The title compounds are active in the polymerization of lactide and ϵ -caprolactone and in contrast to other related compounds their reactions are faster in THF relative to DCM. Other compounds show a marked preference for DCM relative to THF.

TMPZnN(SiMe₃)₂, [TMPZn(μ -OⁱPr)]₂ and TMPZn[OCMe₂C(O)OEt]. Their role in the Ring-Opening of *rac*-lactide and ϵ -caprolactone where TMP = 1,5,9-trimesityldipyrromethene

Vagulejan Balasanthiran^a, Malcolm H. Chisholm^{a*}, Kittisak Choojun^b, Christopher B. Durr^a, and Pasco M. Wambua^a

^a Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, 43210

^b Catalytic Chemistry Research Unit, Department of Chemistry, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand, 10520

*Chisholm@chemistry.ohio-state.edu

KEYWORDS (Polylactic acid, Polycaprolactone, Ring-Opening Polymerization)

Abstract

From the reaction between Zn[N(SiMe₃)₂]₂ and TMP-H (1 equiv.) in toluene at room temperature TMPZn[N(SiMe₃)₂] was prepared and subsequently reacted with PrⁱOH (1 equiv.) and HOOCMe₂C(O)OEt (1 equiv.) to give [TMPZn(μ -OPrⁱ)]₂ and TMPZn[OCMe₂C(O)OEt], respectively. The three compounds were each crystallized and characterized by single crystal X-ray diffraction. The compound TMPZn[N(SiMe₃)₂] was a three coordinated N₃Zn compound with an anagostic N(SiMe₃)₂ ligand where one SiMe₃ was annexed to the Zn²⁺ ion. The compound [TMPZn(μ -OPrⁱ)]₂ has a molecular C₂ axis and is dimeric in toluene-*d*₈ solution having a N₂ZnO₂ core for each Zn²⁺ ion. In TMPZn[OCMe₂C(O)OEt] compound the Zn 2+ ion is four-coordinated. This too is present in solution (IR) and also present in toluene-*d*₈ and THF

where there is evidence of fluxionality with $T_c \sim 15^\circ\text{C}$ and -85°C , respectively. The compound $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ polymerizes both ϵ -caprolactone (ϵ -CL) and *rac*-lactide (*rac*-LA) to give polycaprolactone (PCL) and polylactic acid (PLA), respectively. The rate of the reactions are ϵ -CL > LA and are influenced by the nature of solvent, THF > $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$. The nature of PLA derived from *rac*-LA is heterotactic: $P_r = 0.96$ in THF and $P_r = 0.75$ in $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$. In the copolymerization of *rac*-LA: ϵ -CL by both $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ and $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$ only PLA is produced, PCL is not formed.

Introduction

My remembrance of Jack Lewis is dominated by the kindness to which he showed his visitors, so many of whom became friends. My first visit with Jack was in 1976 when I had decided to leave Princeton and work elsewhere. He was an adorable host in Cambridge and offered me a position in the department. With time I grew to know Jack well, as well as his dear wife Freddie, who often entertained me, my wife and my children. Indeed, when I told one of my sons that Jack had died, he said it was like losing an uncle. So for many reasons, I will always hold dear the friendship that Jack and Freddie offered me and my family. Sadly, I never attended Cambridge except as a visiting professor, but I hold a house there and in every sense Cambridge is my second home, and this owes much to Jack.

Jack was a memorable chemist, one of the most distinguished in the second half of the 20th century. He had the ability to captivate the presence of Inorganic Chemistry at its prime. He pioneered the field of magnetism, ligand field theory, applications of mass spectrometry and during his time at Cambridge, was a prominent organometallic chemist. Many a journal entry will testify to his strengths as a chemist, particularly those of his Royal Society Memoir.¹ He

always kept up with the times and with Paul Raithby, worked so hard with platinum alkynyl polymers that showed interesting photo physical-properties.^{2,3} Indeed, some of these had particularly attractive properties for photovoltaics.⁴ It was perhaps toward his retirement that the age of chemistry from renewable resources became popular. Given Jack's long term interest in the chemistry of the environment, this is perhaps one area of chemistry that he would have pioneered.

In the ring-opening polymerization, ROP, of lactide, LA, and ϵ -caprolactone, ϵ -CL, the influence of both the metal and the attendant ligands are similarly important.⁵ For a given set of ligands we generally note the order of reactants being $\text{Mg}(2+) > \text{Zn}(2+) > \text{Al}(3+)$ with that of $\text{Ca}(2+)$ being omitted since it is notably larger, 1.0 Å related to $\text{Mg}(2+) \sim \text{Zn}(2+)$, 0.8 Å and that of $\text{Al}(3+)$ 0.6 Å.⁶ This often causes the same ligands not to work as well for $\text{Ca}(2+)$ since ligand rearrangements may well interfere. The lanthanides are also important and, in general, $\text{Ln} > \text{Mg}$,⁷ though the ligands tend to be different as the larger lanthanides are not as susceptible to encapsulation by smaller ligands which are capable of complexing Mg ions. We compared the complexes TMP (1,5,9-trimesityldipyrromethene) and BDI (2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-ene) and noted that TMP was slightly more sterically demanding⁸ (See figure 1).

Figure 1: Best superposition of the molecular structures of (BDI)MgBuⁿ(THF) in red and (TMP)MgBuⁿ(THF) in blue showing the relative disposition of the aryl ligands and the greater steric pressure of mesityl groups in the pyrromethene ligand, TMP, on the pocket of the *n*-butyl group. Originally published in reference 8.

As part of our study of these molecules we now report on the reactions of [TMPZn(μ -OPr^{*i*})]₂ in its role as an initiator in the ROP of *rac*-LA and ϵ -CL together with related reactions involving TMPZn[N(SiMe₃)₂] and TMPZn[OCMe₂C(O)OEt] as shown in Scheme 1. These are compared to the reactions of BDI bound to both Mg and Zn and show an inverse solvent effect. With TMP ligands the ROP of LA and CL is faster in THF relative to DCM, whereas for BDI the order is DCM greater than THF. This is suggested due to the role the solvent and metal during catalysis.

Results and Discussion

Synthesis

The reaction between $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ and TMP-H in toluene (1 equiv.) yielded the compound $\text{TMPZn}[\text{N}(\text{SiMe}_3)_2]$. This was a dark-orange compound which was subsequently employed in the synthesis of $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ and $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$ as shown in Scheme 1.

Scheme 1: Synthesis of TMP zinc complexes

The latter two compounds are bright orange; all are stable in a dry N₂ atmosphere at room temperature. The ¹H and ¹³C NMR data are recorded in the experimental and will be discussed individually. All three compounds were studied by single-crystal X-ray crystallography.

Solid-State and Molecular Structures

TMPZn[N(SiMe₃)₂] crystallized with one independent molecule in the asymmetric unit. The cell parameters are given in Table 1 as they are for the other structures. The molecular structure is shown in Figure 2 where it can be seen that the Zn²⁺ ion is raised above the TMP ligand (C-N-N) core by 0.6 Å.

Figure 2: Two views of the molecular structure of TMPZn[N(SiMe₃)₂] drawn at 50% probability. Where Brown = Zinc, Blue = Nitrogen, Scarlet = Oxygen, and Gray = Carbon. Hydrogens are omitted for clarity. In addition methyl groups are removed from the mesityls in the side view.

Table 1: Crystallographic Data Collection Parameters for TMPZn[N(SiMe₃)₂], TMPZn[OCMe₂C(O)OEt] and [TMPZn(μ-OPr^{*i*})₂].

Compound	TMPZn[N(SiMe ₃) ₂]	TMPZn[OCMe ₂ C(O)OEt]	[TMPZn(μ-OPr ^{<i>i</i>}) ₂]
Chemical Formula	C ₄₂ H ₅₅ N ₃ Si ₂ Zn	C ₄₂ H ₄₈ N ₂ O ₃ Zn	C ₇₈ H ₈₈ N ₄ O ₂ Zn ₂
Formula Weight	723.44	694.19	1244.26
Temperature (K)	150(2)	150(2)	150(2)
Space Group	Monoclinic, P2 ₁ /c	Monoclinic, P2 ₁ /c	Monoclinic, C2/c
<i>a</i> (Å)	12.8501(2)	13.1220(5)	28.6695(8)
<i>b</i> (Å)	16.1086(3)	21.1057(6)	12.2437(3)
<i>c</i> (Å)	19.8251(3)	13.3316(6)	25.3442(6)
α (°)			
β (°)	96.535(1)	94.504(2)	122.003(1)
γ (°)			
<i>V</i> (Å ³)	4077.07(12)	3680.8(2)	7544.3(3)
<i>Z</i>	4	4	4
D _{calc} (Mg/m ³)	1.179	1.253	1.095
Crystal Size (mm)	0.35 X 0.35 X 0.19	0.27 X 0.23 X 0.15	0.31 X 0.31 X 0.15
Theta range for data collection	1.595 to 27.479°	1.557 to 25.048°	1.68 to 25.02°
μ (mm ⁻¹) [Mo, K α]	0.692	0.707	0.679
<i>F</i> (000)	1544	1472	2640
Reflections collected	70290	43322	51292
Unique reflections	9328 [R(int)= 0.058]	6503 [R(int)= 0.048]	6674 [R(int)= 0.040]
Data Completeness to [θ]	100.0% [25.242]	99.9% [25.00]	100.0% [25.02]
Data/restraints/parameters	9328 / 0 / 448	6503 / 70 / 474	6674 / 0 / 399
R1a (%) (all data)	4.36 (7.59)	3.89 (5.87)	3.39 (4.92)
wR2b(%) (all data)	10.60 (11.93)	9.83 (11.21)	8.73 (9.21)
Goodness-of-fit on <i>F</i> ²	1.045	1.053	1.058
Largest diff. peak and hole (e Å ⁻³)	0.477 and -0.409	0.458 and -0.427	0.465 and -0.244

$$^a \text{R1} = \Sigma ||\text{F}_o| - |\text{F}_c|| / \Sigma |\text{F}_o| \times 100$$

$$^b \text{wR2} = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma (w |F_o|^2)^2]^{1/2} \times 100$$

Indeed this variation generates a departure from the trigonal geometry and also raises question of how the $\text{N}(\text{SiMe}_3)_2$ coordinates to the Zn^{2+} ion. The ligand may be assumed to be anagostic with the estimated $\text{C-H} \cdots \text{Zn}$ being ~ 2.9 Å. The distinction between agostic is $\text{C-H} \cdots \text{Zn}$ of $1.8 - 2.3$ Å and anagostic being $2.3 - 2.9$ Å.⁹ The chelate $\text{N} - \text{Zn} - \text{N}$ angle is 94.5° and the other $\text{N} - \text{Zn} - \text{N}'$ angles are 133.2° and 129.3° . The $\text{Zn} - \text{N}$ distances to the chelate are 1.98 Å and the $\text{Zn} - \text{N}_{\text{amide}}$ is 1.89 Å.

The molecular structure of $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$ is shown in Figure 3. Here there is an essential N_2ZnO_2 core that is suitably disposed as being derived from a T_d geometry. The $\text{N} - \text{Zn} - \text{N}$ chelate angle is 96.8° and the $\text{O} - \text{Zn} - \text{O}$ angle is 83.5° . The $\text{Zn} - \text{O}$ distances are 1.88 Å for the alkoxide oxygen and 2.12 Å for the ketonic oxygen. The $\text{Mg} - \text{N}$ distances are 1.98 Å.

Figure 3: Molecular structure of $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$ drawn at 50% probability. Where Brown = Zinc, Blue = Nitrogen, Scarlet = Oxygen, and Gray = Carbon. Hydrogens and disorder omitted for clarity.

The molecular structure of $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ is shown in Figure 4 and involves two rather severely distorted tetrahedral molecules. Here each Zn^{2+} ion is nearly trigonally disposed with the TMP ligand binding in a bidentate fashion, ZnN_2 , and OPr^i bridging the two metal centers. There is only a molecular C_2 axis of symmetry and each $\mu\text{-OPr}^i$ ligand is disposed in a similar manner being downward in the view shown in Figure 4. This makes a significant difference to the methyl groups of the mesityl ligands which we shall describe later. The $\text{N} - \text{Zn} - \text{N}$ angles are 91.0° which is notably smaller than in the other structure. The $\text{O} - \text{Zn} - \text{O}'$ angles are 83.1° and $\text{Zn} - \text{O} - \text{Zn}'$ angles are 96.8° . The $\text{Zn} - \text{N}$ distances are $2.01 \text{ \AA}$ and the $\text{Zn} - \text{O/O}'$ distances are 1.93 and $2.03 \text{ \AA}$, respectively.

Full data, including the handling of interstitial solvents and disorder, are recorded in the supporting information for all structures.

Figure 4: Molecular structure of $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ drawn at 50% probability. Where Brown = Zinc, Blue = Nitrogen, Scarlet = Oxygen, and Gray = Carbon. Hydrogens and mesityl groups omitted for clarity.

¹H NMR data

From the crystallographic data recorded for $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$ we see that there are two rather different Zn – O bond distances, one shorter, belonging to the alkoxide, and one longer belonging to the ketonic oxygen atom. Looking at the structure we would expect to see two signals for the H_z aromatic protons when the chelate is closed. If, however, the chelate is open as in a trigonal planar structure we see just one H_z signal. Then as we look at the ¹H NMR as a function of solvent we see in toluene- d_8 that at 15 °C there is a coalescence behavior. However, in neat THF we only see a coalescence of H_z at -85 °C, 100 °C colder than in neat toluene- d_8 . This exchange process can be (i) by dissociation in neat toluene- d_8 or by (ii) an associative process described in THF where a five-coordinate intermediate possessing two axial sites occupied by THF ligands. These two spectra are shown in comparison in Figure 5 and 6.

Figure 5: Expanded aromatic region of dynamic (variable temperature) NMR studies showing stacked ¹H NMR spectra of (TMP)Zn(OCMe₂COOEt) (0.035M) compound in toluene-d₈. The coalescence temperature (T_c) is approximately 15 °C

Figure 6: Expanded aromatic region of dynamic (variable temperature) NMR studies showing stacked ^1H NMR spectra of (TMP)Zn(OCMe₂COOEt) (0.035M) compound in THF-d₈. The coalescence temperature (T_c) is approximately -85 °C

For the complex $[\text{TMPZn}(\mu\text{-OPr}^i)_2]$ we see a spectrum in neat THF which is consistent with a planar molecule. We see four signals for the methyl groups of w, z, y, and x in the ratio 2:4:2:2, respectively. For the aromatic protons we see H_w and $H_z = 1:2$, respectively and H_x and H_y as 1:1. Similarly the OPr^i ligand looks like a CH septet, 2H, and a doublet CMe, 6H. See the supporting information. (See the Figure S7)

Now if we record the spectrum in toluene- d_8 we observe something quite different. The region from 3.5 to 0.5 ppm is shown in Figure 7. Here we see at 27 °C a more complicated pattern. For a molecule having two four-coordinate molecules containing a mirror plane we might expect a 1:2:2:2:2 pattern assuming there is restricted rotation about the N – C group of the mesityl ligand attached to the N atoms. However, at 27 °C we see a more complicated pattern with a ratio of 1:1:2:2:2:1. Here we can state that the molecule lacks a plane of symmetry and that the methyl groups are c,c' and b, b' are now inequivalent. This would be consistent with the element of C_2 symmetry leading to a more complicated behavior and the OPr^i methyls which collapse to give two signals at -90 °C. This is consistent with the C_2 molecular symmetry observed in the solid state.

Figure 7: Expanded methyl region variable temperature ^1H 500 MHz NMR of 0.035mM $[(\text{TMP})\text{ZnO}^i\text{Pr}]_2$ in toluene- d_8 .

If we follow the signals associated with the aromatic region here we see H_x and H_y become inequivalent upon cooling, again further indicating a lack of a mirror plane of symmetry. Similarly if we look at the ^1H NMR of the z aromatic protons we see at room temperature there are two resonances and upon lowering the temperature these split to give four. Again a sufficient sign of the lack of a plane of symmetry at room temperature and a consistent sign of no

symmetry or C_2 symmetry present at low temperature. The spectrum shown for these aromatic protons is given in Figure 8.

Figure 8: Expanded aromatic-mesityl region variable temperature ^1H 500 MHz NMR of 0.035mM $[(\text{TMP})\text{ZnOiPr}]_2$ in toluene- d_8 . (* = Toluene- d_8 protio impurities)

Again these are quite different from what we see in neat THF which leads us to suggest that in neat THF we have $\text{TMPZnOPr}^i(\text{THF})$ where THF exchanges rapidly with free THF.

Homopolymerization

In a J-Young tube the reaction between *rac*-LA and $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ in CD_2Cl_2 at 25 °C showed first order kinetics in $[\text{Zn}]$ as seen in Figure 9. The $k_p = 0.57 \text{ M}^{-1}\text{s}^{-1}$ which is slower than that observed for the reaction in THF. The rate of reaction of ϵ -CL with this alkoxide is faster in CH_2Cl_2 , as can be seen in Figure 10, and still faster in neat THF. The Plot of molecular weight (M_n) and polydispersity index (PDI) vs % conversion of ϵ -caprolactone in THF using $[\text{TMPZnO}^i\text{Pr}]_2$ at 0 °C is shown in Figure 11.

Figure 9: Polymerization of *rac*-LA in CD_2Cl_2 at 25 °C using $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ as an initiator ($[\text{rac-LA}]_0 = 0.347 \text{ M}$; (■) $[\text{rac-LA}]_0/[\text{cat.}] = 34.8$, $k_{\text{app}} = 6.52 \times 10^{-2} \text{ min}^{-1}$ (linear fit, $R^2 = 0.99$); (▲) $[\text{rac-LA}]_0/[\text{cat.}] = 47.0$, $k_{\text{app}} = 4.80 \times 10^{-2} \text{ min}^{-1}$ (linear fit, $R^2 = 0.99$); (×) $[\text{rac-LA}]_0/[\text{cat.}] = 77.1$, $k_{\text{app}} = 2.84 \times 10^{-2} \text{ min}^{-1}$ (linear fit, $R^2 = 0.99$).

Figure 10: Polymerization of ϵ -CL at 25°C using $[(\text{TMP})\text{ZnOPr}^i]_2$ as an initiator ($[\epsilon\text{-CL}]_0 = 0.298$ M, $[(\text{TMP})\text{ZnOPr}^i]_2 = 6.02$ mM; (■) CH_2Cl_2 , $k_{\text{app}} = 0.0434 \text{ min}^{-1}$ (linear fit, $R^2 = 0.99$); (◆) THF, $k_{\text{app}} = 0.710 \text{ min}^{-1}$ (linear fit, $R^2 = 0.99$))

Based on these studies we note that the reaction in neat THF is faster than that in CD_2Cl_2 / CH_2Cl_2 and based on ^1H NMR studies it is most likely due to the presence of the monomer rather than the dimeric structure as seen in neat toluene- d_8 . This is quite contradictory to what we saw for $(\text{BDI})\text{M}^n\text{Bu}(\text{THF})^{1f}$ where $\text{M} = \text{Mg}$ or Zn and also different from that of $(\text{TMP})\text{Mg}^n\text{Bu}(\text{THF})$. Also when we look at the selectivity for *rac*-LA to give heterotactic PLA we see that the faster reaction in THF gives the higher $P_r = 0.96$ relative to the slower reaction in CD_2Cl_2 where $P_r = 0.75$, again indicating a different mechanism since a slower reaction normally enhances the selectivity of the reaction.

Figure 11: Plot of molecular weight (Mn) and polydispersity index (PDI) vs % conversion of ϵ -caprolactone in THF using $(\text{TMPZnO}^i\text{Pr})_2$ at 0 °C.

In the separate reactions between $\text{TMPZn}[\text{N}(\text{SiMe}_3)_2]$ and $\epsilon\text{-CL}$ and *rac*-LA in neat THF, we see that at room temperature $\epsilon\text{-CL}$ is converted to PCL and *rac*-LA to PLA. However, in non-coordinating solvents (C_6D_6 , CH_2Cl_2 or CD_2Cl_2) once the reaction starts to proceed the reaction is fast as shown in Figure 12. Here we believe that the induction period involves the initial reaction of $\epsilon\text{-CL}$ with the zinc amide as shown in Figure 13.

Figure 12: Ring-opening polymerization plot of $\epsilon\text{-CL}$ in C_6D_6 (♦) and THF-d_8 (■) using $\text{TMPZnN}(\text{SiMe}_3)_2$ at room temperature ($[\text{Catalyst}] = 6.90 \text{ mM}$, $[\epsilon\text{-CL}] = 0.34 \text{ M}$)

Figure 13: Possible induction routes in the reactivity of $\text{TMPZnN}(\text{SiMe}_3)_2$ with $\epsilon\text{-CL}$ in both non-coordinating solvents (C_6D_6 or CD_2Cl_2) and THF, respectively.

Concluding Remarks

The reactions of Mg and Zn supported by BDI and TMP are very similar with those containing Mg being faster than those of Zn. As we have shown here the dimeric nature of the alkoxide $[\text{TMPZn}(\text{O}^i\text{Pr})]_2$ is indicated by variable temperature ^1H NMR studies in toluene but not in THF. In contrast to other reagents involving BDI supported Mg and Zn reagents where reactions in THF are slower than those in non-coordinating solvents, we find here that the reactions are faster in THF. We assume that in THF we are dealing with a monomer while in the non-coordinating solvent we are dealing with a dimeric species.

Experimental

General considerations

All reactions were carried out under a purified nitrogen gas employing standard Schlenk line and drybox techniques. Dichloromethane, toluene, and THF were distilled at least twice under nitrogen from calcium hydride. *rac*-Lactide (*rac*-LA), ϵ -caprolactone (ϵ -Cl), were purchased from Sigma-Aldrich. Benzene- d_6 , THF- d_8 and chloroform- d_1 were purchased from Cambridge Isotopes. Anhydrous zinc chloride was purchased from Alfa Aesar and used as received. Lithium bis(trimethylsilyl)amide was purchased from Sigma-Aldrich. *rac*-LA was triple sublimed and crystallized twice in toluene, then dried under a dynamic vacuum at 50 °C overnight prior to use. ϵ -Caprolactone was stirred over calcium hydride overnight under nitrogen and distilled under reduced pressure at 90 °C prior to use.

Measurements

^1H and ^{13}C NMR spectra were acquired in C_6D_6 and CDCl_3 on Bruker DPX-400 and 500 NMR Spectrometers. All chemical shifts were determined using the residual protio impurity peaks; (C_6D_6 - 7.16 ppm, C_7D_8 - 2.08 and CDCl_3 - 7.26 ppm) and for C (C_6D_6 - 128.06 ppm, C_7D_8 - 20.43 ppm and CDCl_3 - 77.16 ppm).

Synthesis

$\text{Zn}[\text{N}(\text{SiMe}_3)_2]^{10}$: In a glovebox anhydrous zinc chloride (4.80 g, 35.2 mmol) and approximately two equiv. of lithium bis(trimethylsilyl)amide (12.0 g, 71.7 mmol) were charged into two separate 250 ml Schlenk flasks. These were then connected to a Schlenk line and placed under

nitrogen. THF (75 ml) was introduced into the flasks and then partially frozen in liquid nitrogen. The thawing solution of lithium bis(trimethylsilyl)amide was added drop wise into the thawing solution of zinc chloride. The reaction was allowed to stir for six hours at room temperature before removing the THF under vacuum. Toluene (50 ml) was added to extract the title compound and precipitate out lithium chloride. The toluene solution was filtered through a medium porosity frit with celite. The solution was concentrated in vacuum to afford colorless oil (10.0 g, 73.5% yield). ^1H NMR (400 MHz, C_6D_6): singlet at 0.21 ppm.

(TMP)ZnN(SiMe₃)₂: A 50ml Schlenk flask was charged with TMPH (1.23 g, 2.47 mmol) and $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ (1.00 ml, 2.47 mmol) in toluene (35 ml) inside the glovebox. This was refluxed for 15 h. The solution was cooled to room temperature before all volatiles were dried under dynamic vacuum to give the title compound as a brick red solid in quantitative yield (1.76 g, 98% yield). Crystals were grown overnight in a concentrated toluene solution at -25°C . ^1H NMR (400 MHz, C_6D_6): 6.84 (s, 4H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.82 (s, 2H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.71 (d, $J_{\text{HH}} = 4\text{Hz}$, 2H, pyrrole C–H), 6.13 (d, $J_{\text{HH}} = 4\text{Hz}$, 2H, pyrrole C–H), 2.27 (s, 12H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.24 (s, 6H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.23 (s, 3H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.18 (s, 6H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), -0.036 (s, 18H, CH_3) ppm. ^{13}C { ^1H } NMR (100 MHz, C_6D_6): δ/ppm 162.6, 145.9, 140.7, 138.6, 136.9, 135.8, 133.2, 132.9, 129.1, 120.1, 21.3, 21.2, 19.9, 4.98.

MALDI-TOF calculated most abundant MW for $[\text{M}+\text{THF}]$: 793.4. Found $[\text{M}+\text{THF}]$: 792.9

[(TMP)ZnOPr^{*i*}]₂: To a solution of (TMP)ZnN(SiMe₃)₂ (0.62 g, 0.86 mmol) in toluene (10 ml) at 0°C was added 2-propanol (66 μL , 0.86 mmol). The solution was stirred for 30 minutes before the solvent was removed under dynamic vacuum to give a bright orange solid. This was washed one time with 5 ml dry benzene to remove trace impurities (0.40 g, 75% yield). Crystals were

grown from a concentrated toluene solution overnight at -25°C. ^1H NMR (400 MHz, Toluene- d_8): 7.02 (s, 1H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.94 (s, 2H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.81 (s, 1H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.73 (s, 2H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.66 (d, $J_{\text{HH}} = 4\text{Hz}$, 2H, pyrrole C–H), 6.09 (d, $J_{\text{HH}} = 4\text{Hz}$, 2H, pyrrole C–H), 2.99 (m, 1H, $\text{OCH}(\text{CH}_3)_2$), 2.63 (s, 3H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.31 (s, 3H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.24 (s, 6H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.14 (s, 6H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.12 (s, 6H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.04 (s, 3H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 0.32 (d, 6H, $J_{\text{HH}} = 5.9\text{Hz}$, $\text{OCH}(\text{CH}_3)_2$) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, Toluene- d_8): δ/ppm 145.4, 142.9, 138.7, 138.5, 137.6, 137.5, 137.0, 136.6, 134.8, 133.5, 120.2, 65.7, 28.6, 21.9, 21.9, 21.6, 21.5, 19.9.

MALDI-TOF calculated most abundant MW for [M]: 1242.5. Found [M]: 1242.1

TMPZn(OCMe₂COOEt): A 50ml Schlenk flask was charged with (TMP)ZnN(SiMe₃)₂ (0.70 g, 0.97 mmol) in toluene (15 ml) and placed in an ice bath. Ethyl 2-hydroxy -2-methyl propanoate (HOCMe₂COOCH₂CH₃) was added using a 1 ml syringe (0.13 ml, 0.97 mmol). The solution was stirred for 30 minutes before removing all volatiles under dynamic vacuum to give the title compound as a bright orange solid (0.62 g, 0.93 mmol, 92.5 %). X-ray quality crystals were grown from a concentrated solution of dichloromethane in a freezer (-23 °C) overnight. ^1H NMR (400 MHz, THF- d_8): 6.97 (s, 2H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.75 (s, 4H, *m*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.54 (d, $J_{\text{HH}} = 4\text{Hz}$, 2H, pyrrole C–H), 6.13 (d, $J_{\text{HH}} = 4\text{Hz}$, 2H, pyrrole C–H), 4.06 (q, 2H, -OCH₂CH₃), 2.36 (s, 3H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.20 (s, 6H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.18 (s, 6H, *p*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.08 (s, 12H, *o*- $\text{C}_6\text{H}_2(\text{CH}_3)_3$), 1.18 (t, 3H, -OCH₂CH₃), 0.362 (s, 6H, -C(CH₃)₂) ppm. ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, Toluene- d_8): δ/ppm 161.9, 146.0, 140.7, 133.8, 132.4, 119.1, 74.18, 62.8, 29.5, 13.9, 1.36.

MALDI-TOF calculated most abundant MW for [M]: 692.3. Found [M]: 692.9

General procedure for studying the kinetics of *rac*-LA and ϵ -CL polymerization

A Schlenk flask was charged with a 0.298 M ϵ -CL solution in THF and DCM, respectively. A 6.02 mM solution of $[(\text{TMP})\text{ZnOPr}^i]_2$ was introduced to the respective flasks. At appropriate time intervals, 0.50 - 1.00 mL aliquots were taken out of the stirred solution and immediately quenched with one drop of acidified methanol. The aliquots were then dried under a dynamic vacuum and analysed by ^1H NMR spectroscopy. In cases where J-young tubes were used, respective ϵ -CL and *rac*-LA solutions were introduced via 1 mL syringe inside the glovebox. The respective catalysts/initiators were then introduced, quickly capped and the sample was inserted in the NMR spectroscopy where acquisitions were made at specified intervals.

Single Crystal X-ray Diffraction

Single crystals of $\text{TMPZn}[\text{N}(\text{SiMe}_3)_2]$, $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$ and $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$ were isolated as orange blocks, chunks and plates, respectively, and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with $\text{Mo K}\alpha$ radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack.¹¹ The structures were solved by the direct methods program in SHELXS-13 for $\text{TMPZn}[\text{N}(\text{SiMe}_3)_2]$ and $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$, and SHELXS-97 for $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$.¹² Full-matrix least-squares refinements based on F^2 were performed in SHELXS-13 for $\text{TMPZn}[\text{N}(\text{SiMe}_3)_2]$ and $\text{TMPZn}[\text{OCMe}_2\text{C}(\text{O})\text{OEt}]$, and SHELXS-97 for $[\text{TMPZn}(\mu\text{-OPr}^i)]_2$, as incorporated in the WinGX package.¹³ For each methyl group, the

hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5U_{eq}$ (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2U_{eq}$ (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.¹⁴ $TMPZn[OCMe_2C(O)OEt]$ contained disorder in the ethoxy group of the $OCMe_2C(O)OEt$ ligand. This disorder was modeled in two locations and allowed to refine on a free variable. Similarity restraints and ridged bond restraints were used to ensure reasonable bond lengths and thermal parameters for the disorder. $[TMPZn(\mu-OPr^f)]_2$ crystallized with a highly disordered toluene molecule on an inversion center. After numerous attempts to rationally model the solvent, it was removed using the SQUEEZE¹⁵ protocol of PLATON.¹⁶ Ultimately 66 electrons were removed from a void of $353 \text{ \AA}^3$ which corresponds to the toluene used in crystallization. Further details can be found embedded in the supporting CIF.

CCDC 986713, 1032738 – 1032739 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

AUTHOR INFORMATION

Corresponding Author

*Chisholm@chemistry.ohio-state.edu

Funding Sources

We thank the Department of Energy, Office of Basic Sciences, Chemistry Division for support of this project.

ACKNOWLEDGMENT

We thank the Department of Energy, Office of Basic Sciences, Chemistry Division for support of this project.

REFERENCES

-
- ¹ B. F. G. Johnson, W. P. Griffith, R. J. H. Clark, J. Evans, B. H. Robinson, P. R. Raithby, *Dalton Trans.* 44 (2015) 3896.
- ² (a) M. S. Khan, A. K. Kakkar, N. J. Long, J. Lewis, P. Raithby, P. Nguyen, T. B. Marder, F. Wittmann, R. H. Friend, *J. Mater. Chem.* 4 (1994) 1227. (b) J. Lewis, N. J. Long, P. R. Raithby, G. P. Shields, W.-Y. Wong, M. Younus, *J. Chem. Soc., Dalton Trans.* (1997), 4283. (c) J. Lewis, P. R. Raithby, W.-Y. Wong, *J. Organomet. Chem.* 556 (1998) 219. (d) W.-Y. Wong, W.-K. Wong, P. R. Raithby, *J. Chem. Soc., Dalton Trans.* (1998) 2761. (e) W.-Y. Wong, K.-H. Choi, G.-L. Lu, J.-X. Shi, *Macromol. Rapid Commun.* 22 (2001) 461. (f) W.-Y. Wong, S.-M. Chan, K.-H. Choi, K.-W. Cheah and W.-K. Chan, *Macromol. Rapid Commun.* 21 (2000) 453. (g) W.-Y. Wong, *Dalton Trans.* (2007) 4495. (h) W.-Y. Wong, *Coord. Chem. Rev.* 251 (2007) 2400. (i) C.-L. Ho, W.-Y. Wong, *Coord. Chem. Rev.* 257 (2013) 1614. (j) W.-Y. Wong, P. D. Harvey, *Macromol. Rapid Commun.* 31 (2010) 671. (k) G.-J. Zhou, W.-Y. Wong, *Chem. Soc. Rev.* 40 (2011) 2541
- ³ D. Beljonne, H.F. Wittmann, A. Köhler, S. Graham, M. Younus, J. Lewis, P.R. Raithby, M.S. Khan, R.H. Friend and J.L. Brédas, *J. Chem. Phys.*, 105 (1996) 3868.
- ⁴ (a) W.-Y. Wong, C.-L. Ho, *Acc. Chem. Res.* 43 (2010) 1246. (b) N. Chawdhury, A. Köhler, R. H. Friend, W.-Y. Wong, J. Lewis, M. Younus, P. R. Raithby, T. C. Corcoran, M. R. A. Al-Mandhary, M. S. Khan *J. Chem. Phys.* 110 (1999) 4963. (c) W.-Y. Wong, X.-Z. Wang, Z. He, A. B. Djurišić, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S. K. Mak, W.-K. Chan, *Nat. Mater.* 6 (2007) 521. (d) W.-Y. Wong, *Macromol. Chem. Phys.* 209 (2008), 14. (e) L. Liu, C.-L. Ho, W.-Y. Wong, K.-Y. Cheung, M.-K. Fung, W.-T. Lam, A. B. Djurišić, W.-K. Chan *Adv. Funct. Mater.* 2008, 18, 2824-2833. (f) Q. Wang, W.-Y. Wong *Polym. Chem.* 2 (2011) 432. (g) H. Zhan, S. Lamare,

A. Ng, T. Kenny, H. Guernon, W.-K. Chan, A. B. Djurišić, P. D. Harvey, W.-Y. Wong, *Macromolecules* 44 (2011) 5155. (h) X.-Z. Wang, Q. Wang, L. Yan, W.-Y. Wong, K.-Y. Cheung, A. Ng, A. B. Djurišić, W.-K. Chan, *Macromol. Rapid Commun.* 31 (2010) 861. (i) C. Qin, Y. Fu, C.-H. Chui, C.-W. Kan, Z. Xie, L. Wang, W.-Y. Wong, *Macromol. Rapid Commun.* 32 (2011) 1472.

⁵ a) R. H. Platel, L. M. Hodgson, C.K. Williams, *Polymer Reviews*, 48 (2008) 11., b) M. J. Stanford and A. P. Dove *Chem. Soc. Rev.* 39 (2010) 486., c) P. Wongmahasirikun, P. Prom-on, P. Sangtrirutnugul, P. Kongsaree, K. Phomphrai, *Dalton Trans.* 44(2015) 12357. d) V. Balasanthiran, M. H. Chisholm, K. Choojun, C. B. Durr, *Dalton Trans.* 43 (2014) 2781., e) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* 122 (2000) 11845., f) V. Balasanthiran, M. H. Chisholm, K. Choojun, C. B. Durr, P. M. Wambua. *Polyhedron*, doi:10.1016/j.poly.2015.02.024 g) V. Balasanthiran, M. H. Chisholm, C. B. Durr, J. C. Gallucci, *Dalton Trans.* 42 (2013) 11234. h) V. Balasanthiran, C. Chatterjee, M. H. Chisholm, N. D. Harrold, T. V. RajanBabu, G. A. Warren, *J. Am. Chem. Soc.* 137 (2015) 1786.

⁶a) M. H. Chisholm, J. C. Huffman, K. Phomphrai, *J. Chem. Soc., Dalton Trans.* (2001) 222., b) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Organomet. Chem.* 683 (2003) 137., c) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J Am Chem Soc.* 123 (2001) 3229., d) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* 43 (2004) 6717.

⁷ a) C. Bakewell, A. J. P. White, N. J. Long, and C. K. Williams *Angew. Chem. Int. Ed.* 53 (2014) 9226. b) T.-P.-A. Cao, A. Buchard, X. F. Le Goff, A. Auffrant, C. K. Williams, *Inorg Chem.* 51 (2012) 2157., c) B. M. Chamberlain, B. A. Jazdzewski, M. Pink, M. A. Hillmyer, W. B. Tolman, *Macromolecules* 33 (2000) 3970.

⁸ Chisholm, M.; Choojun, K.; Gallucci, J.; Wambua, P. *Chem. Sci.* 3 (2012) 3445.

⁹ Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 250 (1983) 395.

¹⁰ D. J. Darensbourg, M. W. Holtcamp, G. E. Struck, M. S. Zimmer, S. A. Niezgoda, P. Rainey, J. B. Robertson, J. D. Draper, J. H. Reibenspies, *J. Am. Chem. Soc.* 121 (1999), 107.

¹¹ Z. Otwinowski and W. Minor, *Methods in Enzymology*, Vol. 276: Macromolecular Crystallography, Part A, Academic Press, 1997.

¹² G. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.* 64 (2008) 112.

¹³ L. Farrugia, *J. Appl. Crystallogr.*, 1999, 32, 837.

¹⁴ *International Tables for Crystallography*, Volume C, ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1st edn, 1992.

¹⁵ Sluis, P. v. d.; Spek, A. L., *PLATON/SQUEEZE. Acta Crystallogr., Sect. A* 46 (1990) 194.

¹⁶ Spek, A. L., *Structure Validation in Chemical Crystallography. Acta Crystallogr., Sect. D* 65 (2009) 148.