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Group 4 initiators for the stereoselective ROP of *rac*-β-butyrolactone and its copolymerization with *rac*-lactide†

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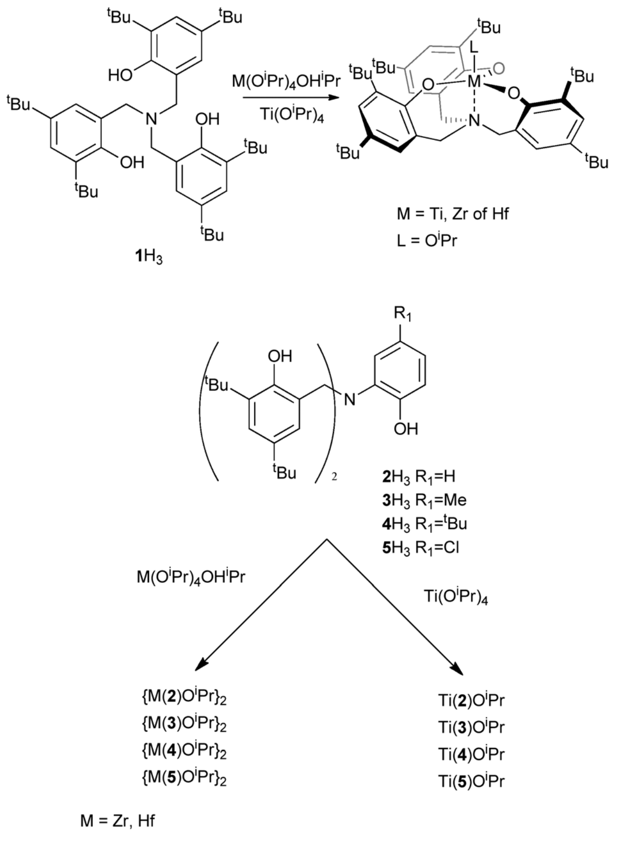
In this paper we demonstrate the utility of Group 4 metals for the well-controlled and stereoselective (syndiotactic) ring opening polymerization (ROP) of *rac*-β-butyrolactone (BBL) and their ability to form copolymers.

Polymers that are available from renewable resources and that are degradable are of considerable interest as potential replacements for petrochemically derived polymers.[1] Polylactide (PLA), arguably the most important of these to date, can be produced by ring-opening polymerization (ROP) of the cyclic ester lactide (LA).[2] The LA monomer can be produced from the fermentation of readily available renewable resources such as starch, and is therefore of commercial and environmental interest.[1,2] Another class of polymers that has garnered recent attention are polyhydroxyalkanoates (PHAs), which can be isolated directly from several species of algae and bacteria.[3,4] Whilst possessing a wide range of properties, the cost of commercial production of PHAs by extraction from microbial species can be prohibitive.[4] For example, processing polyhydroxybutyrate (PHB) can be challenging due to the high crystallinity caused by perfect isotacticity. Therefore, other synthetic approaches to the production of PHAs are of interest. For example, metal-initiated ROP of β-lactones also gives access to PHAs with potentially desirable properties.[4a] The most notable example of this is the ROP of β-butyrolactone (BBL) to produce polyhydroxybutyrate.[3a,5] Highly isotactic PHB can be achieved when optically pure BBL is polymerized, however ROP of *rac*-BBL has led to atactic PHB[6] and, less commonly, syndiotactic[3a,7] and isotactic polymers.[8] For example, Coates[5d] and Carpentier,[7a,9] have recently shown that zinc and yttrium systems, respectively, show high activity for the controlled ROP of *rac*-BBL.

We and others have shown that Group 4 metals can be highly active and selective initiators for ROP of cyclic esters such as LA and caprolactone.[10] To date, very few examples are reported using Group 4 metals for the ROP of *rac*-BBL, however, a recent example is the production of syndiotactic PHB *via* bis(imino)phenoxide complexes of zirconium.[11]

Our initial attempts focused on the ROP of *rac*-BBL with a C_3-symmetric amine tris(phenolate) complex-Zr(**1**)(O^{i}Pr), Scheme 1.[10i] This complex has been shown to be very active for the production of heterotactic PLA, with near quantitative conversion after only 15 mins.[10i] In contrast, when this initiator was used with *rac*-BBL as a monomer, only low molecular weight PHB was observed regardless of monomer conversion. This led us to search for other related initiators that can polymerize BBL more effectively.



Scheme 1 Ligands and complexes prepared in this study.

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Recently we have prepared a series of Ti(IV) and Zr(IV) complexes based on the ligands **2**H_3–**5**H_3 shown in Scheme 1, which interestingly, showed that a slight modification to the C_3-symmetric amine tris(phenolate) turned a highly selective initiator into a non-selective system for *rac*-LA, achieving slight heteroselectivity (P_r = 0.6).[10g] In contrast to the C_3-symmetric amine tris(phenolate) system, when complexes based on ligands **2**H_3–**5**H_3 were tested for the ROP of *rac*-BBL (Table 1), they were shown to be active for the polymerization; giving narrow polydispersities and predictable molecular weights. The Ti(IV) complexes were less active than the Zr(IV) analogues, the latter of which achieved turnover numbers approaching 50 h^{-1}. Encouraged by this success, we prepared Hf(IV) complexes of the ligands. As observed with the previously published Zr(IV) complexes,[10g] the Hf(IV) species exist as dimers in the solid-state, Fig. 1. In solution ($CDCl_3$ or d^8-toluene) a complex equilibrium between monomeric and dimeric species was observed on the NMR timescale, however when measurements were recorded in d^8-THF NMR spectra consistent with monomeric species were obtained. This tentatively suggests that, in the presence of an excess of coordinating BBL, a monomeric initiator is likely to predominate.

To improve the physical properties of commercial polymers, LA is often copolymerized with other cyclic esters (normally caprolactone, valerolactone or glycolide) resulting in either block or random copolymers.[1,12] Although examples exist for the ROP of both monomers investigated herein, interestingly, examples of copolymerization of LA and BBL are rare.[13] We have therefore also investigated the copolymerization of *rac*-LA and *rac*-BBL at a 1 : 1 monomer ratio using {Hf(**2**)O^iPr}$_2$ and {Hf(**4**)O^iPr}$_2$, Table 1.

The zirconium and hafnium complexes all produced PHB with syndiotactic enrichment. The greatest stereocontrol was observed after 6 h with {Hf(**2**)(O^iPr)}$_2$ and {Hf(**4**)(O^iPr)}$_2$ (P_r 0.76 and 0.74, respectively). If the polymerizations were run for 24 h with those catalysts then the M_n and PDI remained relatively constant. Polymerizations carried out at lower temperature and for a longer period of time did not significantly improve the selectivity (P_r 0.77 using {Hf(**4**)(O^iPr)}$_2$). Narrow polydispersities were achieved for most complexes for both monomers suggesting controlled polymerization. The hafnium complexes showed greater control than the zirconium complexes under similar conditions (PDI $<$1.14). Complexes prepared with ligands **3**H_3 and **5**H_3 appeared to be less active than those with **2**H_3 and **4**H_3; with {Hf(**3**)(O^iPr)}$_2$ showing low conversion for both monomers and no appreciable conversion of BBL after 6 h using {Zr(**5**)(O^iPr)}$_2$ or {Hf(**5**)(O^iPr)}$_2$. Analysis of the PHB microstructure *via* $^{13}C\{^1H\}$ NMR spectroscopy showed that all the polymers prepared with Zr(IV) or Hf(IV) initiators have a syndiotactic bias (P_r 0.76–0.58). Analysis *via* MALDI-ToF MS from PHB prepared with {Hf(**2**)(O^iPr)}$_2$ indicated O^iPr and H end groups.

Table 1 Polymerization results[a]

Catalyst	Mon[a]	Time	Con[b]	M_n[c]	PDI[c]	M_n (calc)[e]	P_r[d]
Ti(**2**)O^iPr	BBL	24	15	1200	1.06	3950	0.5
Ti(**3**)O^iPr	BBL	24	38	3300	1.08	9850	0.5
Ti(**4**)O^iPr	BBL	24	3	—	—	—	—
Ti(**5**)O^iPr	BBL	24	38	3400	1.07	9850	0.5
{Zr(**2**)(O^iPr)}$_2$	BBL	6	96	21 800	1.29	24 850	0.65
{Zr(**3**)(O^iPr)}$_2$	BBL	24	94	18 750	1.09	24 350	0.60
{Zr(**3**)(O^iPr)}$_2$	BBL	6	72	9700	1.07	18 650	0.58
{Zr(**4**)(O^iPr)}$_2$	BBL	6	99	26 900	1.19	25 650	0.64
{Zr(**5**)(O^iPr)}$_2$	BBL	24	99	19 000	1.27	25 650	0.58
{Hf(**2**)(O^iPr)}$_2$	BBL	24	96	27 550	1.12	24 850	0.73
{Hf(**2**)(O^iPr)}$_2$	BBL	6	81	21 100	1.06	21 000	0.76
{Hf(**2**)(O^iPr)}$_2$	LA	2	95	27 100	1.12	13 750	0.60
{Hf(**3**)(O^iPr)}$_2$	BBL	24	40	—	—	—	—
{Hf(**3**)(O^iPr)}$_2$	LA	2	25	550	1.01	3650	—
{Hf(**4**)(O^iPr)}$_2$	BBL	24	96	28 500	1.11	24 850	0.74
{Hf(**4**)(O^iPr)}$_2$	BBL	6	56	4950	1.07	14 500	0.74
{Hf(**4**)(O^iPr)}$_2$	LA	2	99	15 950	1.60	14 300	0.60
{Hf(**5**)(O^iPr)}$_2$	BBL	24	96	12 800	1.14	24 850	0.68
{Hf(**5**)(O^iPr)}$_2$	LA	2	25	550	1.01	3650	—

[a] Polymerizations run at 80 °C in toluene; [BBL]/[initiator] = 300; [LA]/[initiator] = 100. [b] Conversion determined *via* ^1H NMR. [c] M_n = number average molecular weight; PDI = polydispersity index, determined from GPC measurements in THF (flow 1 ml min^{-1}, and referenced to polystyrene standards). [d] P_r = probability of racemic enchainment determined by $^{13}C\{^1H\}$ NMR for BBL determined by ^1H NMR for LA. [e] Calculated M_n for 1 polymer chain per metal centre.

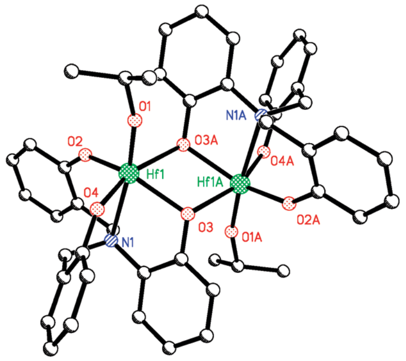

Fig. 1 Molecular structure of {Hf(**2**)(O^iPr)}$_2$ Selected bond lengths (Å) are Hf(1)–O(1) 1.913(3), Hf(1)–O(2) 1.972(3), Hf(1)–O(3) 2.142(3), Hf(1)–O(4) 1.987(3), Hf(1)–N(1) 2.417(4). The ^tBu groups and all hydrogen atoms have been removed for clarity.

Our attentions then turned to studying the kinetics in more detail. The homopolymerizations of BBL and LA indicate that the hafnium initiators {Hf(**2**)O^iPr}$_2$ (Fig. 2) and {Hf(**4**)O^iPr}$_2$ have comparable rates for both monomers, *e.g.* for {Hf(**4**)O^iPr}$_2$ k_{app} = 1.9 × 10^{-3} min^{-1} for *rac*-LA and k_{app} = 2.9 × 10^{-3} min^{-1} for *rac*-BBL.

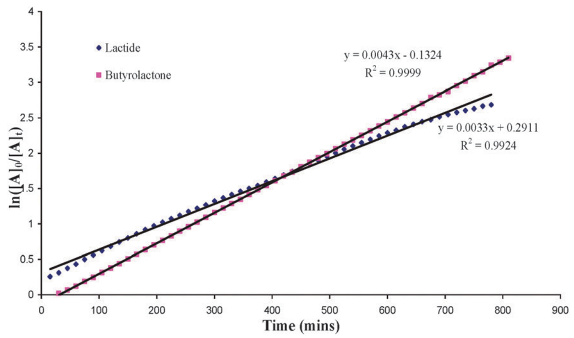

Fig. 2 ^1H NMR kinetic plot for the polymerization with {Hf(**2**)(O^iPr)}$_2$. The gradient represents k_{app} in units of min^{-1}, which are 4.3 × 10^{-3} and 3.3 × 10^{-3} respectively.

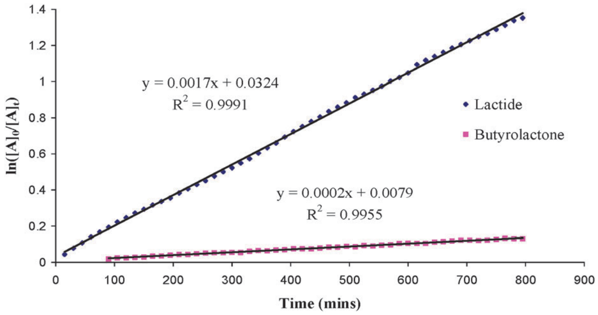

Fig. 3 Copolymerization of *rac*-LA and *rac*-BBL initiated by $\{\mathrm{Hf}(\mathbf{2})\mathrm{O}^i\mathrm{Pr}\}_2$.

Due to their comparable rates it was hoped that a random or alternating copolymer could be achieved under similar conditions to the homopolymerizations *via* $\{\mathrm{Hf}(\mathbf{2})\mathrm{O}^i\mathrm{Pr}\}_2$ and $\{\mathrm{Hf}(\mathbf{4})\mathrm{O}^i\mathrm{Pr}\}_2$ at 150 : 150 : 1 [LA] : [BBL] : [initiator], in one pot with the BBL and LA added simultaneously. The copolymers produced from these reactions have close to a 1 : 1 ratio of PLA : PHB and controlled molecular weight distribution in concurrence with theoretical values. Monomodal GPC traces suggest that a copolymer was produced (M_n = 31 350 g mol^{-1}, PDI = 1.61). From ^{1}H NMR studies, Fig. 3, it is surmised that the rate of insertion of BBL into a M-LA linkage is significantly slower than into the M-BL linkage. This leads to the conclusion that with these initiators and a 1 : 1 ratio of BBL : LA a block copolymer results, albeit with a broad molecular weight distribution. In line with previous reports we have not observed melting points in the DSC for either the homo or block polymers.[12] We also observed no melting temperature if an *L*-PLA-*b*-PHB copolymer is prepared in the same manner (M_n = 64 000 g mol^{-1}, PDI = 1.59). The copolymer was also prepared by sequential addition of the monomers, 150 equivalents of one monomer was initially homopolymerized (24 h, 80 °C) in toluene followed by addition of 150 equivalents of the second monomer and left for a further 24 h at 80 °C. If *rac*-LA is polymerized initially followed by *rac*-BBL then M_n = 38 900 g mol^{-1} and PDI 1.33 and a conversion of 99% of LA and 84% BBL is observed. If the copolymer is prepared initially with *rac*-BBL followed by *rac*-LA, M_n = 41 700 g mol^{-1} and PDI 1.09 and a conversion of 89% of LA and 99% BBL observed. The sequential addition method yielded copolymers with significantly lower PDIs.

In conclusion, a series of Group 4 complexes of four related amine tris(phenolate) ligands has been investigated for the activity of ROP of both *rac*-LA and *rac*-BBL. Interestingly, previously reported C_3-symmetric amine tris(phenolate) complexes that are highly selective for the ROP of LA showed poor control over the ROP of *rac*-BBL. However with a slight ligand modification, the Group 4 initiators reported here, that are non-selective in the production of PLA, produce syndiotactic PHB. The complexes also demonstrate the ability to form copolymers of LA and BBL.

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Notes and references

1 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841–1846.

2 A. C. Albertsson and I. K. Varma, *Biomacromolecules*, 2003, **4**, 1466–1486.

3 (*a*) A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel and J. F. Carpentier, *Angew. Chem., Int. Ed.*, 2006, **45**, 2782–2784; (*b*) A. Amgoune, C. M. Thomas, T. Roisnel and J. F. Carpentier, *Chem.–Eur. J.*, 2006, **12**, 169–179.

4 (*a*) M. C. Serrano, E. J. Chung and G. A. Ameer, *Adv. Funct. Mater.*, 2010, **20**, 192–208; (*b*) M. Avella, E. Martuscelli and M. Raimo, *J. Mater. Sci.*, 2000, **35**, 523–545; (*c*) R. A. J. Verlinden, D. J. Hill, M. A. Kenward, C. D. Williams and I. Radecka, *J. Appl. Microbiol.*, 2007, **102**, 1437–1449; (*d*) K. Sudesh, H. Abe and Y. Doi, *Prog. Polym. Sci.*, 2000, **25**, 1503–1555.

5 (*a*) A. Amgoune, C. M. Thomas and J. F. Carpentier, *Macromol. Rapid Commun.*, 2007, **28**, 693–697; (*b*) E. Brule, S. Gaillard, M. N. Rager, T. Roisnel, V. Guerineau, S. P. Nolan and C. M. Thomas, *Organometallics*, 2011, **30**, 2650–2653; (*c*) Z. Jedlinski, M. Kowalczuk, P. Kurcok, G. Adamus, A. Matuszowicz, W. Sikorska, R. A. Gross, J. Xu and R. W. Lenz, *Macromolecules*, 1996, **29**, 3773–3777; (*d*) L. R. Rieth, D. R. Moore, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 15239–15248; (*e*) N. Tanahashi and Y. Doi, *Macromolecules*, 1991, **24**, 5732–5733.

6 M. Moller, R. Kange and J. L. Hedrick, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 2067–2074.

7 (*a*) N. Ajellal, M. Bouyahyi, A. Amgoune, C. M. Thomas, A. Bondon, I. Pillin, Y. Grohens and J. F. Carpentier, *Macromolecules*, 2009, **42**, 987–993; (*b*) J. E. Kemnitzer, S. P. McCarthy and R. A. Gross, *Macromolecules*, 1993, **26**, 1221–1229.

8 (*a*) R. Reichardt, S. Vagin, R. Reithmeier, A. K. Ott and B. Rieger, *Macromolecules*, 2010, **43**, 9311–9317; (*b*) N. Ajellal, G. Durieux, L. Delevoye, G. Tricot, C. Dujardin, C. M. Thomas and R. M. Gauvin, *Chem. Commun.*, 2010, **46**, 1032–1034; (*c*) A. Leborgne and N. Spassky, *Polymer*, 1989, **30**, 2312–2319.

9 (*a*) J. F. Carpentier, *Macromol. Rapid Commun.*, 2010, **31**, 1696–1705; (*b*) E. Grunova, E. Kirillov, T. Roisnel and J. F. Carpentier, *Organometallics*, 2008, **27**, 5691–5698; (*c*) E. Grunova, E. Kirillov, T. Roisnel and J. F. Carpentier, *Dalton Trans.*, 2010, **39**, 6739–6752.

10 (*a*) 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; (*b*) S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem.*, 2006, **45**, 4783–4790; (*c*) Y. Kim, G. K. Jnaneshwara and J. G. Verkade, *Inorg. Chem.*, 2003, **42**, 1437–1447; (*d*) T. K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem.*, 2011, **50**, 2720–2722; (*e*) Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.*, 2006, 340–350; (*f*) E. L. Whitelaw, M. D. Jones and M. F. Mahon, *Inorg. Chem.*, 2010, **49**, 7176–7181; (*g*) E. L. Whitelaw, M. D. Jones, M. F. Mahon and G. Kociok-Kohn, *Dalton Trans.*, 2009, 9020–9025; (*h*) J. C. Buffet and J. Okuda, *Chem. Commun.*, 2011, **47**, 4796–4798; (*i*) A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones and M. D. Lunn, *Chem. Commun.*, 2008, 1293–1295.

11 T. K. Saha, B. Rajashekhar, R. R. Gowda, V. Ramkumar and D. Chakraborty, *Dalton Trans.*, 2010, **39**, 5091–5093.

12 (*a*) N. Nomura, A. Akita, R. Ishii and M. Mizuno, *J. Am. Chem. Soc.*, 2010, **132**, 1750–1751; (*b*) M. HiljanenVainio, T. Karjalainen and J. Seppala, *J. Appl. Polym. Sci.*, 1996, **59**, 1281–1288; (*c*) Y. Q. Shen, Z. Q. Shen, Y. F. Zhang and K. M. Yao, *Macromolecules*, 1996, **29**, 8289–8295; (*d*) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215–2224; (*e*) D. Pappalardo, L. Annunziata and C. Pellecchia, *Macromolecules*, 2009, **42**, 6056–6062.

13 (*a*) H. Abe, Y. Doi, Y. Hori and T. Hagiwara, *Polymer*, 1998, **39**, 59–67; (*b*) S. Hiki, M. Miyamoto and Y. Kimura, *Polymer*, 2000, **41**, 7369–7379.