Supporting Information

Next Generation of Zinc Bisguanidine Polymerization Catalysts towards Highly Crystalline, Biodegradable Polyesters

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SUPPORTING INFORMATION

1. General information

All steps were performed under nitrogen (99.996%), which was dried with P₂O₅ granulate, using Schlenk techniques. Solvents were purchased in technical purity, dried according to literature and stored under nitrogen.[1] All chemicals were purchased from abcr GmbH, Acros Organics, Grüssing GmbH, Carl Roth GmbH & Co. KG and TCI Deutschland GmbH and were used without further purifications. The used lactide was donated by Total Corbion PLA. Rac-lactide was made from L-lactide PURALACT® B3 resin grade (water < 0.01%, free acid = 3 meq kg⁻¹) and D-lactide PURALACT® D polymer grade (water < 0.01%, free acid = 0.55 meq kg⁻¹) and was used without further purification. L-lactide (PURALACT® L polymer grade, water < 0.01%, free acid = 6 meq kg⁻¹) was recrystallized once from dried toluene. A part of the recrystallized L-lactide was then sublimated at 110 °C. All lactide charges were stored at −35 °C in a nitrogen filled glovebox. ε-caprolactone was dried over CaH₂ for 24 h at room temperature and distilled under reduced pressure. Tin(II) 2-ethylhexanoate was distilled under reduced pressure. A sample of a PLA cup (Art. P60) from Huhtamaki was used as commercially available PLLA sample. The ligand (R,R)-DMEG₃(1,2)ch was synthesized after known procedures from literature.[2]

NMR spectroscopy: NMR spectra were recorded at room temperature on a Bruker Avance II (400 MHz) or a Bruker Avance III (400 MHz). The NMR signals were calibrated to the residual signals of the deuterated solvent [CDCl₃; δ(¹H) = 7.26 ppm and δ(¹³C) = 77.16 ppm] Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constants (Hz), integration). Couplings are expressed by: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof.¹³C NMR spectra are also expressed in parts per million (ppm) and reported as aforementioned. Various 2D NMR experiments (COSY, HSQC, HMBC) were used to assign the ¹H and ¹³C NMR spectra. For PLA and PCL polymer analysis HR mass spectra were obtained with a ThermoFisher Scientific Finnigan MAT95 mass spectrometer for HR EI and a ThermoFisher Scientific LTQ-Orbitrap XL Spectrometer for HR-ESI. The source voltage of the ThermoFisher Scientific LTQ-Orbitrap XLSpectrometer was 4.49 kV, and the capillary temperature was 299.54 °C. The tube lens voltage was between 100 and 130 V. Acetonitrile was used as solvent. EI mass spectra were measured with a source voltage of 5 kV and an electron energy of 70 eV. FTIR spectra were measured with a Shimadzu IRTracer 100 using a CsI beam splitter with an ATR unit (Quest model from Specac utilizing a robust monolithic crystalline diamond) with a resolution of 2 cm⁻¹. Thermo gravimetrical analysis (TGA) of the complexes was performed with a Mettler STARReSW 9.20 with a flow of 60 mL min⁻¹ in a temperature range of 25-150 °C with a heating rate of 10 K min⁻¹ followed by one hour at 150 °C. Elemental analysis was conducted with an elementar varioEL.

Physical methods: Mass spectra were obtained with a ThermoFisher Scientific Finnigan MAT95 mass spectrometer for HR-EI and a ThermoFisher Scientific LTQ-Orbitrap XL Spectrometer for HR-ESI. The source voltage of the ThermoFisher Scientific LTQ-Orbitrap XLSpectrometer was 4.49 kV, and the capillary temperature was 299.54 °C. The tube lens voltage was between 100 and 130 V. Acetonitrile was used as solvent. EI mass spectra were measured with a source voltage of 5 kV and an electron energy of 70 eV. FTIR spectra were measured with a Shimadzu IRTracer 100 using a CsI beam splitter with an ATR unit (Quest model from Specac utilizing a robust monolithic crystalline diamond) with a resolution of 2 cm⁻¹. Thermo gravimetrical analysis (TGA) of the complexes was performed with a Mettler STARReSW 9.20 with a flow of 60 mL min⁻¹ in a temperature range of 25-150 °C with a heating rate of 10 K min⁻¹ followed by one hour at 150 °C. Elemental analysis was conducted with an elementar varioEL.

X-ray diffraction analysis: The single crystal diffraction data for 1 are presented in Table S1 The data were collected on a Bruker D8 goniometer with APEX CCD detector. An Incoatec microsource with Mo-Kα radiation (λ = 0.71073 Å) was used and temperature control was achieved with an Oxford Cryostream 700. Crystals were mounted with grease on glass fibers and data were collected at 100 K in o-scans mode. Data were collected with SMART,[9] integrated with SAINT[9] and corrected for absorption by multi-scan methods with SADABS.[9] The structure was solved by direct and conventional Fourier methods and all non-hydrogen atoms were refined anisotropically with full-matrix least-squares based on F² (XPREP[6], SHELXS-97[5] and ShelXle[6]). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters Uiso(H) = 1.2Ueq(C) and 1.5Ueq(C methyl). All methyl groups were allowed to rotate but not to tip.

Full crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC – 1998353 for 1. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

In 1 it was not possible to model the disordered solvent molecule (THF) in an adequate manner, and the data set was treated with the SQUEEZE routine as implemented in PLATON.[7,8] Furthermore, 1 crystallizes in a Sohnke space group and the values of the Flack parameter are the following: Flack x = 0.072(28) by classical fit to all intensities and 0.082(12) from 2574 selected quotients (Parsons’ method). So the values are closed to zero and a twin refinement is not necessary.
Gel permeation chromatography:

**GPC A:** The average molecular masses and the mass distributions of the obtained polymer samples were determined by GPC in THF as the mobile phase at a flow rate of 1 mL min$^{-1}$. The utilized GPCmax VE-2001 from Viscotek was a combination of an HPLC pump, two Malvern Viscotek T columns (porous styrene divinylbenzene copolymer) with a maximum pore size of 500 and 5000 Å, a refractive index detector (VE-3580), and a viscometer (Viscotek 270 Dual Detector). Universal calibration was applied to evaluate the chromatographic results.

**GPC B:** To establish baseline polymer properties for degradation analysis, GPC was also performed using a system equipped with an intelligent pump AI-12 and three Mz columns from MZ-Analysetechnik GmbH, Mainz, Germany (MZ-Analysetechnik 8 mm diameter, 10 µm particle size, precolumn of 50 mm, 3 x 100 Å of 300 mm). THF (unstabilized - HPLC from Biosolve Chimie, Dieuze, France) was used as GPC eluent with a flow rate of 1 mL min$^{-1}$. The GPC system was calibrated with ten polystyrene standards from Agilent Technologies (MW 575 - 3039000 g mol$^{-1}$). UV spectra were recorded on a Waters 486 Tunable Absorbance Detector. Differential refractive index spectra were recorded using a Viscotek VE-3580 (Malvern Instruments). Data analysis was performed using the Nteq GPC V6.0 software.

If not mentioned otherwise the GPC A was used.

**In situ-Raman spectroscopy:** Raman spectra were measured under process conditions (150 °C, Ar atmosphere) using a RXN1 spectrometer of Kaiser Optical System with a 785 nm laser. The used detector is a TE-Cooled, 1024 CCD detector and the used stirrer corresponds to the model PRE1946 of Premex Reactor AG with a torsional moment of 20 Ncm. A immersion probe with a sapphire lens (d = 0.1 mm) was applied to the autoclave optimized for monitor biphasic reaction mixtures. The obtained time-resolved data were processed with the PEAXACT 4.6 software. Kinetic data were obtained by integration of characteristic peaks of the Raman spectrum. For the polymerization of lactide the lactide peak (656 cm$^{-1}$) and the polylactide peak (872 cm$^{-1}$) were integrated. For the ε-caprolactone polymerization the characteristic monomer peaks at 733 cm$^{-1}$ and 696 cm$^{-1}$ were integrated.

**MALDI-ToF-MS:** Compounds were analyzed using a Bruker MALDI-TOF Ultraflex I system with either 2,5-dihydroxybenzoic acid (DHB) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Samples were dissolved in THF (2-5 mg/mL). The ratio of matrix to compound was 5:1. Spectra were acquired in linear mode in a m/z range 1000-10000. Spectra were analyzed using Bruker Polymerix MALDI software.

**Computational details:** Density functional theory (DFT) calculations were performed with Gaussian 16, Revision B01. The geometry optimizations were started from the geometry of the solid-state structures using the TPSSH functional and with the Ahlrichs type basis set def2-TZVP basis set as implemented in Gaussian 16, Revision B01. NBO calculations were accomplished using the program suite NBO 6.0 delivering the NBO charges and the charge-transfer energies by second order perturbation theory. As empirical dispersion correction, we used the D3 dispersion with Becke–Johnson damping as implemented in Gaussian16, Revision B.01.

**Differential Scanning Calorimetry (DSC):** Differential Scanning Calorimetry (DSC) analysis was conducted using a Mettler-Toledo DSC3 with data automatically analysed using STAR® software. The experiments were performed by heating the samples from −40 to 200°C (heating and cooling scans were repeated, at least in triplicate, to ensure reproducibility). Also, the measurements were carried out at a heating rate of 10 °C/min, in nitrogen atmosphere. The degree of crystallinity ($X_c$) is calculated firstly by obtaining the values for melting enthalpy ($\Delta H_m$) and cold crystallization ($\Delta H_c$) as determined and automatically calculated from the DSC thermogram. The integral, of the corresponding area under the curve, is assigned by the relevant software. The reference enthalpy $\Delta H_m^{\text{ref}}$ at 100% crystallinity is given as: $\Delta H_m^{\text{ref}} = 93 \text{J g}^{-1} \text{(PLA)}$ and 139 J g$^{-1}$ (PCL). $X_c$ is given by the following equation:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^{\text{ref}}} \times 100$$  \hspace{1cm} (1)

**Atomic Absorption Spectroscopy (AAS):** AAS was performed as follows: polymer samples (e.g. 1-PCL 20.1 mg; 1-PLA 20.3 mg) were immersed in 1M NaOH (1 mL - prepared from MilliQ water and solid NaOH) and the solution incubated for 5 days at 100 °C.
**Polymer Mass Loss Studies**: Hydrolytic degradation experiments were performed as follows: a 25-40 mg (approx. dimensions: 5 mm x 3 mm x 2 mm) pellet of either PLA or PCL (1 or Sn(Oct)₂-polymerized) was cut from precipitated bulk substrate. The pellet was placed in a pre-weighed, 2 mL Eppendorf tube and aqueous media (MilliQ (MQ) water, tap water (TW), phosphate-buffered saline (PBS) and 1M HCl) (1.5 mL) was added to the pellet. The resulting Eppendorf tube was then incubated at either 37 °C (thermostat-controlled incubator) (PLA samples 7/11 - Tables S10/11) or 70 °C (heated sand-bath) (all samples Table S10/11) for the appropriate time length (24 h, 72 h, or 168 h). Following the incubation time, if visible mass was still present, the solvent was removed by pipette and the sample exterior washed 3 times with distilled H₂O before careful freeze-drying in the same Eppendorf tube. After at least 24 h under vacuum, the remaining pellet and Eppendorf tube’s mass was obtained. Percentage mass change was calculated using Equation 2. Each experiment (polymer type, hydrolytic condition, incubation time and temperature) were repeated at least in triplicate. The percentage mass loss calculation is given by the following equation:

\[
\text{% Mass Loss} = \left( \frac{\text{Pre Incubated Pellet Mass}}{\text{Post Incubated or Freeze dried Pellet Mass}} \times 100 \right) - 100
\]

**Polymer Mass Loss Studies under “Environmental Conditions”**: Mass loss degradation experiments were performed as follows: a 50-100 mg pellet (approx. dimensions: 10 mm x 5 mm x 3 mm) of PLA (1 or Sn(Oct)₂-polymerized) was cut from precipitated bulk substrate (samples 7 and 11: Table S10/11). The pellet was placed in a pre-weighed, 15 mL Falcon tube and either filtered pond water (10 mL) or soil (~ 10 cm³) (see details below) was added to the pellet. The resulting Falcon tube, having had two holes punctured into the lid, was then stored outside on a west-facing balcony at the Heinrich-Heine-University Düsseldorf from 21.11.19 to 5.12.2019 under a partially elevated (using lab-jacks), top-weighted, transparent plastic box. Two time-points were used: 7 and 14 days. Each experiment (polymer type, hydrolytic condition, incubation time and temperature) were repeated at least in triplicate.

Following the incubation time, if visible mass was still present, the solvent was removed by pipette and the pellet exterior washed 3 times with distilled H₂O before careful freeze-drying in the same Falcon tube (Further washings to remove excess soil/associated coloration was conducted). After at least 24 h under vacuum, the remaining pellet and Falcon tube’s mass was obtained. Percentage mass change was calculated using Equation 2.

Pond water was obtained from a pond residing between buildings 26.32 and 26.33 of HHU Düsseldorf on 21.11.19. It was resultantly filtered and applied to the sample pellet. Soil was, also, obtained from the local environment around campus buildings 26.32/26.33. For weather conditions see Figure S34.

**Enzymatic Degradation**: See Polymer Mass Loss Studies above for full operational details except that the pellet was placed in a pre-weighed, 2 mL Eppendorf tube and immersed in enzyme-containing PBS (25 mg lyophilized enzyme in 50 mL PBS + 0.05% NaN₃; esterase derived from porcine liver CAS#: 9016-18-6) (1.5 mL) before incubation at 37 °C (thermostat-controlled incubator) for the appropriate time length (24 h, 72 h, or 168 h). Selected samples were used (samples 7 and 11 Table S10/11).

2. Experimental section

2.1. Complex synthesis

Complex 1 was synthesized as crystalline solid (for XRD) as well as amorphous solid. IR spectra verify the identity of the samples which enables to use the amorphous solid as catalyst in the ROP.
Method A: Zinc(II) trifluoromethylsulfonate (31.0 mg, 0.100 mmol, 1.0 eq) was dissolved under heating in THF (6 mL). Ligand (R,R)-DMEG (15.0 mg, 0.040 mmol, 0.4 eq) was also dissolved under heating in THF (4 mL). The solutions were combined while adding the zinc(II) trifluoromethylsulfonate solution to the ligand solution. Colorless crystals (10.0 mg, 9.54 \times 10^{-3} \text{ mmol}, 10\%) were obtained after four days at room temperature.

Method B: The complex synthesis as amorphous solid material was carried out analogously to method A. However, the amount of substance was used tenfold with the same volume of solvent. After combining the salt solution to the ligand solution, colourless solid precipitated. The solid was filtered and then washed first with tetrahydrofuran (THF) and subsequently with diethyl ether (Et\,2O) several times and dried under vacuum. A yield of 80\% (337 mg, 0.321 mmol) was obtained.

\[ \alpha_{25} \] due to the insolubility of the complex in any solvent at room temperature, the specific amount of rotation could not be determined.

\[^{1}H\text{ NMR}\] (400 MHz, CDCl\(_3\)): \(\delta = 3.76–3.73\) (m, 4H, \(\text{CH}_{\text{aliph.}}, \text{c}\)), 3.70–3.16 (m, 16H, \(\text{CH}_{2}\text{, g-h}\)), 3.01–2.75 (m, 24H, \(\text{CH}_{3}\text{, e,f}\)), 2.30–2.15 (m, 4H, \(\text{CH}_{2}\text{,aliph.}, \text{b}\)), 1.80–1.67 (m, 4H, \(\text{CH}_{2}\text{,aliph.}, \text{a}\)), 1.06–0.97 (m, 4H, \(\text{CH}_{2}\text{,aliph.}, \text{a}'\)) ppm.

\[^{13}C\text{ NMR}\] (100 MHz, CDCl\(_3\)):\(\delta = 165.9\) (C\(_{\text{gua}}, \text{d}\)), 68.1 (CH\(_{\text{aliph.}}, \text{c}\)), 50.6/48.7 (CH\(_{2}\text{, g-h}\)), 36.6/36.4 (CH\(_{3}\text{, e,f}\)), 31.9 (CH\(_{2}\text{,aliph.}, \text{b/b'}\)), 24.8/24.7 (CH\(_{2}\text{,aliph.}, \text{a/a'}\)) ppm.

\[\text{IR}\] (ATR), crystalline solid: \(\tilde{\nu} = 2939\) (w, \(\nu(\text{CH}_{\text{aliph.}})\)), 2862 (w, \(\nu(\text{CH}_{\text{aliph.}})\)), 1560 (s, \(\nu(\text{C=N}_{\text{gua}})\)), 1504 (m), 1421 (m), 1407 (m), 1384 (w), 1345 (w), 1264 (vs, \(\nu(\text{CF}_{3})\)), 1222 (m, \(\nu(\text{SO}_{3})\)), 1080 (w), 1063 (w), 1029 (vs, \(\nu(\text{SO}_{3})\)), 979 (w), 954 (w), 931 (w), 866 (m), 790 (w), 751 (w), 741 (m), 665 (w), 636 (vs, \(\delta_{d}(\text{SO}_{3})\)), 611 (m), 516 (m, \(\delta_{d}(\text{CF}_{3})\)), 477 (w), 434 (w), 407 (w) cm\(^{-1}\).

\[\text{IR}\] (ATR), amorphous solid: \(\tilde{\nu} = 2939\) (w, \(\nu(\text{CH}_{\text{aliph.}})\)), 2863 (w, \(\nu(\text{CH}_{\text{aliph.}})\)), 1560 (s, \(\nu(\text{C=N}_{\text{gua}})\)), 1505 (m), 1420 (m), 1407 (m), 1384 (w), 1346 (w), 1262 (vs, \(\nu(\text{CF}_{3})\)), 1222 (m, \(\nu(\text{SO}_{3})\)), 1136 (s, \(\nu(\text{SO}_{3})\)), 1081 (w), 1063 (w), 1029 (vs, \(\nu(\text{SO}_{3})\)), 979 (w), 954 (w), 931 (w), 865 (m), 790 (w), 753 (w), 741 (m), 665 (w), 635 (vs, \(\delta_{d}(\text{SO}_{3})\)), 611 (m), 516 (m, \(\delta_{d}(\text{CF}_{3})\)), 478 (w), 435 (w), 407 (w) cm\(^{-1}\).

\[\text{HRMS}\] (ESI): \(m/z\) calculated for C\(_{33}\)H\(_{60}\)F\(_{3}\)N\(_{12}\)O\(_{3}\)SZn\(^{+}\): 825.3868 [M - OTf\(^{-}\)]; found: 825.3863.

\[\text{EA}\] calculated (\%) for C\(_{38}\)H\(_{68}\)F\(_{6}\)N\(_{12}\)O\(_{7}\)S\(_{2}\)Zn (1048.53 g mol\(^{-1}\)): C: 43.53, H: 6.54, N: 16.03; found: C: 43.13, H: 6.58, N: 15.56.

The NMR data were deposited as original data in the repository Chemotion and are published under an Open Access model. The link to the original data is the following one: https://dx.doi.org/10.14272/RVBYFQZFRUDCA-WAFKZFKJSA-L.
2.2. NMR of complex 1

Figure S1: $^1$H-NMR spectrum of complex 1 (CDCl$_3$, 400 MHz). *: THF which is included in the crystal.
Figure S2: $^{13}$C-NMR spectrum of complex 1 (CDCl$_3$, 101 MHz). *: THF which is included in the crystal.
2.3. IR spectroscopy of complex 1

Figure S3: IR spectra of complex 1 as crystalline and amorphous solid sample.

The overlapping of the IR bands of the amorphous and crystalline solid sample shows identical bands for both solids. Therefore, the complex can also be used as an amorphous solid in the ROP.

2.4. Crystal data for complex 1:

Table S1: Crystallographic data for complexes 1.

| parameter                           | value                                      |
|-------------------------------------|--------------------------------------------|
| empirical formula                   | C_{38}H_{68}F_{6}N_{12}O_{7}S_{2}Zn         |
| formula mass [g mol^{-1}]           | 1048.53                                    |
| temperature [K]                      | 100(2)                                     |
| wavelength [Å]                       | 0.71073                                    |
| crystal system                       | Orthorhombic                               |
| space group                          | P2_12_12_1                                 |
| dimensions of the primitive unit cell| a = 10.1710(7) Å, α = 90°                  |
|                                     | b = 19.3775(14) Å, β = 90°                 |
|                                     | c = 24.3689(17) Å, γ = 90°                 |
| V [Å^3]                             | 4802.8(6)                                  |
| Z                                   | 4                                          |
| \(\rho_{cal} [\text{mg m}^{-3}]\)   | 1.350                                      |
| Absorption coefficient [mm^{-1}]    | 0.674                                      |
| F(000)                              | 2048                                       |
| crystal size [mm^3]                  | 0.350 x 0.150 x 0.100                      |
| \(\theta\)-range for data collection [°] | 1.343 to 30.508                              |
| limiting indices                    | -14 ≤ h ≤ 14, -27 ≤ k ≤ 27, -33 ≤ l ≤ 34 |
| independent reflections             | 14147                                      |
reflections collected 74457
$R_{int}$ 0.1409
completeness to $\theta=25.242$ [%] 100.0
absorption correction semi-empirical from equivalents
refinement method full-matrix least squares on $F^2$
data/restraints/parameters 14147/1/559
goodness-of-fit on $F^2$ 1.018
final R indices [I>2\sigma(I)] $R_1 = 0.0910$, $wR_2 = 0.2242$
R indices (all data) $R_1 = 0.1497$, $wR_2 = 0.2573$
absolute structure parameter 0.082(12)
extinction coefficient n/a
largest diff. peak and hole [e Å$^{-3}$] 1.262 and -0.760

Figure S4: Molecular structure of the complex cation [Zn{(R,R)-DMEG$_2$(1,2)ch}$_2$]$_2^+$ in crystals of 1 (ellipsoids drawn at the 50% probability level). The hydrogen atoms and the triflate anions are omitted for clarity.

2.5. Comparison of crystal structures

Table S2: Selected bond lengths, angles and structure parameters to compare complex 1 with literature known complex.

| Bond length [Å] | [Zn{(R,R)-DMEG$_2$(1,2)ch}$_2$]$_2$·THF (1) | [Zn(DMEG$_2$e)$_2$]([OTf]$_2$)$_2$[18] |
|-----------------|-------------------------------------------|----------------------------------|
| Zn–N$_{imin,qua}$ | 1.991(6), 2.067(8), 2.008(7), 2.004(7) | 2.028(3), 1.996(3), 2.021(3), 2.004(3) |

| Bond angle[Å] | |
|---------------|-----------------|-----------------|
| N–Zn–N       | 86.2(3), 138.0(3), 108.6(3), 111.0(3), 134.7(3), 145.3(1), 106.0(1), 85.5(1), 85.2(1), 105.3(1), 143.1(1) |

| Structure parameters | |
|----------------------|-----------------|
| $\rho$               | 0.95, 0.96      |
| $\tau$               | 0.62            |

$\rho = 2a/(b + c)$,[20] $\tau = [360° - (\alpha + \beta)]/141°$.[20]
SUPPORTING INFORMATION

2.6. Computational results

Table S3: NBO charges (in e⁻ units) and charge transfer energies (in kcal/mol) for selected atoms for the cation of 1 and the cation of [Zn(DMEG₂e)₂][OTf]₂ (NBO6.0. TPSSH/def2-TZVP and the empirical dispersion correction with Becke-Johnson damping)

|                      | Cation of 1 | Cation of [Zn(DMEG₂e)₂][OTf]₂ |
|----------------------|-------------|-------------------------------|
| **NBO charges**      |             |                               |
| Zn                   | 1.66        | 1.65                          |
| N(gua)               | -0.79       | -0.79                         |
| **Charge transfer energies** |         |                               |
| N(gua) → Zn          | 29.5        | 33.0                          |

Figure S5: Visualization of the lone-pair of the guanidine moiety of the cation in 1 (right) and the cation in [Zn(DMEG₂e)₂][OTf]₂ (left). The depicted angle is 39° for the cation in 1 and 34° for the cation in [Zn(DMEG₂e)₂][OTf]₂.

2.7. TGA of complex 1

The thermal stability of complex 1 was tested at 150 °C and 200 °C for one hour in each case. A mass loss percentage of about 10% is detected during the heating phase for both measurements. This can be assigned to the residual THF in the crystal structure, which evaporates at around 65 °C. During the isothermal conditions of 150 °C and 200 °C no further significant mass loss was detected.

Figure S6: Left: TGA measurement of the zinc-guanidine complex 1 at 150 °C. Right: TGA measurement of the zinc-guanidine complex 1 at 200 °C.
2.8. Polymerization monitored by in situ-Raman spectroscopy

The reactor was heated at 150 °C under vacuum and flashed three times with argon. The reactions were conducted under argon atmosphere and a stirrer speed of 260 rpm was applied. Sample collection started after the reaction mixture insertion as soon as the reactor was closed. The reaction time was adjusted to the [M]/[I]-ratio.

**Lactide polymerization**: Either non-purified technical grade *rac*-lactide or sublimated *L*-lactide were used. In a nitrogen filled glovebox, lactide (8.00 g, 55.5 mmol) and the catalyst were weighted in and mixed thoroughly in a mortar. The reaction mixture was filled in a glass vial and removed from the glovebox. The reaction mixture was transferred to the pre-heated reactor in argon counterflow and the *in situ*-Raman measurement started.

**ε-caprolactone polymerization**: In a nitrogen filled glovebox ε-caprolactone (8.00 mL, 8.64 g, 75.7 mmol, 1.08 g cm⁻¹) was added in a glass vial via single-channel pipette with variable volume (100–1000 μL). The catalyst was weighted out and added to the glass vial. Due to the solubility of the catalyst in ε-caprolactone, homogeneity could be ensured. The glass vial including the reaction mixture was removed from the glovebox and the reaction mixture was transferred to the pre-heated reactor in argon counterflow.

After the polymerizations (LA- or CL polymerization) were stopped, the reaction mixture was removed from the reactor and a ¹H NMR spectrum was collected to determine the conversion. The polymer was dissolved in an appropriate amount of DCM, then precipitated in ethanol at room temperature and dried under vacuum. To determine the molar mass, the dried polymer was characterized via GPC.

2.9. Polymerization in Schlenk tubes (solvent polymerization)

For a polymerization in Schlenk tubes recrystallized *L*-lactide was used. In a nitrogen filled glovebox, lactide (1.153 g, 8.00 mmol) and the catalyst were weighted in. Schlenk tubes with stirring bars were filled with the respective [M]/[I] ratio of the mixture, closed air-proof with a Young closure and removed from the glovebox. The solvent (dry THF, toluene or diphenylehter) was added to the Schlenk tube under inert gas atmosphere. After fixing the Schlenk tubes in an oil bath of 55 °C, 100 °C or 150 °C and 260 rpm, the reaction time started. After a defined reaction time, aliquots for NMR spectroscopy and GPC characterization were taken from the Schlenk tube with a glass pipette. To stop the polymerization the Schlenk tube was removed from the oil bath and cooled down under running water. The conversion was determined via ¹H NMR spectroscopy for each sample after removing the solvent out of the samples. Samples with high polymer conversion were dissolved in an appropriate amount of DCM, then precipitated in ethanol at room temperature and dried under vacuum. To determine the molar mass, the dried polymer was characterized via GPC.
3. Data of polymerization experiments

3.1. Solvent-free polymerization of lactide

Table S4: Polymerization details for the polymerization of non-purified technical rac-LA with complex 1.

| Entry | [M]/[I] ratio | $k_{app}[b]$ [s$^{-1}$] | $t$ [s] | conv.[c] [%] | $M_{n,exp}[d]$ [g mol$^{-1}$] | $M_{n,calc}$ [g mol$^{-1}$] | $ar{D}[e]$ |
|-------|---------------|------------------------|--------|-------------|-----------------|-----------------|----------|
| 1     | 500:1         | 0.0359                 | 150    | 94          | 33900           | 67700           | 1.6      |
| 2     | 500:1         | 0.0346                 | 321    | 94          | 39800           | 67700           | 1.4      |
| 3     | 1250:1        | 0.0225                 | 441    | 89          | 83600           | 160000          | 1.6      |
| 4     | 2000:1        | 0.0185                 | 700    | 82          | 90800           | 236000          | 1.6      |
| 5     | 2500:1        | 0.0177                 | 886    | 80          | 71900           | 288300          | 1.5      |
| 6     | 2500:1        | 0.0159                 | 611    | 70          | 67600           | 252000          | 1.5      |
| 7[a]  | 5000:1        | 0.0011                 | 2416   | 32          | -               | 231000          | -        |
| 8[f]  | 5000:1        | 0.0323                 | 231    | 74          | 146000          | 533000          | 1.7      |

[a] Polymerization conditions: catalyst 1, 150 °C, non-purified technical grade rac-LA, solvent-free polymerization, stirrer speed: 260 rpm. [b] The rate constant $k_{app}$ was determined by plotting ln([LA]$_0$/[LA]) vs. $t$. [c] Determined by $^1$H NMR spectroscopy. [d] Determined by GPC in THF. [e] Polymers could not precipitate because of too short chains. Moreover, at these low catalyst loadings, the reproducibility is limited. [f] Use of sublimated L-LA.

The apparent polymerization rate constant $k_{app}$ was obtained by linear regression of the semilogarithmic plot. For error determination the corresponding experiment was reproduced. The average value of $k_{app}$ and the standard deviation of the double determination was plotted in the $k_p$ graph (Figure 2). The polymerization was carried out to high conversion and stopped at a high viscosity of the samples, resulting in different reaction times.

Figure S8: Semi-logarithmic plots for the polymerization of non-purified technical rac-LA catalyzed by 1.

A few graphs in Figure S8 show a delayed gradient because the added lactide sometimes takes a few seconds to melt completely in the reactor. The high reaction rate of complex 1 impedes the in situ measurements for a sufficient amount of kinetic data points (Figure S8).
**Figure S9:** *in situ-*Raman spectrum with LA peak at 656 cm\(^{-1}\) and PLA peak at 872 cm\(^{-1}\). Polymerization conditions: [M]/[I] ratio of 1250:1, 150 °C, 260 rpm, non-purified technical grade rac-LA.

**Figure S10:**

*A:* colorless, transparent PLA polymerized with L-LA ([M]/[I] ratio: 2000:1) (left) and with rac-LA ([M]/[I] ratio: 1000:1) (right). 

*B:* PLA foil produced with complex 1.
Figure S11: Semi-logarithmic plot for the polymerization of technical grade rac-LA catalyzed by 1. [M]/[I] ratio: 5000:1, T = 150 °C, measured by in situ-Raman spectroscopy.

The decreased activity at around 200 s is due to the impurities of e.g. water and lactic acid residues in the used technical grade rac-LA.

Figure S12: Semi-logarithmic plot for the polymerization of sublimated L-LA catalyzed by 1. [M]/[I] ratio: 5000:1, T = 150 °C, measured by in situ-Raman spectroscopy.

The delayed gradient at the beginning is caused by the fact that it takes a few seconds until lactide is molten completely in the reactor. The flattening at about 100 s is due to high viscosity (compare Table S4).
Figure S13: Extract from a homonuclear decoupled $^1$H NMR spectrum from the LA polymerization with complex 1, [M]/[I] ratio of 500:1 at 298 K, with i = isotactic and s = syndiotactic; $P_r$ value of 0.55.
### 3.2. ε-Caprolactone polymerization

**Table S5:** Polymerization details for the polymerization of ε-CL with complex 1 and Sn(Oct)$_2$.

| Entry | catalyst  | [M]/[I] ratio | $k_{\text{app}}$ | $t$ [s] | conv.[c] [%] | $M_n,\text{exp.}$ | $M_n,\text{calc}$ | $\Theta$[d] |
|-------|-----------|---------------|------------------|--------|-------------|----------------|----------------|-----------|
| 1     | 1         | 500:1         | 8.18            | 1096   | 60          | 128000        | 34200          | 1.5       |
| 2     | 1         | 500:1         | 9.12            | 531    | 55          | 129000        | 31400          | 1.5       |
| 3     | 1         | 1000:1        | 4.28            | 1696   | 52          | 116000        | 59400          | 1.5       |
| 4     | 1         | 1500:1        | 2.91            | 2596   | 60          | 101000        | 103000         | 1.5       |
| 5     | 1         | 2000:1        | 1.76            | 3165   | 53          | 107000        | 121000         | 1.5       |
| 6     | 1         | 2500:1        | 1.27            | 5131   | 42          | 105000        | 120000         | 1.6       |
| 7     | 1         | 2500:1        | 0.950           | 6871   | 37          | 87000         | 106000         | 1.4       |
| 8[e]  | 1         | 5000:1        | 0.400           | 7621   | 12          | -             | 68500          | -         |
| 9     | Sn(Oct)$_2$ | 500:1        | 6.23            | 1500   | 71          | n.d.          | n.d.           | n.d.      |
| 10    | Sn(Oct)$_2$ | 500:1        | 5.37            | 1500   | 56          | n.d.          | n.d.           | n.d.      |
| 11    | Sn(Oct)$_2$ | 750:1        | 4.06            | 2100   | 53          | n.d.          | n.d.           | n.d.      |
| 12    | Sn(Oct)$_2$ | 1000:1       | 3.34            | 2700   | 64          | n.d.          | n.d.           | n.d.      |
| 13    | Sn(Oct)$_2$ | 2000:1       | 2.10            | 4500   | 66          | n.d.          | n.d.           | n.d.      |
| 14    | Sn(Oct)$_2$ | 2500:1       | 1.87            | 5400   | 75          | n.d.          | n.d.           | n.d.      |
| 15    | Sn(Oct)$_2$ | 2500:1       | 1.43            | 5400   | 53          | n.d.          | n.d.           | n.d.      |

[a] Polymerization conditions: catalyst 1, 150 °C, ε-CL, solvent-free polymerization, stirrer speed: 260 rpm. [b] The rate constant $k_{\text{app}}$ was determined by plotting $\ln([\text{LA}]_0/[\text{LA}]_t)$ vs. $t$. [c] Determined by $^1$H NMR spectroscopy. [d] Determined by GPC in THF. [e] Polymers could not precipitate because of too short chains. n.d. = not determined.

The apparent polymerization rate constant $k_{\text{app}}$ was obtained by linear regression of the semilogarithmic plot. For error determination the corresponding experiment was reproduced. The average value of $k_{\text{app}}$ and the standard deviation of the double determination was plotted in the $k_p$ graph (Figure 3). The polymerization was carried out to high conversion and stopped at a high viscosity of the samples, resulting in different reaction times.
Figure S14: Semi-logarithmic plots for the polymerization of ε-CL catalyzed by 1.

Figure S15: Semi-logarithmic plots for the polymerization of ε-CL catalyzed by Sn(Oct)₂.
Figure S16: in situ-Raman spectrum with $\varepsilon$-CL peaks at 733 cm$^{-1}$ and 696 cm$^{-1}$. Polymerization conditions: [M]/[I] ratio of 500:1, 150 °C, 260 rpm, distilled $\varepsilon$-CL.

Figure S17: Left: colorless PCL polymerized with complex 1 ([M]/[I] ratio: 1000:1). Right: colorless PCL polymerized with Sn(Oct)$_2$ ([M]/[I] ratio: 1000:1).
3.3. Solution polymerization of lactide

Table S6: Polymerization details for the solvent polymerization of recrystallized \(L\)-LA with complex 1 and Sn(Oct)$_2$.

| Entry | catalyst | solvent | [M]/[I] ratio | \(k_{\text{app}}\) $10^{-3}$ [s$^{-1}$] | \(t\) [min] | conv.\(^{c}\) [\%] | \(M_{n,\text{exp}}\) \(^{d}\) [g mol$^{-1}$] | \(M_{n,\text{calc}}\) \(^{d}\) [g mol$^{-1}$] | \(D\) \(^{d}\) |
|-------|----------|---------|---------------|--------------------------------|----------|----------------|----------------|----------------|-------|
| 1     | 1        | THF     | 500:1         | -                               | 1440     | -              | -              | -              | -     |
| 2     | 1        | toluene | 300:1         | 1.37                            | 15       | 65             | 43600          | 28100          | 1.3   |
| 3     | 1        | toluene | 300:1         | 1.28                            | 15       | 61             | 39300          | 26400          | 1.3   |
| 4     | 1        | toluene | 400:1         | 1.11                            | 15       | 43             | n.d.           | n.d.           | n.d.  |
| 5     | 1        | toluene | 400:1         | 0.914                           | 15       | 47             | n.d.           | n.d.           | n.d.  |
| 6     | 1        | toluene | 500:1         | 0.962                           | 15       | 51             | n.d.           | n.d.           | n.d.  |
| 7     | 1        | toluene | 500:1         | 0.632                           | 15       | 35             | n.d.           | n.d.           | n.d.  |
| 8\[a\] | 1        | toluene | 750:1         | 0.463                           | 15       | 28             | -              | -              | -     |
| 9\[a\] | 1        | toluene | 750:1         | 0.351                           | 15       | 18             | -              | -              | -     |
| 10\[a\] | 1   | toluene | 1000:1        | 0.363                           | 15       | 24             | -              | -              | -     |
| 11    | 1        | toluene | 1000:1        | 0.524                           | 15       | 37             | 36000          | 53300          | 1.2   |
| 12\[f\] | 1   | toluene | 500:1:1       | 2.7                             | 15       | 72             | 37200          | 25900          | 1.1   |
| 13\[f\] | 1   | toluene | 500:10:1      | 7.7                             | 15       | 96             | -              | -              | -     |
| 14    | 1        | diphenyl ether | 1000:1      | 3.0                            | 5        | 46             | n.d.           | n.d.           | n.d.  |
| 15    | Sn(Oct)$_2$ | toluene | 100:1         | 0.178                           | 45       | 35             | n.d.           | n.d.           | n.d.  |
| 16    | Sn(Oct)$_2$ | toluene | 100:1         | 0.167                           | 45       | 33             | n.d.           | n.d.           | n.d.  |
| 17\[f\] | Sn(Oct)$_2$ | toluene | 300:1         | 0.0686                          | 20       | 8              | -              | -              | -     |
| 18\[f\] | Sn(Oct)$_2$ | toluene | 350:1         | 0.0859                          | 20       | 6              | -              | -              | -     |
| 19\[f\] | Sn(Oct)$_2$ | toluene | 400:1         | 0.0827                          | 45       | 18             | -              | -              | -     |
| 20\[f\] | Sn(Oct)$_2$ | toluene | 500:1         | 0.0705                          | 45       | 15             | -              | -              | -     |
| 22\[f\] | Sn(Oct)$_2$ | toluene | 600:1         | 0.0710                          | 45       | 16             | -              | -              | -     |
| 23\[f\] | Sn(Oct)$_2$ | toluene | 600:1         | 0.0534                          | 45       | 12             | -              | -              | -     |

\[a\] Polymerization conditions: complex 1, recrystallized \(L\)-LA, \(c(L\)-LA \(= 1.0\) mol L$^{-1}$, \(T(\text{THF}) = 55\) °C, \(T(\text{toluene}) = 100\) °C, \(T(\text{diphenyl ether}) = 150\) °C; stirrer speed: 260 rpm. \[b\] The rate constant \(k_{\text{app}}\) was determined by plotting ln([LA]$\Rightarrow$[LA]) vs. \(t\). \[c\] Determined by \(^1\)H NMR spectroscopy. \[d\] Determined by GPC in THF. \[e\] Polymers could not precipitate because of too short chains. \[f\] Used co-initiator benzyl alcohol, [M]/[Co–I]/[I], n.d. = not determined.

The apparent polymerization rate constant \(k_{\text{app}}\) was obtained by linear regression of the semilogarithmic plot. For error determination the corresponding experiment was reproduced. The average value of \(k_{\text{app}}\) and the standard deviation of the double determination was plotted in the \(k_p\) graph (Figure 4).
Figure S18: Semi-logarithmic plots for the polymerization of recrystallized L-LA catalyzed by 1 in toluene. Sometimes it takes a few seconds to melt the lactide completely in solution which explains the delayed gradient at the beginning.

Figure S19: Semi-logarithmic plots for the polymerization of recrystallized L-LA catalyzed by Sn(Oct)$_2$ in toluene.
Table S7: Polymerization details for the solvent polymerization with complex 1 at 500:1.

| Entry | t [min] | conv. [%] | $M_{n,exp}$ [g mol$^{-1}$] | $M_{n,calc}$ [g mol$^{-1}$] | $D$ |
|-------|---------|-----------|-----------------|-----------------|-----|
| 1     | 1       | 0         | -               | -               | -   |
| 2     | 3       | 4         | -               | -               | -   |
| 3     | 5       | 13        | -               | -               | -   |
| 4     | 7       | 24        | -               | -               | -   |
| 5     | 9       | 36        | 32100           | 25900           | 1.2 |
| 6     | 11      | 45        | 37500           | 32400           | 1.2 |
| 7     | 13      | 51        | 32400           | 36800           | 1.3 |
| 8     | 15      | 46        | 35700           | 33100           | 1.2 |
| 9     | 30      | 77        | 47000           | 55490           | 1.3 |

[a] Polymerization conditions: complex 1, [M]/[I] ratio: 500:1, recrystallized L-LA in toluene, c(L-LA) = 1.0 mol L$^{-1}$, 100 °C, stirrer speed: 260 rpm. Samples with a shorter reaction time resulted in short chain polymers, which could not be determined via GPC. [b] Determined by $^1$H NMR spectroscopy. [c] Determined by GPC in THF.

Table S8: Polymerization details for the solvent polymerization with complex 1 and benzyl alcohol as co-initiator at 500:1:1.

| Entry | [M]/[I] ratio | t [min] | conv. [%] | $M_{n,exp}$ [g mol$^{-1}$] | $M_{n,calc}$ [g mol$^{-1}$] | $D$ |
|-------|---------------|---------|-----------|-----------------|-----------------|-----|
| 1     | 500:1:1       | 1       | 2         | -               | -               | -   |
| 2     | 500:1:1       | 3       | 13        | -               | -               | -   |
| 3     | 500:1:1       | 5       | 44        | -               | -               | -   |
| 4     | 500:1:1       | 7       | 64        | -               | -               | -   |
| 5     | 500:1:1       | 9       | 70        | 37500           | 25200           | 1.04|
| 6     | 500:1:1       | 11      | 75        | 39900           | 27000           | 1.1 |
| 7     | 500:1:1       | 13      | 72        | 48600           | 25900           | 1.1 |
| 8     | 500:1:1       | 15      | 72        | 37200           | 25900           | 1.1 |
| 9     | 500:1:1       | 30      | 91        | 52300           | 32800           | 1.1 |

[a] Polymerization conditions: complex 1, benzy alcohol as co-initiator, [M]/[Co-I]/[I] ratio 500:1:1, recrystallized L-LA in toluene, c(L-LA) = 1.0 mol L$^{-1}$, 100 °C, stirrer speed: 260 rpm. Samples with a shorter reaction time resulted in short chain polymers, which could not be determined via GPC. [b] Determined by $^1$H NMR spectroscopy. [c] Determined by GPC in THF.
Figure S20: Determination of $k_{\text{app}}$ of complex 1 with recrystallized L-LA in diphenylether. With a [M]/[I] ratio of 1000:1, at 150 °C, 260 rpm, c(LA) = 1.0 mol L$^{-1}$.

3.4. Conversion determination by 1H NMR spectroscopy

Figure S21: Example of $^1$H NMR spectrum of lactide polymerization. rac-LA, [M]/[I] = 1000:1.
Figure S22: Example of $^1$H NMR spectrum of $\varepsilon$-caprolactone polymerization. $[M]/[I] = 2000:1$. 

polycaprolactone

caprolactone
3.5. MALDI-ToF-MS

Figure S23: MALDI-ToF-MS results for PLA, sample produced by catalyst 1 and co-initiator BnOH with [M]/[I]/[Co-I] ratio 50:1:1. Exemplary calculations: 2147.70 = 28 x repeating unit (72.02 g mol⁻¹) + BnOH + Na⁺; 2151.70 = 16 x repeating unit + complex + Na⁺.
Figure S24: MALDI-ToF-MS results for PCL, sample produced by catalyst 1 and co-initiator BnOH with [M]/[I]/[Co-I] ratio 50:1:1. Exemplary calculations: 2070.24 = 17 \times \text{repeating unit} (114.07 \text{ g mol}^{-1}) + \text{BnOH} + \text{Na}^+; 2075.25 = 9 \times \text{repeating unit} + \text{complex} + \text{THF} + \text{Na}^+.
### Table S9: End groups determined by MALDI-ToF-MS for PLA and PCL.

| End groups | PLA[^b] | PCL[^c] |
|------------|---------|---------|
| OH         | yes     | yes     |
| EtOH       | yes     | yes     |
| Ligand     | yes     | yes     |
| Ligand-Zn  | yes     | yes     |
| Complex    | yes     | yes     |
| Co-initiator[^d] | yes | yes |

[^a]: reaction conditions: [M]/[I]/[Co-I] ratio 50:1:1, 150 °C, 260 rpm. [^a]: reaction time: 80 s, 46%. [^b]: reaction time: 180 s, conversion 69%. [^d]: Benzyl alcohol.

The observation of ethanol as end group can be traced back to its use for polymer precipitation; the presence of water as end group originates from the impurity of technical grade LA.
4. Degradation studies

Following catalyst characterization, extensive degradation studies were conducted on PCL and PLA samples produced using 1 and Sn(Oct)$_2$.

4.1. Polymer Sample Baseline Properties

Table S10: Collated macromolecular properties for PCL and PLA samples.

| Sample | Material | Catalyst | $t$ [min] | conv. [%] | $M_w$ [g mol$^{-1}$] | $M_n$ [g mol$^{-1}$] | $D$ |
|--------|----------|----------|-----------|-----------|---------------------|---------------------|-----|
| 1      | CL       | 1        | 40        | 60        | 169000              | 104000              | 1.6 |
| 2      | CL       | 1        | 40        | 66        | 305000              | 174000              | 1.8 |
| 3      | CL       | 1        | 40        | 66        | 236000              | 139000              | 1.7 |
| Average| CL       | 1        | -         | -         | 237000              | 139000              | 1.7 |
| 4      | CL       | Sn(Oct)$_2$ | 40  | 78        | 121000              | 79100               | 1.5 |
| 5      | CL       | Sn(Oct)$_2$ | 40  | 92        | 270000              | 156000              | 1.7 |
| 6      | CL       | Sn(Oct)$_2$ | 40  | 70        | 274000              | 161000              | 1.7 |
| Average| CL       | Sn(Oct)$_2$ | -   | -         | 222000              | 132000              | 1.7 |
| 7      | L-LA     | 1        | 8         | 93        | 118000              | 72500               | 1.6 |
| 8      | L-LA     | 1        | 8         | 92        | 190000              | 125000              | 1.6 |
| 9      | L-LA     | 1        | 8         | 92        | 190000              | 112000              | 1.7 |
| 10     | L-LA     | 1        | 8         | 92        | 196000              | 127000              | 1.6 |
| Average| L-LA     | 1        | -         | -         | 176000              | 109000              | 1.6 |
| 11     | L-LA     | Sn(Oct)$_2$ | 12  | 70        | 119000              | 67900               | 1.8 |
| 12     | L-LA     | Sn(Oct)$_2$ | 12  | 76        | 182000              | 120000              | 1.5 |
| 13     | L-LA     | Sn(Oct)$_2$ | 12  | 63        | 224000              | 158000              | 1.4 |
| 14     | L-LA     | Sn(Oct)$_2$ | 12  | 84        | 139000              | 82800               | 1.7 |
| Average| L-LA     | Sn(Oct)$_2$ | -   | -         | 166000              | 107000              | 1.6 |
| 15     | rac-LA   | 1        | 6         | 83        | 834000              | 499000              | 1.7 |
| 16     | rac-LA   | Sn(Oct)$_2$ | 9   | 66        | 503000              | 31700               | 1.6 |

[a] CL = ε-caprolactone; L-LA = L-lactide; rac-LA = racemic-lactide; Sn(Oct)$_2$ = tin(II) bis(2-ethylhexanoate). Polymerization conditions: 150 °C, solvent-free polymerization, stirrer speed: 260 rpm. The polymerization was stopped at a high viscosity of the samples, resulting in different reaction times. [b] Determined by $^1$H NMR spectroscopy. [c] Determined by GPC-B in THF.

See below for molecular weight distributions graphs for each of the samples in Table S10.
### Supporting Information

#### Entry 1 - 1-PCL

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 2 - 1-PCL

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 3 - 1-PCL

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 4 - Sn-PCL

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 5 - Sn-PCL

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 6 - Sn-PCL

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 7 - 1-PLA

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0

#### Entry 8 - 1-PLA

**Molecular Mass (g mol\(^{-1}\))**

- **Relative Intensity**
  - 0.0
  - 0.5
  - 1.0
4.1.1. NMR spectroscopy

*Figure S25: $^1$H NMR comparison (Sn-PCL-4 (above-turquoise) vs. 1-PCL-1 (below-red)).*
Figure S26: $^1$H NMR comparison (Sn-PLA-7 (above-turquoise) vs. 1-PLA-11 (below-red)).

Figure S27: $^1$H NMR spectra of the methine region of PLA using recrystallized L-LA. Decoupled peaks are labeled with corresponding stereosequences. A: 1-PLA. B: homonuclear decoupled PLA\textsuperscript{[21]} polymerized with complex 1. C: Sn-PLA and D: homonuclear decoupled PLA polymerized with complex Sn(Oct)$_2$. 
Figure S28: \(^1\)H NMR spectra of the methine region of PLA using recrystallized L-LA. Decoupled peaks are labeled with corresponding stereosequences. **A**: Sn-PLA with Co-Initiator. **B**: homonuclear decoupled PLA\(^{[21]}\) prepared with Sn(Oct)_2 and benzyl alcohol, [M]:[I]:[Co-I] = 1000:1:10. **C**: commercially available PLA and **D**: homonuclear decoupled PLA of the commercially available PLA sample.
### 4.1.2. Differential Scanning Calorimetry

Table S11: Collated thermal properties for PLA and PCL samples as determined by DSC.

| Sample | Monomer | Catalyst | T\(_g\) [°C] | T\(_m\) [°C] | \(\Delta H_m\) [J.g\(^{-1}\)] | \(\chi_c\) [%] |
|--------|---------|----------|-------------|-------------|----------------------------|--------------|
| 1      | CL      | 1        | N.M.        | 55          | 62                        | 44           |
| 2      | CL      | 1        | N.M.        | 56          | 63                        | 45           |
| 3      | CL      | 1        | N.M.        | 56          | 64                        | 46           |
| **Average** | **CL** | **1** | **N.M.** | **55 ± 0.5** | **63 ± 1** | **45 ± 1** |
| 4      | CL      | Sn(Oct)\(_2\) | N.M.    | 57          | 61                        | 44           |
| 5      | CL      | Sn(Oct)\(_2\) | N.M.    | 57          | 65                        | 47           |
| 6      | CL      | Sn(Oct)\(_2\) | N.M.    | 56          | 67                        | 48           |
| **Average** | **CL** | **Sn(Oct)\(_2\)** | **N.M.** | **56 ± 0.5** | **64 ± 3** | **46 ± 2** |
| 7      | L-LA    | 1        | 60          | 176         | 57                        | 61           |
| 8      | L-LA    | 1        | 56          | 175         | 57                        | 61           |
| 9      | L-LA    | 1        | 56          | 176         | 52                        | 56           |
| 10     | L-LA    | 1        | 58          | 175         | 56                        | 60           |
| **Average** | **L-LA** | **1** | **58 ± 2** | **175 ± 0.5** | **55 ± 2** | **60 ± 2** |
| 11     | L-LA    | Sn(Oct)\(_2\) | 34        | 171         | 38                        | 41           |
| 12     | L-LA    | Sn(Oct)\(_2\) | 49        | 176         | 44                        | 47           |
| 13     | L-LA    | Sn(Oct)\(_2\) | 56        | 175         | 51                        | 55           |
| 14     | L-LA    | Sn(Oct)\(_2\) | 53        | 175         | 42                        | 45           |
| **Average** | **L-LA** | **Sn(Oct)\(_2\)** | **48 ± 9** | **174 ± 2** | **43 ± 5** | **47 ± 6** |
| 15     | rac-LA  | 1        | 48          | N.D.        | N.D.                      | N.D.         |
| 16     | rac-LA  | Sn(Oct)\(_2\) | 46        | N.D.        | N.D.                      | N.D.         |
| 17\[^b\] | L-LA    | 51        | 149         | 19          | 20                        |               |

[a] CL = ε-caprolactone; L-LA = L-lactide; rac-LA = racemic-lactide; Sn(Oct)\(_2\) = tin(II) bis(2-ethylhexanoate); N.M. = not measured; N.D. = not determined, the standard deviation of the mean is the associated error. [b] Thermal properties of commercially available PLLA, a cup sample (Art. P60) from Huhtamaki.

See below for the normalized curves for all entries in Table S11.
SUPPORTING INFORMATION

Entry 1: 1-PCL

Sample mass: 3.94 mg
$\Delta H_m$ integral: 246.67 mJ
$T_m$ peak: 55.7 °C

Entry 2: 1-PCL

Sample mass: 7.58 mg
$\Delta H_m$ integral: 401.29 mJ
$T_m$ peak: 56.6 °C

Entry 3: 1-PCL

Sample mass: 7.62 mg
$\Delta H_m$ integral: 491.71 mJ
$T_m$ peak: 56.5 °C

Entry 4: Sn-PCL

Sample mass: 5.35 mg
$\Delta H_m$ integral: 328.69 mJ
$T_m$ peak: 57.8 °C

Entry 5: Sn-PCL

Sample mass: 6.85 mg
$\Delta H_m$ integral: 451.70 mJ
$T_m$ peak: 57.1 °C

Entry 6: Sn-PCL

Sample mass: 12.42 mg
$\Delta H_m$ integral: 841.75 mJ
$T_m$ peak: 56.9 °C

Entry 7: 1-PLA (L-LA)

Sample mass: 3.83 mg
$\Delta H_m$ integral: 220.81 mJ
$T_m$ peak: 176.1 °C
$T_o$ onset: 57.5 °C

Entry 8: 1-PLA (L-LA)

Sample mass: 5.58 mg
$\Delta H_m$ integral: 323.42 mJ
$T_m$ peak: 175.8 °C
$T_o$ onset: 53.3 °C
Entry 17: commercially available PLA (J-LA)

Sample mass: 5.88 mg
$\Delta H_m$ integral: 110.12 mJ
$T_m$ peak: 149.2 °C
$T_g$ onset: 51.1 °C

Calibration Standard
1-PCL
1-PLA
Blank Aqueous Solution

Concentration / mg L$^{-1}$ vs. Absorbance Reading

Concentration / mg L$^{-1}$ vs. Absorbance Reading

Concentration / mg L$^{-1}$ vs. Absorbance Reading
### Table: Zn Content

|                      | PCL       | PLA       |
|----------------------|-----------|-----------|
| Zn concentration (10 mL solution) | 0.7 mg/L  | 0.5 mg/L  |
| Zn content per gram polymer         | 0.3 mg/g  | 0.3 mg/g  |
| Zn weight % in precipitated polymer | 0.03 %    | 0.03 %    |

Figure S29: Above: Graph displaying Zn concentration as determined by atomic absorption spectroscopy with two expansions (error bars represent standard deviation across all samples tested). Below: Zn content as derived from atomic spectroscopy in 10 mL sample solution, calculated Zn content in original polymer samples, and their % weight content.

Figure S30: Compiled mass loss studies for all polymer samples in MilliQ H$_2$O incubated at 70 °C for either 1, 3, or 7 days (7 day averages reported in Figure 5 - error bars represent the standard error of the mean).

Figure S31: 1-PLA (entry 7) mass loss studies at 37 °C in MilliQ (MQ), tap water (TW), PBS, and 1M HCl after 1, 3, 7 days. Each point represents at least 3 replicates. Error bars represent the standard error of the mean.
### Figure S32: Sn-PLA (entry 11) mass loss studies at 37 °C in MilliQ (MQ), tap water (TW), PBS, and 1M HCl after 1, 3, 7 days. Each point represents at least 3 replicates. Error bars represent the standard error of the mean.

![Graph showing mass loss studies for Sn-PLA](image)

### Figure S33: Comparison of mass loss studies for PLA samples in either PBS (taken from Figure S31/32) or an esterase-PBS solution maintained at 37 °C for either 1, 3, or 7 days. Error bars represent the standard error of the mean.

![Graph showing comparison of mass loss studies](image)
Figure S34: Weather information pertaining to minimum and maximum temperatures and rainfall (worldweatheronline.com).

Figure S35: PLA mass loss studies having been kept under "real world" conditions for either 7 or 14 days immersed in filtered pond water. Each point represents at least 3 replicates. Error bars represent the standard error of the mean.
Figure S36: PLA mass loss studies having been kept under "real world" conditions for either 7 or 14 days immersed in soil. Each point represents at least 3 replicates. Error bars represent the standard error of the mean.

5. References

[1] W. L. F. Ammarenge, Purification of Laboratory Chemicals, 8th ed., Elsevier Inc., Oxford, 2017.
[2] A. Metz, P. McKown, B. Esser, C. Gohlke, K. Kröckert, L. Laurini, M. Schechenbach, S. N. McCormick, M. Oswald, A. Hoffmann, M. D. Jones, S. Herres-Pawlis, *Eur. J. Inorg. Chem.* 2017, 5557–5570.
[3] Bruker, SMART (Version 5.6.01), SAINT (Version 8.3.7A) and SADABS (Version 2008/1), Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
[4] Bruker, XPREP Vers 5.1/NT, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
[5] G. S. SHELXS, Acta Crystallogr., Sect. A, 1990, 46, 467–473.
[6] C. B. Höschle, G. M. Sheldon, B. Dittrich, *J. Appl. Crystalogr.* 2011, 44, 1281–1284.
[7] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands), 2008.
[8] A. L. Spek, Acta Crystallogr. D 2009, 65, 148–155.
[9] S. Hardy, I. M. de Wispelaere, W. Leitner, M. A. Liauw, *Analyst* 2013, 138, 819–824.
[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Peters, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, R. E. Stratmann, J. C. Cammi, N. Ochterski, M. Katsoulis, M. F. Rega, G. A. Peters, H. N. Ayala, P. Morokuma, N. Rajh, J. A. Foresman, J. V. Ortiz, K. E. Cioslowski, Q. Cui, I. Li, B. B. P. Stewart, M. Gomperts, E. S. Martin, K. D. Fox, D. J. Fox, R. Gomperts, W. Chai, S. Mennucci, M. P. Hratchian, J. V. Ortiz, J. Cioslowski, D. J. Fox, J. Compu. Chem. 2010, 31, 1684–1687.
[11] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, Phys. Rev. Lett. 2003, 91, 146401; b) V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, J. Chem. Phys. 2003, 119, 12129–12137; c) V. N. Staroverov, G. E. Scuseria, J. Tao, J. P. Perdew, J. Chem. Phys. 2004, 121, 11507–11507.
[12] a) F. Weinigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297–3305; b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* 1994, 100, 5829–5835; c) K. Eichkorn, F. Weinigend, O. Treutler, R. Ahlrichs, Theor. Chem. Acc. 1997, 97, 119–124.
[13] a) E. D. Glendening, C. R. Landis, F. Weinhold, J. Compu. Chem. 2013, 34, 1429–1437; b) F. Weinhold, C. R. Landis, Valency and bonding: a natural bond orbital donor-acceptor perspective, Cambridge University Press, New York, 2005; c) E. Glendening, J. Badenhoop, A. Reed, J. Carpenter, J. Bohmann, C. Morales, C. Landis, F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.
[14] a) S. Grimme, S. Ehrlich, L. Goerigk, *J. Computational Chem.* 2011, 32, 1456–1466; b) L. Goerigk, S. Grimme, *Phys. Chem. Chem. Phys.* 2011, 13, 6670–6688; c) For TPSN, the values of the original paper have been substituted by the corrected values kindly provided by S. Grimme as private communication and published in; d) A. Hoffmann, R. Grunzke, S. Herres-Pawlis, *J. Comput. Chem.* 2014, 35, 1943–1950.
[15] E. W. Fischer, H. J. Stierzel, G. Wegner, *Kolloid-Zeitschrift und Zeitschrift für Polymere* 1973, 251, 980–990.
[16] S. M. Davachi, B. Shiroud Hedari, I. Hejazi, J. Seyfi, E. Ollaei, A. Farzaneh, H. Rashedi, *Carbohydr. Polym.* 2017, 155, 336–344.
[17] E. L. Whitelew, G. Loraine, M. F. Mahon, M. D. Jones, *Dalton Trans.* 2011, 40, 11469–11473.
[18] J. Börner, S. Herres-Pawlis, U. Flörke, K. Huber, *Eur. J. Inorg. Chem.* 2007, 5645–5651.
[19] V. Raad, K. Harms, J. Sundermeyer, B. Kovačević, Z. B. Maksić, J. Org. Chem. 2003, 68, 8790–8797.
[20] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* 2007, 955–964.
[21] B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* 2001, 123, 3229–3238.