Supporting Information for

A robust Zirconium *N*-heterocyclic carbene complex for the living and highly stereoselective ring-opening polymerization of *rac*-lactide

Charles Romain, Benoît Heinrich, Stéphane Bellemin Laponnaz, Samuel Dagorne

Laboratoire DECOMET and Service de Radiocristallographie, Institut de Chimie, CNRS-Université de Strasbourg, 1 rue Blaise Pascal, 67070 Strasbourg

IPCMS (Institut de Physique et Chimie des Matériaux de Strasbourg), CNRS-Université de Strasbourg, 23 rue du Loess BP 43, F-67034 Strasbourg, France

Chemical Communications

General Procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane and tetrahydrofuran were collected after going through drying columns (SPS apparatus, MBraun) and stored over activated molecular sieves (4 Å) for 24h in a glovebox prior to use. Tetrahydrofuran was distilled over Na/benzophenone and stored over activated molecular sieves (4 Å) for 24h in a glovebox prior to use. CH_2Cl_2, CD_2Cl_2, and C_6D_6 were distilled from CaH_2, degassed under a N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. Anhydrous BnOH (99.8%) was purchased from Aldrich and stored over activated molecular sieves (4 Å) for 24h in a glovebox prior to use. All deuterated solvents were obtained from Eurisotop (CEA, Saclay, France). *rac*-lactide (98% purity) was purchased from Aldrich and was either used as is or sublimed once prior to use. All other chemicals were purchased from Aldrich and were used as received, with the exception of trimethylene carbonate purchased from either T.C.I. Europe Corporation or Boehringer: it was recrystallized twice from dry Et_2O prior to use. The NMR spectra were recorded on Bruker AC 300 or 400 MHz NMR spectrometers in Teflon-valved J-Young NMR tubes at ambient temperature. ^1H and ^{13}C chemical shifts are reported vs. $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. Elemental analysis for all compounds were performed at the Service de Microanalyse of the Université de Strasbourg (Strasbourg France). GPC analyses were performed either on a system equipped with a Shimadzu RID10A refractometer detector using HPLC-grade THF as an eluant (with molecular weights and polydispersity indices (PDIs) calculated using polystyrene standards). In the case of molecular weight number (M_n), these were corrected with appropriate correcting factors for the M_n values. Some SEC analysis of polymers were performed at the Institut Charles Sadron (Strasbourg, France) on a system equipped with a Shimadzu RID10A refractometer detector and a TREOS (WYATT Techn.) multiple angles light scattering detector, allowing direct access to the real masses of the synthesized polymers. MALDI-TOF mass spectroscopic analyses were performed at the Service de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg and run in a positive mode: samples were prepared by mixing a solution of the polymers in CH_2Cl_2 with a 0.5 mg/100 mL concentration; 2,5-dihydroxybenzoic acid (DHB) was used as the matrix in 5:1 volume ratio. A TA Instruments Q-1000 DSC was used for standard DSC and TMDSC analysis. All measurements were carried out with ca. ~ 5 mg samples from -40°C to 180 °C under a nitrogen environment. In the standard DSC analysis, a heating rate of 2 °C/min was used unless indicated. The TMDSC measurements were performed with a heating rate of 0.1 °C/min having an oscillation period of 40 s and amplitude of 0.106 °C for samples previously heated 2 h above the glass transition temperature. The T_g was taken as the midpoint of the glass transition step in the heat capacity curve.

[$^{t\text{Bu}}$(OCO)]Zr(O^{i}Pr)(Cl)(THF) (2). In a nitrogen-filled glovebox, a THF solution (5 mL) of Zr(O^{i}Pr)$_{4,}$ $^{\text{i}}$PrOH (752.6 mg, 1.94 mol) was added at room temperature via a pipette to a stirring THF solution (100 mL) of the imidazolium chloride salt **1** (1.0 g, 1.94 mmol). The initial colorless solution slowly turned yellow/green after addition of the zirconium reagent. The reaction mixture was stirred overnight at room temperature and evaporated to dryness to quantitatively yield L^{1}Zr(Cl)(O^{i}Pr)(THF) an yellow/green solid residue. **Elemental Analysis**: Anal. Calcd. (%) : C, 62.13; H, 8.09; N, 3.81. Found : C,62.17; H, 8.10; N, 3.81. **^{1}H NMR (300 MHz, CD_2Cl_2)** 7.21 (d, J = 2 Hz, 2H, aryl-*H*), 6.98 (d, J = 2 Hz, 2H, aryl-*H*), 4.48-4.21 (m, 4H, NCH_2), 4.18 (hept, J = 6 Hz, 1H, O^{i}Pr), 3.76-3.63 (m, 4H, THF), 1.77-1.69 (m, 4H, THF), 1.56 (s, 18H, ^{t}Bu), 1.37 (s, 18H, ^{t}Bu), 0.94 (d, J = 6 Hz, 6H, CH_3-O^{i}Pr). **^{13}C NMR (75MHz, CD_2Cl_2)** 200.0 (N*C*N), 149.1 (C_{ipso}, O-aryl), 139.8 (C_{quat}, aryl), 138.2 (C_{quat}, aryl), 130.6 (C_{quat}, aryl), 119.8 (CH, aryl), 112.7 (CH, aryl), 73.9 (*C*H, O^{i}Pr), 70.2 (CH_2, THF), 48.1 (CH_2, NCH_2), 36.0 (C_{quat}, ^{t}Bu), 34.8 (C_{quat}, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 30.2 (CH_3, ^{t}Bu), 26.6 (CH_3, O^{i}Pr), 25.7 (CH_2, THF).

Typical polymerization procedure. In a glovebox, the initiator (complex **2**) was charged in a vial equipped with a TeflonTM-tight screw-cap and a monomer solution ($[M]_0$= 1 M, THF or CH_2Cl_2) was added *via* a syringe all at once. The solution was vigorously stirred the appropriate time and at the chosen temperature conditions. When the desired time was reached, aliquots were taken and analyzed by ^{1}H NMR spectroscopy to estimate the conversion. The reaction mixture was quenched with cold MeOH provoking the precipitation of the polymer, which was then washed several times with MeOH, dried in *vacuo* until constant weight and subsequently analyzed by ^{1}H NMR and SEC. In some cases, a MALDI-TOF-MS analysis was performed.

“Immortal” polymerization conditions. An identical procedure to that above was used but with the addition of a monomer solution ($[M]_0$ = 1 M, THF or CH_2Cl_2) containing the desired quantities of benzylic alcohol (BnOH) onto complex **2**.

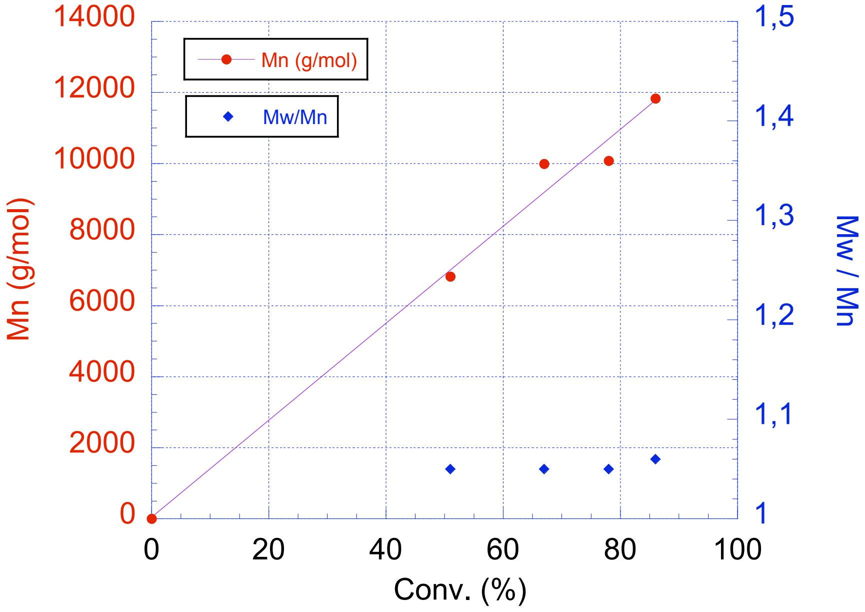


Figure S1. Dependence of M_n (●) and polydispersity index (M_w/M_n ◆) of PLA on monomer (M) conversion for *rac*-lactide polymerization by the Zr complex **2** 100 (M_n and PDI determined by GPC). Conditions: CH_2Cl_2, r.t., $M_0/I = 100$.

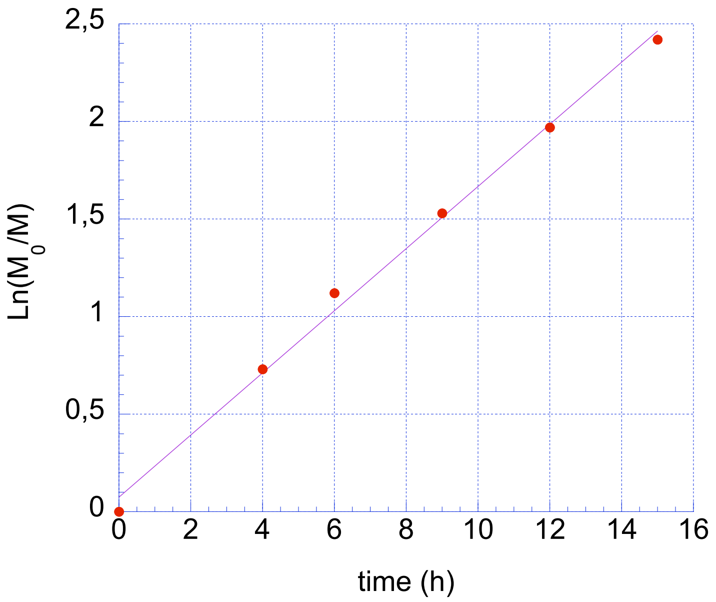


Figure S2. Plot [$\ln(M_0/M)$] vs. time (showing the ROP of *rac*-lactide initiated complex **2** to be first order in monomer). Conditions: CH_2Cl_2, r.t., $M_0/I = 100$.

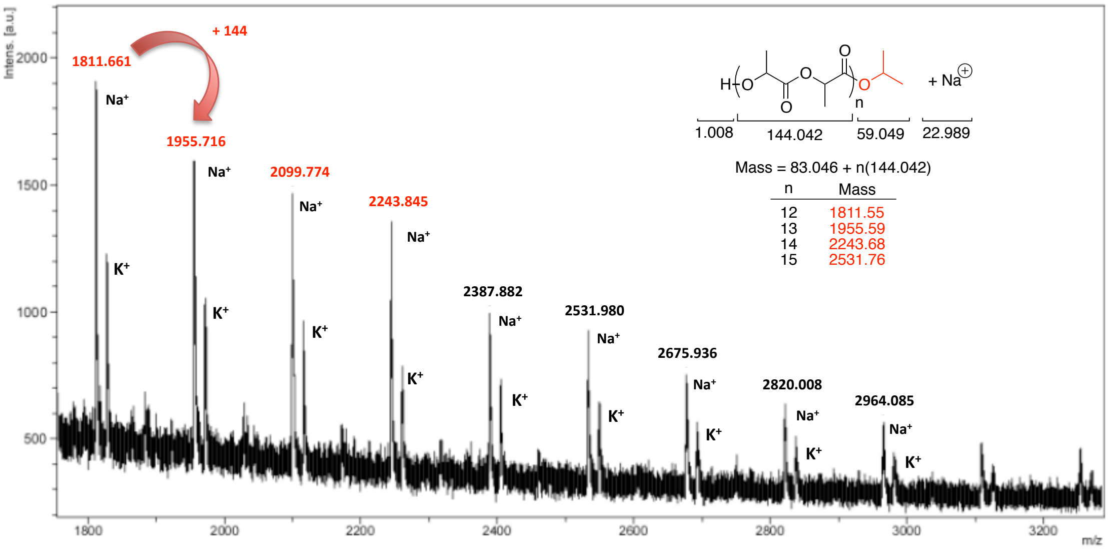


Figure S3. MALDI-TOF mass spectrum of linear PLA prepared *via* the ROP of *rac*-lactide initiated by complex **10-THF.** Reaction conditions: $M_0/I = 10$, r.t., CH_2Cl_2 (100% conv.).

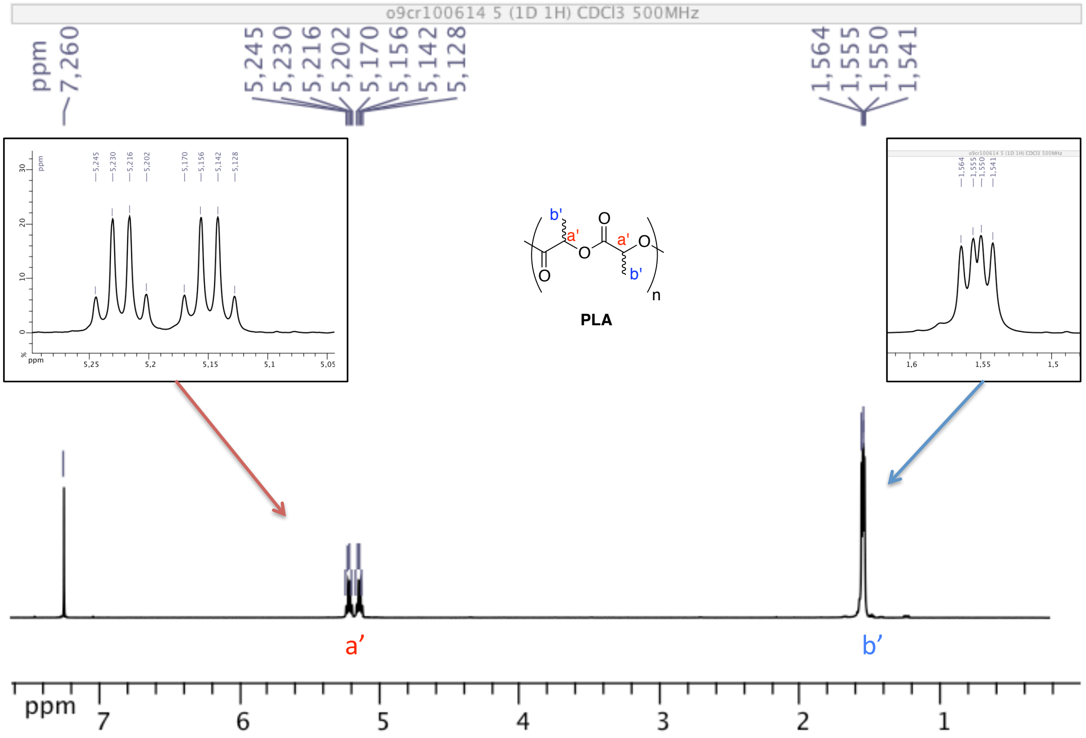


Figure S4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of highly heterotactic PLA ($P_r = 0.97$) *via* ROP of *rac*-lactide initiated by complex **2**. Reaction conditions: $M_0/I = 100$, r.t., CH_2Cl_2, 15h, 91% conv. to PLA (table 1, entry 1).

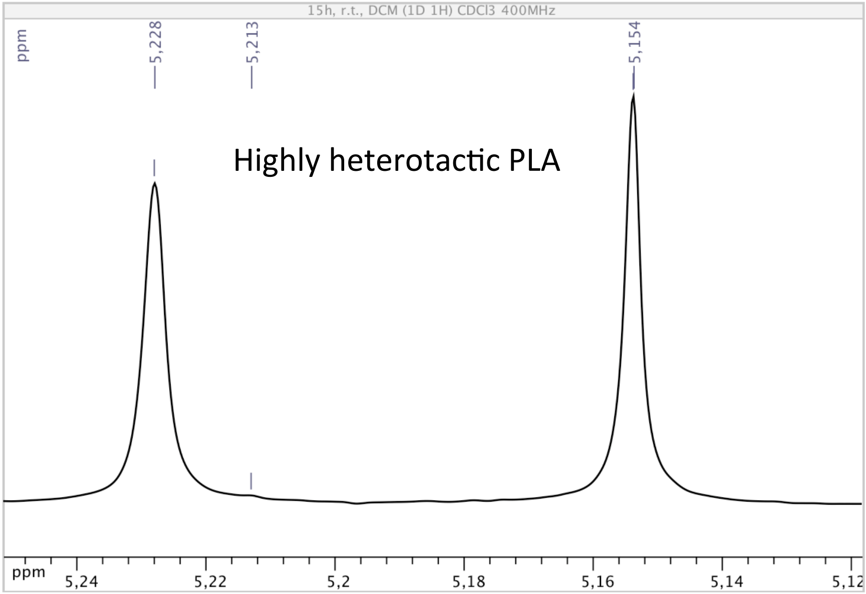


Figure S5. Decoupled ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of highly heterotactic PLA (P_r = 0.97) via ROP of *rac*-lactide initiated by complex **2**. Reaction conditions: $M_0/I = 100$, r.t., CH_2Cl_2, 15h, 91% conv. to PLA (table 1, entry 1).

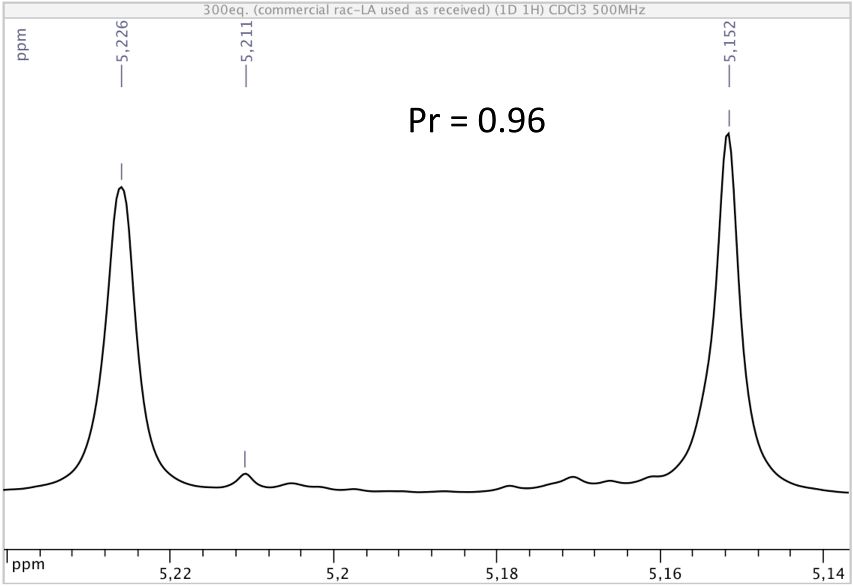


Figure S6. Decoupled ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of highly heterotactic PLA (P_r = 0.96) via ROP of **commercial** *rac*-lactide (**used as is**) initiated by complex **2**. Reaction conditions: $M_0/I = 300$, r.t., CH_2Cl_2, 15h, 90% conv. to PLA (table 1, entry 4).

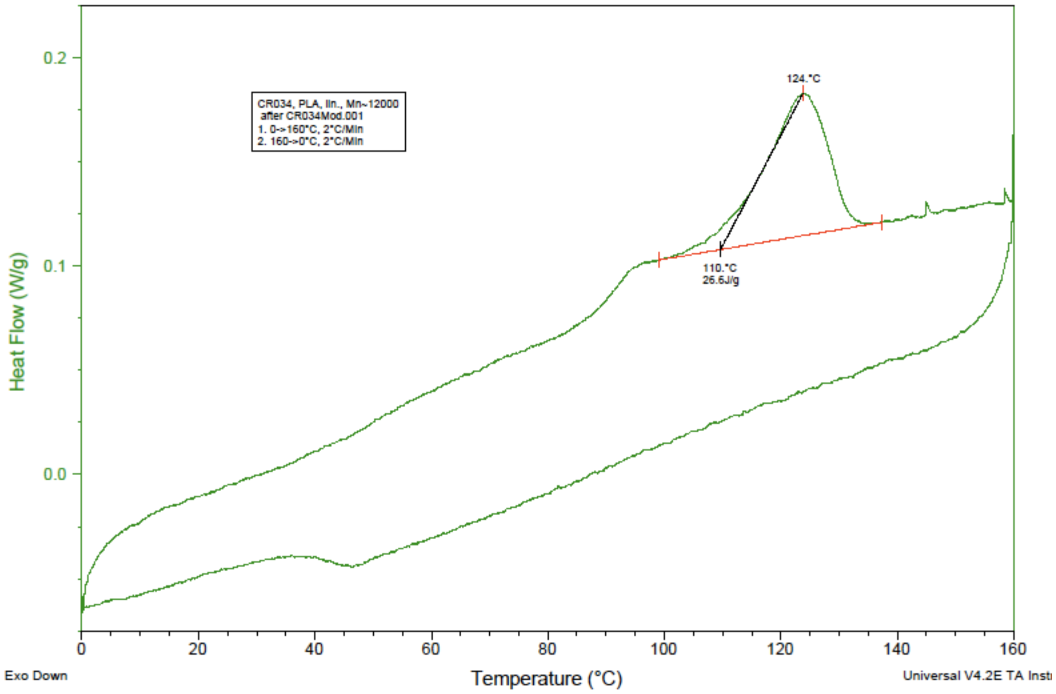


Figure S7. DSC analysis of heterotactic PLA (prepared by ROP of *rac*-LA carried out in THF and subsequent precipitation of the reaction mixture with MeOH). Reaction conditions: THF, r.t., 15h, $M_0/I = 100$, $M_0 = 1$ M, 95% conv., $M_n = 10900$ g/mol, $M_w/M_n = 1.10$ (table 1, entry 5).

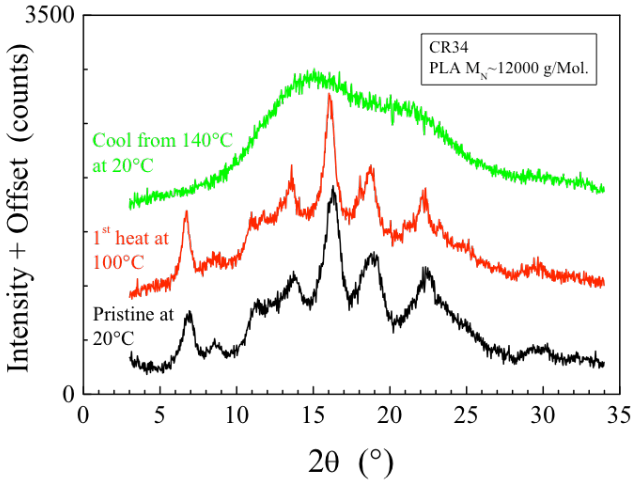


Figure S8. XRD analysis of heterotactic PLA (prepared by ROP of *rac*-LA carried out in THF and subsequent precipitation of the reaction mixture with MeOH). Reaction conditions: THF, r.t., 15h, $M_0/I = 100$, $M_0 = 1$ M, 95% conv., $M_n = 10900$ g/mol, $M_w/M_n = 1.10$ (table 1, entry 5).

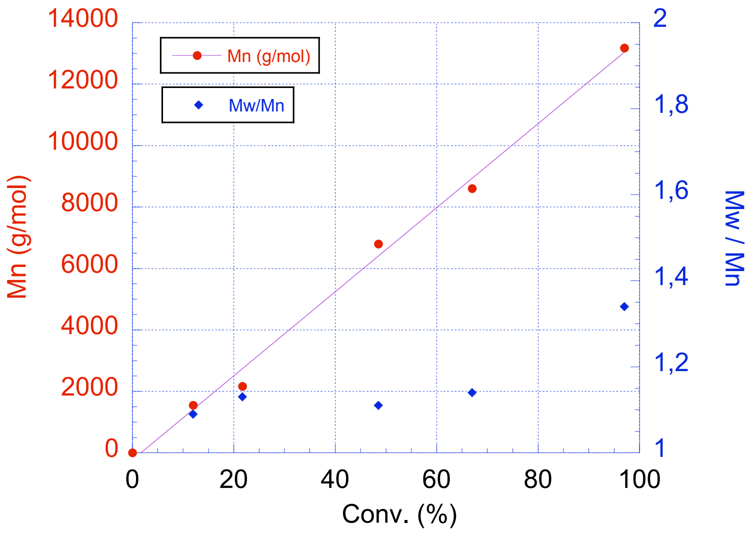


Figure S9. Plot of M_n (●) and of the PTMC polydispersity index (M_w/M_n ◆) versus TMC (M) conversion in the ROP of TMC initiated by complex **2** (M_n and PDI determined by GPC). Conditions: CH_2Cl_2, r.t., $M_0/I = 100$.

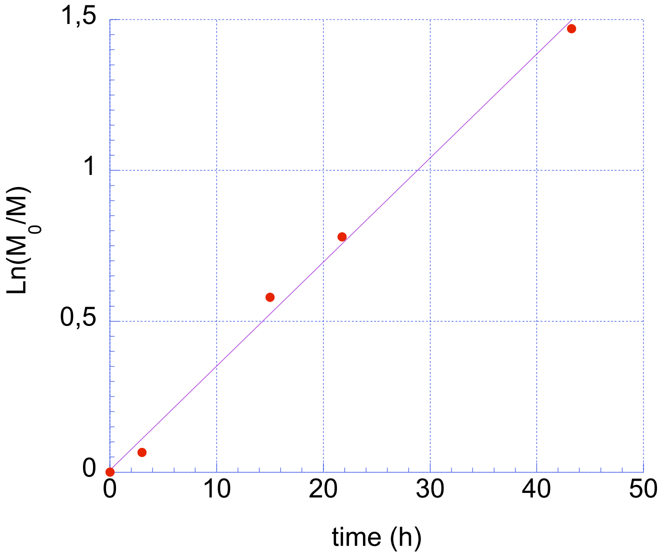


Figure S10. Plot [$\ln(M_0/M)$] vs. time (showing the ROP of TMC initiated by complex **2** to be first order in monomer). Conditions: CH_2Cl_2, r.t., $M_0/I = 100$.

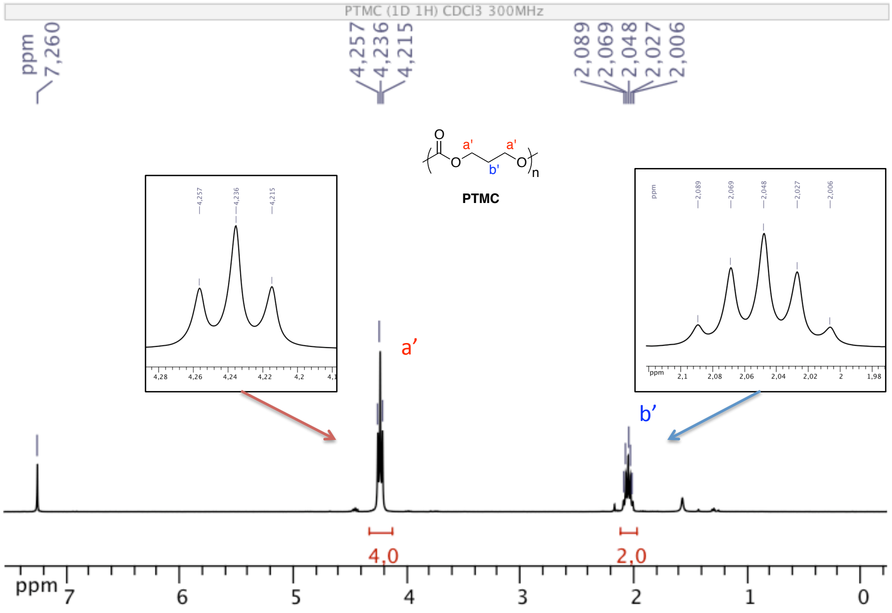


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated poly-TMC (PTMC) *via* ROP of TMC initiated by complex **2**. Reaction conditions: $M_0/I = 100$, r.t., CH_2Cl_2, 15h, 97% conv. to PTMC.

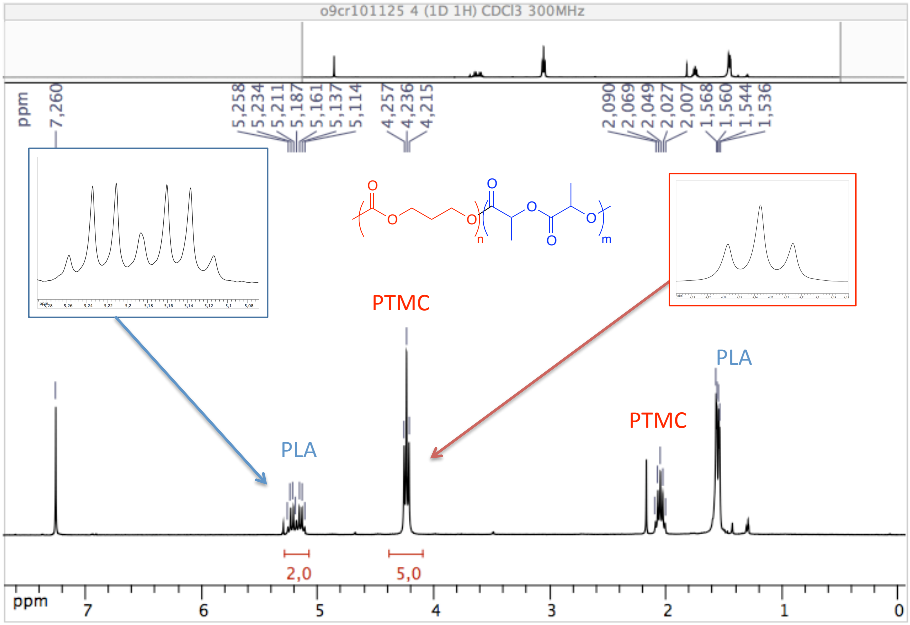


Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of isolated (heterotactic)-PLA-*b*-PTMC via sequential ROP of TMC and *rac*-lactide initiated by complex **2**. Reaction conditions: $M_0/I = 40$ (for *rac*-lactide) and $M_0/I = 60$ (for TMC), r.t., CH_2Cl_2, quantitative conversion.

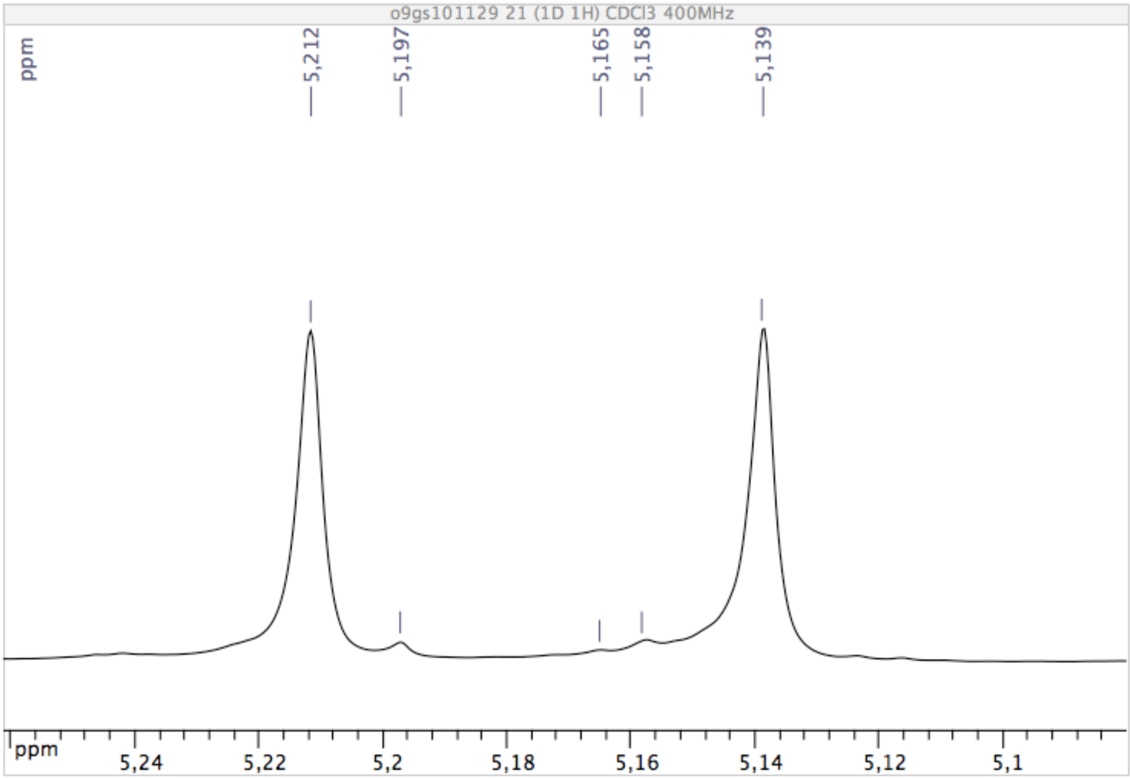
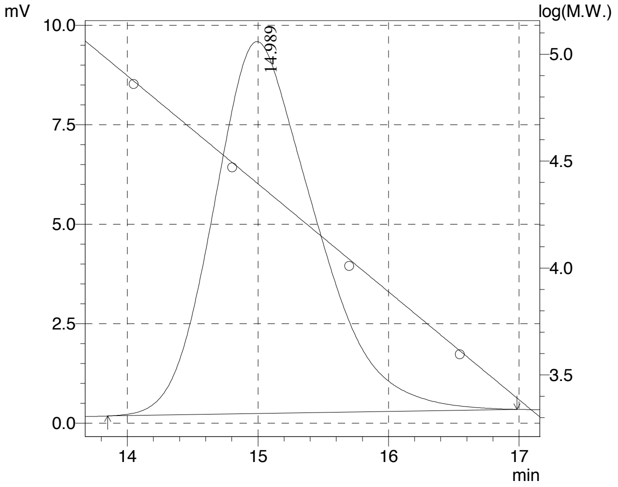


Figure S13. Methine region of the decoupled ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of isolated (heterotactic)-PLA-*b*-PTMC via sequential ROP of TMC and *rac*-lactide initiated by complex **2** (consistent with Pr > 0.95).

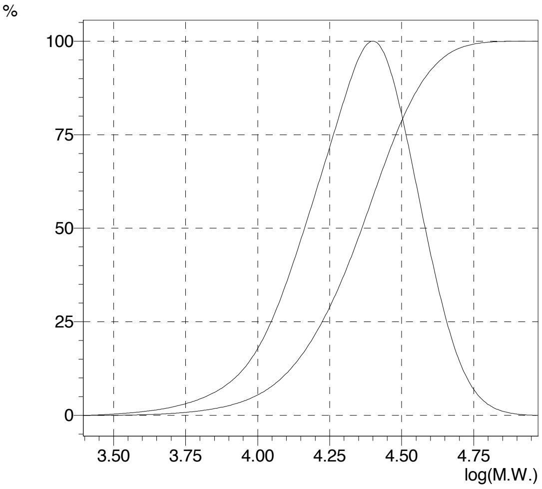
==== Shimadzu LCsolution GPC Analysis Report ====

Acquired by : Admin
Sample Name : CRIII-156
Sample ID :
Vail# :
Injection Volume : 100 uL
Data Filename : CRIII156-TMC-LA.lcd
Method Filename : Etalon PS.lcm
Batch Filename :
Report Filename : Default.lcr
Date Acquired : 26/11/2010 14:20:20
Data Processed : 26/11/2010 19:05:06

Chromatogram & Calibration Curve



Molecular Weight Distribution Curve



GPC Calculation Results

Peak#:1 (Detector A Ch1)
[Peak Information]

	Time(min)	Volume(mL)	Molecular Weight	Height
Start	13.850	13.850	94366	183
Top	14.989	14.989	25098	9346
End	16.983	16.983	2468	351

Area : 505181
Area% : 100.0000

[Average Molecular Weight]

Number Average Molecular Weight(Mn)	19679
Weight Average Molecular Weight(Mw)	24354
Z Average Molecular Weight(Mz)	28831
Z+1 Average Molecular Weight(Mz1)	33259
Mw/Mn	1.23754
Mv/Mn	0.00000
Mz/Mw	1.18380

Detector A Ch1
[Average Molecular Weight(Total)]

Number Average Molecular Weight(Mn)	19679
Weight Average Molecular Weight(Mw)	24354
Z Average Molecular Weight(Mz)	28831
Z+1 Average Molecular Weight(Mz1)	33259
Mw/Mn	1.23754
Mv/Mn	0.00000
Mz/Mw	1.18380

Figure S14. GPC traces of isolated (heterotactic)-PLA-*b*-PTMC *via* sequential ROP of TMC and *rac*-lactide initiated by complex **2**.

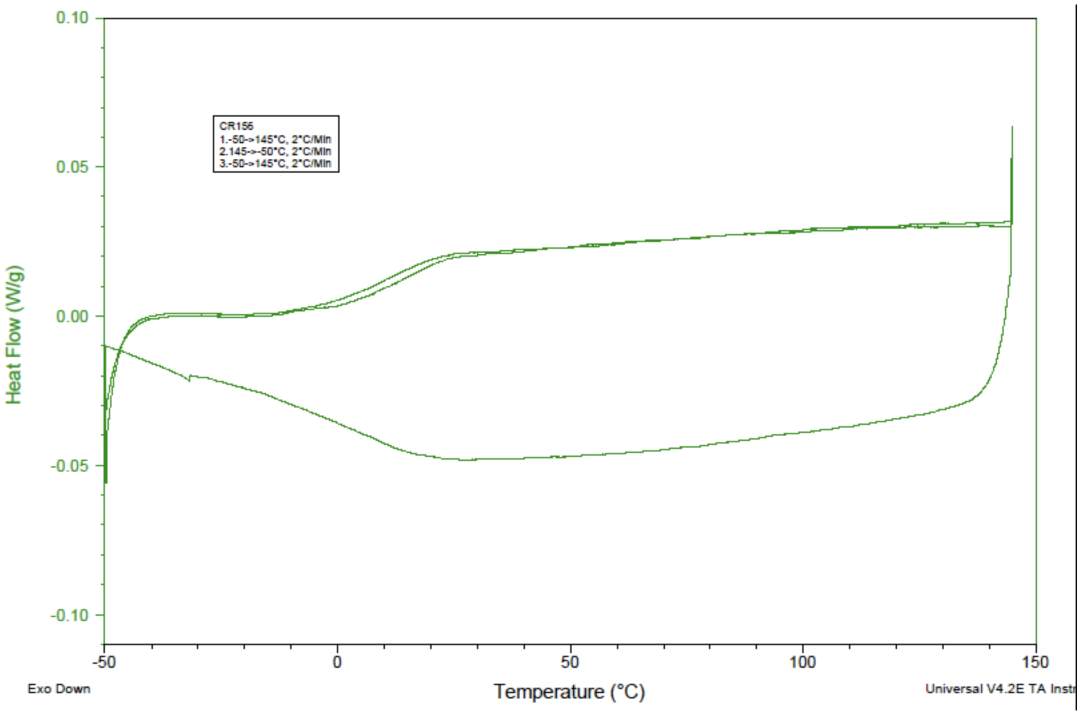


Figure S15. DSC analysis of isolated (heterotactic)-PLA-*b*-PTMC, consistent with an amorphous material with no phase separation.

Table S1. Reaction conditions for the ROP of trimethylene carbonate (TMC) using the Zr-NHC complex **2.**[a]

Entry	t (h)	conv.[b] (%)	$M_{n(calc.)}$[c] (g/mol.)	$M_{n(GPC)}$[d] (g/mol)	PDI[d]
1	3	14	1440	1546	1.09
2	6	24	2469	2163	1.13
3	16	48	4939	6800	1.11
4	19	67	6894	8590	1.14
5	43	97	9991	13177	1.34

a) Conditions: M_0 = 1 M, CH_2Cl_2, $M_0/I=100$; b) determined by ^1H NMR spectroscopy; c) calculated using the following formula M_n = conv. x M_0/I x 102.09 ; d) determined by gel permeation chromatography (GPC) with polystyrene standards and corrected by the corresponding factor.

X-ray crystallographic characterization of complex 2 (CCDC number : 847683)

A single crystal of complex **2** was mounted on glass fibers and data collected on a Nonius Kappa-CCD or Bruker APEX II DUO Kappa-CCD area detector diffractometer ($MoK_a\ l$ = 0.71073 Å). The complete conditions of data collection (Denzo software)[1] and structure refinements are in appendix section. The structure was solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software.[2] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.

Table S2. Crystal data and structure refinement for complex **2** (CCDC number : 847683)

	2
Chemical formula	$C_{38}H_{59}ClN_2O_4Zr$
Formula Mass	734.54
Crystal system	Monoclinic
a/Å	15.7565(5)
b/Å	13.8949(3)
c/Å	19.2220(7)
α/°	90.00
β/°	110.9160(10)
γ/°	90.00
Unit cell volume/Å³	3931.1(2)
Temperature/K	173(2)
Space group	*P21/c*
No. of formula units per unit cell, Z	4
Radiation type	MoKα
Absorption coefficient, μ/mm⁻¹	0.386
No. of reflections measured	23159
No. of independent reflections	8890
R_{int}	0.1371
Final R_1 values ($I > 2\sigma(I)$)	0.0777
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2000
Final R_1 values (all data)	0.0878
Final $wR(F^2)$ values (all data)	0.2142
Goodness of fit on F^2	1.082

---

[1] *Kappa CCD Operation Manual*, Nonius B. V., Ed.; Delft: The Netherlands, 1997.

[2] G.-M. Sheldrick, *SHELXL97, Program for the refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.