular transesterification exist under appropriate reaction conditions. The low and high molar mass cycles formed in absence of initiators exclusively result from ete-cyclization. Furthermore, revPOCs with low or moderate conversions were found which do not involve formation of cycles. Hence, it may be concluded that the JS theory is not useful as a general theory of revPOCs. These results suggest formulation of a new concept of revPOCs based on the definition of three classes of polycondensations (Class I-III). All three classes have in common that when the conversion approaches 100% of functional groups, the final polymerization product almost exclusively consists of cycles with a broad molecular weight distribution. Class I and class III have in common that all cycles small and large ones, are formed by ete-cyclization, whereas in the case of class II both, back-biting” and ete-cyclization contribute to the formation of cycles. The three classes of polycondensations defined above should not be considered as three isolated regimes of polycondensation, but as three corners of triangle (see TOC graphic) which encompasses almost real experiments.

**Author contributions**

HRK – Project administration, Conceptualization, Synthesis, Writing original draft, SMW – Investigation, Methodology, Validation, Visualization, Writing – review & editing, JF – Investigation, Methodology, Visualization
ARTICLE

Conflicts of interest

There are no conflicts to declare.

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