Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Hybrid Block Copolymers of Polyester/Polycarbonate and Polypeptide Synthesized via One-Pot Sequential Ring-Opening Polymerization

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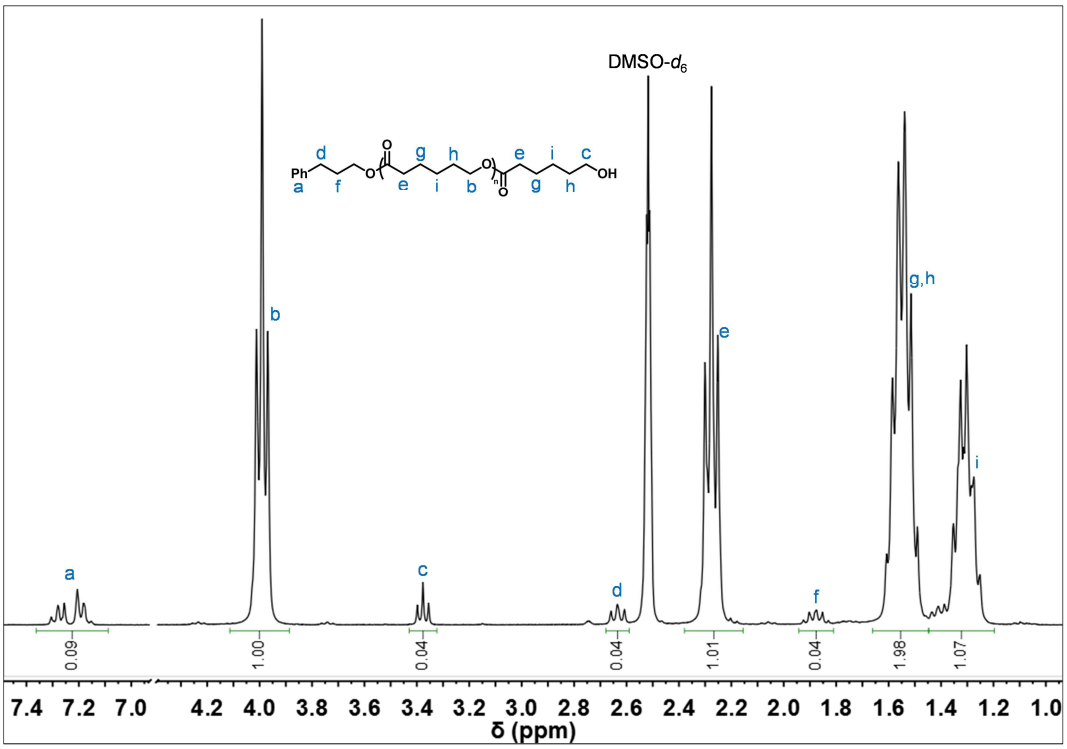

Figure S1. ^{1}H NMR spectrum of the PCL homopolymer. M_n of the PCL was determined from the integral ratio of the signals for the main chain CH_2 groups and the terminal CH_2 groups at the chemical shifts of 3.99 ppm (b) and 3.38 ppm (c), respectively.

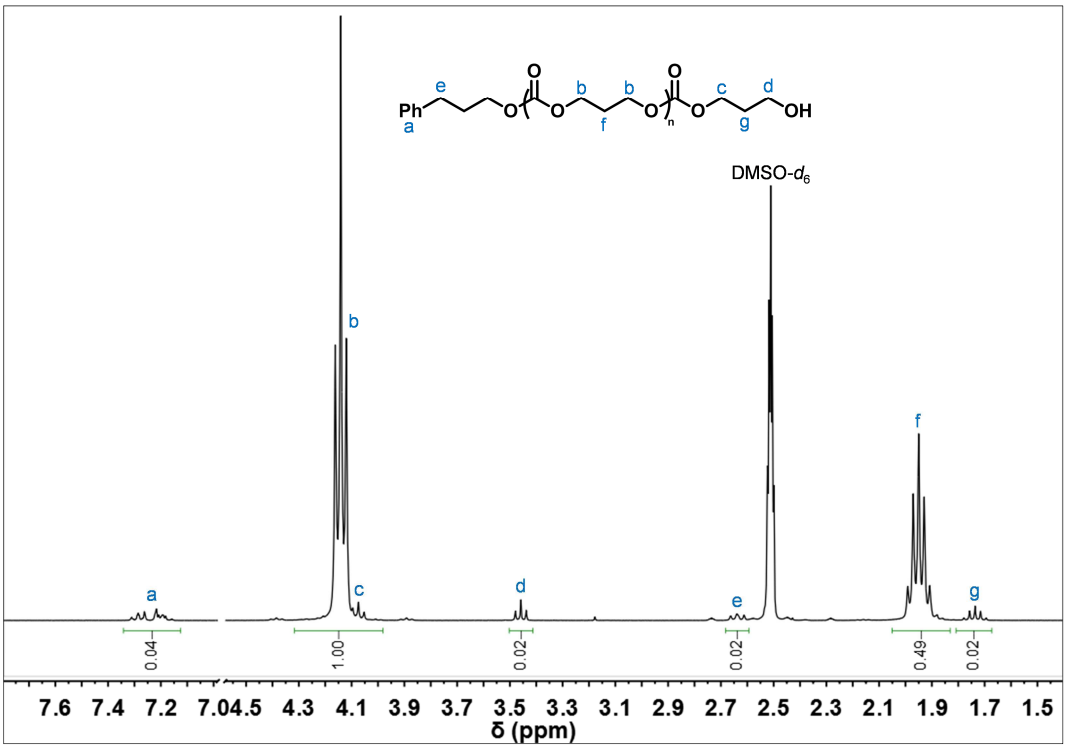

Figure S2. ^{1}H NMR spectrum of the PTMC. M_n of 2.9 kg mol^{-1} was determined for this homopolymer from the integral ratio of the signals for the main chain CH_2 groups and the terminal CH_2 groups at the chemical shifts of 4.14 ppm (b) and 3.46 ppm (d) taking into account content of the difunctional homopolymer in the sample which was estimated to be 5 mol% as determined from a difference between the signal at 3.46 ppm (d) of the end-groups and signal at 2.64 ppm (e) of the PPA initiator group.

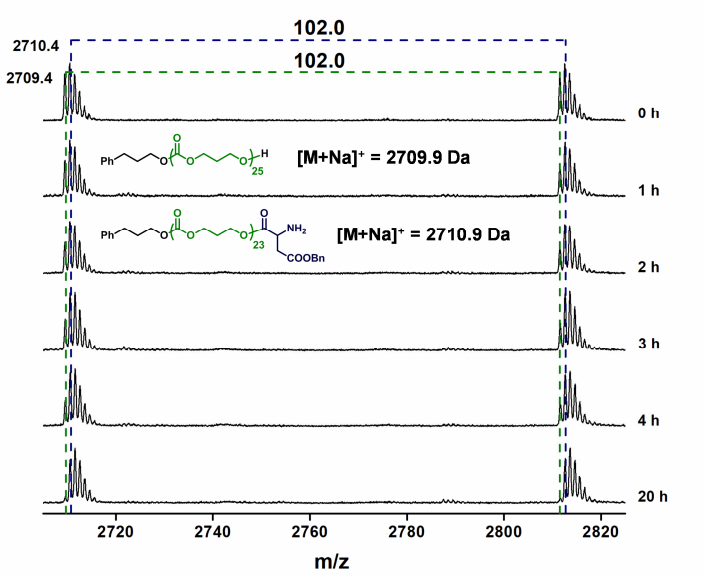

Figure S3. Enlarged MALDI-TOF mass spectra of the reaction aliquots withdrawn at different time of initiation of BLA NCA with PTMC. The measured monoisotopic signals are denoted together with the calculated exact masses ionized with the sodium ion for the proposed structures.

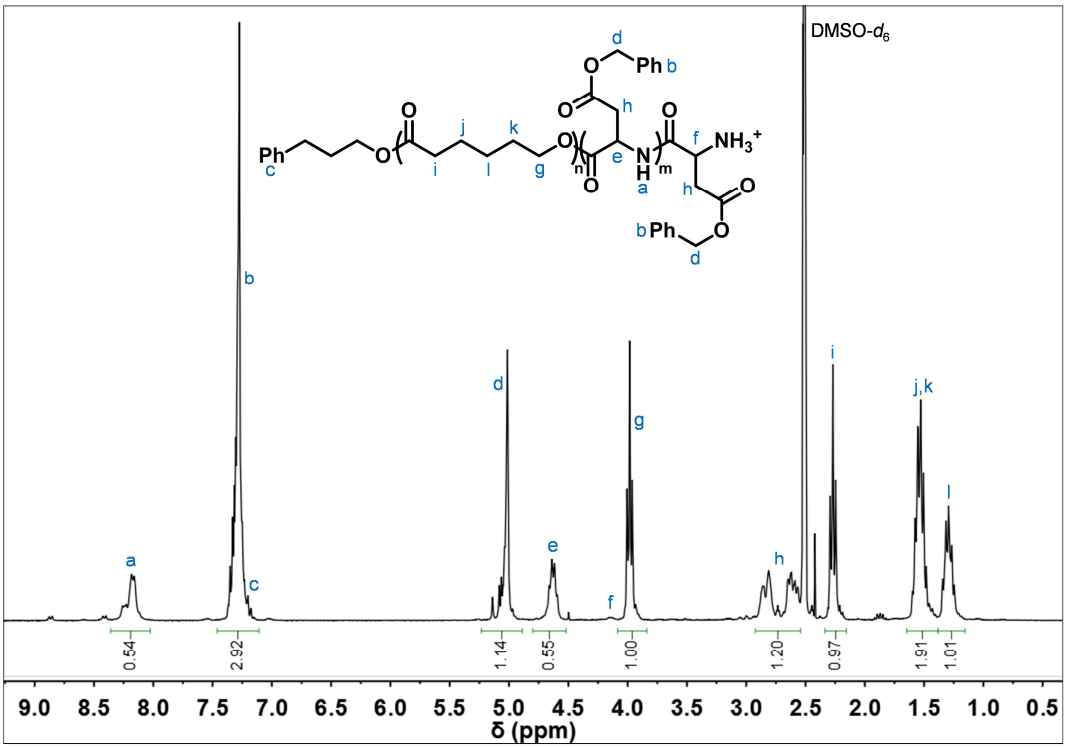

Figure S4. ^{1}H NMR spectrum of the PCL-*b*-PBLA$_{25}$ copolymer.

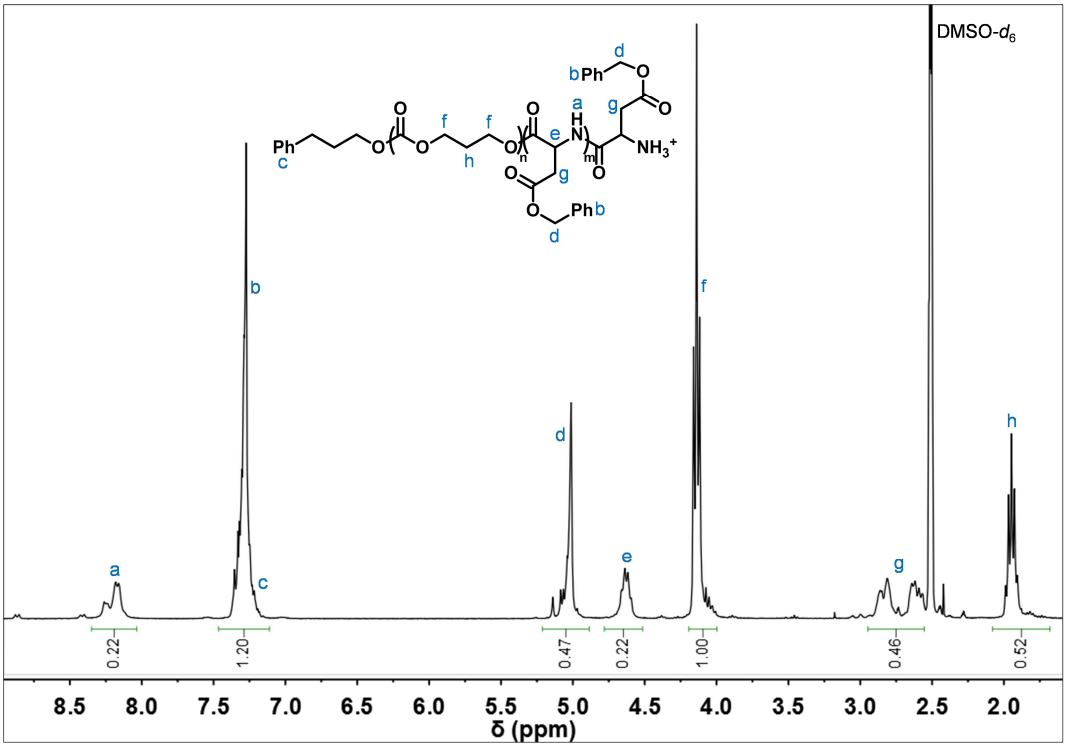

Figure S5. ^{1}H NMR spectrum of the PTMC-*b*-PBLA$_{25}$ copolymer.

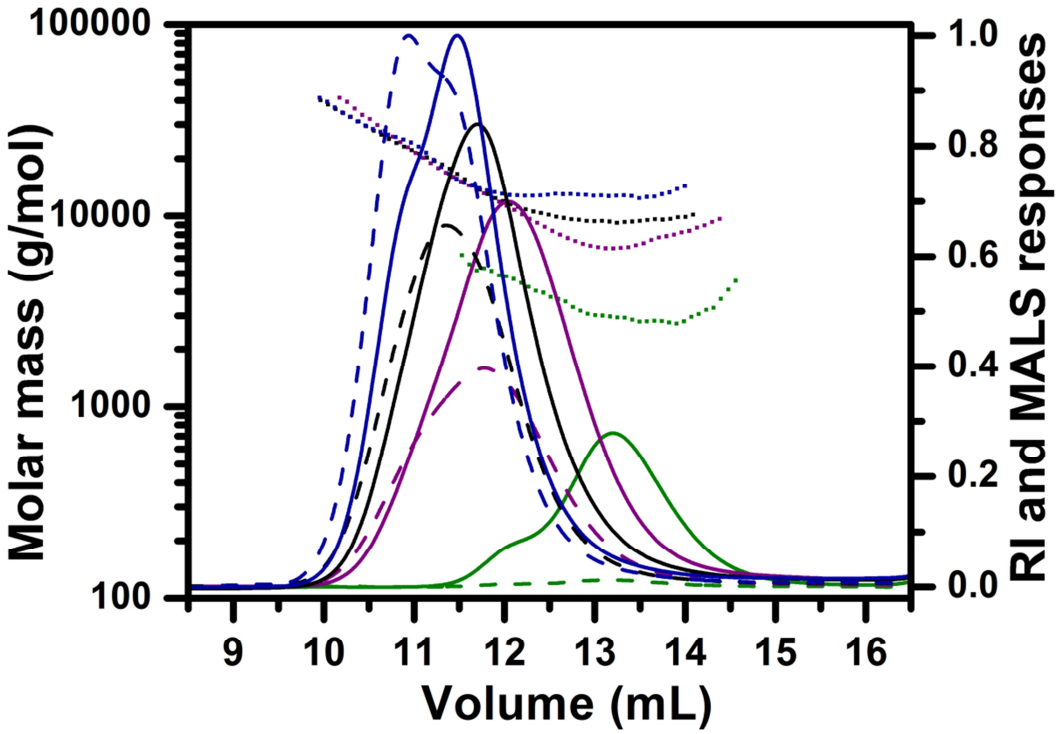

Figure S6. SEC-MALS chromatograms of PTMC (green) and PTMC-*b*-PBLA$_{25}$ (purple), PTMC-*b*-PBLA$_{40}$ (black), PTMC-*b*-PBLA$_{55}$ (blue) copolymers. Solid curves: refractive index detector responses; dashed curves: light-scattering detector responses at 90° angle; dotted curves: molar mass as a function of elution volume.

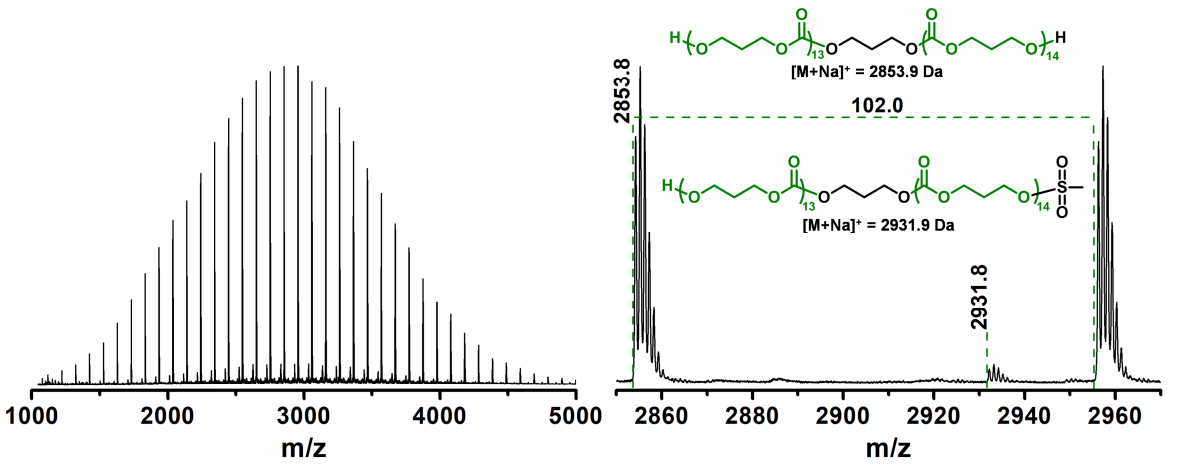

Figure S7. MALDI-TOF mass spectrum of the difunctional PTMC homopolymer prepared by ROP of TMC initiated by the 1,3-propanediol in the presence of MSA. The measured monoisotopic signals are denoted in the enlarged region of the mass spectrum together with the calculated exact masses ionized with the sodium ion for the proposed structures. MALDI-TOF mass spectrum shows beside the expected distribution of peaks also an additional distribution of much lower intensity, corresponding to the chains terminated by a methanesulfonyl group at one chain terminus. The low intensity peak distribution most likely resulted from a side reaction of the hydroxyl end-groups with the MSA impurities[1] since the difunctional PTMC was prepared with a higher MSA amount.

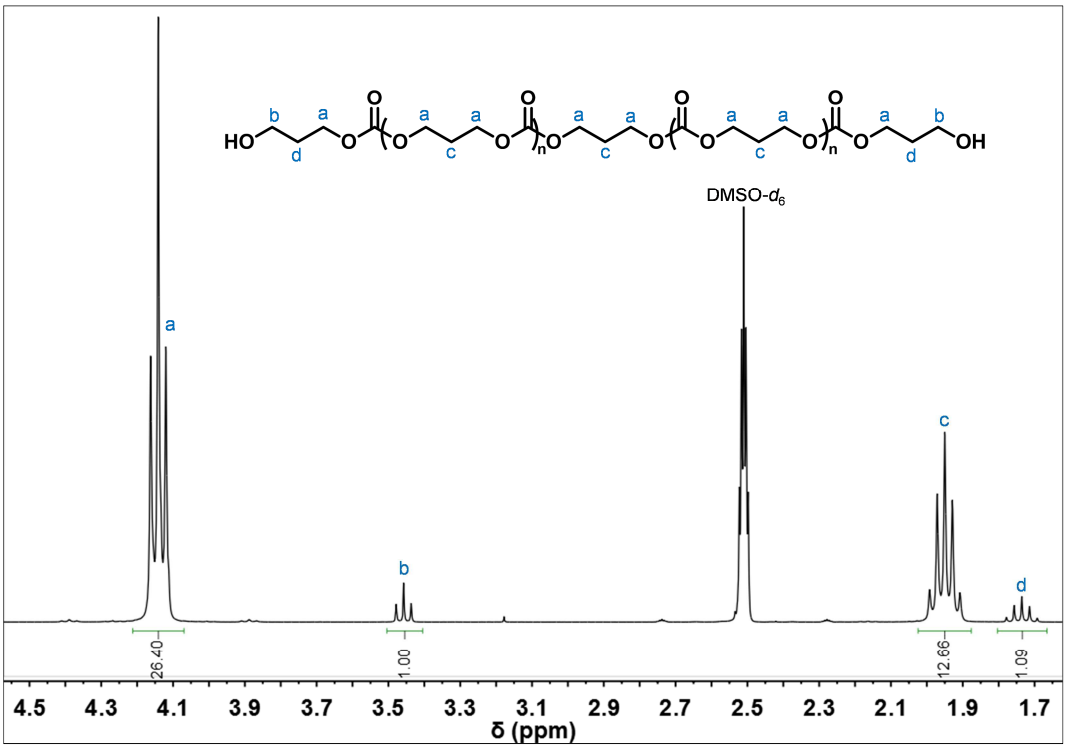

Figure S8. ^{1}H NMR spectrum of the difunctional PTMC prepared by ROP of TMC initiated by the 1,3-propanediol. M_n of 2.8 kg mol^{-1} was determined for this homopolymer from the integral ratio of the signals for the main chain CH_2 groups and the terminal CH_2 groups at the chemical shifts of 4.14 ppm (a) and 3.46 ppm (b).

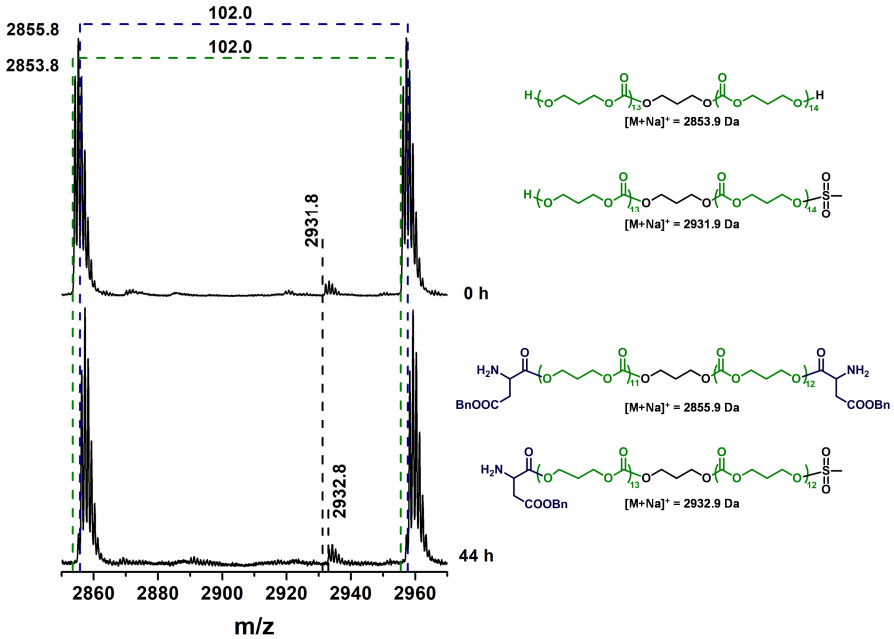

Figure S9. Enlarged MALDI-TOF mass spectra of the reaction aliquots withdrawn at the beginning and at the end of the initiation of BLA NCA with the 1,3-propanediol-initiated PTMC homopolymer. The measured monoisotopic signals are denoted together with the calculated exact masses ionized with the sodium ion for the proposed structures.

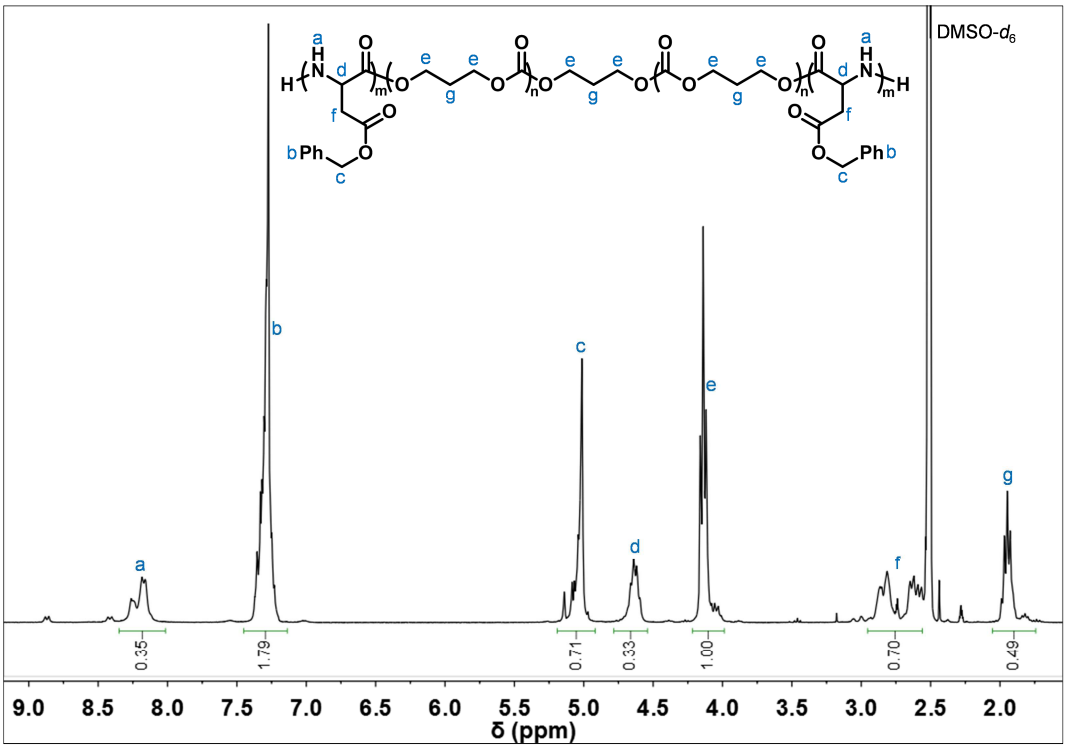

Figure S10. ^{1}H NMR spectrum of the PBLA$_{20}$-*b*-PTMC-*b*-PBLA$_{20}$ triblock copolymer prepared by ROP of BLA NCA with the 1,3-propanediol-initiated PTMC homopolymer.

References

1 D. J. Snodin, *Regul. Toxicol. Pharmacol.,* 2006, **45**, 79-90.