

Cationic and zwitterionic rare earth and alkaline earth initiators for the living and immortal ring-opening polymerisation of *rac*-lactide

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Poly(lactide) (PLA) based plastics are important renewable, biocompatible and biodegradable materials. The preferred method of synthesis from both an industrial and academic perspective is ring-opening polymerisation (ROP) of the cyclic diester, lactide (LA).^[1] Well-behaved coordination-insertion events lead to living ROP (one PLA chain per metal, of well-defined molecular weight). In the presence of a chain transfer agent, immortal ROP (*i*ROP) can be induced, leading to multiple PLA chains per initiator.

In the first part of this presentation we will report the synthesis of new zwitterionic and dicationic rare earth initiators for the ROP and *i*ROP of *rac*-LA, along with amine co-initiated *i*ROP (Fig. 1), the first fast and well-controlled example of this process.^[2]

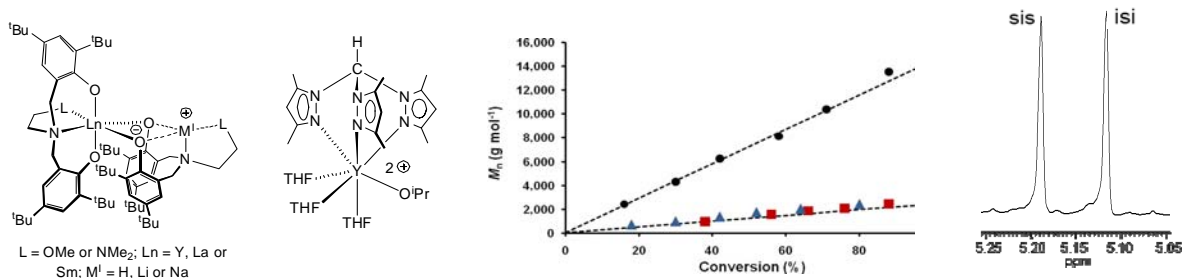


Figure 1. Zwitterionic and dicationic initiators for the ROP and *i*ROP of *rac*-LA; M_n vs. conversion for ROP in the absence (upper) and presence (lower) of BnNH₂ or ^tPrOH; selectively decoupled partial ¹H NMR spectrum of the highly heterotactic amine-terminated PLA formed with BnNH₂ co-initiator.

We have also been interested to extend the scope of recently reported neutral and cationic rare earth borohydride initiators for the ROP of cyclic esters^[3] to the neighbouring alkaline earth metals. In the second part of the presentation we will briefly report on the synthesis and ROP capability of new cationic and charge neutral calcium borohydrides for the synthesis of telechelic, highly heterotactic PLA (Fig. 2).^[2]

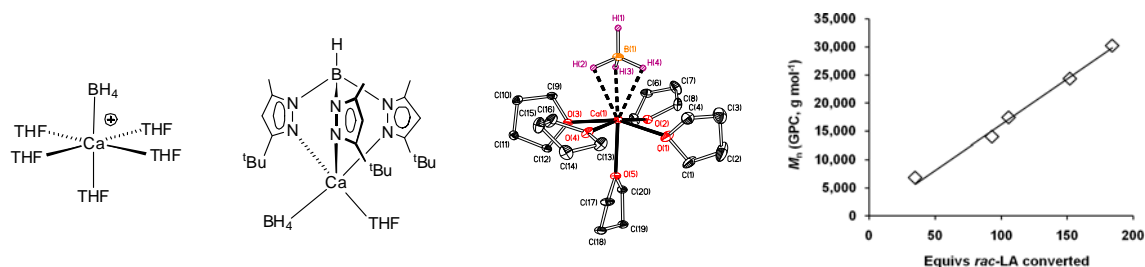


Figure 2. Cationic and charge-neutral calcium borohydrides; example solid state structure; example M_n vs. conversion plot for the ROP of *rac*-LA.

References

- [1] Selected reviews: A. P. Dove, *Chem. Soc. Revs.* **2010**, 39, 486; C. K. Williams, *Chem. Soc. Revs.* **2007**, 36, 1573; J.-F. Carpentier *et al.*, *Pure Appl. Chem.* **2007**, 79, 2013.
- [2] P. Mountford *et al.*, *Chem. Commun.* **2010**, 46, 273 & unpublished results.
- [3] Selected examples: J. Okuda *et al.*, *Dalton Trans.* **2008**, 2667; S. G. Guillaume *et al.*, *Chem. Eur. J.* **2007**, 13, 1511; P. Mountford *et al.*, *Organometallics* **2010**, DOI: 10.1021/om100513.