Electronic Supplementary Information

Controlled bulk polymerization of L-Lactide and lactones by dual activation with Organo-Catalytic Systems

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Figure S1. $^1$H NMR spectrum of raw sample (top) and precipitated sample (bottom) of run 10 (Table 1)
Figure S2. $M_{n,SEC}$ versus L-LA conversion for experiments presented in Table 1.

Figure S3. DSC thermograms of PLLA synthesized in bulk at 100°C (runs 14, 15 and 16 from Table 1).
Figure S4. $^1$H NMR spectrum of raw sample of run 21 (Table 2)
Figure S5. $^1$H NMR spectrum of raw sample of run 26 (Table 2)
Figure S6. $^1$H NMR spectrum of raw sample of run 27 (Table 2)
Figure S7. MALDI-TOF mass spectra of polylactides initiated with PeOH after 2, 5 and 10 min of reaction (DMAP/DMAP.HOTf, bulk, 100 °C).

Figure S8. Evolution of molar masses of polylactides initiated with PeOH with conversion (DMAP/DMAP.HOTf, bulk, 100 °C), dashed line is the theoretical molar mass.
Figure S9. DSC thermograms of PLLA synthesized in bulk at 100°C (runs 17, 21, 24 and 26 from Table 2)
Figure S10. $^1$H NMR spectrum of raw sample of run 34 (Table 3)

Figure S11. ROP of caprolactone ([M]/[I]=20 and [M]/[I]=100) catalyzed with DMAP/DMAP.HOTf catalytic system
Figure S12. MALDI-TOF mass spectra of run 29 in Table 3 (top: full spectrum; bottom: zoom)
Figure S13. MALDI-TOF mass spectra of run 37 in Table 3 (top: full spectrum; bottom: zoom)
Figure S14. $^1$H NMR spectrum of raw sample of run 40 (Table 4)

![NMR spectrum](image)

Figure S15. ROP of valerolactone ([M]/[I]=100) catalyzed with DMAP/DMAP.HOTf catalytic system

![Graph](image)
Figure S16. MALDI-TOF mass spectra of run 39 in Table 4 (top: full spectrum; bottom: zoom)
Figure S17. $^1$H and $^{13}$C NMR spectra of a PCL-b-PLLA.
Figure S18. $^1$H and $^{13}$C NMR spectra of a PVL-$b$-PLLA.
Figure S19. DSC thermogram of a PCL-\textit{b}-PLLA.

Figure S20. DSC thermogram of a PVL-\textit{b}-PLLA.