



Cite this: *Chem. Commun.*, 2014, 50, 15967

Received 6th October 2014,  
Accepted 3rd November 2014

DOI: 10.1039/c4cc07871c

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# Zirconium complexes of bipyrrrolidine derived salan ligands for the isoselective polymerisation of *rac*-lactide†

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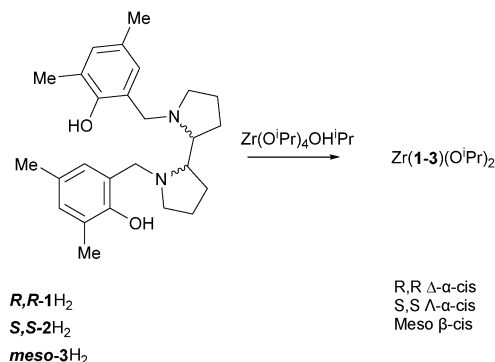
**Herein we report the synthesis and characterisation of a series of Zr(IV) 2,2'-bipyrrrolidine–salan derived complexes and their exploitation for the ring opening polymerisation of *rac*-lactide to afford highly isotactically enriched polymers.**

Poly(lactic acid) is unequivocally a success story in modern sustainable chemistry.<sup>1</sup> This is in no small part due to the desirable properties of the resultant polymer—namely biodegradability and the fact that the monomer is sourced from annually renewable raw materials.<sup>2</sup> Poly(lactic acid) (PLA) is currently commercially produced using tin(II) octanoate as the initiator. However, there is a desire to prepare new initiators that are faster and able to control the microstructure of the resultant polymer.<sup>3</sup> The stereochemistry of PLA dramatically affects the properties of the material—for example isotactic PLLA (or PDLA) has a melting point of *ca.* 170 °C, moreover for stereoblock/gradient PLA with isotactic sequences of L- and D-lactide the *T<sub>m</sub>* increases to 180–220 °C.<sup>4</sup> There are many impressive examples in the literature reporting the stereo-selective polymerisation of *rac*-lactide (*rac*-LA).<sup>3,5</sup> Compared to the number of initiators that are active for the production of heterotactic PLA, isoselective initiators are rare. The metal centres that are typically used for the production of isotactic PLA from *rac*-LA are Zn(II),<sup>6</sup> Al(III)<sup>5c,7</sup> and Y(III).<sup>3,8</sup> Du and co-workers have recently reported a series of Zn(II)–amido-oxazolinato complexes for the ring opening polymerisation (ROP) of *rac*-LA, which afforded high isoselectivity in toluene at 50 °C. Full conversion was achieved after 30 min with a *P<sub>m</sub>* (probability of isotactic enchainment) up to 0.8.<sup>6</sup> When the temperature was lowered to 23 °C this could be increased to 0.91, but full conversion was only reached in 44 hrs at

this temperature. Williams has recently shown that Yttrium phosphasalen complexes can produce PLA with a *P<sub>m</sub>* of up to 0.84, very rapidly.<sup>3</sup> Examples of Al(III) include the early work of Spassky, Feijen and Nomura with salen derived complexes.<sup>7a–d</sup> Whilst there have been many elegant examples of the utility of group 4 complexes for the ROP of *rac*-LA, the vast majority produce atactic or heterotactic PLA.<sup>9</sup> However, Davidson and co-workers have shown that *C<sub>2</sub>*-symmetric Zr(IV) amine-bis(phenolates) are capable of producing moderate isotacticity (*P<sub>m</sub>* = 0.7).<sup>10</sup> More recently Kol and Okuda have prepared a series of Zr(IV) complexes with ONSO ligands, which depending upon the flexibility of the backbone, produce either heterotactically (*P<sub>r</sub>* up to 0.87) or isotactically inclined PLA (*P<sub>m</sub>* up to 0.67).<sup>11</sup> Group 4 initiators have the added advantage of being easy to prepare, relatively moisture stable and can be trialled under the industrially preferred melt conditions.

In this paper we report the preparation of three Zr(IV) complexes based on a 2,2'-bispyrrrolidine and their exploitation in the ROP of *rac*-LA. Examples based on such ligands are rare in the literature<sup>12</sup> and this is only the second example of the use of this *meso*-ligand in catalysis<sup>13</sup> (Scheme 1).

The ligands were prepared by modified Mannich reactions involving either enantiopure (*R,R* or *S,S*) or *meso* variants of 2,2'-bispyrrrolidine.<sup>12c</sup> All ligands have been characterised by NMR spectroscopy, HR-MS and the solid-state structure has been



Scheme 1 Synthesis of the complexes under investigation.

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† Electronic supplementary information (ESI) available: Full experimental data. CCDC 1027438–1027441. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc07871c



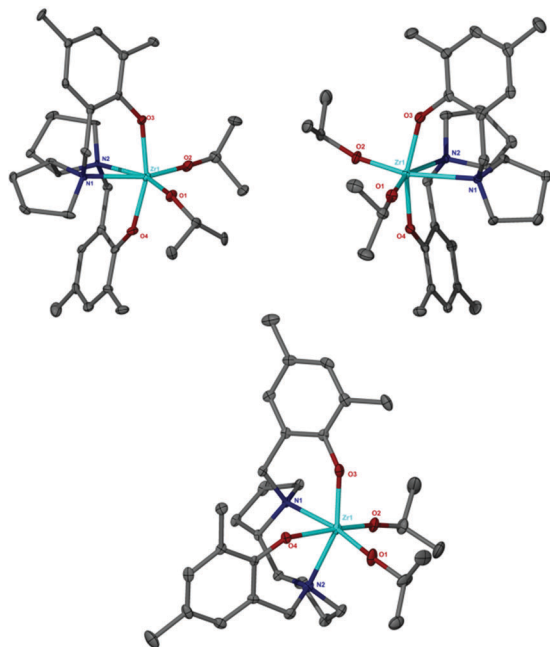


Fig. 1 The solid state structures of  $\Delta$ -Zr(1)(O<sup>i</sup>Pr)<sub>2</sub> (left) and  $\Delta$ -Zr(2)(O<sup>i</sup>Pr)<sub>2</sub> (right) and Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> (bottom) ellipsoids are shown at the 30% probability level and hydrogen atoms have been removed for clarity.

determined for the meso ligand (3H<sub>2</sub>); see ESI<sup>†</sup> for full details. All Zr(IV) complexes were characterised by single crystal X-ray diffraction. The metric data for the complexes are similar and are in agreement with literature reported salan complexes.<sup>10</sup> The *R,R* and *S,S* ligands coordinate to Zr(IV) in a *fac-fac* fashion with the *R,R* enantiomer forming the  $\Delta$ -isomer and the *S,S* enantiomer the  $\Lambda$ -isomer exclusively in the solid-state (Fig. 1). Zr(1)(O<sup>i</sup>Pr)<sub>2</sub> crystallises in the chiral space group *P*<sub>4</sub><sub>1</sub> whereas Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> in *P*<sub>4</sub><sub>3</sub>. This is in agreement with Kol and co-workers for related Ti(IV) complexes where the ligands lead to a predetermined chirality at the metal centre.<sup>14</sup> The <sup>1</sup>H NMR spectra of complexes Zr(1/2)(O<sup>i</sup>Pr)<sub>2</sub> were indicative of the solid-state structure being maintained in solution, see ESI<sup>†</sup>. The ligands are locked in position as indicated by discrete doublets for the methylene CH<sub>2</sub> moieties, furthermore there are no exchange peaks observed in the NOESY/EXSY spectrum at 298 K (CDCl<sub>3</sub>).

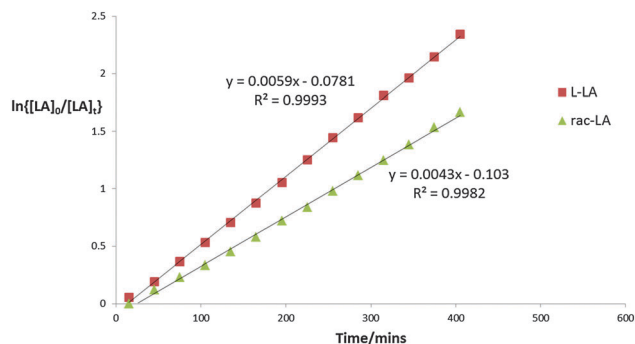
In the solid state Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> crystallises in the monoclinic *P*<sub>2</sub><sub>1</sub>/*c* space group, with both enantiomers (the  $\Lambda$  and  $\Delta$  forms) present, arbitrarily the  $\Delta$ -isomer is shown in Fig. 1. Compared to the chiral ligands a different coordination mode of the salan (*fac-mer*) was observed, this is presumably due to the *syn* relationship of the hydrogen atoms pertaining to the C–C bond between the five membered rings (*cf.* antiperiplanar for the chiral complexes). When this complex was recrystallised from toluene, the room temperature solution state NMR spectrum (in either CDCl<sub>3</sub> or d<sup>8</sup>-THF) was complicated, with clearly more than one species present in solution. The ground state energies of various isomers have been studied *via* DFT methods.<sup>†</sup> Unsurprisingly the observed structure is the most thermodynamically stable, however the *trans* isomer is only 8.3 kcal mol<sup>−1</sup> higher. Fortunately, when Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> was recrystallised in hexane the product gave an NMR

spectrum that was consistent with the *fac-mer* isomer, with discrete doublets for the methylene CH<sub>2</sub> moieties being observed along with two observed resonances for the methine isopropoxides and four resonances in the aryl region. Room temperature NOESY/EXSY measurements showed the presence of exchange peaks, indicating that in solution an equilibrium exists which potentially is  $\Delta$ -isomer  $\rightleftharpoons$   $\Lambda$ -isomer.<sup>†</sup> Presumably, these enantiomers are interconverting in solution at room temperature giving rise to the exchange peaks, which were absent in the chiral complexes Zr(1/2)(O<sup>i</sup>Pr)<sub>2</sub>.

The majority of examples of the polymerisation of *rac*-LA using group 4 initiators use sublimation methods to purify the monomer. In this study we have simply used recrystallised monomer to mimic more industrially relevant conditions (entries 4 and 11 use sublimed monomer as a comparison). The selectivity and dispersity appear to be relatively similar for the sublimed monomer compared to recrystallised, although similar conversions are achieved in a slightly shorter time frame for the sublimed monomer. The solution polymerisations of *rac*-LA are incredibly well controlled with low dispersities obtained. For Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> in the melt (entries 3 and 4) the dispersity of the polymer is slightly higher indicating a degree of transesterification.

Interestingly, the Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> yielded PLA with a high isotactic bias (*P*<sub>m</sub> = 0.86 in solution), which to the best of our knowledge is the highest reported isotactic initiator in the literature to date utilising a group 4 initiator. Analysis of this highly isotactic polymer prepared in solution *via* DSC showed there to be a major endothermic peak at 190 °C, indicative of stereoblock isotactic PLA.<sup>4b</sup> Moreover, in the case of Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> the *sis* tetrad is significantly smaller than the *sii*, *iis* and *isi* tetrads indicating isotactic PLA of a blocky nature.<sup>5g,15</sup> Furthermore, the MALDI-ToF analysis has a repeat unit of 144 g mol<sup>−1</sup>, this coupled with the low *M*<sub>w</sub>/*M*<sub>n</sub> (1.05) indicates a controlled polymerisation with little transesterification occurring. The expected H- and -O<sup>i</sup>Pr end groups from the coordination insertion mechanism were also observed. The solution state kinetics of the polymerisation were investigated with Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> at room temperature in CDCl<sub>3</sub> (100 : 1 LA : Init), for *rac*-LA *k*<sub>app</sub> = 4.3 × 10<sup>−3</sup> min<sup>−1</sup> was observed, Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> polymerises L-LA significantly faster with a *k*<sub>app</sub> = 5.9 × 10<sup>−3</sup> min<sup>−1</sup>, Fig. 2. Both Zr(1–2)(O<sup>i</sup>Pr)<sub>2</sub> complexes were inactive for the solution state polymerisation of *rac*-LA in CDCl<sub>3</sub> at room temperature. However, the chiral complexes were active at 70 °C in toluene – with *ca.* 50% conversion being achieved after 4 and 8 hours respectively, with a strong isotactic bias observed and *T*<sub>m</sub> = 178 °C, from DSC (Table 1, entry 5) and *T*<sub>m</sub> = 176 °C, from DSC (Table 1, entry 7). In the case of Zr(1–2)(O<sup>i</sup>Pr)<sub>2</sub> the mechanism of polymerisation is presumably enantiomeric site control. There does appear to be a slight difference in selectivity with reaction time (entries 5 *vs.* 7 and 6 *vs.* 8), at low conversion (*ca.* 10%) *P*<sub>m</sub> = 0.75 similar to the 4 h run (entries 5 and 6). Only *ca.* 50% conversion of *rac*-LA could be achieved in solution with the chiral complexes compared to 85% with the *meso* complex in the same timeframe (*N.B.* the Zr(3)(O<sup>i</sup>Pr)<sub>2</sub> test was at 20 °C *cf.* 70 °C for Zr(1/2)(O<sup>i</sup>Pr)<sub>2</sub>). The polymerisation was investigated further with L-LA, where  $\Delta$ -Zr(2)(O<sup>i</sup>Pr)<sub>2</sub> was active (*k*<sub>app</sub> = 4.1 × 10<sup>−4</sup> min<sup>−1</sup> after 37 h, conversion to PLLA = 58% *M*<sub>n</sub> = 6900, *M*<sub>w</sub>/*M*<sub>n</sub> = 1.07) and  $\Delta$ -Zr(1)(O<sup>i</sup>Pr)<sub>2</sub> was slow (*k*<sub>app</sub> = 0.97 × 10<sup>−4</sup> min<sup>−1</sup> after 37 hrs, conversion to PLLA = 18%) Fig. 3.<sup>16</sup>



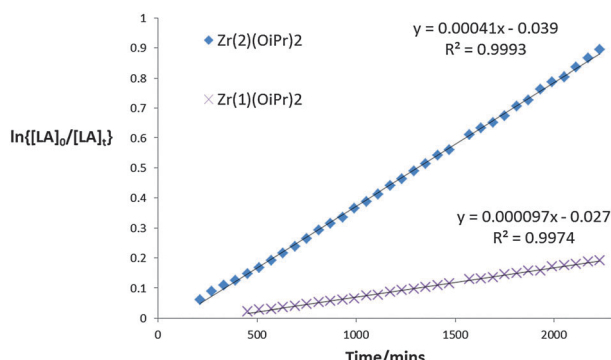


**Fig. 2** Semi-logarithmic plots of the polymerisation of L-LA and rac-LA ( $[LA]_0 = 0.56 \text{ mol dm}^{-3}$ )  $[LA] : [Init] = 100 : 1$ ,  $Init = Zr(3)(O^iPr)_2$ .

**Table 1** Polymerisation data for rac-LA with initiators  $Zr(1-3)(O^iPr)_2$

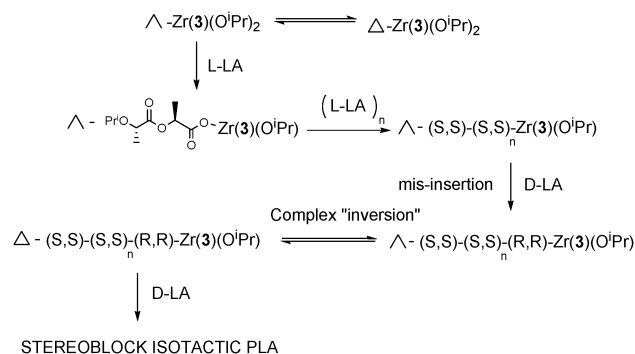
Entry	Initiator	Time (h)	Conv. <sup>d</sup> (%)	$M_n^e$	$M_w/M_n^e$	$P_m^f$
1	$Zr(1)(O^iPr)_2^a$	0.17	55	16 650	1.13	0.70
2	$Zr(2)(O^iPr)_2^a$	0.17	45	15 950	1.09	0.71
3	$Zr(3)(O^iPr)_2^a$	0.17	90	81 400	1.21	0.66
4	$Zr(3)(O^iPr)_2^a$	0.1	89	60 250	1.17	0.65
5	$Zr(1)(O^iPr)_2^b$	4	48	6200	1.08	0.75
6	$Zr(2)(O^iPr)_2^b$	4	51	7250	1.07	0.75
7	$Zr(1)(O^iPr)_2^b$	8	54	8000	1.07	0.80
8	$Zr(2)(O^iPr)_2^b$	8	60	9600	1.06	0.80
9	$Zr(3)(O^iPr)_2^c$	8	85	16 500	1.05	0.86
10	$Zr(3)(O^iPr)_2^c$	4	45	7650	1.05	0.85
11	$Zr(3)(O^iPr)_2^c$	6	79	22 000	1.04	0.84
12	$Zr(3)(O^iPr)_2^b$	8	94	16 400	1.22	0.75

<sup>a</sup> Conditions:  $[M]/[I] = 300$ ,  $130^\circ\text{C}$ , solvent free. <sup>b</sup> Conditions:  $[M]/[I] = 100$ , toluene,  $T = 70^\circ\text{C}$ . <sup>c</sup> Conditions:  $[M]/[I] = 100$ ,  $CDCl_3$ ,  $T = 20^\circ\text{C}$ . <sup>d</sup> As determined via  $^1\text{H}$  NMR spectroscopy. <sup>e</sup> Determined from GPC (in THF) referenced to polystyrene. <sup>f</sup>  $P_m$  is the probability of isotactic enchainment, calculated from the  $^1\text{H}$  homonuclear decoupled NMR spectra. *N.B.* entries 4 and 11 are using sublimed lactide as a comparison, all others use recrystallised lactide.



**Fig. 3** Semi-logarithmic plots of the polymerisation of L-LA ( $[LA]_0 = 0.56 \text{ mol dm}^{-3}$ )  $[LA] : [Init] = 100 : 1$ ,  $Init = Zr(1 \text{ or } 2)(O^iPr)_2$ .

Both  $Zr(1/2)(O^iPr)_2$  are “locked”, in solution as single enantiomers ( $\Delta$ - $Zr(1)(O^iPr)_2$  and  $\Delta$ - $Zr(2)(O^iPr)_2$  respectively). The data clearly show a strong preference for  $\Delta$ - $Zr(2)(O^iPr)_2$  to specifically polymerise L-LA compared to  $\Delta$ - $Zr(1)(O^iPr)_2$ . It is thus hypothesised if we consider the polymerisation of rac-LA with the chiral complex  $\Delta$ - $Zr(1)$  when an L-LA inserts a significantly less active catalytic species will form (the same is true when D-LA inserts into  $\Delta$ - $Zr(2)$ ). Essentially this is an



**Scheme 2** Proposed mechanism for the polymerisation of rac-LA with  $Zr(3)(O^iPr)_2$ .

enantiomeric site controlled mechanism. As discussed previously  $Zr(3)(O^iPr)_2$  is fluxional in solution,  $\Delta$ - $Zr(3)(O^iPr)_2 \rightleftharpoons \Lambda$ - $Zr(3)(O^iPr)_2$ , and initially the chirality of  $\Delta/\Lambda$ - $Zr(3)(O^iPr)_2$  controls which monomer is inserted in a site controlled manner ( $\Delta \rightarrow$  D-LA,  $\Lambda \rightarrow$  L-LA). However, we tentatively suggest that if the “wrong” insertion occurs the complex can convert to the other form and now the chirality of the metal and chain end complement each other again, Scheme 2, and propagation continues leading to stereoblock isotactic PLA. It is also interesting to note that the rate of ROP of L-lactide with  $Zr(3)(O^iPr)_2$  is significantly faster than that of  $\Delta$ - $Zr(2)(O^iPr)_2$ , this may well be due to the difference in coordination of the ligand around the Zr(IV) centre.

Work is currently on-going to investigate the mechanism in more detail, the applicability of the initiators with other cyclic esters and for co-polymer formation. Encouragingly,  $Zr(3)(O^iPr)_2$  is active for the ROP of rac-butyrolactone ( $[M] : [Init] = 300 : 1$ ,  $T = 80^\circ\text{C}$  solvent free; conversion = 75%,  $M_n = 19\,500$ ,  $M_w/M_n = 1.10$  after 4 hours to produce atactic polymer).

Zirconium(IV) complexes have been prepared and screened for the polymerisation of rac-LA. Stereoblock isotactic PLA is prepared with the *meso* salan complex  $Zr(3)(O^iPr)_2$ , which is significantly faster than either of the chiral complexes  $Zr(1/2)(O^iPr)_2$ . It is hypothesised that this reflects the fluxionality of  $Zr(3)(O^iPr)_2$ . We wish to thank the EPSRC (EP/G03768X/1), the EPSRC UK National Service for Computational Chemistry Software (CHEM752), Corbion for lactide and support of the CDT at Bath and the University of Bath for funding.

## Notes and references

- (a) R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835–864; (b) R. J. Pounder and A. P. Dove, *Polym. Chem.*, 2010, **1**, 260–271; (c) M. Vert, *Biomacromolecules*, 2005, **6**, 538–546.
- S. Slomkowski, S. Penczek and A. Duda, *Polym. Adv. Technol.*, 2014, **25**, 436–447.
- C. Bakewell, C. Thi-Phuong-Anh, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 20577–20580.
- (a) M. J. Stanford and A. P. Dove, *Chem. Soc. Rev.*, 2010, **39**, 486–494; (b) K. Fukushima and Y. Kimura, *Polym. Int.*, 2006, **55**, 626–642.
- (a) D. C. Aluthge, B. O. Patrick and P. Mehrkhodavandi, *Chem. Commun.*, 2013, **49**, 4295–4297; (b) B. Gao, R. Duan, X. Pang, X. Li, Z. Qu, Z. Tang, X. Zhuang and X. Chen, *Organometallics*, 2013, **32**, 5435–5444; (c) P. Hornmair, E. L. Marshall, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2004, **126**, 2688–2689; (d) N. Nomura, R. Ishii, M. Akakura and K. Aoi, *J. Am. Chem. Soc.*, 2002, **124**, 5938–5939;



- (e) T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 4072–4073; (f) A. Pilone, K. Press, I. Goldberg, M. Kol, M. Mazzeo and M. Lamberti, *J. Am. Chem. Soc.*, 2014, **136**, 2940–2943; (g) H. Wang and H. Ma, *Chem. Commun.*, 2013, **49**, 8686–8688; (h) Z. Y. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291–11298.
- 6 S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689–692.
- 7 (a) G. Montaudo, M. S. Montaudo, C. Puglisi, F. Samperi, N. Spassky, A. LeBorgne and M. Wisniewski, *Macromolecules*, 1996, **29**, 6461–6465; (b) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem. – Eur. J.*, 2007, **13**, 4433–4451; (c) N. Spassky, M. Wisniewski, C. Pluta and A. LeBorgne, *Macromol. Chem. Phys.*, 1996, **197**, 2627–2637; (d) M. Wisniewski, A. LeBorgne and N. Spassky, *Macromol. Chem. Phys.*, 1997, **198**, 1227–1238; (e) P. Hormnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh and A. J. P. White, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15343–15348.
- 8 (a) C. Bakewell, R. H. Platel, S. K. Cary, S. M. Hubbard, J. M. Roaf, A. C. Levine, A. J. P. White, N. J. Long, M. Haaf and C. K. Williams, *Organometallics*, 2012, **31**, 4729–4736; (b) A. Alaaeddine, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Organometallics*, 2009, **28**, 1469–1475; (c) R. Heck, E. Schulz, J. Collin and J.-F. Carpentier, *J. Mol. Catal. A: Chem.*, 2007, **268**, 163–168.
- 9 (a) A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007–9023; (b) A. L. Zelikoff, J. Kopilov, I. Goldberg, G. W. Coates and M. Kol, *Chem. Commun.*, 2009, 6804–6806; (c) A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones and M. D. Lunn, *Chem. Commun.*, 2008, 1293–1295.
- 10 A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250–7257.
- 11 (a) J.-C. Buffet, A. N. Martin, M. Kol and J. Okuda, *Polym. Chem.*, 2011, **2**, 2378–2384; (b) A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, **45**, 698–704; (c) A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, **53**, 9140–9150.
- 12 (a) X. Gu, Y. Zhang, Z.-J. Xu and C.-M. Che, *Chem. Commun.*, 2014, **50**, 7870–7873; (b) R. Mayilmurugan, P. Traar, J. A. Schachner, M. Volpe and N. C. Moesch-Zanetti, *Eur. J. Inorg. Chem.*, 2013, 3664–3670; (c) M. Miller and E. Y. Tshuva, *Eur. J. Inorg. Chem.*, 2014, 1485–1491; (d) E. Sergeeva, J. Kopilov, I. Goldberg and M. Kol, *Inorg. Chem.*, 2009, **48**, 8075–8077; (e) E. Sergeeva, K. Press, I. Goldberg and M. Kol, *Eur. J. Inorg. Chem.*, 2013, 3362–3369.
- 13 V. A. Yazerski, P. Spannring, D. Gatineau, C. H. M. Woerde, S. M. Wieclawska, M. Lutz, H. Kleijn and R. J. M. K. Gebbink, *Org. Biomol. Chem.*, 2014, **12**, 2062–2070.
- 14 E. Sergeeva, J. Kopilov, I. Goldberg and M. Kol, *Chem. Commun.*, 2009, 3053–3055.
- 15 T. M. Ovitt and G. W. Coates, *J. Polym. Sci., Polym. Chem. Ed.*, 2000, **38**, 4686–4692.
- 16 It was found using D-LA it was necessary to sublime the monomer prior to use (N.B. for L-LA this was not the case). Using sublimed D-LA for  $\text{Zr(1)(O}^i\text{Pr)}_2$   $k_{\text{app}} = 7.5 \times 10^{-4} \text{ min}^{-1}$   $\text{Zr(2)(O}^i\text{Pr)}_2$   $k_{\text{app}} = 0.7 \times 10^{-4} \text{ min}^{-1}$ . These results clearly show that  $\text{Zr(1)(O}^i\text{Pr)}_2$  has a much stronger preference for D-LA and  $\text{Zr(2)(O}^i\text{Pr)}_2$  has a stronger preference for L-LA.

