Supporting Information for:

Continuous cyclo-polymerisation of L-lactide by reactive extrusion using atoxic metal-based catalysts: easy access to well-defined polylactide macrocycles

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1. $^1$H NMR Spectra of PLA’s

Figure SI1. $^1$H NMR spectrum (CDCl$_3$) of the crude PLA formed with Sm(BH$_4$)$_3$(THF)$_3$ (4) by reactive extrusion polymerisation (run 24).
Figure S12. $^1$H NMR spectrum (CDCl$_3$) of the crude PLA formed with La(BH$_4$)$_3$(THF)$_3$ (5) by reactive extrusion polymerisation (run 30).
2. MALDI-TOF mass spectra of PLA’s

Mass spectra of PLA’s synthesized by reactive extrusion polymerisation

Figure S13. MALDI-TOF mass spectrum of the PLA formed with Nd(BH₄)₃(THF)₃ (3) by reactive extrusion polymerisation (run 18). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1200 – 1650 amu. Mass = (n × 72.07) + 22.99 corresponding to cyclic PLA.
Figure S14. MALDI-TOF mass spectrum of the PLA formed with La(BH₄)₃(THF)₃ (5) by reactive extrusion polymerisation (run 30). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1350 – 1780 amu. Main population, Mass = (n × 72.07) + 22.99, corresponding to cyclic PLA (o). Small fraction of linear H-PLA-OH (Δ), Mass = (n × 72.07) + 18 + 22.99.
Mass spectra of PLA’s synthesized by bulk polymerisation

**Figure SI5.** MALDI-TOF mass spectrum of the PLA formed with Nd(BH₄)₃(THF)₃ (3) by bulk polymerisation (run 7). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1870 – 2210 amu. Main population, Mass = \((n \times 72.07) + 22.99\), corresponding to cyclic PLA, (o). Small fraction of linear PLA (H-PLA-OH), Mass = \((n \times 72.07) + 18 + 22.99\) (-).
Figure S16. MALDI-TOF mass spectrum of the PLA formed with La(BH$_4$)$_3$(THF)$_3$ (5) by bulk polymerisation (run 13). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1380 – 1790 amu. Main population, Mass = (n × 72.07) + 22.99, corresponding to cyclic PLA, (o). Small fraction of linear PLA (H-PLA-OH), Mass = (n × 72.07) + 18 + 22.99 (-).
**Figure SI7.** MALDI-TOF mass spectrum of the PLA formed with La(BH$_4$)$_3$(THF)$_3$ (5) by bulk polymerisation (run 14). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1380 – 1790 amu. Main population, Mass = (n × 72.07) + 22.99, corresponding to cyclic PLA, (o). Small fraction of linear PLA (H-PLA-OH), Mass = (n × 72.07) + 18 + 22.99 (-).