

Well-defined Polymethylene-Based Block Co/Terpolymers by Combining Anthracene/Maleimide Diels-Alder Reaction with Polyhomologation

Supplementary Information

Nazeeha Alkayal and Nikos Hadjichristidis*

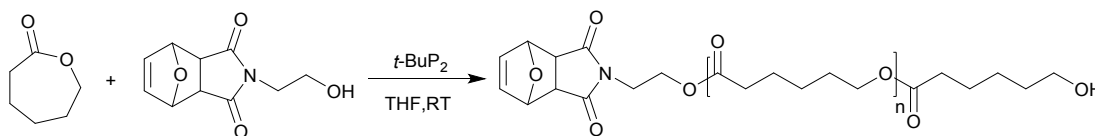
King Abdullah University of Science and Technology (KAUST), Physical Sciences and Engineering Division,
KAUST Catalysis Center, Polymer Synthesis Laboratory, Thuwal 23955, Saudi Arabia

Experimental Information

Synthesis of dimethylsulfoxonium methylide ¹

In a three-necked flask connected to a condenser and an argon/vacuum line, 6.8 g of NaH (dispersed in mineral oil, 60% in weight) was introduced and washed with dry petroleum ether (20 mL × 3). The residual solvent was removed under vacuum conditions, followed by the addition of 20 g of dry trimethylsulfoxonium chloride and 200 mL of THF. The entire operation was performed under argon flow. The mixture was heated and refluxed at 70°C until cessation of the gas (4–5 h). After the reaction, the THF was removed under low pressure and 50 mL of dry toluene was added. The solution was filtered by dry celite-545 aid (2–3 cm). The flask and filtration cake was washed with 200 mL fresh toluene. A clear solution with a light yellow color was obtained, which was titrated with a standard HCl aqueous solution (0.73 mmol/mL).

Synthesis of furan-protected-maleimide-terminated poly(ϵ -caprolactone) (PCL₅₀-MI)



The reaction was performed in a 100 mL Schlenk flask. 0.056 g of 4-(2-hydroxyethyl)-10-oxa-4-azatricyclo [5.2.1.0.2, 6] dec-8-ene-3, 5-dione ² was dissolved in 1.5 mL of THF and added to the reactor. Then, the THF was evaporated, and 0.13 mL of *t*-BuP₂ in THF was injected, followed by the addition of 6 mL of THF and 3 mL of ϵ -CL monomer. The reaction solution was stirred under Ar at room temperature, followed by quenching with acetic acid after three days. The polymer was precipitated in cold methanol and dried in a vacuum oven at 40°C (yield = 1.9 g, 63%, $M_{n,NMR}$ = 5700 g/mol, M_w/M_n =

1.10, PS standards). The values for the ^1H NMR (600 MHz, CDCl_3) included 6.58 ppm (s, 2H, $\text{CH}=\text{CH}$, vinyl protons), 5.27 ppm (s, 2H, $-\text{CHO}$, bridge-head protons), 4.27 ppm (t, 2H, $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$), 4.02 ppm (t, $\text{CH}_2\text{OC}=\text{O}$ of PCL), 3.77-3.64 ppm (m, 4H, $\text{NCH}_2\text{CH}_2\text{OC}=\text{O}$ and CH_2OH end-group of PCL), 2.85 ppm (s, 2H, $\text{CH}-\text{CH}$, bridge protons), 2.33 ppm (t, $\text{C}=\text{OCH}_2$ of PCL), and 1.63-1.35 ppm (m, CH_2 of PCL).

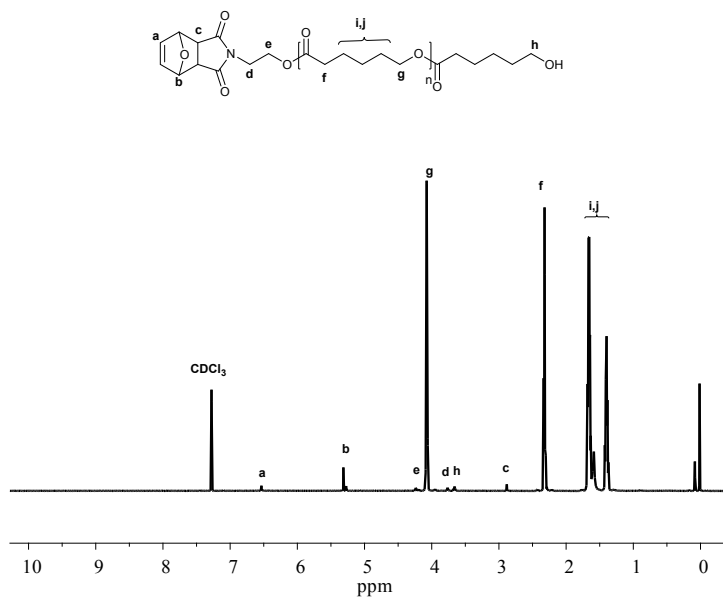


Figure S1. The ^1H NMR spectrum of furan- protected-maleimide-terminated poly (ϵ -caprolactone) (PCL₅₀-MI) in CDCl_3 (600MHz).

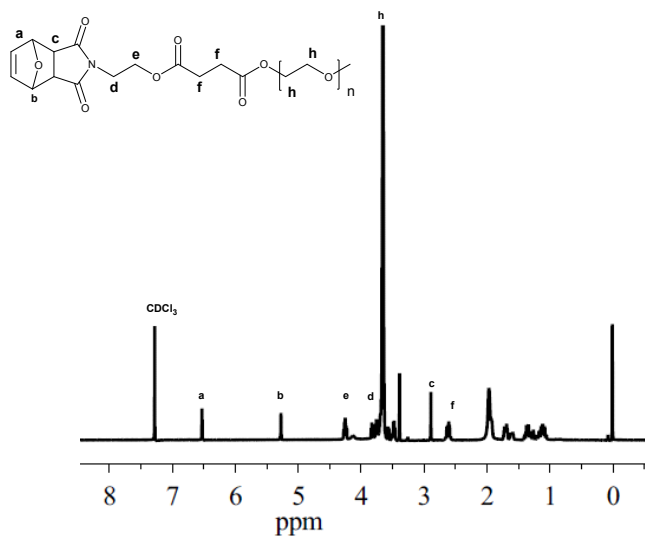


Figure S2. ^1H NMR spectrum of furan-protected-maleimide-terminated polyethylene glycol (PEG₁₀₀-MI) in CDCl_3 (600MHz).

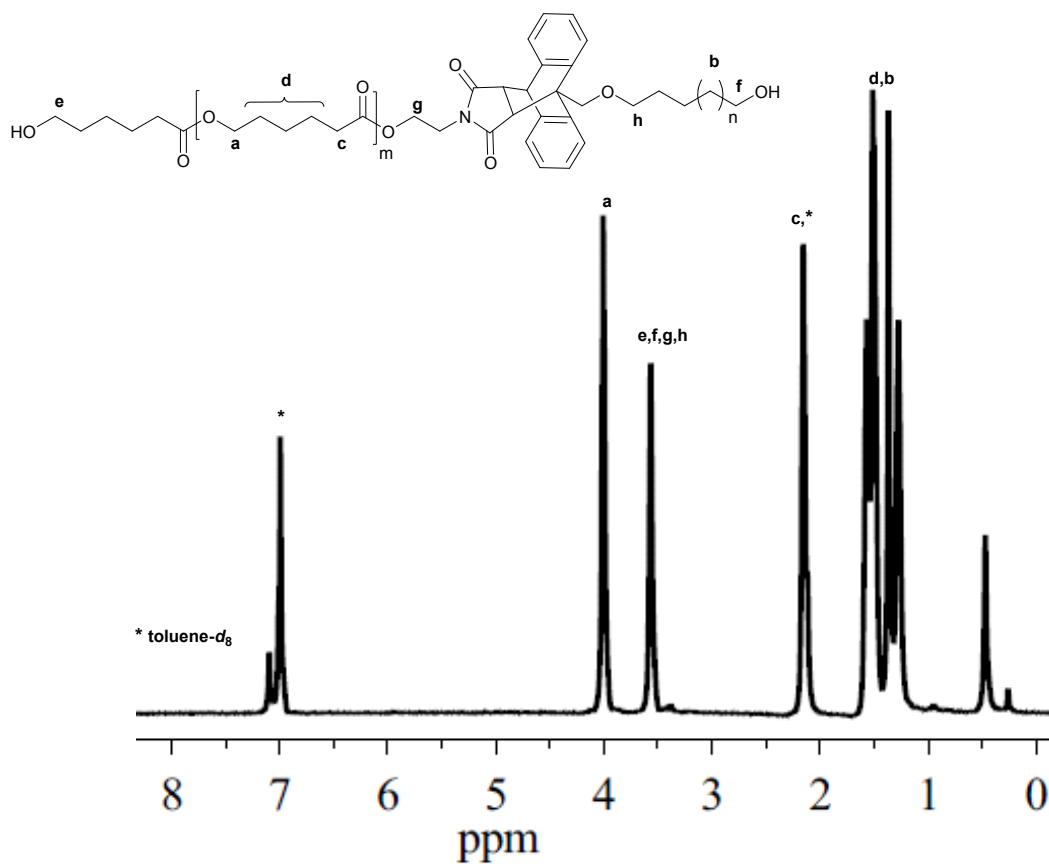


Figure S3. ^1H NMR spectrum of the diblock copolymer ($\text{PM}_{100}\text{-}b\text{-PCL}_{50}$) in toluene- d_8 at 80°C (600MHz).

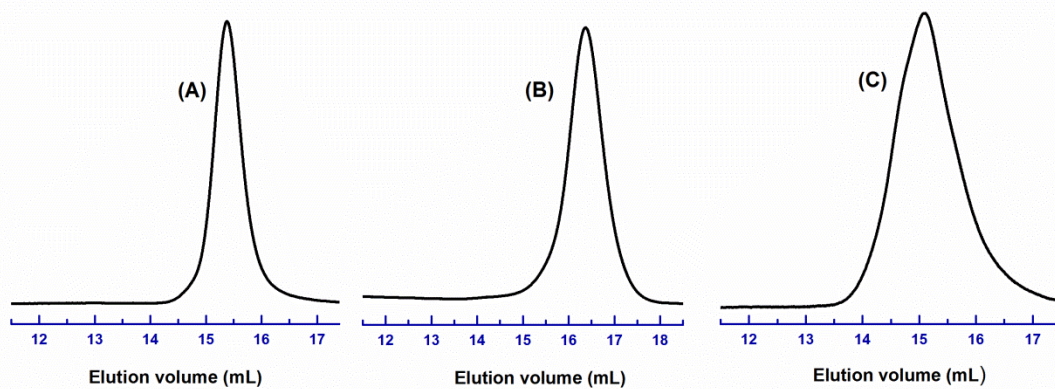


Figure S4. HT-SEC chromatograms of ant- $\text{PM}_{100}\text{-OH}$ (A), $\text{PCL}_{50}\text{-MI}$ from THF-SEC (B), and diblock copolymer $\text{PM}_{100}\text{-}b\text{-PCL}_{50}$ from HT-SEC (C).

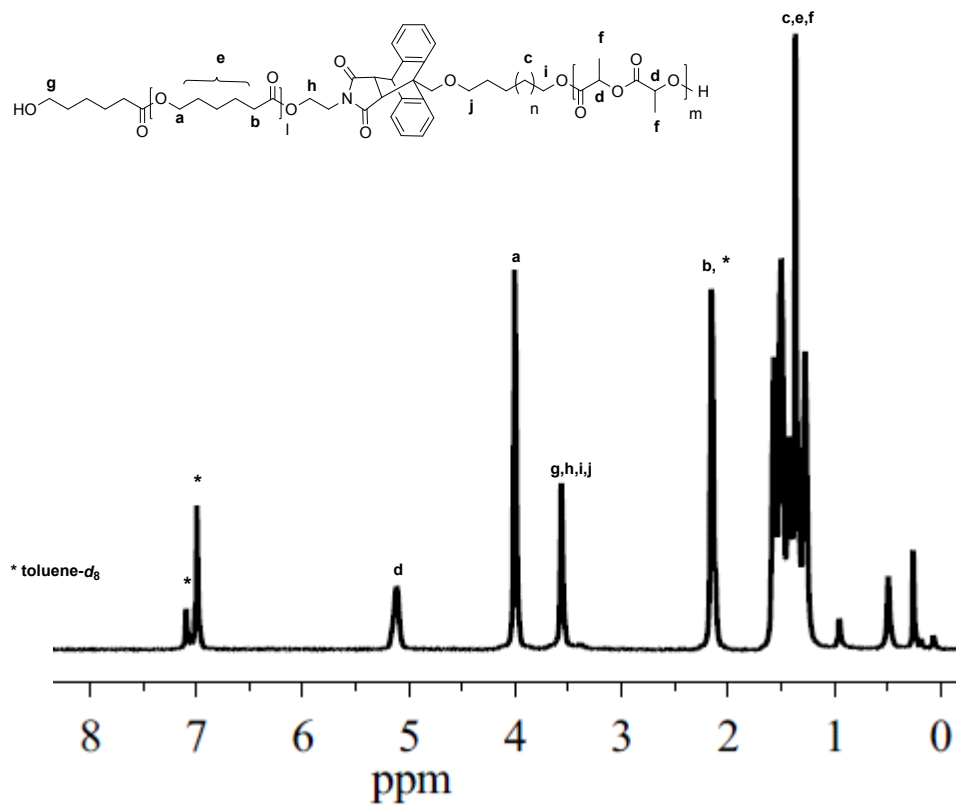


Figure S5. ^1H NMR spectrum of the triblock terpolymer ($\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$) in $\text{toluene-}d_8$ at 80°C (600MHz).

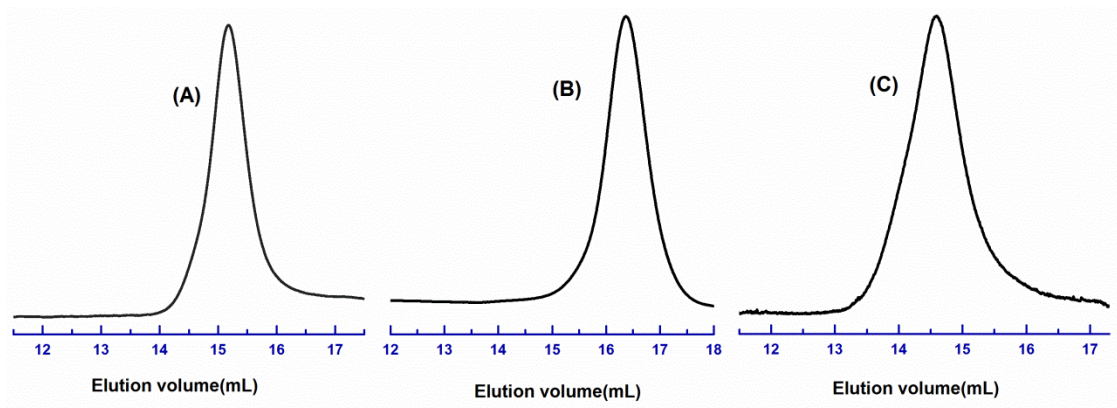


Figure S6. HT-SEC chromatograms of $\text{ant-PM}_{100}\text{-}b\text{-PLA}_{20}\text{-OH}$ (A), $\text{PCL}_{50}\text{-MI}$ from THF-SEC (B), and the triblock terpolymer $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$ from HT-SEC (C).

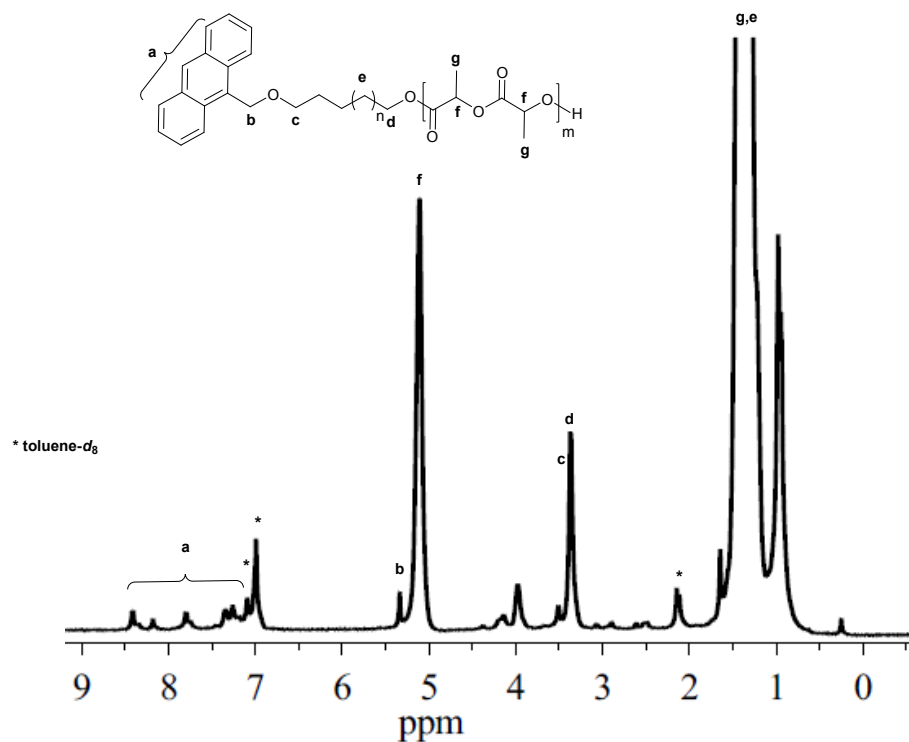


Figure S7. ^1H NMR spectrum of the diblock copolymer ($\text{ant-PM}_{100}\text{-}b\text{-PLA}_{20}$) in $\text{toluene-}d_8$ at 80°C (600MHz).

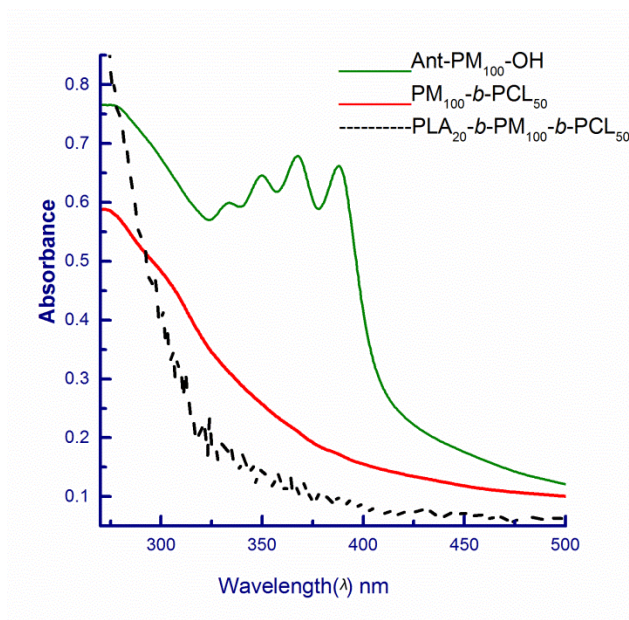


Figure S8. UV-VIS spectra of $\text{ant-PM}_{100}\text{-OH}$ ($C_0 = 6.2 \times 10^{-5} \text{ M}$), $\text{PM}_{100}\text{-}b\text{-PCL}_{50}$ ($C = 1.36 \times 10^{-5} \text{ M}$), and $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ ($C = 1.03 \times 10^{-5} \text{ M}$) in 1,2-dichloroethane at 80°C .

References

- 1 B. B. Busch , M. M. Paz , K. J. Shea , C. L. Staiger , J. M. Stoddard , J. R. Walker , X.-Z. Zhou , and H. Zhu *J. Am. Chem. Soc.*, 2002, **124**, 3636–3646.
- 2 G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. J. L. M. Cornelissen and K. Velonia, *J. Am. Chem. Soc.* 2005, **127** , 2966–2973.