Electronic Supplementary Material (ESI) for RSC Advances.

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).

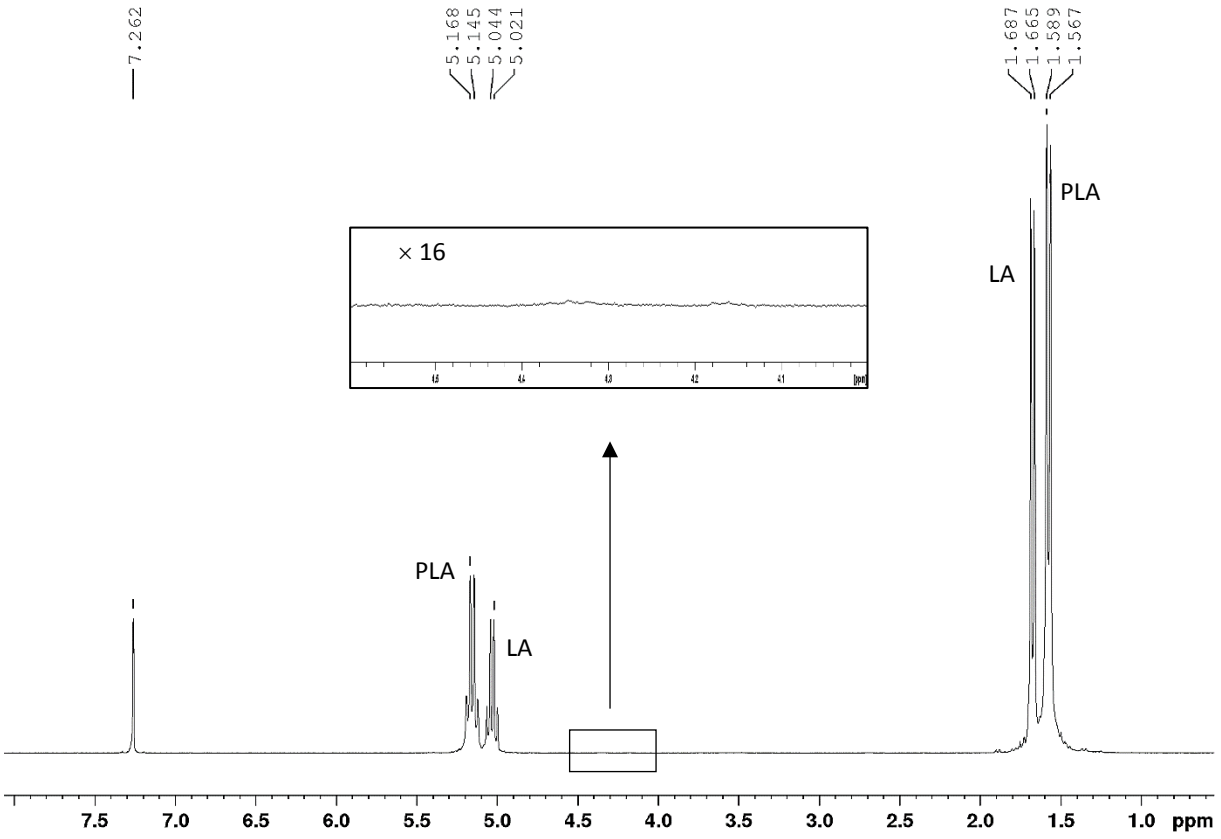
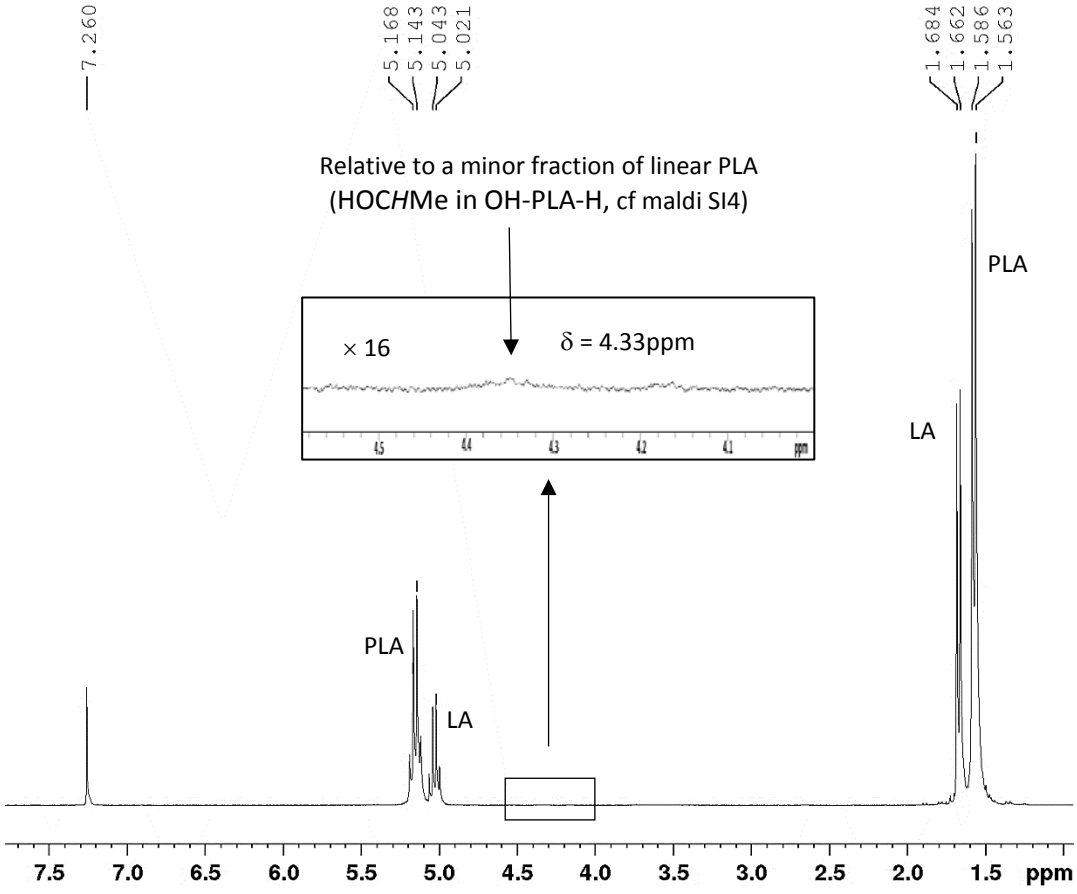


Figure SI2. ^{1}H NMR spectrum ($CDCl_3$) of the crude PLA formed with $La(BH_4)_3(THF)_3$ (**5**) by reactive extrusion polymerisation (run 30).

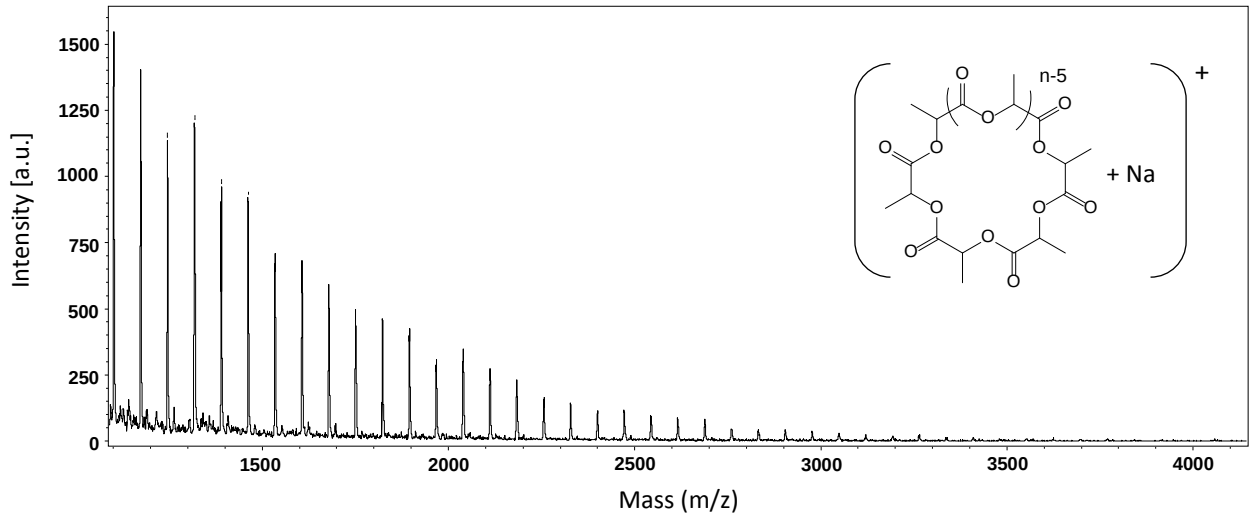


2. MALDI-TOF mass spectra of PLA's

Mass spectra of PLA's synthesized by reactive extrusion polymerisation

Figure SI3. MALDI-TOF mass spectrum of the PLA formed with $Nd(BH_4)_3(THF)_3$ (**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.

(a)



(b)

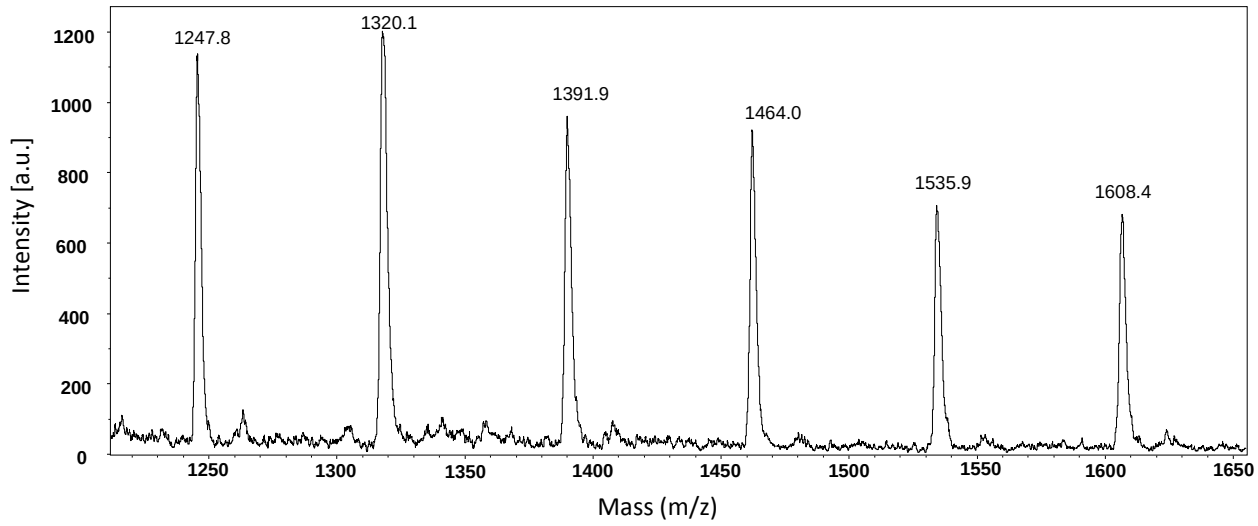
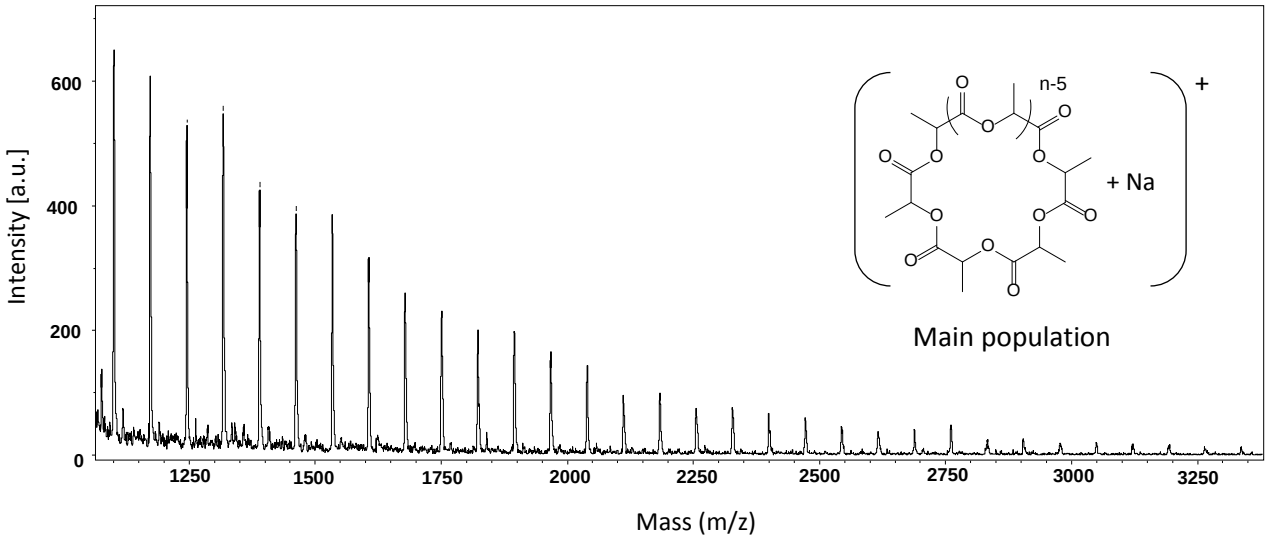
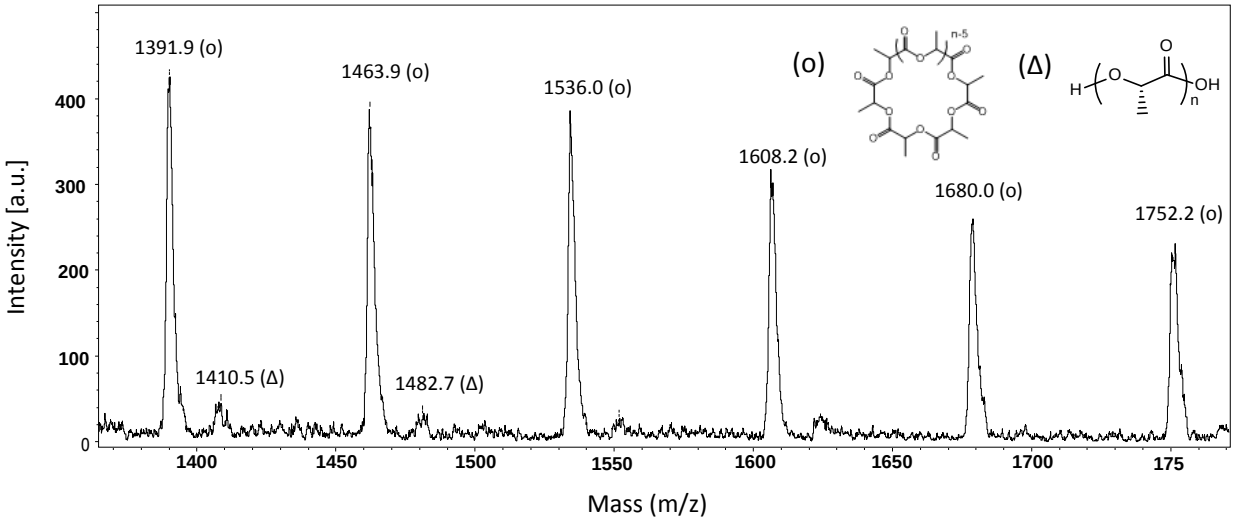


Figure SI4. MALDI-TOF mass spectrum of the PLA formed with $La(BH_4)_3(THF)_3$ (**5**) by reactive extrusion polymerisation (run 30). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1350 – 1780 amu. Main population, Mass = (n × 72.07) + 22.99, corresponding to cyclic PLA (o). Small fraction of linear H-PLA-OH (Δ), Mass = (n × 72.07) + 18 + 22.99.

(a)



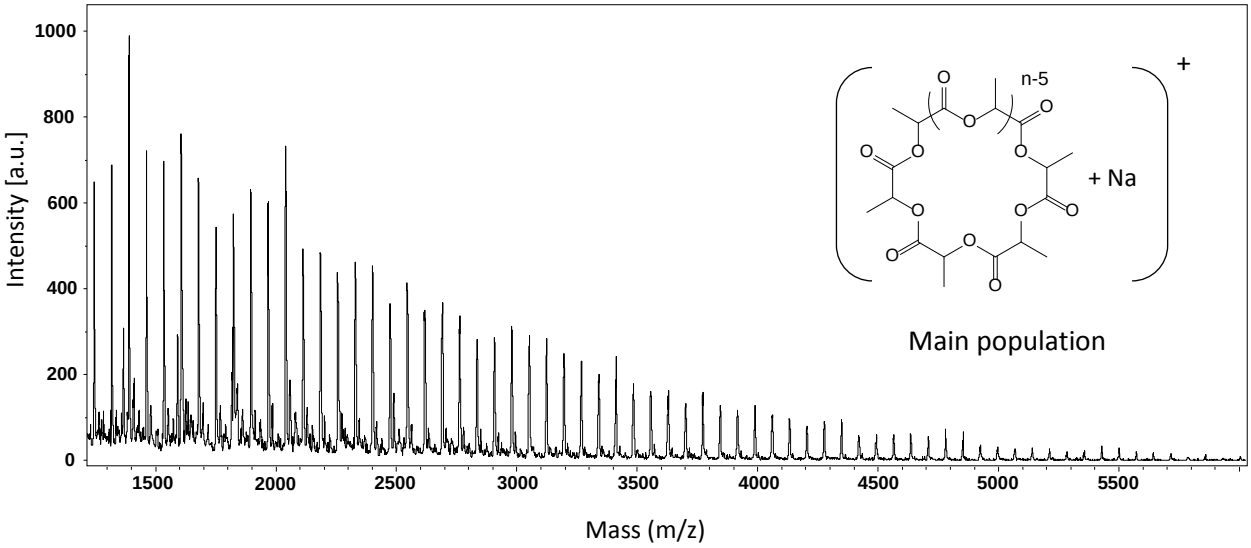
(b)



Mass spectra of PLA's synthesized by bulk polymerisation

Figure SI5. MALDI-TOF mass spectrum of the PLA formed with $Nd(BH_4)_3(THF)_3$ (**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 × 72.07) + 22.99, corresponding to cyclic PLA, (o). Small fraction of linear PLA (H-PLA-OH), Mass = (n × 72.07) + 18 + 22.99 (-).

(a)



(b)

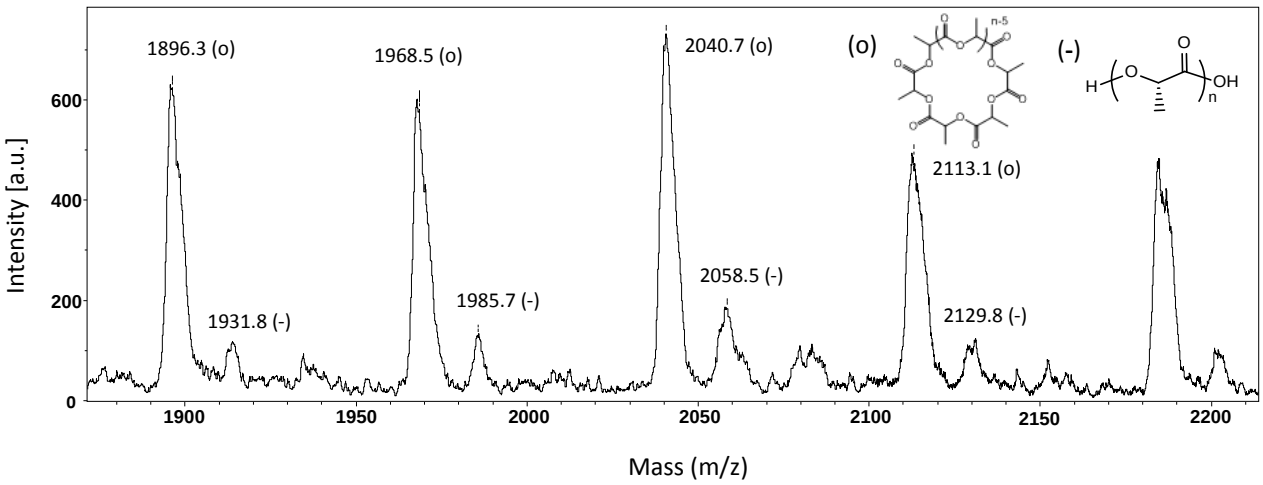


Figure SI6. MALDI-TOF mass spectrum of the PLA formed with $La(BH_4)_3(THF)_3$ (**5**) by bulk polymerisation (run 13). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1380 – 1790 amu. Main population, Mass = (n × 72.07) + 22.99, corresponding to cyclic PLA, (o). Small fraction of linear PLA (H-PLA-OH), Mass = (n × 72.07) + 18 + 22.99 (-).

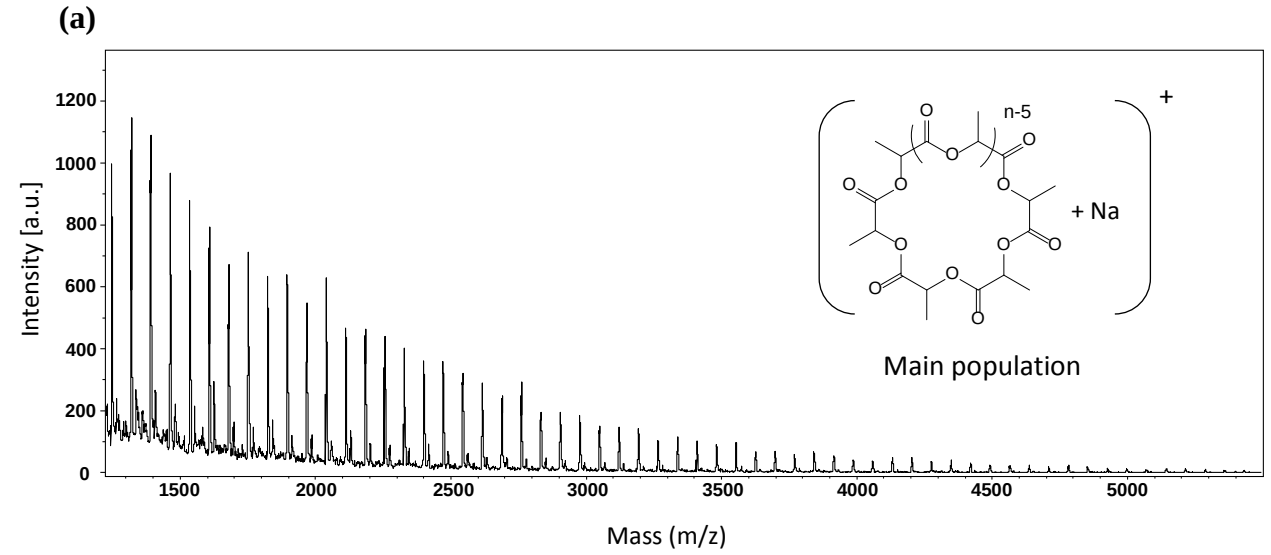
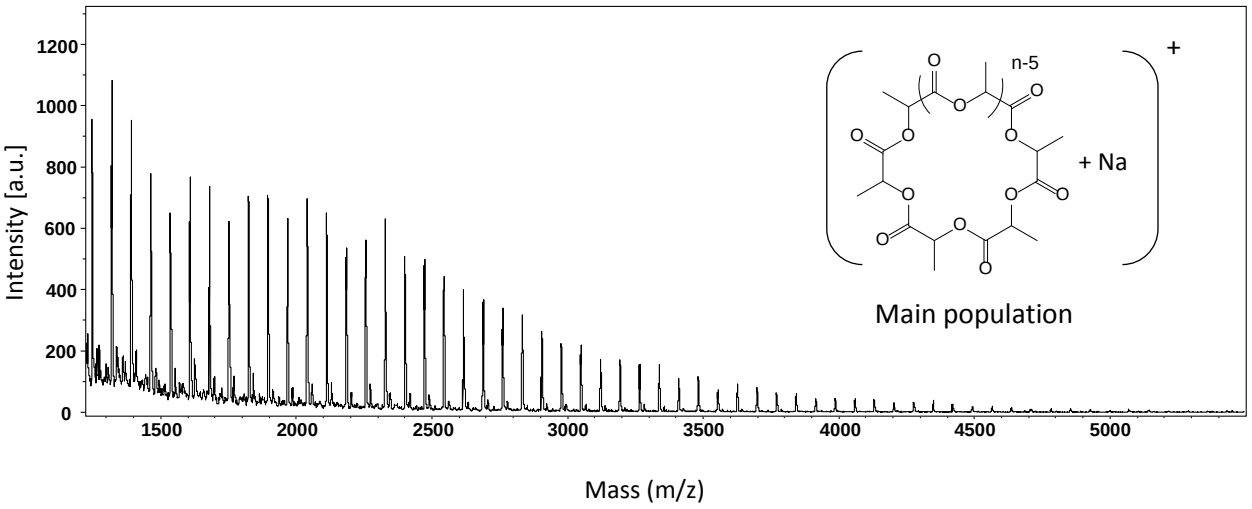


Figure SI7. MALDI-TOF mass spectrum of the PLA formed with $La(BH_4)_3(THF)_3$ (**5**) by bulk polymerisation (run 14). (a) full spectrum (b) expansion of the spectrum in the range m/z = 1380 – 1790 amu. Main population, Mass = (n × 72.07) + 22.99, corresponding to cyclic PLA, (o). Small fraction of linear PLA (H-PLA-OH), Mass = (n × 72.07) + 18 + 22.99 (-).

(a)



(b)