

SUPPORTING INFORMATION

Injectable Thermoresponsive Hydrogels Based on (Me)PEG-Poly(Menthide) Amphiphilic Block Copolymers from Bioderived Lactone

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Processing Parameters of HPLC for Paclitaxel Anticancer Drug

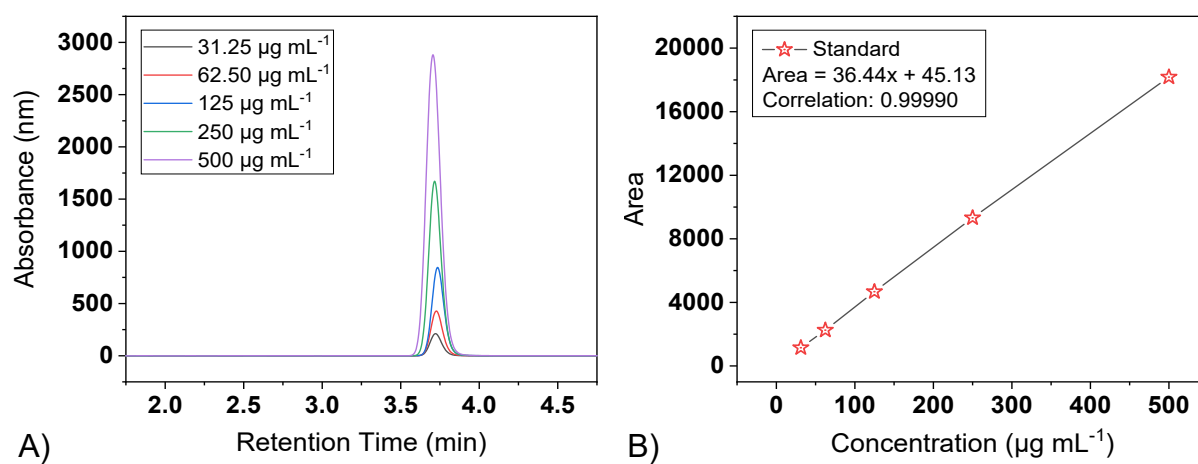


Figure S1. Typical HPLC chromatogram (A) and calibration curve (B) for various concentrations of paclitaxel anticancer drug at 227 nm.

Spectroscopic Characterization: ATR-FTIR Spectra

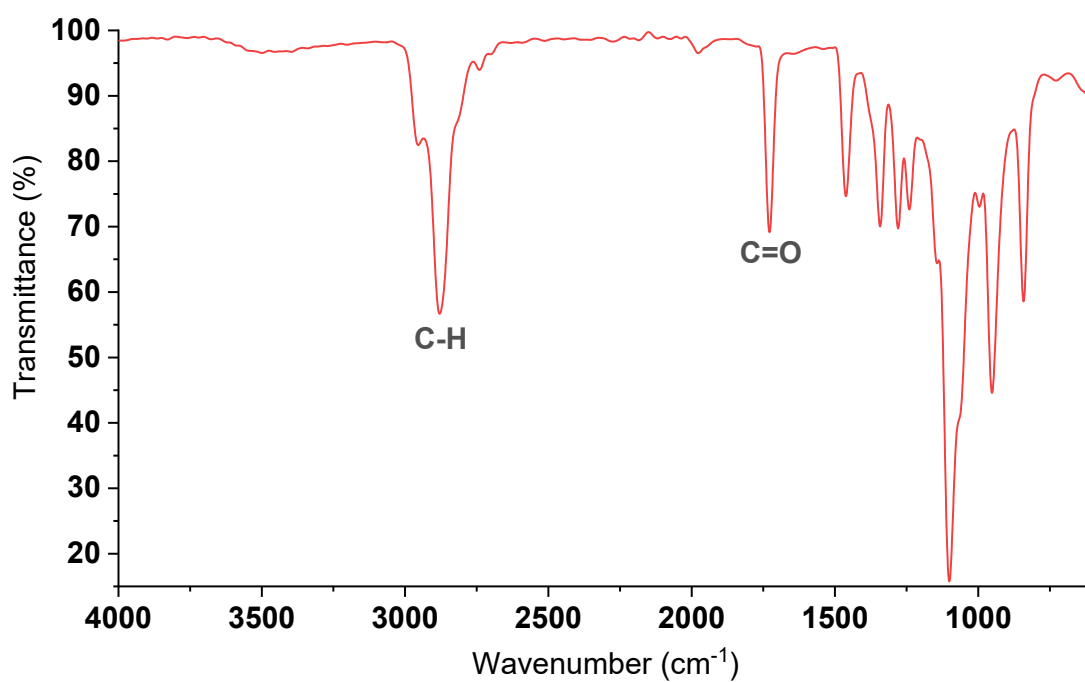


Figure S2. ATR-FTIR spectrum of MePEG-PM diblock copolymer **5**

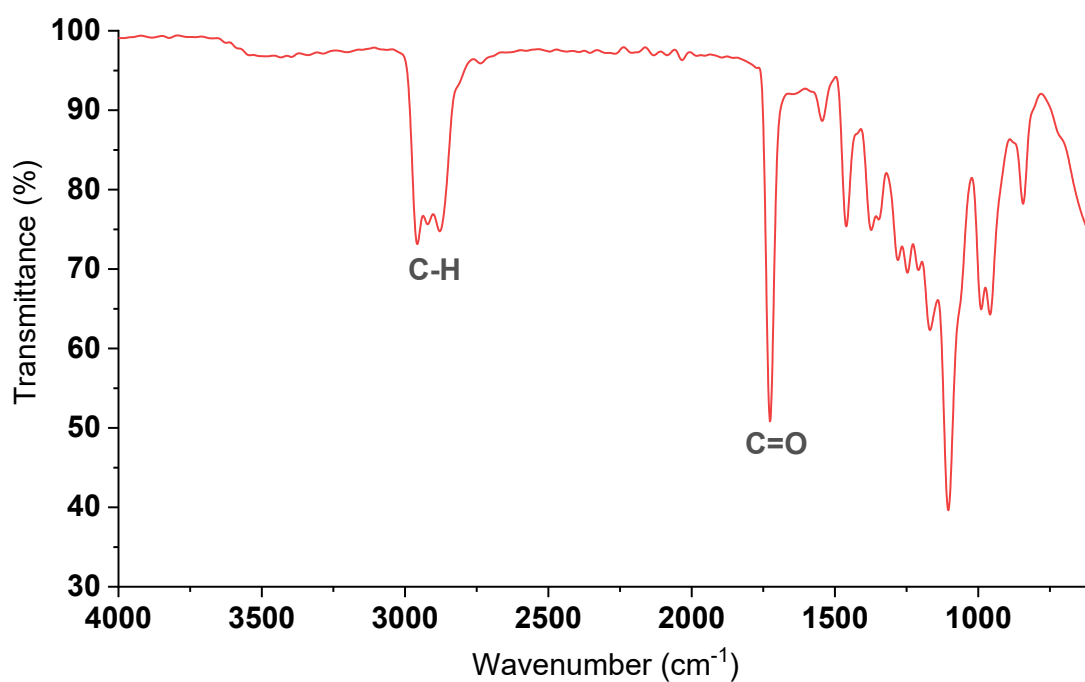


Figure S3. ATR-FTIR spectrum of MePEG-PM diblock copolymer **6**

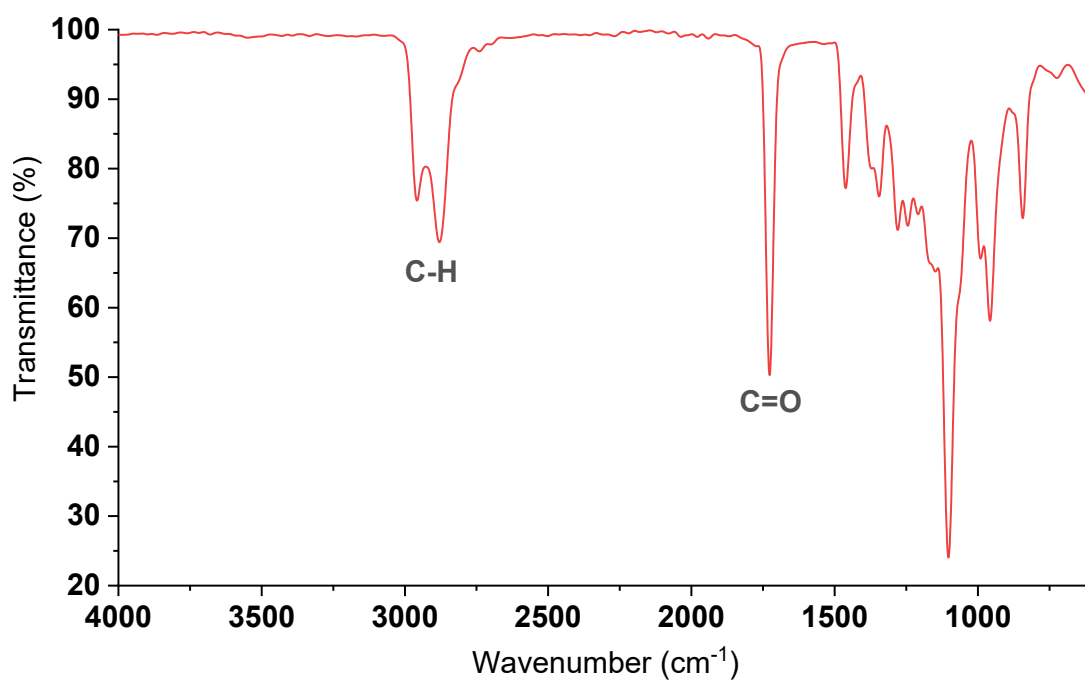


Figure S4. ATR-FTIR spectrum of MePEG-PM diblock copolymer **7**

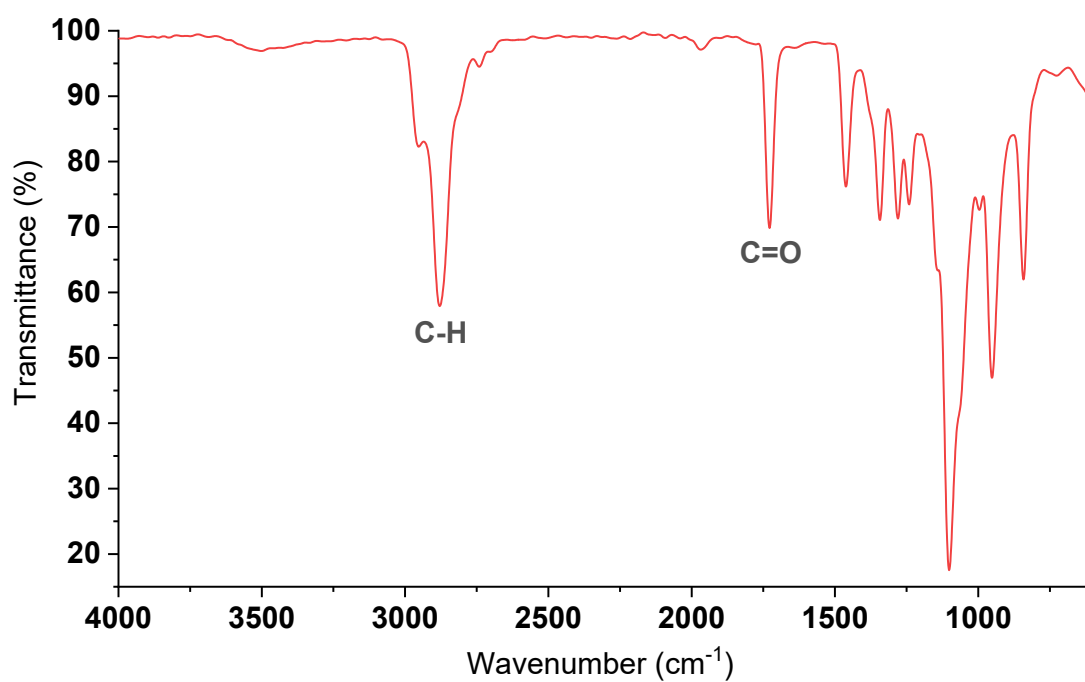


Figure S5. ATR-FTIR spectrum of PM-PEG-PM triblock copolymer **9**

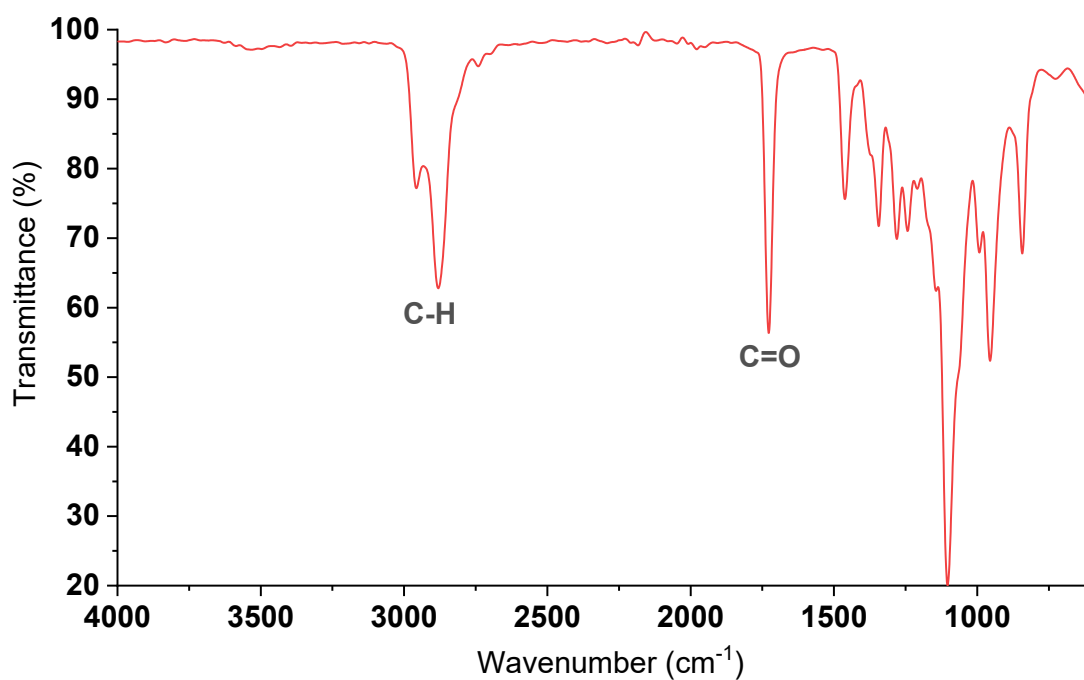


Figure S6. ATR-FTIR spectrum of PM-PEG-PM triblock copolymer **10**

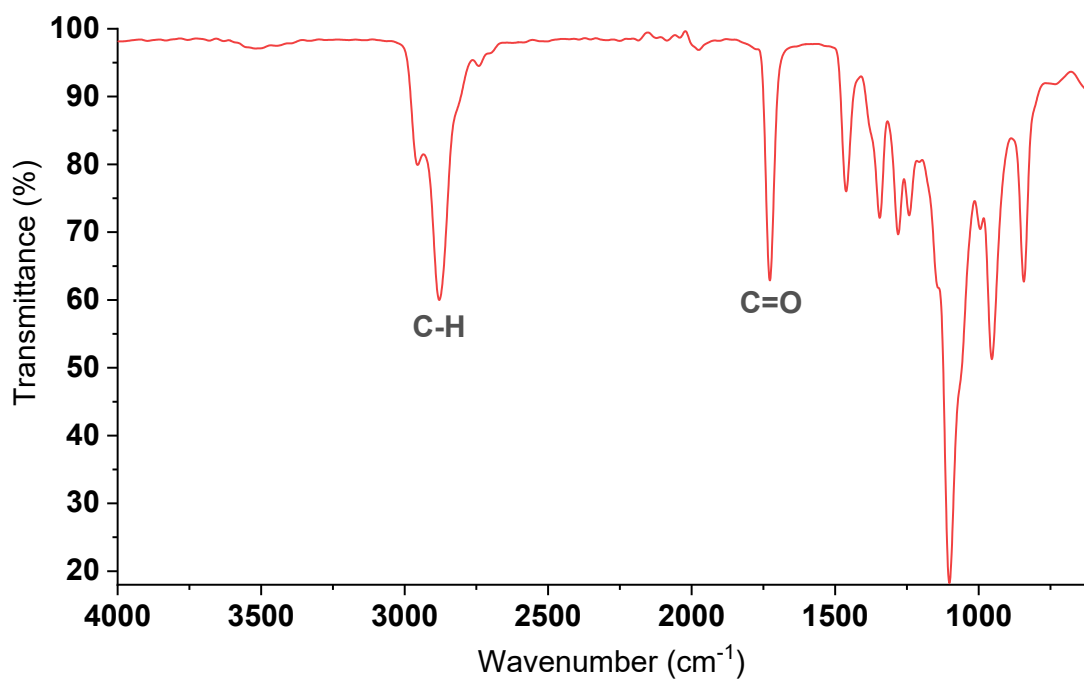


Figure S7. ATR-FTIR spectrum of PM-PEG-PM triblock copolymer **11**

Spectroscopic Characterization: 1D NMR Spectra

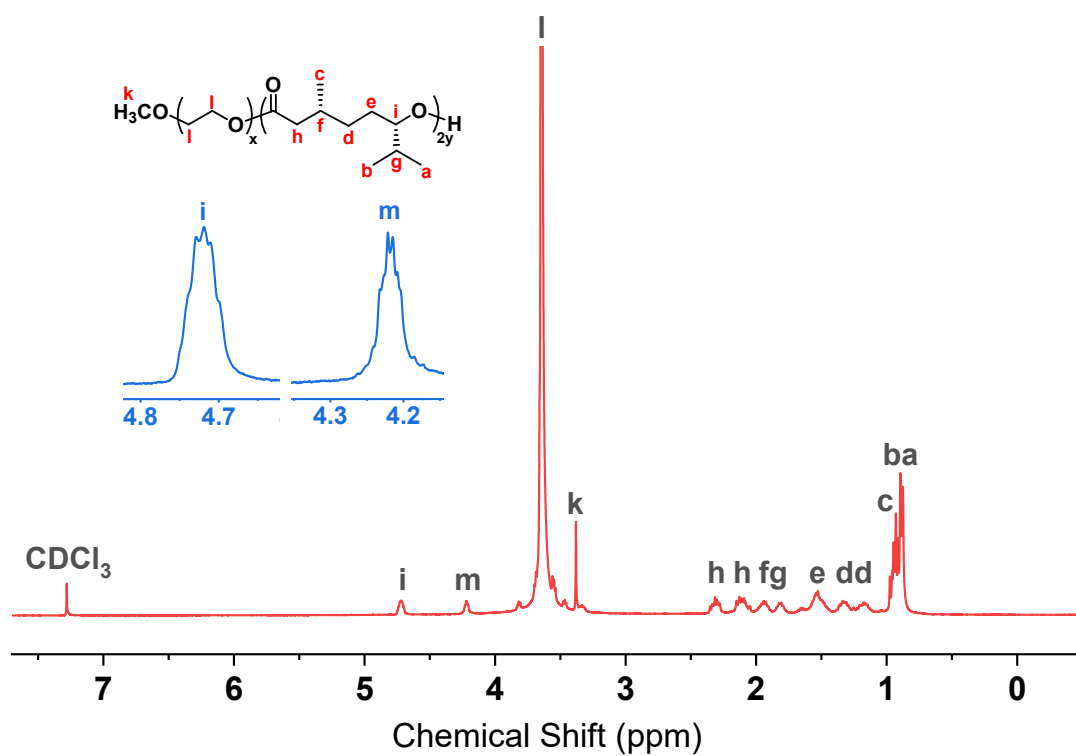


Figure S8. ¹H NMR spectrum of MePEG-PM diblock copolymer 5

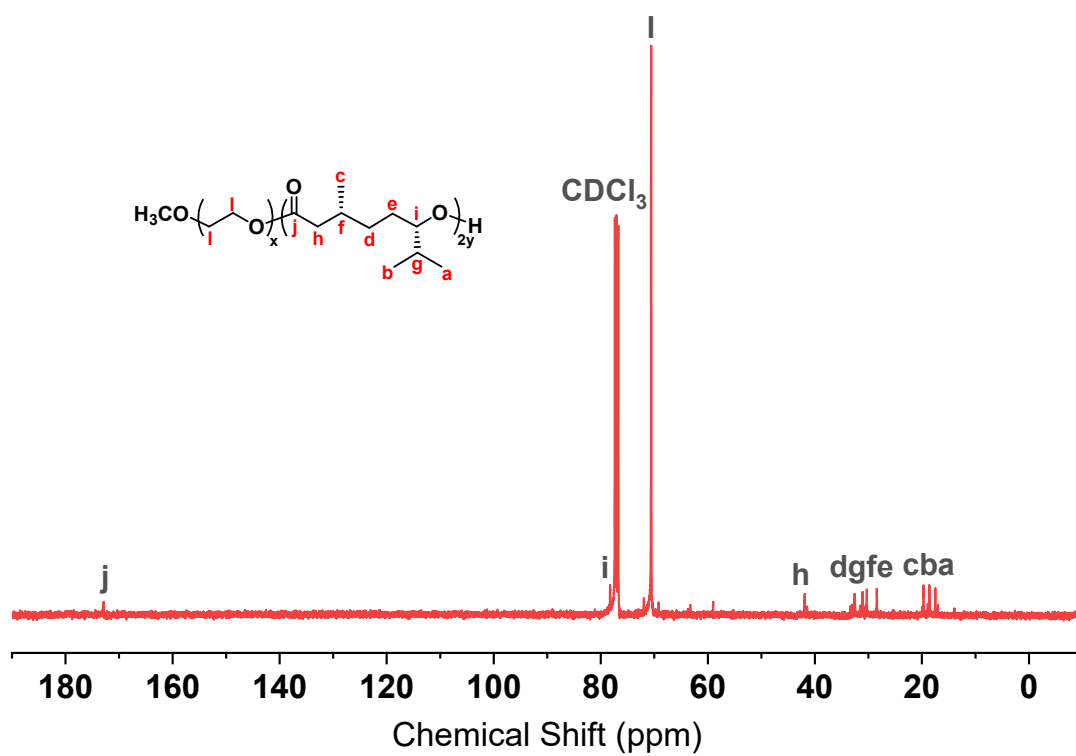


Figure S9. ¹³C NMR spectrum of MePEG-PM diblock copolymer 5

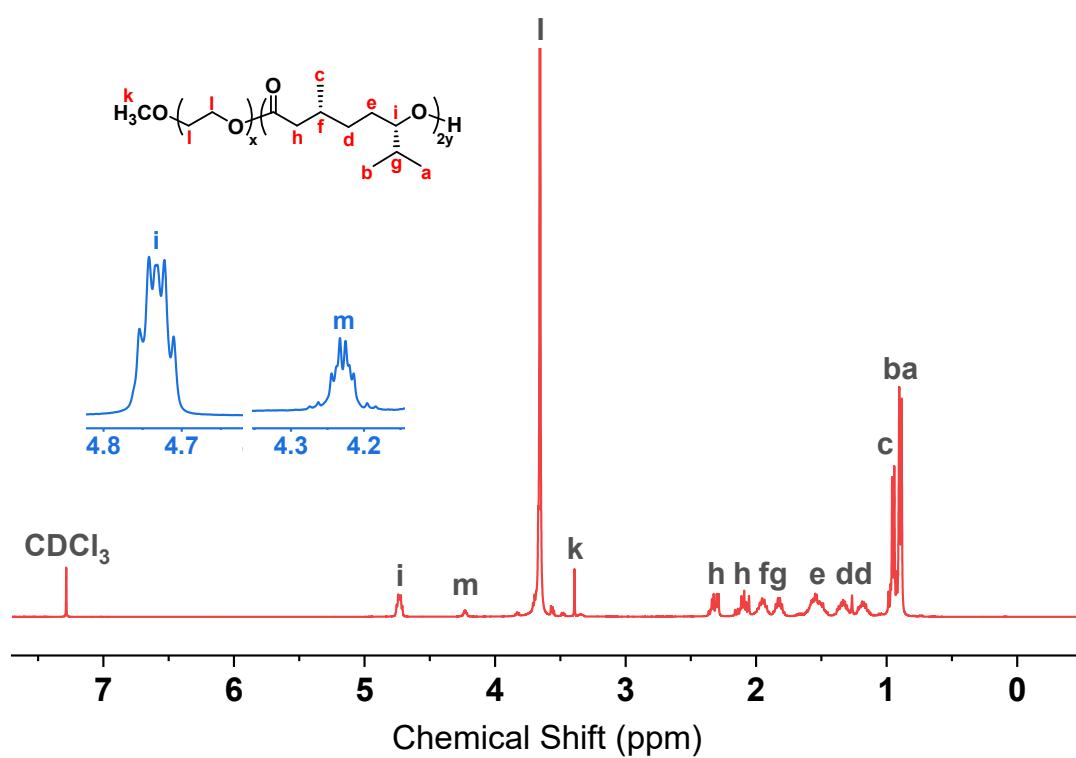


Figure S10. ¹H NMR spectrum of MePEG-PM diblock copolymer **6**

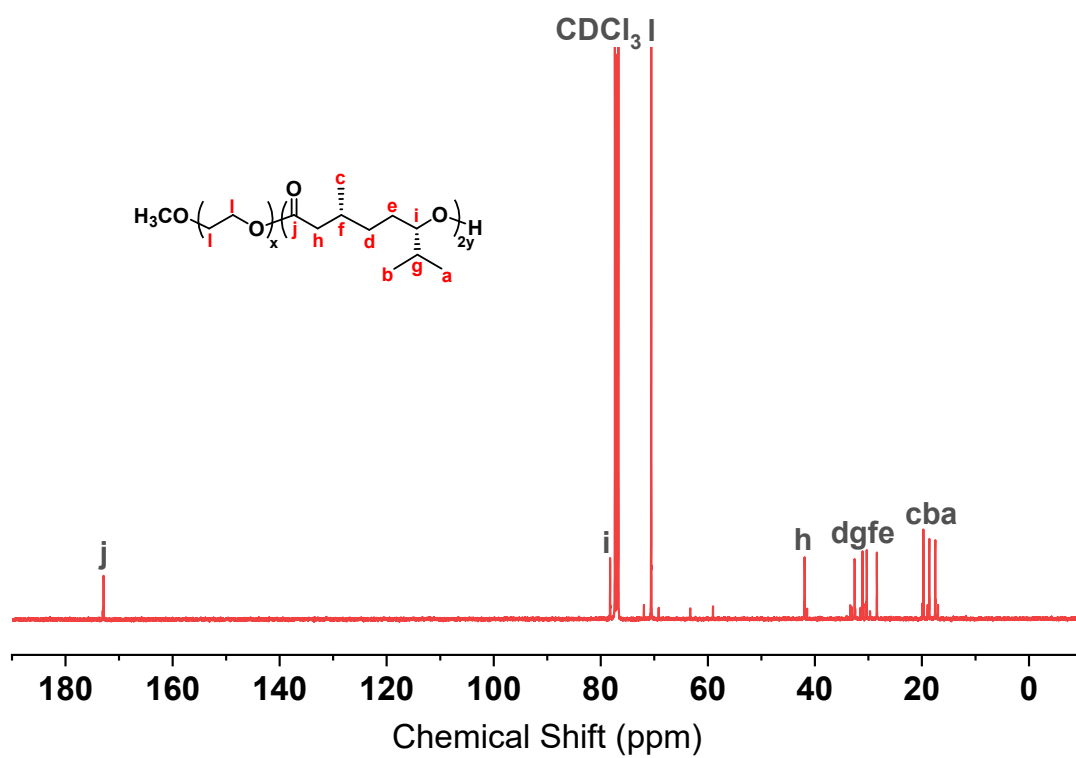


Figure S11. ¹³C NMR spectrum of MePEG-PM diblock copolymer **6**

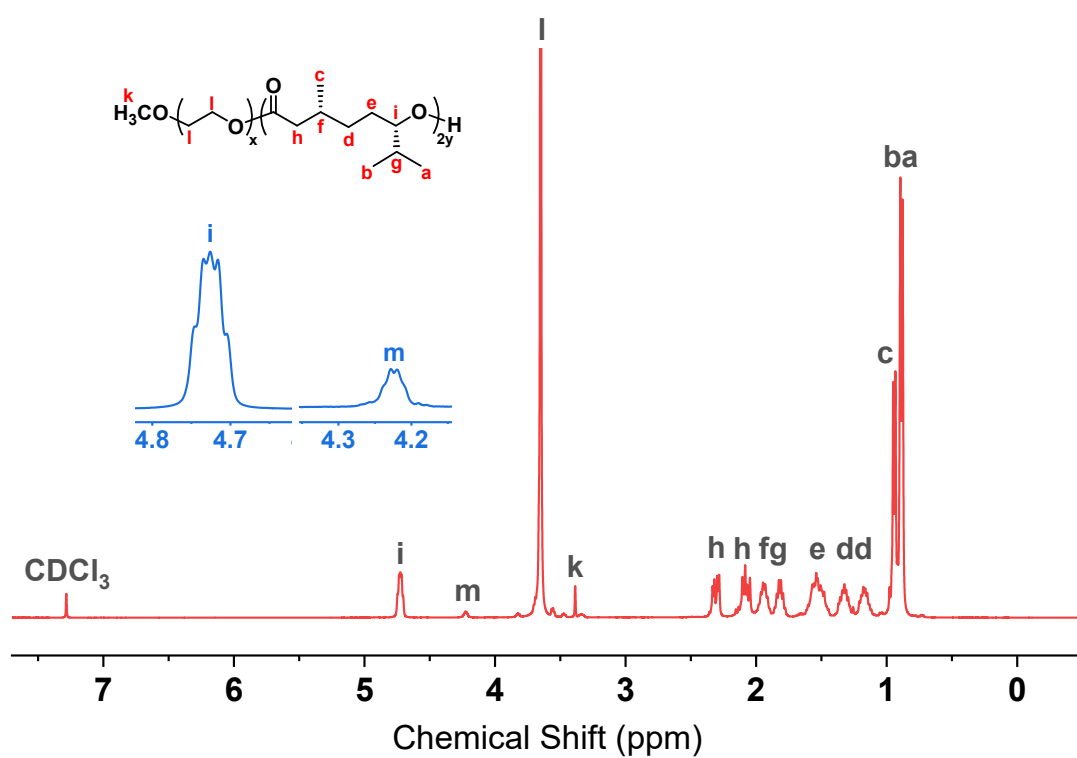


Figure S12. ^1H NMR spectrum of MePEG-PM diblock copolymer 7

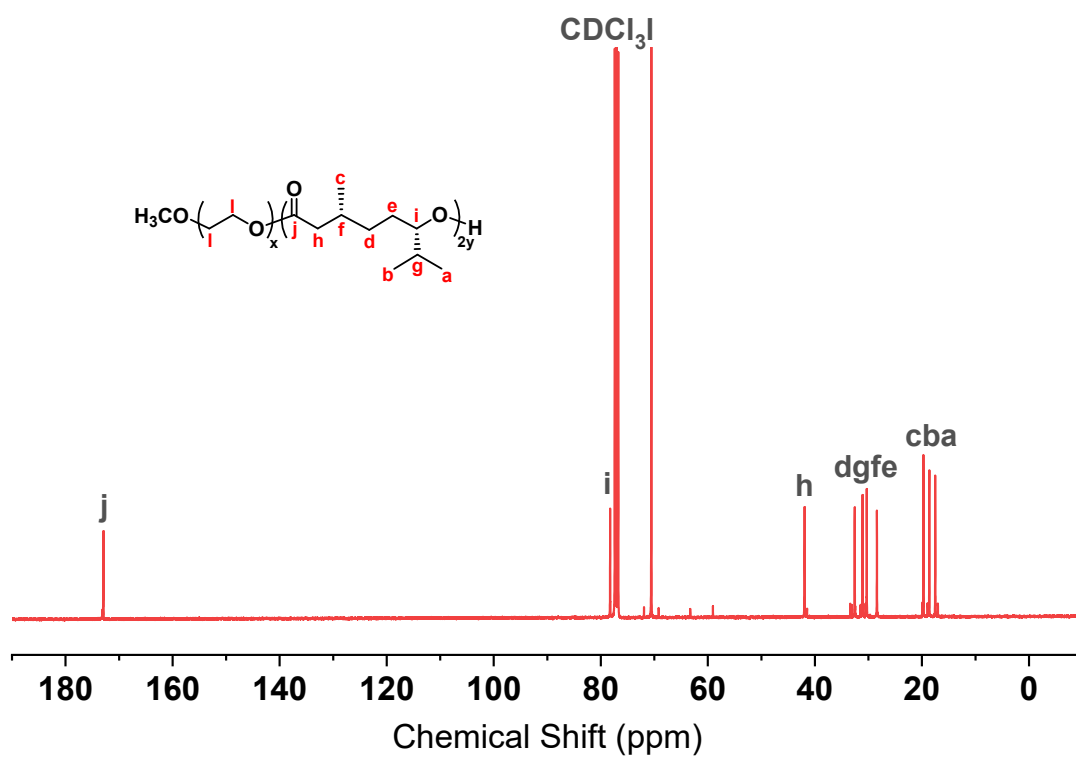


Figure S13. ^{13}C NMR spectrum of MePEG-PM diblock copolymer 7

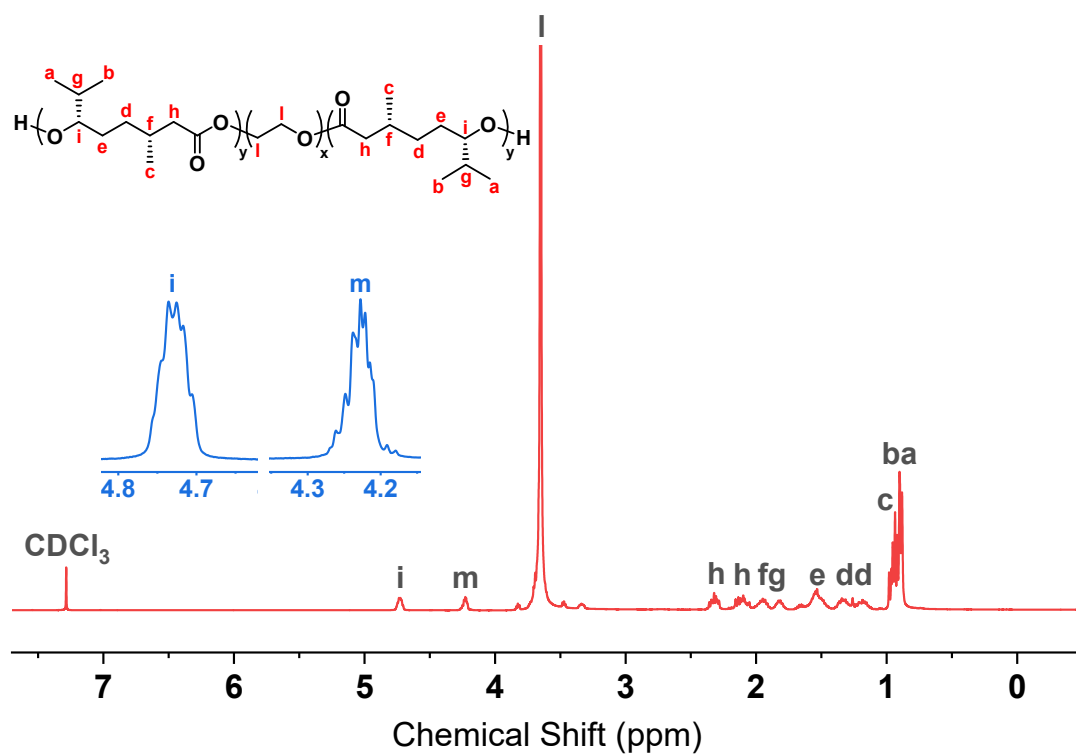


Figure S14. ¹H NMR spectrum of PM-PEG-PM triblock copolymer **9**

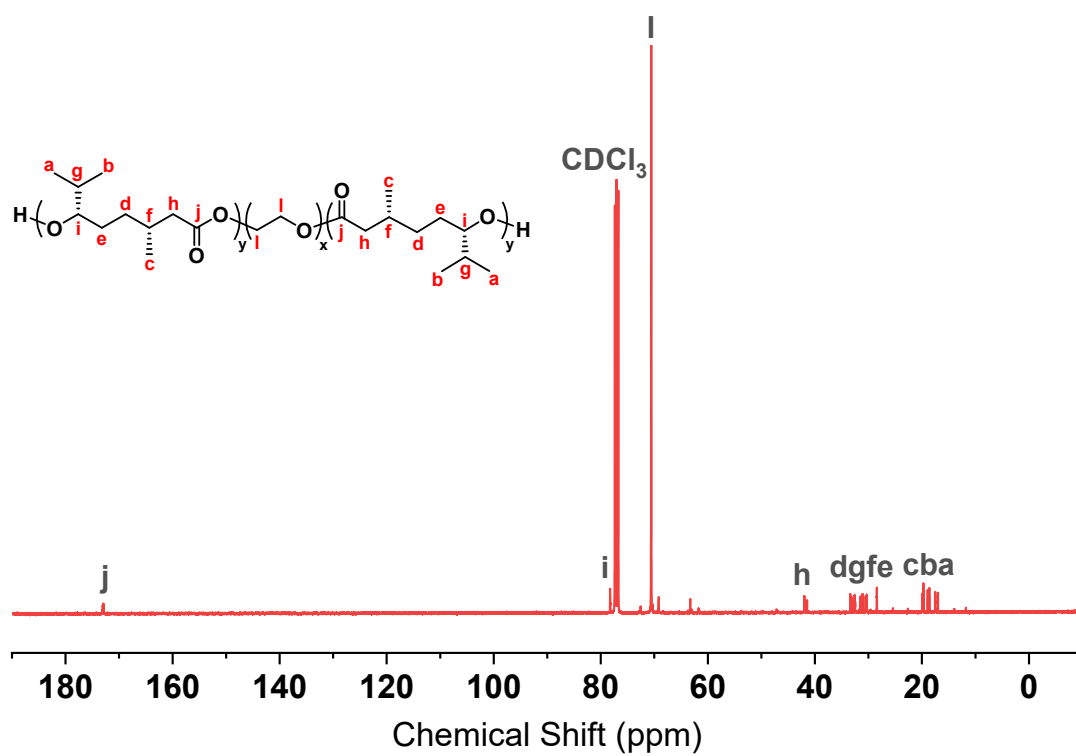


Figure S15. ¹³C NMR spectrum of PM-PEG-PM triblock copolymer **9**

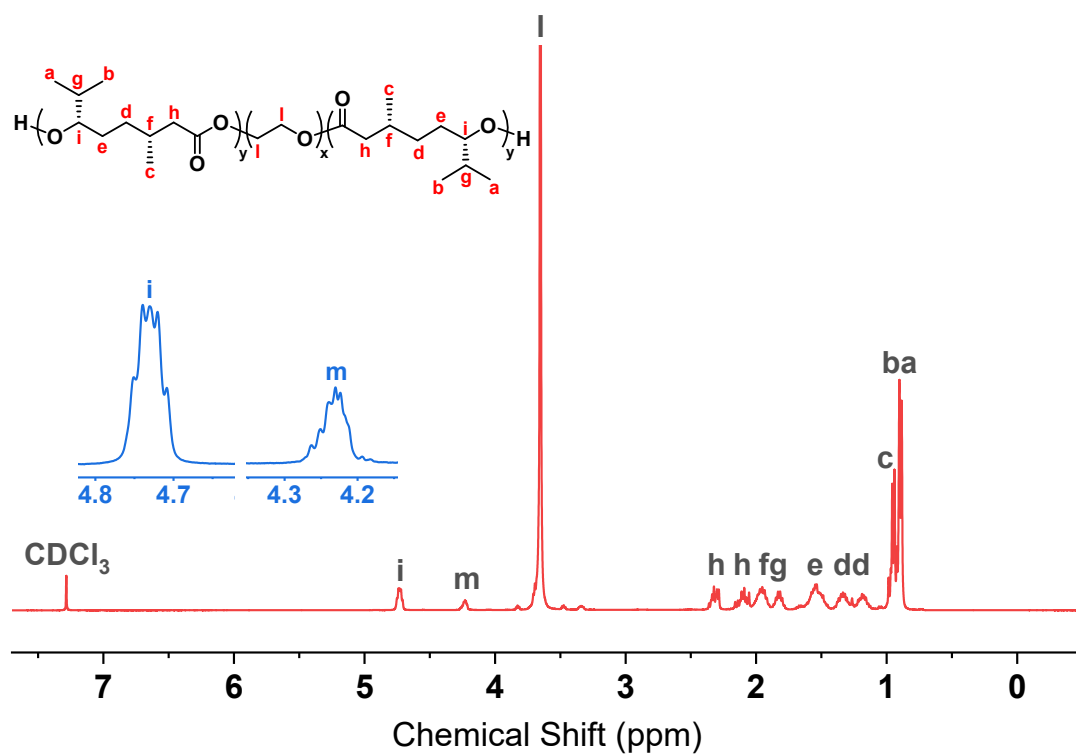


Figure S16. ^1H NMR spectrum of PM-PEG-PM triblock copolymer **10**

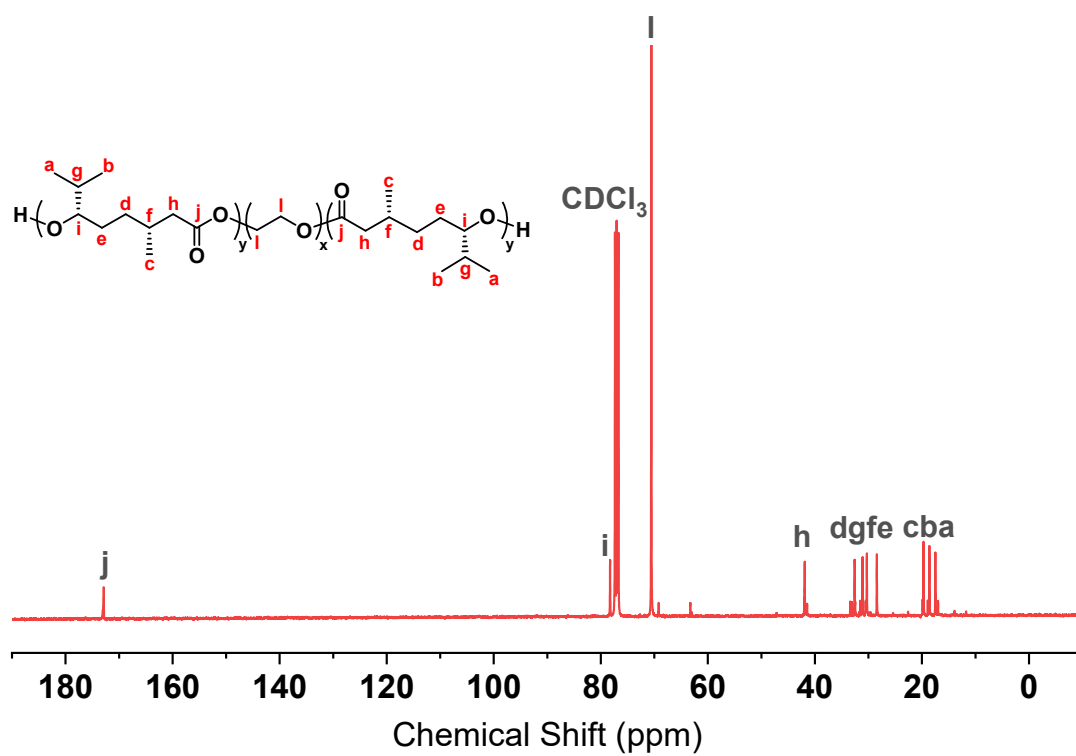


Figure S17. ^{13}C NMR spectrum of PM-PEG-PM triblock copolymer **10**

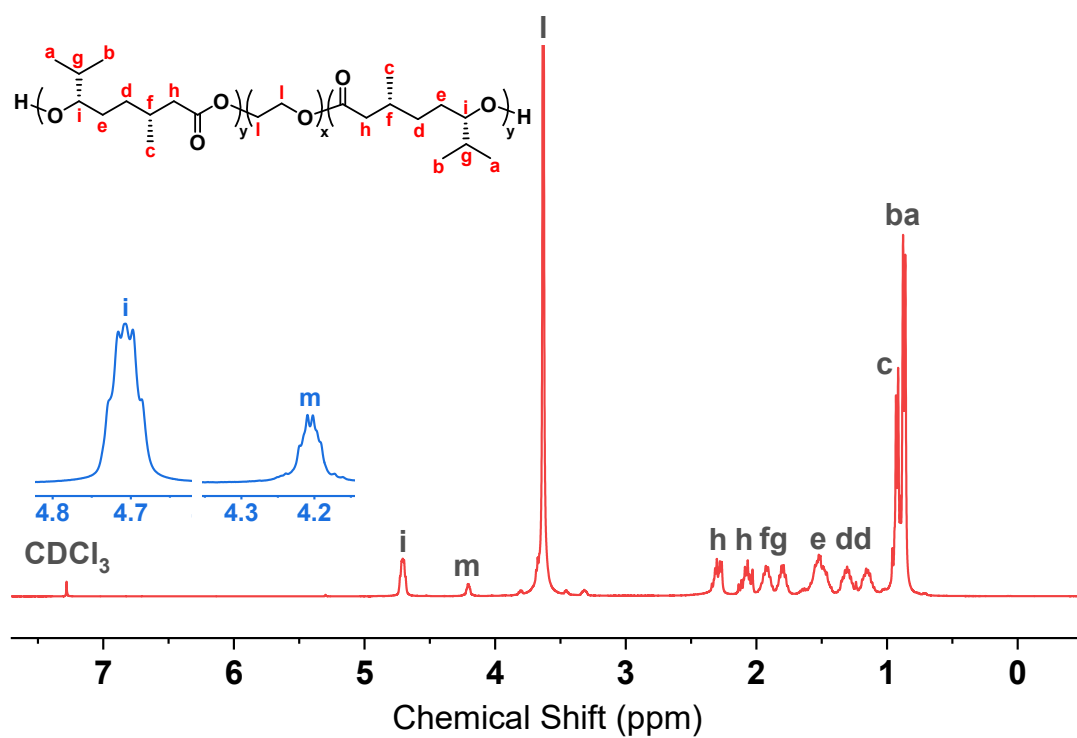


Figure S18. ^1H NMR spectrum of PM-PEG-PM triblock copolymer 11

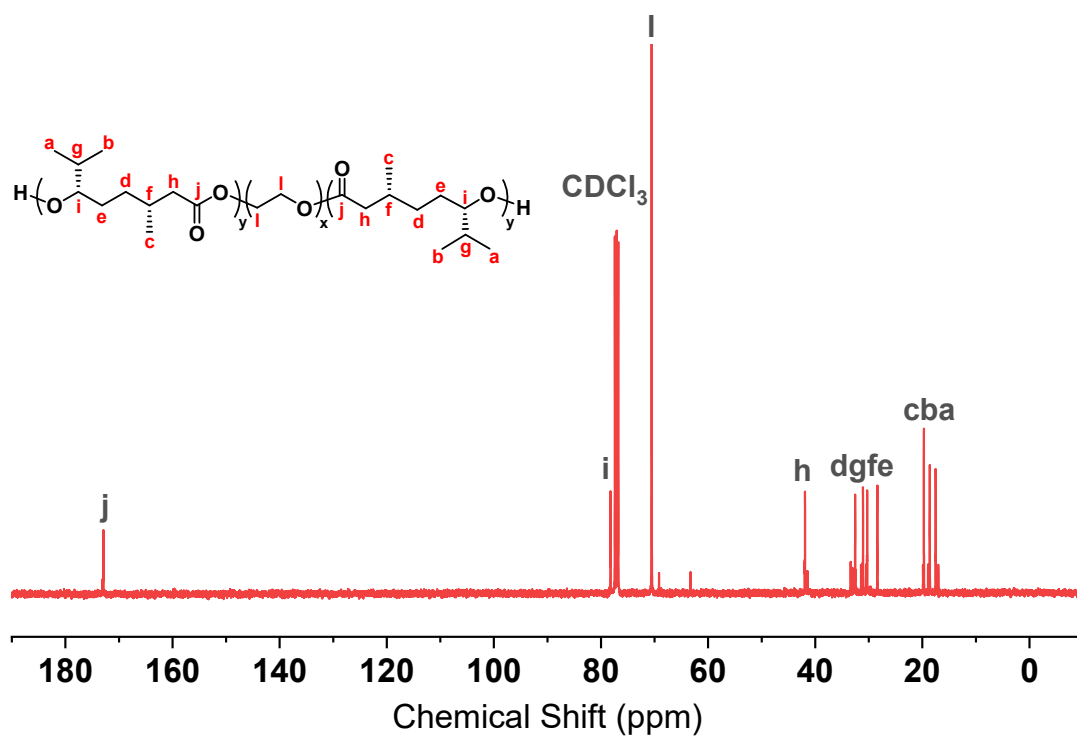


Figure S19. ^{13}C NMR spectrum of PM-PEG-PM triblock copolymer 11

Spectroscopic Characterization: 2D NMR Spectra

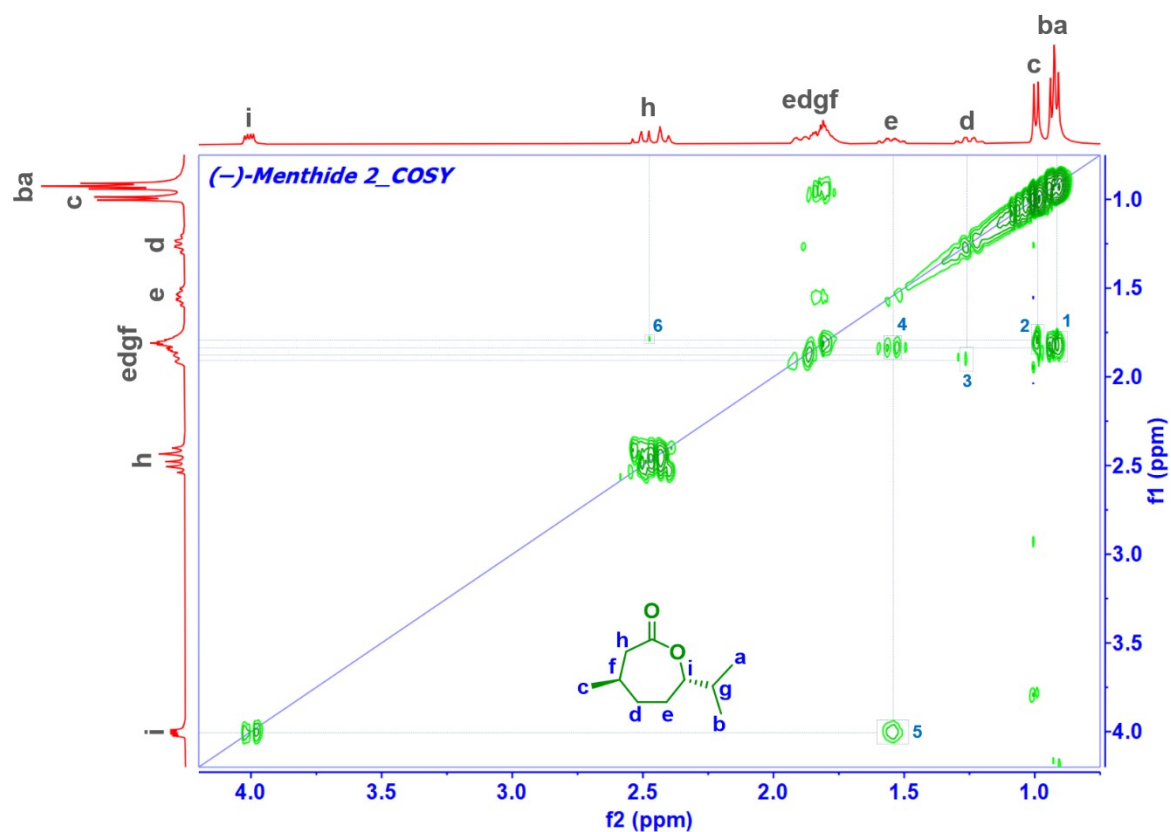


Figure S20. COSY 2D NMR spectrum (in CDCl_3) of (-)-menthoxide (2)

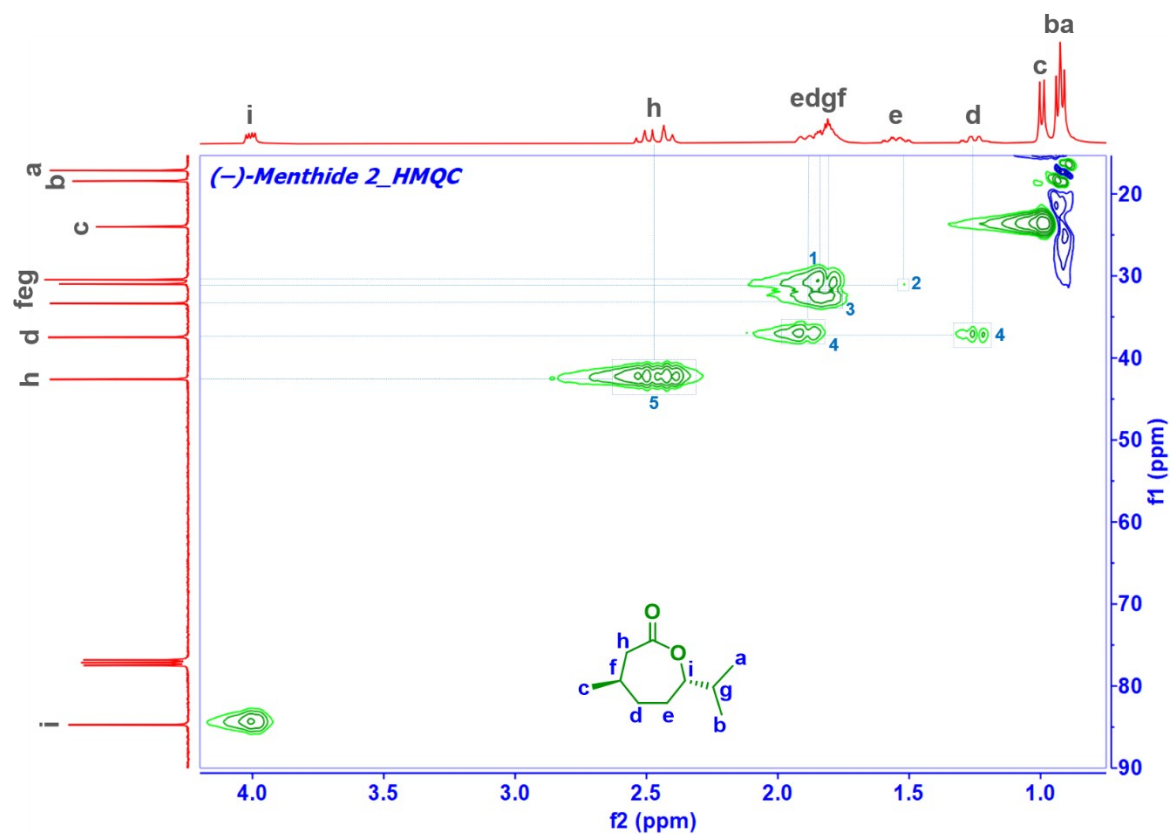


Figure S21. HMBC 2D NMR spectrum (in CDCl_3) of (-)-menthoxide (2)

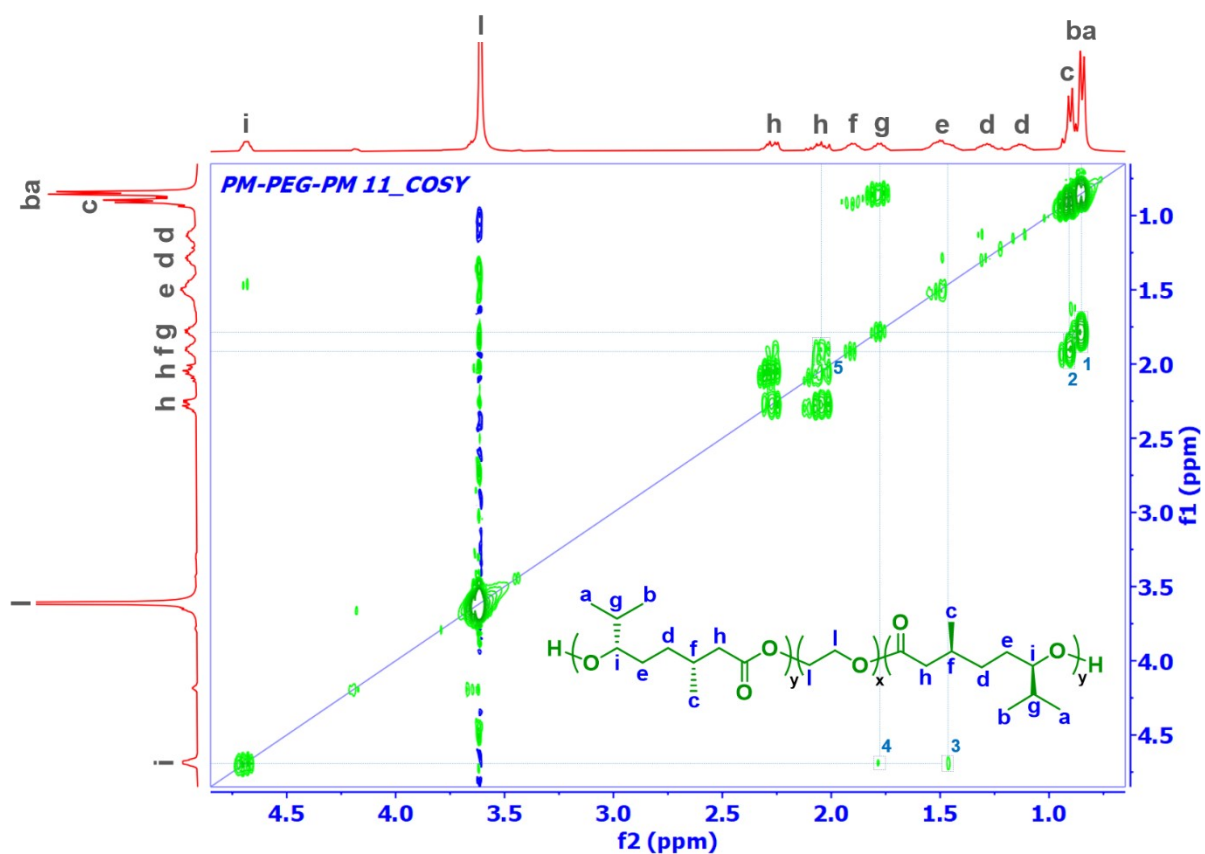


Figure S22. COSY 2D NMR spectrum (in CDCl_3) of PM-PEG-PM triblock copolymer **11**

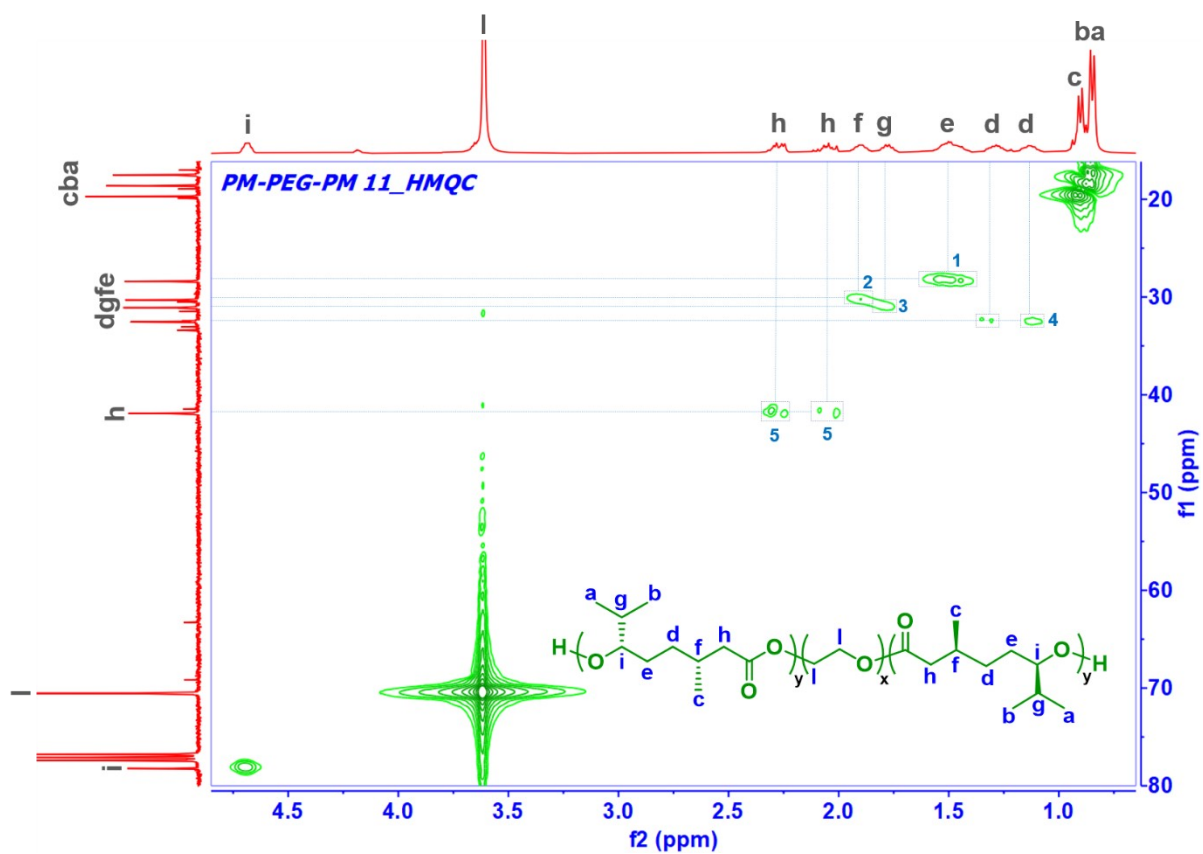


Figure S23. HMQC 2D NMR spectrum (in CDCl_3) of PM-PEG-PM triblock copolymer **11**

DLS Analysis

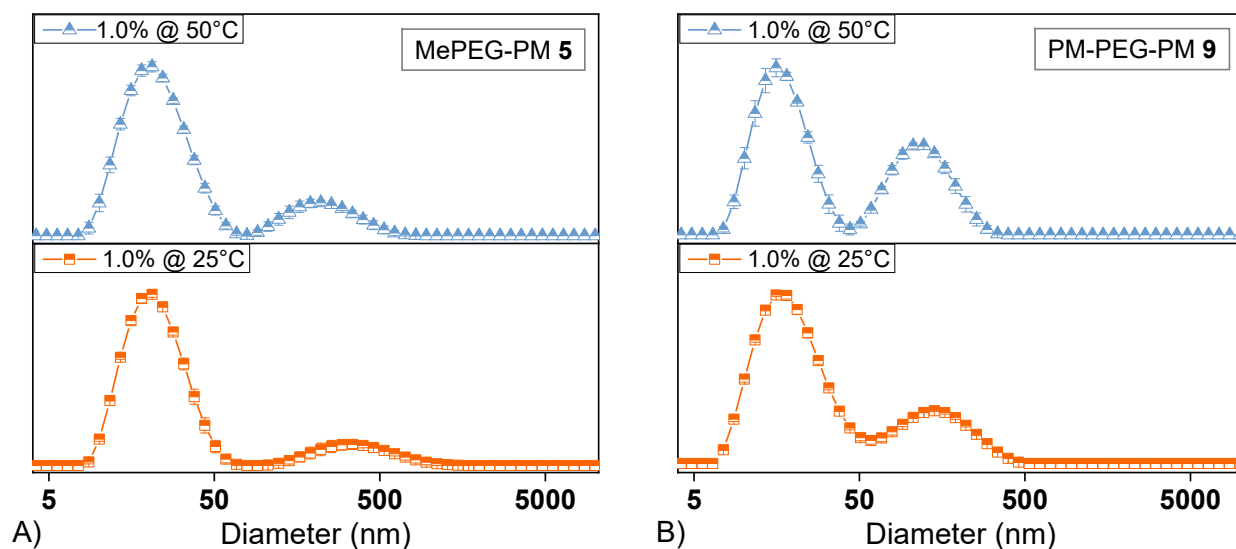


Figure S24. DLS curves of diblock hydrogel **5** (1.0 wt%) (A) and triblock hydrogel **9** in water (1.0 wt%) at different temperatures (B).

Table S1. Hydrodynamic diameters of diblock hydrogels **5**, **6** and triblock hydrogels **9**, **10** at 1.0 wt% concentration by DLS

ID	Temperature (°C)	Peak 1		Peak 2		Peak 3	
		Average ± S.D.	% ± S.D.	Average ± S.D.	% ± S.D.	Average ± S.D.	% ± S.D.
MePEG-PM 5	25 °C	23.2 ± 0.6	86.4 ± 1.8	404.8 ± 71.0	13.6 ± 1.9		
	50 °C	23.5 ± 0.5	82.7 ± 1.2	248.6 ± 29.6	17.3 ± 1.1		
MePEG-PM 6	25 °C	41.6 ± 0.4	95.2 ± 1.0			2600 ± 1016	4.8 ± 1.0
	50 °C	38.5 ± 1.2	91.6 ± 1.6			963.4 ± 325.6	8.4 ± 1.6
PM-PEG-PM 9	25 °C	21.1 ± 0.1	74.2 ± 0.3	155.2 ± 3.2	25.8 ± 0.3		
	50 °C	17.7 ± 0.8	61.6 ± 1.4	124.9 ± 5.0	38.4 ± 1.4		
PM-PEG-PM 10	25 °C			172.6 ± 4.3	100.0 ± 0.0		
	50 °C			202.6 ± 25.9	100.0 ± 0.0		

Release Profiles

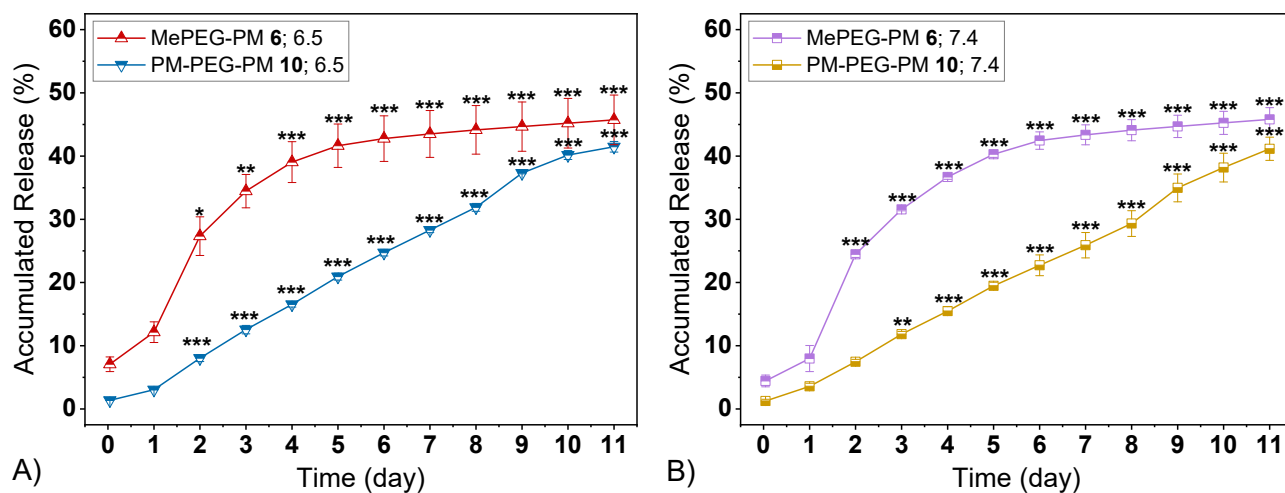


Figure S25. Comparison of the release profiles of diblock hydrogel **6** and triblock hydrogel **10** at pH 6.5 (A) and pH 7.4 with statistical significance (B). Data are presented as mean values $\pm$ SDs ($n = 3$; one-way ANOVA; * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$; compared with the respective control groups of paclitaxel release at 1st h).