Polymer Chemistry

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Supporting Information

New Biomaterials from Renewable Resources - Amphiphilic Block Copolymers from δ-Decalactone

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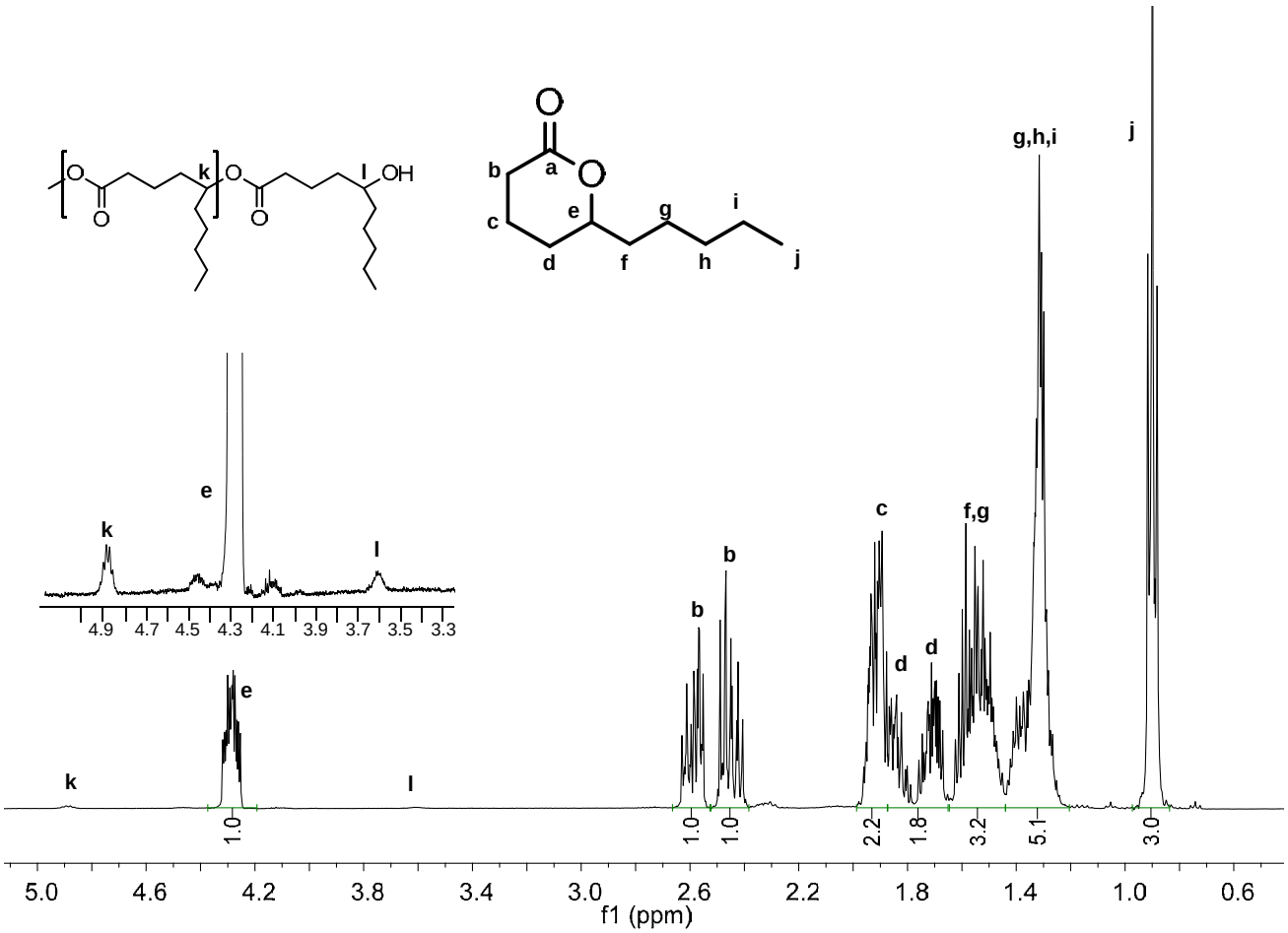


Figure S1 ^{1}H NMR of commercially available δ-decalactone acquired in $CDCl_3$. Inset showing enlarged region of spectrum between 3.3 and 5.0 ppm.

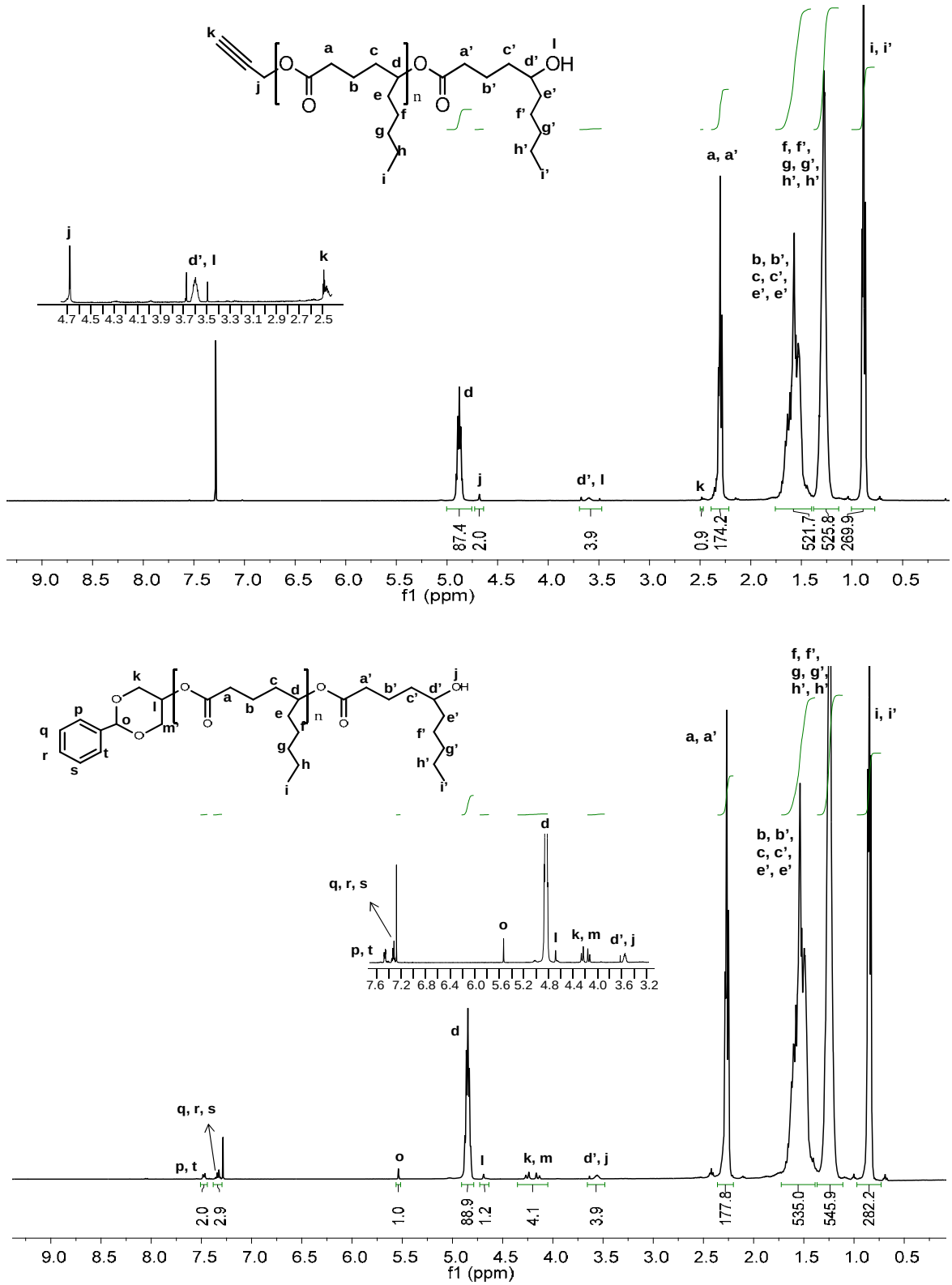


Figure S2 ^{1}H NMR spectra of propargyl-PDL and BZD-PDL in $CDCl_3$. Inset showing enlarged area of ^{1}HNMR to aid visualisation of diagnostic proton peaks. Lettering adjacent to positions on the chemical structures refer to protons labelled on the NMR spectra

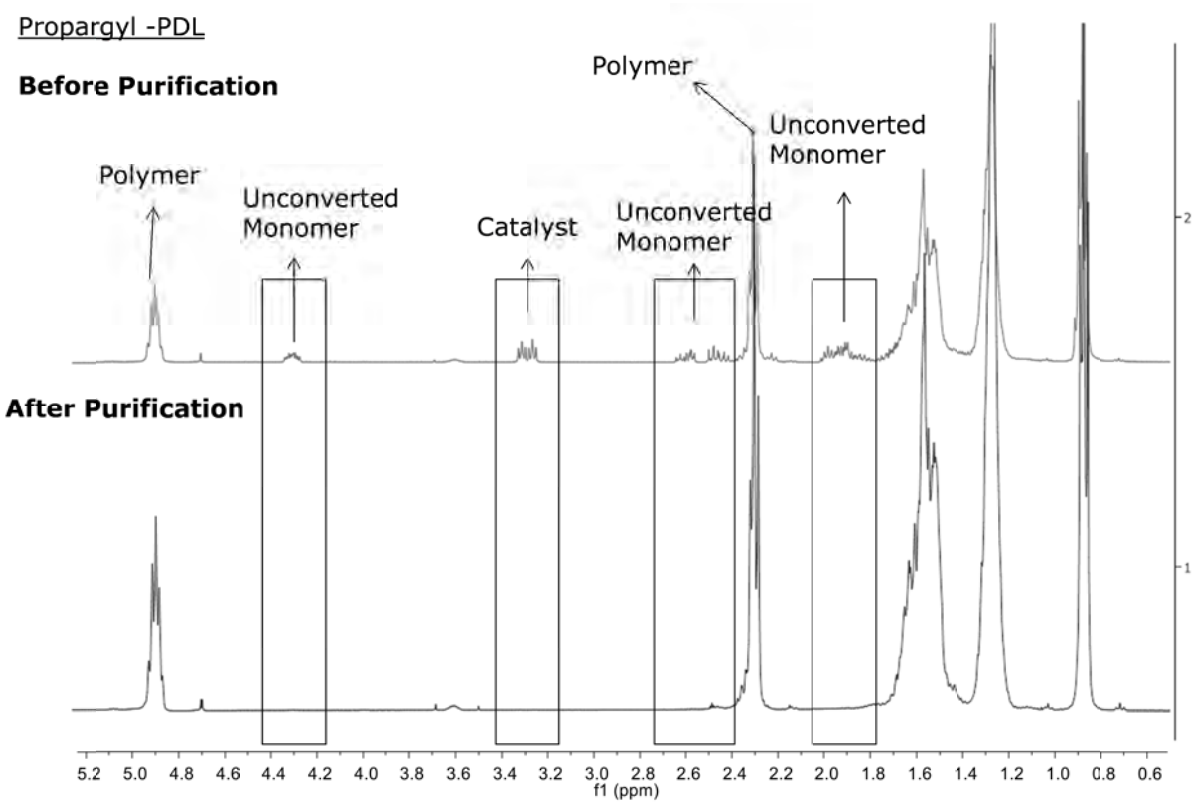


Figure S3 ^{1}H NMR spectra of propargyl PDL before and after purification of polymer by precipitation of quenched reaction mixtures in cold methanol.

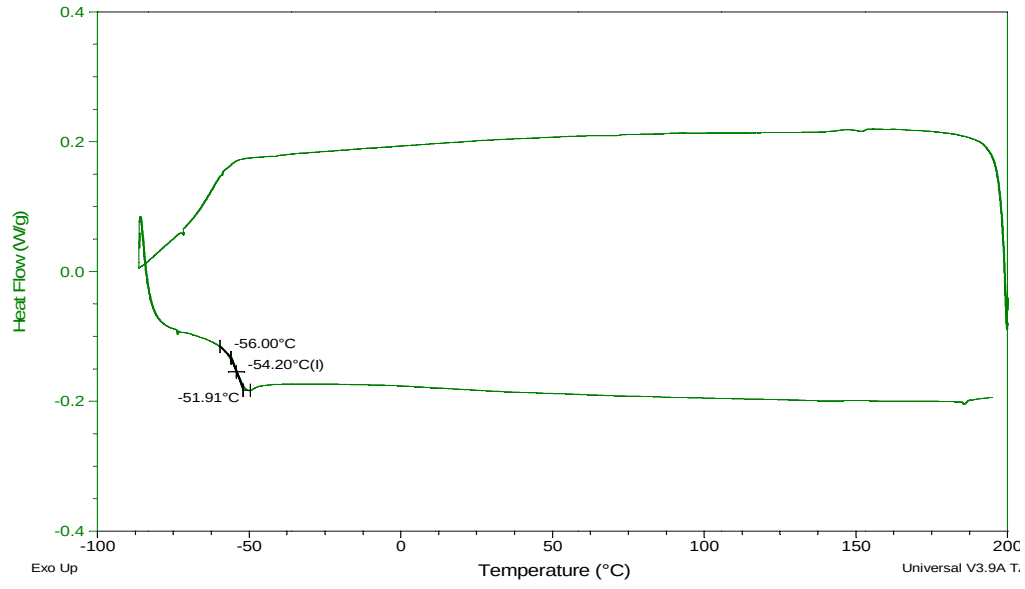


Figure S4. DSC plot of Propargyl PDL. The presented trace was acquired from the second heating/cooling cycle.

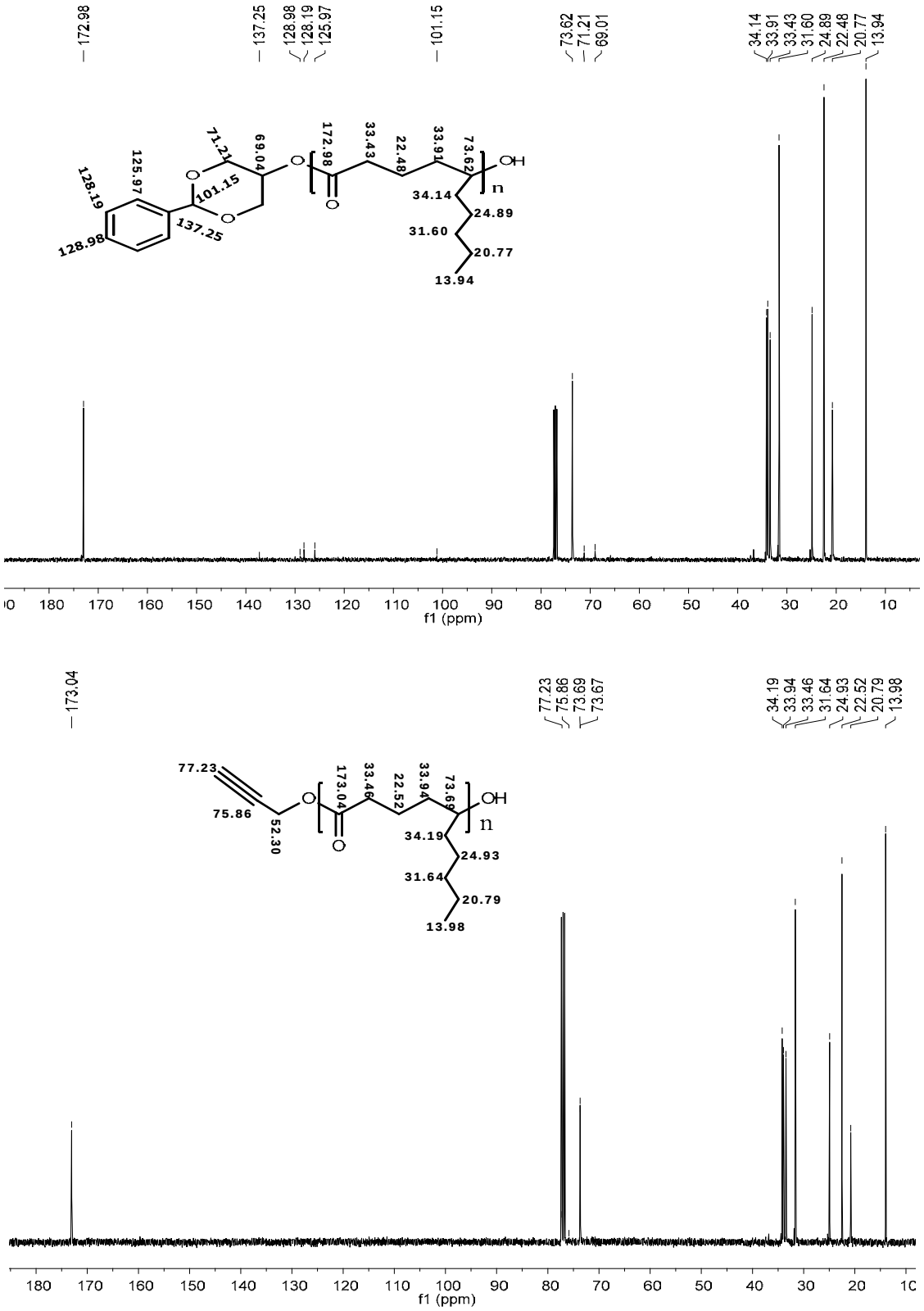
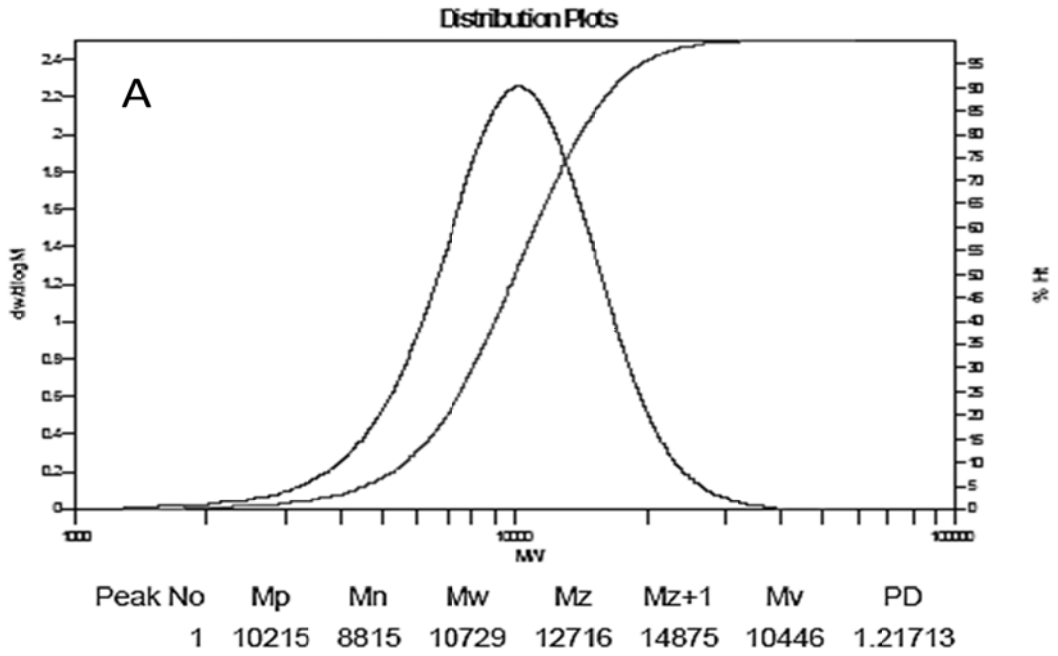
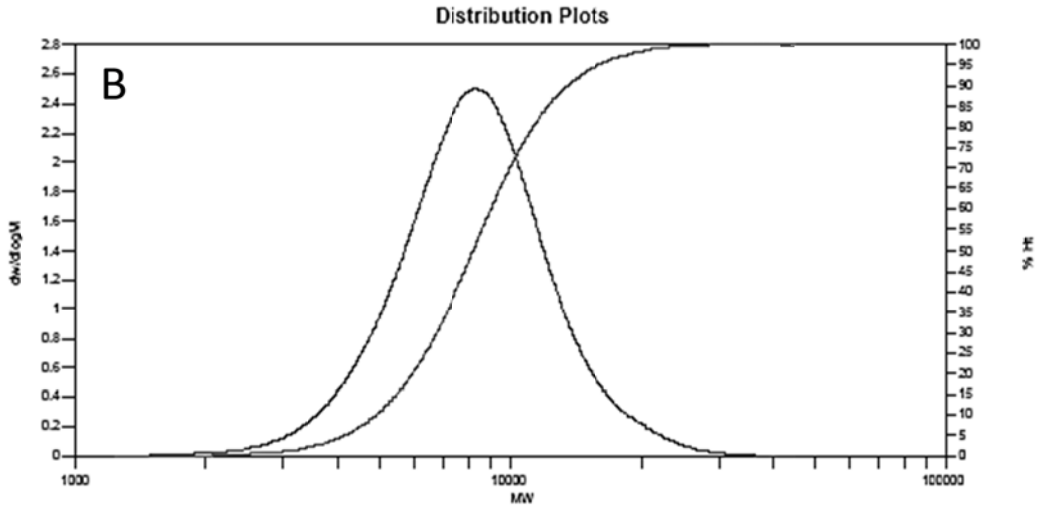


Figure S5. ^{13}C NMR of BZD-PDL and propargyl-PDL in $CDCl_3$.



Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	10215	8815	10729	12716	14875	10446	1.21713



Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	8341	7491	8834	10417	12369	8621	1.17928

Figure S6. SEC traces of (A) BZD-PDL and (B) propargyl-PDL, which were acquired using chloroform as the mobile phase. Average molecular weights were calculated against polystyrene as the molar mass standard.

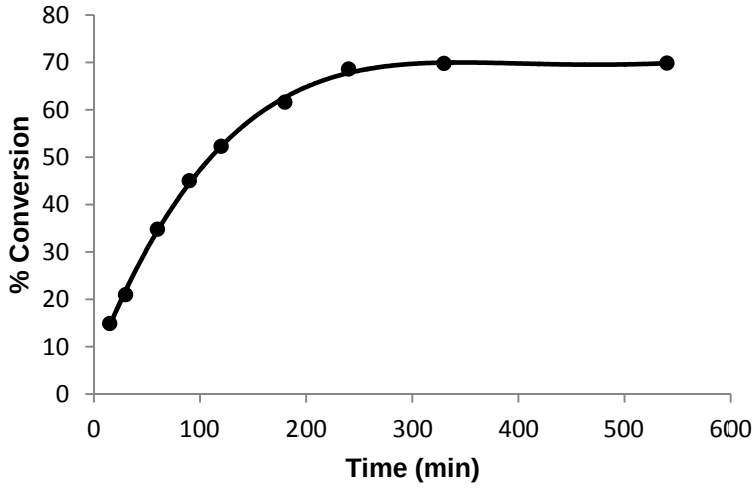


Figure S7. Conversion of monomer with time for ROP of δ-decalactone using mPEG as initiator and TBD (5 mol %) as the catalyst.

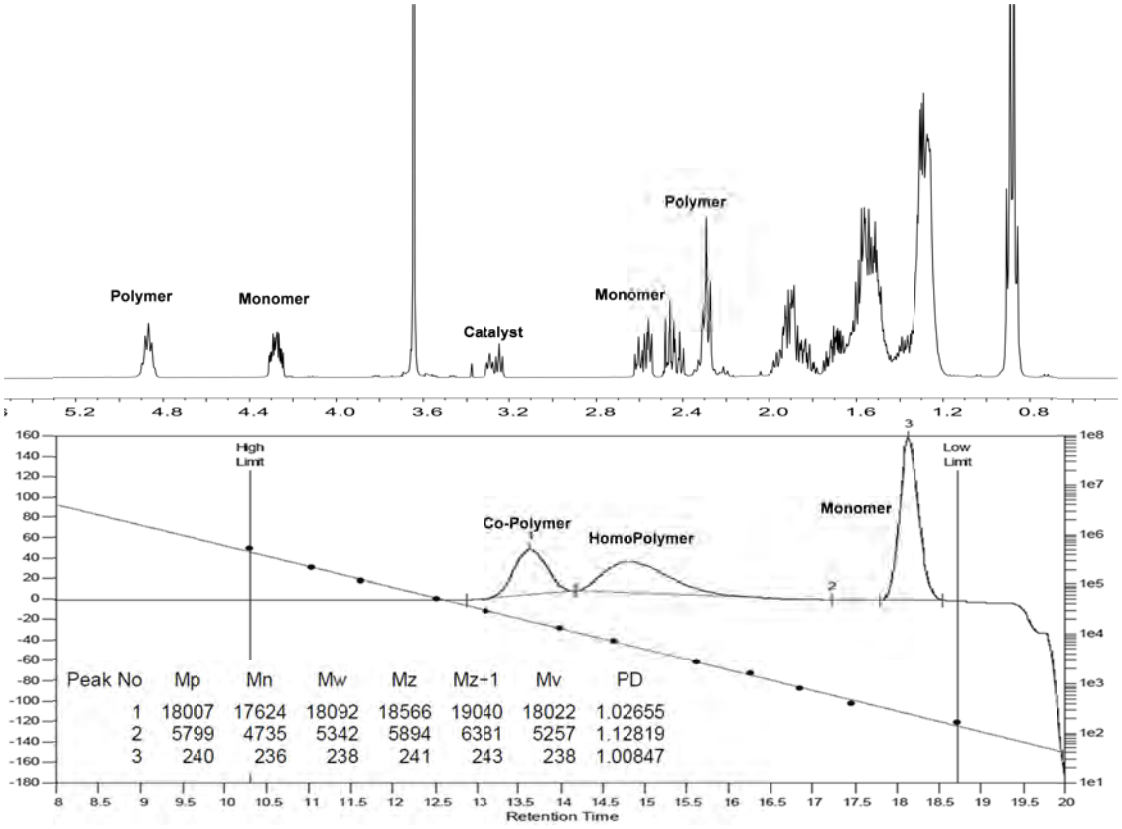


Figure S8. ^{1}H NMR spectrum and SEC trace of mPEG-b-PDL (during kinetic study) after 9 h containing 5% of TBD as the catalyst. SEC traces were obtained using chloroform as the mobile phase and polystyrene as molar mass standard. For ^{1}H NMR analysis the sample was dissolved in $CDCl_3$.

Table S1. Data obtained from the kinetics analysis of mPEG-b-PDL synthesis. As shown in figure S8, peaks 1 and 2 correspond to copolymer and homopolymer respectively. (PD-Polydispersity Index)

Time	Conversion by NMR (%)	$M_{n,SEC}$ Peak 1 (kDa)	PD Peak1	$M_{n,SEC}$ Peak 2 (kDa)	PD Peak 2
15 min	15	12.6	1.02	1.2	1.36
30 min	21	13.7	1.02	1.7	1.37
1 h	35	15.2	1.02	2.8	1.23
1.5 h	45	15.8	1.02	3.3	1.21
2 h	52	16.4	1.02	3.9	1.16
3 h	62	17.2	1.02	4.5	1.14
4 h	69	17.3	1.02	4.6	1.13
5.5 h	70	17.6	1.02	4.7	1.13
9 h	70	17.6	1.02	4.7	1.12

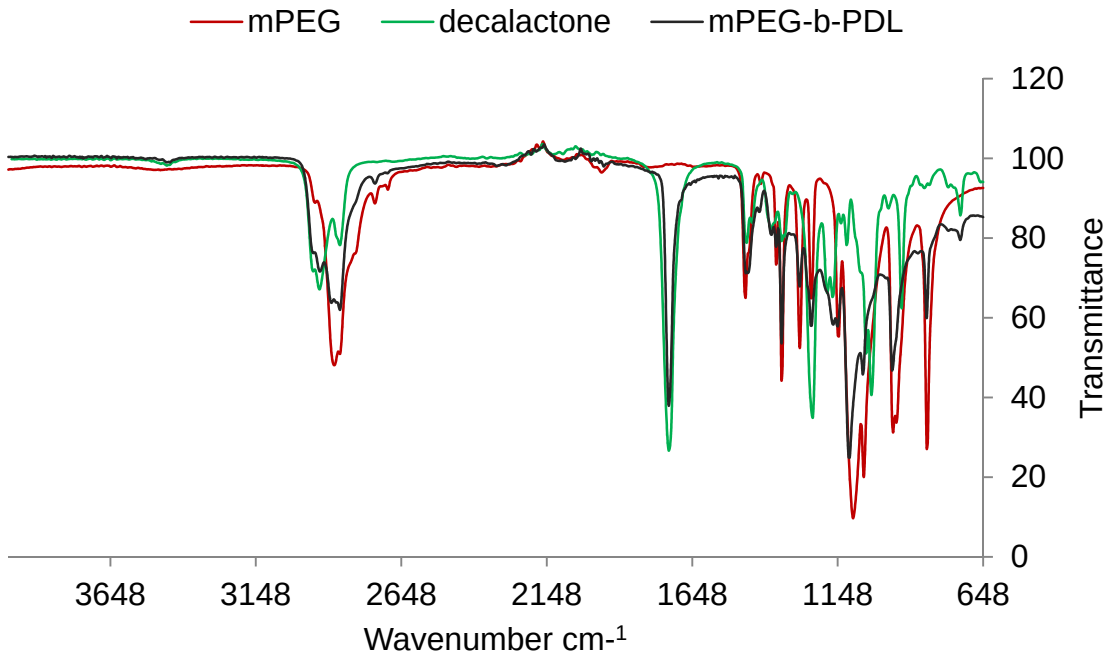


Figure S9 Overlaid FTIR spectra of mPEG, δ-decalactone monomer and mPEG-b-PDL copolymer.

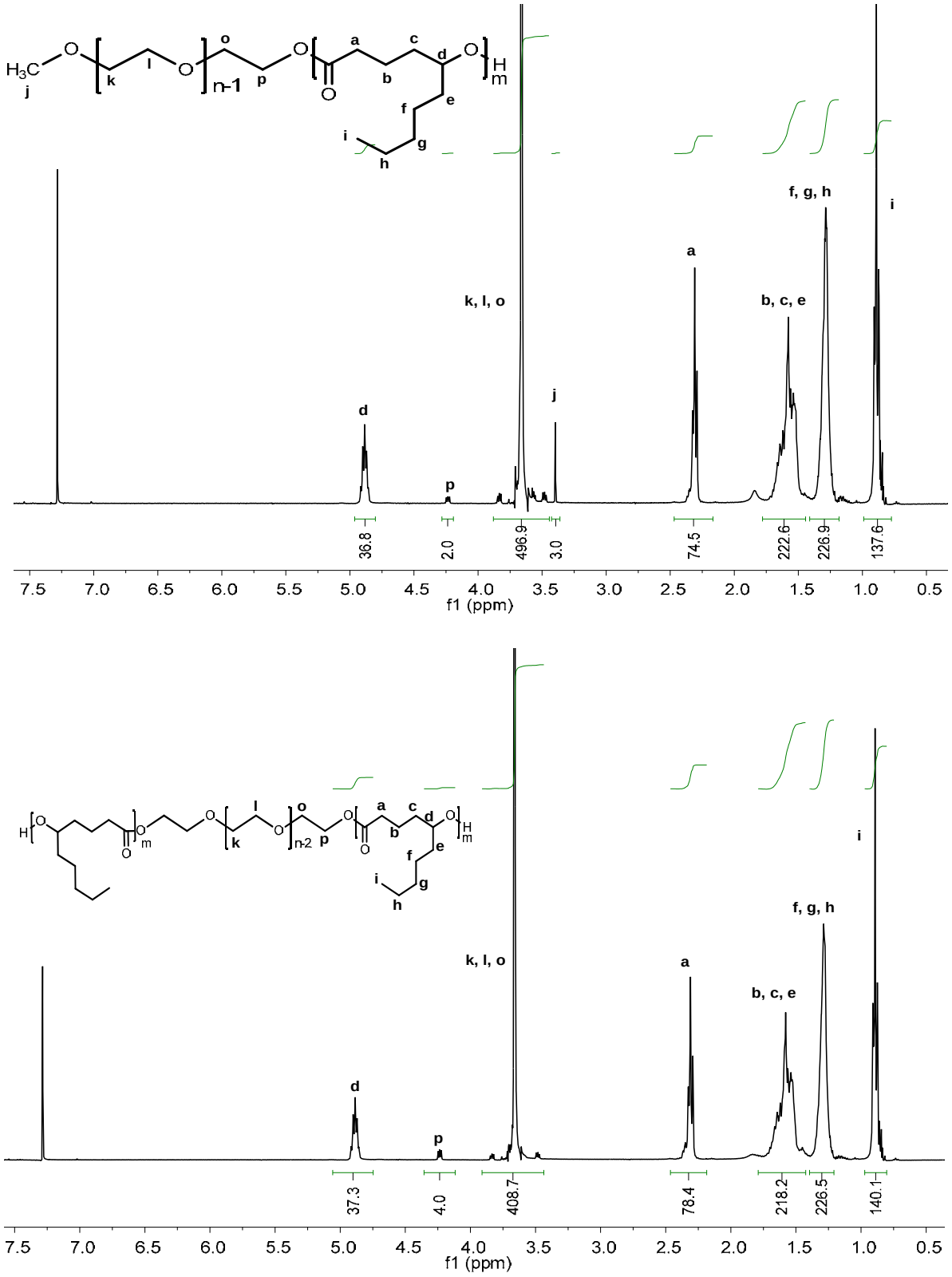


Figure S10. ^{1}H NMR of mPEG-b-PDL and PDL-b-PEG-b-PDL copolymer in $CDCl_3$

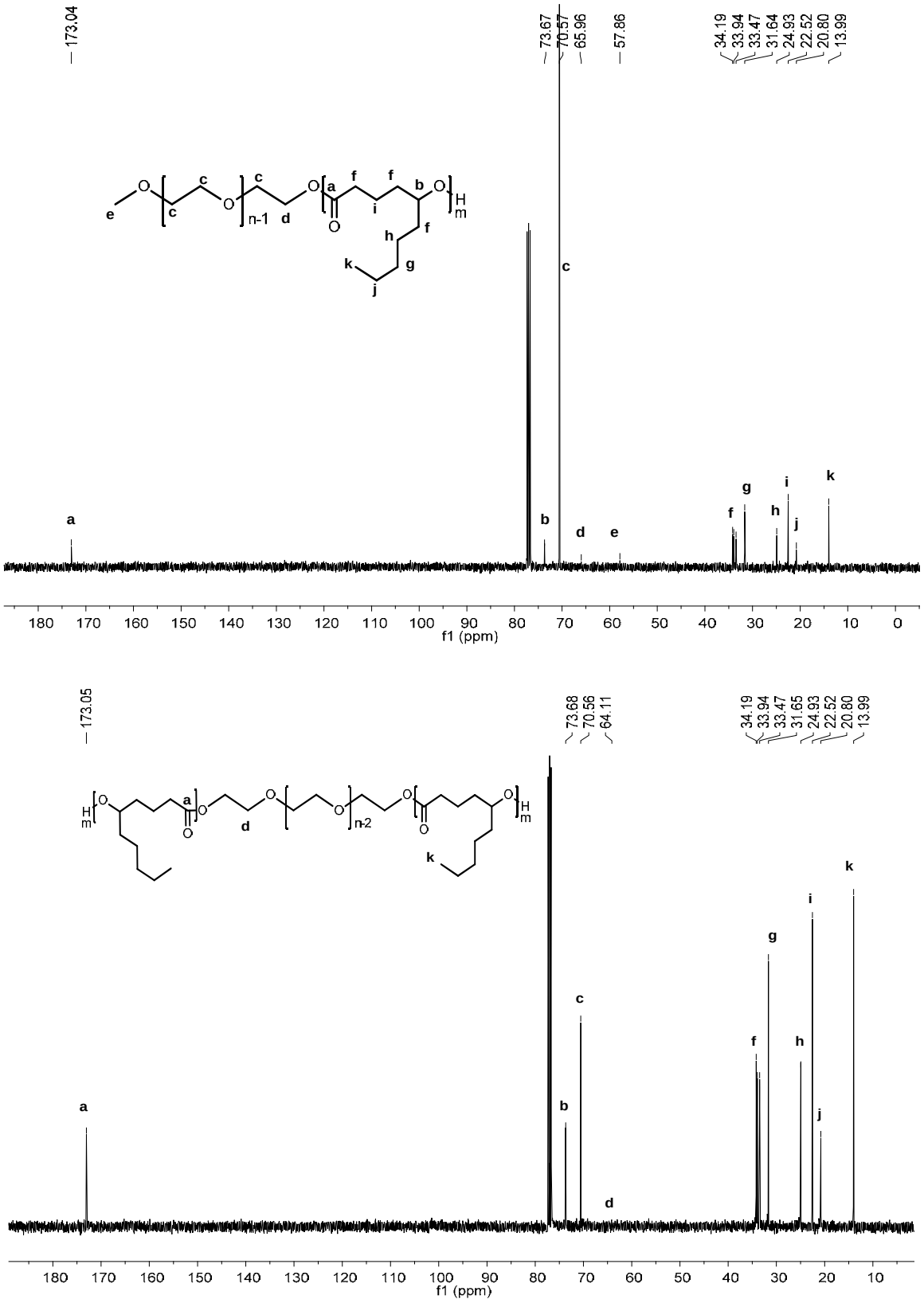


Figure S11. ^{13}C NMR of mPEG-b-PDL and PDL-b-PEG-b-PDL copolymer in $CDCl_3$.

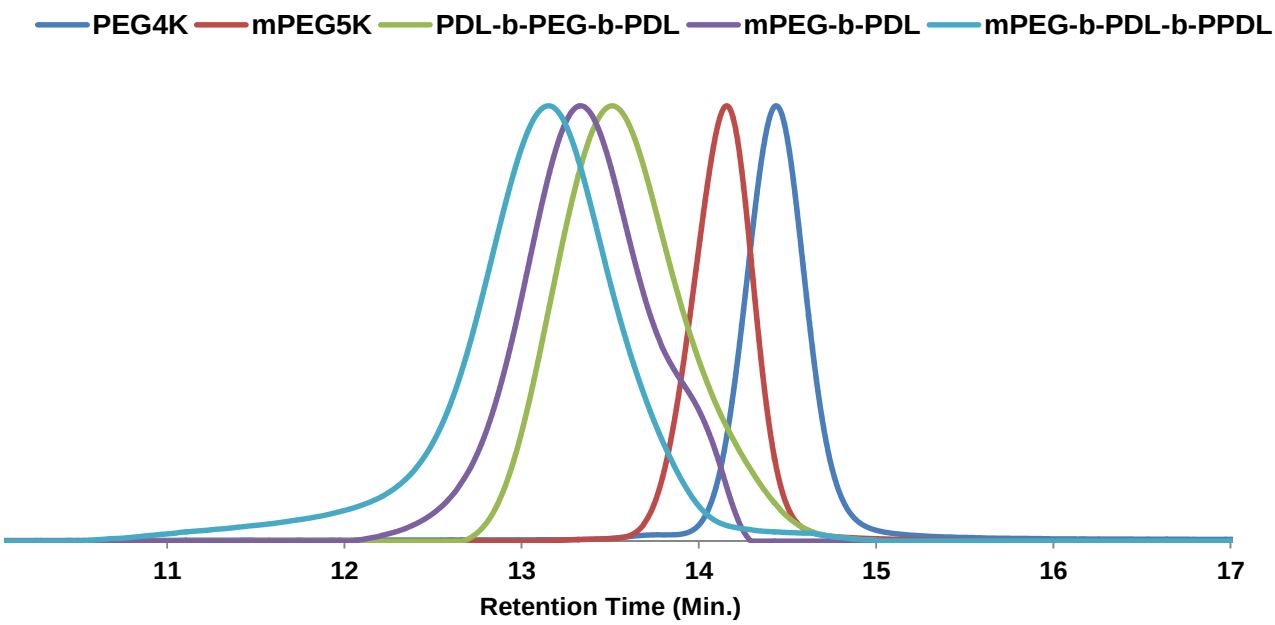


Figure S12. SEC traces of PEG macroinitiators and different block copolymers of decalactone, which were obtained using chloroform as the mobile phase. Polystyrene standards were used to calibrate the SEC.

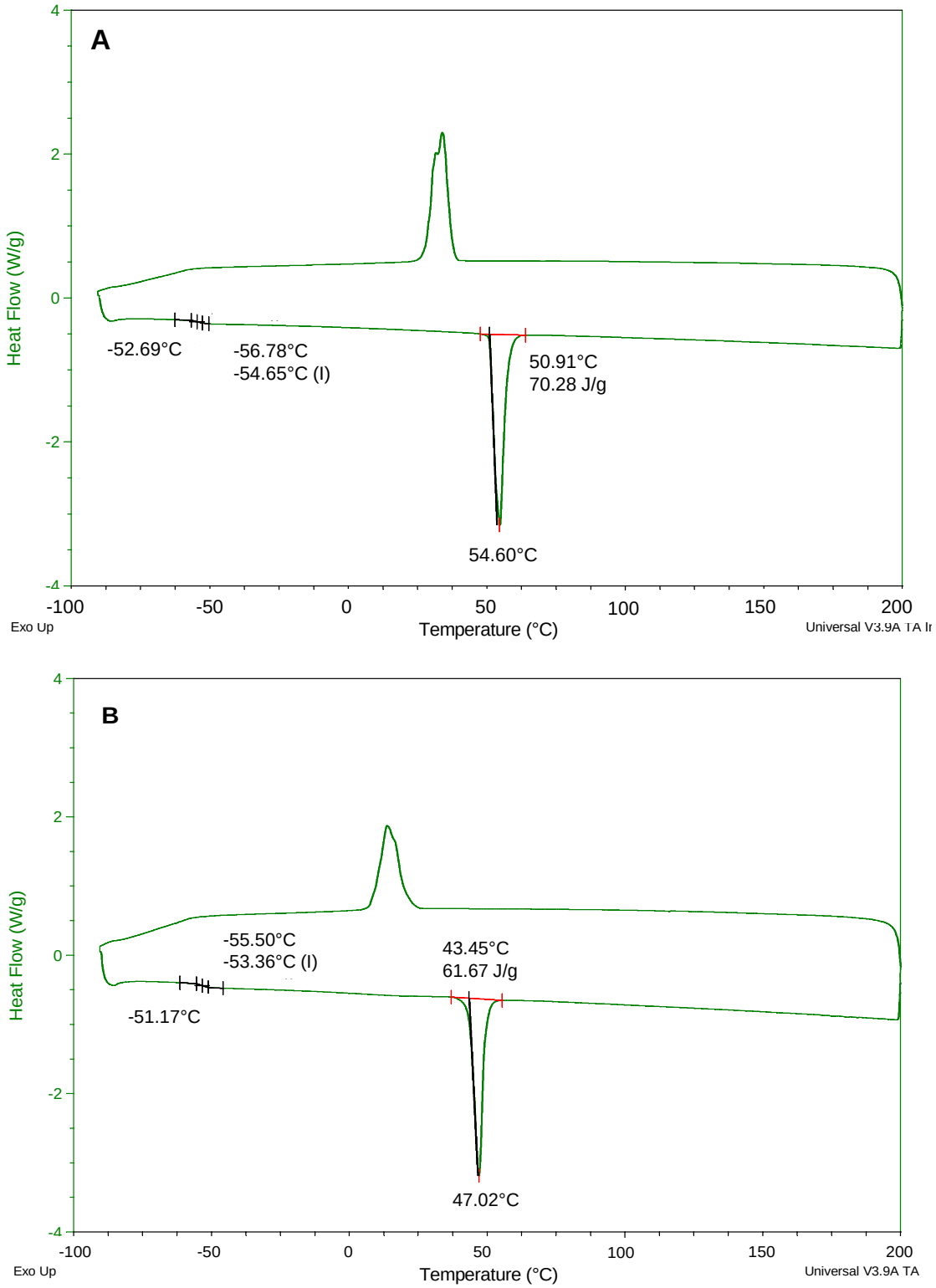


Figure S13. DSC plots of (A) mPEG-b-PDL and (B) PDL-b-PEG-b-PDL, obtained from second heating/cooling cycle.

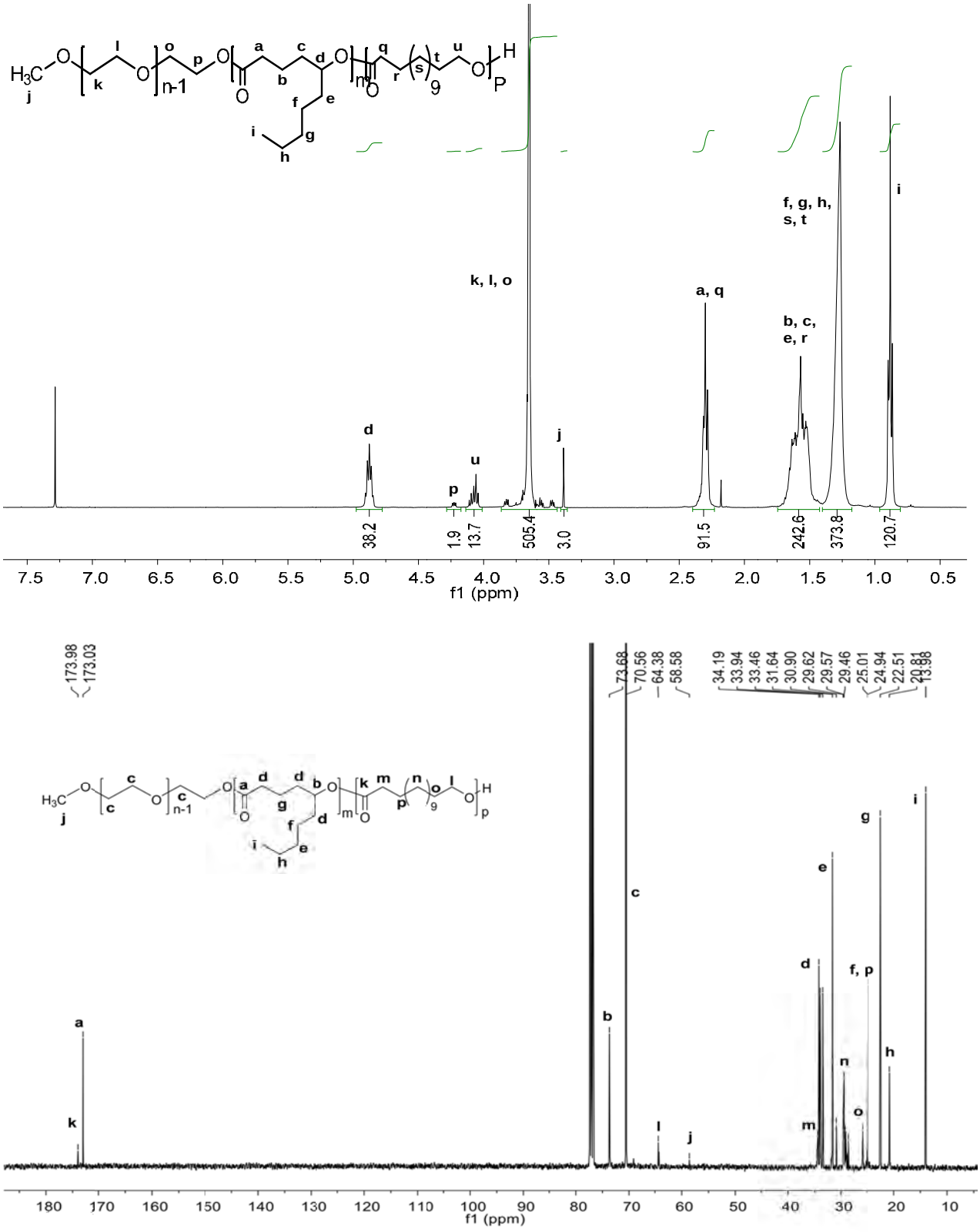


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of mPEG-b-PDL-b-PPDL in $CDCl_3$.

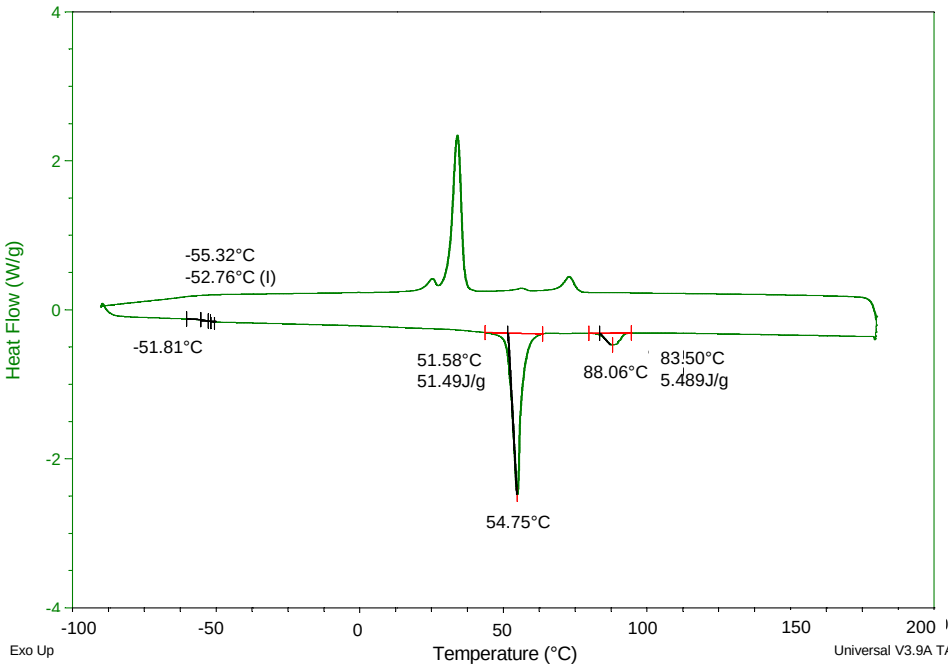
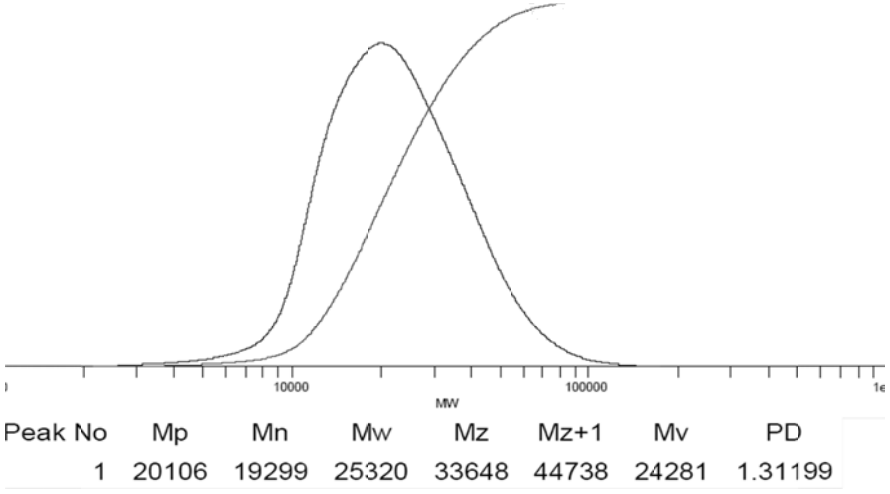


Figure S15 DSC plots of mPEG-b-PDL-b-PPDL from second heating/cooling cycle.



Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	20106	19299	25320	33648	44738	24281	1.31199

Figure S16. SEC trace of mPEG-b-PCL obtained using chloroform as the mobile phase. Polystyrene standards were used to calibrate the SEC.

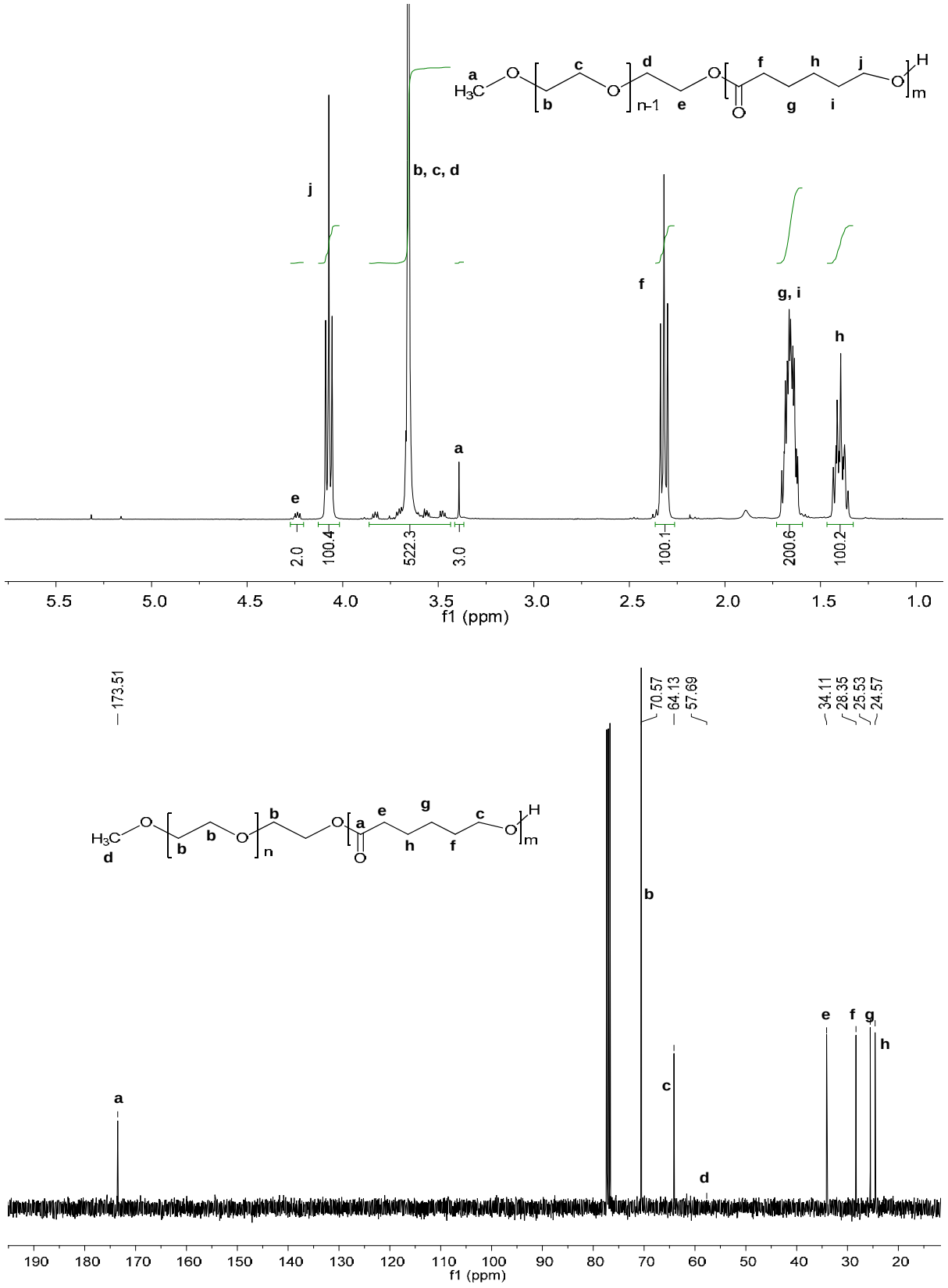


Figure S17. ^{1}H NMR and ^{13}C NMR of mPEG-b-PCL in $CDCl_3$.

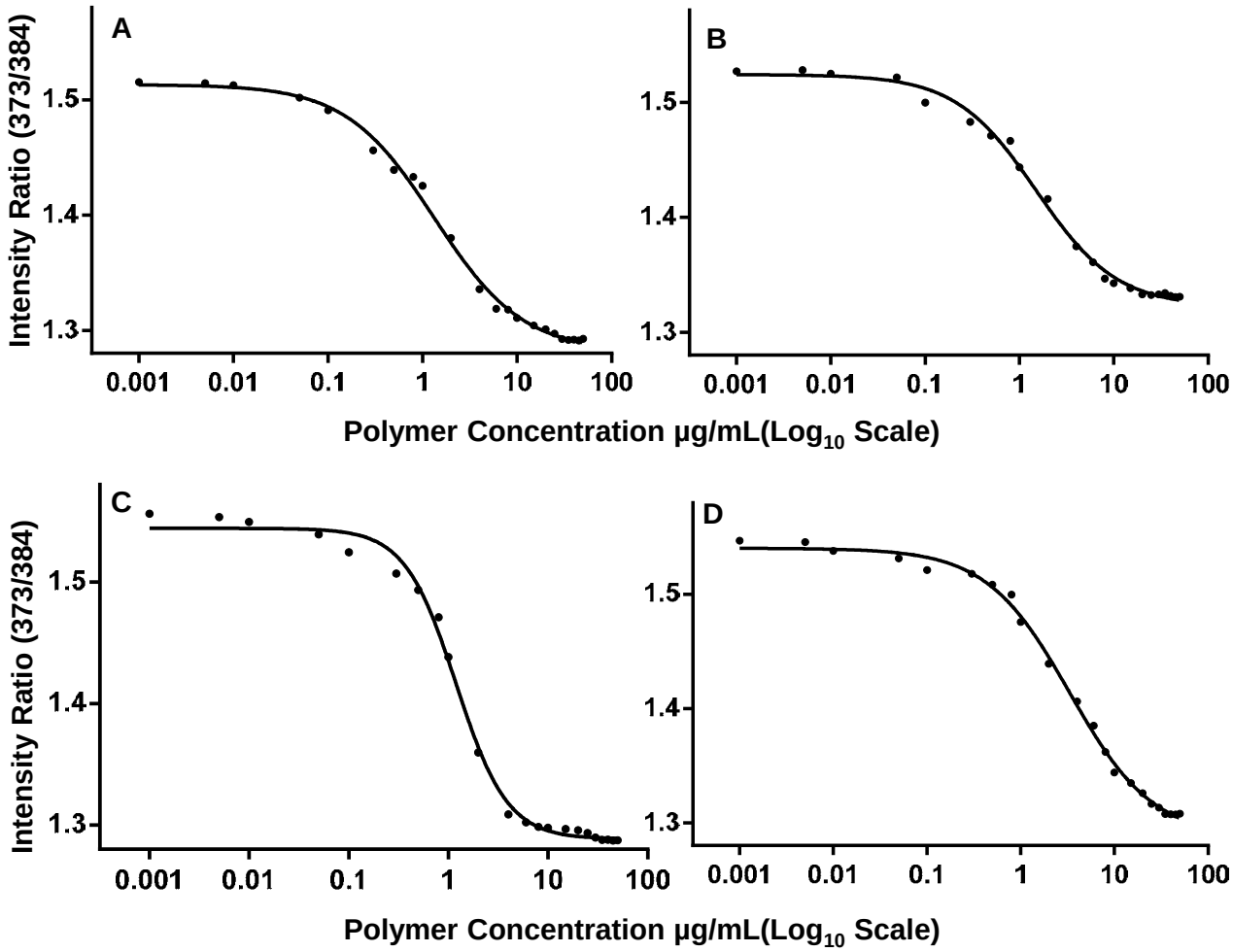


Figure S18. CMC plot for (A) mPEG-b-PDL, (B) PDL-b-PEG-b-PDL, (C) mPEG-b-PDL-b-PPDL and (D) mPEG-b-PCL obtained by the pyrene 1:3 peak ratio method in water.

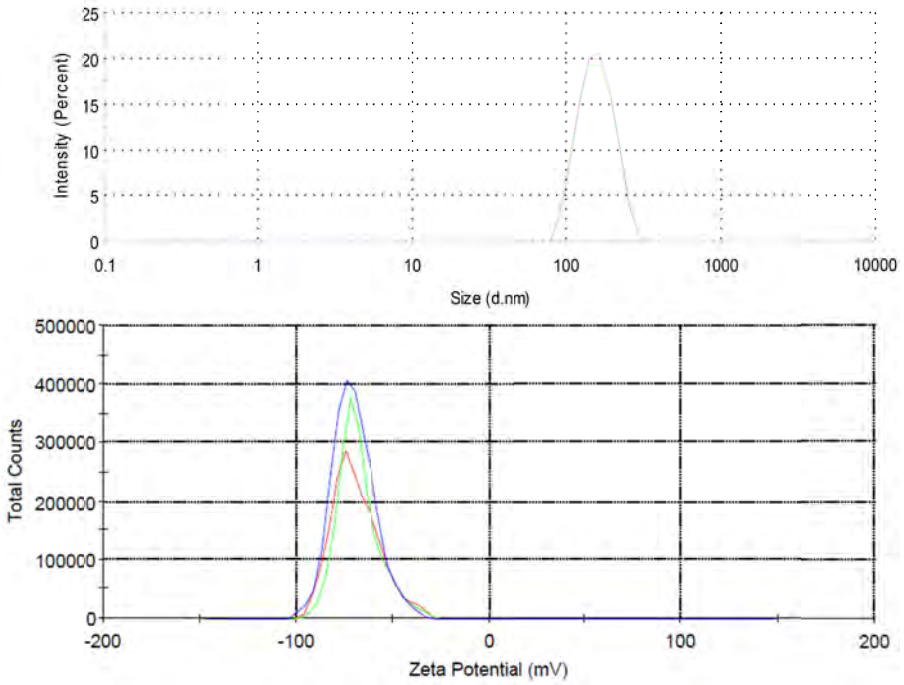


Figure S19. Size and Zeta potentials of propargyl-PDL nano emulsion. Size was determined in HPLC grade water whereas zeta potential was measured in 10 mM HEPES buffer.

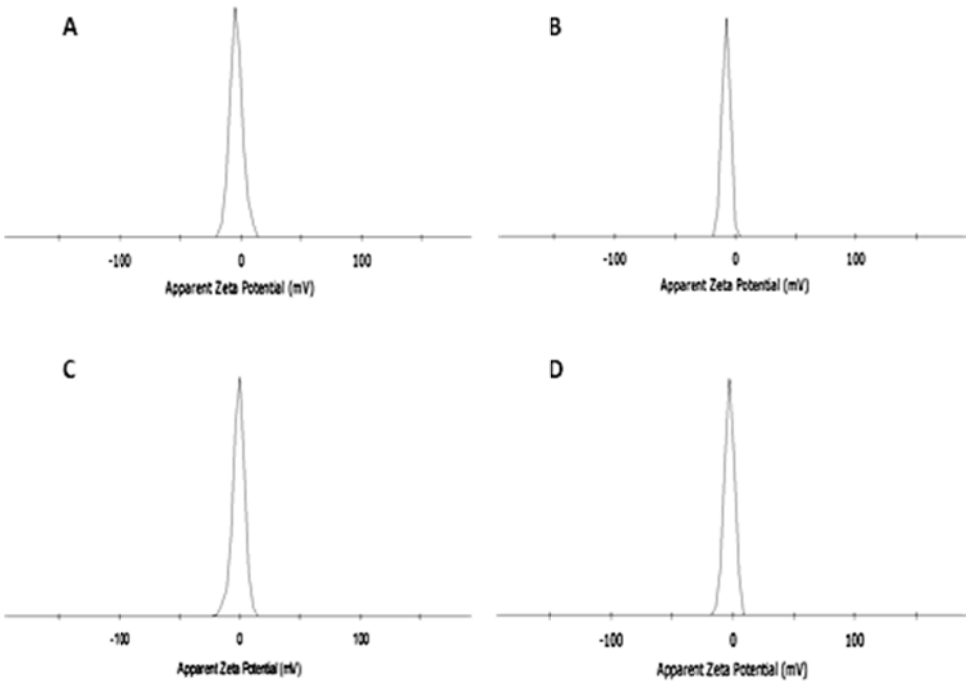


Figure S20. Zeta potential measurements of (A) mPEG-b-PDL, (B) PDL-b-PEG-b-PDL„ (C) mPEG-b-PCL and (D) mPEG-b-PDL-b-PPDL micelles acquired in HEPES 10 mM buffer (pH 7.4).

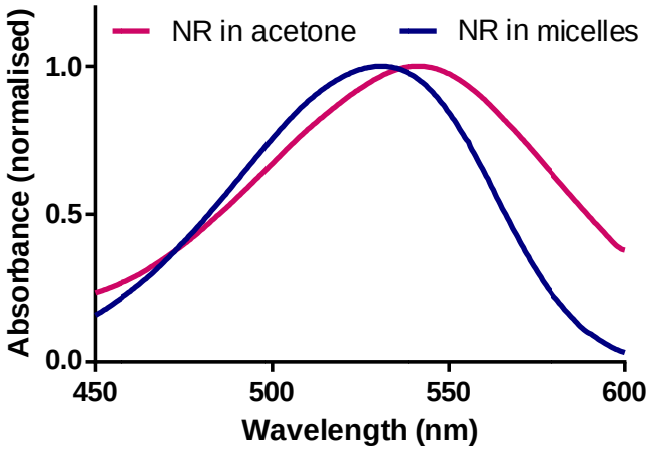


Figure S21. UV-Visible absorbance spectra of Nile red (NR) in acetone and micelles. Micelle samples contained encapsulated NR in mPEG-b-PDL micelles dispersed in water.

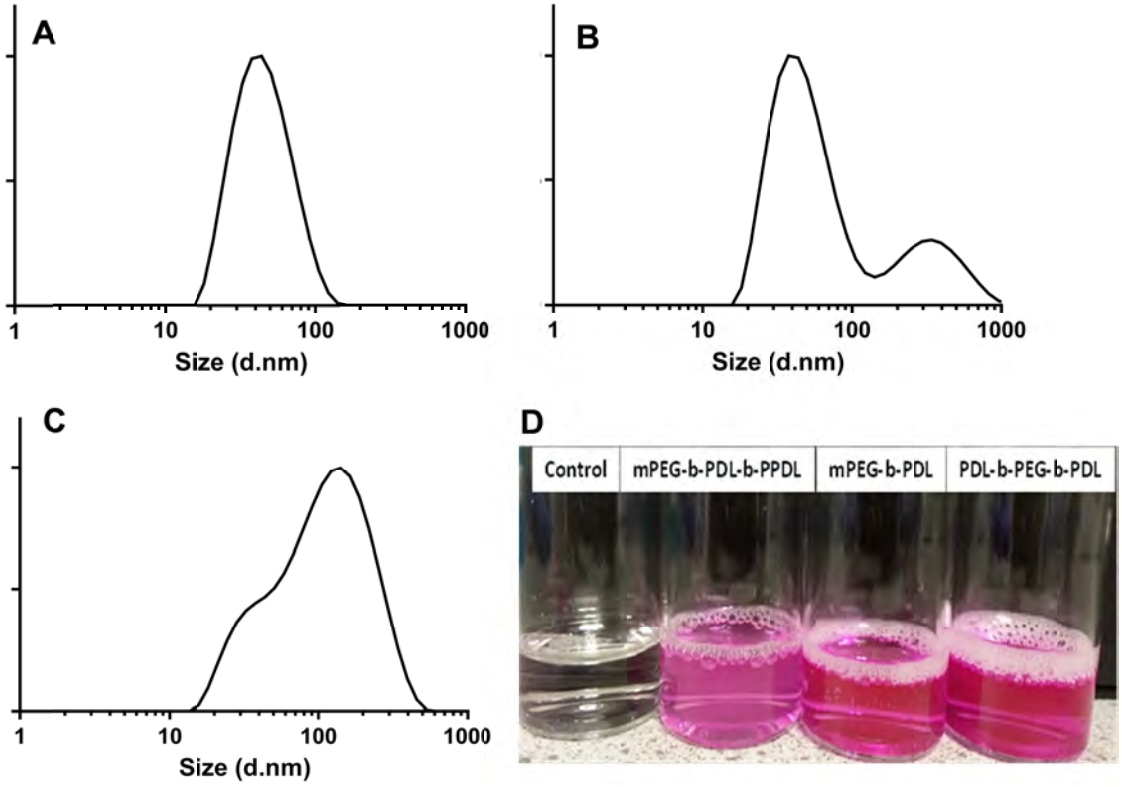


Figure S22. Size distribution curve by intensity of (A) mPEG-b-PDL, (B) PDL-b-PEG-b-PDL and (C) mPEG-b-PDL-b-PPDL acquired by DLS in water. (D) Appearance of micellar solutions and control (formulation without polymer) after Nile red loading.

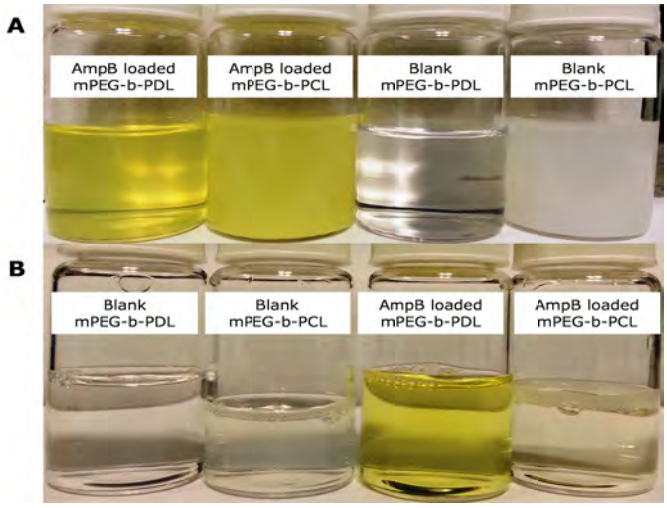


Figure S23. Physical appearance of micellar suspension (obtained via nanoprecipitation method) in water (A) before and (B) after filtration through 0.22 µm syringe filter.

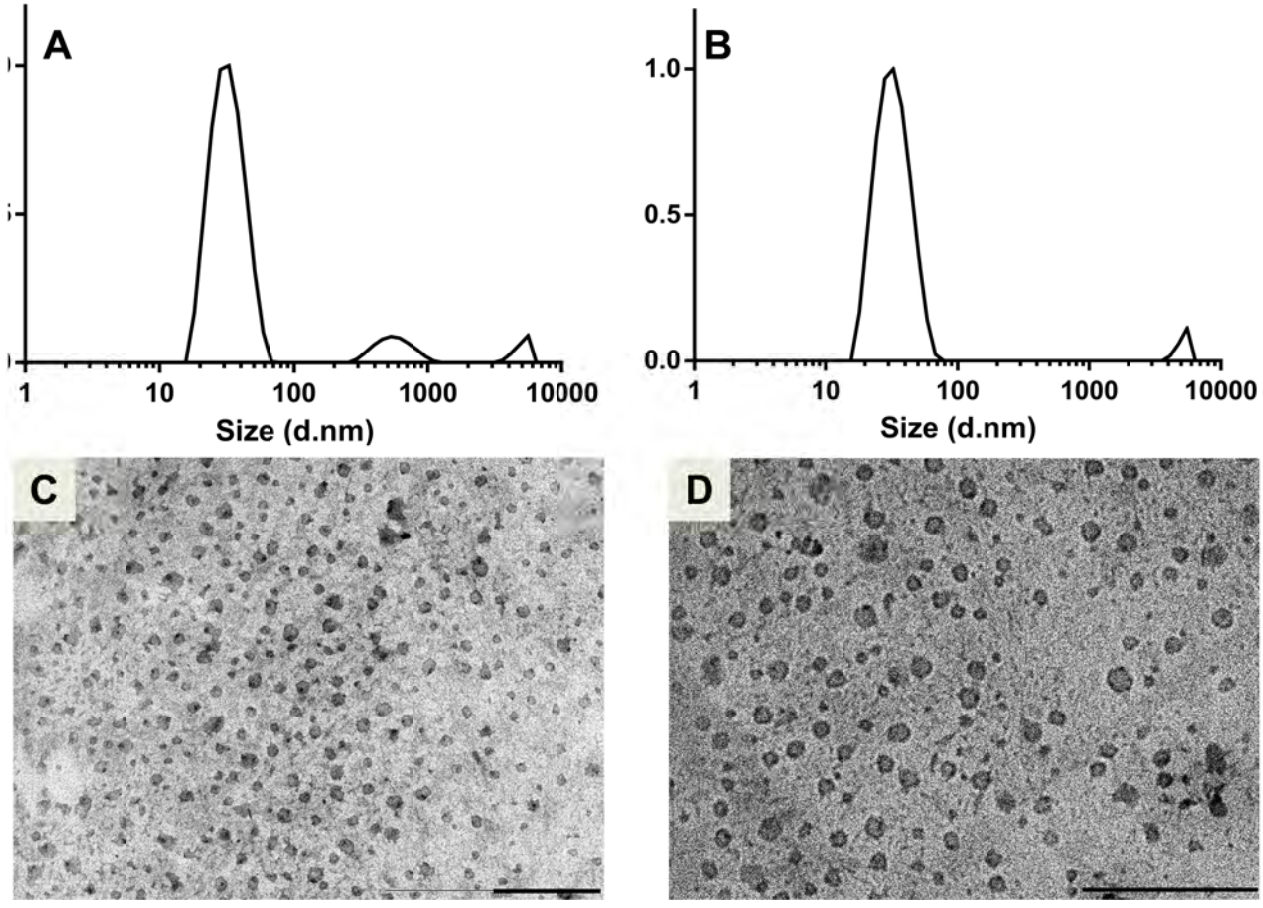


Figure S24. Size distribution curves by intensity of (A) Blank mPEG-b-PCL, (B) AmpB loaded mPEG-b-PCL, and TEM image of (C) Blank mPEG-b-PCL and (D) AmpB loaded mPEG-b-PCL micelles. The images were recorded without staining. Scale bar – 500 nm.

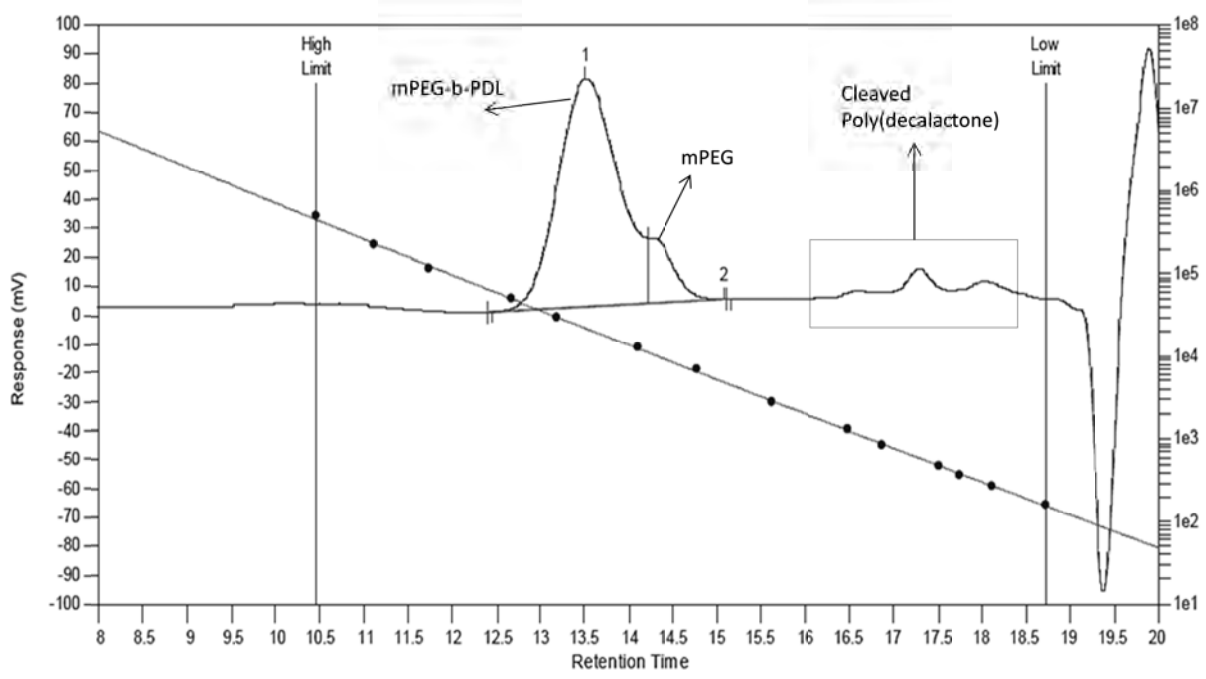


Figure S25. SEC trace of mPEG-b-PDL after 120 days of storage at pH 7.4 (temperature – 37°C). The SEC instrument was calibrated using polystyrene standards and chloroform was used as the mobile phase.