Supporting Information

Tuning a robust system: N,O Zinc Guanidine Catalysts for the ROP of Lactide

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1. Ligand synthesis

Methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate (TMG4NMe₂asme, L1):



Fig SI 1. ¹H NMR spectrum of the ligand L1 TMG4NMe₂asme (methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate).



Fig SI 2. ¹³C NMR spectrum of the ligand L1 TMG4NMe₂asme (methyl 2-((bis(dimethylamino)methylene)amino)-4-(dimethylamino)benzoate).



Methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate (TMG5Clasme, L2):

Fig SI 3. ¹H NMR spectrum of the ligand L2 TMG5Clasme (methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate).



Fig SI 4. ¹³C NMR spectrum of the ligand L2 TMG5Clasme (methyl 2-((bis(dimethylamino)methylene)amino)-5-chlorobenzoate).



Methyl 2-((bis(dimethylamino)methylene)amino)-5-methylbenzoate (TMG5Measme, L3):

Fig SI 5. ¹H NMR spectrum of the ligand L3 TMG5Measme (methyl 2-((bis(dimethylamino)methylene)amino)-5methylbenzoate).



Fig SI 6. ¹³C NMR spectrum of the ligand L3 TMG5Measme (methyl 2-((bis(dimethylamino)methylene)amino)-5-methylbenzoate).

Methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate (TMG5NMe₂asme, L4):



Fig SI 7. ¹H NMR spectrum of the ligand L4 TMG5NMe₂asme (methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate).



Fig SI 8. ¹³C NMR spectrum of the ligand L4 TMG5NMe₂asme (methyl 2-((bis(dimethylamino)methylene)amino)-5-(dimethylamino)benzoate).

2. Complex synthesis

[ZnCl₂(TMG4NMe₂asme)] (C1):





[ZnCl₂(TMG5Clasme)] (C2):







Fig SI 12. ¹³C NMR spectrum of the complex C2 [ZnCl₂(TMG5Clasme)].

[ZnCl₂(TMG5Measme)] (C3):







[ZnCl₂(TMG5NMe₂asme)] (C4):





3. Kinetics



Fig SI 17. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C1** [ZnCl₂(TMG4NMe₂asme)] [M]/[I] = 500:1, 150 °C, 260 rpm, Schlenk tube-technic, conversion determined by ¹H NMR spectroscopy.



Fig SI 18. Semi-logarithmic plot of the polymerisations of non-purified *rac*-LA (determined twice) with **C2** [ZnCl₂(TMG5Clasme)] [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S1. Polymerisation data for *rac*-LA with catalyst **C2**.^[a]

GPC (in THF), M_{n,theo}: 72 000 g mol⁻¹ for 100% conversion.

init.	k _{app} [s ⁻¹] ^[b]	time	conv. [%] ^[c]	M _{n,theo} [g mol ⁻¹]	<i>M</i> _n [g mol ⁻¹] ^[d]	PD
C2	2.39 x 10 ⁻⁴	53 min	25	18 000	43 900	1.4
C2	2.38 x 10 ⁻⁴	60 min	28	20 000	43 000	1.3
[a] Conditions: 15	0 °C, solvent free, nor	-purified techn	ical grade <i>rac</i> -l	_A, [M]/[I] = 500:1. [[b] Determined fro	m the
slope of the plots	s of In([LA] ₀ /[LA] _t) vers	sus time. [c] As	determined b	y ¹ H NMR spectroso	copy. [d] Determir	ed by



Fig SI 19. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C3** [ZnCl₂(TMG5Measme)] [M]/[I] = 500:1 ($k_{app} = 2.95 \times 10^{-2} \text{ min}^{-1}$), 750:1 ($k_{app} = 1.56 \times 10^{-2} \text{ min}^{-1}$), 1000:1 ($k_{app} = 0.91 \times 10^{-2} \text{ min}^{-1}$) and 1250:1 ($k_{app} = 0.65 \times 10^{-2} \text{ min}^{-1}$) at 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S2. Polymerisation data for rac-LA with catalyst C3.^[a]

1]	M]/[I]	k _{app} [min ⁻¹] ^[b]	time	conv. [%] ^[c]	M _{n,theo} [g mol ⁻¹]	<i>M</i> _n [g mol ⁻¹] ^[d]	PD
	500	2.95 x 10 ⁻²	36 min	68	49 000	85 500	1.5
	750	1.56 x 10 ⁻²	78 min	63	68 000	74 700	1.5
1	1000	0.91 x 10 ⁻²	170 min	58	83 500	56 300	1.4
	1250	0.65 x 10 ⁻²	322 min	54	97 200	46 400	1.3
110		<u> </u>					c

[a] Conditions: 150 °C, solvent free, non-purified technical grade *rac*-LA. [b] Determined from the slope of the plots of $ln([LA]_0/[LA]_t)$ versus time. [c] As determined by ¹H NMR spectroscopy. [d] Determined by GPC (in THF), $M_{n,theo}$: 72 000 g mol⁻¹ for 100% conversion.



Fig SI 20. Plot of k_{app} versus [init.] for **C3**. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 500:1, 750:1, 1000:1, 1250:1. No conversion is detected below a catalyst concentration of 0.004 mol L⁻¹, this is presumably due to deactivation by impurities in the monomer feed. Above 0.004 mol L⁻¹ conversion is observed.



Fig SI 21. Semi-logarithmic plot of the polymerisations of non-purified *rac*-LA (determined twice) with **C4** [ZnCl₂(TMG5Clasme)] [M]/[I] = 500:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman and IR spectroscopy.

Table S3. Polymerisation data for *rac*-LA with catalyst **C4**.^[a]

init.	k_{app} [min ⁻¹] ^[b]	time	conv. [%] ^[c]	M _{n,theo} [g mol ⁻¹]	<i>M</i> _n [g mol ⁻¹] ^[d]	PD			
C4	5.48 x 10 ⁻²	30 min	69	50 000	55 000	1.3			
C4	5.29 x 10 ⁻²	120 min	81	58 000	71 000	1.4			
[a] Conditions: 15	[a] Conditions: 150 °C, solvent free, non-purified technical grade rac-LA, [M]/[I] = 500:1. [b] Determined from the								
slope of the plots	s of ln([LA] ₀ /[LA] _t) versu	ıs time. [c] As	determined b	y ¹ H NMR spectroso	copy. [d] Determin	ed by			
GPC (in THF), M _{n,t}	_{heo} : 72 000 g mol ⁻¹ for 1	.00% conversio	on.						



Fig SI 22. Semi-logarithmic plot of the polymerisations of non-purified *rac*-LA (determined twice) with **C4** [ZnCl₂(TMG5Clasme)] [M]/[I] = 2000:1, 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S4. Polymerisation data for rac-LA with catalyst C4.^[a]

init.	k_{app} [min ⁻¹] ^[b]	time	conv. [%] ^[c]	M _{n,theo} [g mol ⁻¹]	<i>M</i> _n [g mol ⁻¹] ^[d]	PD
C4	7.38 x 10 ⁻³	40 min	27	50 000	-	-
C4	11.03 x 10 ⁻³	46 min	29	58 000	-	-
[a] Conditions: 15	0 °C, solvent free, non	-purified tech	nical grade rac	-LA, [M]/[I] = 2000:	1. [b] Determined	l from
the slope of the p	lots of $ln([LA]_0/[LA]_t) v$	ersus time. [c]	As determine	d by ¹ H NMR spectr	oscopy. [d] Deterr	mined

by GPC (in THF), $M_{n,theo}$: 72 000 g mol⁻¹ for 100% conversion.



Fig SI 23. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C4** [ZnCl₂(TMG5NMe₂asme)] [M]/[I] = 500:1 ($k_{app} = 5.48 \times 10^{-2} \text{ min}^{-1}$), 625:1 ($k_{app} = 3.86 \times 10^{-2} \text{ min}^{-1}$), 1000:1 ($k_{app} = 0.97 \times 10^{-2} \text{ min}^{-1}$) and 2000:1 ($k_{app} = 0.20 \times 10^{-2} \text{ min}^{-1}$) at 150 °C, 260 rpm, conversion determined by *in situ* Raman spectroscopy.

Table S5. Polymerisation	data for	rac-LA	with	catalyst	C4.[a]
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[M]/[I]	k _{app} [min ⁻¹] ^[b]	time	conv. [%] ^[c]	M _{n,theo} [g mol ⁻¹]	<i>M</i> _n [g mol ⁻¹] ^[d]	PD				
500	5.48 x 10 ⁻²	30 min	69	49 000	55 500	1.3				
625	3.86 x 10 ⁻²	38 min	73	68 000	70 000	1.4				
1000	0.97 x 10 ⁻²	90 min	49	83 500	45 000	1.2				
2000	0.20 x 10 ⁻²	46 min	29	97 200	-	-				
[a] Conditions: 15	[a] Conditions: 150 °C, solvent free, non-purified technical grade rac-LA. [b] Determined from the slope of the									
plots of ln([LA] ₀ /[l	_A] _t) versus time. [c] A	s determined l	by ¹ H NMR spe	ctroscopy. [d] Dete	rmined by GPC (in	THF),				
M _{n,theo} : 72 000 g n	nol ⁻¹ for 100% convers	ion.								



Fig SI 24. Plot of *k*_{app} versus [init.] for **C4**. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 500:1, 625:1, 1000:1, 2000:1.



Fig SI 25. Semi-logarithmic plot of the polymerisation of non-purified *rac*-LA with **C4** [ZnCl₂(TMG5NMe₂asme)] and (3,5-bis(trifluoromethyl)benzyl alcohol) (co-init.), [M]/[I] = 625:1:1, 150 °C, 260 rpm, Schlenk tube-technic, conversion determined by ¹H NMR spectroscopy. $k_{app} = 14.14 \times 10^{-4} \text{ s}^{-1}$.



Fig SI 26. Plot of k_{app} versus [init.] for Sn(Oct)₂. Conditions: *rac*-LA, 150 °C, 260 rpm, non-purified lactide; [M]/[I] = 1000:1, 1250:1, 1500:1, 2500:1, 5000:1.



Fig SI 27. ¹H NMR spectrum of the polymerisation of non-purified *rac*-lactide ([M]/init.] = 500:1) using TMG5NMe₂asme at 150 °C, 260 rpm. Conversion of 9% after 90 min, no polymer has been obtained for further characterisations. Formation of *meso*-lactide (1.72 ppm, d) during the reaction.



Fig SI 28. ¹H NMR spectrum of the polymerisation of non-purified *rac*-lactide ([M]/[init.]/[co-init.] = 500:1:1) using TMG5NMe₂asme (init.) and (3,5-bis(trifluoromethyl)benzyl alcohol) (co-init.) at 150 °C, 260 rpm. Conversion of 9% after 90 min, no polymer has been obtained for further characterisations. Formation of *meso*-lactide (1.72 ppm, d) during the reaction.

4. End-group analysis

4.1. MALDI-ToF

End group analysis was performed by MALDI-ToF on a Bruker ultrafleXtreme equipped with a 337 nm smartbeam laser in the reflective mode. THF solutions of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (5 μ L of a 20 mg/mL solution), sodium trifluoroacetate (0.1 μ L of a 10 mg/mL solution), and analyte (5 μ L of a 10 mg/mL) were mixed and a droplet thereof applied on the sample target. Protein 1 calibration standard is the name of the protein mixture used for calibration. For spectra 4000 laser shots with 24% laser power were collected. The laser repetition rate was 1000 Hz. The homopolymer analysis was performed using Polymerix software (Sierra analytics).

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Fig SI 29. Stack of MALDI-ToF spectra obtained for a polymerisation initiated with **C4** [ZnCl₂(TMG5NMe₂asme)] and the coinitiator (3,5-bis(trifluoromethyl)benzyl alcohol) ([M]/[init.]/[co-init.] = 100:1:1) 1.5 min, 150 °C, 260 rpm, subl. *rac*-LA,. M_n : 17.000 g mol⁻¹, M_w : 20.300 g mol⁻¹, PD: 1.2, conversion: 79%.

4.3. NMR spectroscopy



Fig SI 30. ¹H NMR spectrum of the polymer initiated with [ZnCl₂(TMG5NMe₂asme)] and the co-initiator (3,5-bis(trifluoromethyl)benzyl alcohol) ([M]/[init.]/[co-init.] = 50:1:1), 2 min, 150 °C, 260 rpm, non-purified *rac*-LA,. *M*_n: 10.000 g mol⁻¹, *M*_w: 14.300 g mol⁻¹, *PD*: 1.2, conversion: 94%.



Fig SI 31. ¹⁹F NMR spectrum of the polymer initiated with $[ZnCl_2(TMG5NMe_2asme)]$ and the co-initiator (3,5-bis(trifluoromethyl)benzyl alcohol) ([M]/[init.]/[co-init.] = 50:1:1), 2 min, 150 °C, 260 rpm, non-purified *rac*-LA,. M_n : 10.000 g mol⁻¹, M_w : 14.300 g mol⁻¹, PD: 1.2, conversion: 94%.

4.4. Polymerisation without co-initiator

The polymerisations with a ratio of 10:1 and 30:1 have been performed in Schlenk-tubes using sublimed rac-lactide (500 mg) and the catalyst C4.

[M]/[I] = 10:1, conversion: 94% (45 s), $M_n = 32.600 \text{ g mol}^{-1}$, $M_w = 51.000 \text{ g mol}^{-1}$, PD = 1.6; [M]/[I] = 30:1, conversion: 41% (60 s), $M_n = 44.100 \text{ g mol}^{-1}$, $M_w = 53.700 \text{ g mol}^{-1}$, PD = 1.2;



5. Thermogravimetrical analysis (TGA)

RWTH-Aachen IAC : METTLER Fig SI 32. Results of TGA measurements. Whole measurement.



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RWTH-Aachen IAC : METTLER

Fig SI 33. Results of TGA measurement. No significant mass loss was detected while the temperature was constantly at 150 °C for 1 hour.

6. Tacticity



7. Crystallographic data

Table S6. Crystallographic data and parameters of the Zn complexes [ZnCl₂(TMG4NMe₂asme)] (**C1**), [ZnCl₂(TMG5Clasme)] (**C2**), [ZnCl₂(TMG5Measme)] (**C3**) and [ZnCl₂(TMG5NMe₂asme)] (**C4**).^[a]

Parameter	[ZnCl ₂ (TMG4NMe ₂ asme)] (C1)	[ZnCl ₂ (TMG5Clasme)] (C2)	[ZnCl ₂ (TMG5Measme)] (C3)	[ZnCl ₂ (TMG5NMe ₂ asme)] (C4)
empirical formula	$C_{15}H_{24}CI_2N_4O_2Zn$	$C_{13}H_{18}Cl_3N_3O_2Zn$	$C_{14}H_{21}Cl_2N_3O_2Zn$	$C_{15}H_{24}Cl_2N_4O_2Zn$
formula mass [g mol ⁻¹]	428.65	420.02	399.61	428.65
Crystal size [mm]	0.48 x 0.25 x 0.23	0.25 x 0.14 x 0.13	0.23 x 0.22 x 0.18	0.16 x 0.14 x 0.07
<i>т</i> [К]	100(2)	100(2)	100(2)	100(2)
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
space group	Pbca	P21/n	P21/n	P21/c
a [Å]	15.010(2)	9.4998(4)	9.5828(4)	17.377(4)
b [Å]	12.9027(19)	16.0292(7)	16.0067(7)	8.0888(16)
c [Å]	20.065(3)	11.7929(5)	11.7969(5)	13.258(3)
∨[ų]	3886.0(10)	1734.20(13)	1748.53(13)	1863.5(7)
α[°]	90	90	90	90
β[°]	90	105.0450(10)	104.9170(10)	90.439(4)
γ[°]	90	90	90	90
Ζ	8	4	4	4
$ ho_{ m calcd} [m g cm^{-3}]$	1.465	1.609	1.518	1.528
μ [mm ⁻¹]	1.554	1.886	1.719	1.620
λ[Å]	0.71073	0.71073	0.71073	0.71073
F(000)	1776	856	824	888
hkl range	−18 ≤ <i>h</i> ≤18	-13≤h≤13	−13 ≤ <i>h</i> ≤13	-21≤h≤21
	−16 ≤ <i>k</i> ≤16	-22≤k≤23	-23≤k≤22	-10≤k≤10
	-25≤/≤25	-16≤/≤16	-17≤/≤16	-16≤/≤16
reflections collected	44 769	26 252	26 572	22 033
independent reflections	3991	5186	5265	3855
R _{int}	0.0983	0.0320	0.0307	0.0922
number of parameters	224	204	205	224
$R_1[I>2 \sigma(I)]$	0.0359	0.0274	0.0261	0.0418
wR ₂ (all data)	0.0877	0.0667	0.0678	0.1039
goodness-of-fit	1.038	1.071	1.047	1.024
largest diff. peak, hole [e ⁻ Å-3]	0.500, -0.453	0.514, -0.308	0.468, -0.257	0.644, -0.385