Supporting Information

For

Functional Degradable Polymers by Radical Ring-Opening Copolymerization of MDO and Vinyl Bromobutanoate: Synthesis, Degradability and Post-Polymerization Modification.

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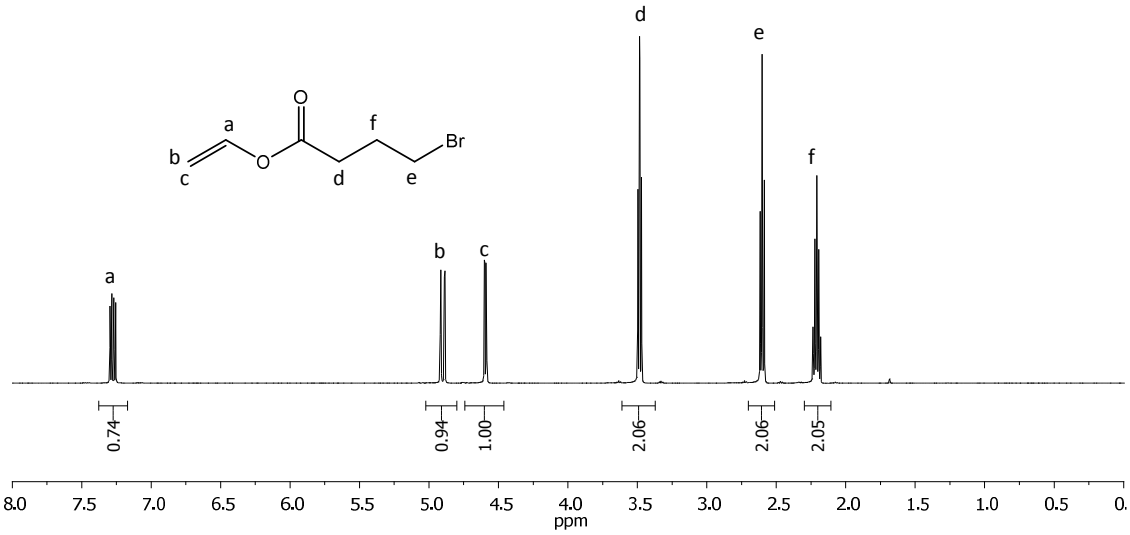


Figure S1. ^{1}H NMR spectrum of vinyl bromobutanoate synthesized by palladium catalyzed vinyl exchange reaction between 4-bromo butyric acid and vinyl acetate (300 MHz, 293 K, $CDCl_3$).

Figure S2. ^{13}C NMR spectrum of vinyl bromobutanoate synthesized by palladium catalyzed vinyl exchange reaction between 4-bromo butyric acid and vinyl acetate (125 MHz, 293 K, $CDCl_3$).

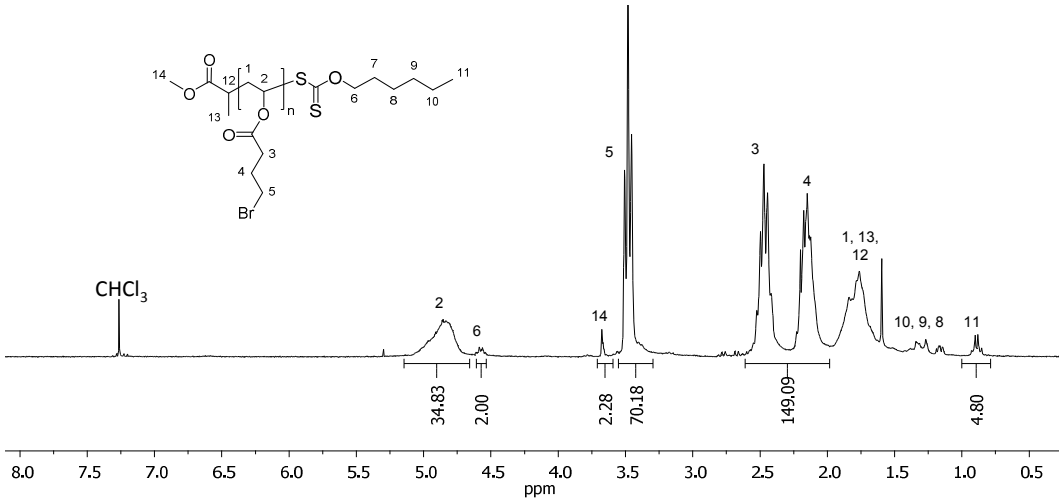


Figure S3. ^{1}H NMR spectrum of poly(VBr) using **1** as the chain transfer agent (400 MHz, $CDCl_3$).

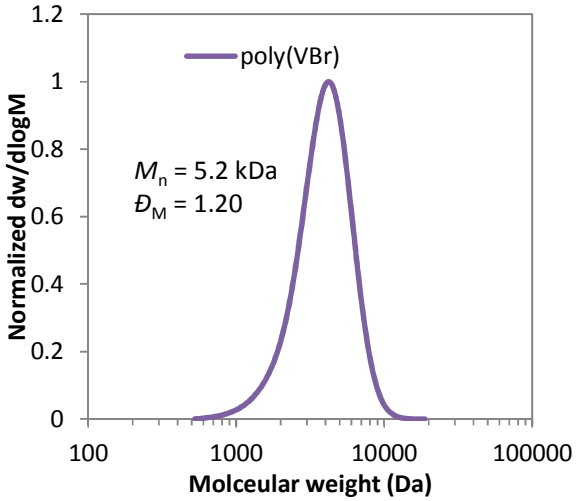


Figure S4. Size exclusion chromatogram of poly(VBr) obtained by RAFT/MADIX polymerization using **1** as the chain transfer agent after 16 h, (SEC, $CHCl_3$).

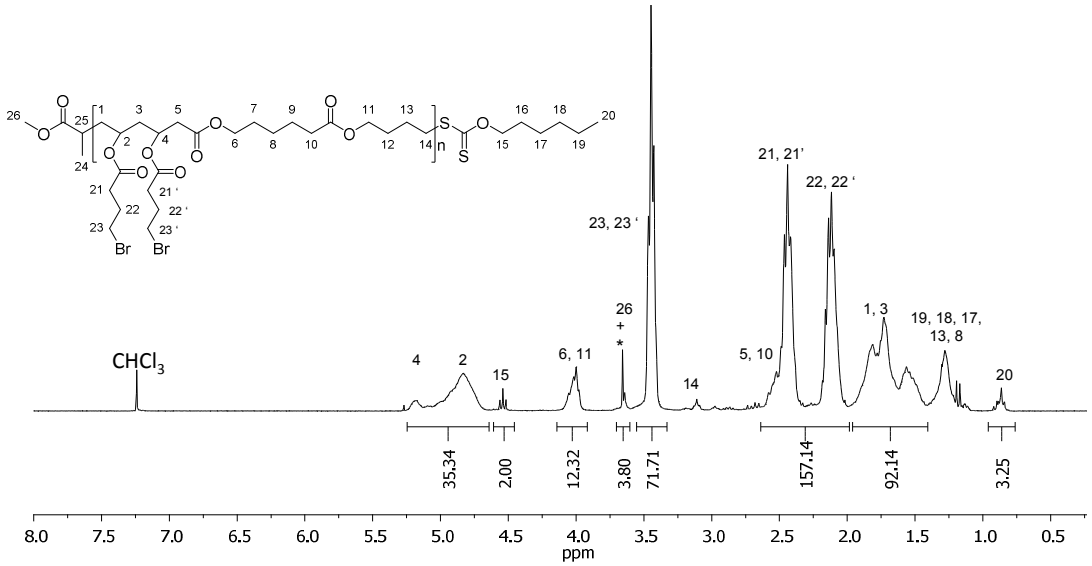


Figure S5. ^{1}H NMR spectrum of poly(MDO-*co*-VBr) using **1** as the chain transfer agent, * indicates a small portion of MDO ring-retained in the copolymer, (400 MHz, $CDCl_3$).

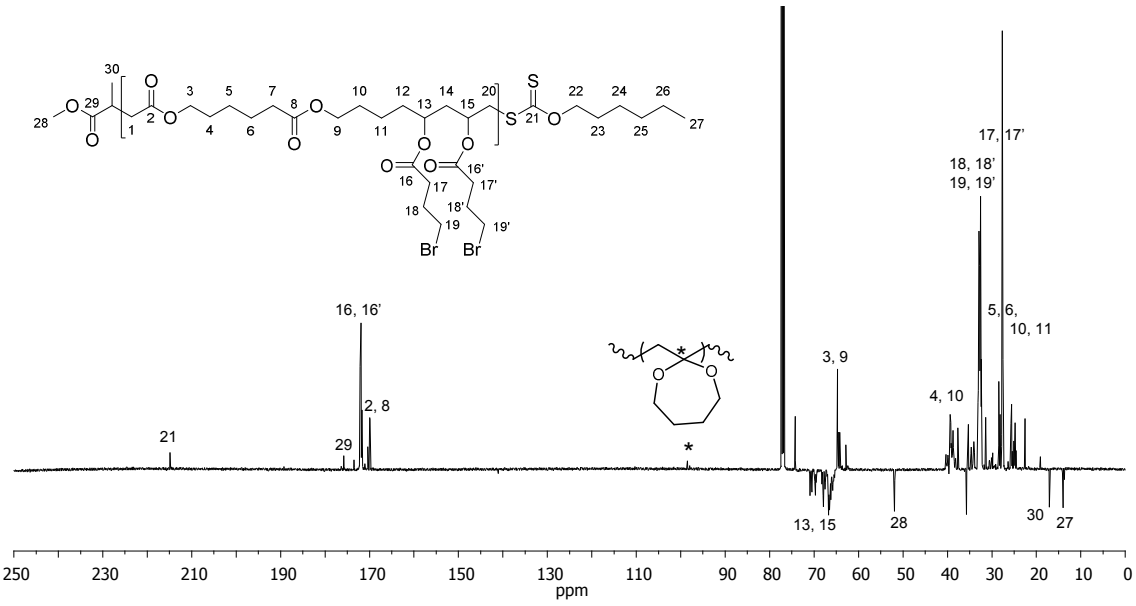


Figure S6. ^{13}C NMR spectrum of poly(MDO-*co*-VBr) using **1** as the chain transfer agent, * indicates a small portion of MDO ring-retained in the copolymer, (125 MHz, $CDCl_3$).

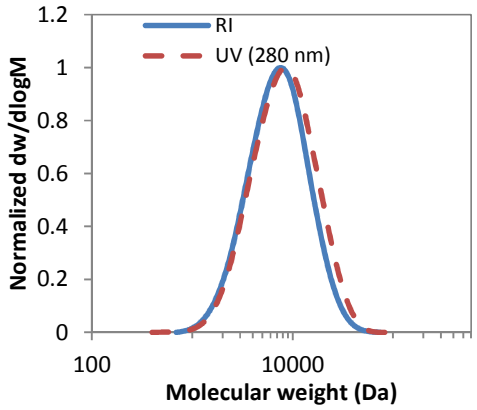


Figure S7. Size exclusion chromatograms of poly(MDO-*co*-VBr) (30/70 mol%) obtained by RAFT/MADIX polymerization after 9 h, blue trace using RI detection and dash trace using UV detection at 280 nm, (SEC, $CHCl_3$).

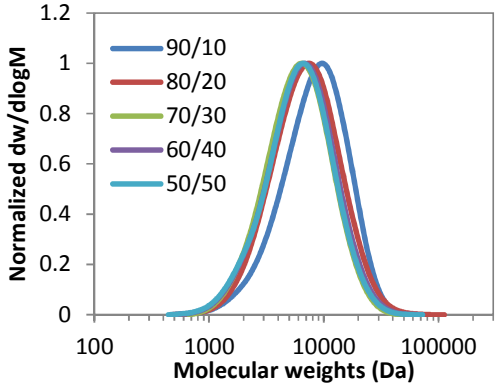


Figure S8. Size exclusion chromatograms of poly(MDO-*co*-VBr) obtained by RAFT/MADIX polymerization for different monomer feeds, (SEC, $CHCl_3$).

Table S1. Mole fractions of monomer in the initial feed and copolymers using CTA **1** in benzene (15 wt%).

Target composition		**Conversions (%)**		**Actual initial comp.**		**Polymer comp.**	
MDO	*VBr*	*MDO*	*VBr*	*MDO*	*VBr*	*MDO*	*VBr*
0.10	0.90	5	4	0.08	0.92	0.10	0.90
0.20	0.80	6	5	0.19	0.81	0.22	0.78
0.30	0.70	4.5	5	0.32	0.67	0.33	0.67
0.40	0.60	8	9	0.38	0.62	0.36	0.64
0.50	0.50	9	11	0.50	0.50	0.45	0.55
0.60	0.40	9	12	0.59	0.41	0.52	0.48
0.70	0.30	10	8	0.65	0.35	0.69	0.31
0.80	0.20	6	5	0.77	0.23	0.80	0.20
0.90	0.10	11	8	0.91	0.09	0.93	0.07

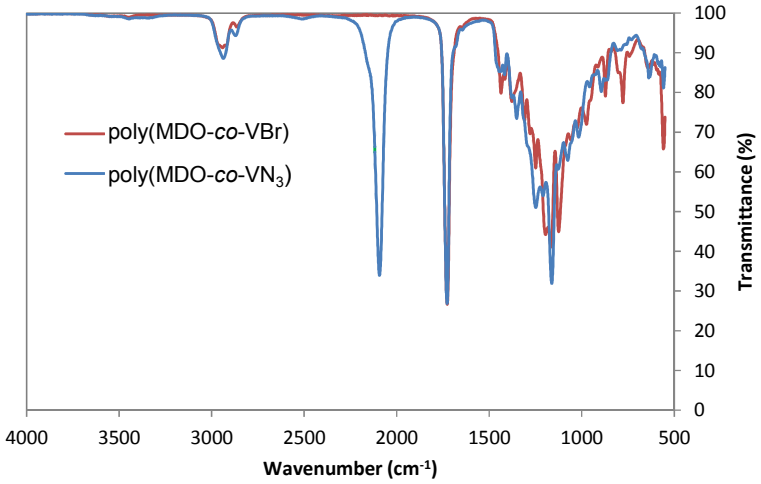


Figure S9. FTIR spectrum of the poly(MDO-*co*-VBr) (30/70 mol%) before and after azidation using NaN_3.

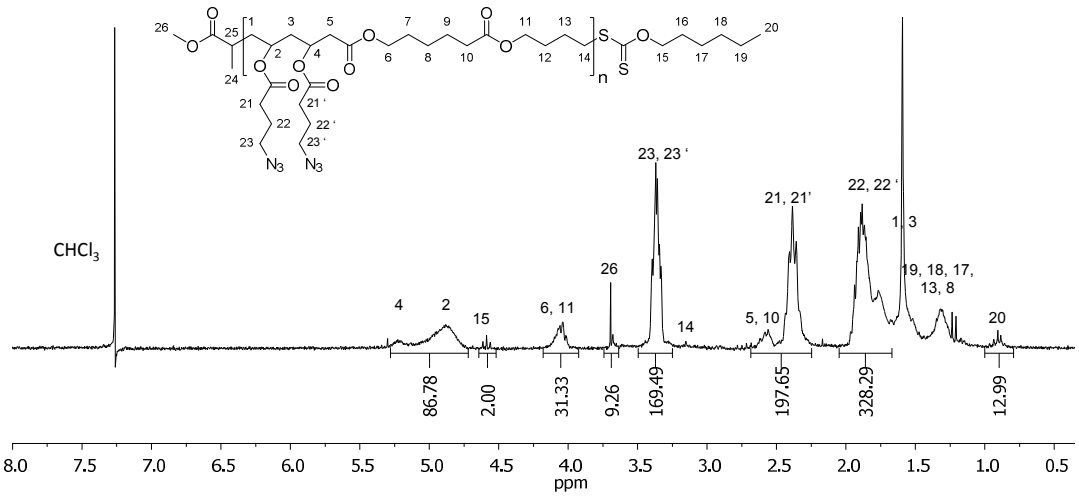


Figure S10. ^{1}H NMR spectrum of poly(MDO-*co*-VBr) (30/70 mol%) after azidation using NaN_3 (400 MHz, $CDCl_3$).

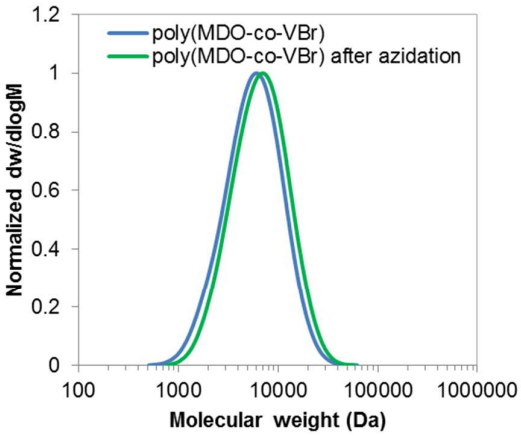


Figure S11. Size exclusion chromatograms of poly(MDO-*co*-VBr) (30/70 mol%) before and after reaction with NaN_3 proving that the modification had no deleterious effect on the polymer sample (SEC, $CHCl_3$).

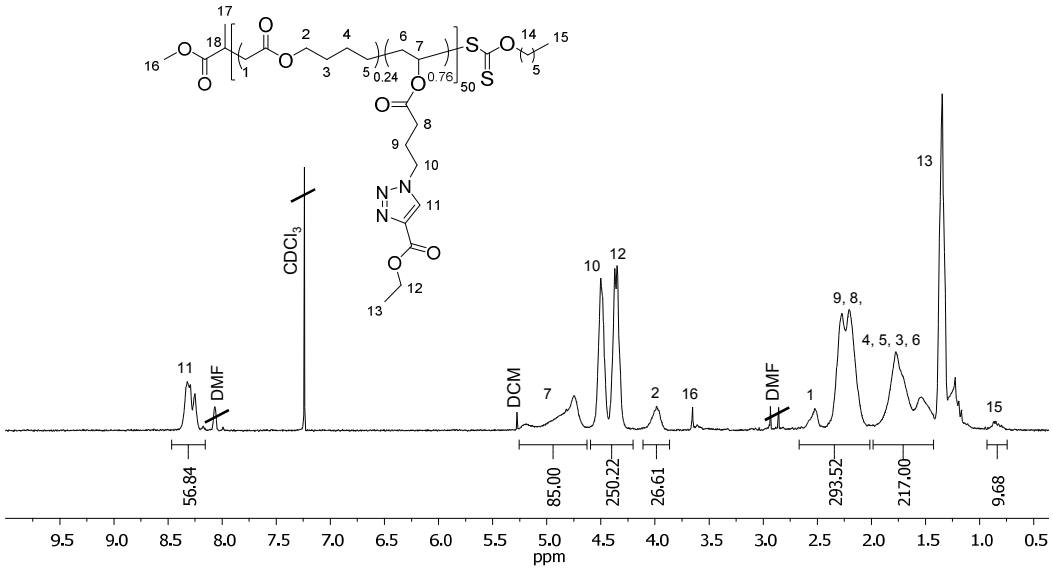


Figure S12. ^{1}H NMR spectra of the copolymer, poly(MDO-*co*-VBr) (30/70 mol%) after 1,3-dipolar cycloaddition post-polymerization modification using ethyl propiolate (400 MHz, $CDCl_3$).

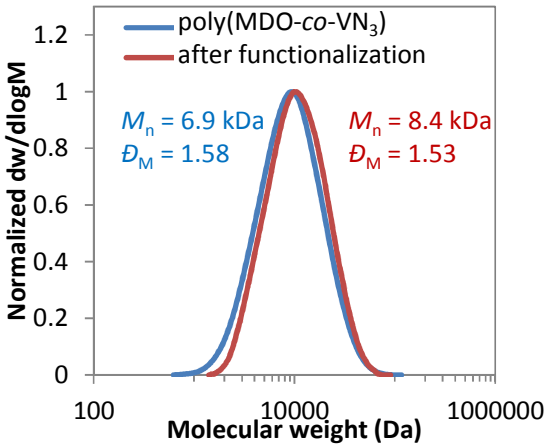


Figure S13. Size exclusion chromatograms of poly(MDO-*co*-VN_3) before and after 1,3-dipolar cycloaddition reaction with ethyl propiolate, (SEC, $CHCl_3$).

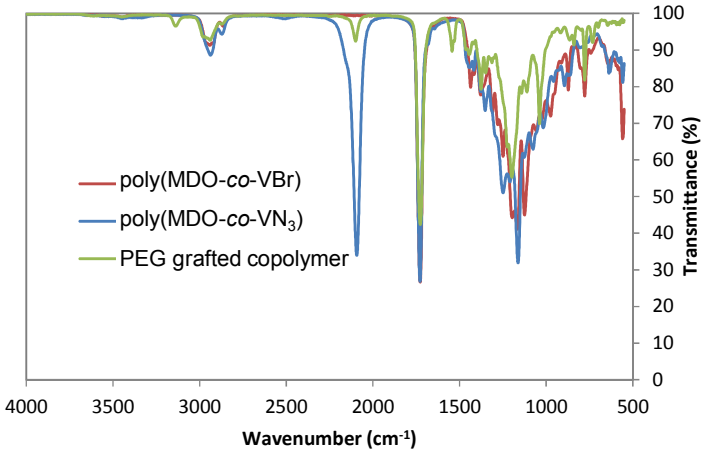
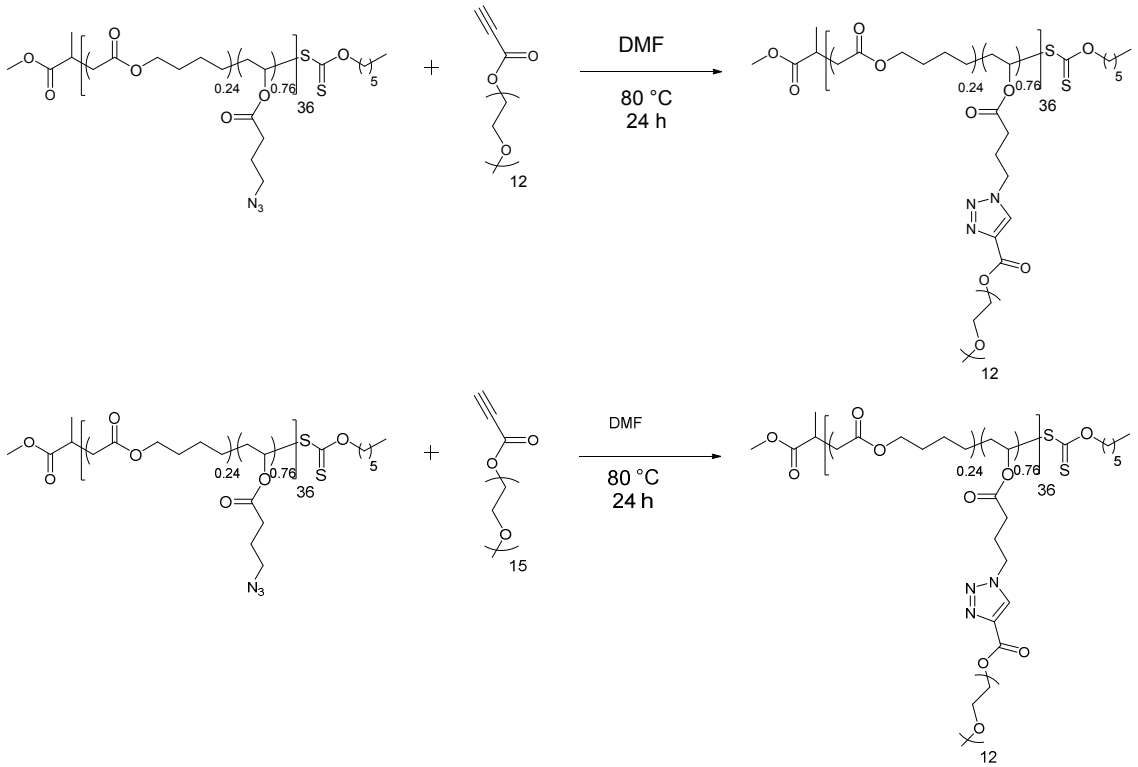


Figure S14. FTIR spectrum of poly(MDO-*co*-VBr), poly(MDO-*co*-VN_3) and the PEG grafted-copolymer.



Scheme S1. Post-polymerization modification of poly(MDO-*co*-VN_3) using cycloaddition reaction with PEG alkyne.

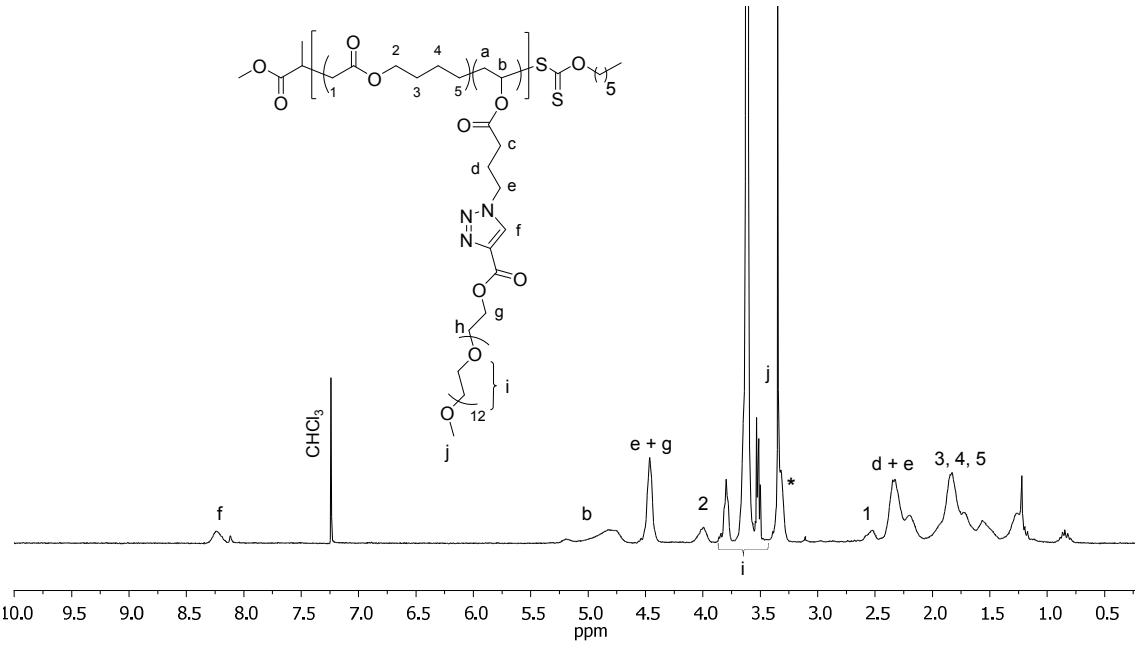


Figure S15. ^{1}H NMR spectra of the copolymer after post-polymerization modification *via* 1,3-dipolar cycloaddition with PEG alkyne, M_n = 550 Da, DP = 12, (400 MHz, $CDCl_3$). * indicates the residual azide pendent groups unreacted during the reaction.

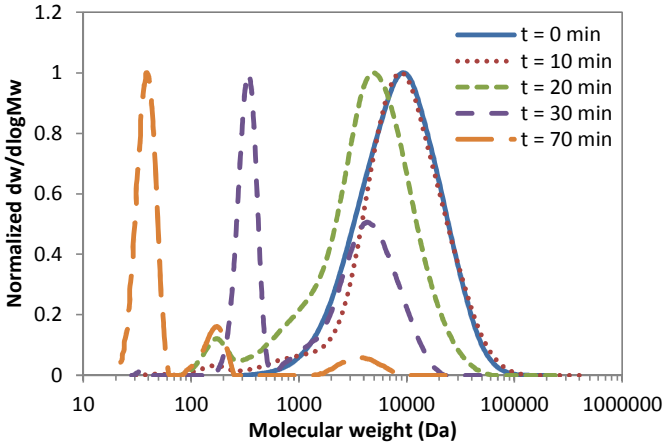


Figure S16. Size exclusion chromatograms of the degradation of poly(MDO-*co*-VBr) in a solution of KOH in methanol (0.1 M) at 40 °C for different time points, (SEC, $CHCl_3$).

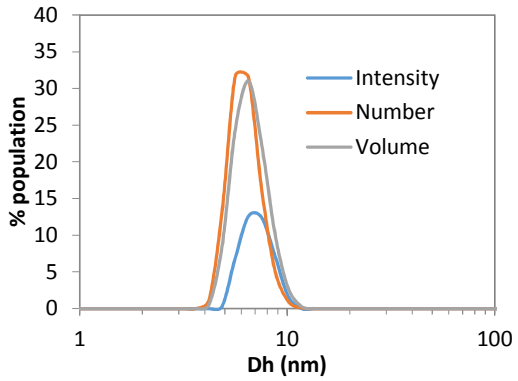


Figure S17. DLS traces for the particles obtained from direct dissolution of the PEG grafted-copolymer in water.

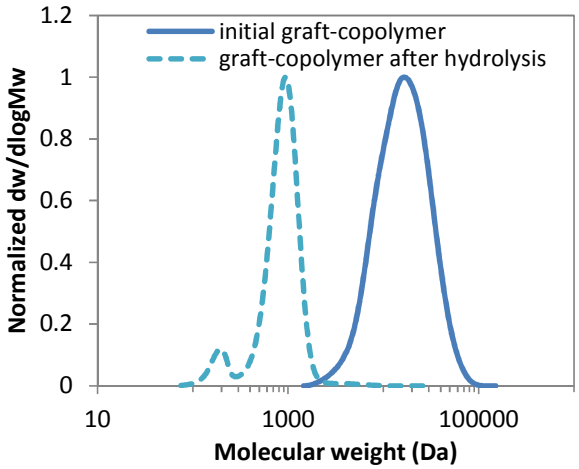


Figure S18. Size exclusion chromatograms of the PEG grafted-copolymer before and after degradation in KOH solution (0.1 M in MeOH) at 40 °C, (SEC, $CHCl_3$).

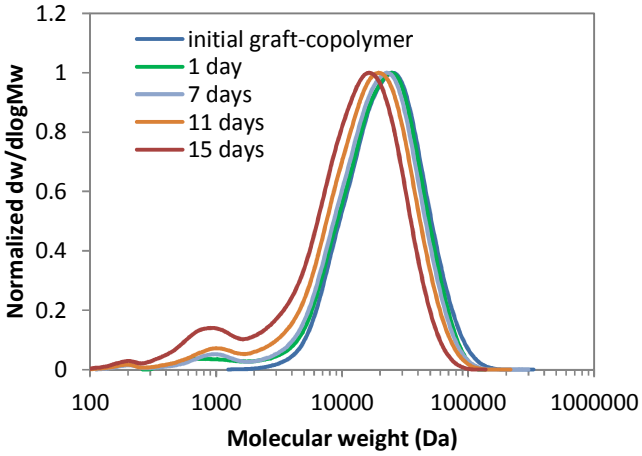


Figure S19. Size exclusion chromatograms of the PEG grafted-copolymer during degradation in PBS, pH = 7.40, at 37 °C for different time points. (SEC, $CHCl_3$).