Metal-Size Influence in Iso-Selective Lactide Polymerization**

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Abstract: Iso-selective initiators for the ring-opening polymerization (ROP) of rac-lactide are rare outside of Group 13. We describe the first examples of highly iso-selective lutetium initiators. The phosphasalen lutetium ethoxide complex shows excellent iso-selectivity, with a $P_i$ value of 0.81–0.84 at 298 K, excellent rates, and high degrees of polymerization control. Conversely, the corresponding La derivative exhibits moderate heteroselectivity ($P_i = 0.74$, 298 K). Thus, the choice of metal center is shown to be crucial in determining the level and mode of stereocontrol. The relative order of rates for the series of complexes is inversely related to metallic covalent radius: that is, $\text{La} > \text{Y} > \text{Lu}$.

Poly(lactide) (PLA), a degradable polymer obtained from renewable resources, is one of the leading alternatives to petrochemical plastics.¹ PLA is produced by the metal-catalyzed ring-opening polymerization (ROP) of lactide (LA).² The central challenge in this field of catalysis is to combine high rates with excellent stereocontrol, ideally without the need for expensive chiral auxiliaries or ligands.³ Iso-selectivity using rac-LA is especially important and useful because the product, stereoblock/complex PLA, has superior properties.⁴ For example, it is a crystalline polymer with a higher melting temperature ($T_m$) and better mechanical properties than isotactic poly-L-lactide (PLLA). In some cases, $T_m$ is elevated by as much as 50°C, greatly improving thermal stability and enabling PLA to compete as an engineering polymer.⁵ However, rac-LA iso-selective catalysts remain scarce, with the majority being chiral aluminum salen complexes or derivatives.⁶⁻⁷ Although these compounds show impressive degrees of stereocontrol, they are often extremely slow and require unacceptably high catalyst loadings, typically taking hours or days to reach completion even at 1 mol% catalyst loading. There are only a handful of other, non-aluminum based, iso-selective catalysts.⁷ The structures of three of the most selective of these are shown in Figure 1.⁸ In 2008, Arnold and co-workers reported the homochiral yttrium phosphasalen complex (Figure 1, structure A).⁸⁻¹² Herein, we report the performance of lutetium and lanthanum phosphasalen complexes. For such Group 3 lanthanide complexes, the coordination geometries are predominantly influenced by steric factors. In this regard, it is relevant that lutetium has a slightly smaller covalent radius than yttrium (1.87 Å versus 1.90 Å), whilst lanthanum is significantly larger (2.07 Å).⁹

The use of different lanthanide centers enables an investigation of the influence of atomic size and coordination environment on polymer tacticity. Both metals have precedent in lactide ROP catalysis,¹⁰ although lutetium is rarely investigated.¹⁰⁻¹⁶ Okuda and co-workers reported hetero-selective (syndiotactic) dithiaalkanediyl-bridged bis(phenolato) yttrium and lutetium catalysts, but found that the stereocontrol decreased from Y to Lu.¹⁹ To our knowledge, there is no precedent for any iso-selective lutetium initiators.

The initiators were prepared in good overall yields, from the phosphasalen ligand, which was synthesized using an established procedure (Scheme 1).¹⁶ First, the ligand was deprotonated using potassium bis(trimethylsilyl)amide (5 equivalents), leading to quantitative conversion into the salt, as observed by the upfield shift ($\delta_p = 23$ ppm) of the signal for the phosphorus center in the $\text{H}^1$ NMR spectrum. The lutetium phosphasalen chloride complex was formed, but not isolated, by reaction with LuCl₃. One signal was observed for this species at $\delta = 35$ ppm in the $\text{H}^1$ NMR spectrum. Addition of the relevant potassium alkoxide (ethoxide or tert-butoxide) led to the formation of the lutetium phosphasalen alkoxide complexes (1 and 2). A slight upfield shift was again observed for resonances in the $\text{H}^1$ NMR spectra of both complexes ($\delta_p = 34$ ppm). Compounds 1 and 2 were isolated in good yields after recrystallization (55% and 75%, respectively). The complexes were fully characterized by NMR spectroscopy and elemental analysis. At room temperature, the $\text{H}^1$ NMR spectra of both 1 and 2 show broad resonance...
signals, indicative of fluxional processes, however, at 360 K coalescence occurs and clearly distinguishable signals are observed (see Figure S9 in the Supporting Information). At 298 K, the $^{31}$P[1H] NMR spectrum of compound 1 shows two signals in a 1:7 ratio, but on heating to 360 K a single sharp signal is observed at $\delta = 34$ ppm. The phosphasalen lanthanum tert-butyl alkoxide complex (3) was formed in an analogous fashion, albeit in a slightly lower yield (34%). The intermediate chloride complex showed a single signal at $\delta = 33$ ppm in the $^{31}$P[1H] NMR spectrum. Addition of potassium tert-butoxide led to the formation of 3, which exhibited a single peak at lower chemical shift ($\delta_b = 30$ ppm). Crystals of all three new complexes suitable for single-crystal X-ray diffraction were isolated from solutions of the complexes in mixtures of cyclohexane and hexane (note that complex 3 crystallized with two independent molecules, 3A and 3B).

The structures of the complexes (Figure 2, Figures S1–S4) all show a severely distorted octahedral geometry at the metal center with trans angles in the ranges 144.52(14)–158.87(12)$^\circ$, 141.9(3)–159.3(3)$^\circ$, 127.11(16)–149.44(13)$^\circ$, and 123.71(18)–146.96(13)$^\circ$ for 1, 2, 3A, and 3B, respectively. The yttrium analogue A [8c] has a similar geometry to those observed for 1 and 2. In each case, the pentacoordinate ligand occupies one hemisphere, leaving the alkoxide ligand isolated in the other hemisphere (Figure 2). The geometries of 1 and 2 are very similar, as would be expected with the only difference between the two complexes being a change in the alkoxide co-ligand. The lanthanum structure 3, however, shows marked differences. In addition to the expected elongation of all of the M–X bonds (Table S1) and the even greater distortion from ideal octahedral coordination angles at the metal center (see above), the O1–O21 phenoxo--phenoxo separation is markedly increased (3.074(4), 3.107(9), 3.154, 3.603(5), and 3.354(5) Å, measured for 1, 2, A (yttrium analogue), 3A, and 3B, respectively). Similarly, the “hole” in which the alkoxide ligand sits is larger in 3A and 3B than in either 1, 2, or yttrium analogue A. [8c] The closest approaches between the methyl group of the alkoxide and a carbon atom of the proximal phenyl ring are approximately 3.74, 3.83, 3.81, 4.67, and 4.13 Å for complexes 1, 2, A, 3A, and 3B, respectively. All four structures adopt asymmetric conformations that place one phenyl ring of one of the two PPh$_2$ units—specifically a phenyl ring attached to P15—much closer to the alkoxide than the other three phenyl rings. There are noticeable differences in geometry between 3A and 3B, which are chemically identical, suggesting a distinct degree of flexibility in both the ligand and the coordination environment in 3. The most visually obvious difference is the orientation of the C48-containing phenyl ring bound to the P15 atom (the phosphorus closest to the alkoxide): in 3A this ring is oriented approximately orthogonally to the N14–P15 bond, whereas in 3B it is almost parallel to this bond (see Figures S3, S4).

Compounds 1–3 were tested as initiators for the ROP of rac-LA. Initially the experiments were conducted under standard conditions, using a 1 m solution of LA in THF at 298 K and with a 2 mm concentration of initiator. The progress of the polymerization was monitored by taking regular aliquots. All the new compounds (1–3) showed very good to very good activities (Table 1). Based on the time required to achieve complete conversion of rac-LA into PLA, the order of activity decreased: La > Y > Lu. To quantify these observations, the polymerization kinetics were monitored (Figures S11, S12).

In all cases, a first-order dependence of the conversion rate on lactide concentration was observed, as evidenced by the linear fit of data to plots of $\ln([\text{LA}]_0)/[\text{LA}]_t$ versus time, from which the gradient corresponds to the $k_{\text{obs}}$ value. For 1 and 2, the $k_{\text{obs}}$ values are comparable at 6.3 × 10$^{-5}$ s$^{-1}$ and 7.5 × 10$^{-5}$ s$^{-1}$, respectively (Figure S11). This similarity is in line with expectations as the two compounds differ only in the nature of the alkoxide which is the initiating group. The two lutetium complexes 1 and 2 are approximately an order of magnitude slower than yttrium complexes A and B ($k_{\text{obs}} = 6.9 × 10^{-4}, 7.9 × 10^{-4}$ s$^{-1}$). This finding is consistent with other examples of lutetium complexes. [10f,b,11] In contrast, lanthanum complex 3 was an extremely fast initiator, enabling almost complete conversion of 1000 equivalents of LA (versus initiator, in the presence of isopropyl alcohol (2 equivalents)) in less than 20 seconds (Table 1). Such rates are beyond the limit of polymerization monitoring using

**Scheme 1.** Synthesis and structure of initiators 1–3. a) Reaction conditions: 1) KN(SiMe$_3$)$_2$ (5 equiv), THF, 2 h, 298 K; 2) LuCl$_3$ or LaCl$_3$, THF, 4 h, 298 K; 3) KOR, THF, 4 h, 298 K.

**Figure 2.** Schematic representation of the single-crystal X-ray structures of complex 1 (M = Lu, R = tBu), 2 (M = Lu, R = Et) and 3 (molecules A and B, M = La, R = tBu).
Table 1: Polymerization data obtained using initiators 1–3 in THF, 298 K. [LA] = 1 m.

| l | [L] | [pPrOH] | [LA] | t [h] | Conversion [%] | $M_{\text{mon}}$ [g mol$^{-1}$] | $M_{\text{zuk}}$ [g mol$^{-1}$] | PDI | $P^{*}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1:500 [f] | 8 | 81 | 101 700 | 58 300 | 1.06 | 0.80 |
| 1 | 1:1500 | 9 | 84 | 38 900 | 60 500 | 1.07 | 0.75 |
| 1[a] | 1:0.5 500 | 72 | 84 | 69 600 | 60 500 | 1.02 | 0.84 |
| 1[b,c] | 1:0.5 200 | 48 | 90 | 36 000 | 26 000 | 1.02 | 0.83 |
| 2 | 1:500 [f] | 8.25 | 86 | 53 400 | 61 900 | 1.02 | 0.82 |
| 2[a] | 1:350 | 5.5 | 86 | 38 300 | 43 300 | 1.09 | 0.82 |
| 2[b] | 1:250 | 3.5 | 86 | 34 900 | 31 000 | 1.02 | 0.84 |
| 2[c] | 1:200 | 2.75 | 89 | 27 800 | 25 600 | 1.05 | 0.81 |
| 2[d] | 1:500 | 72 | 75 | 46 300 | 54 000 | 1.01 | 0.89 |
| 2[e] | 1:200 | 48 | 81 | 22 800 | 23 300 | 1.02 | 0.89 |
| 3 | 1:1 500 | 20 s | 98 | 57 300 | 70 600 | 1.05 | 0.28 |
| 3 | 1:2 1000 | 20 s | 93 | 58 000 | 67 000 | 1.03 | 0.28 |

[a] 0.75 m [LA], [b] 0.5 m [LA], [c] 257 K. [d] Determined by integration of the methine region of the $^1$H NMR spectrum (LA, 4.98–5.08 ppm; PLA, 5.09–5.24 ppm). [e] Determined by GPC (gel permeation chromatography) in THF versus polystyrene standards ($M_n$ values are corrected with a 0.58 factor). [f] Determined by analysis of the homonuclear decoupled NMR spectrum according to the method first described by Coudane et al.[15] [g] No pPrOH added. I = initiator.

Figure 3. Plot of $k_{\text{obs}}$ value versus [L]. Polymerization conditions: [LA]$_{0}$ = 1 m, [L] = 2–5 mm, THF, 298 K. Average errors: 1–8%.

aliquote and so no further kinetics studies were undertaken. Instead, the rate law for polymerization using 2 was investigated: $k_{\text{obs}}$ values were determined over a range of different initiator concentrations, ([2] = 2–5 mm; at 298 K maintaining [LA] = 1 m). In each case, the reactions were first-order in lactide concentration. The reactions also showed a first-order dependence on the concentration of initiator 2, as shown by the linear fit to the plot of $k_{\text{obs}}$ value versus the concentration of 2 (Figure 3). Thus, the overall rate law is second-order and the propagation rate constant, $k_p$, is 5.08 x 10$^{-5}$ M$^{-1}$ s$^{-1}$. As the rate depends on both initiator and lactide concentrations, the rate-limiting process could correspond to LA coordination or reverse exchange reactions leading to faster initiation and, in the case of 2, a very good match between the calculated and the experimental $M_n$ values. In contrast, complex 2, containing an ethoxy co-ligand, enables very well-controlled polymerization without the need for any exogeneous alcohol.

Importantly, in addition to high rates and good polymerization control, the lutetium complexes 1 and 2 both polymerize rac-LA with a high iso-selective bias, as assessed by the $P_i$ values which were determined by integration (normalized) of the homonuclear decoupled NMR spectra and comparison with the values predicted by Bernouillan statistics.[12] Compound 1 showed a significantly improved iso-selectivity compared to compound A (yttrium analogue) at 298 K ($P_i$ = 0.80 versus $P_i$ = 0.75). However, when one equivalent of isopropyl alcohol was added, the degree of iso-selectivity dropped ($P_i$ = 0.75 for 1, versus $P_i$ = 0.73 for compound A with pPrOH), presumably because of some scrambling of stereochemistry during chain transfer. Compound 2, which does not require any alcohol, was even more iso-selective at room temperature ($P_i$ = 0.82 ± 0.02) and represents, to our knowledge, the highest iso-selectivity catalyst reported, excluding the aluminium salen complexes.

As mentioned, although $P_i$ values exceeding 0.95 are known for these chiral aluminium salen ligands, their activities are very low and the high loadings (more than 1 mol%) limit their applicability.

We next considered how to control the iso-selectivity. The $P_i$ value remained high over a range of different catalyst loadings and therefore enabled the production of rather high $M_n$ stereoblock PLA (Table 1). Sterecontrol is a kinetic phenomenon, therefore reducing the reaction temperature enables an increase in iso-selectivity, leading to a maximum $P_i$ value of 0.89 at 257 K. Analysis of the defect tetrad signals in the homonuclear decoupled NMR spectrum indicate that iso-selectivity arises from a chain-end control mechanism (approximately a 1:1:1 ratio of $\delta_1$:$\delta_2$:1; Figure S14). Differential scanning calorimetry (DSC) indicated the formation of polymerization, that is, the need for sufficient Lewis acidity to ensure rapid coordination, balanced with an alkoxide bond which is labile to substitution. The order of rates correlates with the metal-alkoxide bond lengths, as determined by single-crystal XRD experiments. The lanthanum–alkoxide bond is significantly longer than the lutetium–alkoxide and yttrium–alkoxide bonds (M–O2I: 2.196(4), 2.060(3), 2.069(6) Å in 3A (La), 1 (Lu), and A (Y), respectively).

Despite the high overall rates, the polymerizations remained very well controlled. In general, there was a close agreement between the theoretical and observed molecular weights, and the PLA had a narrow polydispersity index (PDI < 1.10 in all cases, Table 1). Complexes 1 and 3 contain tert-butyl alkoxide as the co-ligand. This hindered alkoxide has been shown to undergo relatively slower initiation leading to $M_n$ values exceeding those predicted.[8c] To overcome this limitation, isopropyl alcohol (0.5–1 equivalents) was added, which undergoes rapid and reversible exchange reactions leading to faster initiation and, in the case of 1, a very good match between the calculated and the experimental $M_n$ values. In contrast, complex 2, containing an ethoxy co-ligand, enables very well-controlled polymerization without the need for any exogeneous alcohol.
semi-crystalline PLA with a $T_m$ of 178°C (Figure S16). The increased degree of iso-selectivity for complex 1 and 2 (versus yttrium analogues A and B) is tentatively proposed to be as a result of the smaller lutetium metal center enforcing a more sterically encumbered bonding geometry by the phosphasalen ligand.

Thus, we were surprised to discover that the lanthanum initiator, 3, exhibited moderate heteroselectivity ($P_r = 0.72$). This is unexpected as a gradual decrease in stereocontrol on decreasing steric shielding is much more usual.\[10c,d\] We have previously observed that for a series of yttrium phosphasalen complexes, the stereocontrol switches from heterotactic (for tetracoordinate ligands) to isotactic (for pentacoordinate ligands).\[8c\] In contrast, the same pentacoordinate ligand bound herein to a series of lanthanide centers forms compounds with very closely related coordination geometries (see above), which leads to completely opposite stereoselectivities depending on the metal size. Insight into the propensity for an initiator to exhibit iso-selectivity or heteroselectivity can be gained by analysis of the NMR spectra. High-temperature $^1$H NMR experiments of the lutetium compounds suggest that signal coalescence is reached at 360 K (Figure S5, S6). Under the same conditions, resonance signals attributable to the lanthanum complex are still significantly broadened, indicating a more fluxional structure (Figure S7).

2D NMR spectroscopic experiments were even more informative, with the use of rotating-frame nuclear Overhauser effect spectroscopy (ROESY), it is possible to compare the fluxionalities of the complexes by monitoring proton-exchange events. It is important to note that all complexes showed proton exchange in the iminophosphorane bridges, in line with the broadened resonance signals in the $^1$H NMR spectra observed at 298 K. Lutetium complexes 1 and 2 showed limited further exchange, as did the yttrium analogues A and B.\[8c\] However, the lanthanum analogue 3 showed significant exchange of the phenyl ring protons (Figures S3, S4). Furthermore, previous studies showed no further exchange, as did the yttrium analogues A and B.\[8c\] Thus, we were surprised to discover that the lanthanum analogue 3A exhibited free rotation of the phenyl groups using different yttrium derivatives, revealed that heteroselectivity.\[8c\] Thus, these NMR studies add further weight to the hypothesis that iso-selectivity results from sterically congested metal complexes with limited fluxionality of the phosphorus substituents. In contrast, heteroselectivity is observed when using the larger metal center (La) which shows a more open coordination geometry and fluxionality of the phosphorus substituents.

In conclusion, we have reported highly iso-selective lutetium initiators. The phosphasalen lutetium ethoxide complex shows a $P_r$ value of 0.82 ± 0.02 at 298 K, moving to 0.89 at 257 K. In contrast, the analogous lanthanum initiator was heteroselective ($P_r = 0.72$, 298 K). All initiators show excellent rates and high degrees of polymerization control. Both the relative order of rates and the mode and degree of stereocontrol for the series of complexes have been shown to be related to the metallic covalent radius. A larger metal center results in a higher observed rate (La > Y > Lu). The smaller metal center of lutetium promotes high iso-selectivity (higher than the previously reported yttrium), whilst the more open coordination geometry of lanthanum leads to moderate heteroselectivity. The type of stereocontrol appears to be associated with the level of rigidity imposed on the ligand. Thus, from a single ligand, two different modes of stereocontrol are possible: such switching is very unusual and warrants further investigation as an attractive route to control polymer properties.

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