

Electronic Supplementary Information

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

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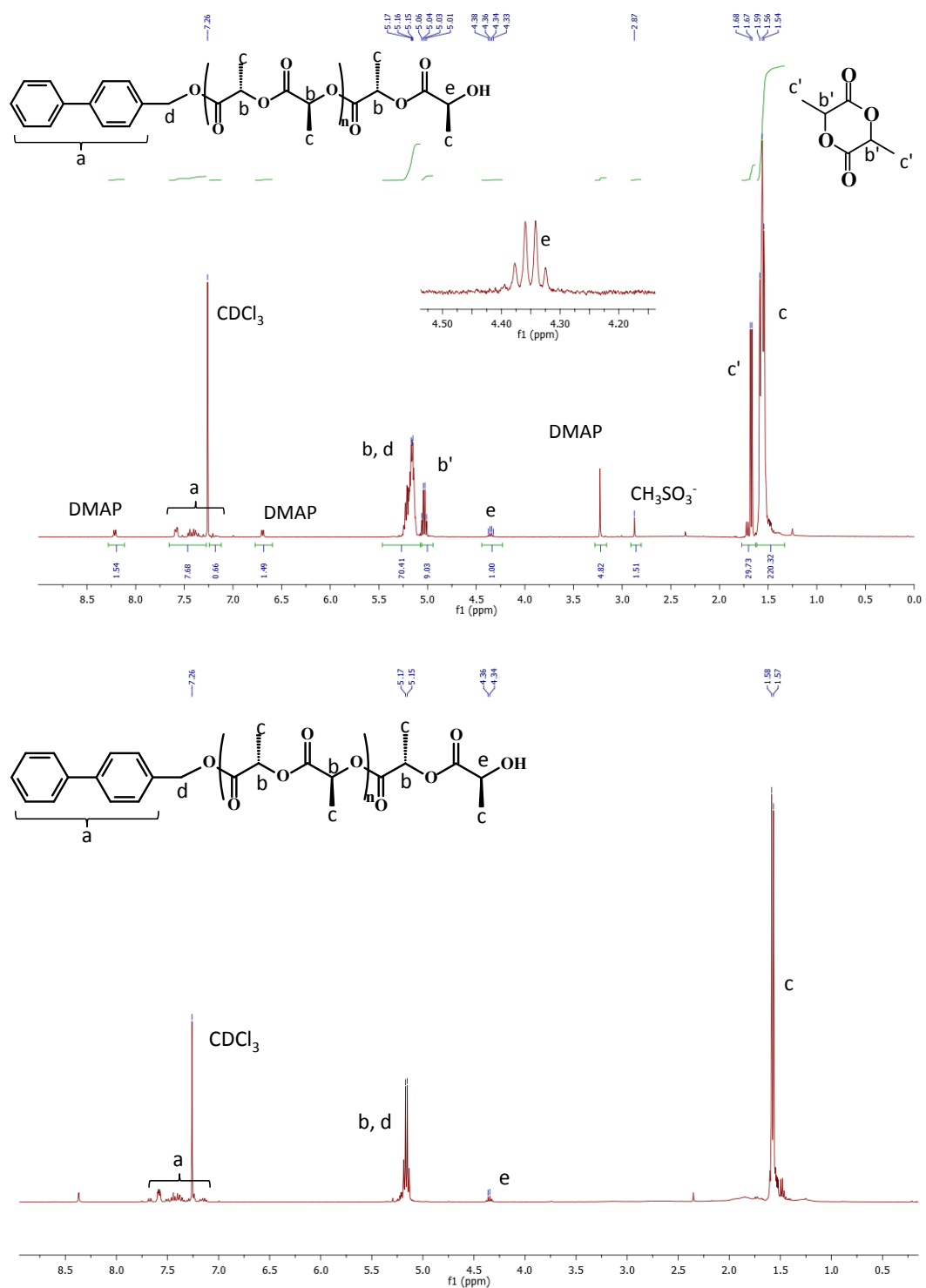


Figure S1. ¹H NMR spectrum of raw sample (top) and precipitated sample (bottom) of run 10 (Table 1)

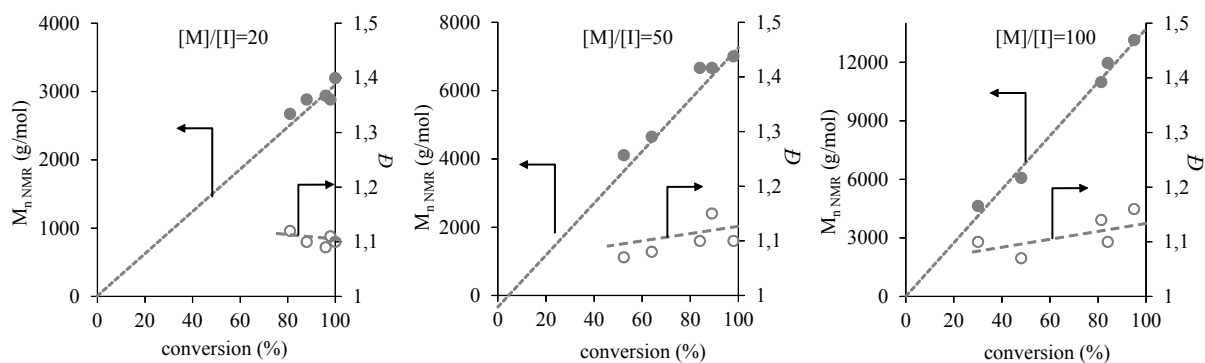


Figure S2. $M_{n,SEC}$ versus L-LA conversion for experiments presented in Table 1

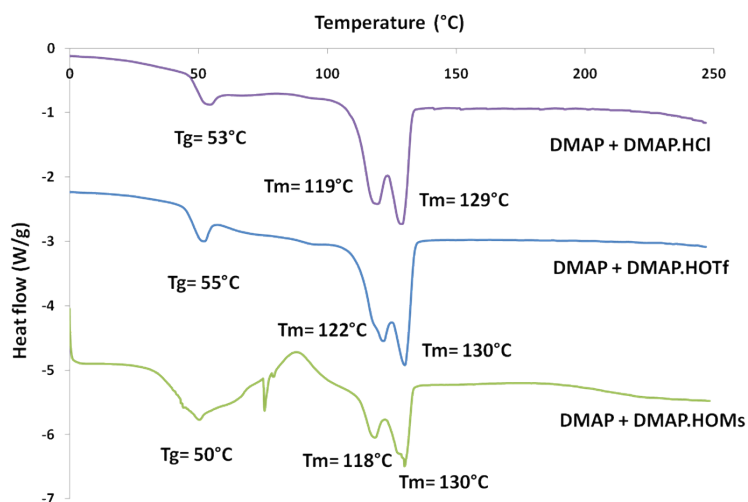


Figure S3. DSC thermograms of PLLA synthesized in bulk at 100°C (runs 14, 15 and 16 from Table 1)

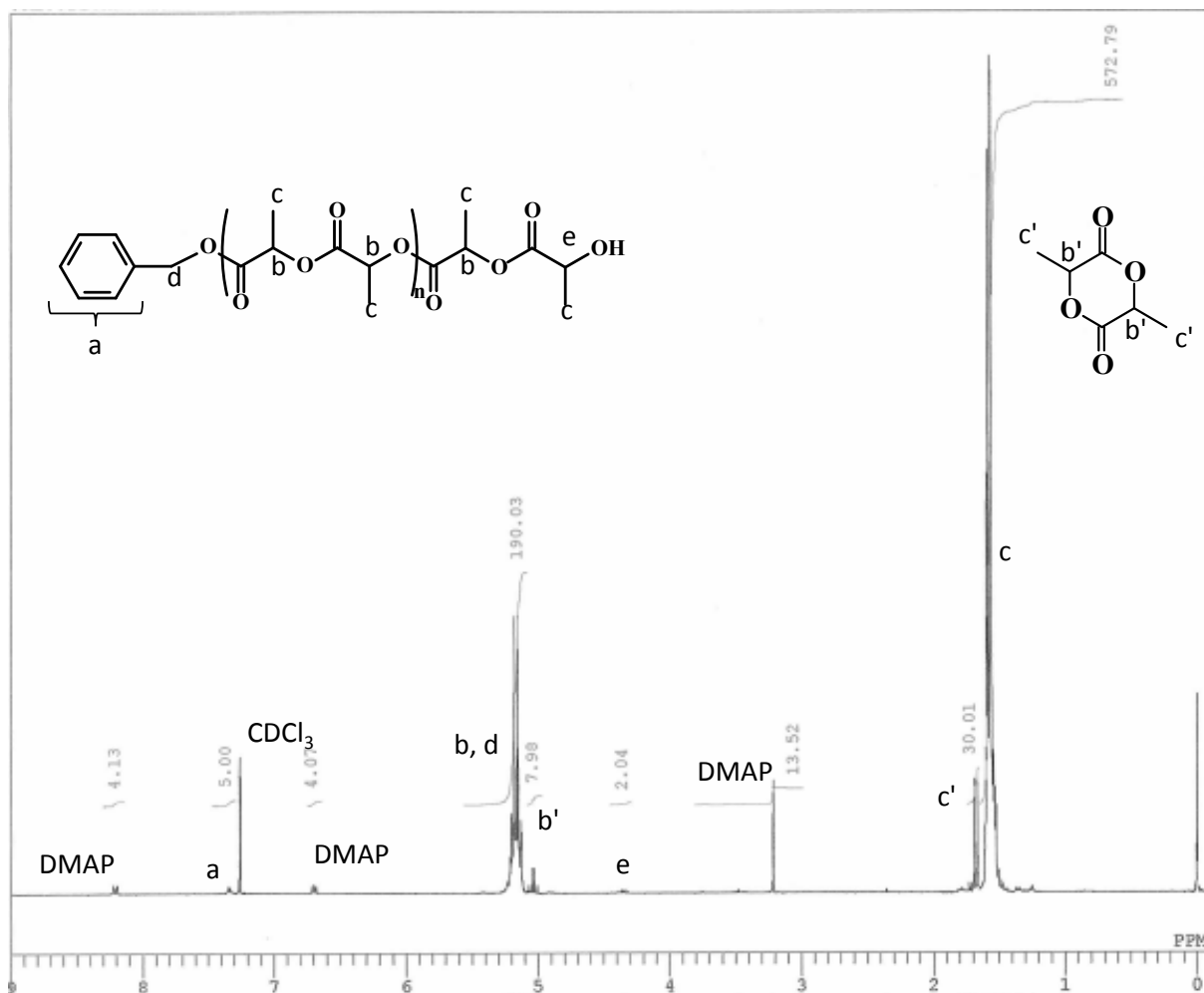


Figure S4. ¹H NMR spectrum of raw sample of run 21 (Table 2)

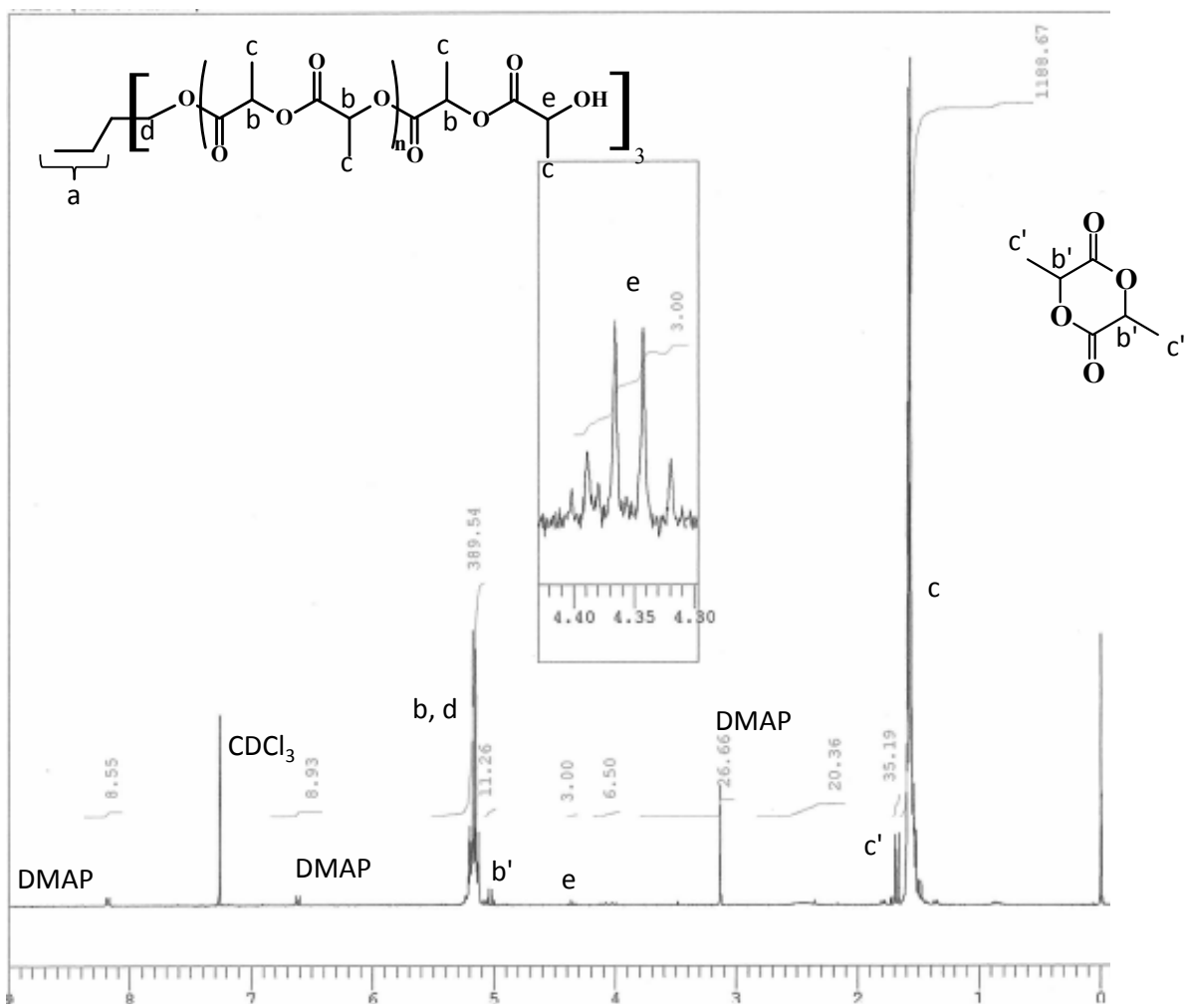


Figure S5. ^1H NMR spectrum of raw sample of run 26 (Table 2)

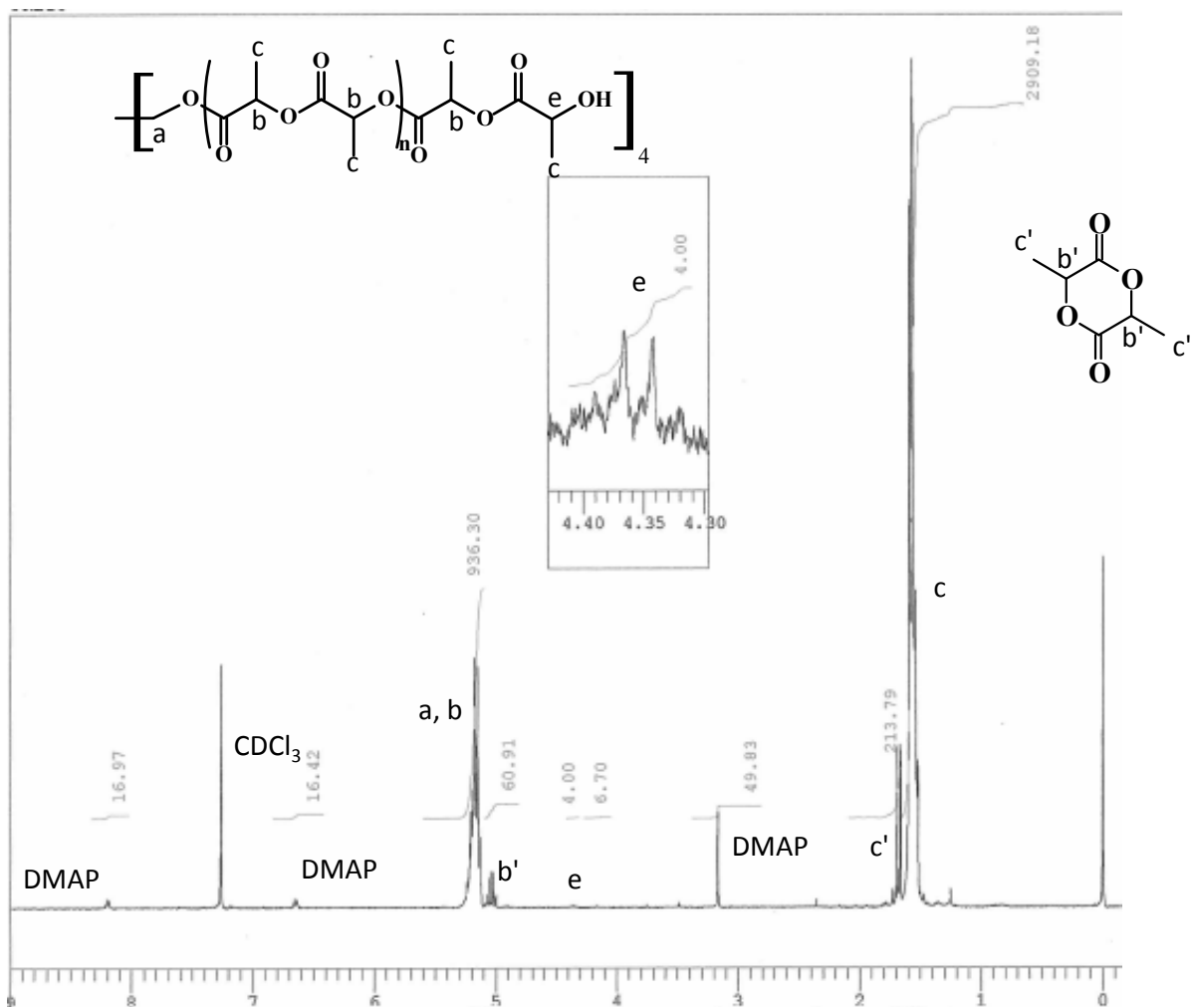


Figure S6. ¹H NMR spectrum of raw sample of run 27 (Table 2)

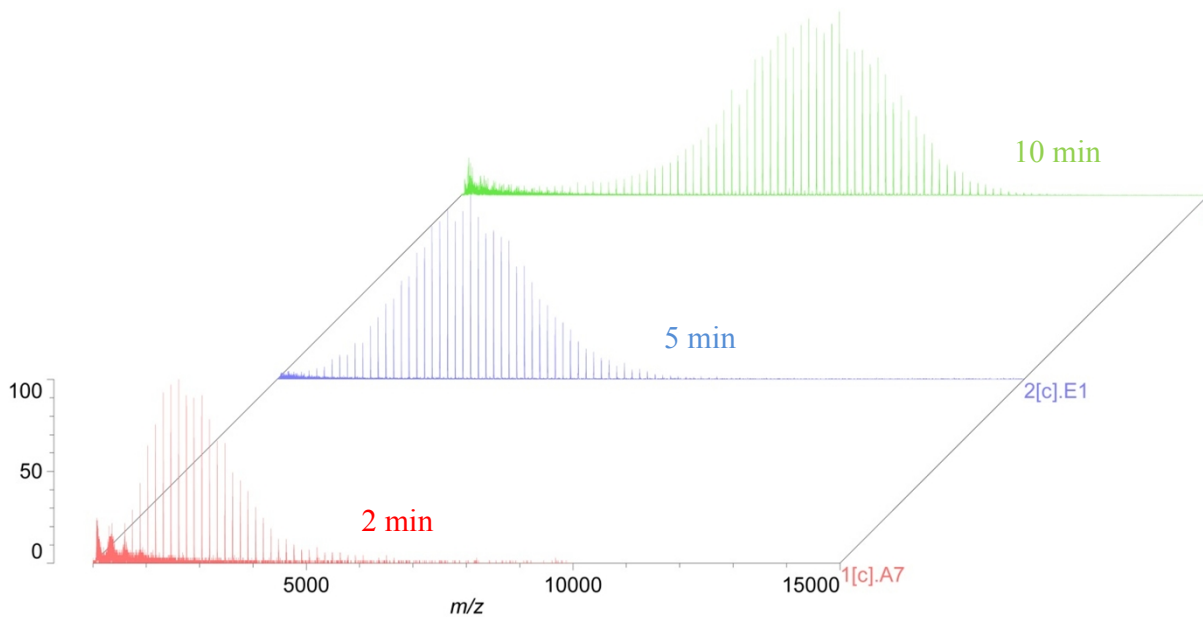


Figure S7. MALDI-TOF mass spectra of polylactides initiated with PeOH after 2, 5 and 10 min of reaction (DMAP/DMAP.HOTf, bulk, 100 °C)

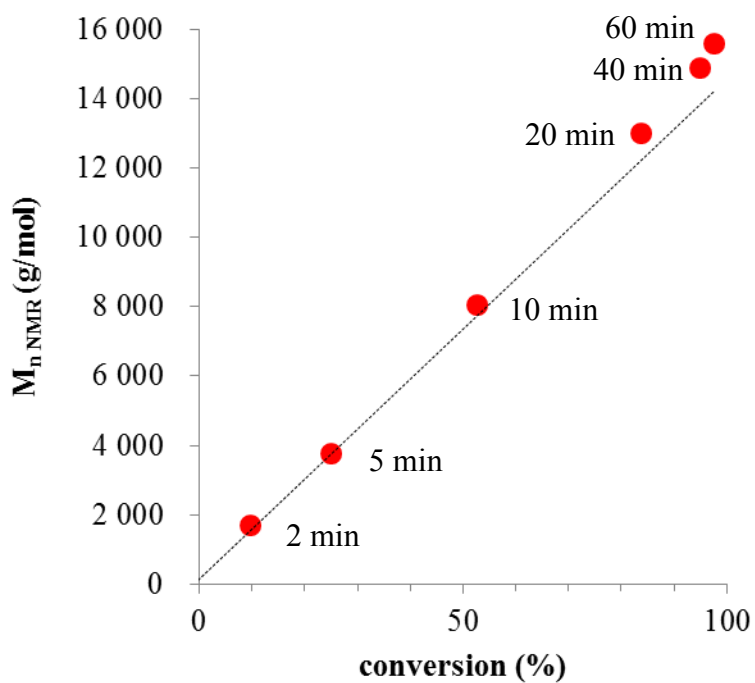


Figure S8. Evolution of molar masses of polylactides initiated with PeOH with conversion (DMAP/DMAP.HOTf, bulk, 100 °C), dashed line is the theoretical molar mass.

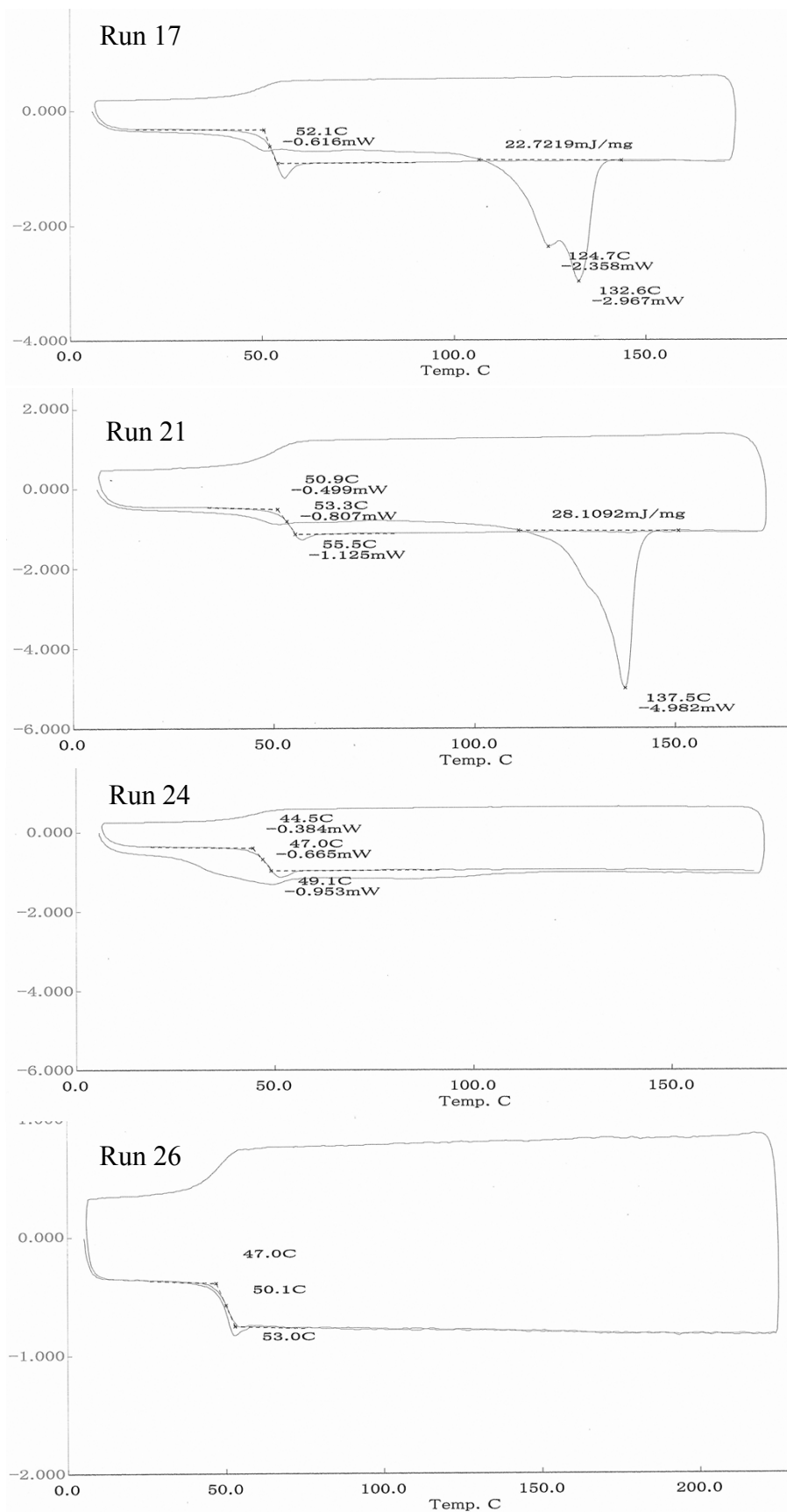


Figure S9. DSC thermograms of PLLA synthesized in bulk at 100°C (runs 17, 21, 24 and 26 from Table 2)

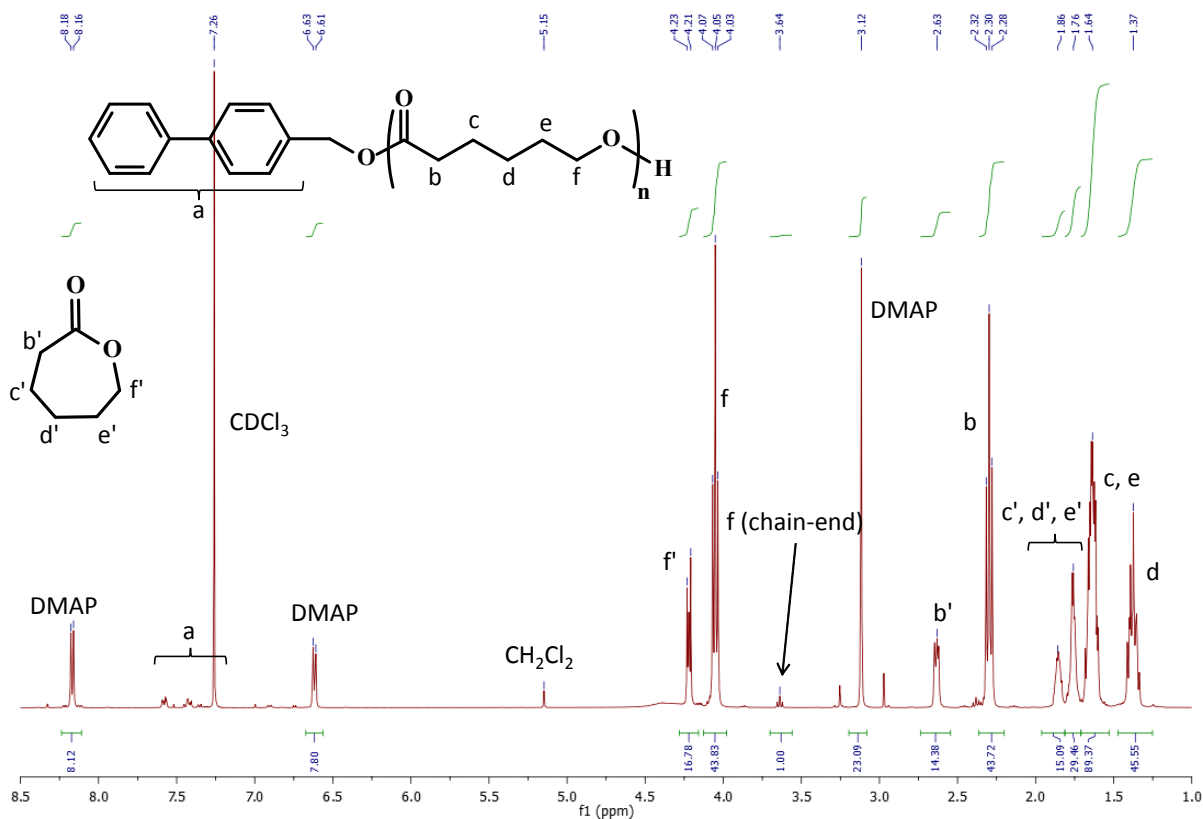


Figure S10. ¹H NMR spectrum of raw sample of run 34 (Table 3)

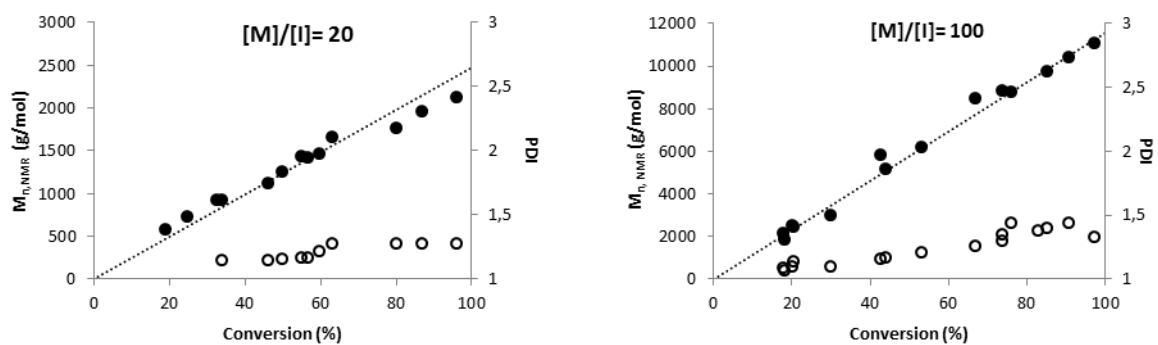


Figure S11. ROP of caprolactone ([M]/[I]=20 and [M]/[I]=100) catalyzed with DMAP/DMAP.HOTf catalytic system

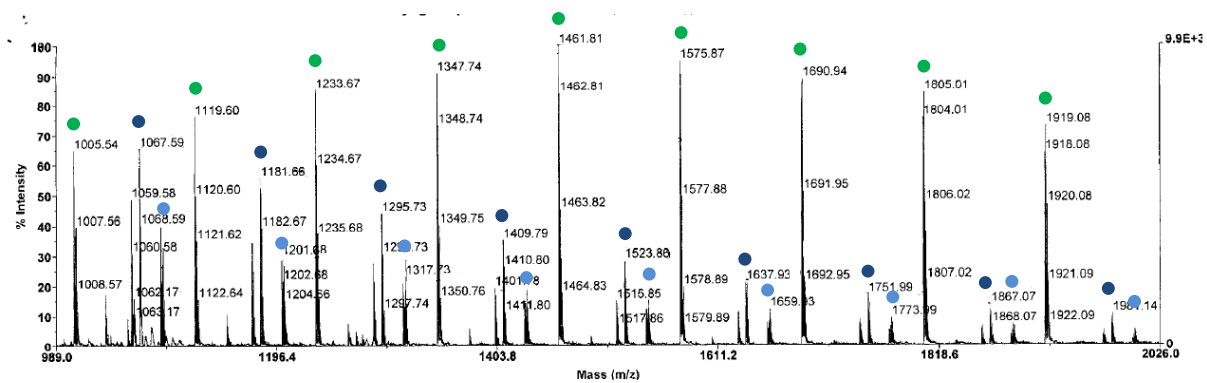
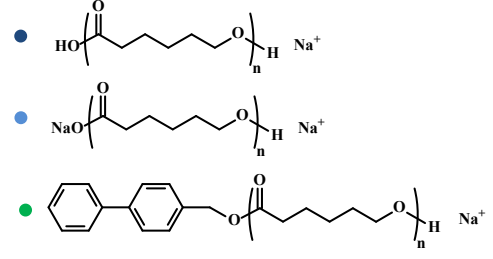
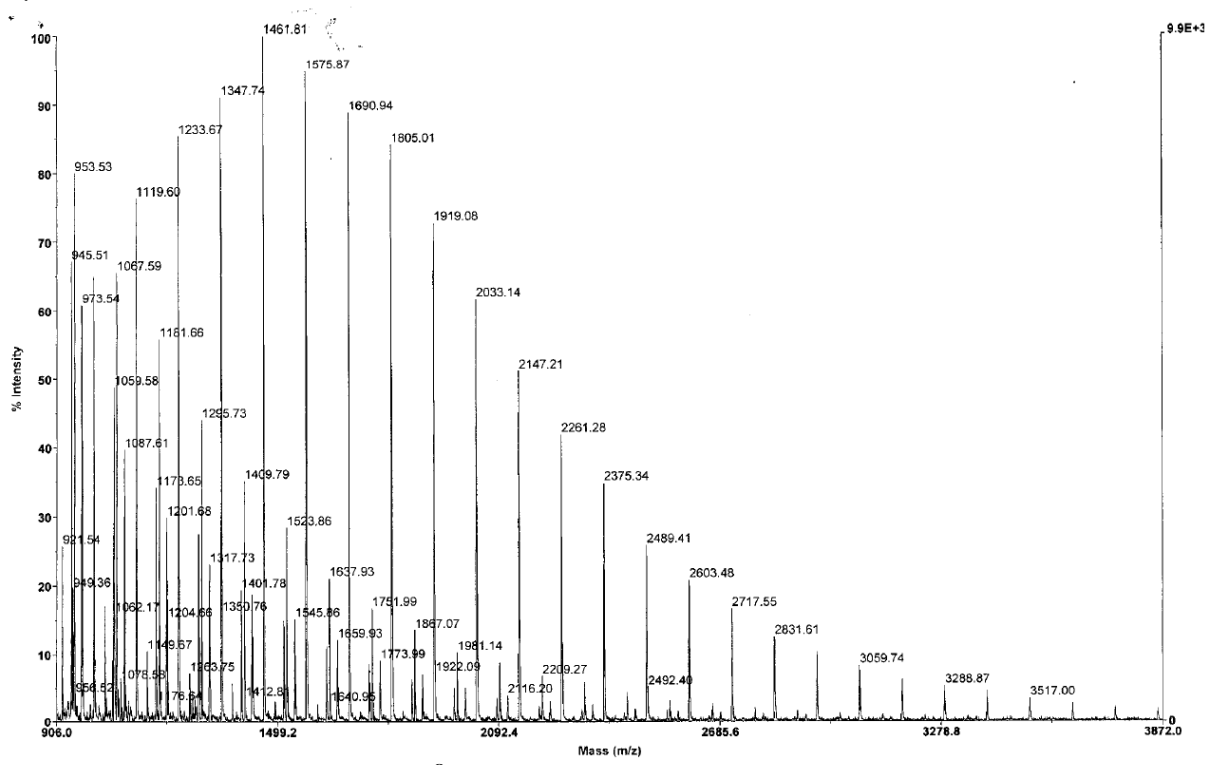


Figure S12. MALDI-TOF mass spectra of run 29 in Table 3 (top: full spectrum; bottom: zoom)

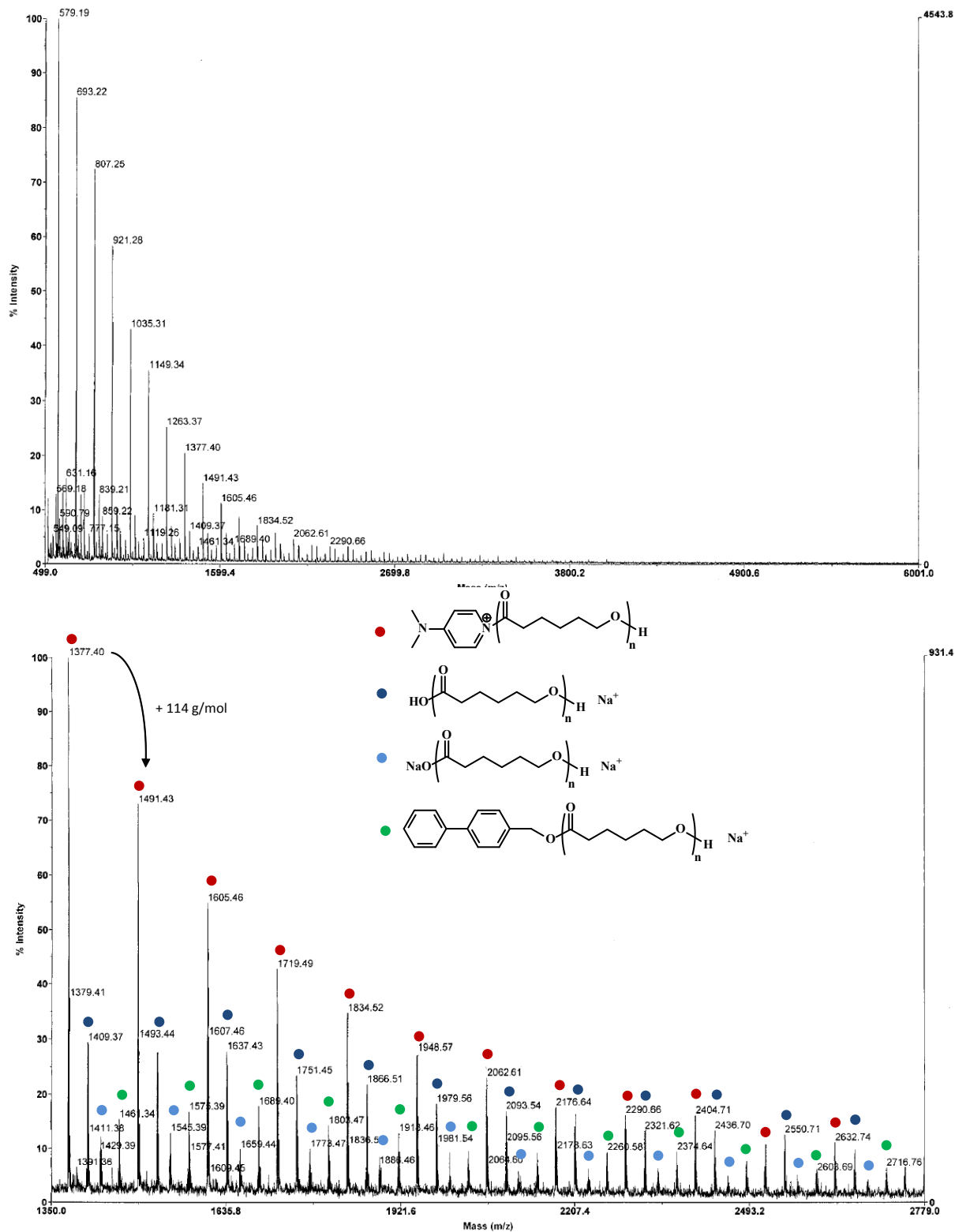


Figure S13. MALDI-TOF mass spectra of run 37 in Table 3 (top: full spectrum; bottom: zoom)

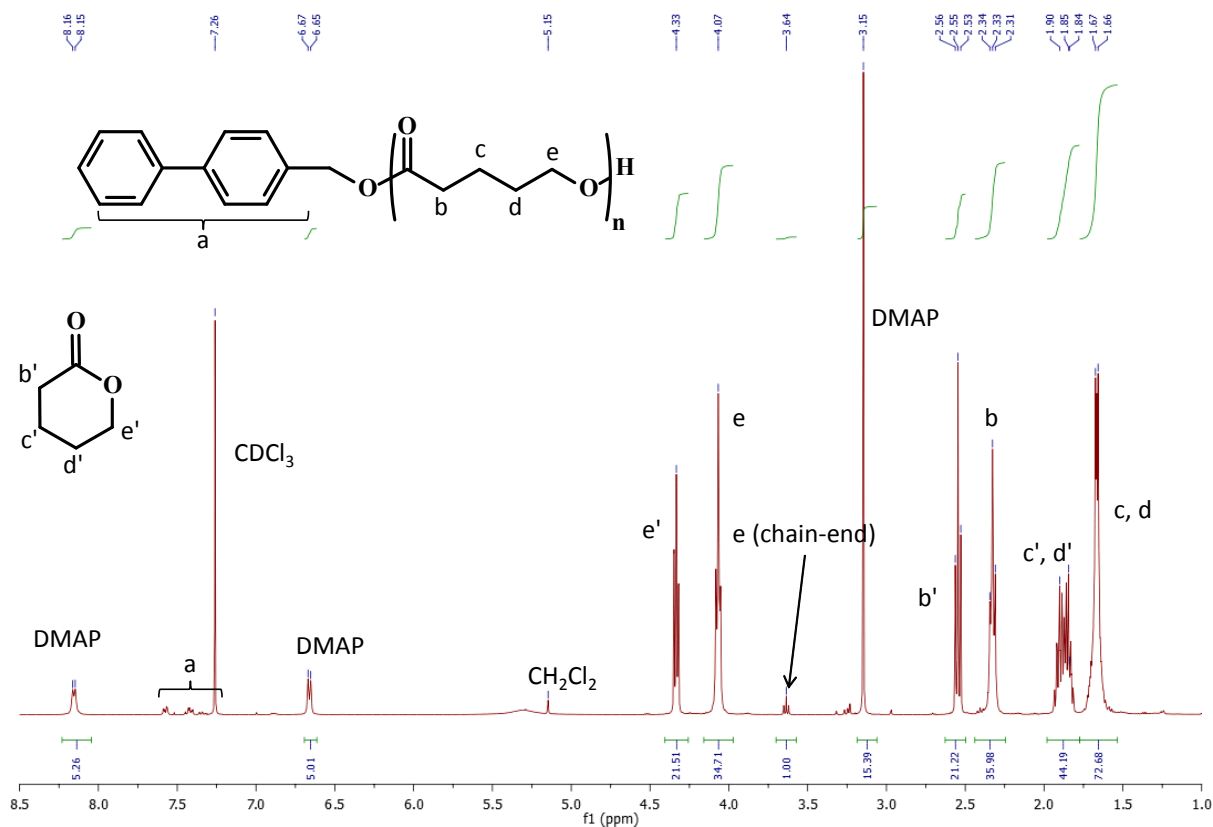


Figure S14. ¹H NMR spectrum of raw sample of run 40 (Table 4)

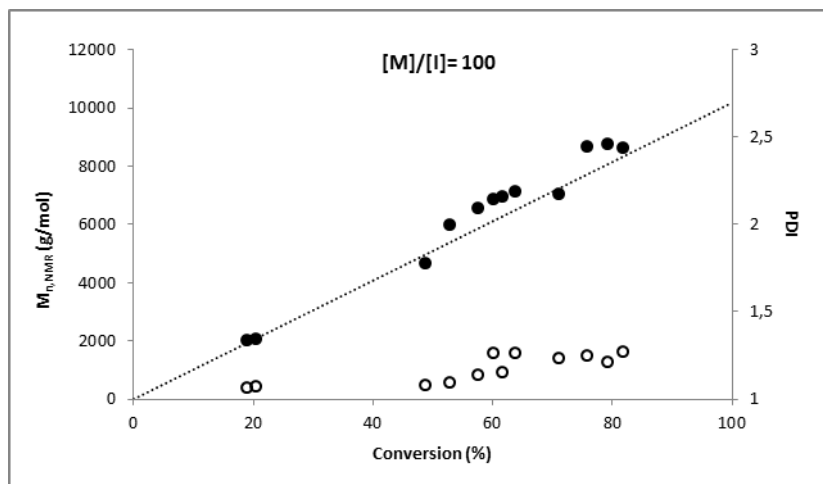


Figure S15. ROP of valerolactone ($[M]/[I]=100$) catalyzed with DMAP/DMAP.HOTf catalytic system

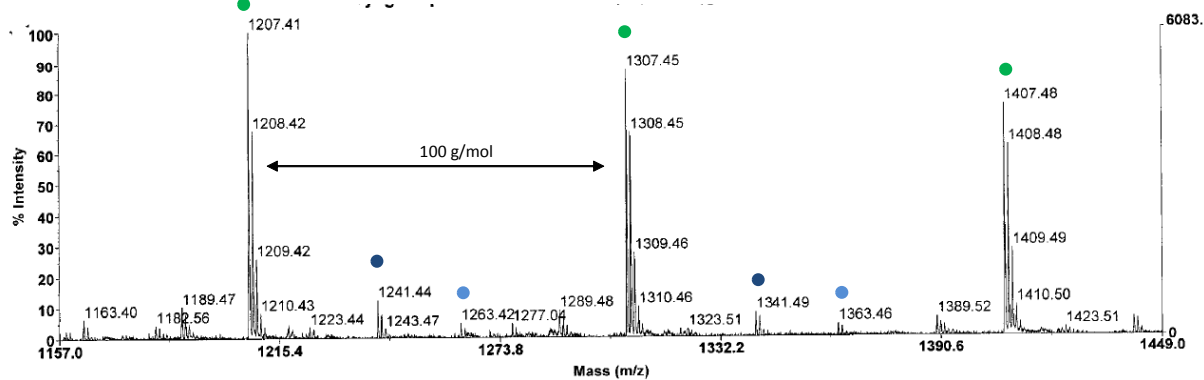
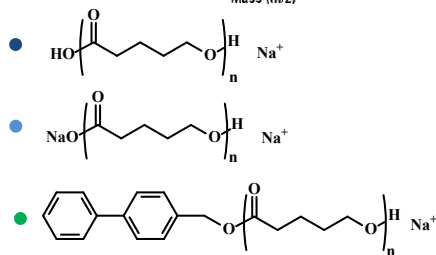
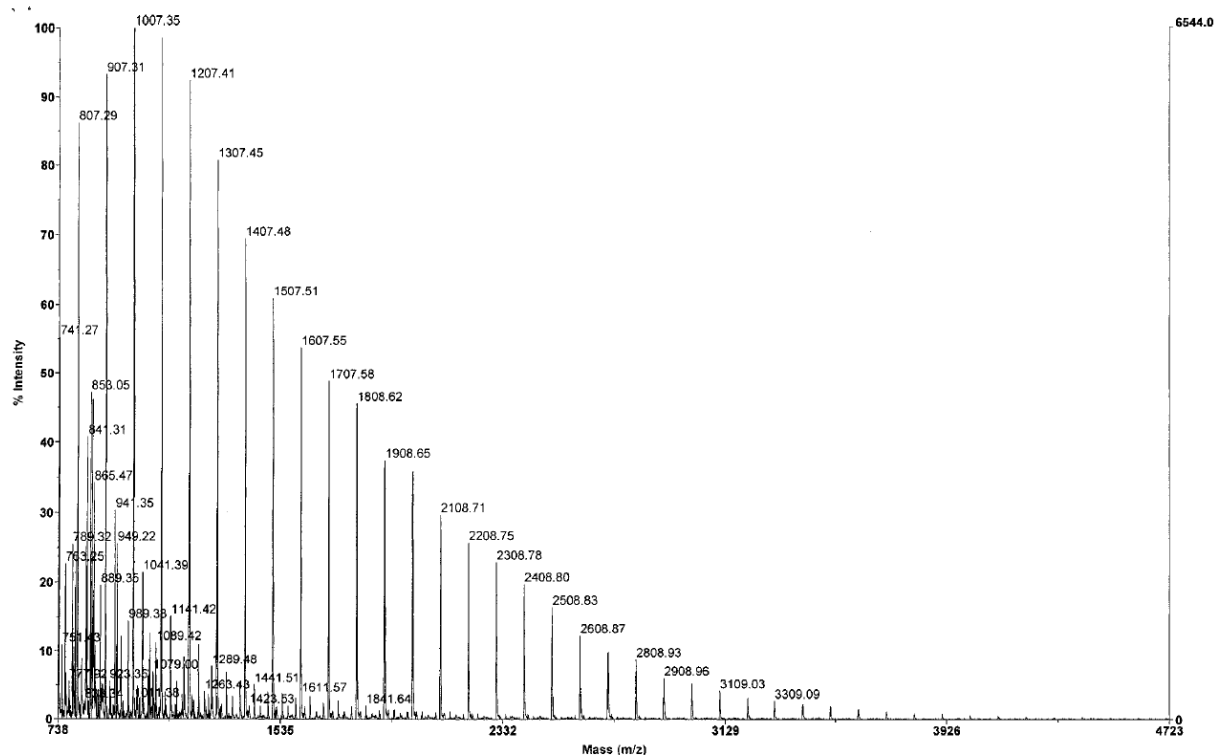


Figure S16. MALDI-TOF mass spectra of run 39 in Table 4 (top: full spectrum; bottom: zoom)

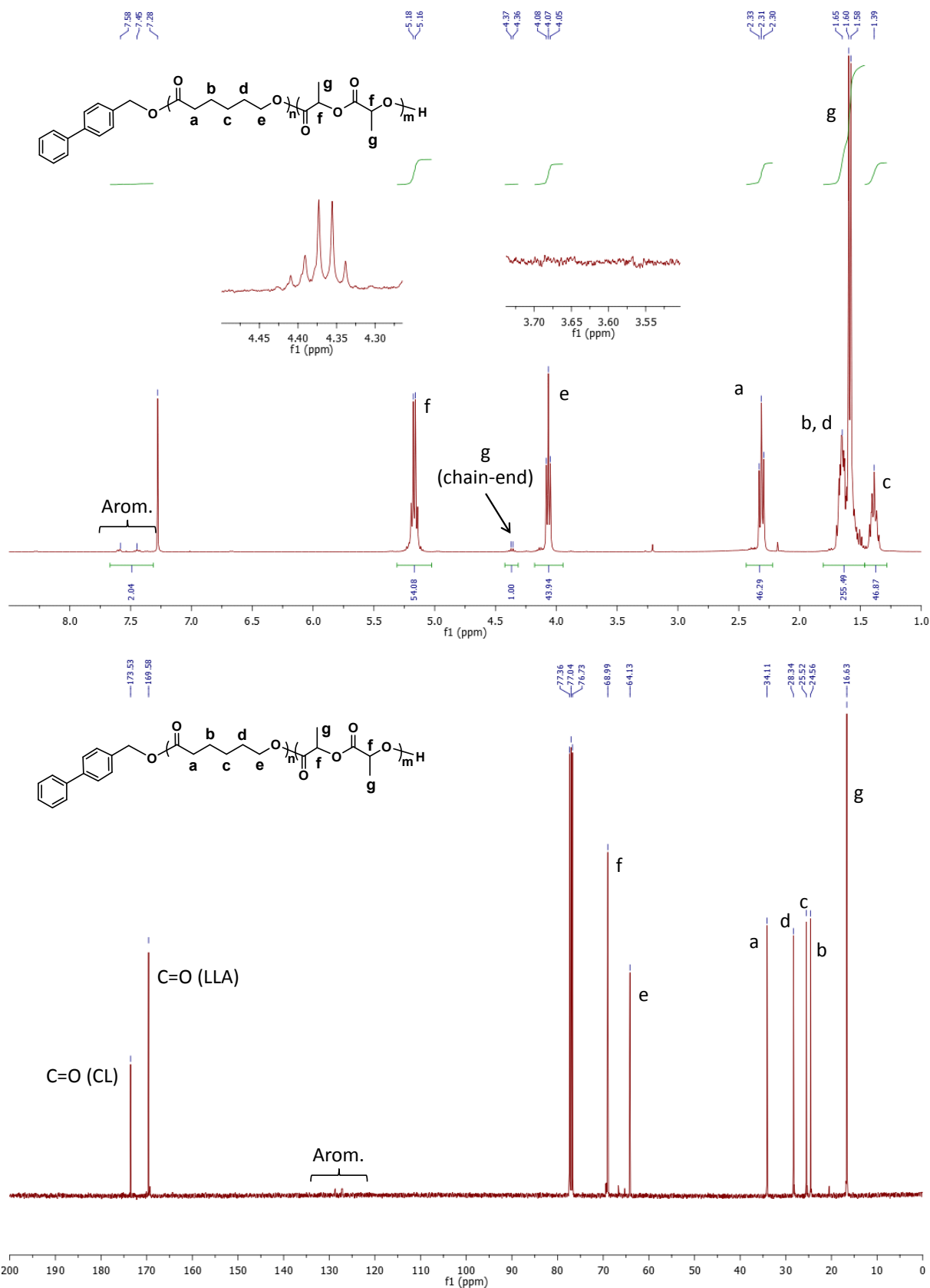


Figure S17. ^1H and ^{13}C NMR spectra of a PCL-*b*-PLLA.

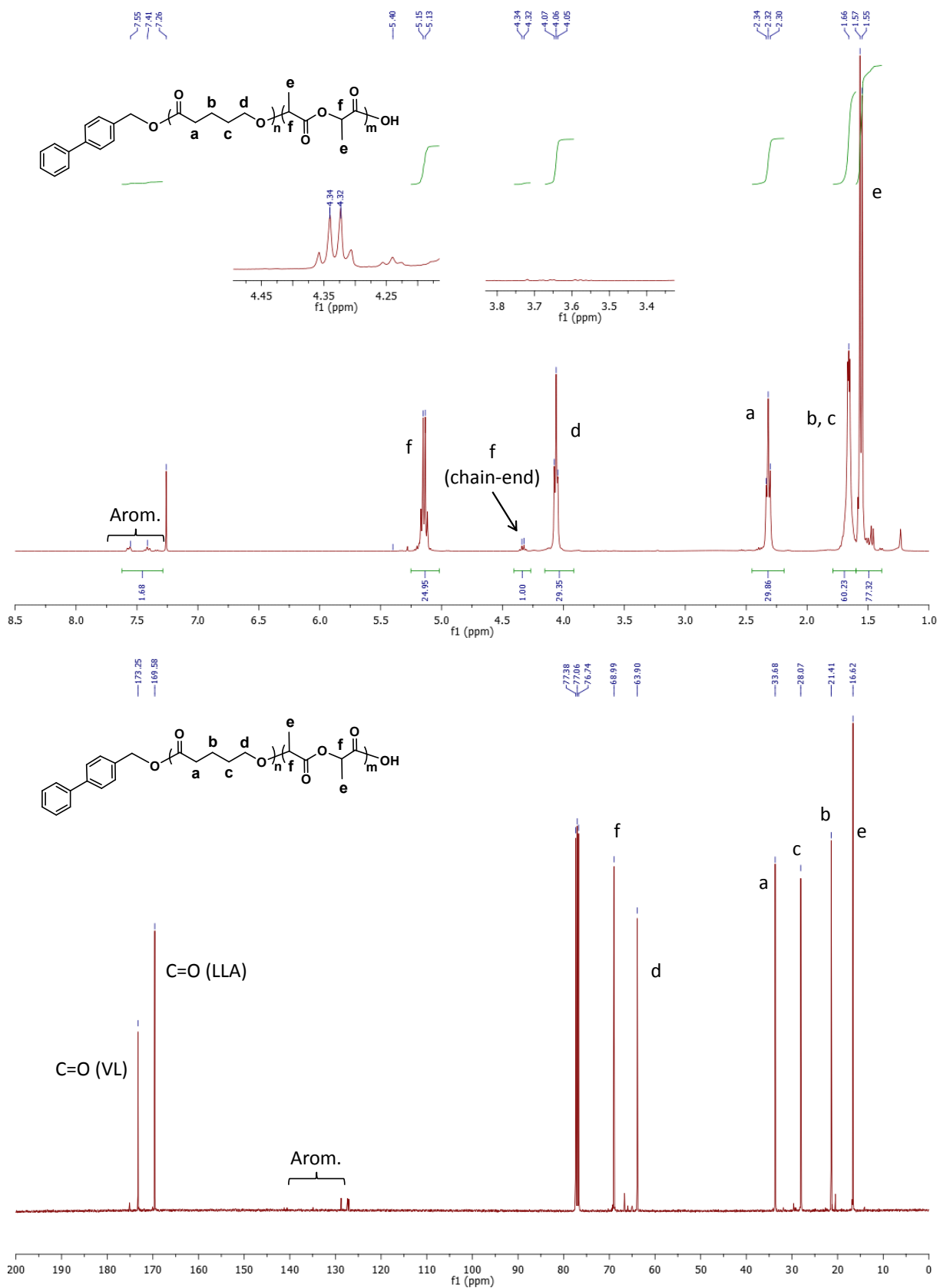


Figure S18. ^1H and ^{13}C NMR spectra of a PVL-*b*-PLLA.

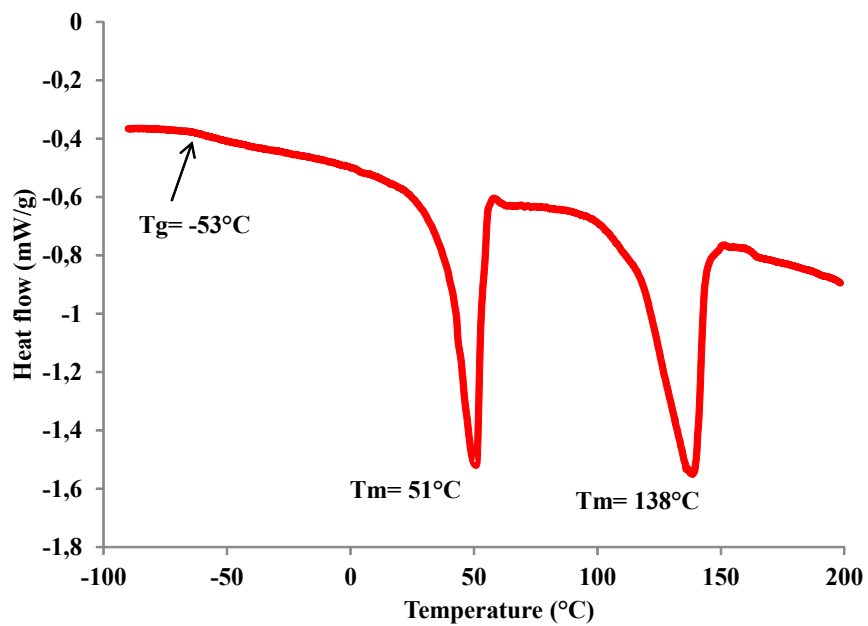


Figure S19. DSC thermogram of a PCL-*b*-PLLA.

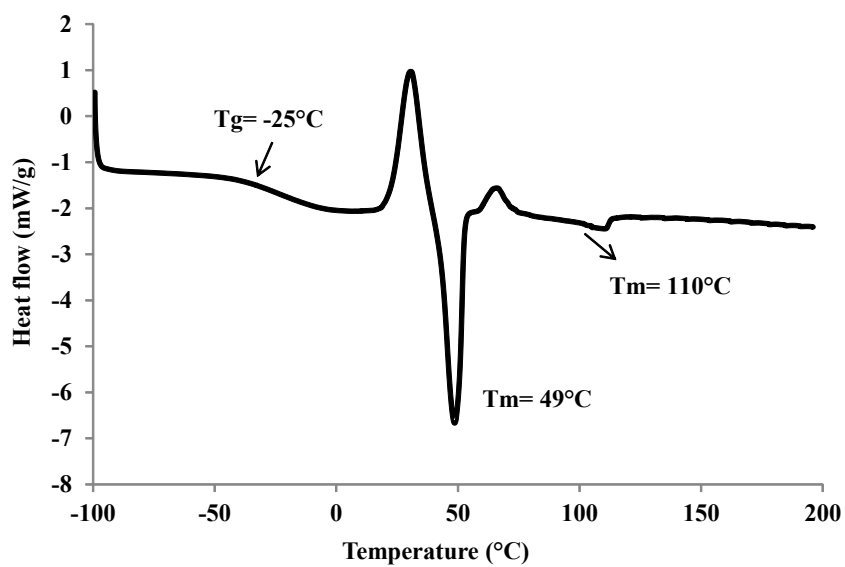


Figure S20. DSC thermogram of a PVL-*b*-PLLA.