Supplementary Information

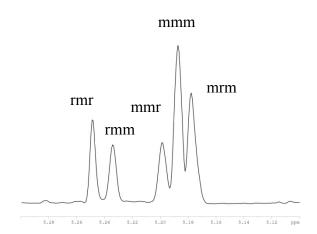
Monoamidinate Titanium complexes: Highly Active Catalysts for the Polymerization and Copolymerization of L-Lactide and ε-Caprolactone.

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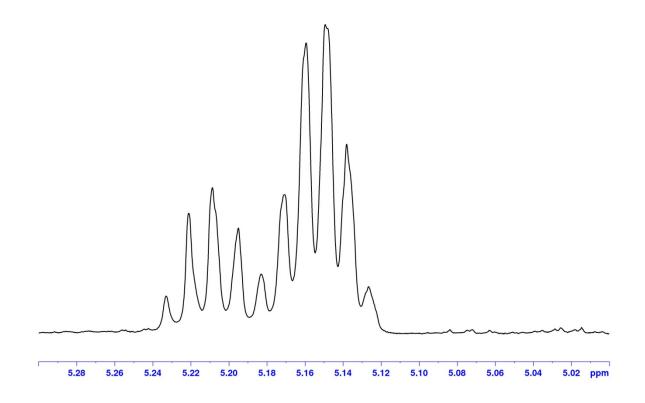


Figure S1. Methine regions (δ =5.00–5.30ppm) of the ${}^{1}H$ and homodecoupled NMR spectra (600 MHz, CDCl₃, 298 K) of the PLA sample obtained by **3**.

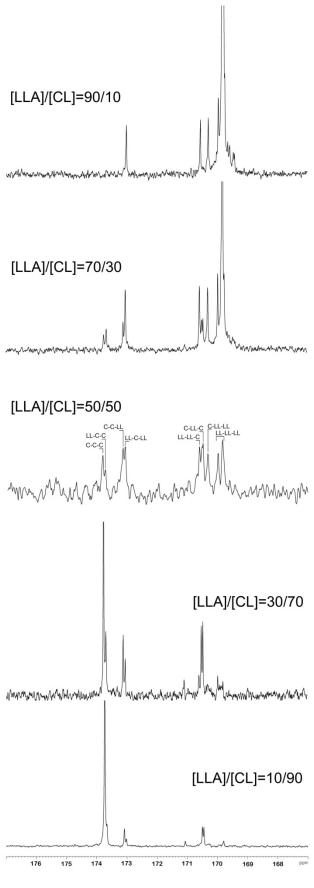


Figure S2. ¹³C NMR spectra (CDCl₃, 25°C) of PCL-co-PLLA copolymers by **3** and triad assignments. C represents the CL unit and L is the lactyl unit.

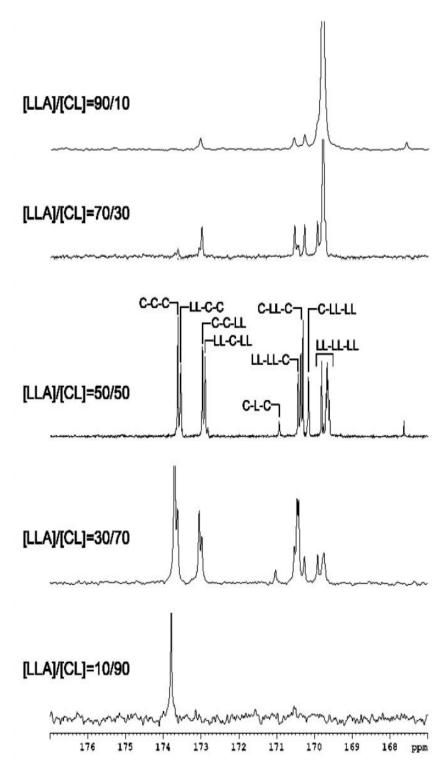


Figure S3. ¹³C NMR spectra (CDCl₃, 25°C) of PCL-co-PLLA copolymers by **1** and triad assignments. C represents the CL unit and L is the lactyl unit.

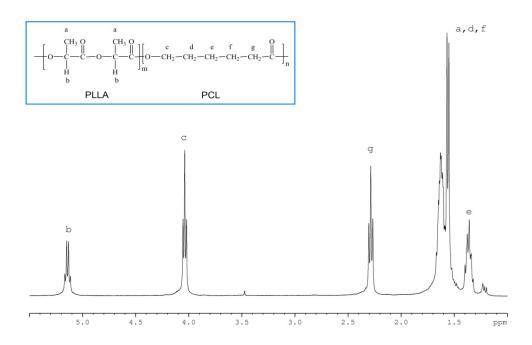


Figure S4. ¹H NMR spectrum (600 MHz, CDCl₃, 298 K) of PCL-block-PLLA copolymer by 3.

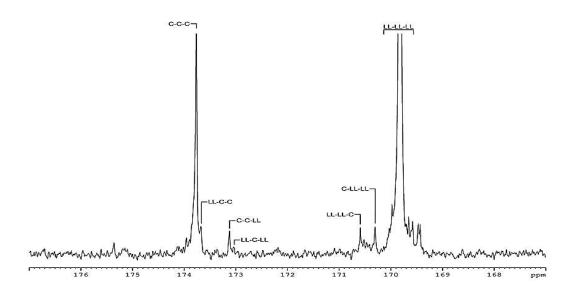


Figure S5. ¹³C NMR spectrum (150 MHz, CDCl₃, 298 K) of PCL-block-PLLA copolymer by 3.

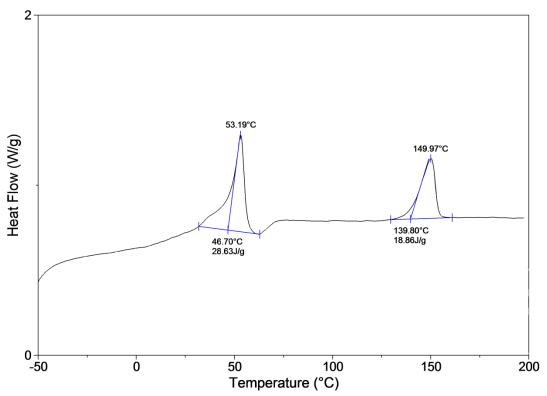


Figure S6. DSC thermogram (second heating cycle, 10°C/min) of the copolymer PCL-b-PLLA obtained with complex **3**.

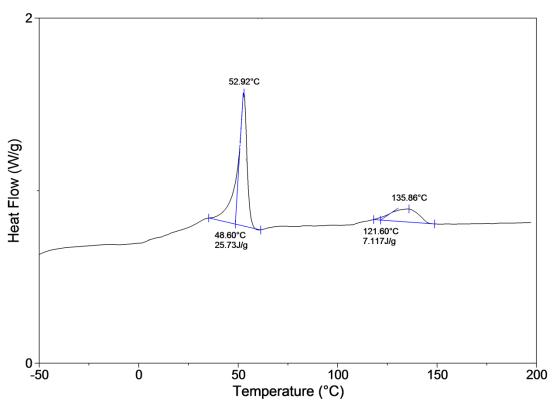


Figure S7. DSC thermogram (second heating cycle, 10°C/min) of the copolymer PCL-b-PLLA obtained with complex 1.

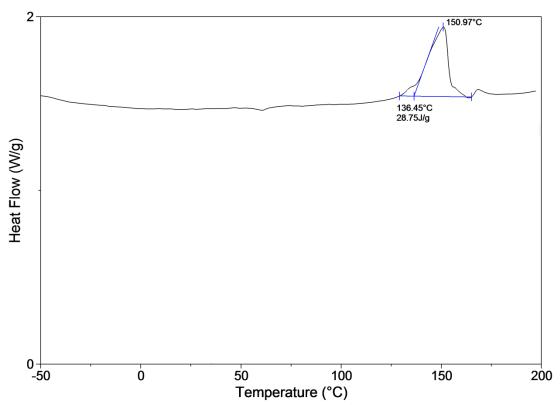


Figure S8. DSC thermogram (second heating cycle, 10°C/min) of the copolymer PLLA-b- PCL obtained with complex **3**.

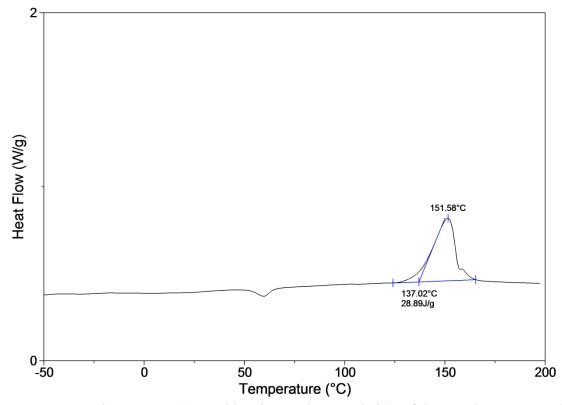
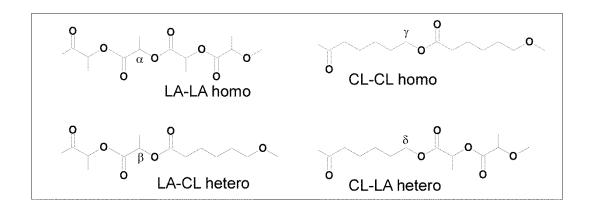


Figure S9. DSC thermogram (second heating cycle, 10°C/min) of the copolymer PLLA-b-PCL obtained with complex 1.



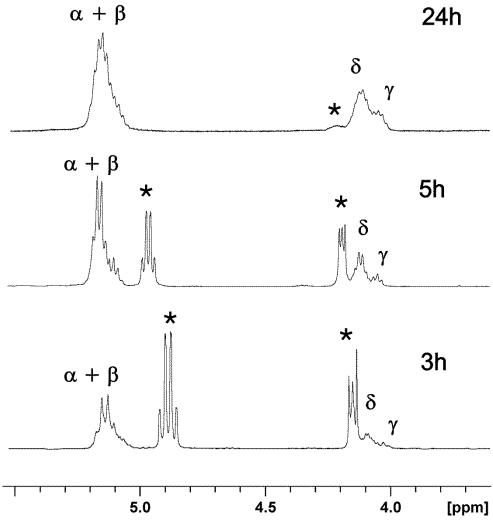


Figure S10. ¹H NMR spectra (300 MHz, CDCl₃, 25 °C) at 3, 5 and 24h of the reaction mixture of run 29 of Table 4. * unreacted monomer.