Amide and alkoxide coordination complexes of calcium supported by β-dinmianato and bulky trispyrazolylborate ligands are reported together with their activity in lactide ring-opening polymerization; some are amongst the most active systems discovered to date.

Well defined coordination complexes\(^1\) have been found to be effective in initiating the ring-opening polymerization (ROP) of lactides to give poly(lactides), PLAs, which are an important emerging class of environmentally friendly and biocompatible polymers, readily available from an inexpensive renewable resource.\(^2\) The β-dinmianato (BDI) ligand \(\text{CH}[\text{CMeN}(2,6'-\text{Pr}_2 \text{C}_6 \text{H}_3)]_2\) \(L\) has proved a particularly effective spectator ligand when attached to Mg\(^{2+}\), Zn\(^{2+}\) and Sn\(^{2+}\) in complexes of the form LMX where X = an amide or alkoxide which acts as an initiator in ring-opening.\(^3\) As with any polymer having commercial interest in the biomedical filed, it is important that the metal be biological benign and that any residual catalyst not impart undesirous properties such as color to an otherwise colorless polymer. In this regard, calcium is an attractive metal.

In comparison to magnesium and zinc, calcium is significantly larger and its organometallic and coordination chemistry is notably different and much less well developed than those of magnesium and zinc. We describe here our initial foray aimed to achieve the metal be biological benign and that any residual catalyst not impart undesirous properties such as color to an otherwise colorless polymer. In this regard, calcium is an attractive metal. In comparison to magnesium and zinc, calcium is significantly larger and its organometallic and coordination chemistry is notably different and much less well developed than those of magnesium and zinc. We describe here our initial foray aimed at preparing complexes of the type LCaX where X = an amide or alkoxide capable of initiating ROP of lactide. These initial results are both extremely promising with regard to the potential utility of well-defined calcium coordination complexes for the ROP of lactide and illuminating with respect to the differences in the coordination chemistry of the elements Ca, Mg, and Zn.

The bulky β-dinmianato ligand LH reacts with KN(SiMe\(_3\))\(_2\) (2 equiv.) in THF and subsequently with CaL\(_2\) to yield the complex LCa[N(SiMe\(_3\))]\(_2\)/THF, 1 (see Fig. 1).\(^4\) However, based on variable temperature \(^1\)H NMR data, this compound is either dimeric at low temperatures or tetradentate or exists in equilibrium with other calcium species. Compound 1 polymerizes rac-lactide to > 90% heterotactic PLA (\(i\_i + \_i s\)) in THF at room temperature.\(^7\) The polymerization approaches 90% conversion in 1 min ([LH]/[CaL\(_2\)] = 200, \(M_n = 37.8\) kg mol\(^{-1}\), PDI = 1.74 and [LA]/[LH] = 200, \(M_n = 40.1\) kg mol\(^{-1}\), PDI = 1.68) (see Fig. 5). Interestingly, the less bulky \([\text{HB}(3-\text{Phpz})_3]\text{MgEt}_{\text{THF}}, 3\) THF shows no stereoselectivity under the same conditions ([LA]/[LH] = 200, 97% conversion in 1 min, \(M_n = 64.0\) kg mol\(^{-1}\), PDI = 1.61).

In examining the relative reactivities of \([\text{HB}(3-\text{Bupz})_3]\text{Ca}\) complexes we note that under identical conditions 100 equiv. of LA are converted to > 90% PLA at room temperature in 1 min.
for mixtures of magnesium and zinc, the magnesium reacted to the exclusion of the zinc amide which remained after consumption of LA.

In conclusion, we have discovered some interesting new coordination compounds of calcium and found that some of these are amongst the most active of all known coordination compounds in the ring-opening polymerization of lactides. Some fascinating comparisons within the coordination chemistry of Ca²⁺, Mg²⁺ and Zn²⁺ are also to be noted. Further studies are in progress.

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Notes and references


Fig. 5 1H NMR spectra (CDCl₃, 400 MHz) of the homodecoupled CH resonance of poly(ε-lactide) prepared in THF using [η-HB3-3HB(3-tertBu)](O-2,6-iPr₂C₆H₃).

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