Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Macromolecular Engineering via Ring-Opening Polymerization (1): L-Lactide/Trimethylene Carbonate Block Copolymers as Thermoplastic Elastomers

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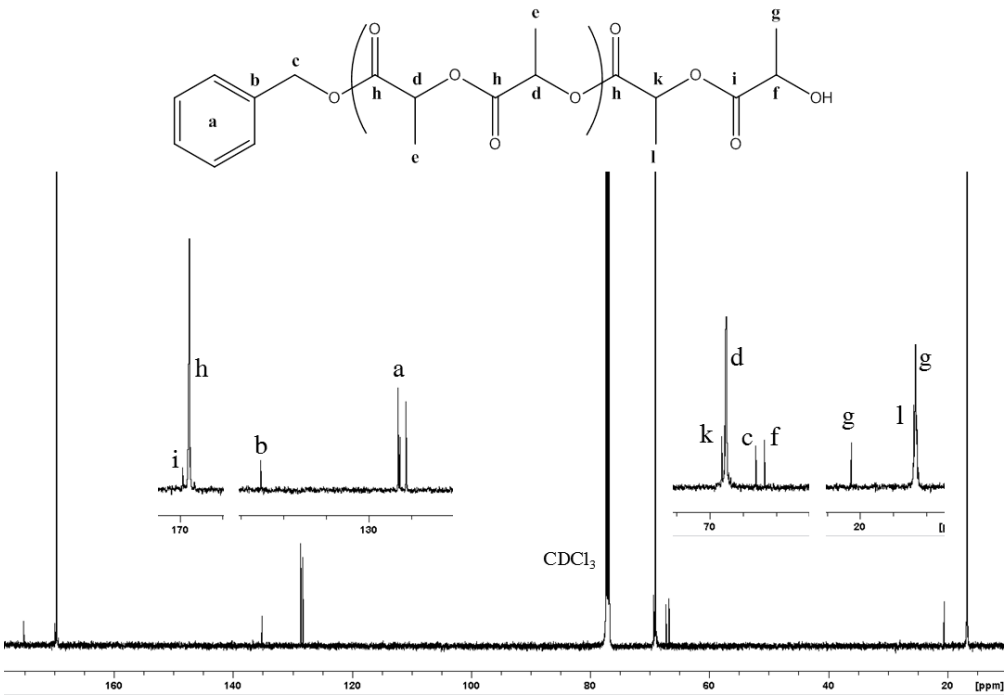

Figure S1. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a PLLA polymer prepared from [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)]/BnOH ($\overline{Mn}_{,NMR}$ = 5 800 g.mol^{-1}).

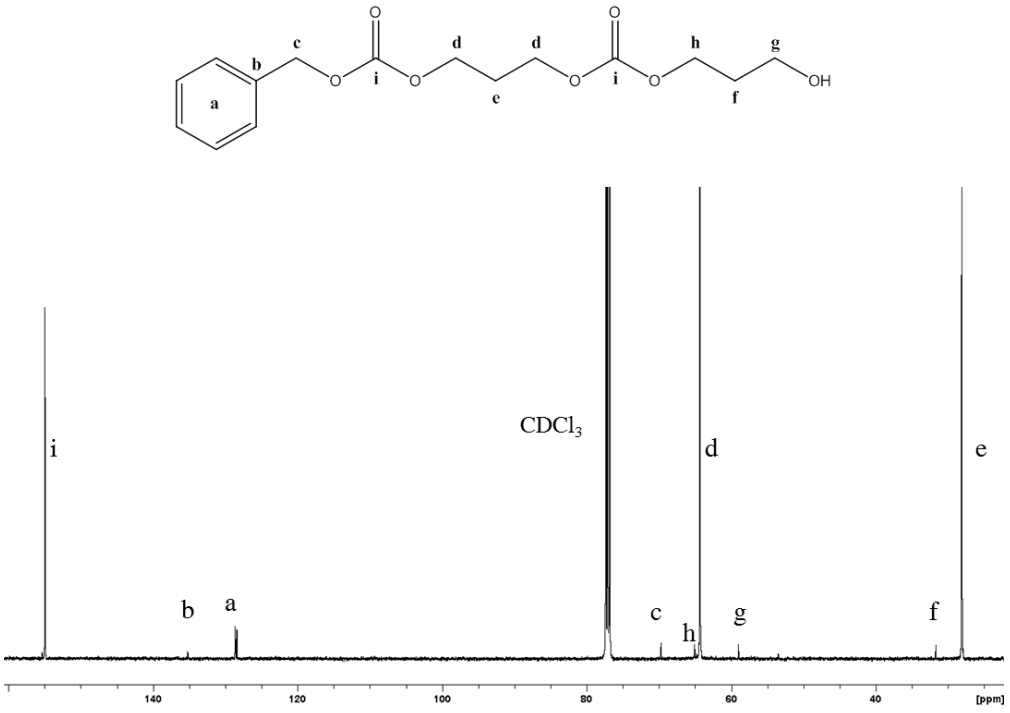

Figure S2. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a PTMC polymer prepared from [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)]/BnOH ($\overline{Mn}_{,NMR}$ = 7 400 g.mol^{-1})

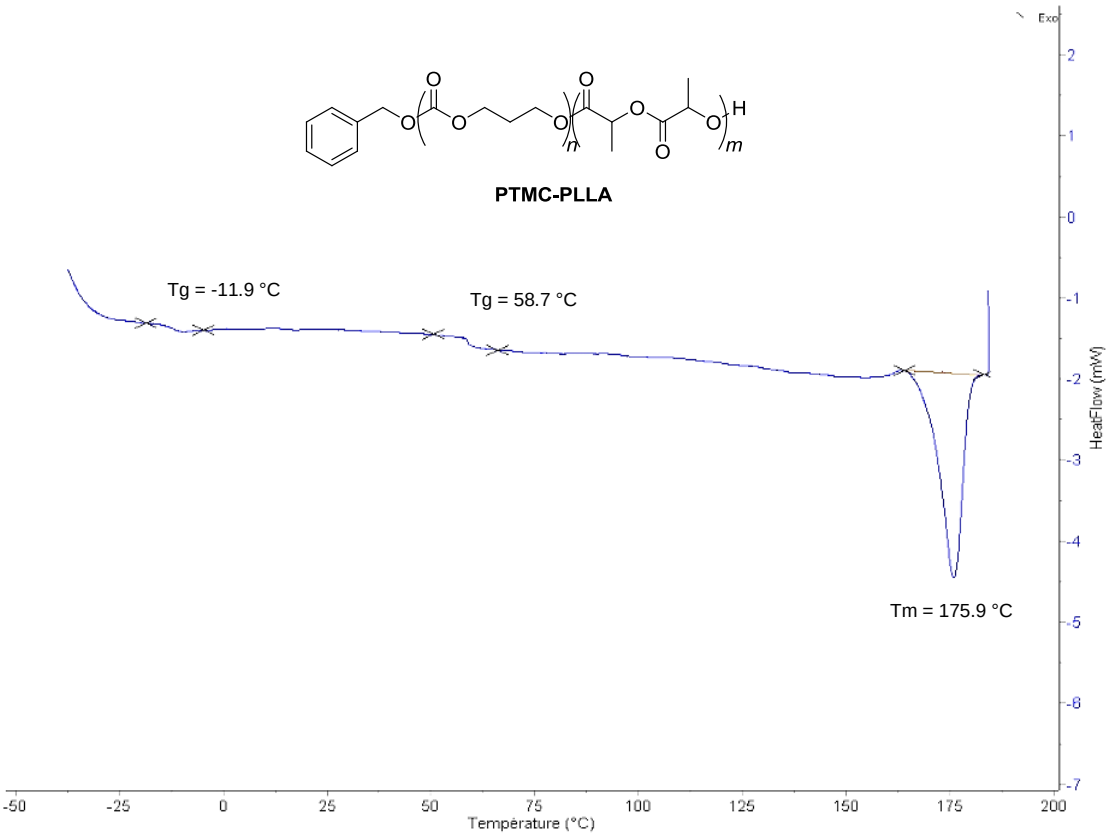

Figure S3. DSC curve (second heating run) of a PTMC-*b*-PLLA sample ($M_{n,SEC}$ = 51 100 g.mol^{-1}; Table 2, entry 4).

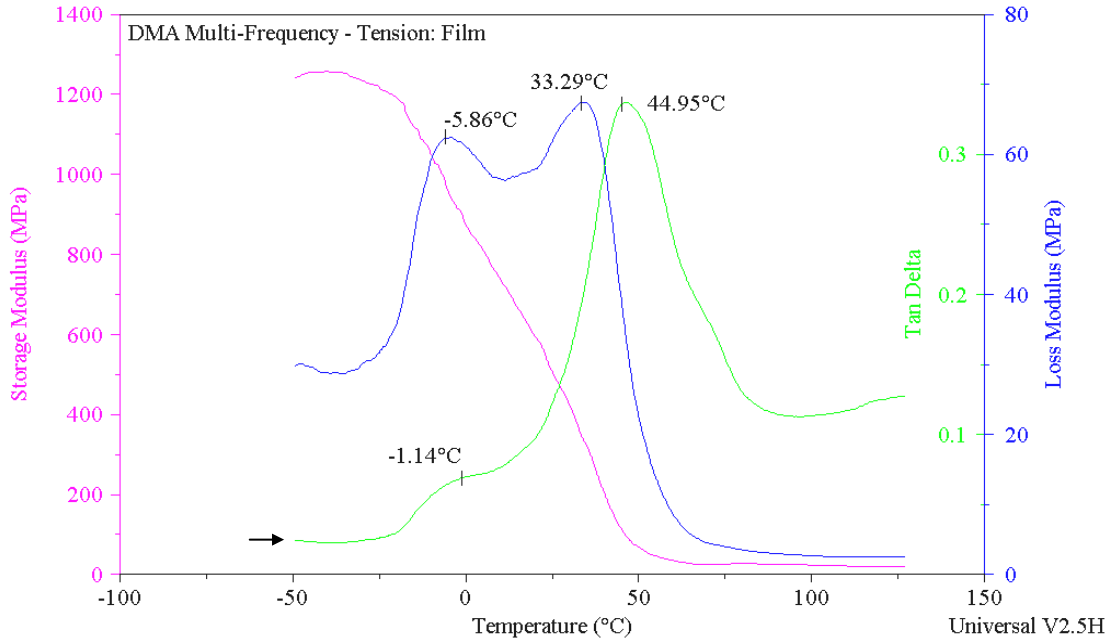

Figure S4. DMA curves of a PTMC-*b*-PLLA sample ($M_{n,SEC}$ = 51 100 g.mol^{-1}; Table 2, entry 4).

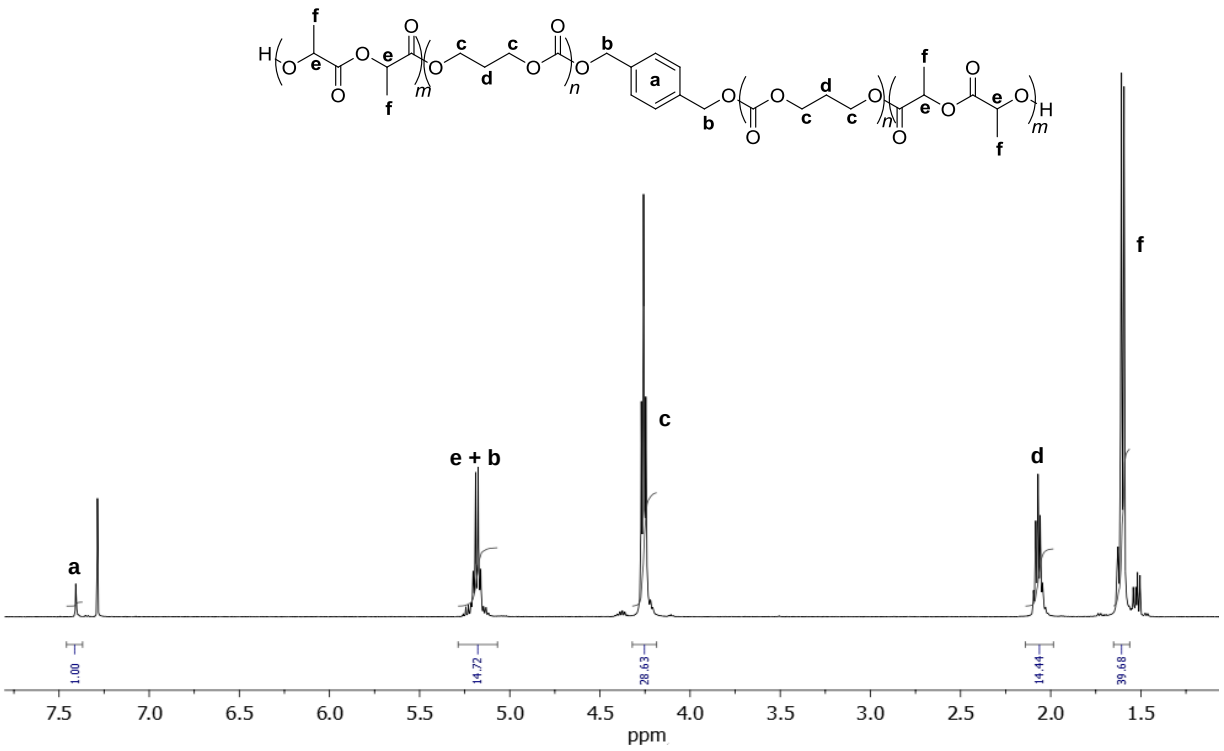

Figure S5. ^{1}H NMR (500 MHz; $CDCl_3$, 298 K) spectrum of a PLLA-*b*-PTMC-*b*-PLLA copolymer prepared from [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)]/BDM ($\overline{Mn}_{,SEC}$ = 7 200 g.mol^{-1}, Table S1, entry 3).

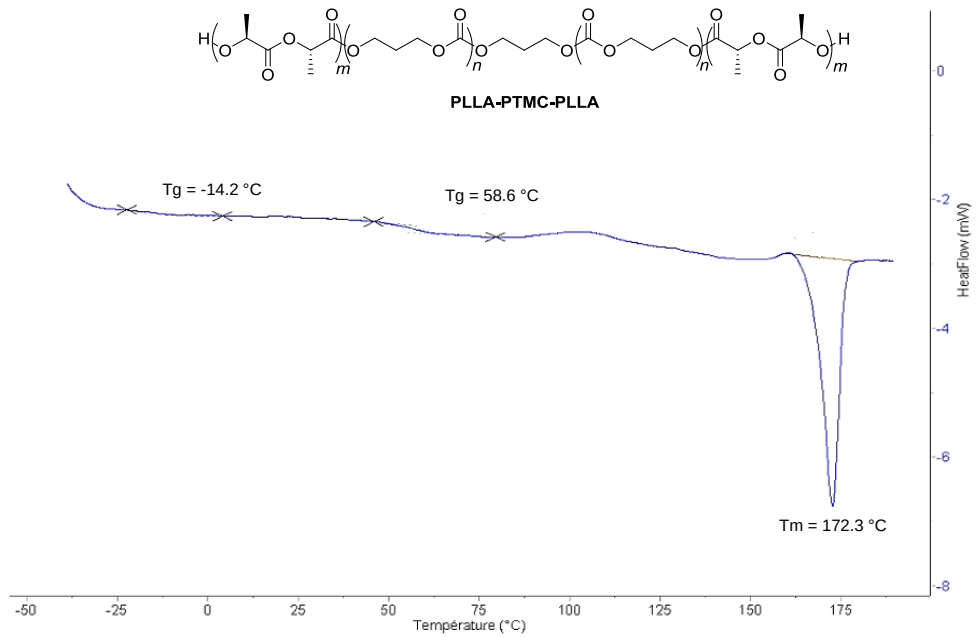

Figure S6. DSC curve (second heating run) of a PLLA-*b*-PTMC-*b*-PLLA sample ($M_{n,SEC}$ = 71 100 g.mol^{-1}; Table 3, entry 3).

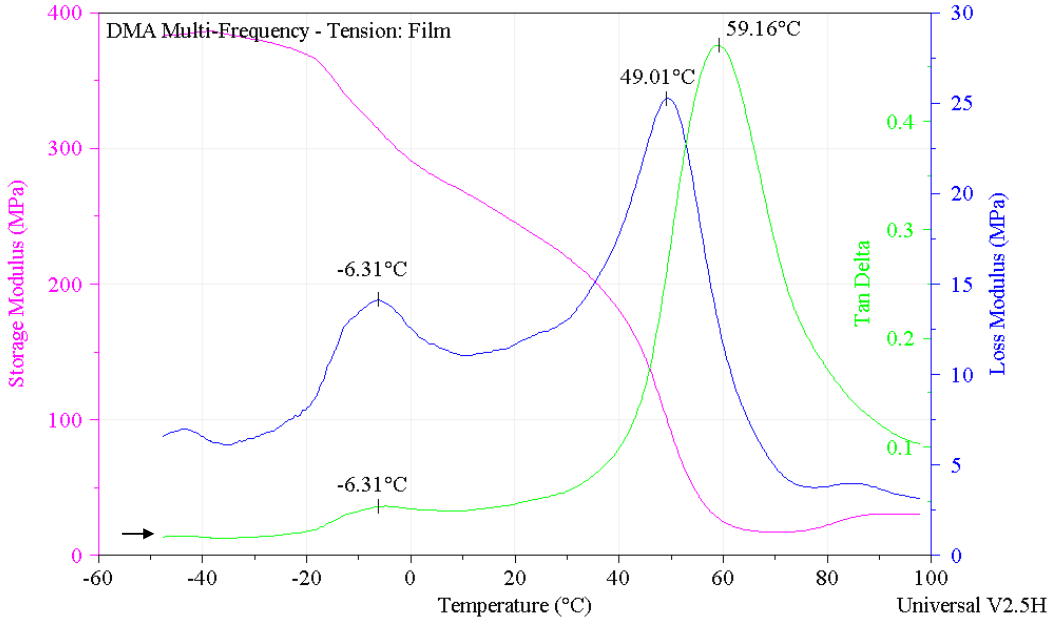

Figure S7. DMA curves of a PLLA-*b*-PTMC-*b*-PLLA sample ($M_{n,SEC}$ = 46 100 g.mol^{-1}; Table 3, entry 1).

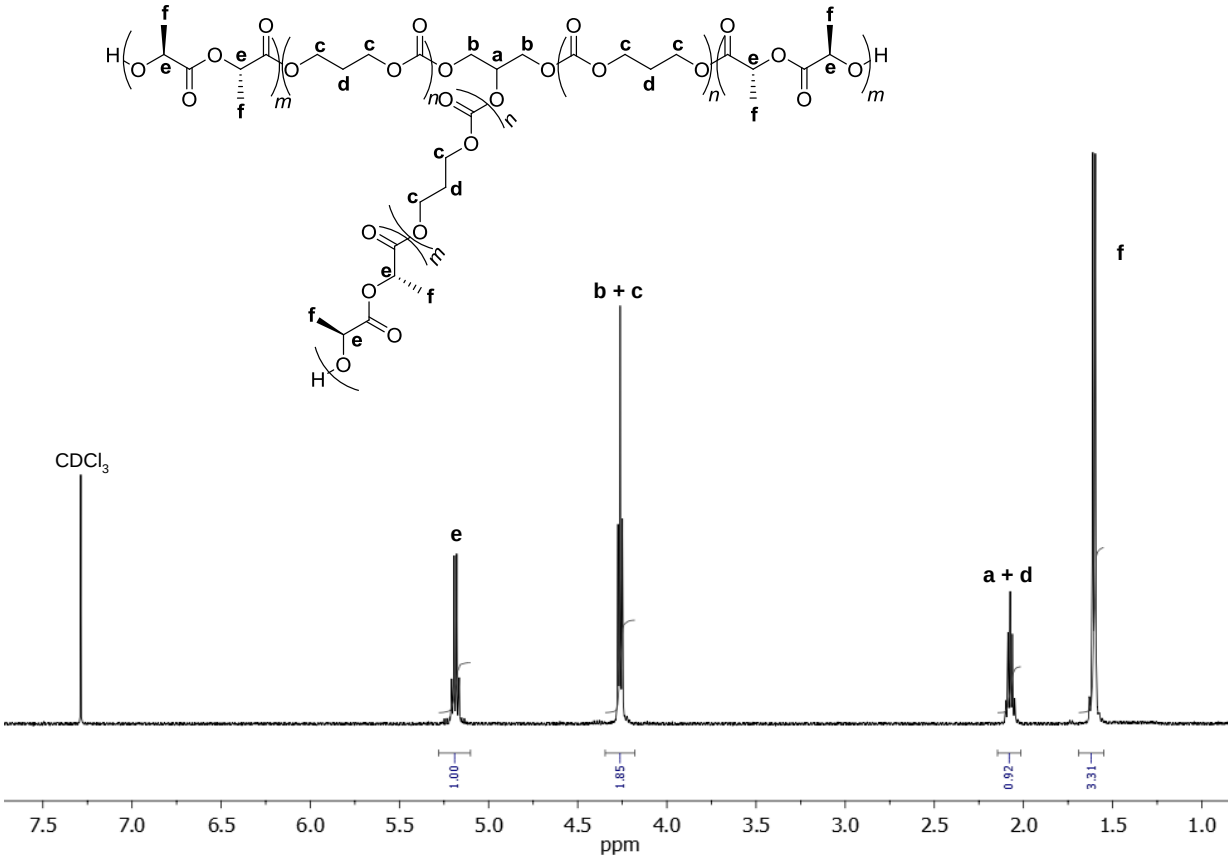

Figure S8. ^{1}H NMR (500 MHz; $CDCl_3$, 298 K) spectrum of a GLY(PTMC-*b*-PLLA)$_3$ copolymer prepared from [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)]/GLY ($M_{n,SEC}$ = 7 600 g.mol^{-1}, Table 4, entry 1).

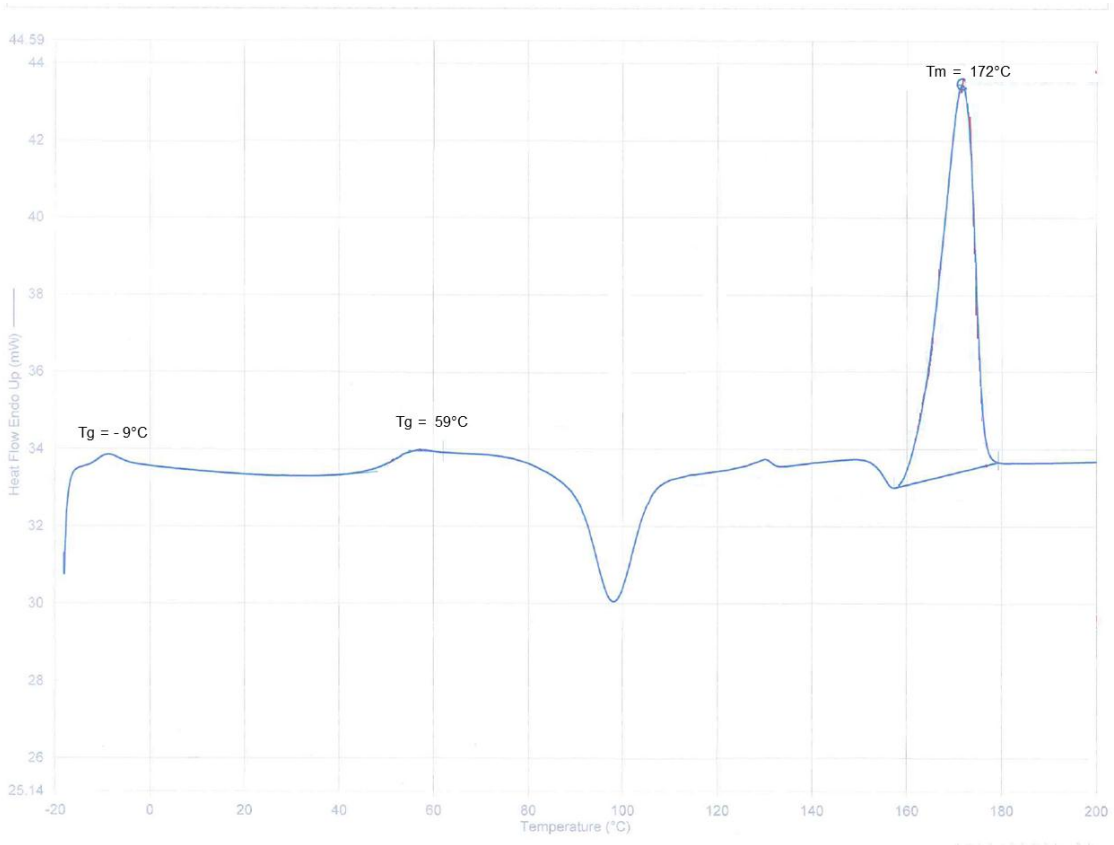

Figure S9. DSC curve (second heating run) of a GLY(PTMC-*b*-PLLA)$_3$ sample ($M_{n,SEC}$ = 29 900 g.mol^{-1}; Table 4, entry 2) (cycles: –20 °C to +200 °C at 20 °C.min^{-1}; +200 °C to –20 °C at 20 °C.min^{-1}.)

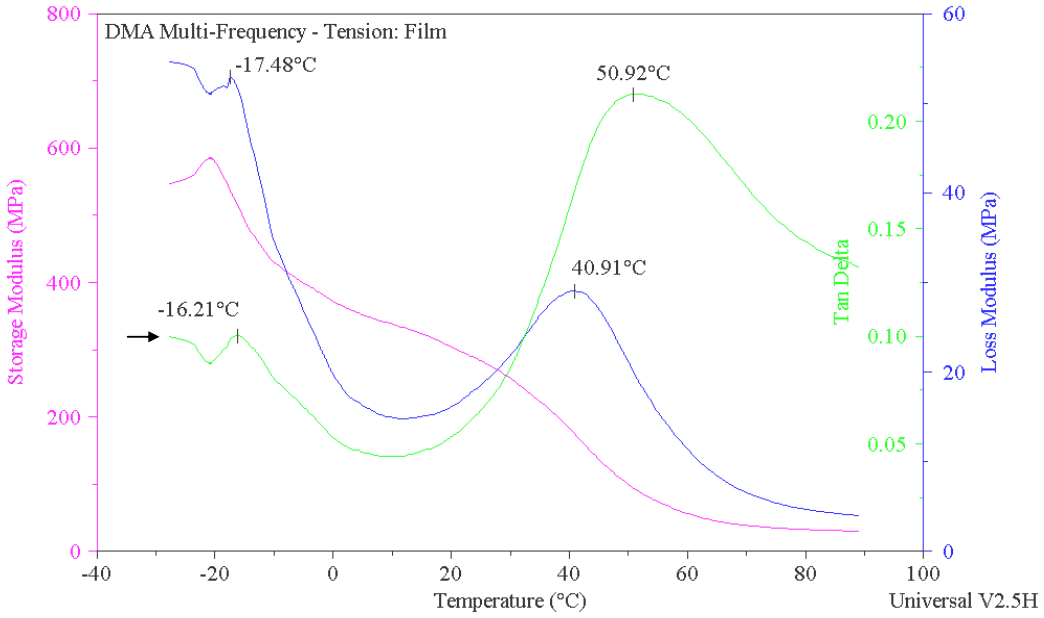

Figure S10. DMA curves of a GLY(PTMC-*b*-PLLA)$_3$ sample ($M_{n,SEC}$ = 29 900 g.mol^{-1}; Table 4, entry 2).

Table S1. ROP of L-LA promoted by [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)]/PTMC-OH$_2$ systems in toluene at 100 °C: synthesis of PLLA-*b*-PTMC-*b*-PLLA.

Entry	M_n [a] (g.mol^{-1}) ($Đ_M$) [b] PTMC-OH$_2$	[LLA]$_0$/[Zn]$_0$/ [PTMC-OH$_2$]$_0$ [c]	Time [d] (h)	L-LA Conv. [e] (%)	TMC/ L-LA [f] (wt-%)	$M_{n,theo}$ [g] (g.mol^{-1})	$M_{n,SEC}$ [a] (g.mol^{-1})	$Đ_M$ [b]
1	3 700 (1.44) **(1)**	200/1/5	1.5	100	40/60	9 460	9 300	1.19
2	13 200 (1.63) **(1)**	1 500/1/5	14	100	41/69	56 400	32 350	1.20
3	4 600 (1.52) **(2)**	200/1/5	3.5	100	64/36	10 360	7 200	1.21

[a] Number average molar mass values (corrected-refer to experimental section) determined by SEC in THF vs. polystyrene standards. [b] Dispersity values determined by SEC in THF. [c] [Zn] = [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)], [L-LA]$_0$ = 4.0 M. [d] The reaction time was not necessarily optimized. [e] Determined by NMR analysis of the crude reaction mixture. [f] TMC/ L-LA weight % in the recovered polymer calculated from the relation: $M_{n,HO\text{-}PTMC\text{-}OBn}/M_{n,SEC} \times 100$. [g] Calculated from the relation: $\{([TMC]_0/[PTMC\text{-}OH_2]_0) \times M_{L\text{-}LA} \times conv._{L\text{-}LA}\} + M_{n,PTMC\text{-}OH2}$ with $M_{L\text{-}LA}$ = 144 g.mol^{-1}.

Note that preliminary investigations on the ROP of L-LA using a low molar mass PTMC-OH$_2$ pre-polymer (Table S1, entries 1,3) previously isolated, revealed, similarly to the analogous

preparation of the related diblock copolymers PTMC-*b*-PLLA, a better control (regarding both $M_{n,SEC}$ vs $M_{n,theo}$ and $Đ_M$ values) than that involving a longer macrodiol (Table S1, entry 2). Also, shorter polymerization times were noted for the two step synthesis of PLLA-*b*-PTMC-*b*-PLLA, as opposed to the sequential approach (Table 4).