Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Combining Oxyanionic Polymerization and Click-Chemistry: A General Strategy for Polyether Polyol Macromonomers

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(D,L-1,2-Isopropylidene glyceryl glycidyl ether) (IGG)

The epoxide monomer (DL-1,2-isopropylidene glyceryl glycidyl) ether (IGG) was synthesized according to a literature procedure.[1] In brief, epichlorohydrine and D,L-1,2-isopropylidene glycerol (solketal) were reacted in a phase transfer reaction. After several washing steps, the solvent was removed. The crude product was purified via distillation under reduced pressure.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 4.3 (m,1H, C*H* acetal), 4.07 (m, 1H, C*H* epoxid), 3.88 – 3.39 (m, 4H, CH_2) 3.17 (m, 2H CH_2 acetal), 2.81 (t, 1H, CH_2 epoxide), 2.63 (q, 1H, CH_2 epoxide), 1.44 (s, 3H, CH_3), 1.38 (s, 3H, CH_3)

1-Azido-6-hydroxyhexane

1-Azido-6-hydroxyhexane was prepared as reported previously.[2] Sodium azide (4.87 g, 0.07 mol, 2 eq.) was dissolved in water (20 mL) and subsequently 1-chloro-6-hydroxyhexane (5 mL, 0.04

mol, 1 eq.) was added via syringe. After stirring over night at 80 °C, the mixture was cooled down to room temperature and extracted with diethyl ether (3 x 50 mL). The combined ether phases were dried over anhydrous sodium sulfate (Na_2SO_4), filtered and the solvent was removed under vacuum. To react residual 1-chloro-6-hydroxyhexane, the crude product was again dissolved in water (40 mL) and sodium azide was added (2.45 g, 0.04 mol, 1 eq.). The mixture was refluxed over night and purified as described above. After removal of residual solvent in a vacuum desiccator at 40 mbar over night the product was obtained as a colorless liquid (4.45 g, 83%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 3.64 (t, 2H, HOCH_2, J = 6.5 Hz,), 3.26 (t, 2H, N_3CH_2, J = 6.9 Hz,), 1.65 – 1.54 (m, 4H, CH_2), 1.43 – 1.34 (m, 4H, CH_2)

1-Azido-3-hydroxypropane

1-Azido-3-hydroxypropane was synthesized as reported elsewhere.[3] Sodium azide (15.55 g, 0.24 mol, 2 eq) and tetrabutyl ammonium hydrogensulfate (40 mg, 1.2 mmol, 0.01 eq) were dissolved in water (15 mL) in a round bottom flask equipped with a reflux condensor. 1-chloro-3 hydroxypropane was added via syringe and the mixture was stirred for 24 hrs at 80 °C. After cooling to room temperature water (20 mL) was added and the mixture extracted with diethyl ether (3 x 80 mL). The collected ether fractions were dried over Na_2SO_4, filtered and distilled under reduced pressure (35 °C, 0.02 mbar) to yield the pure product (11 g, 91%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 3.72 (t, 2H, HOCH_2, J = 6.0 Hz), 3.43 (t, 2H, N_3CH_2, J = 6.6 Hz), 2.11 (s, 1H OH), 1.93 – 1.71 (m, 2H, CH_2).

Azidoalkyl methacrylate

Azidoalkylmethacrylates were prepared similar to a literature procedure.[3] α-Azido-ω-hydroxyalkane (1 eq.), hydroquinone (5 mg) and triethyl amine (TEA, 1.3 eq.) were dissolved in dry dichloromethane (DCM) and cooled to 0°C in an ice bath. Methacryloyl chloride (1.2 eq.) was added slowly over a period of 10 minutes. The ice bath was removed and the mixture was stirred over night at room temperature. After extraction with 1M HCl (3 x 50 mL), 1M NaOH (2 x 50 mL) and brine (2x 50 mL) the organic phase was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was distilled twice (56 °C, 0.03 mbar) for azidopropyl methacrylate (AzPMA) or purified by column chromatography using hexanes and ethyl acetate (5:1.5) as eluent for azidohexyl methacrylate (AzHMA) to yield a colorless liquid.

AzPMA

Yield: 52%

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 6.10 (m, 1H, CH_2=C), 5.57 (m, 1H, CH_2=C), 4.23 (t, 2H, CH_2OOC, J = 6.2 Hz), 3.41 (t, 2H, CH_2N_3, J = 6.7 Hz), 2.05 – 1.86 (m, 5H, CH_3 + CH_2).

AzHMA

Yield: 44%

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) = 6.07 (m, 1H, CH_2=C), 5.53 (m, 1H, CH_2=C), 4.12 (t, 2H, CH_2OOC, J = 6.6 Hz), 3.25 (t, 2H, CH_2N_3, J = 6.9 Hz), 1.92 (m, 3H, CH_3), 1.74 – 1.50 (m, 4H, CH_2), 1.49 – 1.25 (m, 4H, CH_2).

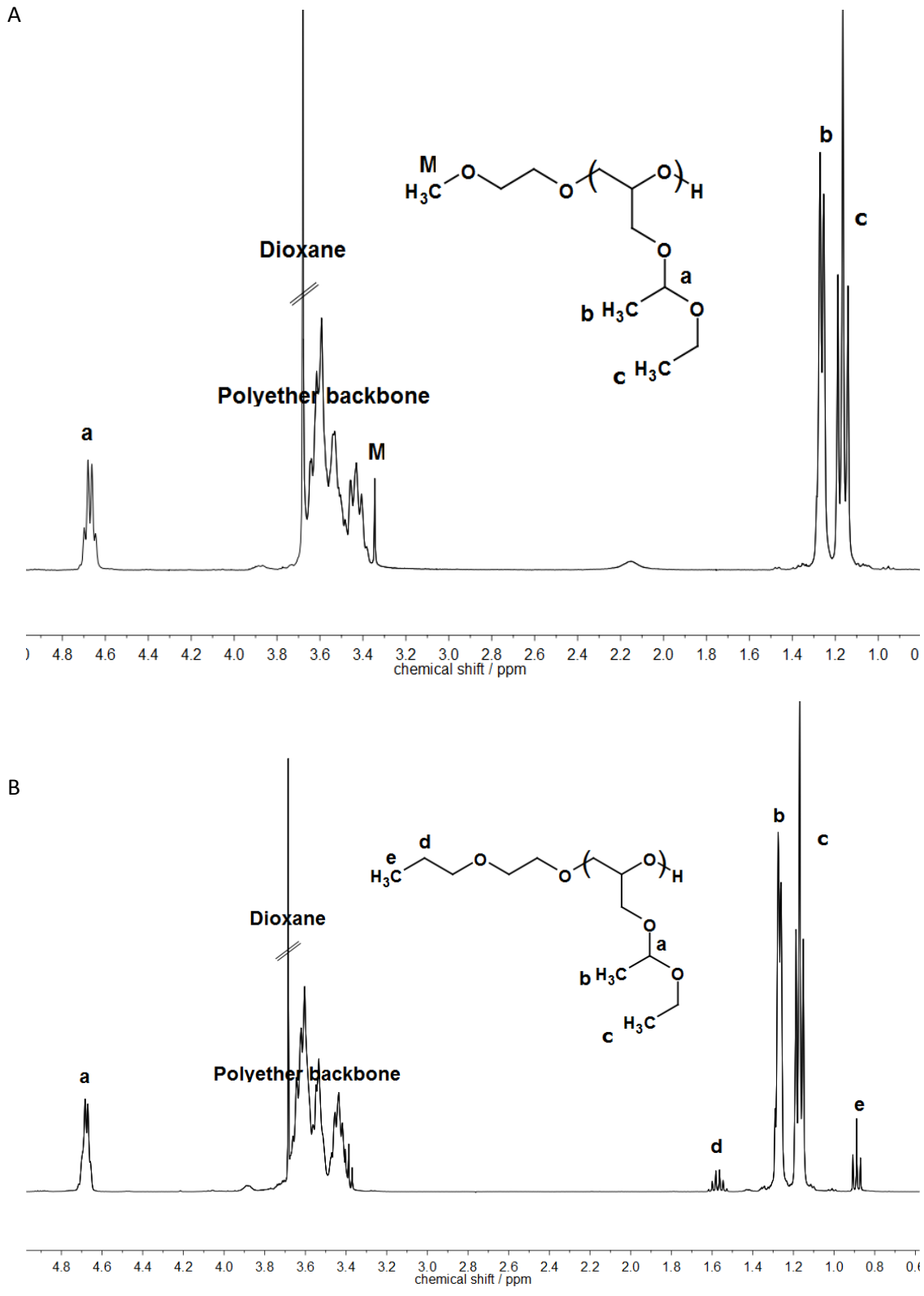


Figure S1 ^{1}H NMR spectra in C*D*Cl$_3$ of P(EEGE) using MEtOH (A, 300 MHz) or PEtOH (B, 400 MHz) as initiator.

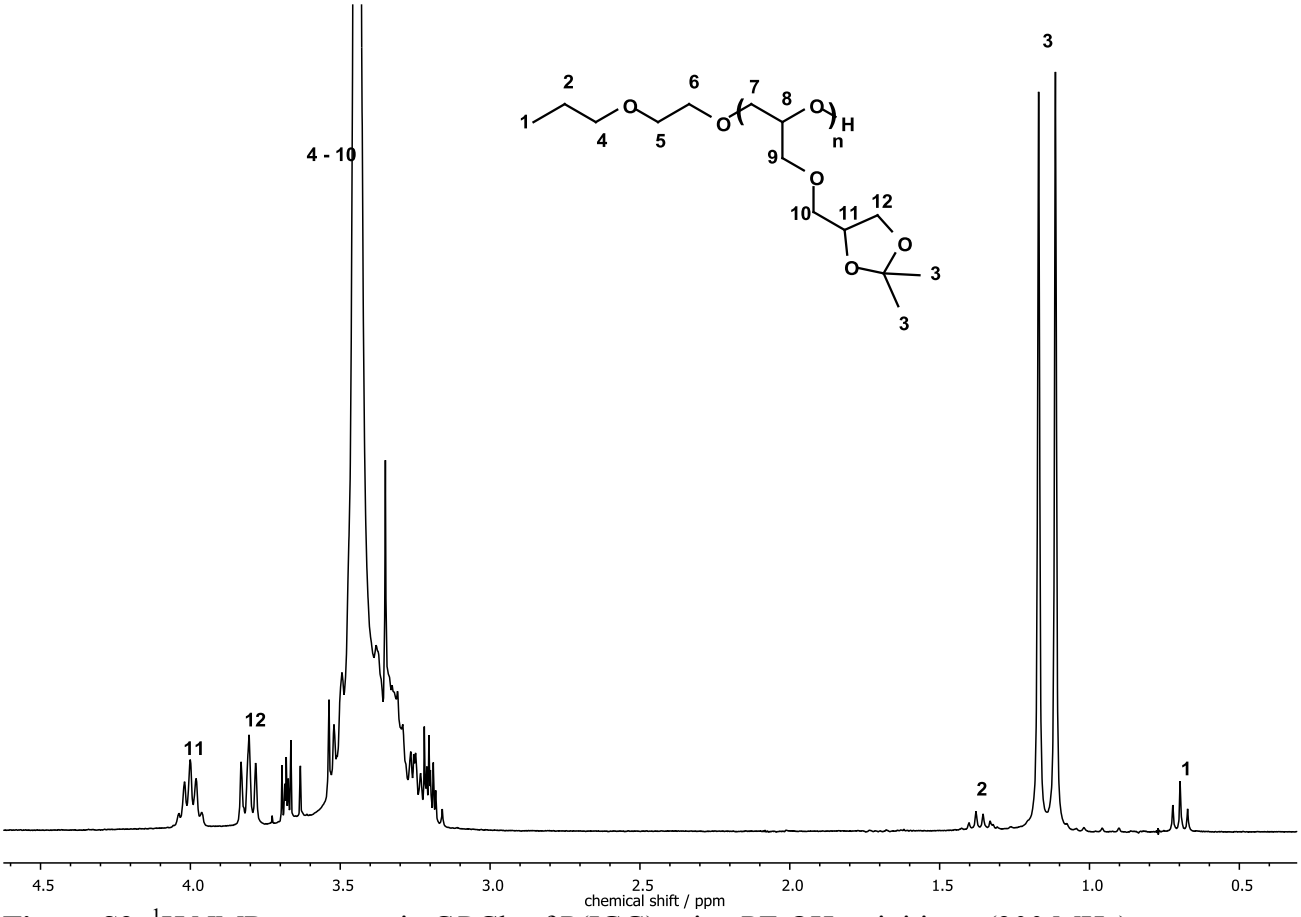


Figure S2. ^{1}H NMR spectrum in C*D*Cl$_3$ of P(IGG) using PEtOH as initiator (300 MHz)

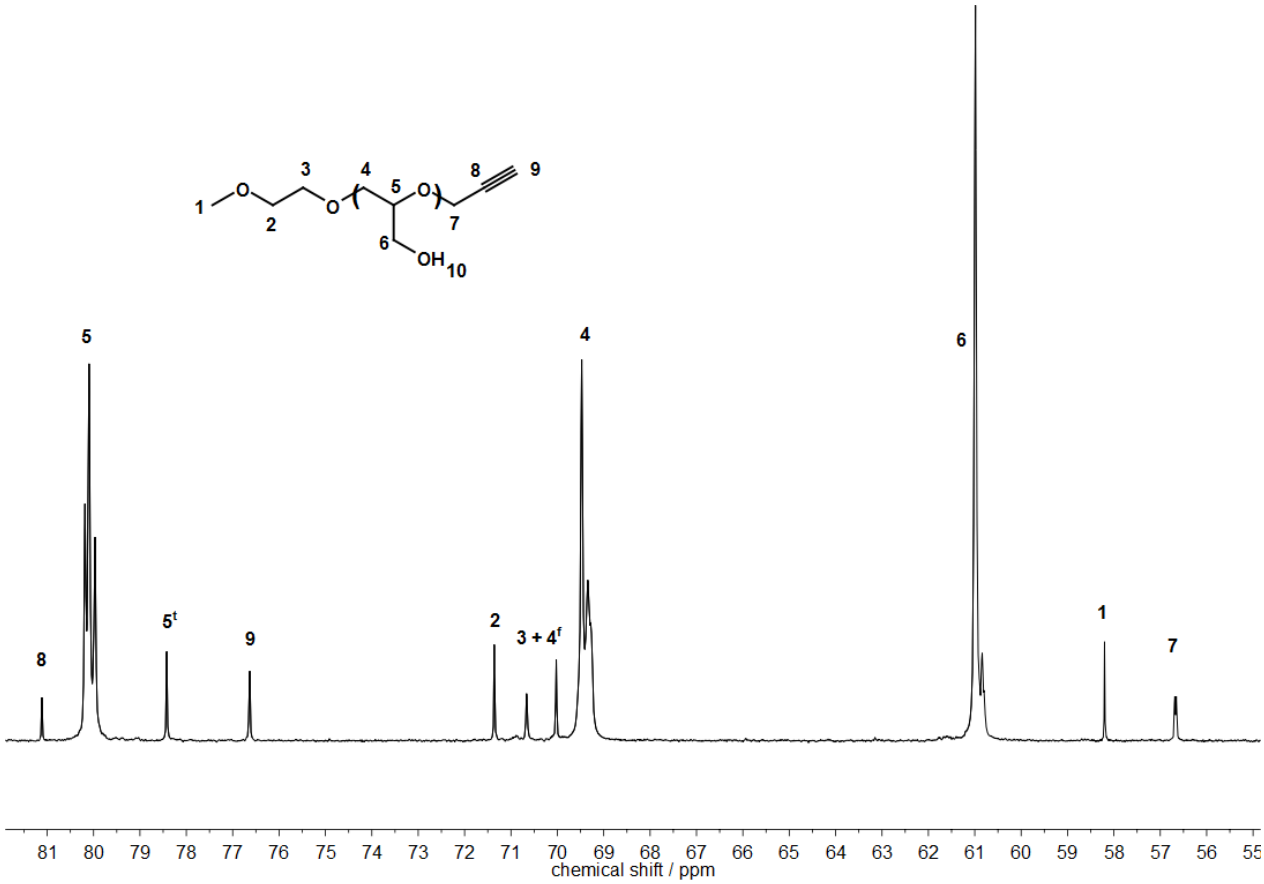


Figure S3. ^{13}C-NMR spectrum for *lin*PPG$_{24}$ (100 MHz, DMSO-d_6).

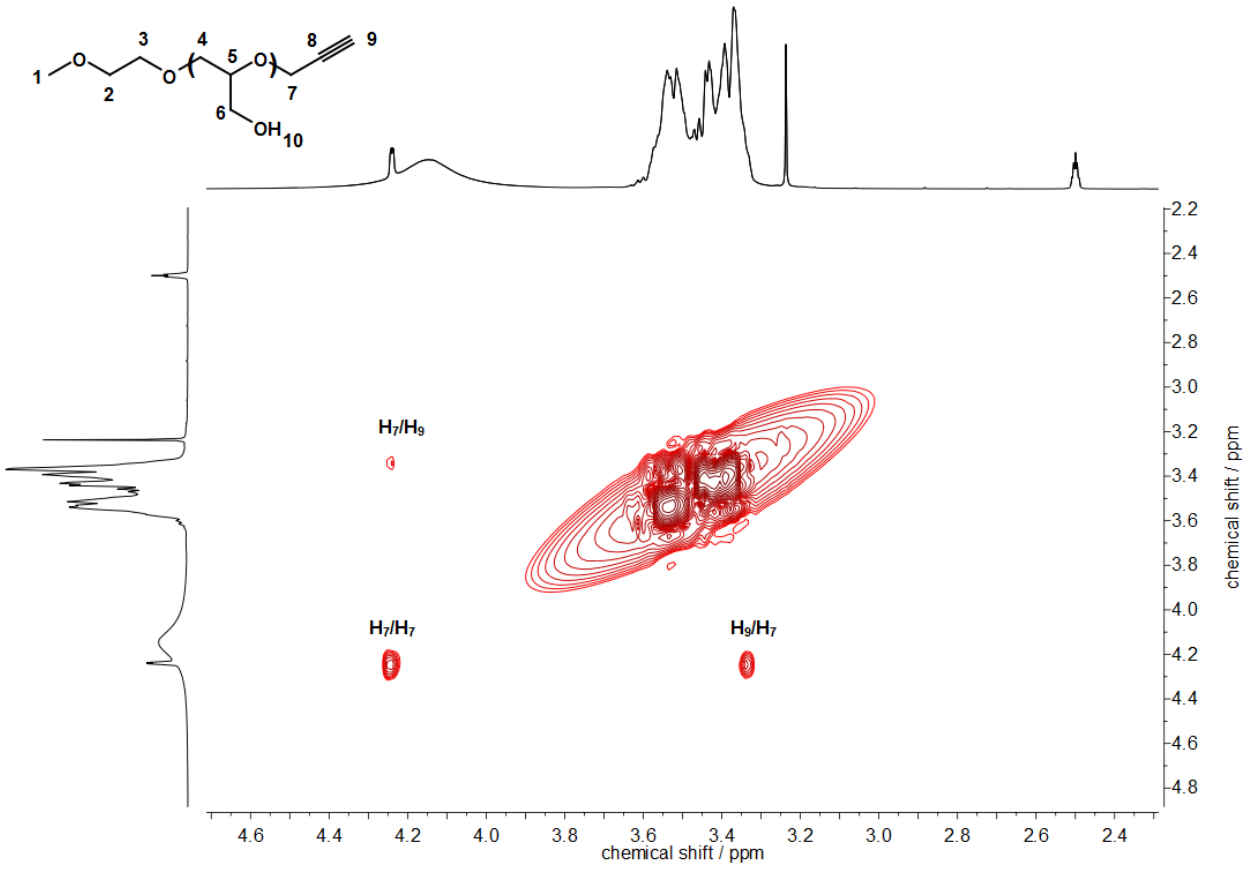


Figure S4. COSY NMR spectrum of *lin*PPG$_{24}$ in DMSO-d_6.

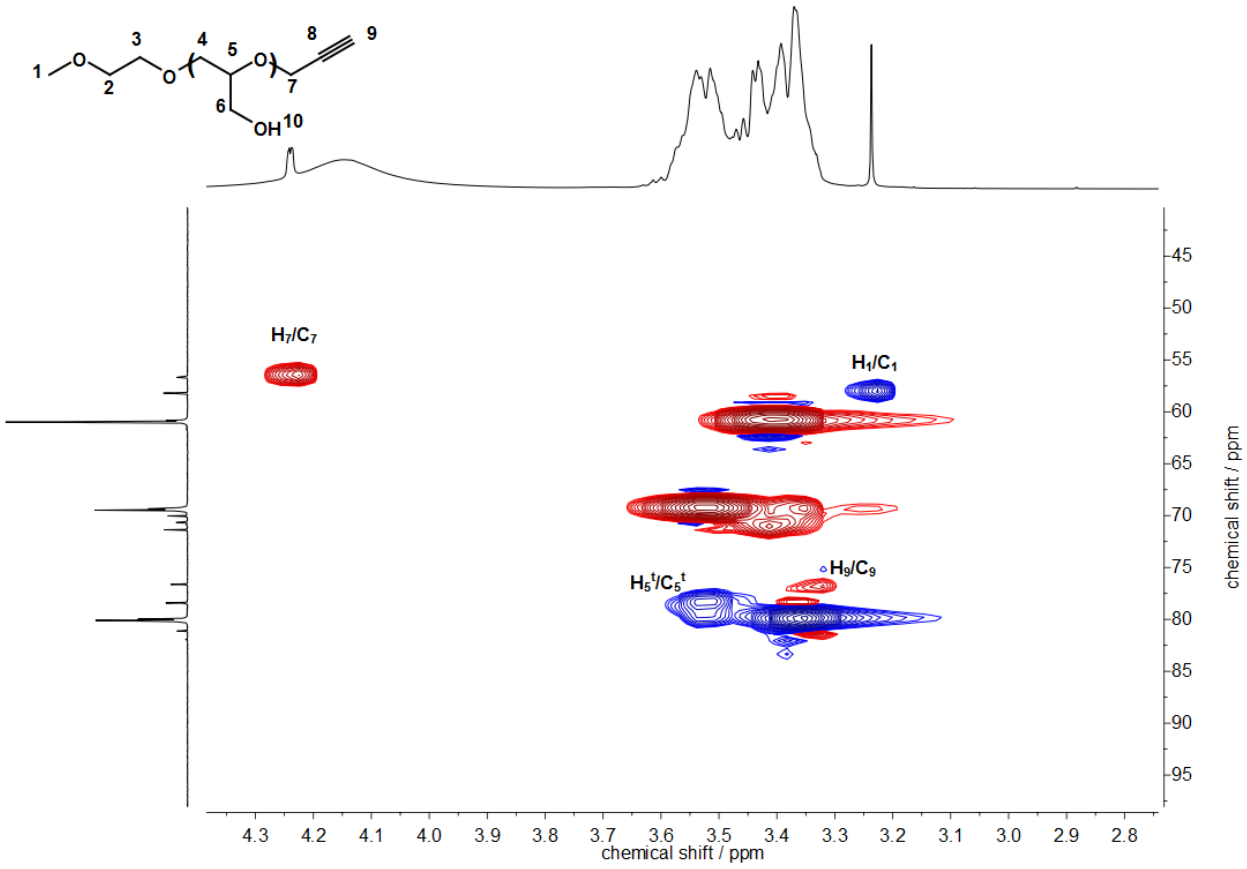


Figure S5. HSQC NMR spectrum for *lin*PPG$_{24}$ in DMSO-d_6.

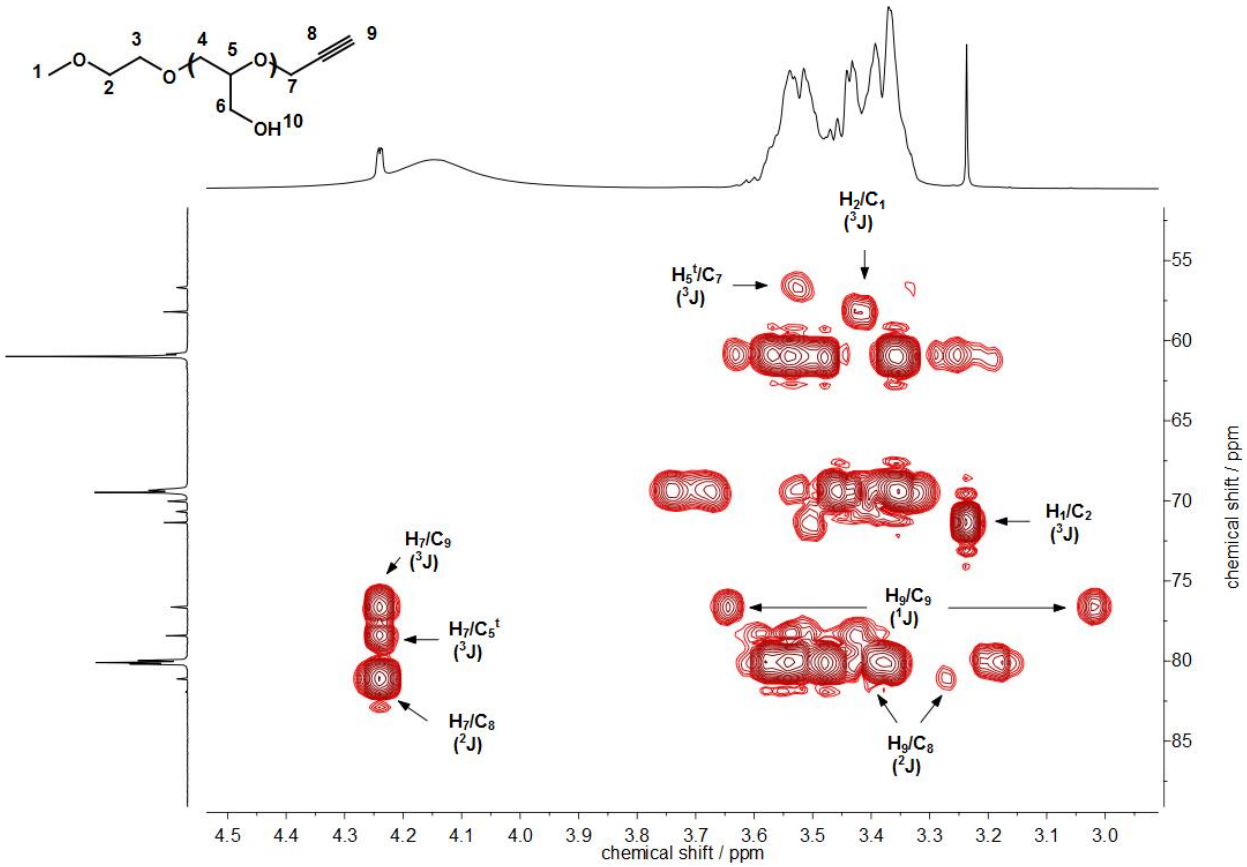


Figure S6. HMBC NMR spectrum for *lin*PPG$_{24}$ in DMSO-d_6.

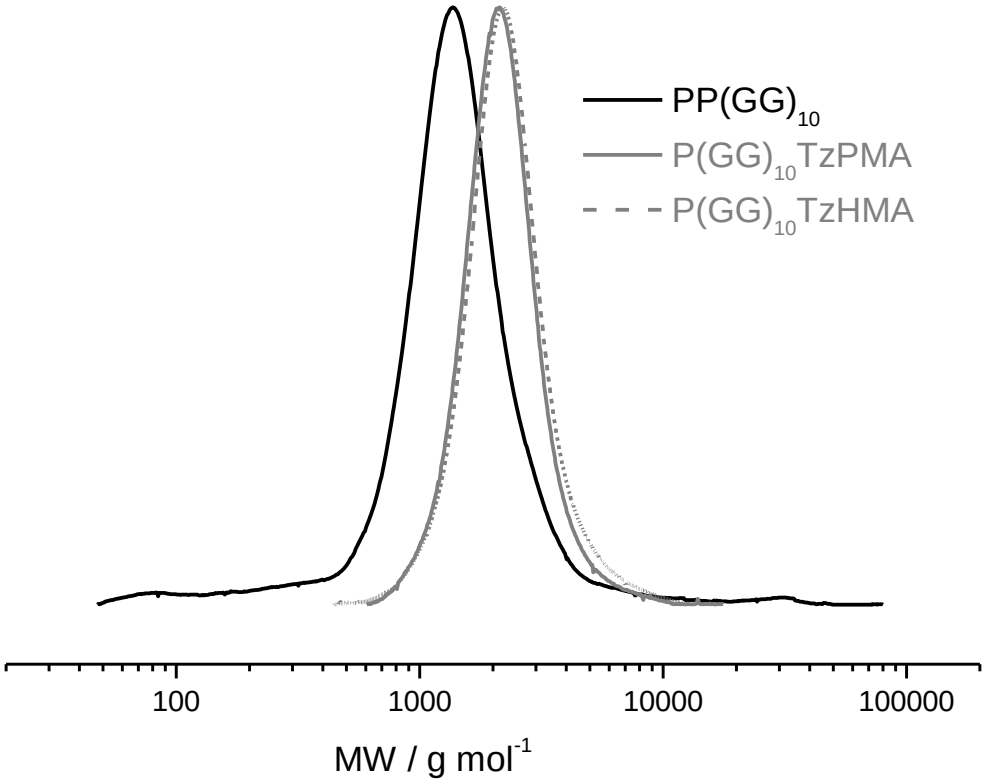


Figure S7. SEC for $PP(GG)_{10}$ (black solid line, sample XI, table 1)), $P(GG)_{10}TzPMA$ (grey solid line, cf. table 2) and $P(GG)_{10}TzHMA$ (grey dashed line, cf. table 2). SEC in DMF, PEG standards, RI signal.

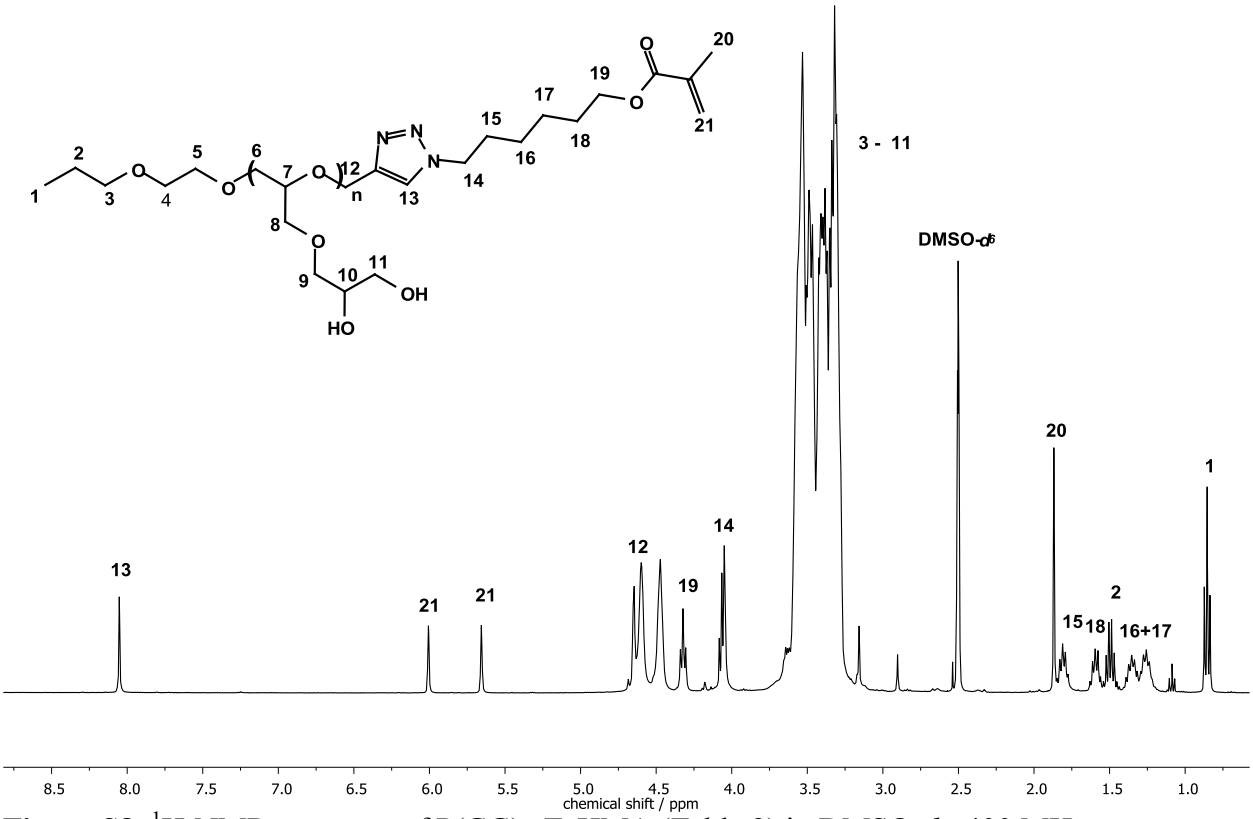


Figure S8. ^{1}H-NMR spectrum of P(GG)$_{10}$TzHMA (Table 2) in DMSO-d_6, 400 MHz.

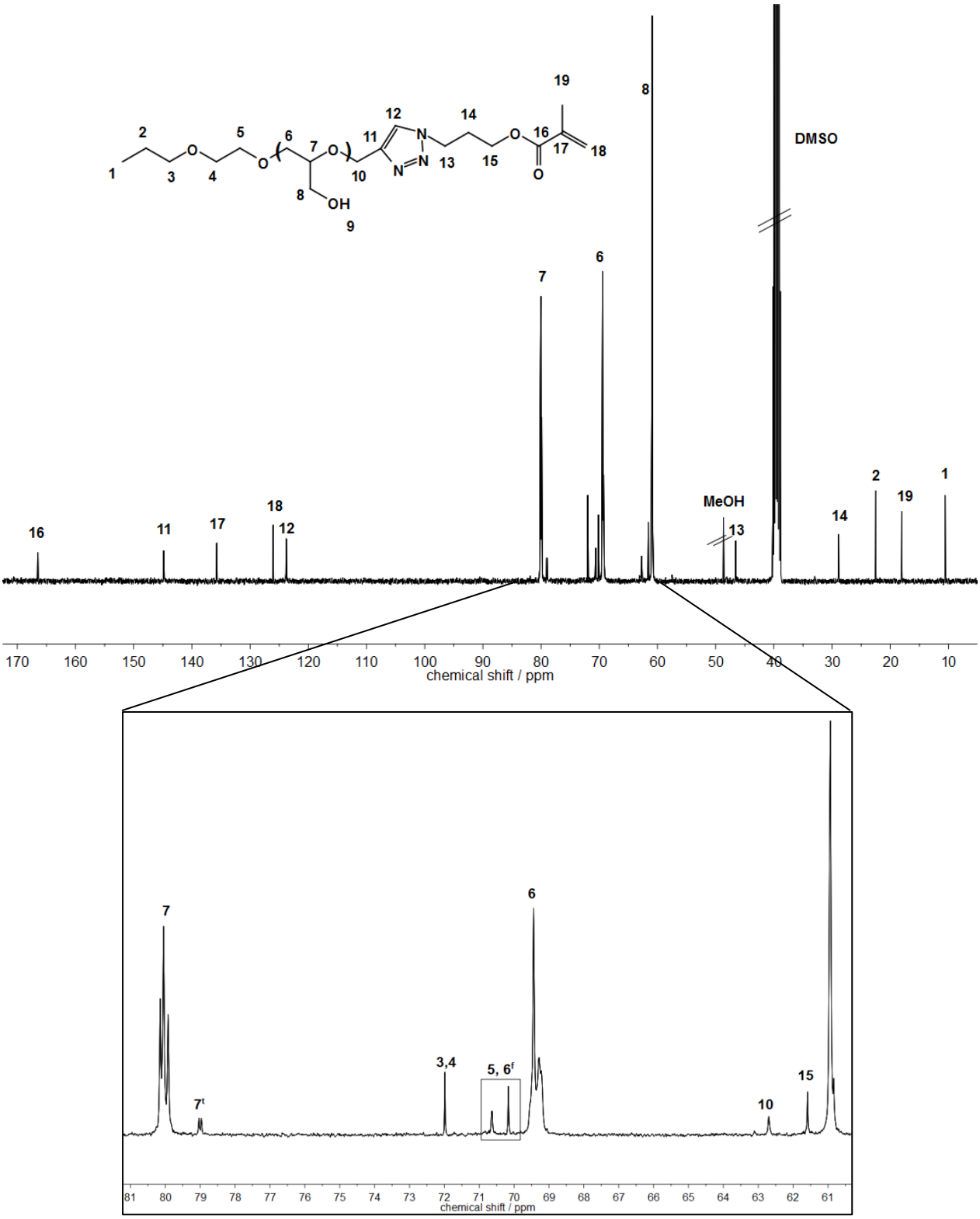


Figure S9. ^{13}C-NMR spectrum for *lin*PG$_{22}$TzPMA (100 MHz, DMSO-d_6).

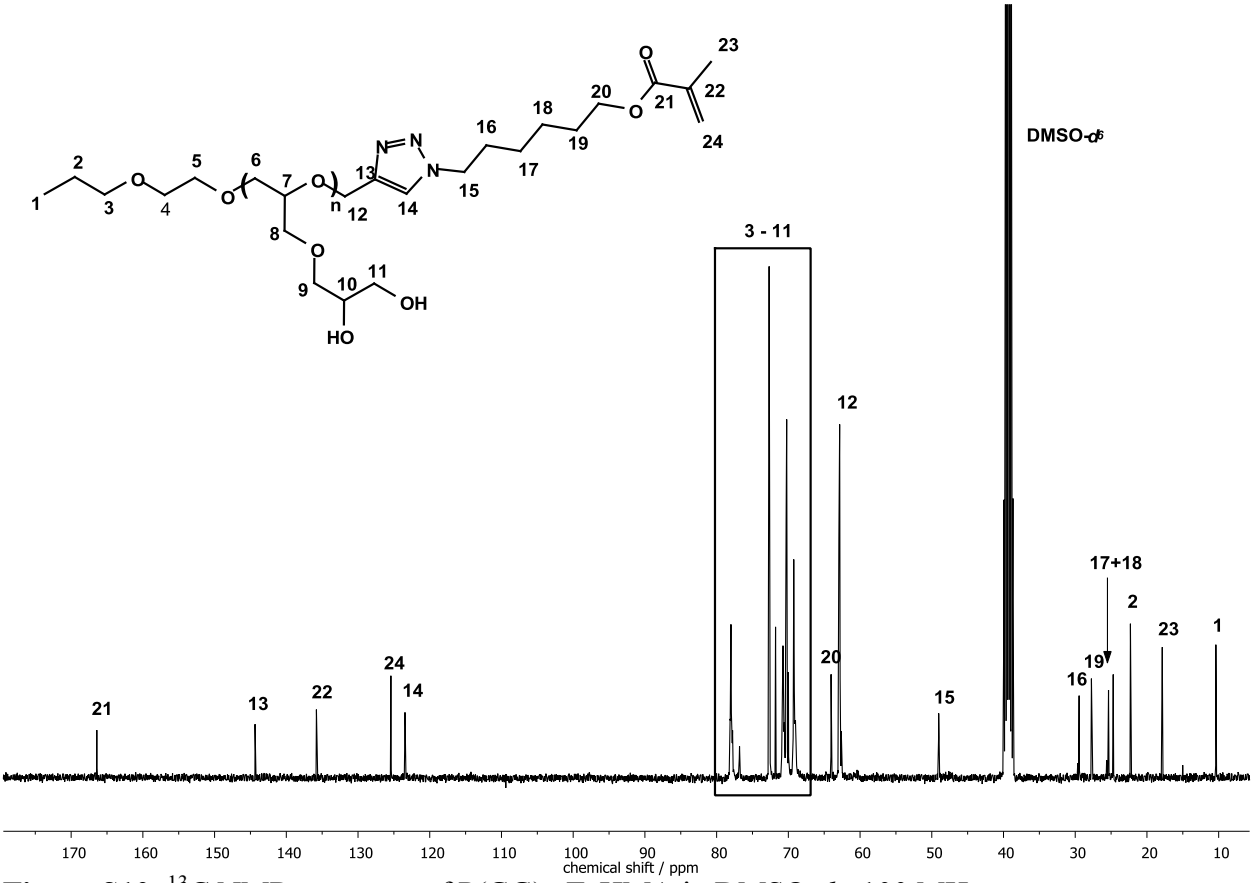


Figure S10. ^{13}C NMR spectrum of P(GG)$_{10}$TzHMA in DMSO-d_6, 100 MHz.

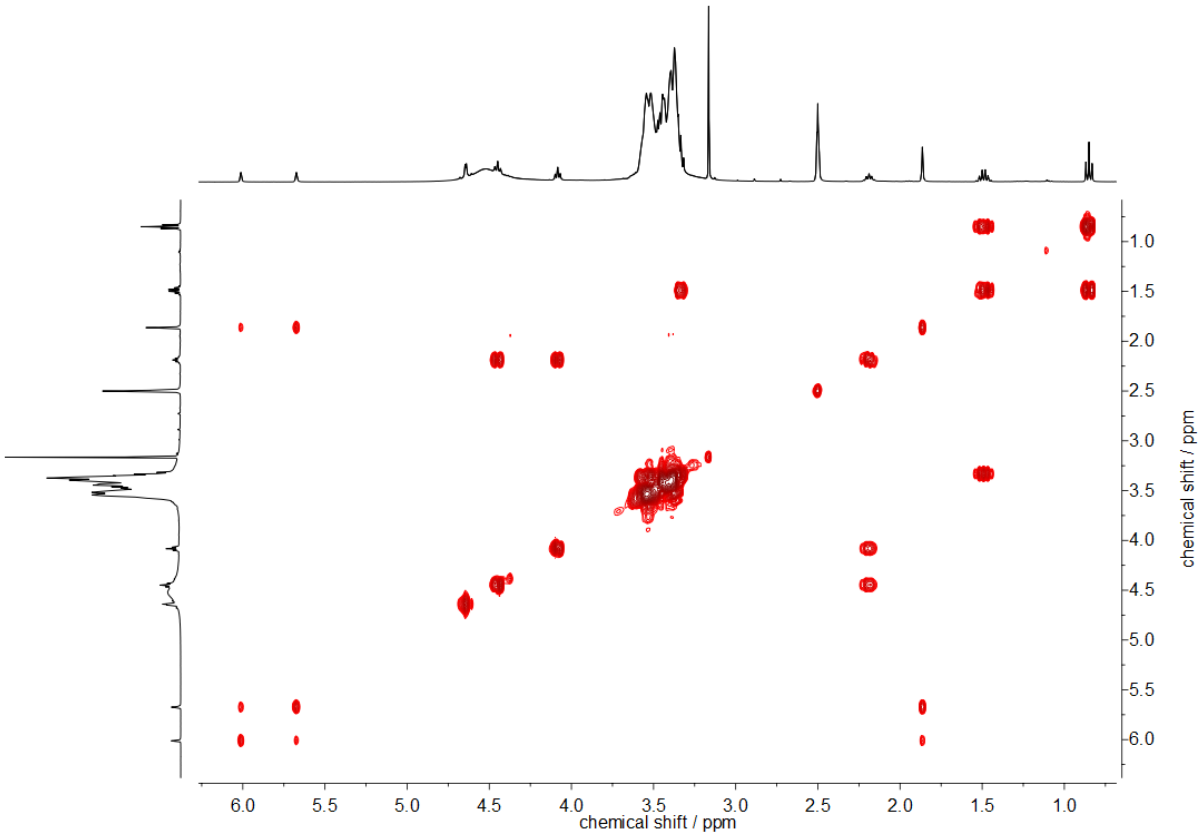


Figure S11. COSY NMR spectrum of *lin*PG_{22}TzPMA (400 MHz, DMSO-d_6).

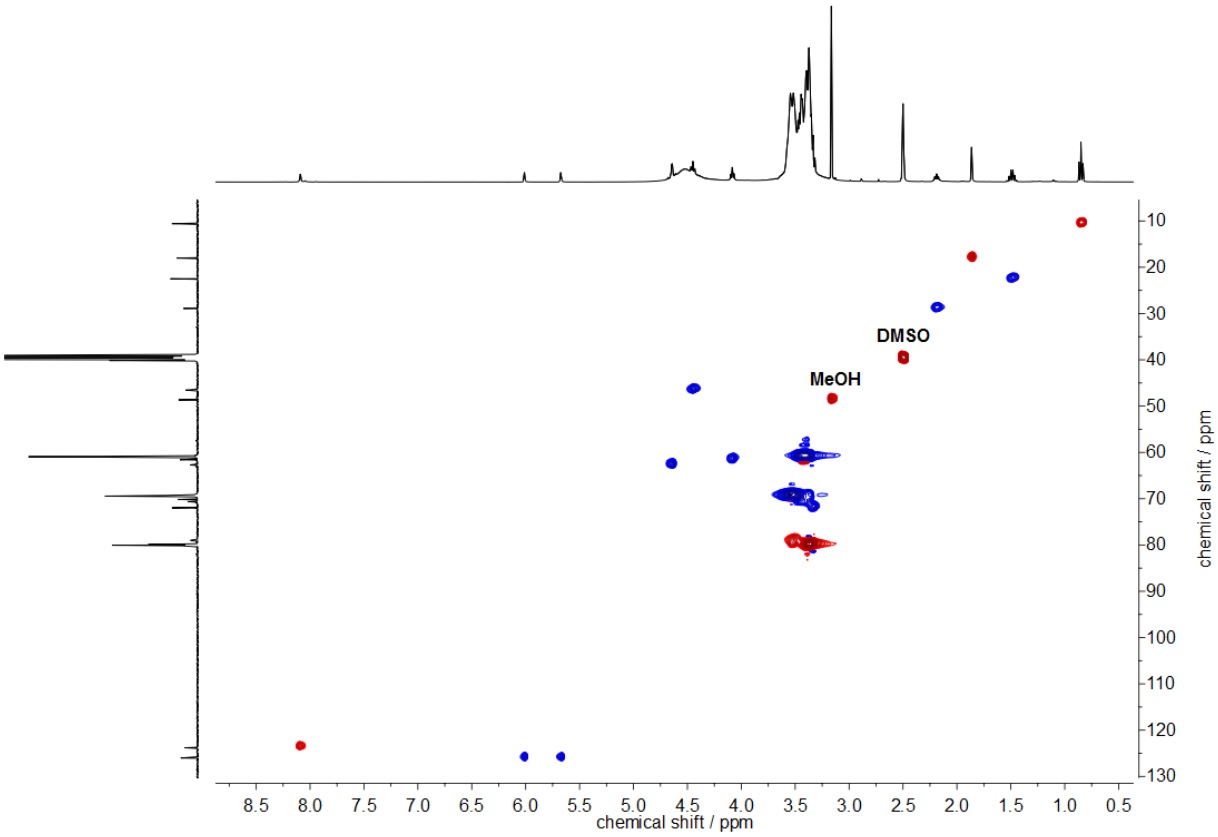


Figure S12. HSQC NMR spectrum for *lin*PG_{22}TzPMA (400 MHz, DMSO-d_6).

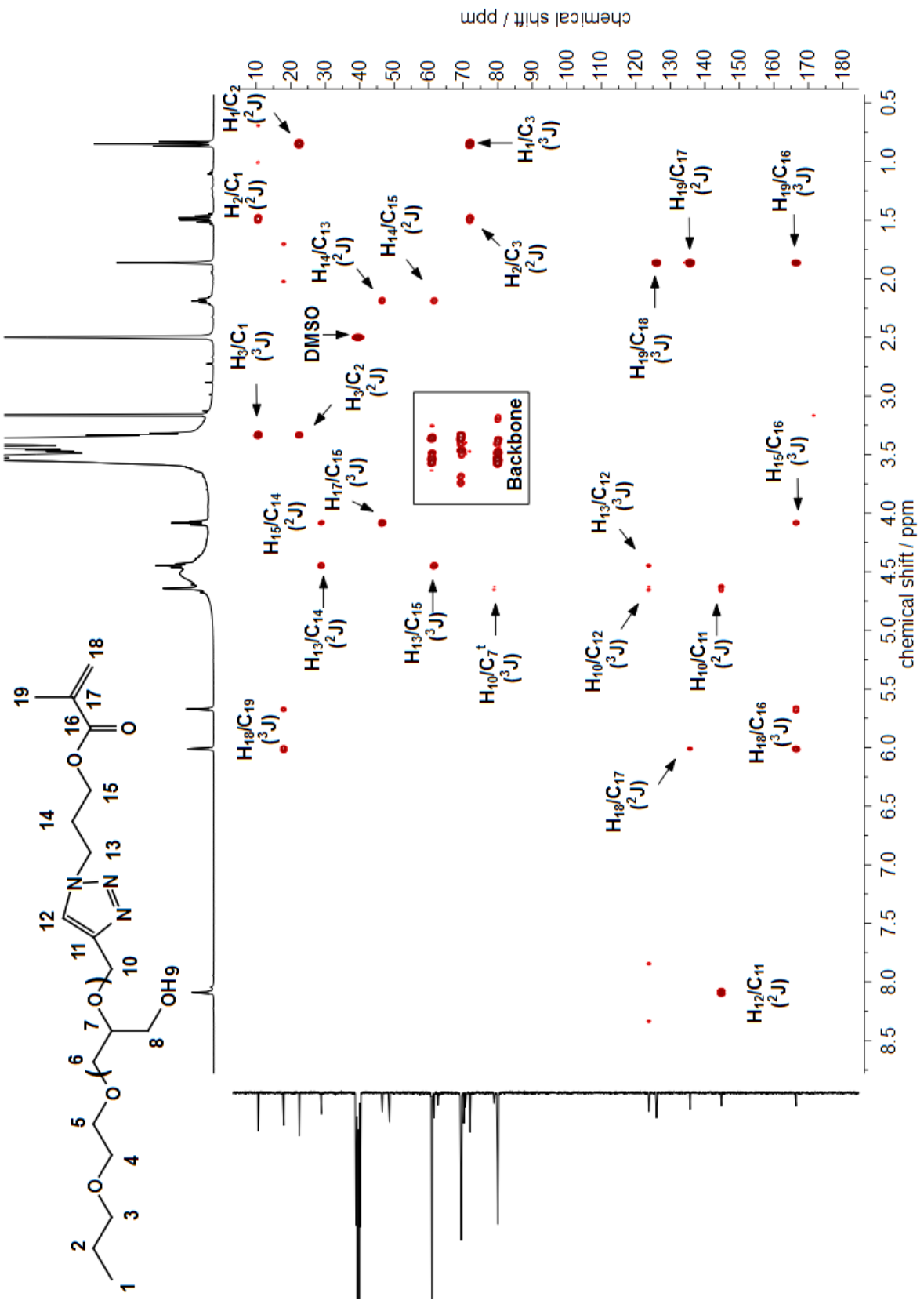
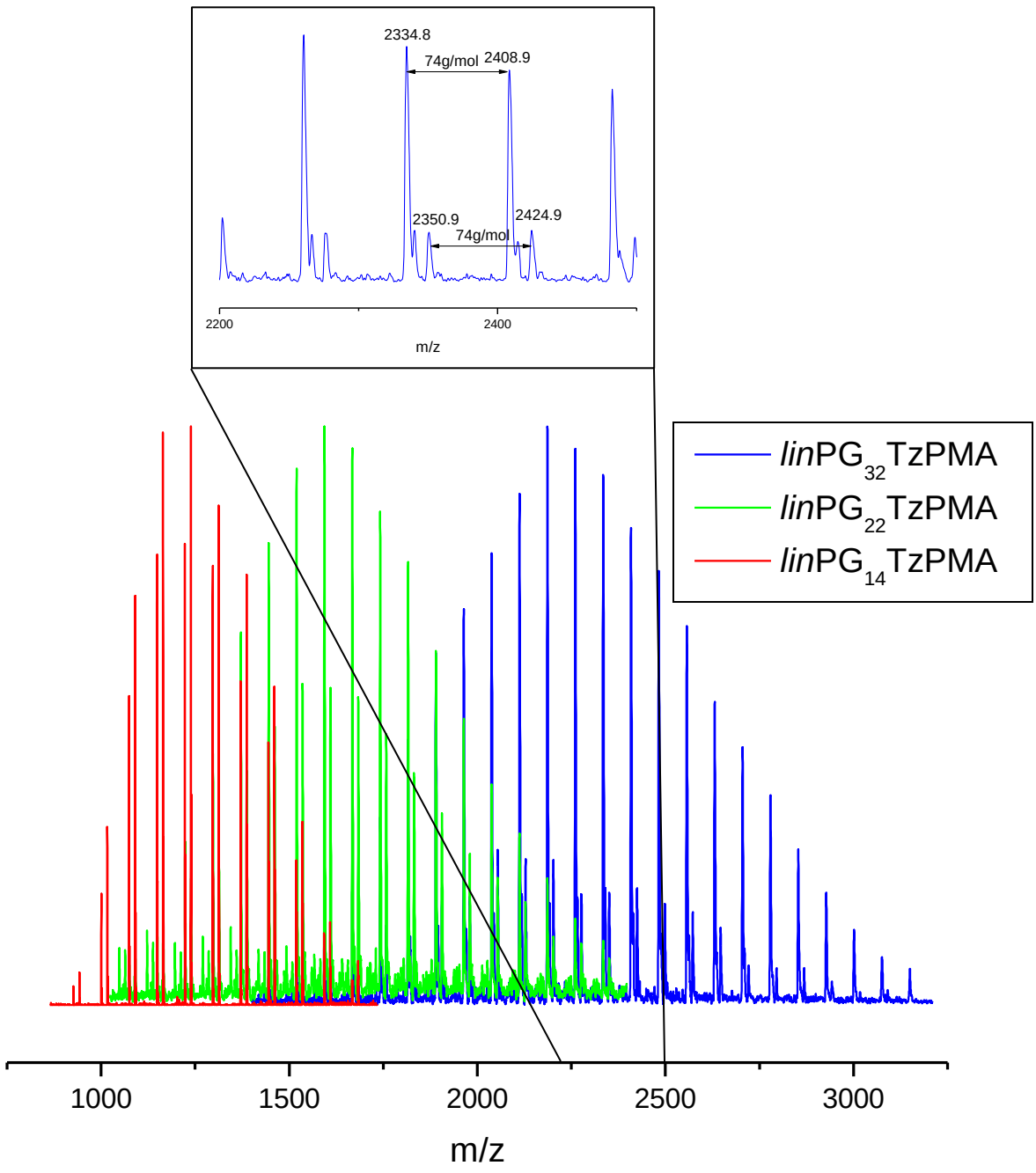


Figure S13. HMBC NMR spectrum for *lin*PG_{22}TzPMA in DMSO-d_6 (400 MHz).

A)



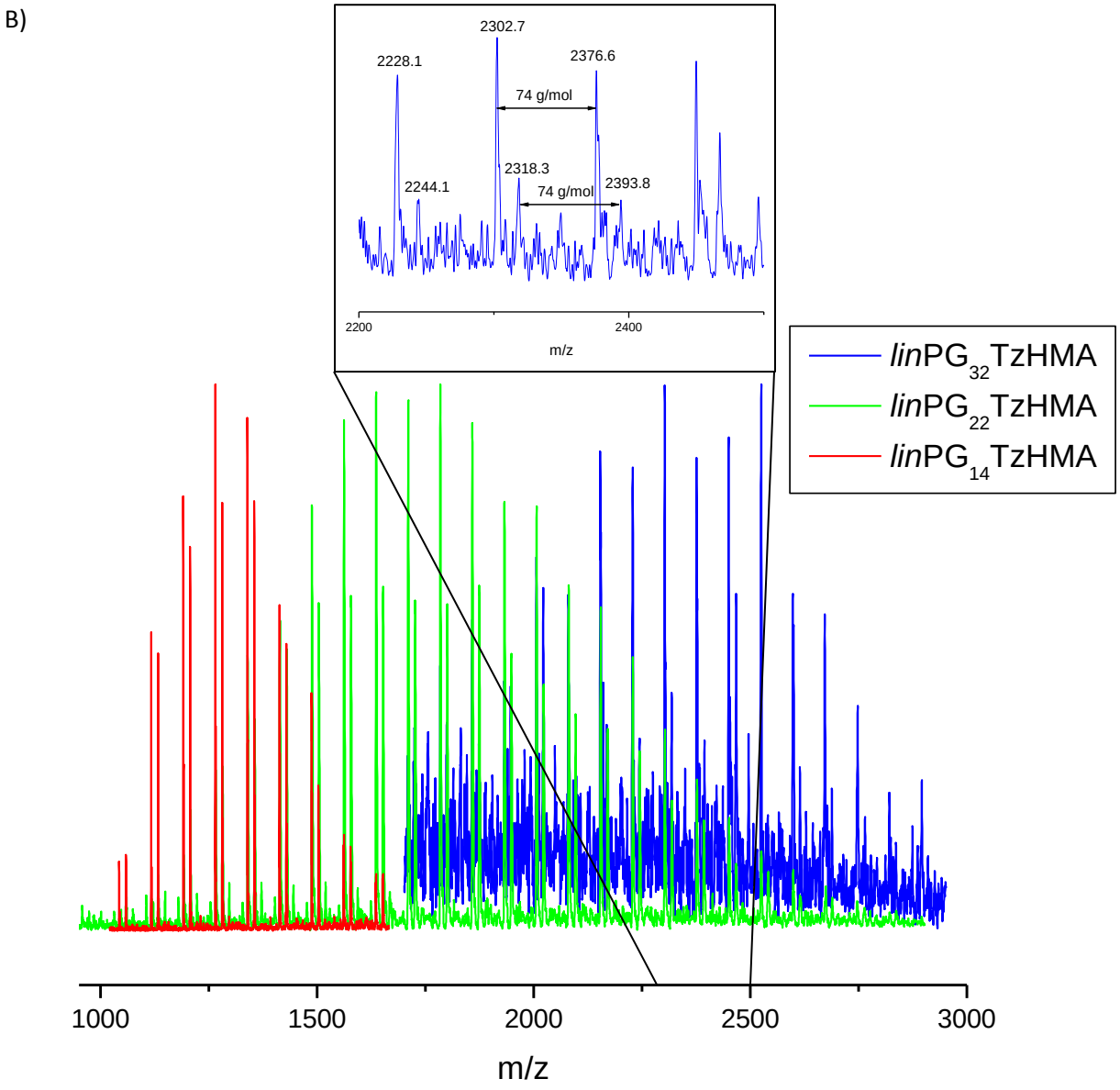


Figure S14. A) MALDI-ToF spectra of *lin*PG_{14}TzPMA (red) *lin*PG_{22}TzPMA (green) *lin*PG_{32}TzPMA (blue) and B) *lin*PG_{14}TzHMA (red,) *lin*PG_{22}TzHMA (green) *lin*PG_{32}TzHMA (blue). The distributions represent the desired macromonomer structures ionized with sodium and potassium, with the mass difference being exactly 74 g/mol (mass of one glycerol unit) for both the sodium and the potassium distribution.

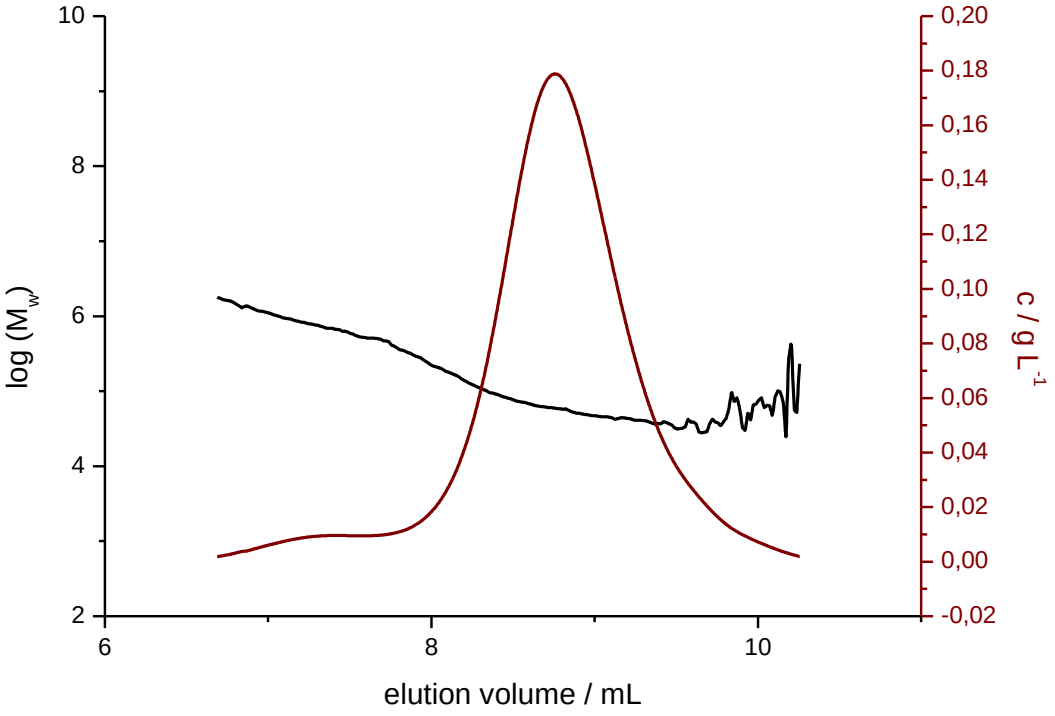


Figure S15. SEC-MALLS measurement for P(*lin*PG$_{32}$TzHMA), sample XVI, table 3.

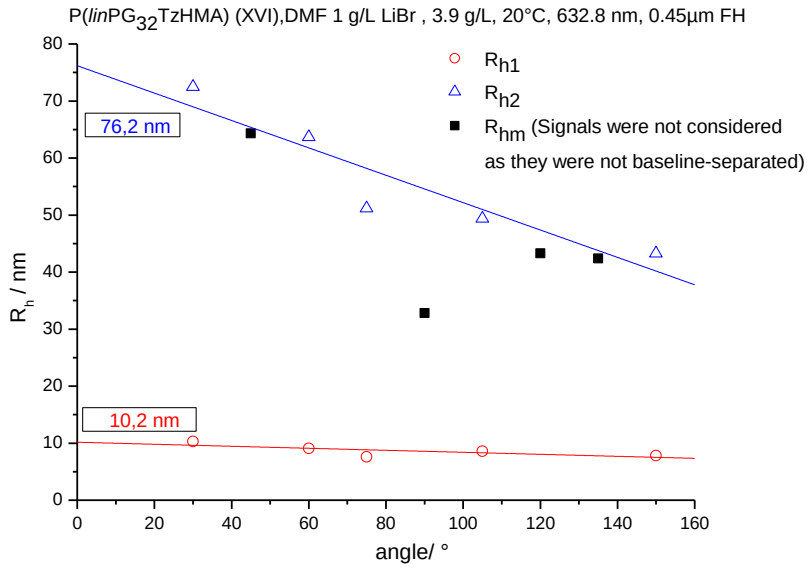


Figure S16. DLS measurement for P(*lin*PG$_{32}$TzHMA), sample XVI, table 3.

1. F. Wurm, J. Nieberle and H. Frey, *Macromolecules*, 2008, **41**, 1909-1911.
2. Y. Li and B. C. Benicewicz, *Macromolecules*, 2008, **41**, 7986-7992.
3. B. S. Sumerlin, N. V. Tsarevsky, G. Louche, R. Y. Lee and K. Matyjaszewski, *Macromolecules*, 2005, **38**, 7540-7545.