

# Zwitterionic yttrium complexes for the amine-initiated, immortal ring-opening polymerisation of *rac*-lactide: facile synthesis of amine terminated, highly heterotactic poly(lactide)

L. Clark, H. E. Dyer, A. D. Schwarz and P. Mountford\*

Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K.



UNIVERSITY OF OXFORD

## Introduction

Poly(lactide) (PLA) is a biodegradable and biocompatible material derived from renewable resources. Ring-opening polymerisation (ROP) of the cyclic ester lactide (LA) is the method of choice for synthesising PLA.<sup>[1]</sup> Rare earth metal complexes supported by bis(phenolate) ligands have been shown to be highly effective catalysts for this process.<sup>[2-6]</sup>

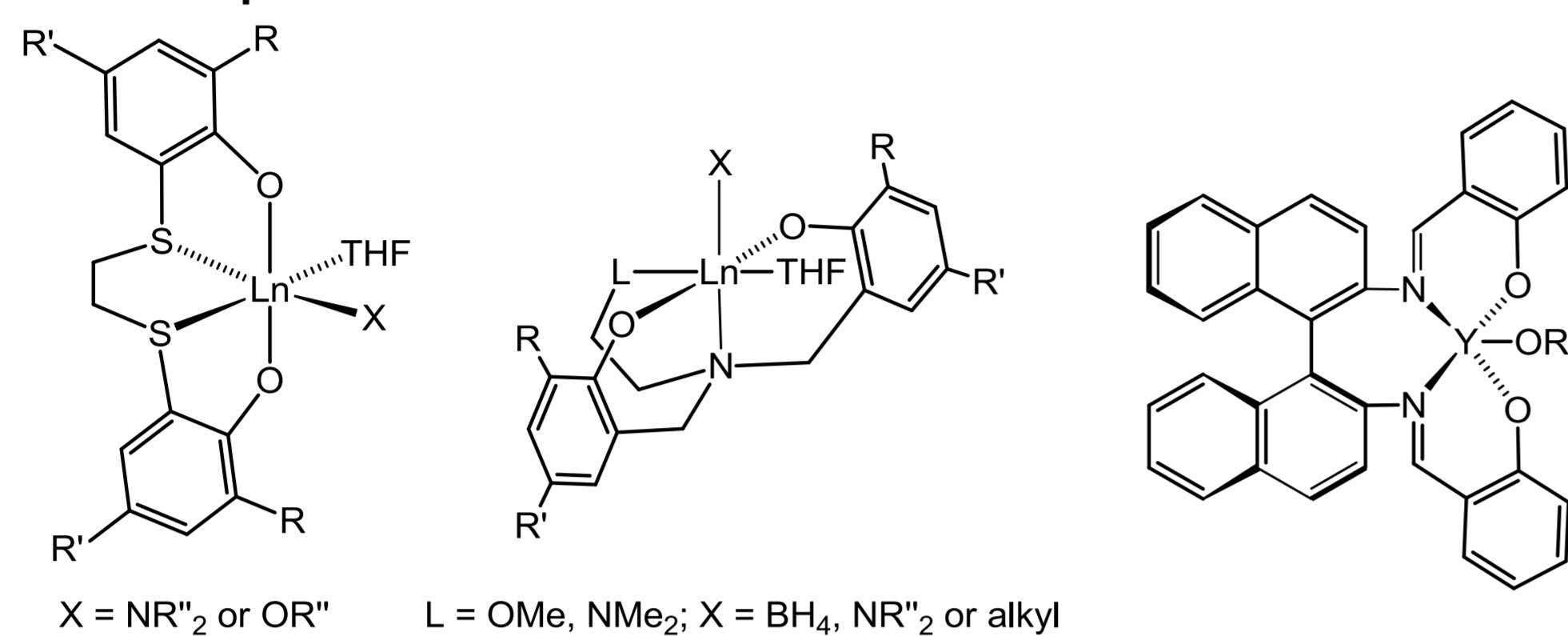
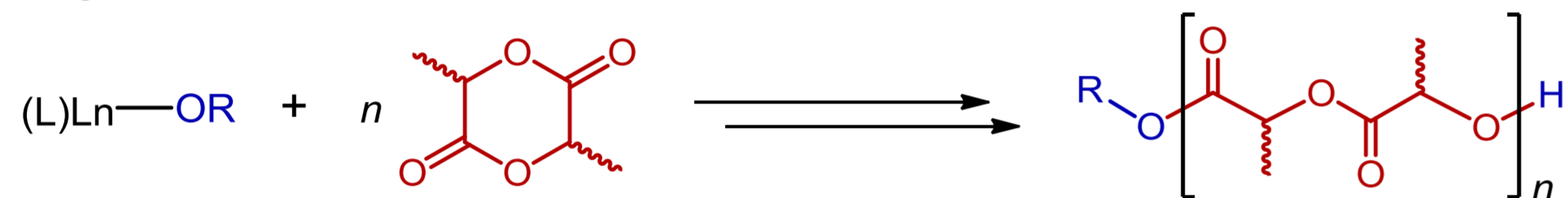
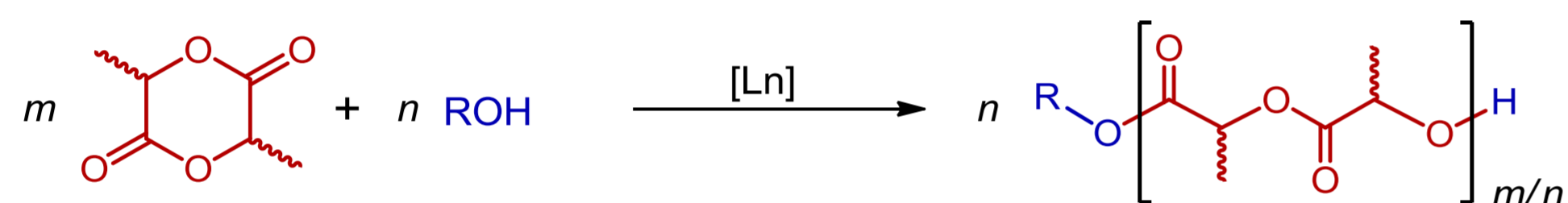


Fig. 1. Bis(phenolate) supported rare earth ROP initiators.

Complexes with alkoxide initiating groups (Fig. 1) have shown excellent control over polymer  $M_n$  and molecular weight distribution. Polymerisation proceeds *via* a coordination-insertion mechanism:



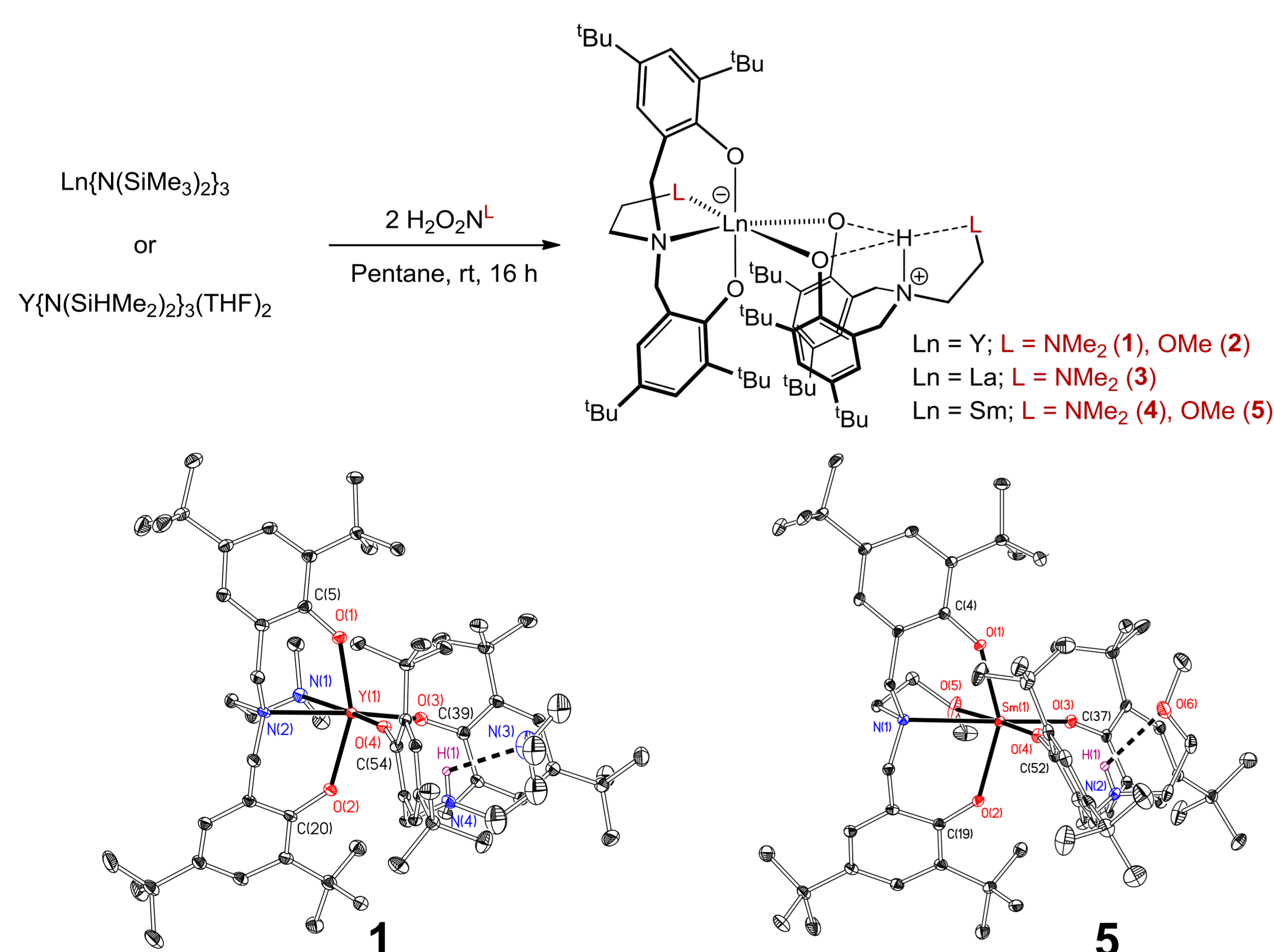
Alcohol chain transfer agents (CTAs)/co-initiators can generate multiple polymer chains per metal centre with the alcohol incorporated as the polymer end-group, a process described as immortal polymerisation:<sup>[7]</sup>



In contrast, there are few ROP-based routes to amine-terminated PLA and metal amides, (L)Ln-NR<sub>2</sub> (Fig. 1), are notoriously prone to poor  $M_n$  control and formation of macrocyclic polyesters.<sup>[3,8]</sup>

## Synthesis

Reaction of two equivalents of protio-bis(phenol)amine and Ln{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub> or Y{N(SiHMe<sub>2</sub>)<sub>2</sub>}<sub>3</sub>(THF)<sub>2</sub> yields zwitterionic complexes supported by a tetradentate [O<sub>2</sub>N<sup>-</sup>] framework in addition to a semi-protonated [HO<sub>2</sub>N<sup>-</sup>] fragment.



Scheme 1. Synthesis of rare earth zwitterions and examples of molecular structures; Y(O<sub>2</sub>N<sup>NMe2</sup>)(HO<sub>2</sub>N<sup>NMe2</sup>) (1) and Sm(O<sub>2</sub>N<sup>OMe</sup>)(HO<sub>2</sub>N<sup>OMe</sup>) (5).

## Amine co-initiated ROP

Zwitterions are highly active initiators for the polymerisation of *rac*-LA but control over  $M_n$  is poor and molecular weight distributions are broad. Addition of BnNH<sub>2</sub>, <sup>n</sup>PrNH<sub>2</sub>, piperidine or BnOH generates one chain per amine or alcohol with excellent control over  $M_n$  (Table 1). Y(O<sub>2</sub>N<sup>NMe2</sup>)(HO<sub>2</sub>N<sup>NMe2</sup>) (1) provides the balance between activity and control over the polymerisation reaction *cf.* La and Sm analogues.  $M_n$  can be tuned by varying [BnNH<sub>2</sub>]<sub>0</sub> and [rac-LA]<sub>0</sub> whilst <sup>1</sup>H-<sup>1</sup>H NMR spectra show that PLAs have high heterotactic enrichment. MALDI-ToF-MS confirmed amide end-groups.<sup>[9]</sup>

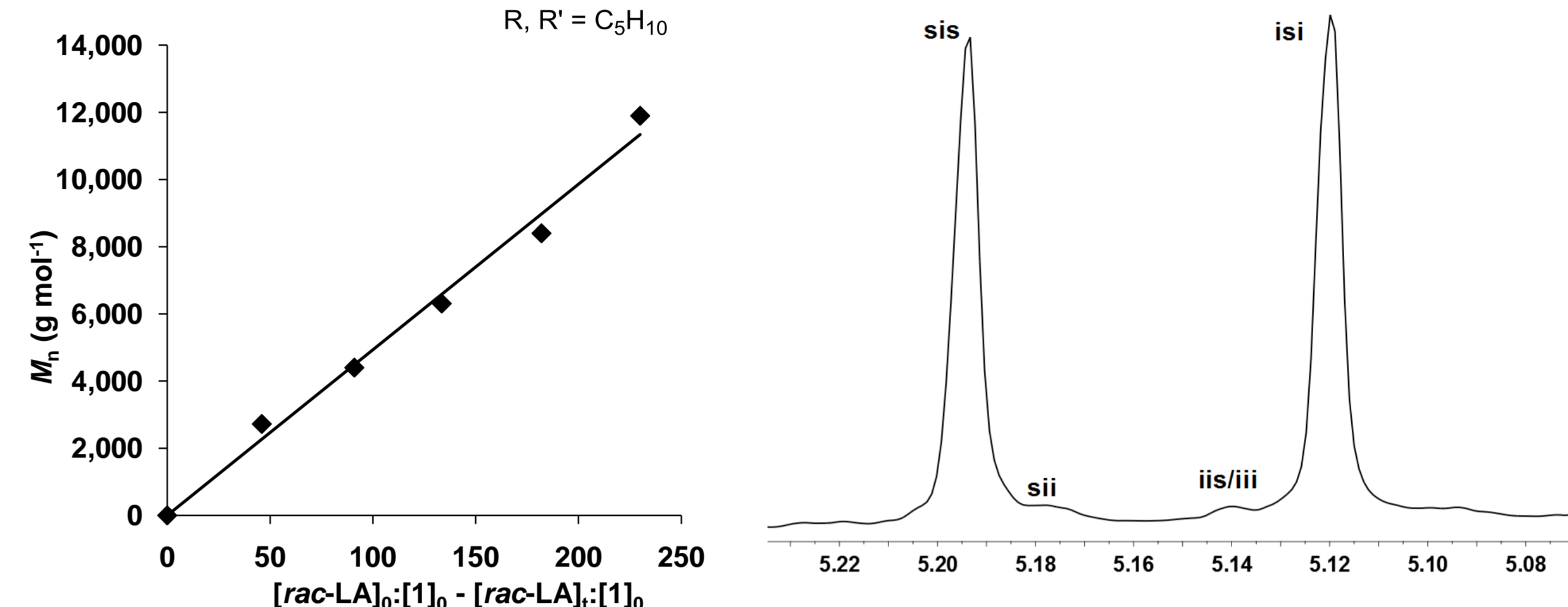
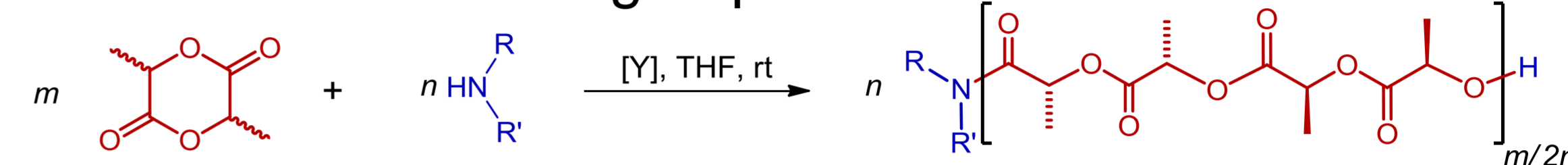


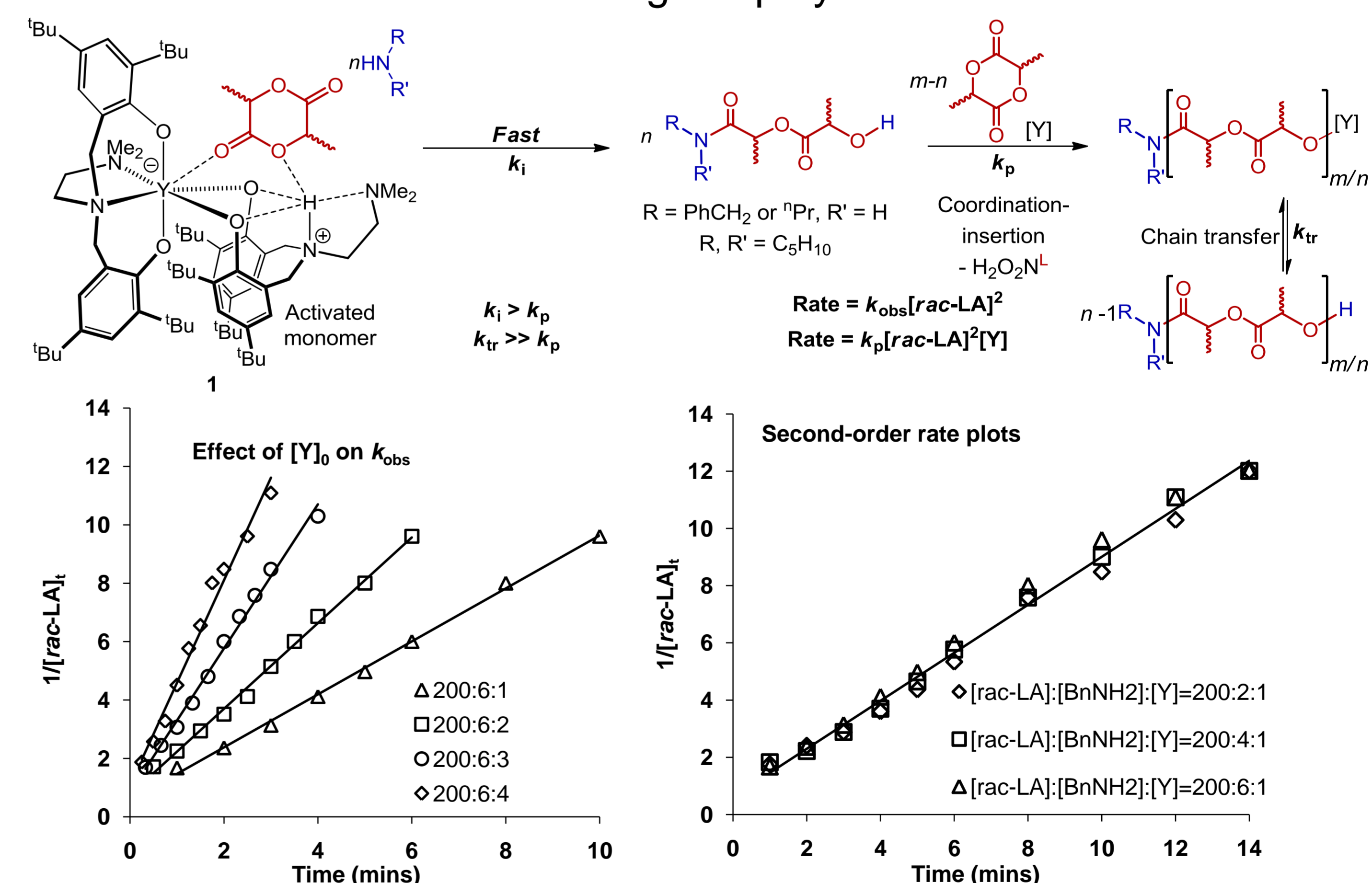
Table 1. Immortal ROP of *rac*-LA catalysed by 1.<sup>a</sup>

Initiator	Conv.(%)	$M_n$ (calcd) <sup>b</sup> / g mol <sup>-1</sup>	$M_n$ (GPC)/ g mol <sup>-1</sup>	PDI	$P_r$
BnNH <sub>2</sub>	89	2670	2460	1.17	0.93
<sup>n</sup> PrNH <sub>2</sub>	91	2680	3030	1.17	0.89
C <sub>5</sub> H <sub>10</sub> NH	90	2680	2810	1.19	0.90
BnOH	90	2700	2620	1.19	0.92

<sup>a</sup> [rac-LA]<sub>0</sub>:[initiator]<sub>0</sub>:[1]<sub>0</sub> = 100:5:1; 2 mL THF, RT, 20 min, [rac-LA] = 0.7 M, % conversion and  $P_r$  determined by <sup>1</sup>H NMR. <sup>b</sup>  $M_n$  (calcd) = (% conv. × 144.1)/5 + initiator RMM.

## Mechanistic Studies

Kinetics studies at ambient temperature have shown a second-order dependence in [rac-LA]<sub>0</sub>.<sup>[10]</sup> From the appropriate runs, a first-order dependence in [1]<sub>0</sub> and zero-order dependences in [amine]<sub>0</sub> or [BnOH]<sub>0</sub> have been determined. <sup>1</sup>H NMR studies show no reaction between 1 and amines in absence of *rac*-LA. Loss of one equivalent of H<sub>2</sub>O<sub>2</sub>N<sup>NMe2</sup> from 1 was shown to occur during the polymerisation reaction.



$k_{obs}$  remained constant at around 0.8 M<sup>-1</sup> min<sup>-1</sup> when [BnNH<sub>2</sub>]<sub>0</sub> was varied between 2, 4 and 6 molar equivs. First-order dependence in [Y]<sub>0</sub> leads to overall rate expression, rate =  $k_p$ [rac-LA]<sup>2</sup>[Y] ( $k_p$  = 240(8) M<sup>-2</sup> min<sup>-1</sup>). Carpentier's compound, Y(O<sub>2</sub>N<sup>NMe2</sup>){N(SiHMe<sub>2</sub>)<sub>2</sub>}(THF) also obeys this rate-law. Initial, rapid consumption of amine generates one macromonomer per amine. Propagation occurs *via* coordination-insertion at the metal centre, with facile exchange between growing and dormant chains.

## Acknowledgements

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## References

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