Electronic Supplementary Material (ESI) for Polymer Chemistry
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Supporting Information

Macromolecular Engineering via Ring-Opening Polymerization (3): Trimethylene Carbonate Block Copolymers derived from Glycerol

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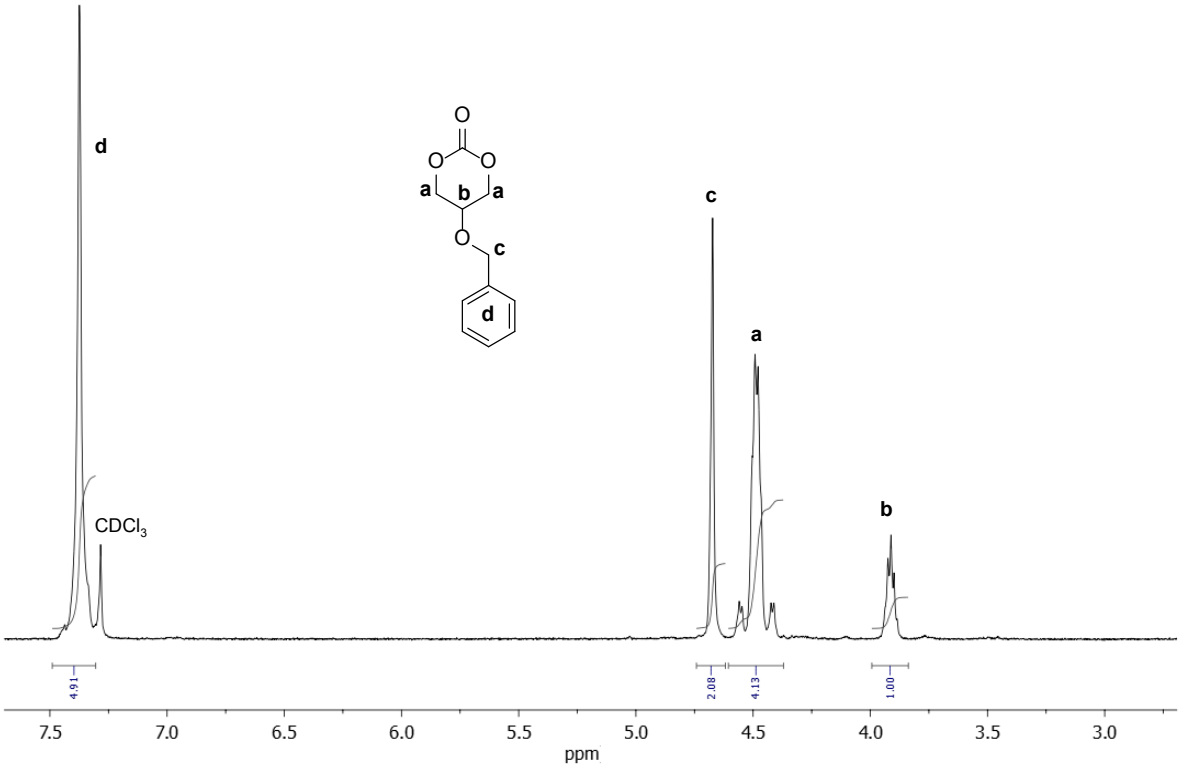

Figure S1. ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C) spectrum of BTMC.

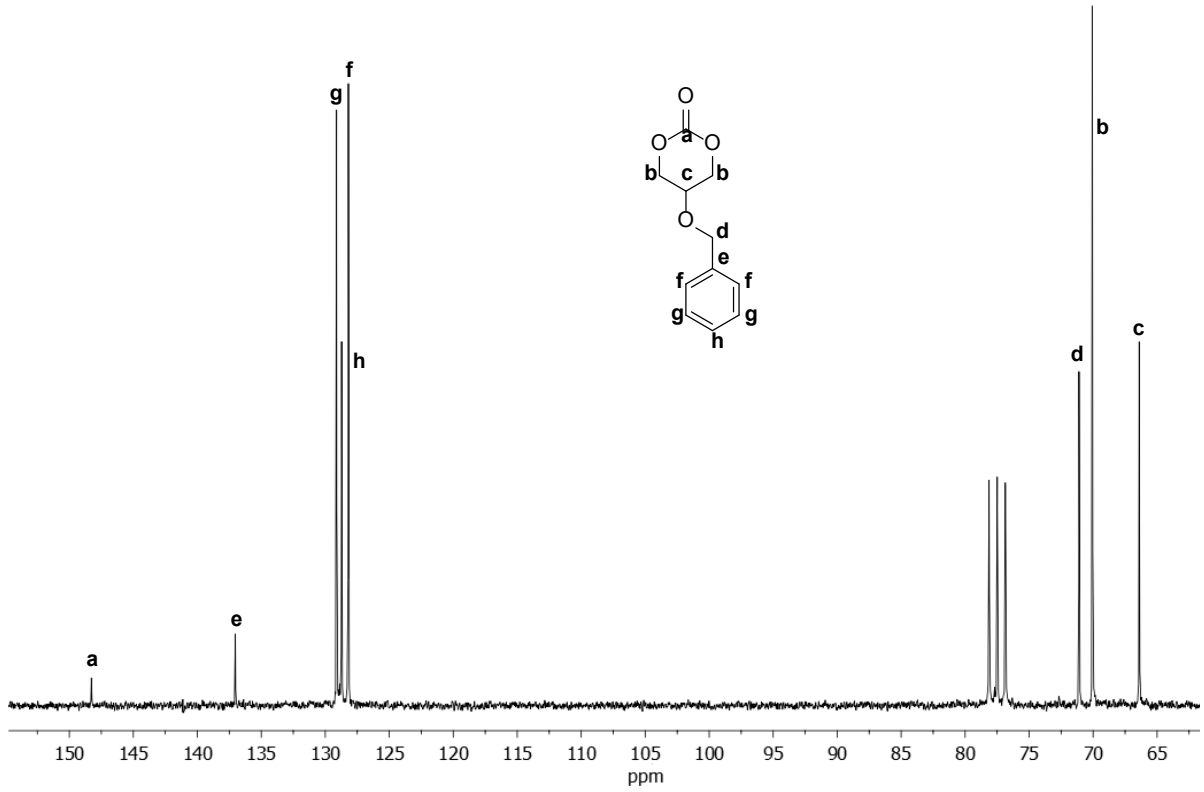

Figure S2. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$, 23 °C) spectrum of BTMC.

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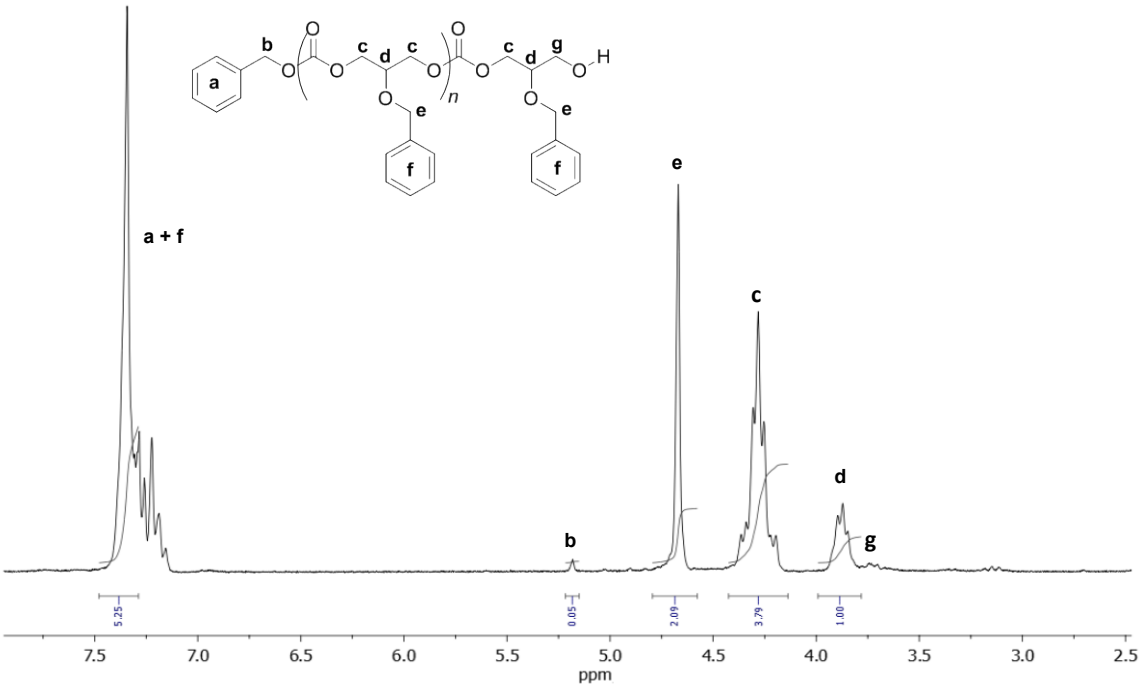

Figure S3. ^{1}H NMR (200 MHz, $CDCl_3$, 23 °C) spectrum of a H–PBTMC–OBn synthesized from [(BDI^{iPr})Zn(N(SiMe$_3$)$_2$)]/BnOH in bulk at 60° C (Table 1, entry 6).

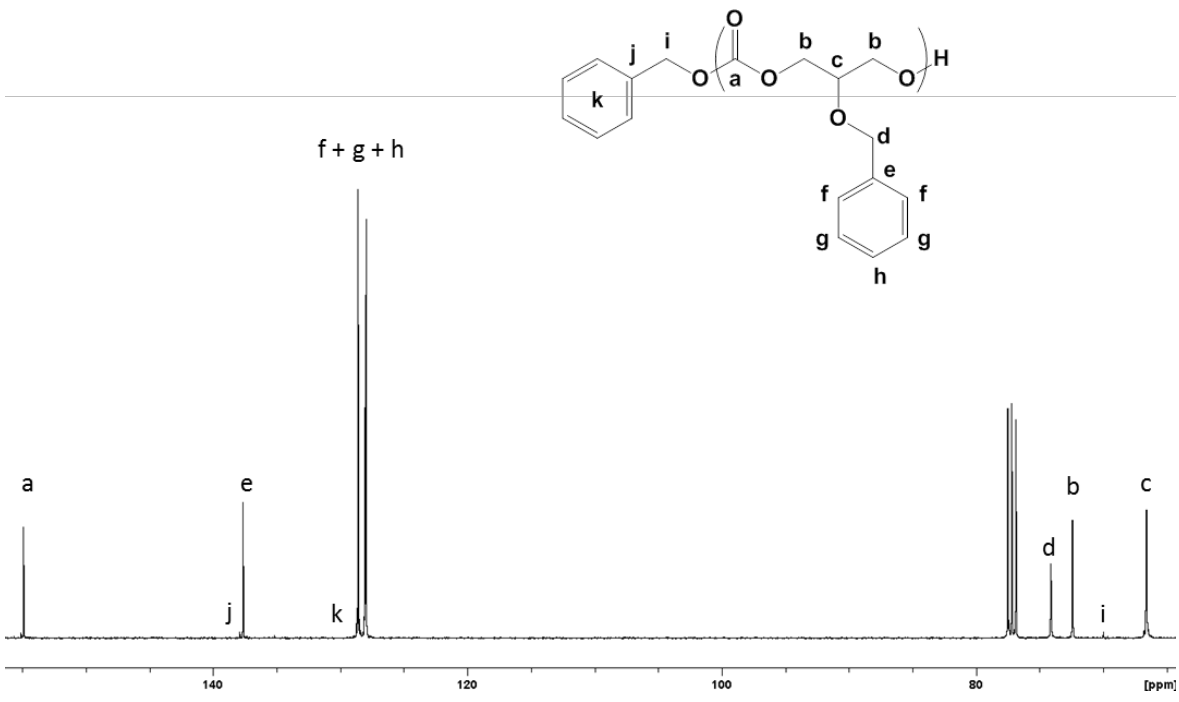

Figure S4. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 23 °C) spectrum of a H–PBTMC–OBn synthesized from BEMP/BnOH in bulk at 60 °C (Table 1, entry 14).

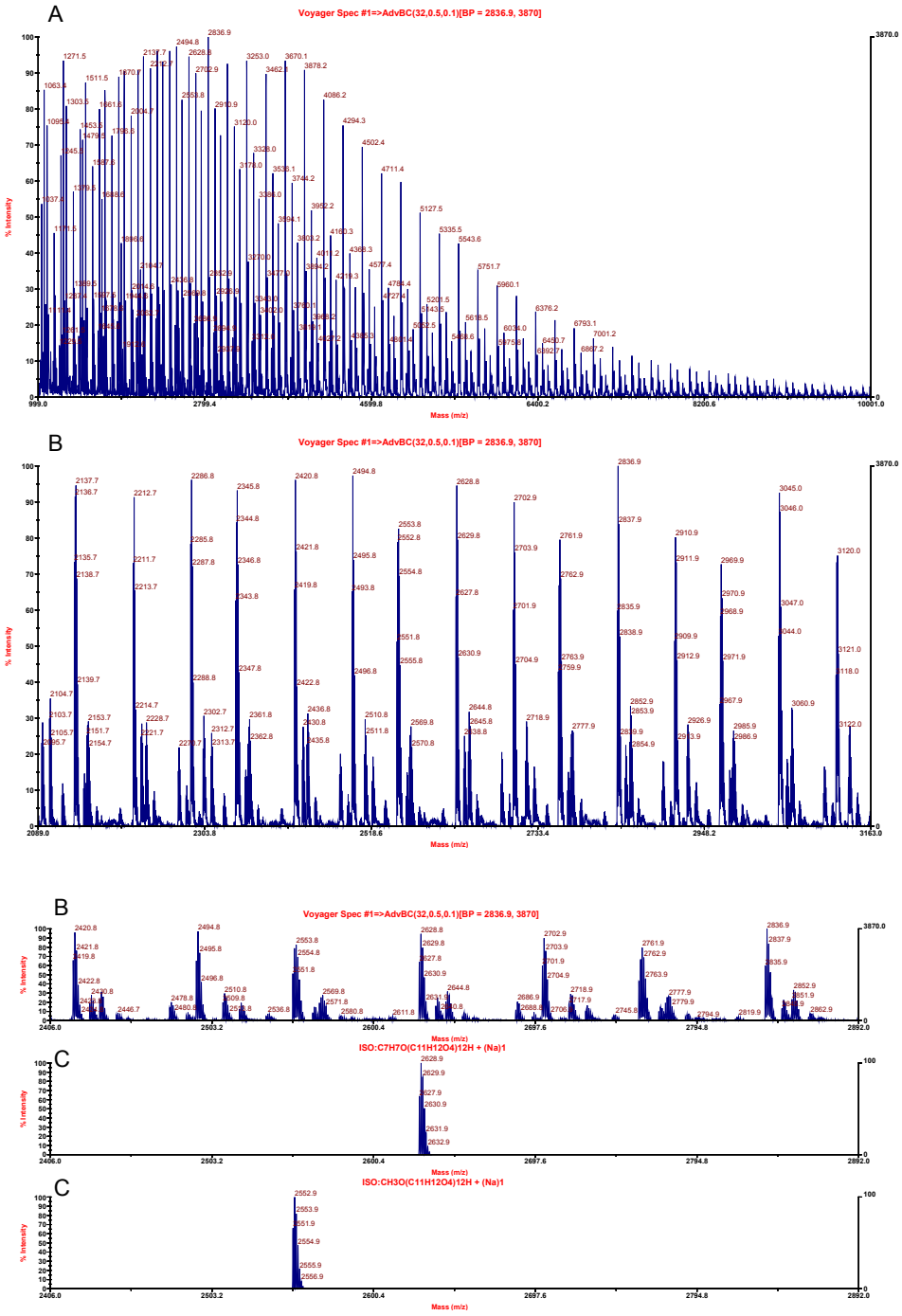

Figure S5. MALDI-ToF mass spectrum of a PBTMC sample produced from BEMP/BnOH using IAA as matrix (Table 1, entry 14): A) full spectrum; B) zoomed region of the spectrum; and C) comparison to the corresponding simulations for n = 12.

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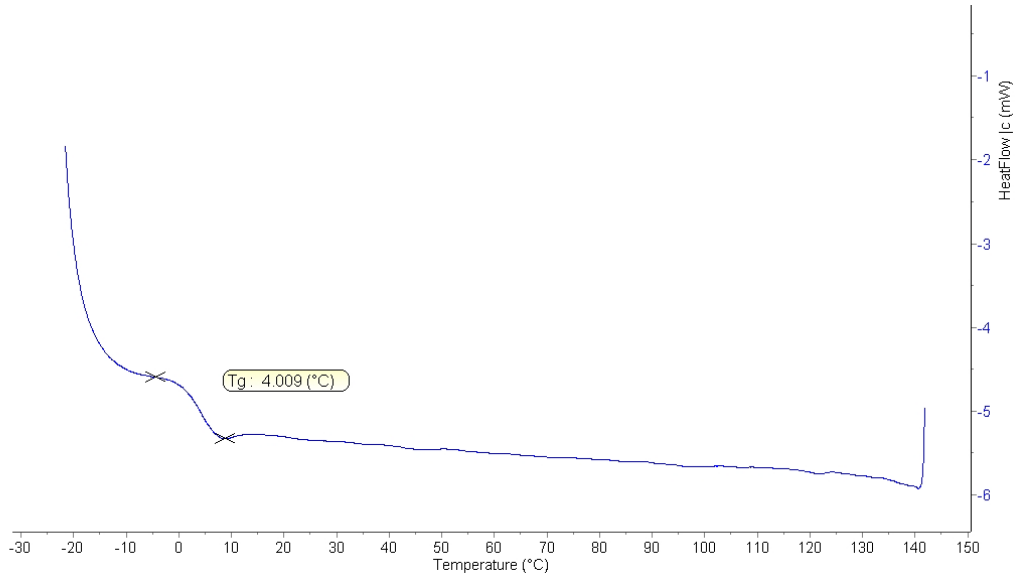

Figure S6. DSC trace of a H–PBTMC–OBn sample synthesized from BEMP/BnOH in bulk at 60 °C, (Table 1, entry 15; 10 °C/min, He).

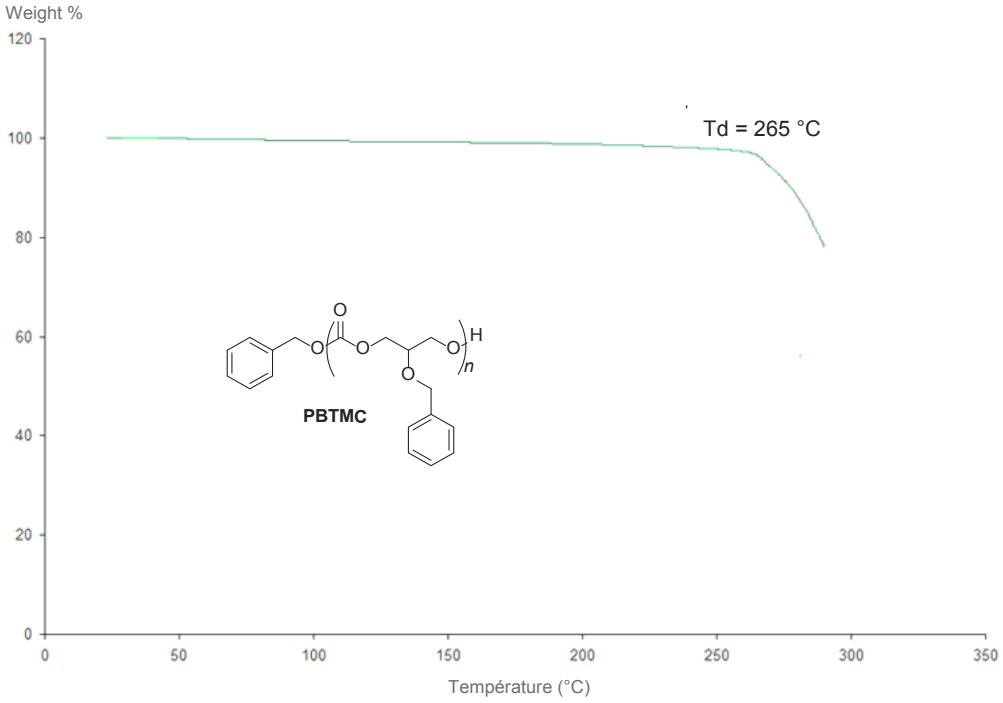

Figure S7. TGA trace (10 °C.min^{-1}, He) of a H–PBTMC–OBn (M_n = 35 000 g.mol^{-1}; Table 1, entry 4).

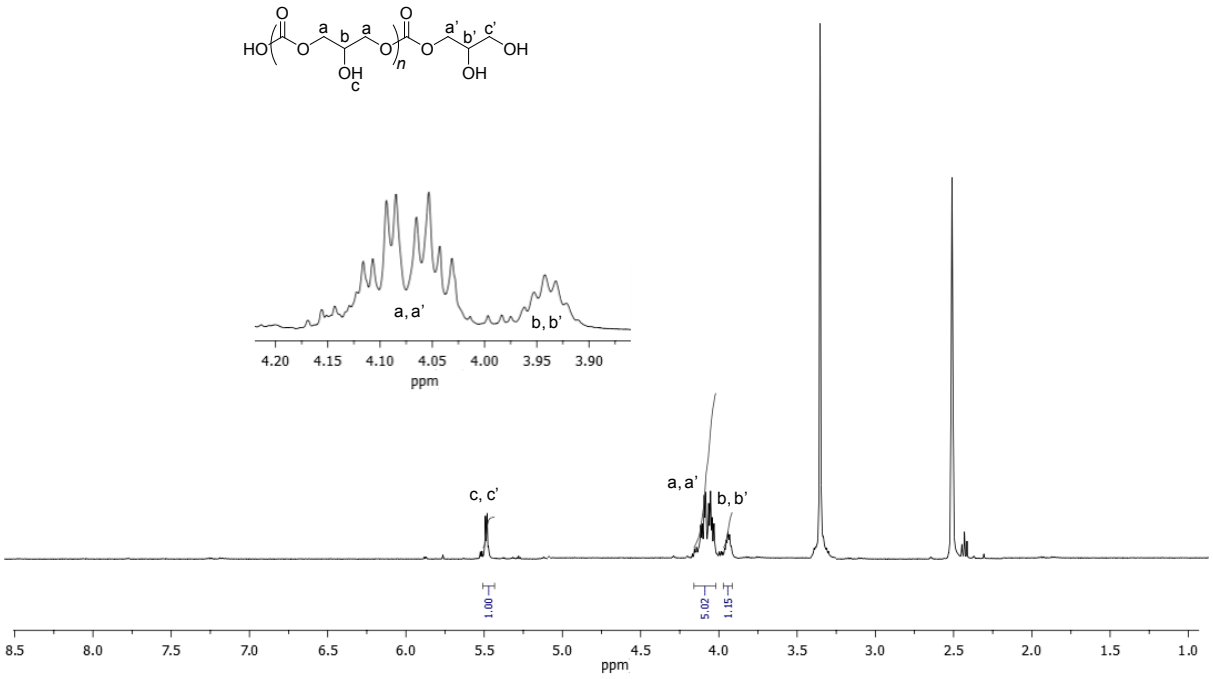

Figure S8. ^{1}H NMR (500 MHz, DMSO, 23 °C) spectrum of a H–PHTMC–OH synthesized upon hydrogenolysis of H–PBTMC–OBn (Table 1, entry 3).

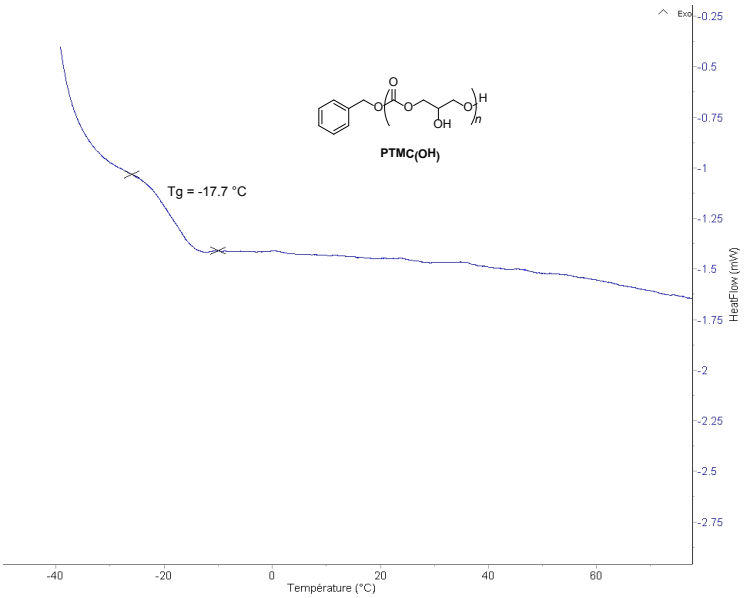

Figure S9. DSC trace of a H–PHTMC–H sample synthesized upon hydrogenolysis of H-PBTMC-H (Table 1, entry 3; 10 °C/min, He).

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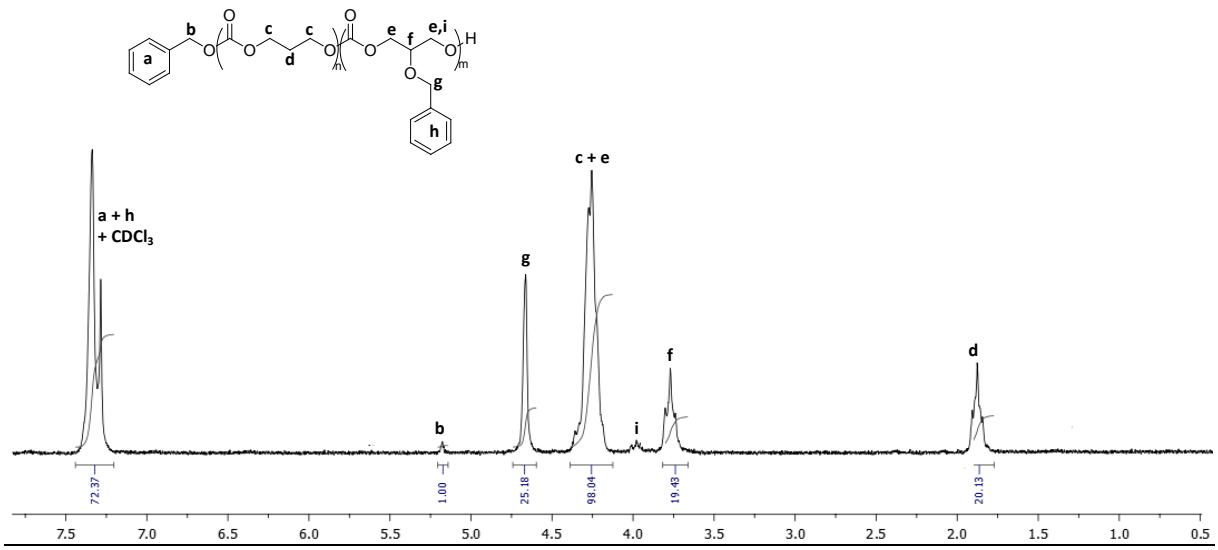


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) spectrum of a H–PBTMC-*b*-PTMC–OBn synthesized by *in situ* sequential copolymerization of TMC and BTMC in toluene from [(BDI^{iPr})Zn[N(SiMe$_3$)$_2$]/BnOH at 60° C (Table 2, entry 2).

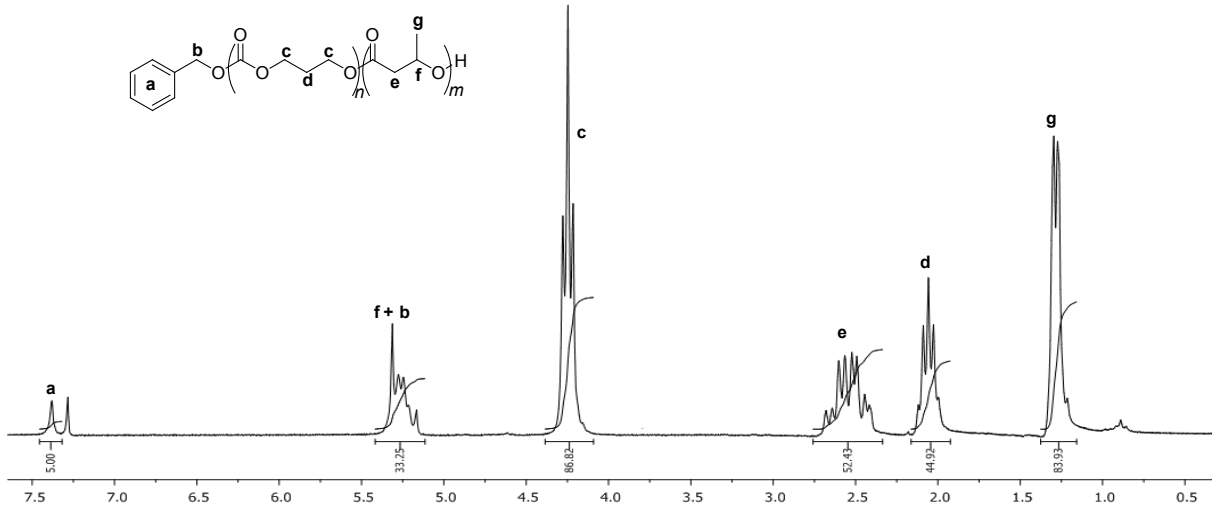


Figure S11. ^{1}H NMR (300 MHz, $CDCl_3$, 23 °C) spectrum of a H–PHB-*b*-PTMC–OBn synthesized by *in situ* sequential copolymerization of TMC and BL in toluene from [(BDI^{iPr})Zn[N(SiMe$_3$)$_2$]/BnOH at 60° C (Table 2, entry 7).

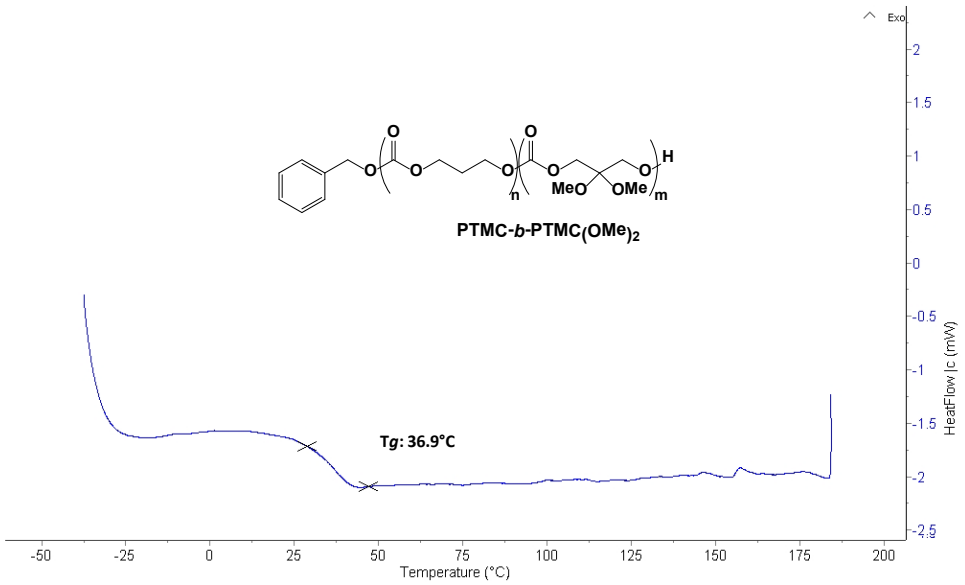


Figure S12. DSC trace (10 °C.min^{-1}, He) of a H–PTMC(OMe)$_2$-*b*-PTMC–OBn sample synthesized by *in situ* sequential copolymerization in toluene from [(BDI^{iPr})Zn[N(SiMe$_3$)$_2$]/BnOH at 60/90° C (Table 2, entry 9).

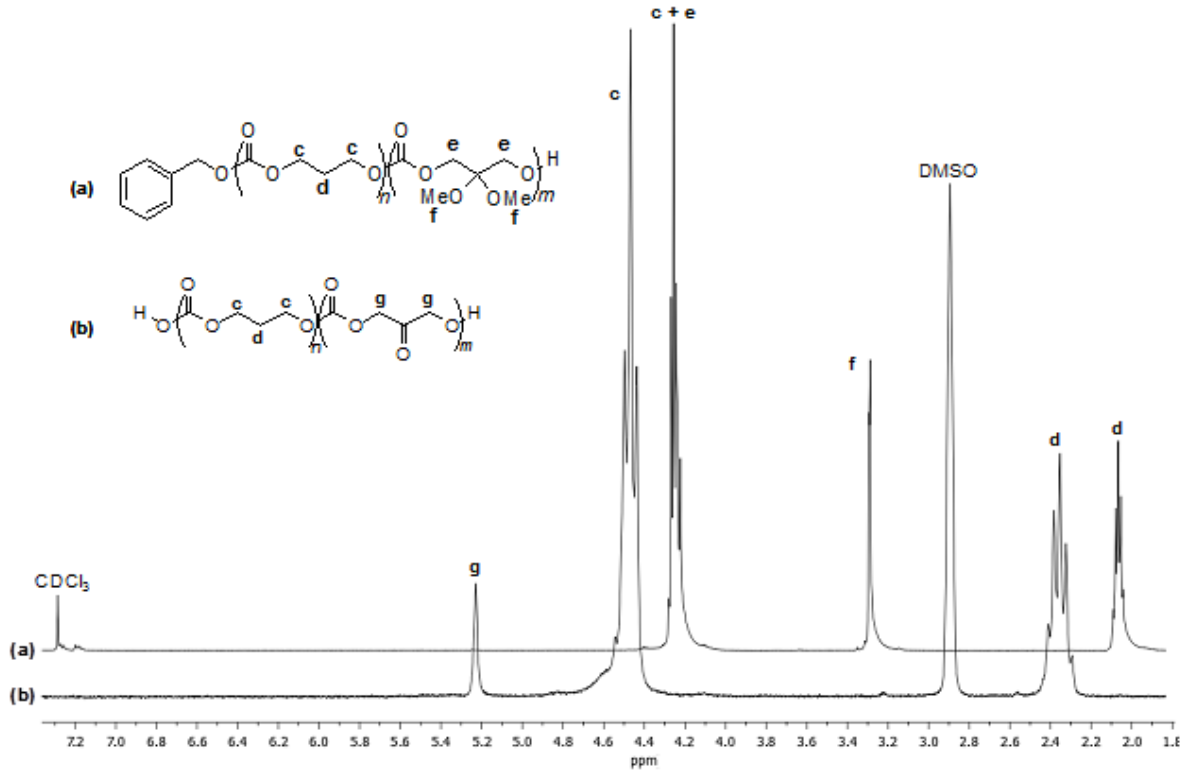


Figure S13: ^{1}H NMR (300 MHz, (a) $CDCl_3$, (b) DMSO, 23 °C) spectra of (a) a PTMC-*b*-PTMC(OMe)$_2$ and (b) a PTMC-*b*-PTMC(O) samples.

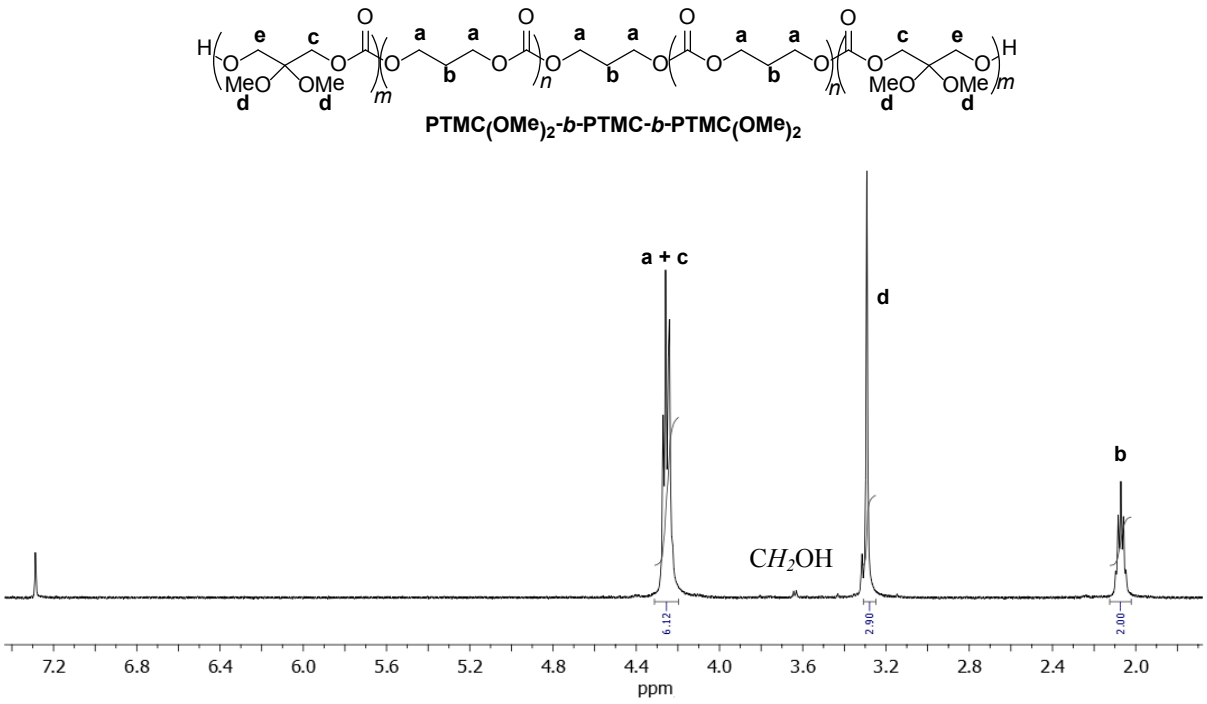
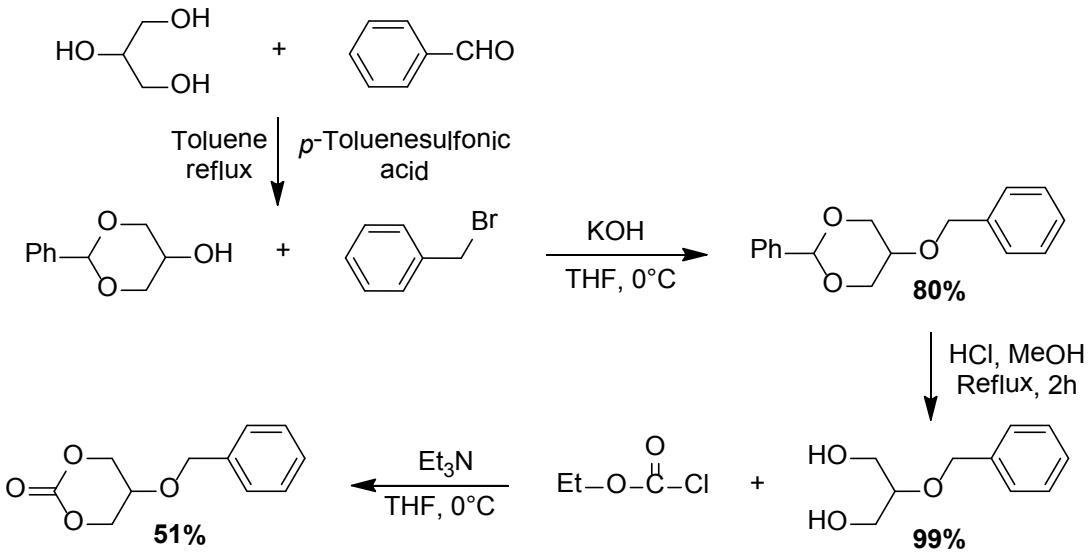


Figure S14: ^{1}H NMR (500 MHz, $CDCl_3$, 23 °C) spectrum of a PTMC(OMe)$_2$-*b*-PTMC-*b*-PTMC(OMe)$_2$ synthesized by *in situ* sequential copolymerization of TMC and TMC(OMe)$_2$ in toluene from [(BDI^{iPr})Zn[N(SiMe$_3$)$_2$]/1,3-propanediol at 60/90° C (Table 4, entry 5).



Scheme S1. Synthesis of BTMC from glycerol.**Error! Bookmark not defined.**

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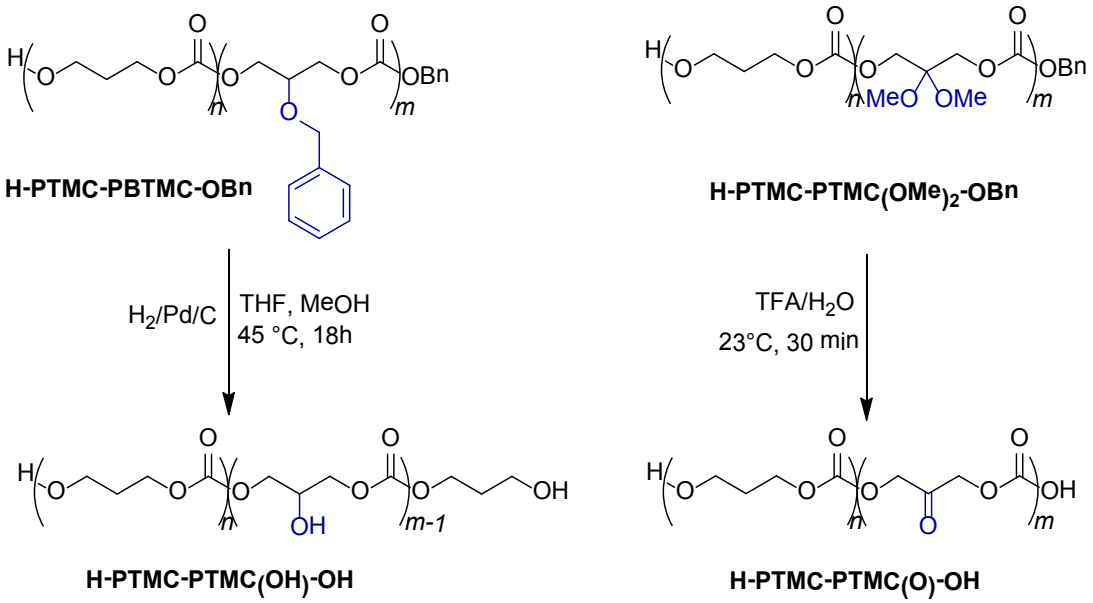

Scheme S2: Deprotection of the acetal and benzylox functions in the PTMC-*b*-PTMC(OMe)$_2$ and PTMC-*b*-PBTMC samples, respectively: synthesis of PTMC-*b*-PTMC(O) and PTMC-*b*-PTMC(OH).