Electronic Supplementary Material (ESI) for Polymer Chemistry.

-Supporting Information-

"Clickable PEG" via Anionic Copolymerization of Ethylene Oxide and Glycidyl Propargyl Ether

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Materials. Ethylene oxide (EO), glycidyl propargyl ether (GPgE), chlorobenzene, Chelex® 100 sodium form (50-100 mesh, dry), Concanavalin A and HEPES buffer were purchased from Sigma-Aldrich. GPgE was freshly distilled from CaH_2 prior to use (see Figure S1-S2 for detailed analysis). Deuterated chlorobenzene was received from Deutero GmbH and dried over CaH_2 and freshly distilled prior to use. Tetra(*n*-butyl) ammonium iodide (TBAI) and all other reagents were reagent grade and purchased from Acros Organics. Anhydrous chlorobenzene was stirred over CaH_2 and freshly distilled before use. If not otherwise stated, the chemicals were used as received.

Note: Ethylene oxide is a toxic gas and precautions must be taken before handling.

General procedures. All reactions involving air or moisture sensitive reagents or intermediates were performed under an inert atmosphere of argon in glassware that was oven dried. Reaction temperatures referred to the temperature of the particular cooling/heating bath. Chromatography was performed using flash chromatography of the indicated solvent system on 35-70 μm silica gel (*Acros Organics*) unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates ($60F_{254}$) using an 1M ethanolic solution of sulfuric acid with 0.2% 3-methoxyphenol and heat as developing agents.

Instrumentation. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded using a Bruker *Bruker Avance-II 400* MHz spectrometer equipped with a 5 mm BBFO-SmartProbe (Z-gradient probe) and an ATM as well as a SampleXPress 60 auto sampler. Chemical shifts were referenced to the deuterated solvent (e.g., for $CDCl_3$, δ = 7.26 ppm and 77.16 ppm for ^{1}H and ^{13}C NMR, respectively) and reported in parts per million (ppm, δ) relative to tetramethylsilane (TMS, δ = 0.00 ppm).[1] (1) Coupling constants (*J*) were reported in Hz and the splitting abbreviations used were: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. SEC measurements were performed in DMF (containing 0.25 g L^{-1} lithium bromide as an

additive) or in THF. For SEC measurements in DMF, an Agilent 1100 Series was used as an integrated instrument, including a PSS HEMA column (300/100/40 · 10^{-10} porosity) as well as a UV (275 nm) and a RI detector. Alternatively, SEC measurements in THF (flow rate 1 mL·min^{-1}) were performed with a MZ-Gel SD plus column (10^5/10^3/100 g mol^{-1}) at 20 °C, using a UV (254 nm) and RI detector. All calibrations were carried out using poly(ethylene glycol) standards purchased from Polymer Standards Service. ^{1}H NMR kinetic studies to monitor copolymerization were conducted on a Bruker Avance III HD spectrometer equipped with a 5 mm BBFO SmartProbe and an ATM as well as a SampleXPress 60 auto sampler. DSC measurements were performed under nitrogen atmosphere using a PerkinElmer DSC 8500 with PerkinElmer CLN2 in the temperature range from – 100 °C to 100 °C (sugar functionalized materials were only heated to 60 °C) at heating rates of 20 and 10 K·min^{-1} for the first and the second heating run, respectively. Specific reactions were monitored by LC-MS on a 1200 HPLC-unit from *Agilent Technologies* with binary pump and integrated diode array detector coupled to a LC/MSD-Trap-mass-spectrometer from *Bruker*. Ionization was achieved by an electron-spray-ionization source (ESI) or an atmospheric-pressure-chemical-ionization source (APCI). Infrared spectra were recorded as FT-IR spectra using a diamond ATR unit and are reported in terms of frequency of absorption (ν, cm^{-1}).

***In situ* ^{1}H NMR kinetic studies of copolymerization.** Measurements were conducted according to a literature procedure.[2] A NMR tube suitable for high pressure and high vacuum Norell S-500-VT-7 NMR tube (equipped with a Teflon stop-cock) was applied. The tube was evacuated and filled with (1) 0.1 mL initiator solution (24 mg TBAI in 0.5 mL chlorobenzene-d_5) followed by (2) 0.3 mL neat chlorobenzene, (3) 60 µL TIBAL solution in toluene (1.1 M, 5 euqiv), (4) 0.2 mL neat chlorobenzene and (5) 21 µL GPgE monomer under argon flow and repeated cooling with an acetone/dry ice bath. Afterwards, the tube was evacuated under cooling and EO was cryo-transferred into the tube (~20 µL). Before the

measurement, the tube was shaking vigorously and subsequently placed in the NMR spectrometer (T = 0 °C). After the temperature in the spectrometer was constant (~10 min, ΔT = 0.1 K), the first spectrum was recorded. Sample spinning was turned off. Spectra were recorded with 16 scans with 2 min-intervals. After 1h at 0 °C, the temperature was raised to 5 °C, all other parameters were kept constant. After another hour, the temperature was set to 10 °C and then to 15 °C. The measurement was stopped after full conversion (~5 h).

Synthesis of poly(ethylene glycol-*co*-glycidyl propargyl ether) (PEG-*co*-PGPgE) copolymers. Here, an exemplary synthesis protocol is described for the synthesis of PEG_{195}-*co*-$PGPgE_5$ with 2.5 mol% GPgE content. TBAI (1 equiv, 83.5 mg) were dissolved in 5 mL benzene and freeze dried under vacuum to remove residual water. The flask was backfilled with argon and 15 ml of chlorobenzene were added via syringe. For the transfer of EO into the flask, vacuum was applied and EO (195 equiv, 2 mL) was cryo-transferred into a graduate ampoule and subsequently into the reaction flask, using an ethanol/liquid nitrogen cooling bath (-80 °C). The flask was sealed, backfilled with argon and 0.12 mL (5 equiv) of freshly distilled GPgE was added via septum by syringe. The reaction was initiated at -15 °C (ice/NaCl bath) by addition of 0.3 mL *i*-Bu_3Al solution in toluene (1.5 equiv, 1.1 M in toluene) and slowly allowed to warm up to room temperature. After 24 h an aliquot was withdrawn from the reaction solution and characterized by ^1H NMR to determine residual epoxide signals and if full conversion was reached, termination was conducted by addition of an excess of ethanol (1 mL). Afterwards, the polymer was precipitated into ice cold diethyl ether. Dialysis in methanol and then DI water (MWCO = 2000 $g \cdot mol^{-1}$) was performed to remove residual tetra(*n*-butyl) ammonium salts. Small loss was observed due to dialysis. Overall yield ≥ 90%. Afterwards, copolymers were dried via lyophilization for DSC measurements. Note, direct purification of the polymers is recommended to extend their shelf-life. Small amounts of basic impurities lead

to crosslinking. Purified polymers were stored in the dark at -18 °C and are stable for several weeks.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.17 (m, 2H, HC≡CCH_2-), 3.81-3.44 (m, 9H, polyether backbone + HC≡CCH_2OCH_2-), 2.45 (m, 1H, HC≡CCH_2-).

Homopolymerization (PGPgE). GPgE was polymerized similar to a literature procedure described for epicyanohydrin by applying monomer-activated AROP.[3] As a typical procedure, TBAI (1 equiv) was added to a Schlenk flask, freeze-dried with benzene overnight and backfilled with argon. Chlorobenzene was added under argon atmosphere via syringe (c = 1 mol·L^{-1}). The solution was cooled to 0 °C before the dry monomer was syringed in, followed by ^{i}Bu$_3$Al solution in toluene (3-4 equiv). Polymerization was conducted under argon atmosphere and the solution was allowed to slowly reach room temperature and was terminated after 24 h by addition of ethanol. Before further purification steps were conducted, an aliquot was withdrawn from the reaction solution and characterized by ^{1}H NMR to determine the monomer conversion. Chlorobenzene was removed under vacuum and the crude polymer was dissolved in THF and precipitated into methanol (room temperature). This purification step was repeated twice to remove tetra(*n*-butyl)ammonium salts and the homopolymer was obtained in quantitative yield. Alternatively, tetra(*n*-butyl)ammonium salts can be removed via consecutive washing of the reaction mixture with saturated $NaHCO_3$ solution, NaCl solution (10%), and water in analogy to reports by Osterwinter et al.[4]

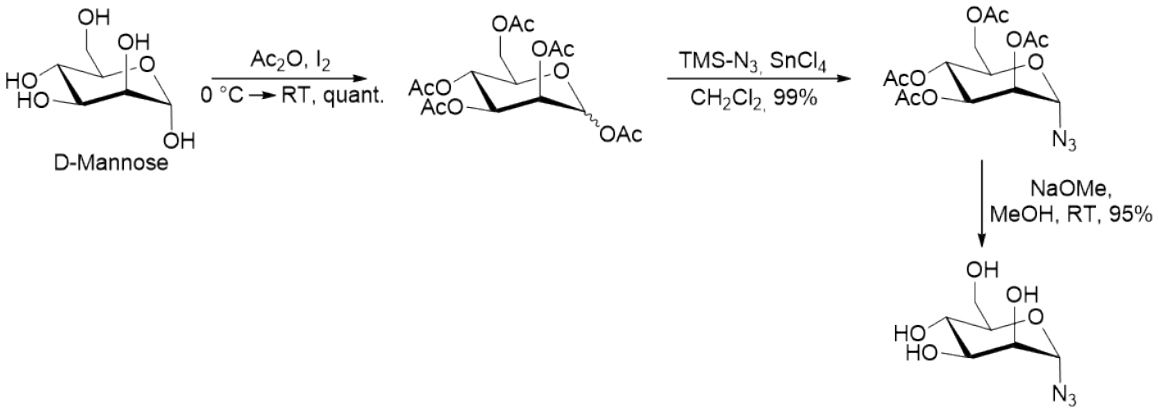
Table S1. Characterization data of additional PGPgE homopolymers.

[^{i}Bu$_3$Al]/[TBAI]	PGPgE[a]	M_n[a]	M_w/M_n[a]
4	28	3180	1.19
5	83	9350	1.34

[a]Determined via SEC (THF, RI signal, PEG standard)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.17 (m, 2H, HC≡CC*H*$_2$-), 3.70-3.55 (m, 5H, polyether backbone + HC≡CCH$_2$OC*H*$_2$-), 2.48 (m, 1H, *H*C≡CCH$_2$-), 2.14 (s, 1H, -OH end group).

Mannopyranosyl azide.



Scheme S1. Synthesis scheme of mannopyranosyl azide, starting from D-mannose.

1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranose. Iodine (560 mg, 2.2 mmol, 0.04 equiv.) and acetic anhydride (50 ml) were mixed under Ar-atmosphere. D-Mannose (10 g, 55.5 mmol, 1 equiv.) was added portion by portion at 0 °C. After stirring for 30 min at 0 °C and additionally for 18 hours at room temperature TLC (cyclohexane/toluene/ethylacetate 3:3:1) showed complete consumption of the starting material. The reaction mixture was diluted with CH_2Cl_2 (50 ml) and was washed twice with cold saturated aqueous Na_2SO_3 solution (2x 80 ml), then with a saturated aqueous solution of $NaHCO_3$ (4x 50 ml). The separated organic layer was dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to afford the desired peracetylated D-mannose (21.5 g, 55.1 mmol, 99%, mixture of both anomers α/β 12:88) as a yellowish high viscous oil.

R_f 0.30 (silica gel, cyclohexane/toluene/ethyl acetate, 3:3:1)

$C_{16}H_{22}O_{11}$ [M]: 390,34 g·mol^{-1}

MS (ESI): *m/z* (%) 413.3 (100) $[M + Na]^+$, 331.5 (6.2) $[M\text{-}OAc]^+$

Signals assignable to α-anomer: ^{1}H NMR, COSY (600 MHz, $CDCl_3$) δ (ppm) = 6.09 (d, ^{3}J = 1.9 Hz, 1H, H-1), 5.34–5.36 (m, 2H, H-3, H-4), 5.25–5.27 (m, 1H, H-2), 4.28 (dd, ^{2}J = 12.4 Hz, ^{3}J = 4.9 Hz, 1H, H-6a), 4.10 (dd, ^{2}J = 12.4 Hz, ^{3}J = 2.5 Hz, 1H, H-6b), 4.03-4.07 (m, 1H, H-5), 2.18, 2.17, 2.10, 2.05, 2.01 (5x s, 15H, COCH_3); ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ (ppm) = 170.8, 170.2, 169.9, 169.7, 168.2 (5x *C*OCH_3), 90.7 (C-1), 70.7 (C-5), 68.8 (C-3), 68.4 (C-2), 65.6 (C-4), 62.2 (C-6), 21.0, 20.9, 20.9, 20.8, 20.8 (5x CO*C*H_3).

The spectral data are in accordance with literature.[5]

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl azide. 1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranose (13.6 g, 34.9 mmol, 1 equiv.) was dissolved in anhydrous CH_2Cl_2 (140 ml) under argon atmosphere. Trimethylsilyl azide (16.1 g, 18.5 ml, 139 mmol, 4 equiv.) and tin(IV) chloride (2.37 g, 1.06 ml, 9.1 mmol, 0.26 equiv.) was added. After stirring for four hours at room temperature, TLC (cyclohexane/toluene/ethylacetate 3:3:1) showed complete consumption of the starting material. The reaction mixture was washed successively with saturated aqueous $NaHCO_3$ solution (100ml), water (100 ml) and brine (100 ml). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (cyclohexane/ ehtylacetate, 3:1) to afford the title compound (12.9 g, 34.4 mmol, 99%) as a clear, colorless oil.

R_f 0.49 (silica gel, cyclohexane/toluene/ethyl acetate, 3:3:1)

$C_{14}H_{19}N_3O_9$ [M]: 373,11 g·mol^{-1}

MS (ESI): *m/z* (%) 396.2 (100) $[M + Na]^+$, 331.7 (10.1) $[M-N_3]^+$

^{1}H NMR, COSY (400 MHz, $CDCl_3$) δ (ppm) = 5.38 (d, ^{3}J = 1.9 Hz, 1H, H-1), 5.14 (dd, ^{3}J = 3.0 Hz, ^{3}J = 1.9 Hz, 1H, H-2), 5.30–5.21 (m, 2H, H-3, H-4), 4.32-4.27 (m, 1H, H-6a), 4.17–4.11 (m, 2H, H-5, H-6b), 2.16, 2.10, 2.04, 1.98 (4x s, 12H, COCH_3); ^{13}C NMR, HSQC,

HMBC (100.6 MHz, $CDCl_3$) δ (ppm) = 170.7, 170.0, 169.9, 169.7 (4x *C*OCH_3), 87.6 (C-1), 70.7 (C-5), 69.3 (C-2), 68.3 (C-3), 65.7 (C-4), 62.2 (C-6), 21.0, 20.8, 20.8, 20.7 (4x CO*C*H_3).

The spectral data are in accordance with literature.[5]

α-D-Mannopyranosyl azide. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl azide (10 g, 26.8 mmol) was dissolved in methanol (100 ml) and sodium methoxide was added until pH 9–10 (approx. 60 mg). The reaction mixture was stirred at room temperature for 16 hours. Subsequently the solution was neutralized by Amberlite 120 H^+ resin until pH 7. The mixture was filtered over Celite which was washed thoroughly with methanol. The solvent was removed *in vacuo* to afford the desired α-D-Mannopyranosyl azide (5.23 g, 25.5 mmol, 95%) as a colorless syrup.

$C_6H_{11}N_3O_5$ [M]: 205,07 g·mol^{-1}

MS (ESI): *m/z* (%) 228.2 (100) $[M + Na]^+$

^{1}H NMR, COSY (400 MHz, $CDCl_3$) δ (ppm) = 5.43 (d, ^3J = 1.9 Hz, 1H, H-1), 3.91–3.87 (m, 1H, H-6a), 3.85 (dd, ^3J = 3.3 Hz, ^3J = 1.9 Hz, 1H, H-2), 3.79–3.69 (m, 3H, H-3, H-5, H-6b), 3.65-3.59 (m, 1H, H-4); ^{13}C NMR, HSQC, HMBC (100.6 MHz, $CDCl_3$) δ (ppm) = 89.7 (C-1), 74.6 (C-5), 69.8, 69.7 (C-2, C-3), 66.3 (C-4), 60.7 (C-6).

The spectral data are in accordance with literature.[5]

Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC). A literature known procedure was applied.[6] For example, 100 mg PEG-*co*-PGPgE (1 equiv) was placed in a Schlenk flask and dissolved in 15 mL DMSO (anhydrous) and mannopyranosyl azide (1.5 equiv per propargyl unit) and diisopropylethylamine (DIPEA) (0.3 equiv per propargyl unit) were added. The mixture was degassed by three freeze-pump-thaw cycles and subsequently copper sulfate pentahydrate (0.3 equiv per propargyl unit) and sodium ascorbic acid (0.6 equiv per propargyl

unit) were added under argon flow. The solution was heated to 50 °C and stirred for 24 h under argon atmosphere. Afterwards, the flask was opened and DMSO was removed under vacuum. The polymer was dissolved in water and Chelex®100 was added and stirred for 12 h, changed and stirred for another 12 h to remove copper traces. Afterwards, the polymer was dissolved in DI water and dialyzed for 1 day (MWCO = 2000 g·mol^{-1}) to remove excess of mannose azide and residual DMSO. Products were obtained after lyophilizing as pale yellow solids (yield = 90%). Functionalized PGPgE homopolymer was treated for 1 week with ion exchange resin (Chelex®100) for sufficient removal of copper traces.

Mannose-functional PEG-*co*-PGPgE:

^{1}H NMR (400 MHz, D_2O) δ (ppm) = 8.24 (m, 1H, triazole), 6.13 (m, 1H, H-1 mannose), 4.76-4.56 (m, 3H, triazole-C*H*$_2$O- + H-3 mannose, strong overlap with D_2O signal), 4.17-4.11 (m, 1H, H-2 mannose), 4.05-3.48 (m, 12H, polyether backbone, H-6 mannose, H-4 mannose), 3.37-3.28 (m, 1H, H-5 mannose).

Mannose-functional PGPgE:

^{1}H NMR (400 MHz, D_2O) δ (ppm) = 8.18 (m, 1H, triazole), 6.07 (m, 1H, H-1 mannose), 4.72 (m, 1H, H-3 mannose, strong overlap with D_2O signal), 4.61 (m, 2H, triazole-C*H*$_2$O-), 4.10 (m, 1H, H-2 mannose), 3.83-3.53 (m, 8H, polyether backbone + H-6 mannose, H-4 mannose), 3.28 (m, 1H, H-5 mannose).

Lectin interaction studies. Lectin binding was investigated in analogy to Schubert and co-workers.[7] Stock solutions of ConA (2 mg·mL^{-1}) and the mannose-functional polyether (2 mg·mL^{-1}) were prepared in HEPES buffer, respectively. Different concentrations of ConA were added to the polymer solution (final concentration of 1 mg·mL^{-1}) and subsequently, the optical transmittance of a light beam at 500 nm was recorded in 2 sec intervals at 25 °C under

stirring (700 rpm). Measurements were conducted on a Jasco V-630 photospectrometer with a Jasco ETC-717 Peltier element through a 1x1 cm sample quartz cell.

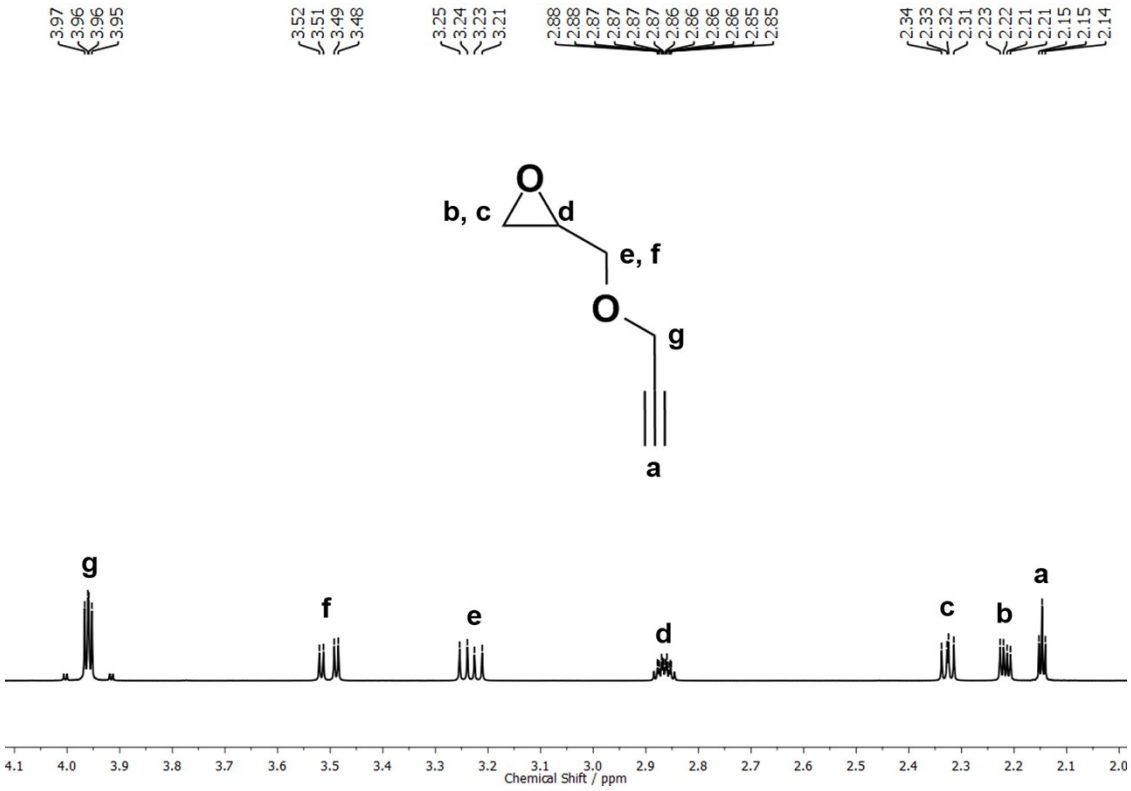


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of commercially available GPgE after purification via distillation.

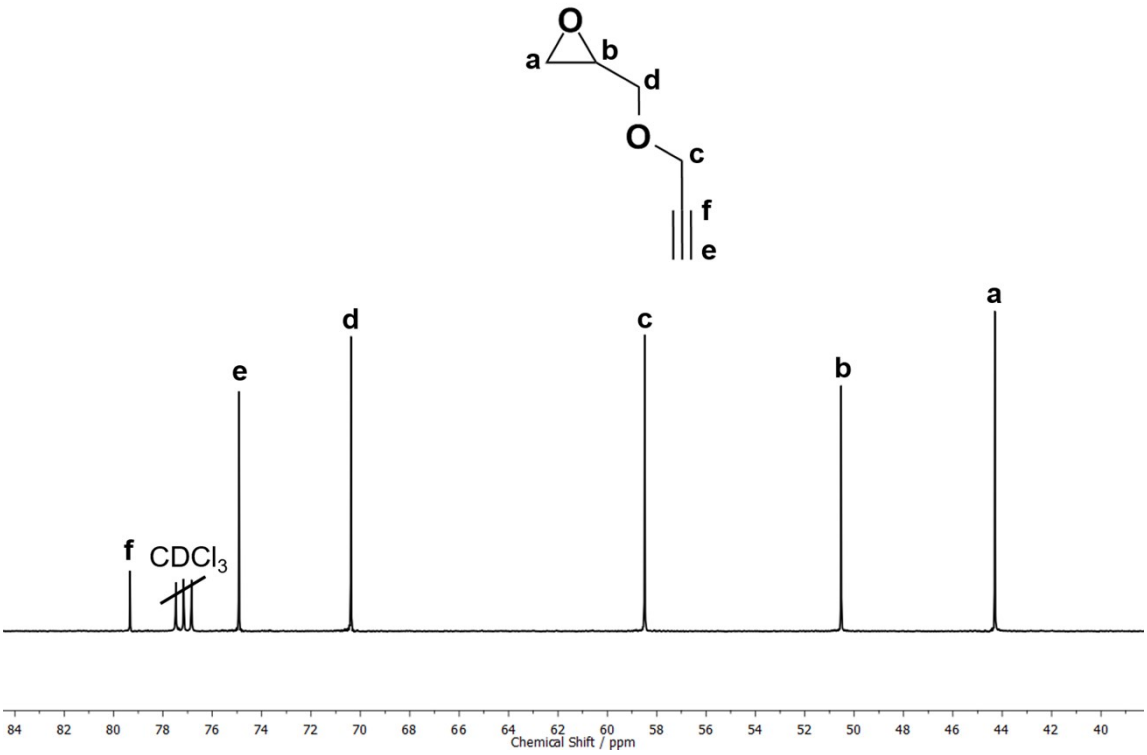


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of commercially available GPgE after distillation.

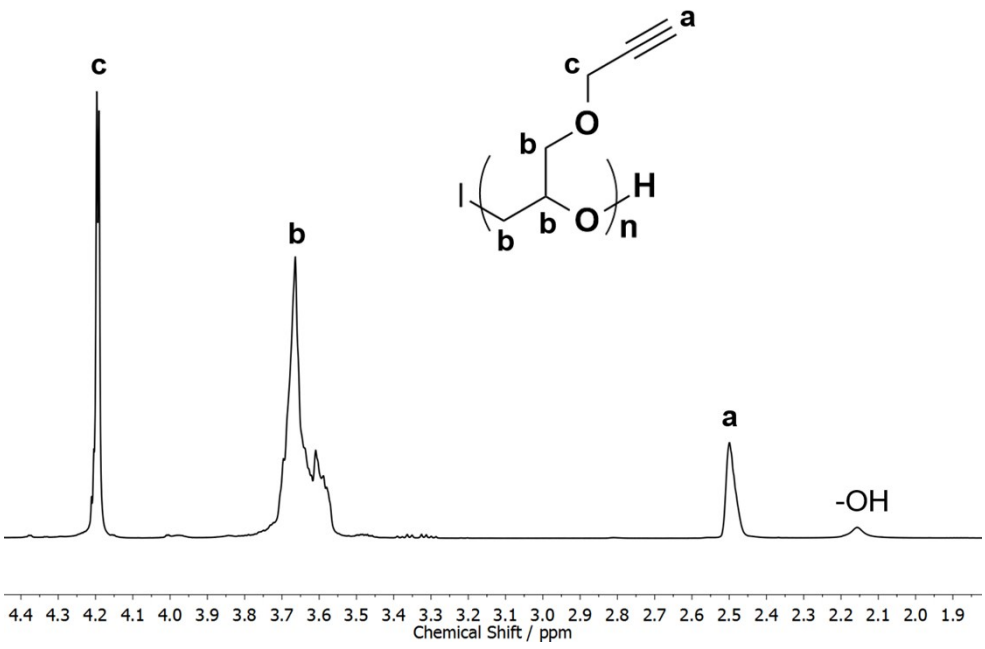


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PGPgE homopolymer.

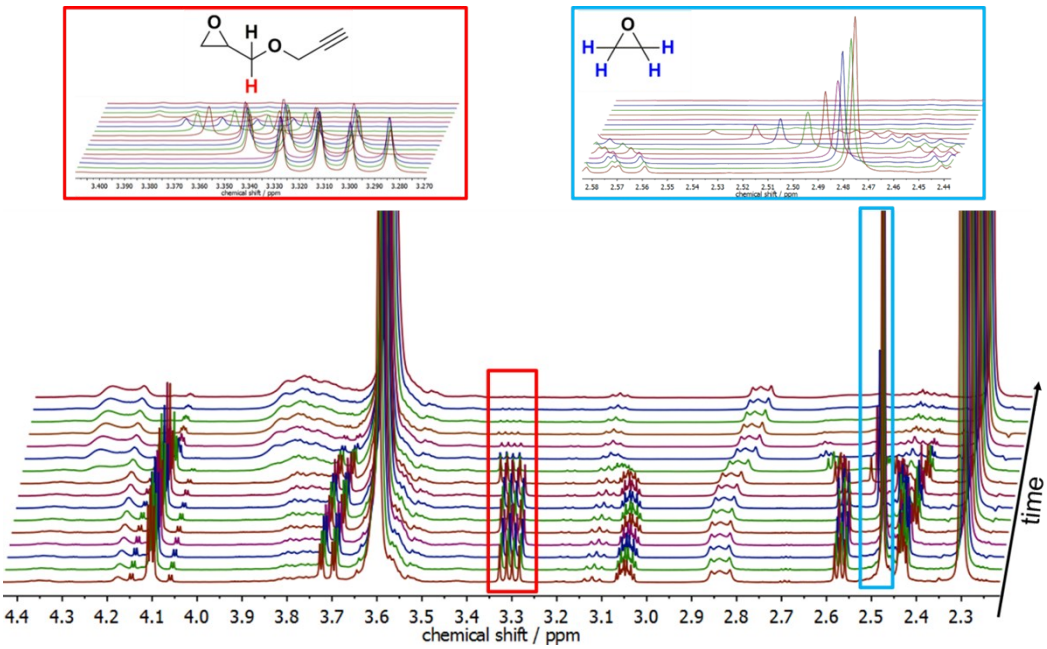


Figure S4. Subset of ^{1}H NMR spectra (400 MHz, chlrobenze-d_5) of the copolymerization of EO with GPgE, applying the activated monomer technique. Insets expand region of interest, showing the proton signals used to calculate the respective monomer conversion (GPgE at 3.30 ppm and EO at 2.47 ppm). Note that each temperature step induces a slight shift of the proton signals. Mole fractions: n(EO) = 59 mol% and n(GPgE) = 41 mol% with a catalyst/initiator ratio of 5, initiated at 0 °C.

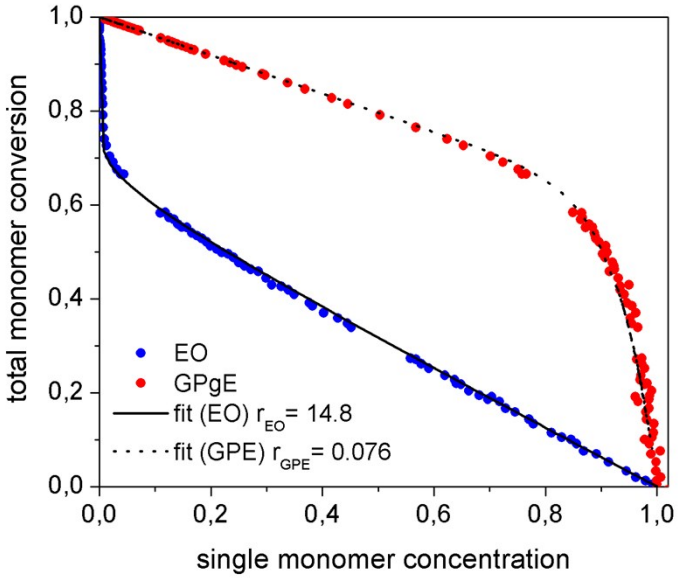


Figure S5. Total monomer conversion plotted as a function of the individual monomer concentration for EO (blue) and GPgE (red). Reactivity ratios are calculated from the respective fits (EO: solid line; GPgE: dashed line) in analogy to literature.[8]

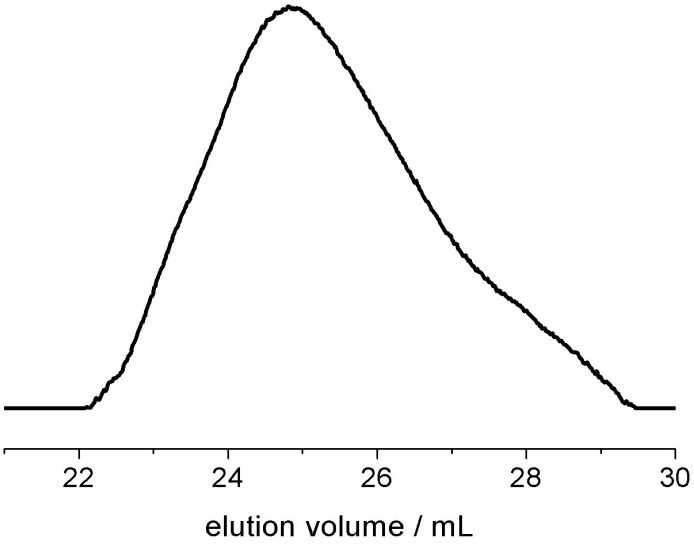


Figure S6. SEC elution trace (THF, RI signal, PEG standard) of PEG-*co*-PGPgE copolymer generated in a NMR tube to study the respective reactivity ratios of EO and GPgE under monomer-activated AROP conditions. Mole fractions: n(EO) = 59 mol% and n(GPgE) = 41 mol% with a catalyst/initiator ratio of 5, initiated at 0 °C. SEC data: M_n = 3000 g·mol^{-1}, PDI = 1.77.

^{13}C triad analysis. Figure S7 shows the IG ^{13}C NMR spectrum of PEG-*co*-PGPgE copolymer. A collection of IG ^{13}C NMR spectra of PGPgE homopolymer and PEG-*co*-PGPgE copolymers with 2.0-15.6 mol% GPgE content in benzene-d_6 is shown in S8. Triad assignment was performed in analogy to literature-known functional PEGs[9] and with the help of 2D spectra and simulated ^{13}C NMR spectra (ChemDraw Ultra 10.0). GPgE units are labeled with *G*, while *a* denotes the methylene carbon and *b* the methine carbon of GPgE. *E* refers to EO units.

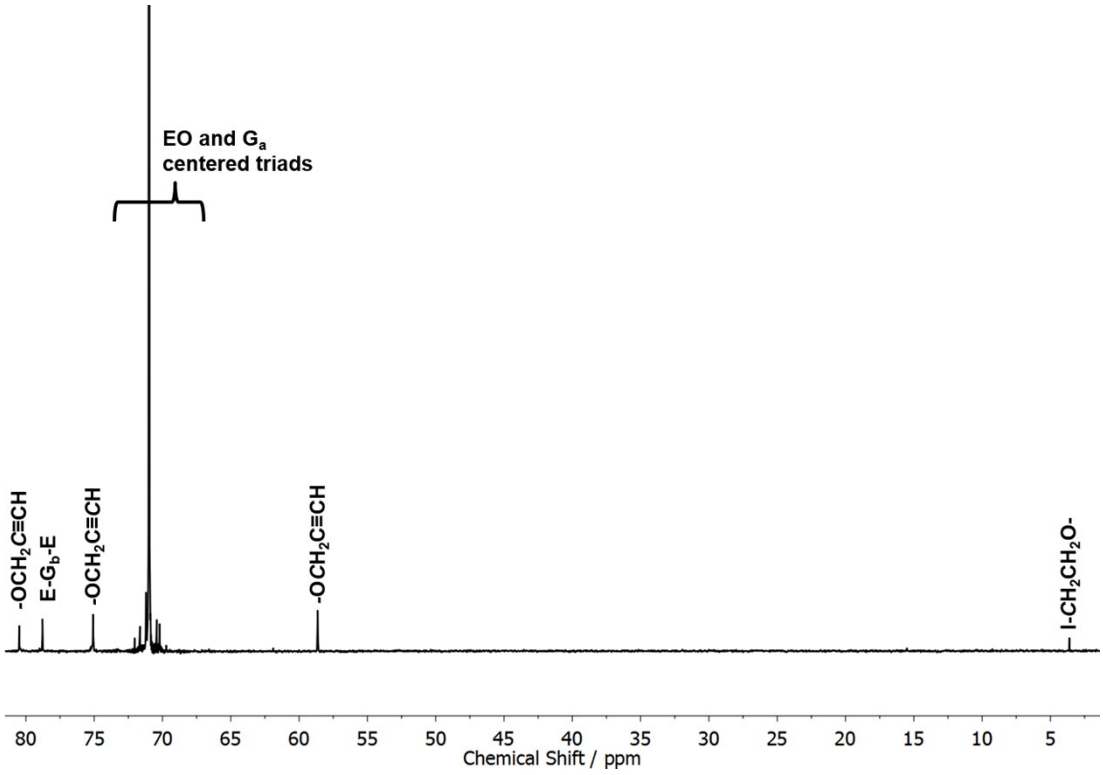


Figure S7. ^{13}C NMR spectrum (100 MHz, benzene-d_6) of PEG-*co*-PGPgE. EO units are abbreviated with E and GPgE units with G, whereas *a* denotes the methylene and *b* the methine carbon.

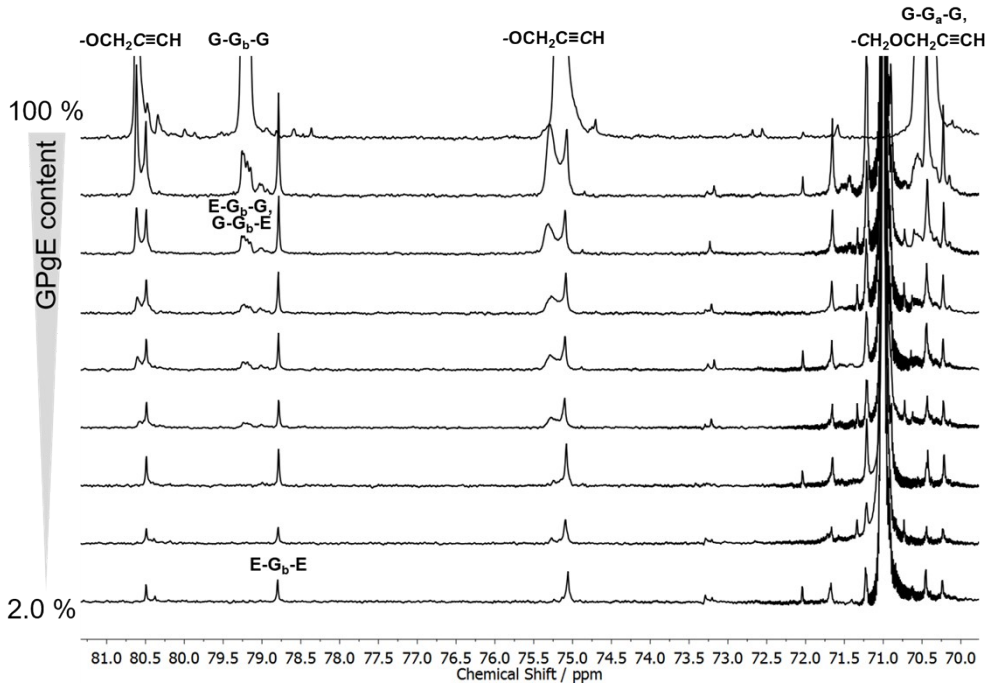


Figure S8. Important region of IG ^{13}C NMR spectra (100 MHz, benzene-d_6) of PGPgE homopolymer and various PEG-*co*-PGPgE copolymers (2.0 - 15.6 mol%).

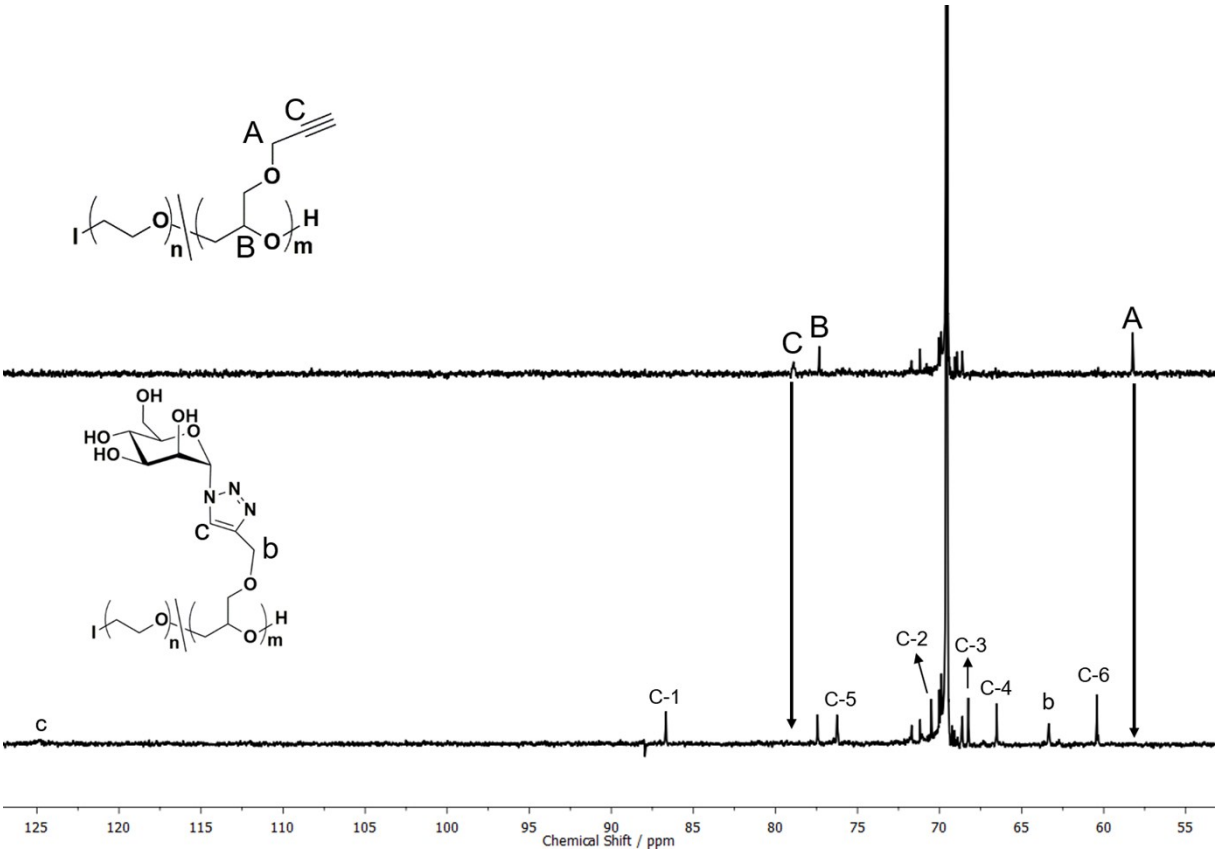


Figure S9. Relevant section of ^{13}C NMR spectra (100 MHz, D_2O) of PEG-*co*-PGPgE before (top) and after click with mannopyranosyl azide (bottom). Peak "c" in bottom spectrum was assigned after HSQC analysis.

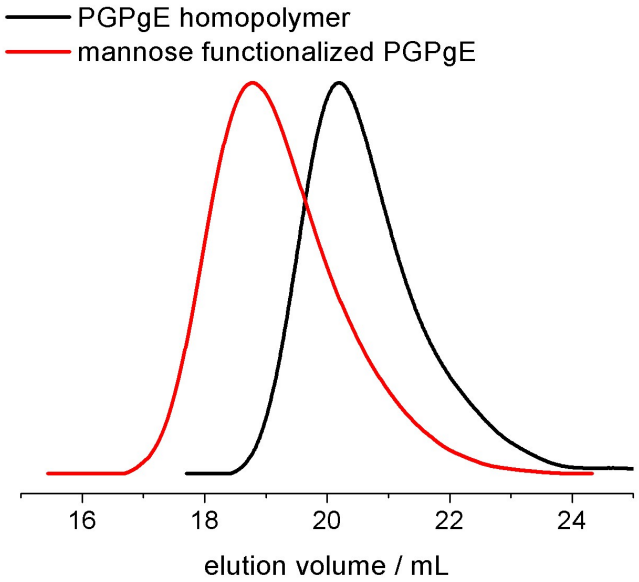


Figure S10. SEC traces (DMF, RI signal, PEG standard) of $PGPgE_{30}$ homopolymer (black line) and mannose-functionalized $PGPgE_{30}$ (red line).

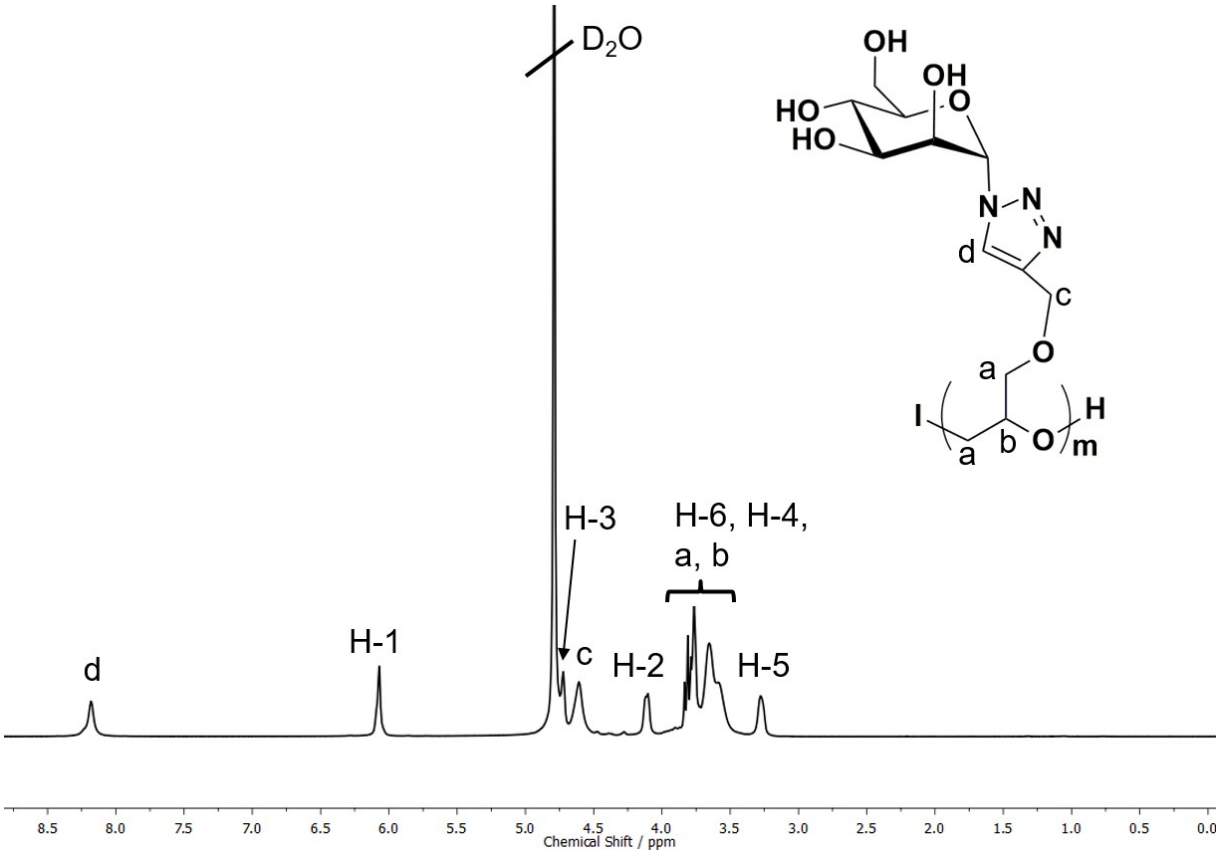


Figure S11. ^{1}H NMR (400 MHz, D_2O) of mannose-functionalized $PGPgE_{30}$ homopolymer.

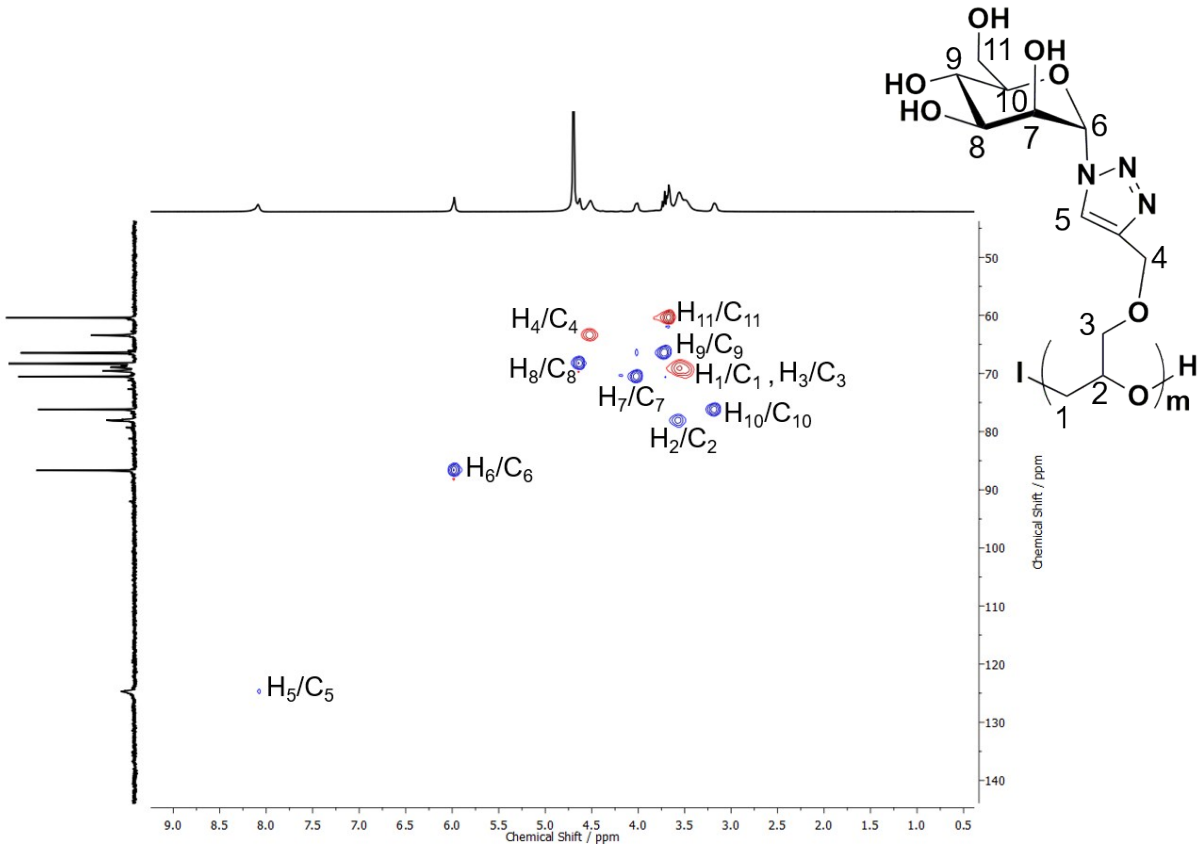


Figure S12. HSQC NMR (400 MHz/100 MHz, D_2O) of mannose-functionalized $PGPgE_{30}$ homopolymer.

Table S2. DSC data of PEG-*co*-PGPgE copolymer and PGPgE homopolymer before and after CuAAC with mannopyranosyl azide.

GPgE / mol%	Functionalization	T_g / °C	T_m / °C	ΔH/J·g^{-1}
2.0	---	-52	52	126
2.0	mannopyranosyl azide	-34	51	109
3.7	---	-51	50	106
3.7	mannopyranosyl azide	-27	48	76
100	---	-39	---	---
100	mannopyranosyl azide	35		

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