

# Zirconocene Alkoxides and Aryloxides for the Polymerization of L- and *rac*-Lactide

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**ABSTRACT:** A family of well-defined cyclopentadienyl and indenyl group 4 complexes has been prepared. The complexes (Cp)<sub>2</sub>ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (1), (Cp)<sub>2</sub>Zr(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (2), (Cp)<sub>2</sub>ZrMe(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (3), (Ind)<sub>2</sub>ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (4), (Ind)<sub>2</sub>ZrMe(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (5), (Ind)<sub>2</sub>ZrMe(O<sup>t</sup>Bu) (6), and *rac*-(EBI)ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (7) were investigated as catalysts for the polymerization of L- and *rac*-lactide. (Ind)<sub>2</sub>ZrMe(O<sup>t</sup>Bu) was shown to be the fastest catalyst. At 100 °C, the rates of polymerization (*k*<sub>obs</sub>) for L- and *rac*-lactide were very similar (0.317 and 0.293 h<sup>-1</sup> respectively). However, it was found that polymerization of L-LA (*k*<sub>obs</sub> = 0.217 h<sup>-1</sup>) was twice as fast as *rac*-LA (*k*<sub>obs</sub> = 0.120 h<sup>-1</sup>) at 80 °C.

## INTRODUCTION

Poly(lactic acids) (PLAs) have been studied intensely over the past few decades because of their biodegradability and biocompatibility.<sup>1,2</sup> PLA possesses versatile physical properties and has been used in tissue engineering and medical applications such as the media for controlled drug release.<sup>3,4</sup> Ring-opening polymerization (ROP) of lactide (LA) by single-site catalysts is the most efficient route to PLAs with controlled molecular weight and narrow molecular weight distribution. Numerous catalysts have been developed over the last twenty years.<sup>5-15</sup> The two stereogenic centers in one lactide molecule result in three distinct configurational isomers (*S,S*)-LA, (*L,L*)-LA, (*R,R*)-LA, (*D,D*)-LA) and (*R,S*)-LA, *meso*-LA. The 1:1 mixture of (*S,S*)-LA and (*R,R*)-LA is referred to as *rac*-LA (Figure 1).

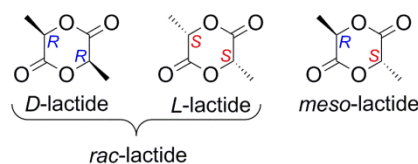


Figure 1. Lactide monomers

Group 4 zirconocenes can be defined as *d*<sup>0</sup> pseudo-tetrahedral organometallic compounds in which the central zirconium atom bears two η<sup>5</sup>-cyclopentadienyl (Cp) type ligands and two σ-type ligands.<sup>16</sup> However, group 4 *ansa*-indenyl metallocenes, which are so influential in olefin polymerization catalysis,<sup>17</sup> have barely been explored in the context of lactide polymerization.<sup>18</sup>

In 2008, Chen and co-workers conducted the first L-lactide polymerization using group 4 metallocenes with enolate leaving groups.<sup>19</sup> They found that these compounds produced 100% isotactic PLA with reasonable activity (92% conversion in 105 min for the C<sub>s</sub>-symmetric catalyst, A); C<sub>2</sub>, B, and C<sub>2v</sub>, C, symmetric zirconocenes were slow catalysts, Chart 1.

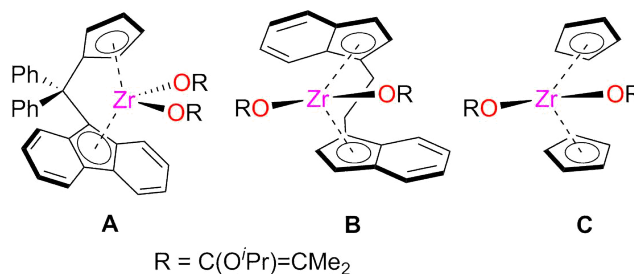


Chart 1. Complexes used by Chen and co-workers.<sup>19</sup>

Recently, we reported a family of well-defined chiral group 4 cyclopentadienyl alkoxide and aryloxide complexes based on the hydropermethylpentalenyl ligand, D in Chart 2, for the polymerization of L- and *rac*-lactide monomers demonstrating extremely high rate of propagation.<sup>20</sup>

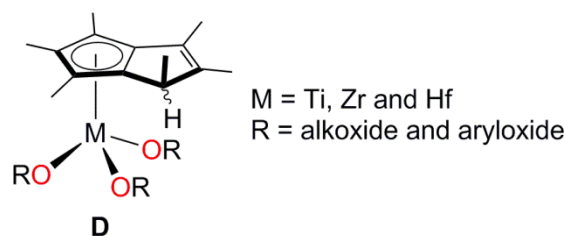


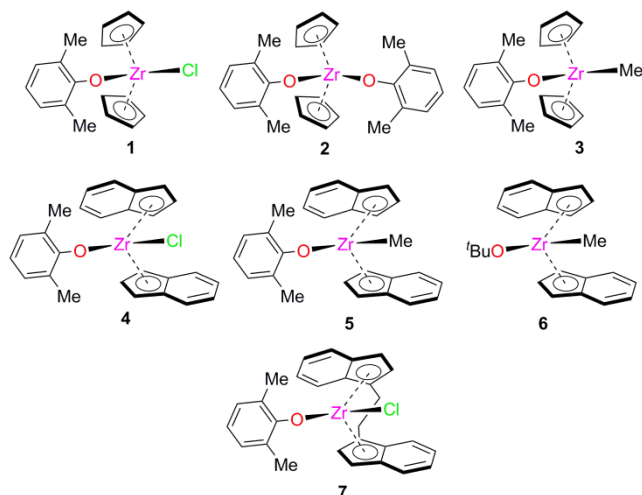
Chart 2. Complexes used by Turner *et al.*<sup>20</sup>

We report here the synthesis and the study of well-defined cyclopentadienyl and indenyl zirconocene alkoxides as catalysts for the polymerization of lactide monomers.

## RESULTS AND DISCUSSION

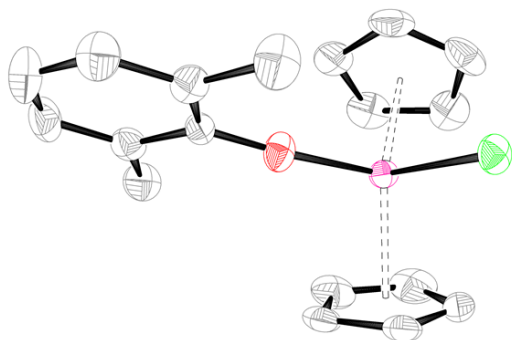
### Synthesis of zirconocene alkoxide and aryloxide complexes.

Seven zirconium alkoxide and aryloxide complexes based on cyclopentadienyl, indenyl and ethylene bridged (bis)indenyl ligands were used for this study, Chart 3.



**Chart 3.** Complexes used in this study.

Complexes **1–3** and **6** were synthesized following adapted literature procedure.<sup>21–22</sup>  $(\text{Cp})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**1**) co-crystallized with  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (**2**) from 50:50 mixture of **1** and **2** in hexane at  $-34^\circ\text{C}$ . The molecular structure of **1** obtained from an X-ray structure analysis of a co-crystal depicted in Figure 2. The full structure of the co-crystal is shown in Figure S11.



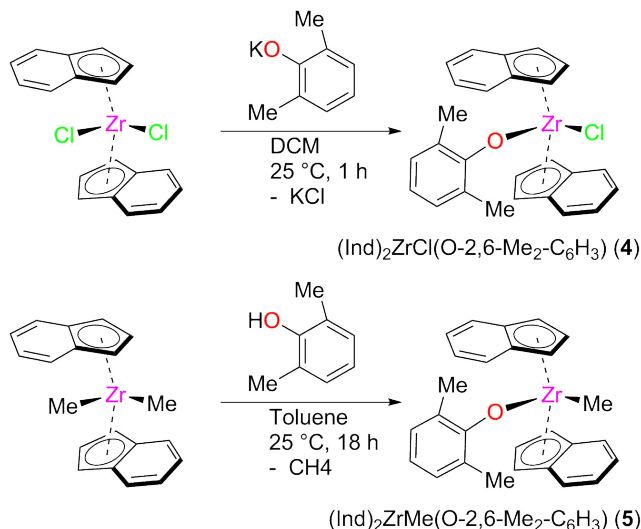
**Figure 2.** Solid-state molecular structure of  $(\text{Cp})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**1**). Ellipsoids are given at 50% probability. Hydrogen atoms omitted for clarity; pink: zirconium, green: chloride, red: oxygen and grey: carbon. Selected bond lengths (Å) Zr–Cp<sub>cent</sub> 2.220, 2.218; Zr–Cl 2.4765(13), and Zr–O 1.955(3).

The average Zr–Cp<sub>cent</sub> distance (2.219 Å) is in agreement with the reported distance for  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (2.235 Å),<sup>22</sup> and  $\text{Cp}_2\text{ZrCl}_2$  (2.203 Å).<sup>23</sup> The Zr–O distance (1.955(3) Å) is in agreement with average bond length of  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (1.9965 Å).<sup>22</sup> The Zr–O–C bond angle ( $171.6(3)^\circ$ ) is very large in comparison to the average angle for  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  ( $146.0^\circ$ ),<sup>22</sup> similar to  $(\text{Cp})_2\text{ZrCl}(\text{O}^t\text{Bu})$  ( $176.2(3)^\circ$ ).<sup>24,25</sup> The Zr–Cl distance (2.4765(13) Å) is within the literature range;<sup>26–27</sup> as is the angle between the two Cp rings ( $52.70^\circ$ ;  $52.3^\circ$  for  $\text{Cp}_2\text{ZrCl}_2$  and  $52.8(5)^\circ$  for  $\text{Cp}_2\text{ZrCl}(\text{O}^t\text{Bu})$ ).<sup>27</sup>

Modified literature procedures were used to prepare  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**4**) and  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**5**), Scheme 1.<sup>28,29</sup> Stoichiometric reaction of  $(\text{Ind})_2\text{ZrCl}_2$  and  $\text{K}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  was carried out in DCM for 1 h. After work-up a yellow solid was afforded in 6% isolated yield. This reactivity was exploited to synthesize

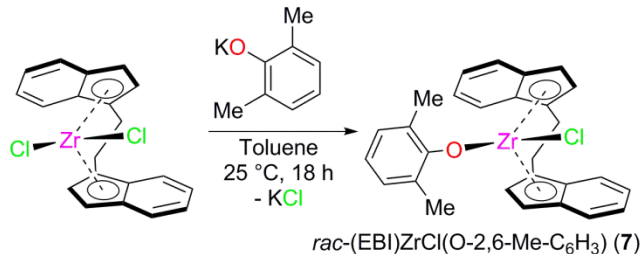
$(\text{Ind})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)\text{Me}$  (**5**). Stoichiometric amounts of  $(\text{Ind})_2\text{ZrMe}_2$  and  $\text{H}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  were stirred in toluene at room temperature for 18 h. After concentration *in vacuo*, **5** was obtained as a colorless deliquescent solid in 75% yield.

**Scheme 1. Synthesis of  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**4**) and  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**5**)**

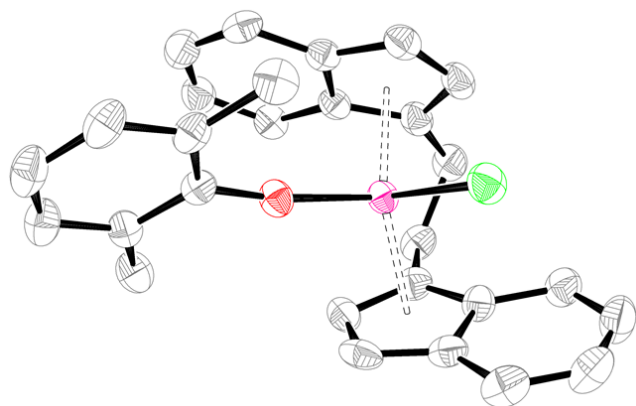


Stoichiometric amounts of  $\text{K}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  and  $\text{rac}(\text{EBI})\text{ZrCl}_2$ , {EBI = ethylenebis(1-indenyl)} were stirred in toluene for 18 h at room temperature, and following work-up,  $\text{rac}(\text{EBI})\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**7**) was isolated as a yellow solid in 80% yield (Scheme 2).

**Scheme 2 Synthesis of  $(\text{EBI})\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**7**)**

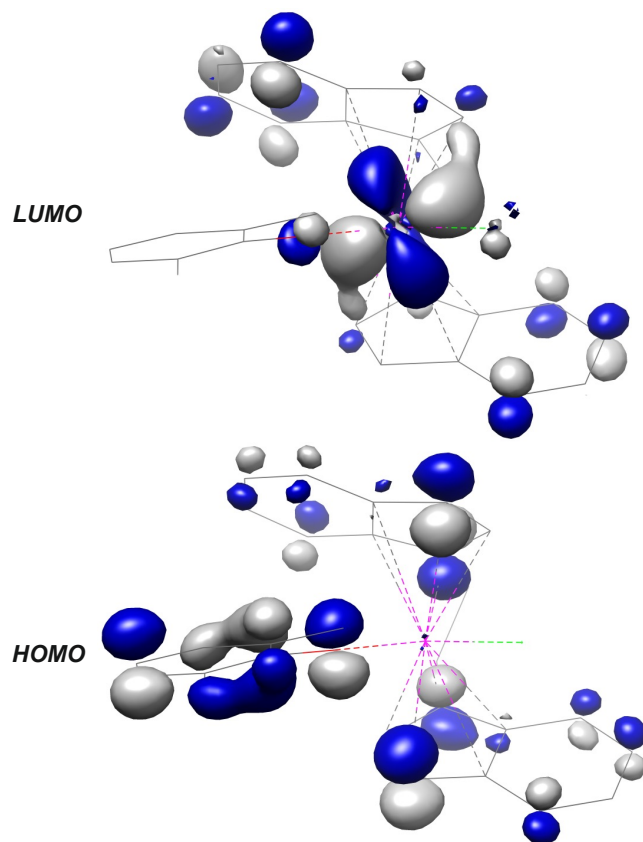


Yellow crystals of  $\text{rac}(\text{EBI})\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**7**) suitable for single-crystal X-ray structure analysis were grown overnight in toluene at room temperature. The molecular structure is shown in Figure 3 and the DFT-computed HOMO and LUMO of the geometry optimized structure is presented in Figure 4. The compound crystallizes in the orthorhombic *Pcab* space group with two molecules in the asymmetric unit. The Zr–O–C bond angle of  $171.4(3)^\circ$  is typical of zirconocene-aryloxide bonds,  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{-C}_6\text{H}_3)\text{Cl}$  has a Zr–O–C bond angle of  $172.7(1)^\circ$ .<sup>30</sup> The carbon-oxygen bond length in **7** (1.352(6) Å) is shorter than in 2,6-dimethylphenol (1.364 Å) suggesting that the geometry of **7** is dominated by steric factors.<sup>30–31</sup> Both Zr–O (1.942(3)°) and Zr–Cl (2.4434(15)°) in **7** are shorter than in complex **1** (1.955(3)° and 2.4765(13)° respectively).



**Figure 3** Molecular structure of (EBI)ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (7). Ellipsoids are given at 50% probability. Hydrogen atoms are omitted for clarity; pink: zirconium, green: chloride, red: oxygen and grey: carbon. Selected bond lengths (Å) and angles (°): Zr-O 1.942(3), Zr-Cl 2.4434(15), O-C2 1.352(6), and O-Zr-Cl 99.35(11).

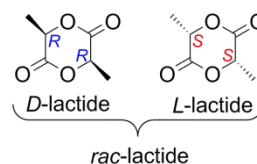
Calculations of complex **7** at the B<sub>3</sub>LYP level of DFT<sup>32,33</sup> resulted in geometry optimized structures which agreed well with the experimental crystallographic data. The HOMO is ligand-based with contributions from C p<sub>z</sub> orbitals of the aryloxy and indenyl groups as well as the p<sub>z</sub> orbital on the aryloxy oxygen. The LUMO is largely metal-based with 12.6% d<sub>z<sup>2</sup></sub>, 17.4% d<sub>x<sup>2</sup>-y<sup>2</sup></sub> character as well as minor contributions from d<sub>xz</sub> and d<sub>xy</sub> orbitals.



**Figure 4** Illustration of the DFT-computed HOMO and LUMO of (EBI)ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (7).

## Polymerization of L- and rac-lactide monomers.

Compounds **1-7** were used in the ring-opening polymerization of L- and rac-lactide monomers (Figure 5). The results are collated in Table 3 and displayed in Figures 6 and 7.



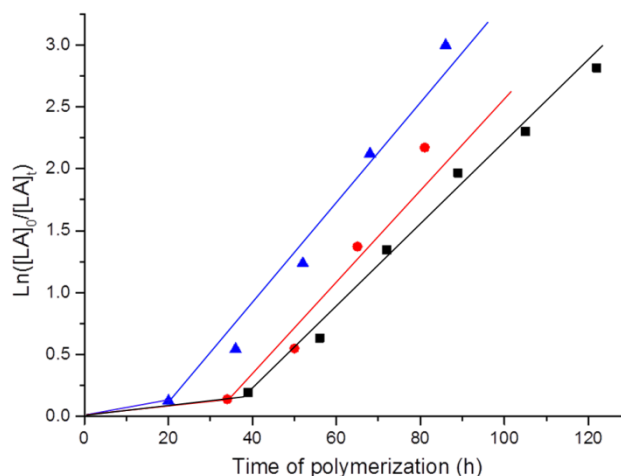
**Figure 5** L- and rac-lactide monomers

**Table 1.** Summary of polymerization data using cyclopentadienyl based complexes **1-3**<sup>a</sup>

Catalyst	T (°C)	LA	$k_{\text{obs}}$ (h <sup>-1</sup> )	$M_n^b$ (g/mol)	$M_w/M_n^b$
<b>1</b>	100	L-	0.044 ± 0.005	16860	1.56
<b>2</b>	100	L-	0.032 ± 0.002	14363	1.43
<b>3</b>	100	L-	0.045 ± 0.003	17928	2.01
<b>2</b>	100	rac-	0.050 ± 0.006	11515	1.62
<b>3</b>	100	rac	0.042 ± 0.005	–	–
<b>3</b>	80	L-	0.029 ± 0.004	7278	1.29
<b>3</b>	60	L-	0.002 ± 0.000	3996	1.57

<sup>a</sup>Polymerization conditions: 100 °C, [LA]<sub>0</sub>/[Zr]<sub>0</sub> = 50, [LA]<sub>0</sub> = 0.5 M, chloroform-*d*<sub>1</sub>. <sup>b</sup>Measured by GPC, calibrated with PS standards in THF.<sup>15</sup>

Pseudo-first-order kinetic data of the polymerization of lactide monomers were recorded using the catalysts (Cp)<sub>2</sub>ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (**1**), (Cp)<sub>2</sub>Zr(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**2**), and (Cp)<sub>2</sub>ZrMe(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (**3**) with a monomer to catalyst ratio of 50 at 100 °C in chloroform-*d*<sub>1</sub>, Figure 6.

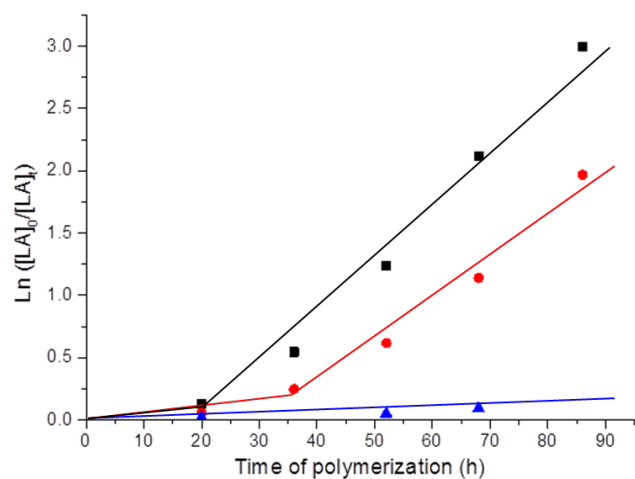


**Figure 6.** L-lactide polymerization using the complexes: (Cp)<sub>2</sub>ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (**1**) (red circle,  $k_{\text{obs}}$  = 0.044±0.005 h<sup>-1</sup>), (Cp)<sub>2</sub>Zr(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**2**) (black square,  $k_{\text{obs}}$  = 0.032±0.002 h<sup>-1</sup>), (Cp)<sub>2</sub>ZrMe(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (**3**) (blue triangle,  $k_{\text{obs}}$  = 0.045±0.003 h<sup>-1</sup>). Polymerization conditions: chloroform-*d*<sub>1</sub> at 100 °C with [LA]<sub>0</sub>/[M]<sub>0</sub> = 50 and [LA]<sub>0</sub> = 0.5 M.

After their initiation periods of between 20 and 40 hours, all complexes show similar rate of polymerization of L-lactide ( $k_{\text{obs}}$  of 0.044, 0.032 and 0.045 h<sup>-1</sup> for **1**, **2**, and **3** respectively),

Figure 6. This is similar to the result reported by Chen and co-workers where  $(\text{Cp})_2\text{Zr}(\text{OC}(\text{OiPr})=\text{CMe}_2)_2$  achieved 7% conversion after 26 h.<sup>19</sup> The molecular weights,  $M_w$ , and polydispersities,  $M_w/M_n$ , are high ( $14363 < M_w < 17928$  g/mol and  $1.43 < M_w/M_n < 2.01$ ), highlighting the presence of transesterifications due to the high temperature needed for the polymerization or that only half of the amount of the catalyst was used (not every metal centre in the reaction is active during polymerization). Similar effects can be seen when complexes  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (**2**),  $(\text{Cp})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**3**) were used for the polymerization of *rac*-lactide at 100 °C. They polymerize *rac*-lactide at the similar rate as for L-lactide (for **2**,  $k_{\text{obs}}$  of 0.032 and 0.050 h<sup>-1</sup> for L- and *rac*-lactide, respectively; for **3**,  $k_{\text{obs}}$  of 0.045 and 0.042 h<sup>-1</sup> for L- and *rac*-lactide, respectively, Table 1). These rate constants are also consistent with those reported for the ROP of *rac*-lactide in the literature.<sup>13a,13b</sup>  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (**2**) is shown to carry out ROP of L- and *rac*-lactide with a similar level of control ( $M_w/M_n$  values of 1.56 and 1.62 respectively) with molecular weights,  $M_n$ , closer to the theoretical value ( $M_n$  of 11515 and 14363 g/mol for *rac*- and L-lactide respectively).

A study of the variation of polymerization activity as a function of temperature was carried out using  $(\text{Cp})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**3**), Figure 7. The polydispersities of the isolated PLA decreased with temperature (Table 1), although there appears to be a more controlled polymerization around 80 °C,  $M_n$  of 7278 g/mol and  $M_w/M_n$  of 1.29.



**Figure 7.** L-lactide polymerization using  $(\text{Cp})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**3**): 100 °C (black square,  $k_{\text{obs}} = 0.045 \pm 0.003$  h<sup>-1</sup>), 80 °C (red circle,  $k_{\text{obs}} = 0.029 \pm 0.004$  h<sup>-1</sup>), 60 °C (blue triangle,  $k_{\text{obs}} = 0.002 \pm 0.000$  h<sup>-1</sup>). Polymerization conditions: chloroform-*d*<sub>1</sub> with  $[\text{LA}]_0/[\text{M}]_0 = 50$  and  $[\text{LA}]_0 = 0.5$  M.

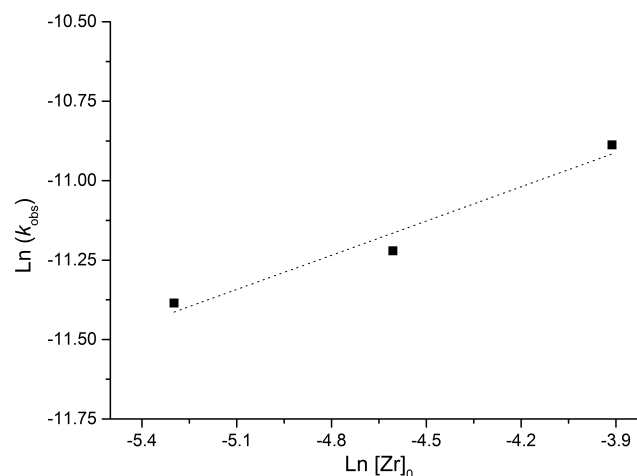
From these polymerization data, it was possible to obtain the activation parameters for the ring-opening polymerization of L-lactide using  $(\text{Cp})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**3**) using Eyring plots. They were found to be  $\Delta H^\ddagger$  of 94.0 kJmol<sup>-1</sup> and  $\Delta S^\ddagger$  of -84.7 Jmol<sup>-1</sup>K<sup>-1</sup>. These values agree with literature values for ROP of lactide.<sup>36</sup> In order to study the effect of varying the monomer to catalyst ratio, pseudo-first-order kinetic data of the polymerization of L-lactide at 100 °C using  $(\text{Cp})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**3**) were collected at various catalyst concen-

trations. The results are collated in Table 2 and illustrated in Figure 8.

**Table 2.** L-lactide polymerization: variation of the catalyst concentration<sup>a</sup>

Catalyst	$[\text{LA}]_0/[\text{Zr}]_0$	$k_{\text{obs}}$ (h <sup>-1</sup> )	$M_n^b$ (g/mol)	$M_w/M_n^b$
3	25	$0.067 \pm 0.003$	8912	2.40
3	50	$0.045 \pm 0.003$	17928	2.01
3	100	$0.041 \pm 0.001$	11212	1.87

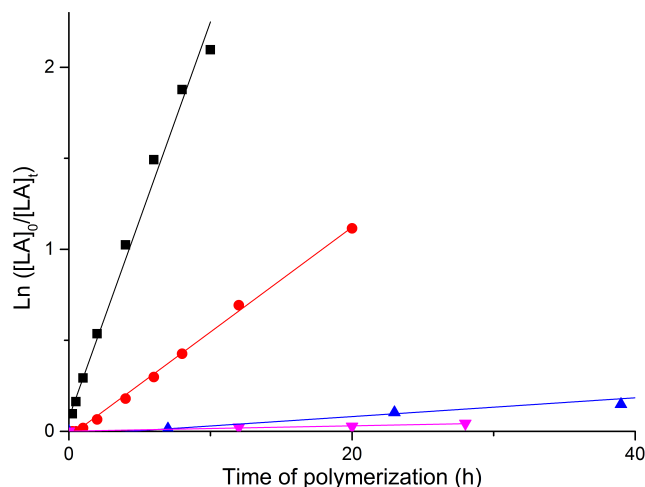
<sup>a</sup>Polymerization conditions: 100 °C,  $[\text{LA}]_0 = 0.5$  M, chloroform-*d*<sub>1</sub>. <sup>b</sup>Measured by GPC, calibrated with PS standards in THF.<sup>15</sup>



**Figure 8.** Plot of  $\ln(k_{\text{obs}})$  vs  $\ln([\text{Zr}]_0)$  using  $(\text{Cp})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**3**): slope:  $0.359 \pm 0.070$  with  $R^2 = 0.981$ . Polymerization conditions: chloroform-*d*<sub>1</sub> at 100 °C with  $[\text{LA}]_0 = 0.5$  M.

These data are consistent with the chain propagation reaction being first order overall in  $[\text{Zr}]$ , which is in agreement with a coordination-insertion mechanism. The polymerization is better controlled at lower concentrations, as demonstrated by decreasing polydispersities with decreasing concentration, Table 2. However, the molecular weight highlights the presence of transesterification processes ( $M_n$  of 8912, 17928 and 11212 g/mol for increasing concentration ratio). Pseudo-first order kinetic data of the polymerization of L-lactide using indenyl based complexes:  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**4**),  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**5**),  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (**6**) and *rac*-(EBI) $\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**7**) are shown in Figure 9. All initial polymerization studies were carried out at 80 °C in chloroform-*d*<sub>1</sub>, with a monomer to catalyst ratio of 50.



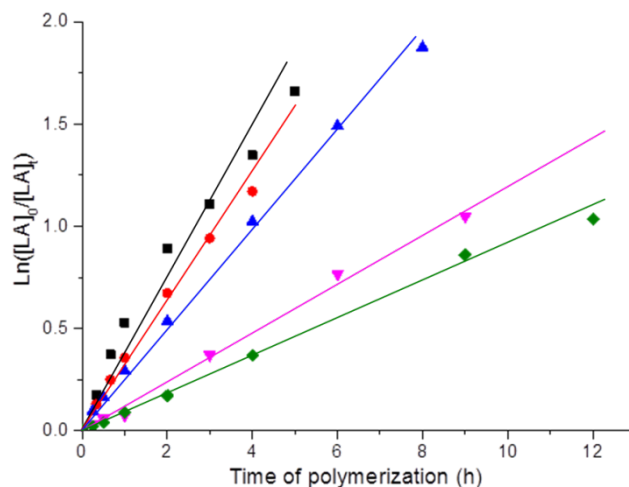


**Figure 9.** L-lactide polymerization using the complexes:  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (4) (blue triangle,  $k_{\text{obs}} = 0.004 \pm 0.000 \text{ h}^{-1}$ ),  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (5) (red circle,  $k_{\text{obs}} = 0.057 \pm 0.001 \text{ h}^{-1}$ ),  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (6) (black square,  $k_{\text{obs}} = 0.217 \pm 0.008 \text{ h}^{-1}$ ) and  $(\text{EBI})\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (7) (pink triangle,  $k_{\text{obs}} = 0.002 \pm 0.000 \text{ h}^{-1}$ ). Polymerization conditions: chloroform- $d_1$  at  $80^\circ\text{C}$  with  $[\text{LA}]_0/[\text{M}]_0 = 50$  and  $[\text{LA}]_0 = 0.5 \text{ M}$ .

Figure 9 shows that  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (6) displayed the highest activity with 84% conversion in 8 h ( $k_{\text{obs}} = 0.217 \text{ h}^{-1}$ ). This is comparable to moderate activities of zirconium catalysts in the literature.<sup>34</sup> Jones and co-workers reported  $k_{\text{obs}}$  of  $0.018 \text{ h}^{-1}$  and  $0.192 \text{ h}^{-1}$  for their hafnium and zirconium salalen complexes in similar polymerisation conditions.<sup>34c,i</sup> Gibson and co-workers reported  $\text{Ti}(\text{salen})(\text{O}^i\text{Pr})_2$  demonstrating a  $k_{\text{obs}}$  of  $0.222 \text{ h}^{-1}$ .<sup>34f</sup> A significantly lower activity was displayed by  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (5), which achieved 74% conversion after 28 h ( $k_{\text{obs}} = 0.057 \text{ h}^{-1}$ ), at a rate 4.5 times slower than  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$ . Interestingly,  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  displayed an initiation period of around half an hour. These observations are rationalized by the increased bulk of the aryl-oxide substituent of 5 compared to the *tert*-butoxide substituent of 6. In comparison,  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (4) and *rac*-(EBI)ZrCl(O-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>) (7) exhibited the lowest catalytic activities ( $k_{\text{obs}}$  of  $0.004$  and  $0.002 \text{ h}^{-1}$  for 4 and 7 respectively), which is comparable for 7 to *rac*-(EBI)Zr(OC(O<sup>*i*</sup>Pr)=CMe<sub>2</sub>) (7% conversion in 18 h at  $80^\circ\text{C}$  in toluene) synthesized by Chen and co-workers.<sup>19</sup> The rate of 7 is two orders of magnitude less than 5 and 6, probably due to both the increased bulk of the aryloxide compared to the *tert*-butoxide and the increased rigidity conferred by the *ansa*-bridged ligand, preventing reorientation of the indenyl moieties. The change of the chloride (4) to a methyl (5) increases the activity by an order of magnitude. Complex  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (4) is seen to polymerize *rac*-lactide over two times faster than L-lactide ( $k_{\text{obs}}$  of  $0.009$  and  $0.004 \text{ h}^{-1}$ , respectively). This behavior has been shown before by Davidson and co-workers with a zirconium alkoxide amine tris-phenolate catalyst,<sup>31</sup> and by Coates and co-workers with zinc  $\beta$ -diiminato catalyst.<sup>8a</sup> Furthermore, molecular weights and polydispersities demonstrate good control ( $M_n$  of  $7296 \text{ g/mol}$  and  $M_w/M_n$  of  $1.36$ ).

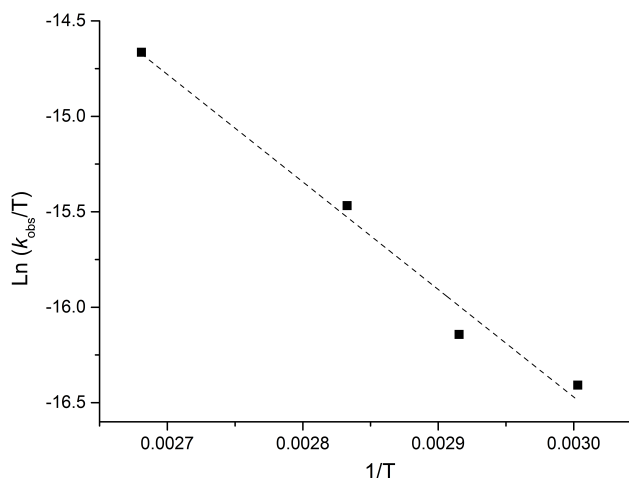
As  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (6) showed the highest rate of polymerization, further studies were carried out to investigate its stereoselectivity and estimate its activation parameters.

Polymerizations using  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (6) as the catalyst were carried out between  $60^\circ\text{C}$  and  $100^\circ\text{C}$ , with the same monomer to catalyst ratio of 50:1, Figure 10.



**Figure 10.** L-lactide polymerization using  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (6): L-lactide,  $100^\circ\text{C}$  (black square,  $k_{\text{obs}} = 0.317 \pm 0.019 \text{ h}^{-1}$ ), *rac*-lactide,  $100^\circ\text{C}$  (red circle,  $k_{\text{obs}} = 0.293 \pm 0.010 \text{ h}^{-1}$ ), L-lactide,  $80^\circ\text{C}$  (blue triangle,  $k_{\text{obs}} = 0.217 \pm 0.008 \text{ h}^{-1}$ ), *rac*-lactide,  $80^\circ\text{C}$  (pink triangle,  $k_{\text{obs}} = 0.120 \pm 0.004 \text{ h}^{-1}$ ) and L-lactide,  $60^\circ\text{C}$  (green diamond,  $k_{\text{obs}} = 0.090 \pm 0.002 \text{ h}^{-1}$ ). Polymerization conditions: chloroform- $d_1$  with  $[\text{LA}]_0/[\text{M}]_0 = 50$  and  $[\text{LA}]_0 = 0.5 \text{ M}$ .

At  $100^\circ\text{C}$ , the rates of polymerization for L- and *rac*-lactide were similar ( $k_{\text{obs}}$  of  $0.317$  and  $0.293 \text{ h}^{-1}$  respectively). However, it was found that polymerization of L-LA ( $k_{\text{obs}} = 0.217 \text{ h}^{-1}$ ) was twice as fast as *rac*-LA ( $k_{\text{obs}} = 0.120 \text{ h}^{-1}$ ) with 7 at  $80^\circ\text{C}$ . At  $60$  and  $70^\circ\text{C}$ ,  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  shows rates of  $0.090$  and  $0.120 \text{ h}^{-1}$  respectively. The enthalpy of activation ( $\Delta H^\ddagger$ ) and the entropy of activation ( $\Delta S^\ddagger$ ) were calculated from a plot of  $\ln(k_{\text{obs}}/T)$  vs.  $(1/T)$  (Figure 11), giving  $\Delta H^\ddagger = 46.9 \text{ kJ.mol}^{-1}$  and  $\Delta S^\ddagger = -193.9 \text{ J.K}^{-1}.\text{mol}^{-1}$ . These values are consistent with the literature.<sup>36</sup>



**Figure 11.** Semi-logarithmic plots of the rate of propagation vs. the inverse of the temperature,  $\Delta H^\ddagger = 46.9 \text{ kJ.mol}^{-1}$  and

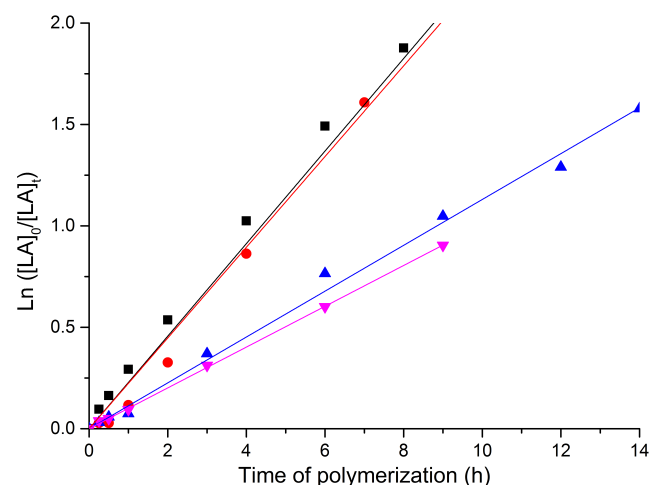
$\Delta S^\ddagger = -193.9 \text{ J.K}^{-1}\text{.mol}^{-1}$ . Polymerization conditions: chloroform- $d_1$ , with  $[\text{LA}]_0/[\text{M}]_0 = 50$  and  $[\text{LA}]_0 = 0.5 \text{ M}$ .

Polymerizations of L-LA and *rac*-LA were repeated at 80 °C with the addition of *tert*-butanol in stoichiometric amounts with  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (**6**), Figure 12 and Table 3.

**Table 3. L-lactide polymerization: alcohol addition<sup>a</sup>**

Catalyst	Alcohol	$k_{\text{obs}}$ ( $\text{h}^{-1}$ )	$M_n^b$ (g/mol)	$M_w/M_n^b$
<i>rac</i> -LA	No	$0.120 \pm 0.004$	11171	1.08
<i>rac</i> -LA	Yes	$0.100 \pm 0.003$	5779	1.10
L-LA	No	$0.217 \pm 0.008$	13813	1.12
L-LA	Yes	$0.211 \pm 0.003$	9065	1.09

<sup>a</sup>Polymerization conditions: 100 °C,  $[\text{LA}]_0/[\text{Zr}]_0 = 50$ , chloroform- $d_1$ . <sup>b</sup>Measured by GPC, calibrated with PS standards in THF.<sup>15</sup>

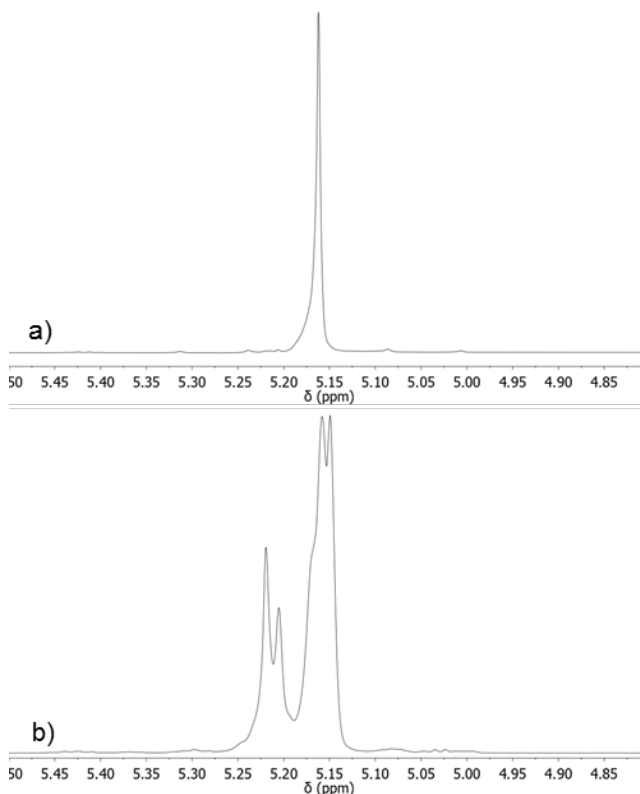


**Figure 12.** L- and *rac*-lactide polymerization using  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (**6**): L-lactide, without alcohol (black square,  $k_{\text{obs}} = 0.217 \pm 0.008 \text{ h}^{-1}$ ), L-lactide, with alcohol (red circle,  $k_{\text{obs}} = 0.211 \pm 0.003 \text{ h}^{-1}$ ), *rac*-lactide, without alcohol (blue triangle,  $k_{\text{obs}} = 0.120 \pm 0.004 \text{ h}^{-1}$ ), and *rac*-lactide, with alcohol (pink triangle,  $k_{\text{obs}} = 0.100 \pm 0.003 \text{ h}^{-1}$ ). Polymerization conditions: chloroform- $d_1$  at 80 °C with  $[\text{LA}]_0/[\text{M}]_0 = 50$  and  $[\text{LA}]_0 = 0.5 \text{ M}$ .

The addition of *tert*-butanol has little effect on  $k_{\text{obs}}$  for both L-LA and *rac*-LA. The rate of polymerization for L-LA without alcohol is similar to the one with ( $k_{\text{obs}}$  of  $0.217 \text{ h}^{-1}$  and  $0.211 \text{ h}^{-1}$  respectively). Similarly, the rates for the polymerization of *rac*-LA ( $k_{\text{obs}}$ ) were of  $0.120 \text{ h}^{-1}$  and  $0.100 \text{ h}^{-1}$  respectively. The molecular weights and polydispersities of the polymerization of L- and *rac*-lactide with and without *tert*-butanol are collated in Table 3. As a catalyst, **6** demonstrated highly controlled polymerization of L- and *rac*-LA at 80 °C with an LA : catalyst ratio of 50 : 1 in chloroform- $d_1$ , as shown by low polydispersities ( $1.08 < M_w/M_n < 1.12$ ). The addition of *tert*-butanol does not affect the polydispersities; however, the experimental molecular weights appear more controlled in the presence of the alcohol, as expected of immortal polymerization shown by Carpentier and co-workers.<sup>37</sup>

The synthesized polylactides were characterized by  $^1\text{H}$ ,  $^1\text{H}\{^1\text{H}\}$ , and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy (Figure 13 and Figure S2-S9). The NMR spectra demonstrated no epimerization

when L-lactide was polymerized and atactic PLA when *rac*-lactide was used.



**Figure 13.**  $^1\text{H}\{^1\text{H}\}$  NMR spectrum (500 MHz, chloroform- $d_1$ , 25 °C) of the polylactide produced using the catalyst  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (**2**), a) L-lactide and b) *rac*-lactide. Polymerization conditions: 100 °C,  $[\text{LA}]_0/[\text{Zr}]_0 = 50$ ,  $[\text{LA}]_0 = 0.5 \text{ M}$ , chloroform- $d_1$ .

## CONCLUSIONS

We have reported the use of seven alkoxides or aryloxides zirconium complexes  $(\text{Cp})_2\text{ZrX}(\text{OR})$  ( $\text{X} = \text{Cl}, \text{Me}$ ;  $\text{R} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3$ ),  $(\text{Cp})_2\text{Zr}(\text{OR})_2$  ( $\text{R} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3$ ), *rac*-( $\text{Ind})_2\text{ZrX}(\text{OR})$  ( $\text{X} = \text{Cl}, \text{Me}$ ;  $\text{R} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3$ ,  $^t\text{Bu}$ ) which were characterized by NMR spectroscopy and two by X-ray crystallography.

All complexes displayed a range of activities for the polymerization of L- and *rac*-lactide.  $(\text{Ind})_2\text{ZrMe}(\text{O}^t\text{Bu})$  (**6**) was shown to be the fastest catalyst. At 100 °C, the rates of polymerization ( $k_{\text{obs}}$ ) for L- and *rac*-lactide were very similar ( $0.317$  and  $0.293 \text{ h}^{-1}$  respectively). However, it was found that polymerization of L-LA ( $k_{\text{obs}} = 0.217 \text{ h}^{-1}$ ) was twice as fast as *rac*-LA ( $k_{\text{obs}} = 0.120 \text{ h}^{-1}$ ) at 80 °C. The synthesized polylactides demonstrated no epimerization for poly-L-lactide and atactic behavior for poly-*rac*-lactide.

## EXPERIMENTAL

**General Details.** Air- and moisture-sensitive compounds were manipulated under an inert atmosphere of nitrogen, using standard Schlenk line techniques on a dual manifold vacuum/nitrogen line or a Braun Unilab glove box. Reaction solvents (pentane, hexane, and toluene) were dried using an MBraun SPS-800 solvent purification system. Hexane, toluene, and pentane were stored over pre-activated 3 Å molecular sieves. Dry solvents were stored in oven-dried ampoules

under an atmosphere of nitrogen, sealed with either Rotaflo or Young's taps. Deuterated solvents used in NMR analysis of air-sensitive compounds were freeze-thaw degassed, vacuum transferred and dried: chloroform- $d_1$  (Sigma-Aldrich) was stored over pre-activated 3 Å molecular sieves. NMR spectra were recorded on a 300 MHz Varian Mercury VX-Works spectrometer, 400 MHz Bruker Avance III HD nanobay spectrometer and a 500 MHz Bruker Avance III spectrometer. NMR spectra were recorded at 25 °C and referenced internally to the residual protio-solvent peak in the deuterated solvent used.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts,  $\delta$ , are given in parts per million (ppm). Selective homonuclear  $^1\text{H}\{^1\text{H}_{\text{Selective}}\}$  NMR spectroscopy was used to determine the tacticity of the polylactide by irradiating the  $\text{CH}_3$  area (ca. 1.57 ppm). Air sensitive samples were prepared under an inert atmosphere in a glove box, using dried solvents in Young's taps NMR tubes.  $(\text{Ind})_2\text{ZrMe}_2$  and  $\text{Cp}_2\text{ZrMe}_2$ , and complexes **1-3** and **6** were synthesized according to literature procedures.<sup>22,23,28,29</sup> *rac*-(EBI)ZrCl $_2$  (Strem) and  $(\text{Ind})\text{ZrCl}_2$  (Strem) were used as received.

**Polymerization procedure.** All polymerizations were carried out in Young's tap NMR tubes containing 40 mg of lactide in a chloroform- $d_1$  solution of catalyst, ensuring that the lactide : catalyst ratio was 50 : 1. Chloroform- $d_1$  was then added to ensure the initial lactide concentration was  $[\text{LA}]_0 = 0.50 \text{ M}$ . Polymerizations involving addition *tert*-butanol were prepared as usual, and *tert*-butanol was added to the chloroform- $d_1$  solution *via* microsyringe, ensuring the lactide : catalyst : *tert*-butanol ratio was 50 : 1 : 1. Gel permeation chromatography studies to determine polymer molecular weights ( $M_n$ ,  $M_w$ ) were performed using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. THF (HPLC grade) was used as an eluent at 30 °C with a flow rate of 1 mL min $^{-1}$ . Linear polystyrenes were used as primary calibration standards, and Mark-Houwink corrections for PLA in THF were applied for the experimental samples.<sup>15</sup>

**X-ray crystallography.** Crystals were mounted on MiTeGen MicroMants using perfluoropolyether oil, and cooled rapidly to 150 K in a stream of cold nitrogen using an Oxford Cryosystems CRYOSTREAM unit.<sup>38</sup> Data collections were performed using an Enraf-Nonius FR590 KappaCCD diffractometer, utilising graphite-monochromated Mo K $_{\alpha}$  X-ray radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Raw frame data were collected at 150(2) K using a Nonius Kappa CCD diffractometer, reduced using DENZO-SMN<sup>39</sup> and corrected for absorption using SORTAV.<sup>40</sup> The structure was solved using SuperFlip<sup>41</sup> and refined using full matrix least-squares using CRYSTALS.<sup>42,43</sup>

Crystallographic data of co-crystal of  $(\text{Cp})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  and  $(\text{Cp})_2\text{Zr}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2$  (**1** and **2**). Single crystals were obtained from a 50:50 mixture of 1:2 in hexane solution at -34 °C,  $\text{C}_{44}\text{H}_{47}\text{ClO}_3\text{Zr}_2$ ,  $M_r = 841.75$ , monoclinic,  $P2_1/c$ ,  $a = 20.9251(5) \text{ \AA}$ ,  $b = 12.7962(2) \text{ \AA}$ ,  $c = 14.8869(3) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 108.663(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3776.56(16) \text{ \AA}^3$ ,  $Z = 4$ ,  $T = 150 \text{ K}$ , block, colorless, 6503 independent reflections,  $R_1 = 0.0407$   $wR_2 = 0.0774$  [ $I > 2\sigma(I)$ ].

Crystallographic data of *rac*-(EBI)ZrCl(O-2,6-Me $_2$ -C $_6$ H $_3$ ) (**7**). Single crystals were grown from a toluene solution at room temperature,  $\text{C}_{28}\text{H}_{25}\text{ClOZr}$ ,  $M_r = 504.15$ , orthorhombic,  $Pcab$ ,  $a = 15.7733(2) \text{ \AA}$ ,  $b = 23.7683(3) \text{ \AA}$ ,  $c = 23.9207(4) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 8968.0(2) \text{ \AA}^3$ ,  $Z = 16$ ,  $T = 150 \text{ K}$ , block, yellow,

10201 independent reflections,  $R_1 = 0.057$   $wR_2 = 0.105$  [ $I > 2\sigma(I)$ ].

**Synthesis of  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**4**).** Stoichiometric amounts of  $(\text{Ind})_2\text{ZrCl}_2$  (0.188 g, 0.48 mmol) and  $\text{K}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (0.092 g, 0.48 mmol) was introduced into a Schlenk tube, to which 10 mL of DCM was added. The reaction mixture was stirred for 1 h at room temperature, then filtered, dried, filtered in hot hexane (10 mL), and dried once more to afford  $(\text{Ind})_2\text{ZrCl}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**4**) as a yellow solid in 6% isolated yield (0.014 g, 0.029 mmol).  $^1\text{H}$  NMR (chloroform- $d_1$ , 25 °C, 400 MHz):  $\delta$  7.65 (d, 2H,  $\text{Ar}_{\text{IndH}}$ ,  $^3J_{\text{HH}} = 8.4 \text{ Hz}$ ), 7.42 (d, 2H,  $\text{Ar}_{\text{IndH}}$ ,  $^3J_{\text{HH}} = 8.5 \text{ Hz}$ ), 7.18 (t, 2H,  $\text{Ar}_{\text{IndH}}$ ,  $^3J_{\text{HH}} = 7.0 \text{ Hz}$ ), 7.01 (t, 2H,  $\text{Ar}_{\text{IndH}}$ ,  $^3J_{\text{HH}} = 7.6 \text{ Hz}$ ), 6.85 (d, 2H,  $\text{ArH}_{\text{meta}}$ ,  $^3J_{\text{HH}} = 7.3 \text{ Hz}$ ), 6.65 (t, 1H,  $\text{ArH}_{\text{para}}$ ,  $^3J_{\text{HH}} = 7.4 \text{ Hz}$ ), 6.37 (m, 2H,  $\text{CpH}$ ), 6.19 (t, 2H,  $\text{CpH}$ ,  $^3J_{\text{HH}} = 3.4 \text{ Hz}$ ), 6.06 (m, 2H,  $\text{CpH}$ ), 1.97 (s, 6H,  $\text{ArMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  128.98 ( $\text{ArH}_{\text{meta}}$ ), 127.74 (O-C), 125.75 ( $\text{Ar}_{\text{IndH}}$ ), 125.69 ( $\text{Ar}_{\text{IndH}}$ ), 124.49 ( $\text{Ar}_{\text{IndH}}$ ), 124.25 ( $\text{Ar}_{\text{IndH}}$ ), 122.16 ( $\text{CpH}$ ), 119.96 ( $\text{ArH}_{\text{para}}$ ), 102.67 ( $\text{CpH}$ ), 101.29 ( $\text{CpH}$ ), 17.77 ( $\text{ArMe}$ ). MS: expected: 476.0485, observed: 476.0730.

**Synthesis of  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (**5**).** One equivalent of  $\text{H}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$  (0.034 g, 0.28 mmol) in toluene (5 mL) was added to one equivalent of  $(\text{Ind})_2\text{ZrMe}_2$  (0.100 g, 0.28 mmol) in toluene (5 mL), at room temperature. The clear, straw-colored solution was stirred for 18 h. Solvent was removed in vacuum to afford  $(\text{Ind})_2\text{ZrMe}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3)$ , **5**, as a colorless oil with a yield of 75% (0.096 g, 0.21 mmol).  $^1\text{H}$  NMR (chloroform- $d_1$ , 25 °C, 300 MHz):  $\delta$  7.48-7.43 (2H, m,  $\text{ArH}$ ), 7.34-7.29 (2H, m,  $\text{ArH}$ ), 7.07-7.00 (2H, m,  $\text{ArH}$ ), 6.92-6.85 (2H, m,  $\text{ArH}$ ), 6.82 (2H, d,  $\text{ArMe}_2\text{H}$ ,  $^3J_{\text{HH}} = 7.4 \text{ Hz}$ ), 6.59 (1H, t,  $\text{ArMe}_2\text{H}$ ,  $^3J_{\text{HH}} = 7.4 \text{ Hz}$ ), 6.20 (2H, m,  $\text{CpH}$ ), 5.91 (2H, m,  $\text{CpH}$ ), 5.76 (2H, t,  $\text{CpH}$ ,  $^3J_{\text{HH}} = 3.4 \text{ Hz}$ ), 1.86 (6H, s,  $\text{ArMe}_2$ ), 0.22 (6H, s,  $\text{ZrMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  159.4 (CO, Ar), 128.0 (2 x CH, Ar), 125.7 (2 x C quaternary, Ar), 124.6 (2 x CH, Ar), 124.3 (2 x CH, Ar), 124.0 (2 x C quaternary, Ar), 123.9 (2 x CH, Ar), 123.8 (2 x C quaternary, Ar), 123.6 (2 x CH, Ar), 118.9 (CH, Ar), 117.6 (2 x CH, Cp), 100.6 (2 x CH, Cp), 99.0 (2 x CH, Cp), 27.8 ( $\text{ZrMe}$ ), 17.6 (2 x  $\text{ArMe}_2$ ).

**Synthesis of *rac*-(EBI)ZrCl(O-2,6-Me $_2$ -C $_6$ H $_3$ ) (**7**).** One equivalent of  $\text{K}(\text{O}-2,6\text{-Me}_2\text{-C}_6\text{H}_3\text{-Me})$  (0.029 g, 0.24 mmol) in toluene (10 mL) was added to one equivalent of *rac*-(EBI)ZrCl $_2$  (0.100 g, 0.24 mmol) in toluene (10 mL), at room temperature. The yellow suspension was stirred for 18 h, resulting in a clear, yellow solution. Solvent was removed *in vacuo* to afford (EBI)ZrCl(O-2,6-Me $_2$ -C $_6$ H $_3$ ) (**7**) as a yellow crystalline solid with a yield of 80% (0.096 g, 0.19 mmol).  $^1\text{H}$  NMR (chloroform- $d_1$ , 25 °C, 300 MHz):  $\delta$  7.84 (1H, dd,  $\text{ArH}$ ,  $^3J_{\text{HH}} = 8.7 \text{ Hz}$ ,  $^4J_{\text{HH}} = 0.9 \text{ Hz}$ ), 7.61 (1H, dd,  $\text{ArH}$ ,  $^3J_{\text{HH}} = 8.6 \text{ Hz}$ ,  $^4J_{\text{HH}} = 0.9 \text{ Hz}$ ), 7.30-7.27 (2H, m,  $\text{ArH}$ ), 7.20-7.10 (2H, m,  $\text{ArH}$ ), 7.03 (1H, t,  $\text{ArMe}_2\text{H}$ ,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ ), 6.78 (2H, d,  $\text{ArMe}_2\text{H}$ ,  $^3J_{\text{HH}} = 7.4 \text{ Hz}$ ), 6.63-6.55 (2H, m,  $\text{ArH}$ ), 6.54 (1H, d,  $\text{CpH}$ ,  $^3J_{\text{HH}} = 3.2 \text{ Hz}$ ), 6.41 (1H, d,  $\text{CpH}$ ,  $^3J_{\text{HH}} = 3.2 \text{ Hz}$ ), 6.15 (1H, d,  $\text{CpH}$ ,  $^3J_{\text{HH}} = 3.2 \text{ Hz}$ ), 6.02 (1H, d,  $\text{CpH}$ ,  $^3J_{\text{HH}} = 3.2 \text{ Hz}$ ), 3.88-3.62 (4H, m, bridge), 1.91 (6H, s,  $\text{ArMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  128.2, 126.6, 125.7, 125.6, 125.4, 123.7, 123.6, 122.7, 121.7, 120.9, 119.5, 115.7, 113.2, 108.4, 106.1 (all non-quaternary ring carbons) 29.6 ( $\text{C}_2\text{H}_4$ ), 28.7 ( $\text{C}_2\text{H}_4$ ), 18.0 (2 x  $\text{ArMe}_2$ ). Quaternary carbons unassigned.

## ASSOCIATED CONTENT

**Supporting Information.** X-ray crystallography and polymerization data including NMR spectroscopy.

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### Author Contributions

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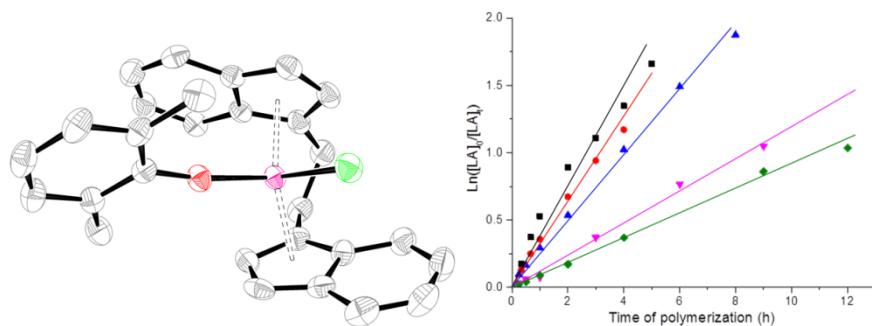
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A family of well-defined cyclopentadienyl and indenyl group 4 complexes has been prepared and use in polymerization of lactide monomers.

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