Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

for

Functional sugar-based polymers and nanostructures comprised of degradable poly(D-glucose carbonate)s

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Experimental section

Materials. All chemicals and reagents were used as received from Sigma-Aldrich, Co. (St. Louis, MO) unless otherwise noted. Tetrahydrofuran (THF), dichloromethane (DCM), and *N*,*N*-dimethylformamide (DMF) were purified by passage through a solvent purification system (J. C. Meyer Solvent Systems, Inc., Laguna Beach, CA). 4-Methylbenzyl alcohol and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were dried over CaH_2 in THF, concentrated under vacuum and stored in a glovebox under Ar atmosphere. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was dried over CaH_2, distilled, degassed, and stored in a glovebox under Ar atmosphere. Dialysis membrane tubing with a molecular weight cut off (MWCO) of 12-14 kDa was purchased from Spectrum Laboratories, Inc. (Rancho Dominguez, CA) and soaked for 5 min in nanopure water at room temperature before use. Column chromatography was performed on a CombiFlash Rf4x (Teledyne ISCO) with RediSep Rf columns (Teledyne ISCO). RAW 264.7 mouse macrophage, and MC3T3 mouse osteoblast precursor cells, as well as MEMα and DMEM media were obtained from the American Type Culture Collection (Manassas, VA). Media additives (fetal bovine serum, penicillin/streptomycin) were obtained from Sigma-Aldrich (St. Louis, MO). Cell culture 96-well round bottom plates were purchased from Corning Costar Co. (Corning, NY).

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Inova 500 spectrometer interfaced to a UNIX computer using VnmrJ software. Chemical shifts were referenced to the solvent resonance signals.

FT-IR spectra were recorded on an IR Prestige 21 system (Shimadzu Corp., Japan), equipped with an ATR accessory, and analyzed using IRsolution v. 1.40 software.

Size exclusion chromatography (SEC) eluting with THF was conducted on a Waters chromatography, Inc. (Milford, MA) system equipped with an isocratic pump model 1515, a differential refractometer model 2414, and a three-column set including a guard column (PLgel 5 μm, 50 × 7.5 mm) and two Styragel columns (PLgel 5 μm Mixed C, 500 Å, and 104 Å, 300 × 7.5 mm columns). The system was operated at 40 °C with a flow rate of 1 mL/min. Data were analyzed using breeze software from Waters Chromatography, Inc. (Milford, MA). Molecular weights were determined relative to polystyrene standards (300–467,000 Da) purchased from Polymer Laboratories, Inc. (Amherst, MA). Polymer solutions were prepared at a concentration of *ca.* 3 mg/mL with 0.05 vol% toluene as flow rate marker and an injection volume of 200 μL was used.

Size exclusion chromatography (SEC) eluting with pre-filtered DMF containing 0.05 M LiBr was conducted on a Waters Chromatography, Inc. (Milford, MA) system equipped with an isocratic pump model 1515, a differential refractometer model 2414, and a four-column set including a 5 μm Guard column (50 × 7.5 mm), a Styragel HR 4 5 μm DMF column (300 × 7.5 mm), a Styragel HR 4E 5 μm DMF column (300 × 7.5 mm), and a Styragel HR 2 5 μm DMF column (300 × 7.5 mm). The system was operated at 70 °C with a flow rate of 1.00 mL/min. Polymer solutions were prepared at a concentration of about 3 mg/mL and an injection volume of 200 μL was used. Data collection and analysis were

performed with Discovery32 v. 1.039.000 software (Precision Detectors, Inc., Bellingham, MA). The system was calibrated with S3 polystyrene standards (Polymer Laboratories, Amherst, MA) ranging from 615 to 442,800 Da.

Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC822® (Mettler-Toledo, Inc., Columbus, OH) under N_2. Measurements of T_g were performed with a heating rate of 5 °C/min and analyzed using Mettler-Toledo Star^e v. 10.00 software. The T_g was taken as the midpoint of the inflection tangent of the third heating scan.

Thermogravimetric analysis (TGA) was performed under Ar atmosphere using a Mettler-Toledo model TGA/DSC 1, with a heating rate of 10 °C/min.

Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry was performed on an Applied Biosystems Voyager-DE STR in reflector ion mode by use of laser pulses at 337 nm. Trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) was used as a matrix.

Electrospray ionization mass spectrometry (ESI-MS) experiments were performed using an Applied Biosystems PE SCIEX QSTAR instrument.

X-ray diffraction (XRD) analysis was performed using a POWDER_SA BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer. The annealed samples were prepared by heating at 160 °C for 18 h.

Transmission electron microscopy (TEM) images were collected on a JEOL 1200EX operating at 100 kV and micrographs were recorded using a SIA-15C CCD camera. Samples for TEM were prepared as follows: 10 μL of dilute polymer solution in nanopure water was deposited onto a carbon coated copper grid, and after 1 min, excess solution was quickly wicked away by a piece of filter paper. The samples were then negatively stained with a 1 wt% phosphotungstic acid (PTA) aqueous solution. After 30 s, the excess staining solution was quickly wicked away by a piece of filter paper and the samples were left to dry under ambient conditions over night.

Dynamic light scattering (DLS) measurements were conducted using a Delsa Nano C instrument from Beckman Coulter, Inc. (Fullerton, CA) equipped with a laser diode operating at 658 nm. Scattered light was detected at 165° angle and analyzed using a log correlator over 70 accumulations for a 0.5 mL of sample in a glass size cell (0.9 mL capacity). The photomultiplier aperture and attenuator were adjusted automatically to obtain a photon counting rate of *ca.* 10 kcps. The calculations of the particle size distribution and distribution averages were performed using CONTIN particle size distribution analysis routines in Delsa Nano 2.31 software. The peak averages of histograms from intensity, volume and number distributions from 70 accumulations were reported as the average diameter of the particles. All measurements were repeated 10 times.

The zeta potential values of the nanoparticles were determined by a Delsa Nano C particle analyzer (Beckman Coulter, Fullerton, CA) equipped with a 30 mW dual laser diode (658 nm). The zeta potential of the particles in suspension was obtained by measuring the electrophoretic movement of the charged particles under an applied electric field. Scattered light was detected at a 30 ° angle at 25 °C. The zeta

potential was measured at five regions in the flow cell and a weighted mean was calculated. These five measurements were used to correct for electroosmotic flow induced in the cell due to the surface charge of the cell wall. All determinations were repeated 9 times.

All experiments were performed according to institutional guidelines provided by Texas A&M's Environmental Health and Safety committee. Experiments involving mouse derived cell lines (RAW 264.7 and MC3T3) were performed according to guidelines provided by Texas A&M's Institutional Biosafety Committee for biosafety level 1 organisms (Protocol Approval Number IBC2014-075).

Synthesis of the monomer methyl-2-O-ethyloxycarbonyl-3-O-propargyloxycarbonyl-4,6-O-carbonyl-α-D-glucopyranoside, 4.

Synthesis* of *methyl-2-O-ethyloxycarbonyl-4,6-O-benzylidene-α-D-glucopyranoside, 1: To a solution of methyl-4,6-O-benzylidene-α-D-glucopyranoside (14.1 g, 50.1 mmol) dissolved in DCM (400 mL) under N_2 at -78 °C, TMEDA (4.5 mL, 30 mmol) was added, followed by the addition of ethyl chloroformate (4.7 mL, 50 mmol) while stirring. Progress was monitored by TLC and the reaction was quenched with water (100 mL) after 60 min. The reaction mixture was washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and DCM was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate) to give ***1*** (12.5 g, 35.3 mmol, 71.1% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 7.53 - 7.49 (m, 2H), 7.41 - 7.35 (m, 3H), 5.55 (s, 1H), 5.01 (d, *J* = 4.0 Hz, 1H), 4.65 (dd, *J* = 10, 4 Hz, 1H), 4.30 (dd, *J* = 10, 5 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.19 (td, *J* = 10 Hz, 1H), 3.84 (td, *J* = 10, 5 Hz, 1H), 3.76 (dd, *J* = 10, 10 Hz, 1H), 3.56 (dd, *J* = 10, 10 Hz, 1H), 3.41 (s, 3H), 1.33 (t, *J* = 7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.66, 136.95, 129.31, 128.35, 126.33, 102.03, 97.50, 81.14, 76.58, 68.84, 68.60, 64.64, 62.03, 55.42, 14.14. FT-IR (ATR) 3456, 2999 - 2809, 1735, 1458, 1374, 1271, 1149, 1095, 1018, 934, 925, 887, 748 cm^{-1}. HRMS (ESI$^+$) $C_{17}H_{22}O_8H^+$ 355.1393, found (M+H$^+$) 355.1405.

Synthesis of methyl-2-O-ethyloxycarbonyl-3-O-propargyloxycarbonyl-4,6-O-benzylidene-α-D-glucopyranoside, ***2***: To a solution of ***1*** (10.0 g, 28.2 mmol) dissolved in DCM (200 mL) under N_2 at 0 °C, TMEDA (2.6 mL, 17 mmol) was added, followed by propargyl chloroformate (3.1 mL, 31 mmol) while stirring. Progress was monitored by TLC and the reaction was quenched with water (50 mL) after 60 min. The reaction mixture was washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and DCM was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate) to give ***2*** (12.2 g, 30.0 mmol, 99.2% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 7.50 - 7.44 (m, 2H), 7.38 - 7.32 (m, 3H), 5.52 (s, 1H), 5.43 (dd, *J* = 10, 10 Hz, 1H), 5.06 (d, *J* = 4 Hz, 1H), 4.79 (dd, *J* = 10, 4 Hz, 1H), 4.73 (d, *J* = 3 Hz, 2H), 4.32 (dd, *J* = 10, 5 Hz, 1H), 4.21 (q, 7 Hz, 2H), 3.94 (td, *J* = 10, 5 Hz, 1H), 3.79 (t, *J* = 10 Hz, 1H), 3.71 (dd, *J* = 10, 10 Hz, 1H), 3.43 (s, 3H), 2.47 (t, *J* = 3 Hz, 1H), 1.32 (t, *J* = 7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.28, 153.60, 136.83, 129.06, 128.16, 126.22, 101.52, 97.48, 79.04, 76.72, 75.89, 74.22, 73.68, 68.72, 64.78,

62.21, 55.66, 55.49, 14.15. FT-IR (ATR) 3407 - 3380, 3287, 3024 - 2800, 1751, 1450, 1373, 1251, 1096, 979, 910 cm^{-1}. HRMS (ESI^+) $C_{21}H_{24}O_{10}H^+$ 437.1448, found ($M+H^+$) 437.1461.

Synthesis of methyl-2-O-ethyloxycarbonyl-3-O-propargyloxycarbonyl-α-D-glucopyranoside, 3: To a solution of ***2*** (12.1 g, 27.5 mmol) in methanol (200 mL), strongly acidic Amberlyst 15 H-form Resin (10 g) was added. The reaction was stirred at room temperature overnight and monitored by TLC until the starting material disappeared completely. The resin was filtered off over a plug of Celite and methanol was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate) to give the carbonate-protected 4,6-diol ***3*** (7.9 g, 23 mmol, 81% yield). ^1H NMR (500 MHz, $CDCl_3$) δ ppm, 5.16 (dd, *J* = 10, 9 Hz, 1H), 4.99 (d, *J* = 4 Hz, 1H), 4.75 (d, *J* = 3 Hz, 2H), 4.65 (dd, *J* = 10, 4 Hz, 1H), 4.19 (qd, *J* = 7, 3 Hz, 2H), 3.86 (dd, *J* = 6, 3 Hz, 2H), 3.84 (d, *J* = 6 Hz, 1H), 3.78 (dd, *J* = 9, 6 Hz, 1H), 3.68 (dt, *J* = 10, 3 Hz, 1H), 3.40 (s, 3H), 2.89 (t, *J* = 6 Hz, 1H), 2.56 (t, *J* = 3 Hz 1H), 1.29 (t, *J* = 7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.55, 154.32, 96.72, 77.40, 76.73, 76.08, 73.80, 71.08, 68.75, 64.71, 61.41, 55.79, 55.37, 14.11. FT-IR (ATR) 3580 - 3348, 3294, 3032-2862, 1744, 1442, 1373, 1248, 1026, 910, 787, 725 cm^{-1}. HRMS (ESI^+) $C_{14}H_{20}O_{10}H^+$ 349.1135, found ($M+H^+$) 349.1144.

Synthesis of monomer methyl-2-O-ethyloxycarbonyl-3-O-propargyloxycarbonyl-4,6-O-carbonyl-α-D-glucopyranoside, ***4***: Pyridine (5.2 mL, 65 mmol) and ***3*** (7.5 g, 22 mmol) were combined in DCM (200 mL) under N_2 while stirring. Triphosgene (4.5 g, 15 mmol) dissolved in DCM (20 mL) was added dropwise over 10-15 minutes and the reaction was heated to 35 °C for 12 h, monitored by TLC. The reaction was cooled in an ice bath, quenched with $NaHCO_{3(aq)}$ (100 mL), extracted with DCM and washed with 5% aq. HCl and brine. The organic layers were combined, dried over anhydrous Na_2SO_4 and removed under reduced pressure. The resulting residue was purified by column chromatography (SiO_2, gradient hexane/ethyl acetate). The product was recrystallized from ethyl acetate : hexanes (1 : 2) to give the monomer ***4*** (4.5 g, 12 mmol, 56% yield). ^1H NMR (500 MHz, $CDCl_3$) δ ppm, 5.41 (t, *J* = 10 Hz, 1H), 5.09 (d, *J* = 4 Hz, 1H), 4.81 (qd, *J* = 15, 3 Hz, 2H), 4.74 (dd, *J* = 10, 4 Hz, 1H), 4.55 (dd, *J* = 10, 5 Hz, 1H), 4.31 (t, *J* = 10 Hz, 1H), 4.26 (dd, *J* = 10, 10 Hz, 1H), 4.25 - 4.19 (m, 3H), 3.47 (s, 3H), 2.57 (t, *J* = 3 Hz, 1H), 1.32 (t, *J* = 7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.08, 153.25, 146.26, 97.73, 76.36, 76.34, 76.21, 73.27, 72.48, 69.26, 65.06, 59.46, 56.24, 56.09, 14.10. FT-IR (ATR) 3302, 3024 - 2808, 1743, 1442, 1389, 1268, 1196, 1119, 1034, 1000, 964, 895, 756 cm^{-1}. HRMS (ESI^+) $C_{15}H_{18}O_{11}H^+$ 375.0927, found ($M+H^+$) 375.0933.

Synthesis of the cyclic D-glucose monomer methyl-2,3-O-ethyloxycarbonyl-4,6-O-carbonyl-α-D-glucopyranoside, 7.

Synthesis of monomer ***7*** was performed similarly as monomer ***4***.

Synthesis of methyl-2,3-O-ethyloxycarbonyl-4,6-O-benzylidene-α-D-glucopyranoside, ***5***: Product was a clear sticky residue (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 7.47 - 7.42 (m, 2H), 7.37 - 7.32 (m, 3H), 5.51 (s, 1H), 5.41 (td, *J* = 10, 2 Hz, 1H), 5.04 (dd, *J* = 4, 2 Hz, 1H), 4.75 (ddd, *J* = 10, 4, 2 Hz, 1H), 4.30 (ddd, *J* = 10, 5, 2 Hz, 1H), 4.25 - 4.16 (m, 4H), 3.93 (tdd, *J* = 10, 5, 2 Hz, 1H), 3.78 (td, *J* = 10, 2 Hz, 1H), 3.68 (td, *J* = 10, 2 Hz, 1H), 3.43 (s, 3H), 1.31 (td, *J* = 7, 2 Hz, 3H), 1.27 (td, *J* = 7, 2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.47, 154.27, 136.99, 129.19, 128.32, 126.30, 101.69, 97.61, 79.30, 74.56, 73.00, 68.94, 64.83, 64.60, 62.35, 55.61, 14.29, 14.25. FT-IR (ATR) 2984 - 2830, 1821, 1748, 1467, 1456, 1371, 1269, 1242, 1153, 1089, 1049, 993, 872, 785 cm^{-1}. HRMS (ESI$^+$) $C_{20}H_{26}O_{10}H^+$ 427.1560, found (M+Li$^+$) 433.1686.

Synthesis of methyl-2,3-O-ethyloxycarbonyl-α-D-glucopyranoside, ***6***: (85% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 5.13 (dd, *J* = 10, 10 Hz, 1H), 4.99 (d, *J* = 4 Hz, 1H), 4.65 (dd, *J* = 10, 4 Hz, 1H), 4.30 - 4.09 (m, 4H), 3.90 - 3.84 (m, 2H), 3.76 (t, *J* = 10 Hz, 1H), 3.70 (dt, *J* = 10, 4 Hz, 1H), 3.40 (s, 3H), 1.31 (td, *J* = 7, 3 Hz, 3H), 1.30 (td, *J* = 7, 3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 155.52, 154.43, 96.79, 76.80, 73.96, 71.24, 64.81, 64.72, 55.42, 14.20, 14.19. FT-IR (ATR) 3462 - 3174, 2984 - 2938, 1748, 1467, 1371, 1273, 1248, 1036, 1007, 908, 871, 786. HRMS (ESI$^+$) $C_{13}H_{22}O_{10}H^+$ 339.1247, found (M+Na$^+$) 361.1111.

Synthesis of monomer methyl-2,3-O-ethyloxycarbonyl-4,6-O-carbonyl-α-D-glucopyranoside, **7**: (51% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 5.38 (dd, *J* = 10, 10 Hz, 1H), 5.06 (dd, *J* = 4, 2 Hz, 1H), 4.70 (ddd, *J* = 10.0, 4, 2 Hz, 1H), 4.55 – 4.52 (m, 1H), 4.28 (td, *J* = 10, 1 Hz, 1H), 4.25 – 4.18 (m, 6H), 3.46 (s, 3H), 1.31 (dt, *J* = 10, 4 Hz, 3H), 1.30 (dt, *J* = 10, 4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.27, 153.87, 146.51, 97.75, 76.75, 76.63, 73.58, 71.83, 69. 41, 65.11, 65.07, 59.62, 56.34, 14.23, 14.21. FT-IR (ATR) 3066 - 2862, 1748, 1467, 1446, 1371, 1271, 1242, 1195, 1101, 1009, 912, 871, 785. HRMS (ESI$^+$) $C_{14}H_{20}O_{11}H^+$ 365.1084, found (M+H$^+$) 365.1079.

General procedure for the organocatalyzed ROP of GC(EPC)

All polymerizations were carried out using standard glovebox and Schlenk line techniques. Monomer ***4*** was dried under vacuum over P_2O_5 for 3 d before transferred to a glovebox for storage under an inert atmosphere. All ROPs were carried out at room temperature in a glovebox under Ar atmosphere, while for those conducted at -78 °C, the reagents were added to a vial inside a glovebox and the reaction conducted in a fume hood. To a solution of ***4*** (401.2 mg, 1.073 mmol) in DCM (1.7 mL), 4-methylbenzyl alcohol (2.6 mg, 0.021 mmol) in DCM (210 µL) was added while stirring. Organocatalyst TBD or DBU (2 mol% relative to monomer, 0.021 mmol) in DCM (210 µL) was added to the reaction under Ar atmosphere. After stirring for a certain period of time (1.5 min to 16 min), the reaction vial was opened to air and quenched by addition of Amberlyst 15 H-form resin. The polymer was purified by precipitation from DCM into methanol (3×) and dried under vacuum to give an average yield of 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 7.26 (d, *J* = 8 Hz, *Ar*), 7.16 (d, *J* = 8 Hz, *Ar*), 5.36 (t, *J* = 10, C^3*H*), 5.20 (m, OCH_2Ar),

5.06 - 4.95 (m, C^1H), 4.94 - 4.82 (m, C^4H), 4.79 - 4.65 (m, C^2H, OCH_2CCH), 4.28 (s, C^6H_2), 4.19 (m, OCH_2CH_3), 4.02 (d, J = 10 Hz, C^5H), 3.45 - 3.34 (s, OCH_3), 2.62 - 2.52 (m, OCH_2CCH), 2.34 (s, CH_3Ar), 1.30 (t, J = 7 Hz, OCH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 154.02, 153.62, 153.52, 96.41, 76.92, 76.17, 74.13, 73.49, 72.19, 66.63, 65.68, 64.77, 55.88, 55.75, 14.11. FT-IR (ATR) 3294, 3039 - 2810, 1751, 1450, 1372, 1234, 1172, 1010, 910, 879, 779. T_g = 105 °C. TGA in Ar, 278 - 378 °C, 80% weight loss.

Kinetic study of the homopolymerization of GC(EPC) via ROP

To a solution of ***4*** (400.5 mg, 1.073 mmol) in DCM (1.7 mL), 4-methylbenzyl alcohol (2.6 mg, 0.021 mmol) was added in DCM (210 µL) while stirring. DBU (2 mol% to monomer, 0.021 mmol, 1.6 µL) in DCM (210 µL) was then added to the reaction. At 30 s, 1, 2, 4, 7, 11, 13 and 16 min, 200 µL of the reaction mixture was removed and quenched over Amberlyst 15 H-form resin in DCM (20 mg in 0.20 mL DCM). The reaction mixture at each time point was removed from the resin and evaporated for analysis by SEC without purification and by ^1H NMR spectroscopy after purification. The kinetic study was repeated three times.

Sequential ROPs of GC (EPC) and GC(EC) to yield PGC(EPC)-b-PGC(EC), 8.

To a solution of ***4*** (1001.6 mg, 2.6781 mmol) in DCM (5.04 mL), 4-methylbenzyl alcohol (10.8 mg, 0.0884 mmol) was added in DCM (100 µL) while stirring. DBU (2 mol% to monomer, 0.054 mmol) in DCM (200 µL) was then added to the reaction. After 20 min, monomer ***7*** (972.4 mg, 2.671 mmol) in 3 mL DCM was added. The reaction was quenched with Amberlyst 15 H-form resin after 30 min. The polymer was purified by precipitation from DCM into methanol (3×) and dried under vacuum to give 1.5 g product (73% yield). ^1H NMR (500 MHz, $CDCl_3$) δ ppm, 7.32 - 7.28 (m, *Ar*), 7.22 (m, *Ar*), 5.33 - 5.24 (m, C^3H), 5.20 (m, OCH_2Ar), 5.10 - 5.02 (m, C^1H), 4.90 (m, C^4H), 4.83 - 4.72 (m, C^2H, OCH_2CCH), 4.44 - 4.15 (m, C^6H_2), 4.13 - 4.00 (m, C^5H, OCH_2CH_3), 3.48 - 3.42 (m, OCH_3), 2.70 - 2.65 (m, OCH_2CCH), 2.37 (s, CH_3Ar), 1.35 - 1.26 (m, OCH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm, 155.28, 154.48, 154.16, 153.97, 153.69, 96.42, 76.85, 75.97, 74.21, 73.39, 72.47, 66.65, 65.80, 64.86, 55.91, 55.55, 13.89. FT-IR (ATR) 3287, 3061 - 2835, 1748, 1447, 1371, 1333, 1240, 1168, 1117, 1091, 1016, 985, 875, 781. M_n (NMR) = 18500 g/mol. M_n (SEC) = 16400 g/mol. $Đ$= 1.04. T_g = 114 °C. TGA in Ar, 286-382 °C, 82% weight loss.

Kinetic study of GC(EC) polymerization upon addition to PGC(EPC)

To a solution of ***4*** (199.6 mg, 0.5337 mmol) in DCM (0.9 mL), 4-methylbenzyl alcohol (1.3 mg, 0.011 mmol) in DCM (100 µL) was added while stirring. DBU (2 mol% to monomer, 0.011 mmol, 1.6 µL) in

DCM (100 µL) was then added to the reaction. After 20 min, monomer ***7*** (193.2 mg, 0.5308 mmol) in 0.4 mL DCM was added. At 0, 1, 3, 6, 10, 15, 20, 30 and 40 min, 150 µL of the reaction mixture was removed and quenched over Amberlyst 15 H-form resin in DCM (20 mg in 0.20 mL DCM). The reaction mixture at each time point was removed from the resin and evaporated for analysis by SEC without purification and then analyzed by ^{1}H NMR spectroscopy after purification. The kinetic study was repeated three times.

Azide-alkyne Huisgen cycloaddition of PGC(EPC)$_{30}$-b-PGC(EC)$_{20}$ with α-methoxy-ω-azido PEG (CH$_3$O-PEG$_{2k}$-azide). A flame-dried Schlenk flask containing a magnetic stir bar was charged with ***8***, PGC(EPC)$_{30}$-*b*-PGC(EC)$_{20}$ (201.5 mg, 11.10 µmol, 1 eq.), α-methoxy-ω-azido PEG (220.6 mg, 110.0 µmol, 10 eq.), *N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 9.5 mg, 56 µmol, 5 eq.) and 5 mL of DMF. The reaction mixture was degassed by several freeze-pump-thaw cycles (>3), during which copper(I) bromide (3.9 mg, 28 µmol, 2.5 eq.) was added. The flask was allowed to return to room temperature after the final cycle and stirred for an additional 3 h under N_2. The solution was subsequently filtered through a neutral alumina column and dialyzed against Chelex® 100 resin in nanopure water in presoaked dialysis tubing (MWCO *ca*. 12-14 kDa) for 2 d to remove copper ions, followed by lyophilization to yield ***9*** as a white powder (361.4 mg, 4.62 µmol, 85.7 % yield). Inductively coupled plasma-mass spectrometry (ICP-MS) confirmed that less than 10 ppm copper was present in the polymer. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm, 7.85 (m, $OCH_2CCHNCH_2$), 7.32 - 7.28 (m, *Ar*), 7.22 (m, *Ar*), 5.33 - 5.2 (m, C^1*H*), 5.2 - 5.1 (m, $OCH_2CCHNCH_2$), 5.04 - 5.00 (m, C^3*H*), 4.9 - 4.75 (m, C^2*H*), 4.51 - 4.59 (m, C^4*H*), 4.33 - 4.12(m, C^5*H*, OCH_2CH_3), 4.09 - 4.01 (m, OCH_2CCH), 3.91 - 3.83 (m, C^6*H*), 3.65 (s, OCH_2CH_2), 3.71 - 3.63 (m, OCH_3), 2.65 (br, OCH_2CCH), 2.28 (s, CH_3Ar), 1.35 - 1.28 (m, OCH_2CH_3). FT-IR (ATR) 3039 - 2800, 1753, 1465, 1371, 1342, 1240, 1143, 1099, 1060, 1033, 960, 873, 842, 783. M_n (NMR) = 28500 g/mol. M_n (SEC) = 19400 g/mol. $Đ$ = 1.16. T_g = 77 °C. TGA in Ar, 210 - 275 °C, 33% weight loss; 275 - 500 °C, 59% weight loss.

General procedure for post-polymerization modification of PGC(EPC)-b-PGC(EC) via thiol-yne reaction. PGC(EPC)-*b*-PGC(EC) (11 µmol), functional thiol (6.6 mmol), and DMPA (0.11 mmol) were dissolved in anhydrous DMF (10 mL), degassed under N_2 for 30 min, and irradiated under UV light (365 nm) for 2 h. The anionic (3-mercaptopropionic acid)-functionalized diblock copolymer was transferred to dialysis tubing and dialyzed against nanopure water at 4 ºC for 3 d to remove excess thiol and photo initiator. The solution was then lyophilized to give the anionic polymer as a white powder. The cationic (cysteamine hydrochloride)-functionalized diblock copolymer was transferred to dialysis tubing and dialyzed against nanopure water with HCl, pH 3.0, at 4 ºC for 3 d, to remove excess thiols and photo initiator byproducts. The solution was then lyophilized to give the modified polymers as white powders. Cationic polycarbonate, ***10***: ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm, 7.65 (br, $SCH_2CH_2NH_2$), 7.32 - 7.28 (m, *Ar*), 7.22 (m, *Ar*), 5.18-5.09 (m, C^1*H*), 5.08 - 5.00 (m, C^3*H*), 4.96 - 4.71 (m, C^2*H,* C^4*H*), 4.46 - 4.23(m, C^5*H*), 4.21 - 4.05 (m, OCH_2CHS, OCH_2CH_3), 4.04 - 3.95 (m, C^6*H*), 3.38 - 3.16 (m, OCH_3, OCH_2CHS),

3.02 - 2.92 (m, $SCH_2CH_2NH_2$), 2.91 - 2.76 (m, OCH_2CHCH_2S), 2.31 (s, CH_3Ar), 1.35 - 1.28 (m, OCH_2CH_3). FT-IR (ATR) 3630 - 3170, 3086 - 2735, 1747, 1604, 1452, 1371, 1240, 1166, 1091, 1016, 873, 779. M_n (NMR) = 23100 g/mol. T_g = 63 °C. TGA in Ar, 160 - 232 °C, 12% weight loss; 232 - 383°C, 72% weight loss. Anionic polycarbonate, ***11***: ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm, 7.28 (m, *Ar*), 7.19 (m, *Ar*), 5.18-5.07 (m, C^1H), 5.05 - 4.97 (m, C^3H), 4.92 - 4.71 (m, C^2H, C^4H), 4.45 - 4.30 (m, C^5H), 4.22 - 4.04 (m, OCH_2CHS, OCH_2CH_3), 4.04 - 3.92 (m, C^6H), 3.34 (s, OCH_3),), 3.20 - 3.09 (m, OCH_2CHS), 2.86 - 2.59 (m, SCH_2CH_2COOH), 2.47 - 2.37 (m, OCH_2CHCH_2S), 2.31 (s, CH_3Ar), 1.2 (m, OCH_2CH_3). FT-IR (ATR) 3115 - 2775, 1747, 1568, 1446, 1394, 1371, 1240, 1168, 1016, 987, 873, 781. M_n (NMR) = 24700 g/mol. T_g = 71 °C. TGA in Ar: 162 - 232 °C, 11% weight loss; 232 - 360°C, 64% weight loss.

Micelle formation

The nonionic diblock copolymer ***9*** (2.0 mg) and positively charged diblock copolymer ***10*** (2.0 mg) were suspended into nanopure water (2.0 mL), followed by sonication for 10 min at room temperature to obtain a clear aqueous solution at a concentration of 1.0 mg/mL. The negatively charged diblock copolymer ***11*** was dissolved into anhydrous DMF to obtain a polymer solution with a concentration of 1.0 mg/mL. Nanopure water (2.0 mL) was then added into the polymer solution (1.0 mL) using a syringe pump at an addition rate of 0.1 mL/min. The mixture was then transferred into presoaked dialysis membrane tubing (MWCO *ca.* 12-14 kDa) and dialyzed against nanopure water for 24 h to remove DMF at room temperature. The final concentration of ***11*** was adjusted to 0.2 mg/mL by addition of nanopure water.

Cytotoxicity assays

RAW 264.7 mouse macrophages (2 x 10^4 cells/well) and MC3T3-E1 mouse osteoblast precursor cells (5 x 10^3 cells/well) were plated in 96-well plate in Dulbecco's Modified Eagle's Medium (DMEM) and Minimum Essential Medium alpha (MEMα) medium respectively (10% fetal bovine serum, and 1% penicillin/streptomycin). Cells were incubated at 37 °C in the humidified atmosphere containing 5% CO_2 for 24 h. Culture medium was replaced by 100 μL serial dilutions of the polymers with a fresh medium (final concentrations ranged from 1.5-3000 μg/mL). Non-ionic and cationic nanoparticle stock solutions were prepared in phosphate buffered saline (PBS). The anionic nanoparticle stock solution was prepared in DMSO. The cells were incubated with the nanoparticle formulations for 72 h and then the medium was replaced with 100 μL of fresh medium prior to the addition of 20 μL MTS combined reagent to each well (Cell Titer 96® Aqueous Non-Radioactive Cell Proliferation Assay, Promega Co., Madison, WI). The cells were incubated with the reagent for 2 h at 37 °C in the humidified atmosphere containing 5% CO_2 protected from light. Absorbance was measured at 490 nm using SpectraMax M5 (Molecular Devices Co., Sunnyvale, CA). The cell viability was calculated based on the relative absorbance to the control-untreated cells. The 0% and 100% cell viabilities were considered as the control medium (no cells) and cells with no treatment, respectively. The calculations of the IC_{50} values were performed using GraphPad Prism four-parameter fit (GraphPad Software, Inc., La Jolla, CA).

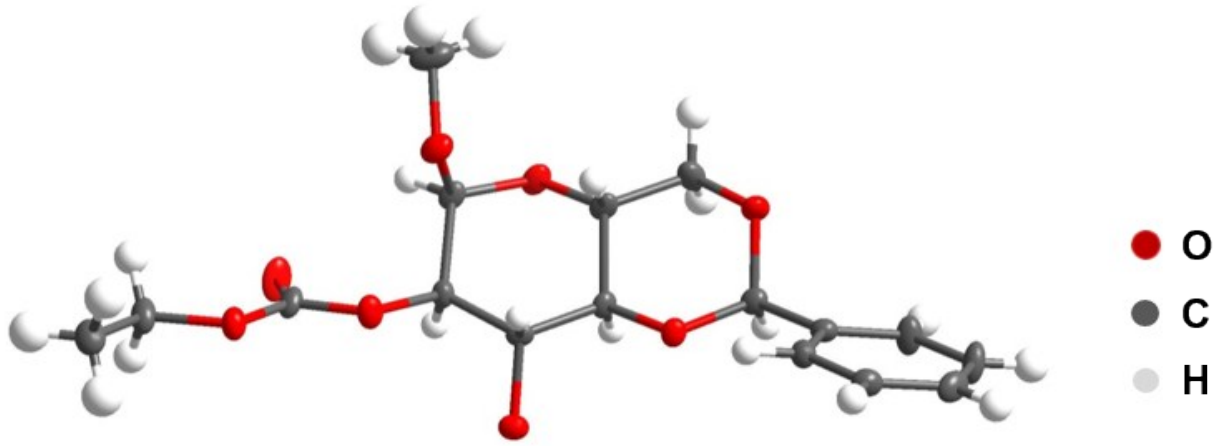

Figure S1. Single-crystal X-ray structure of **1**.

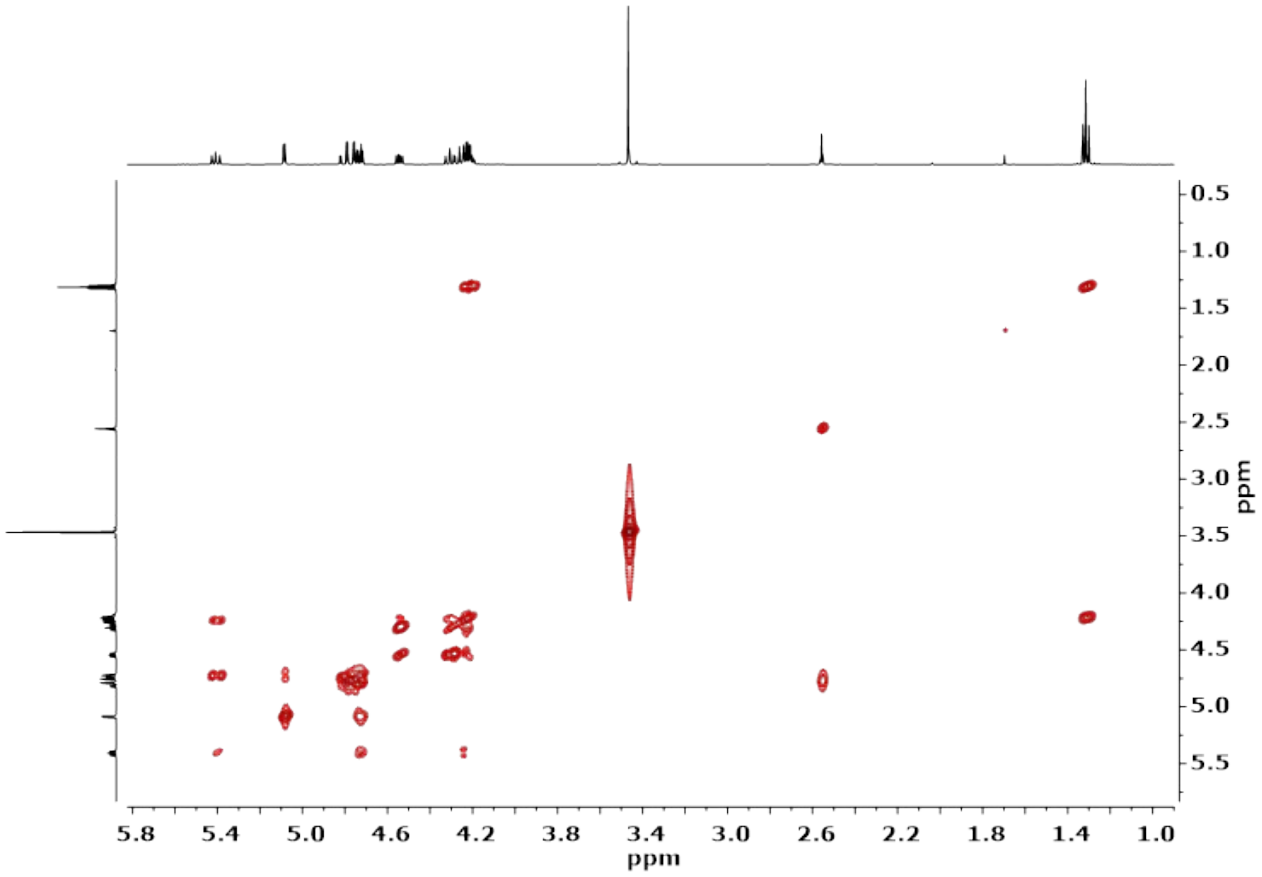

Figure S2. COSY spectrum of **4** in CD_2Cl_2.

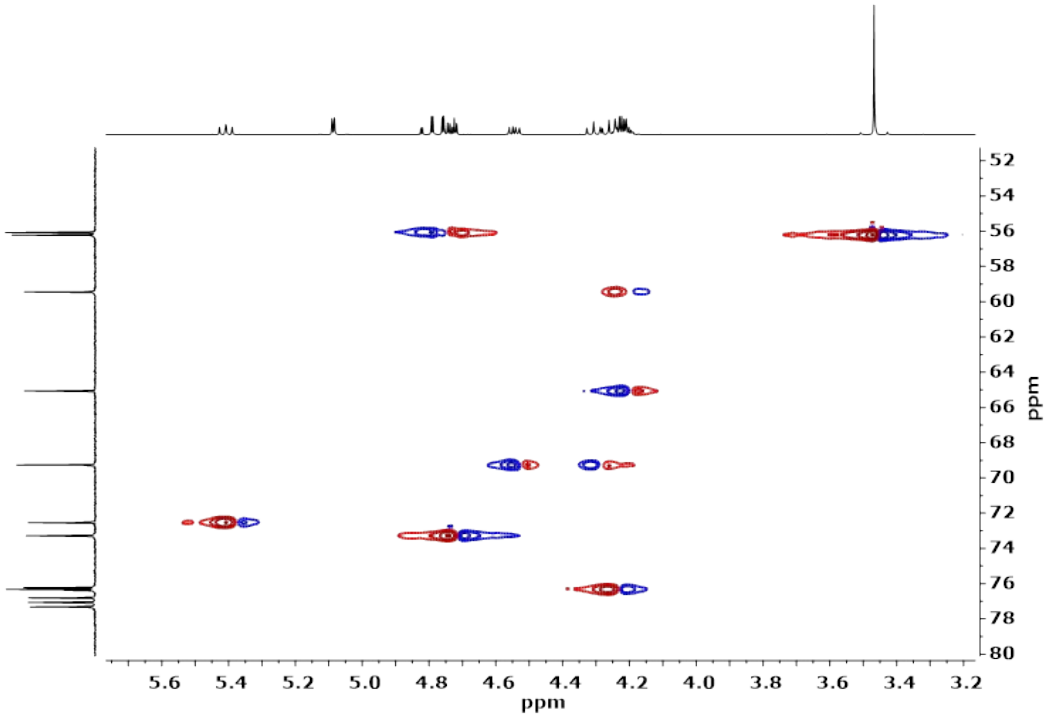

Figure S3. HSQC spectrum of **4** in CD_2Cl_2.

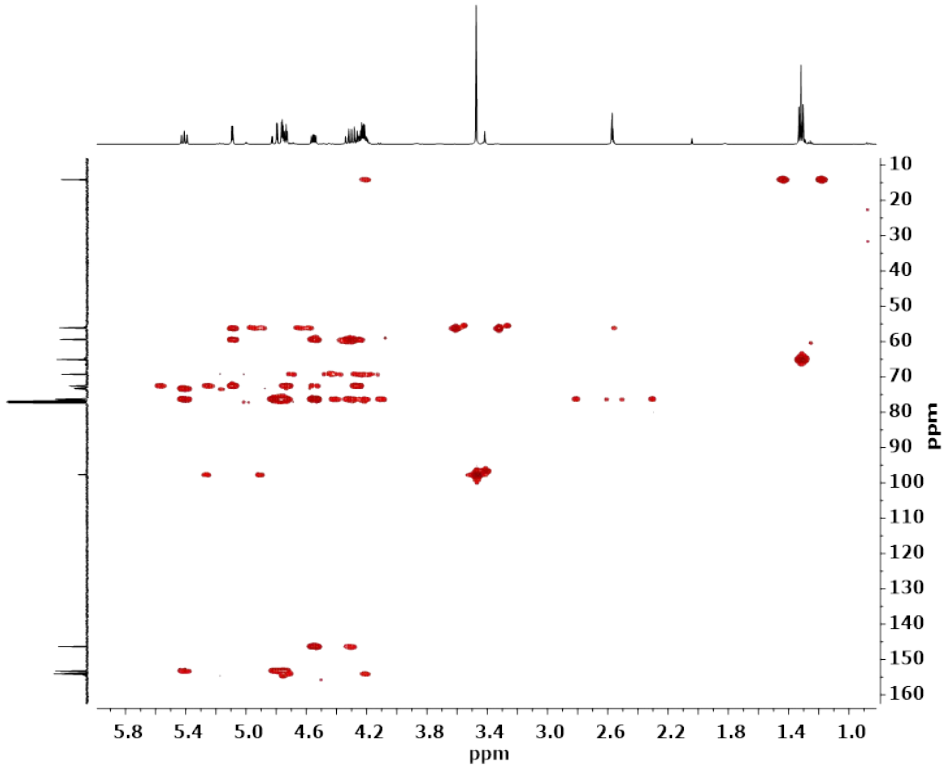

Figure S4. HMBC spectrum of **4** in CD_2Cl_2.

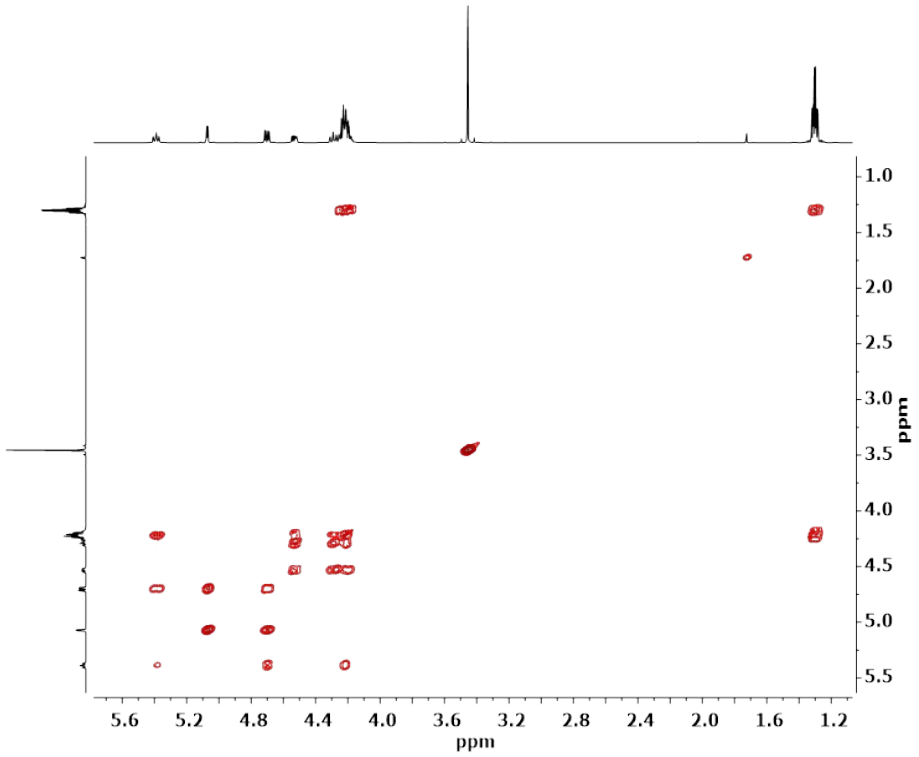

Figure S5. COSY spectrum of **7** in CD_2Cl_2.

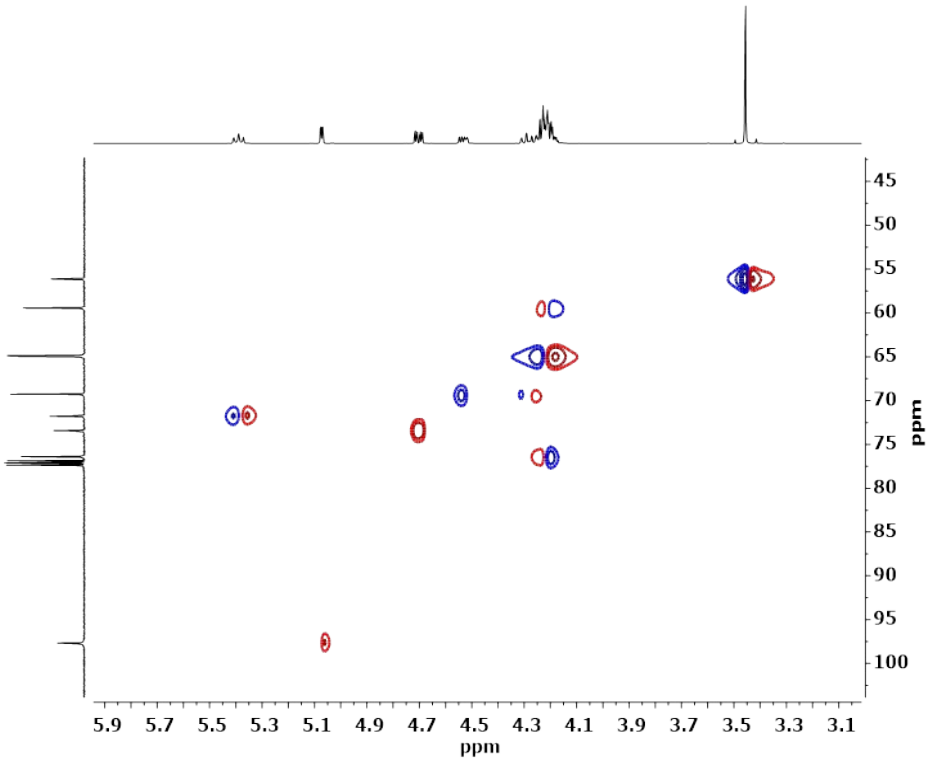

Figure S6. HSQC spectrum of **7** in CD_2Cl_2.

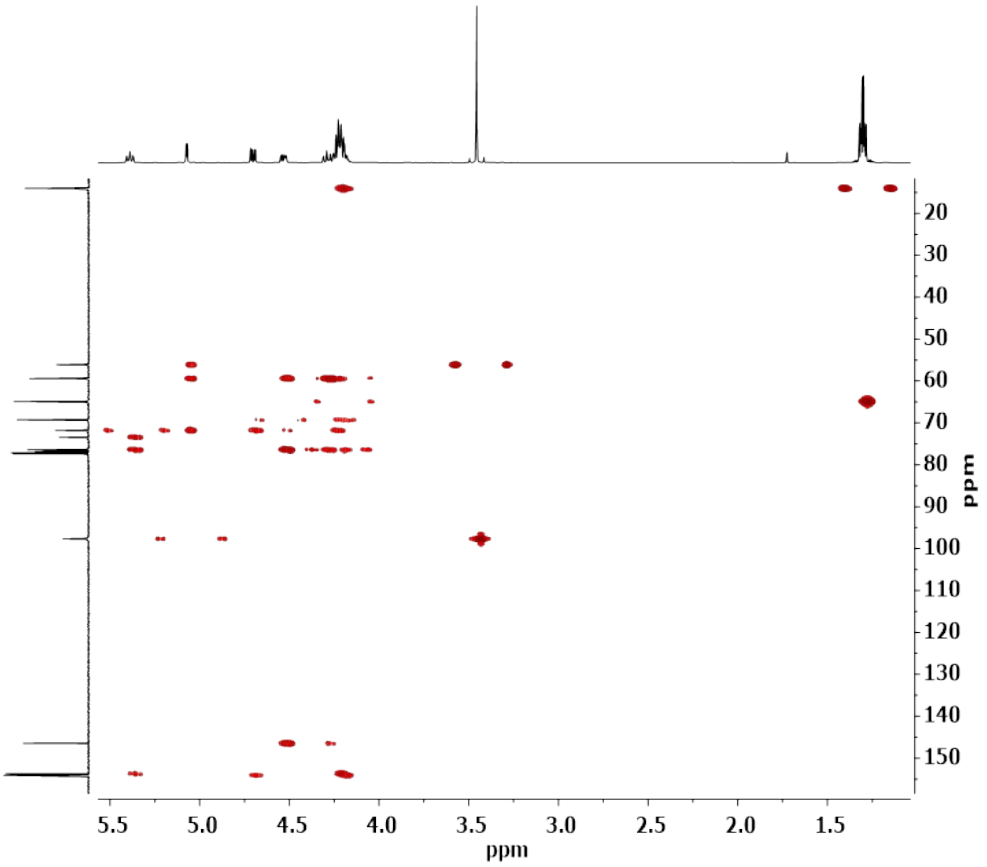

Figure S7. HMBC spectrum of **7** in CD_2Cl_2.

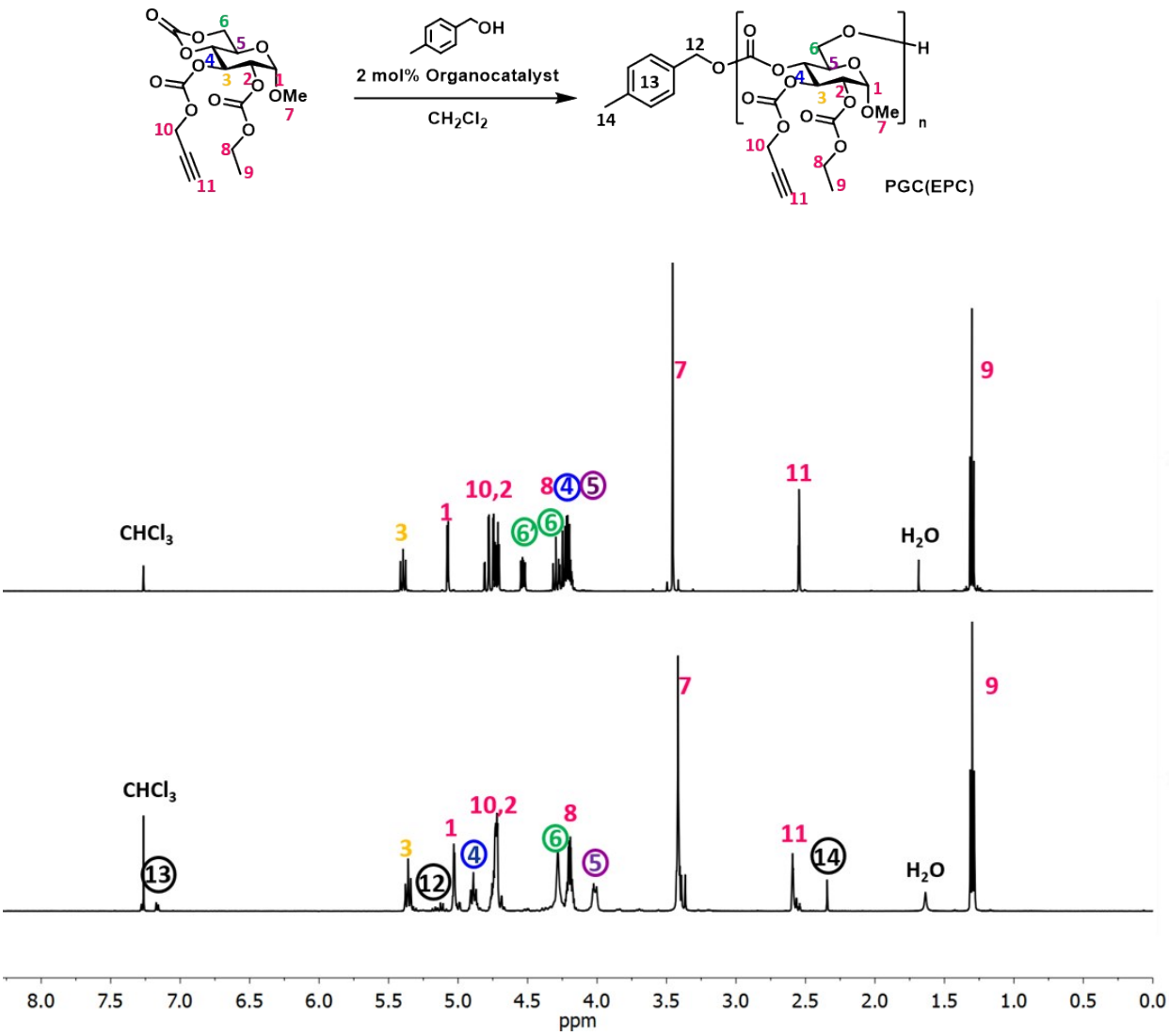

Figure S8. ^{1}H NMR spectra of **4** (upper) and the corresponding polymer PGC(EPC) (lower) in $CDCl_3$, with proton assignments highlighted by circled numbers for protons that undergo a shift or appear from installation of the chain end upon polymerization.

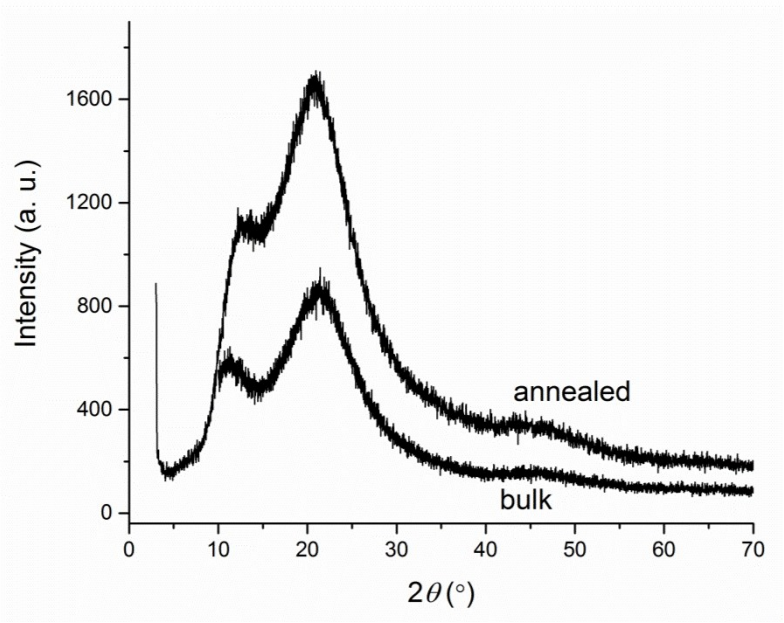

Figure S9. XRD analysis of bulk and annealed samples of PGC(EPC).

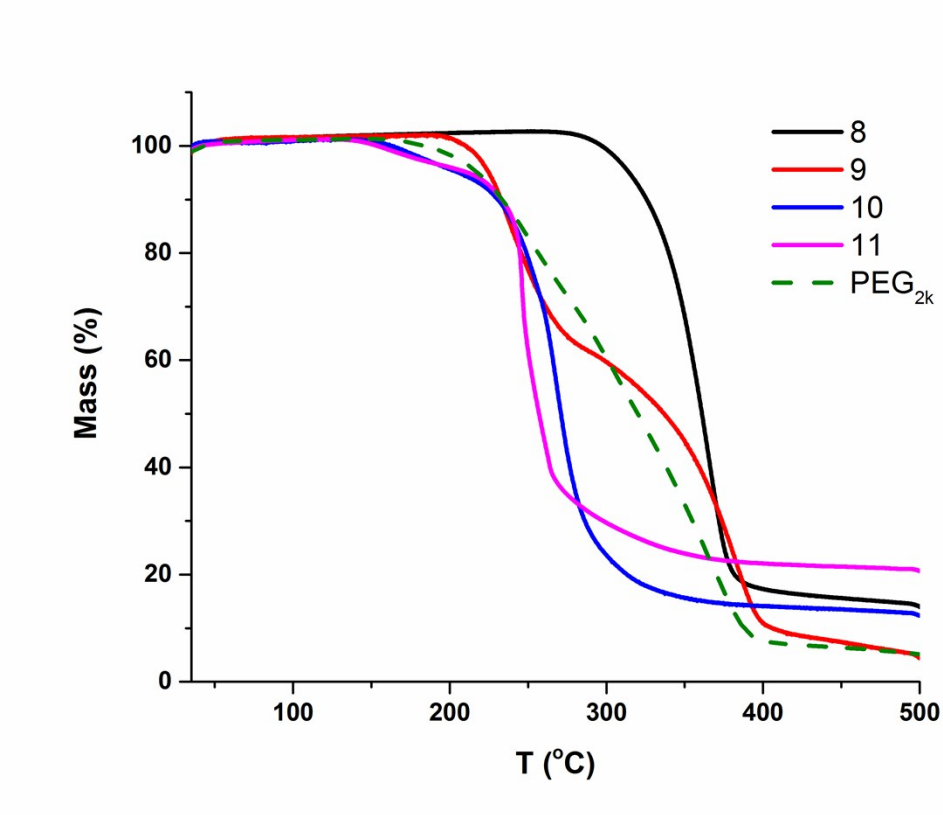

Figure S10. TGA of **8**, **9**, **10**, **11** and PEG_{2k}.

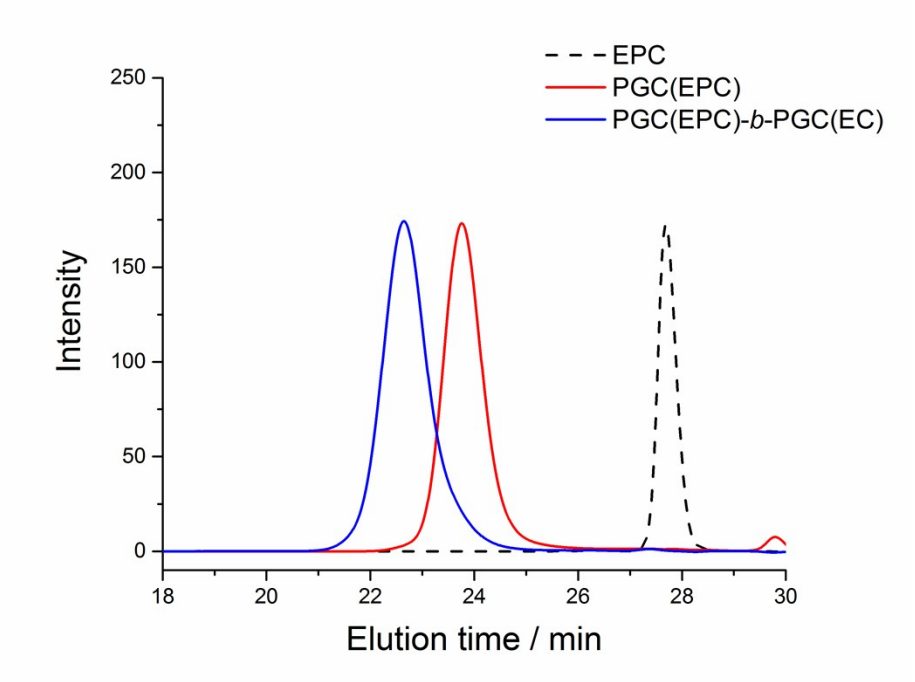

Figure S11. SEC traces of EPC, PGC(EPC)$_{50}$ and PGC(EPC)$_{50}$-*b*-PGC(EC)$_{47}$ in THF.

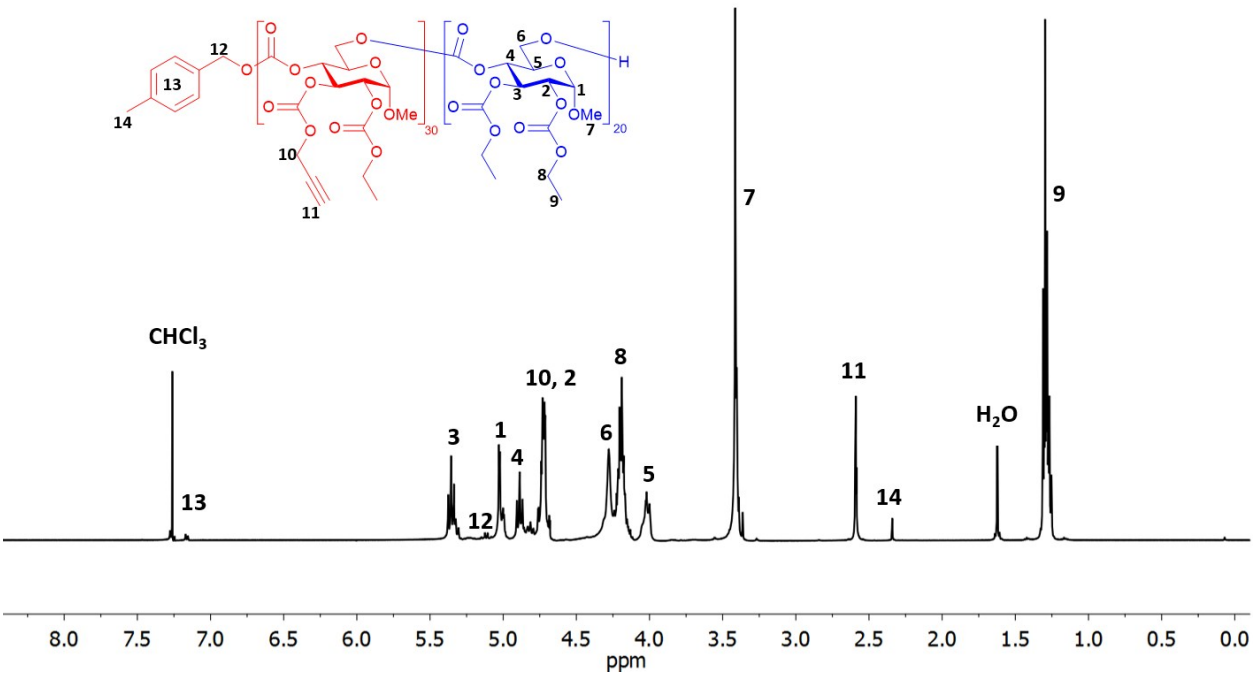

Figure S12. ^{1}H NMR spectra of **8** in $CDCl_3$.

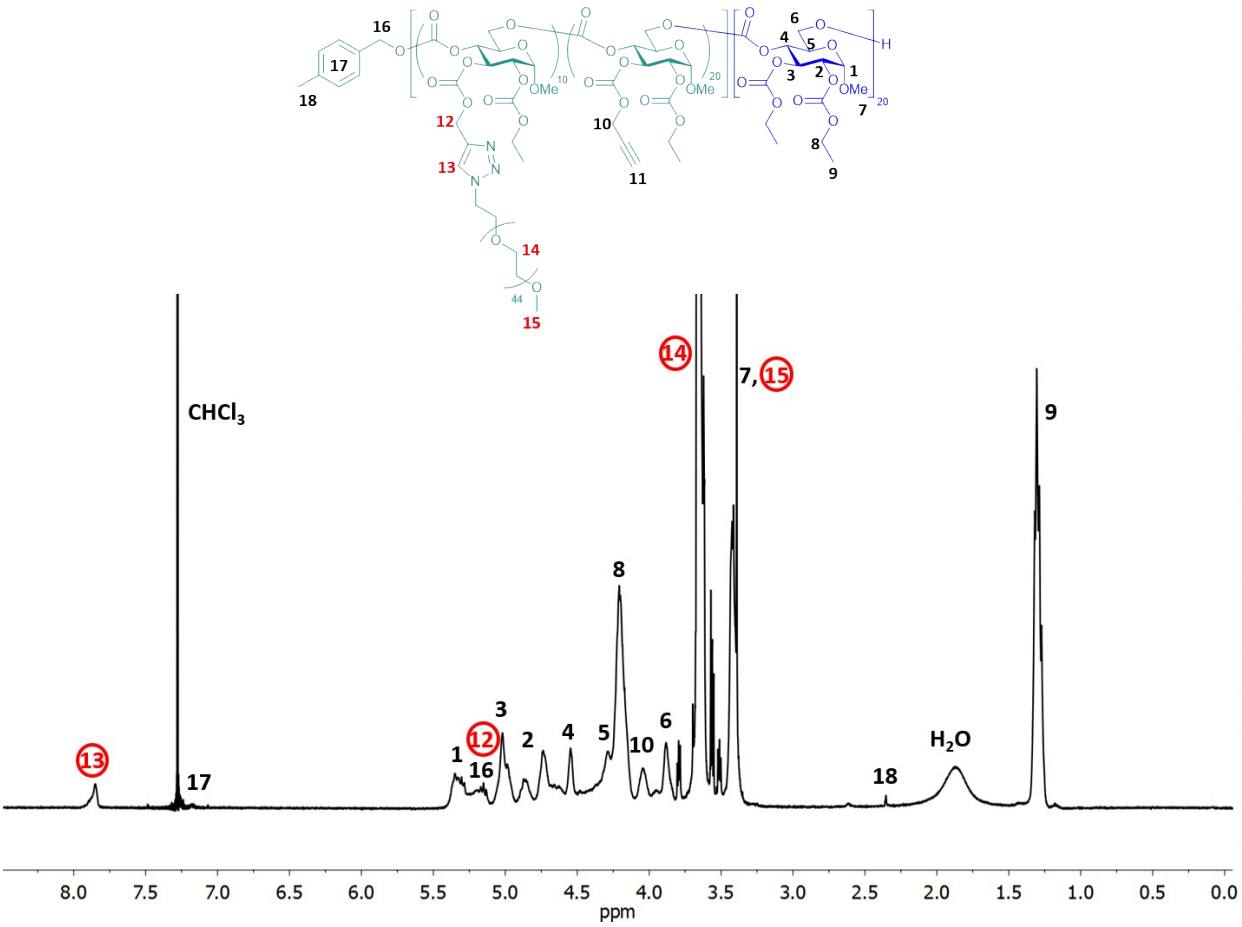

Figure S13. ^{1}H NMR spectrum of **9** in $CDCl_3$ with proton assignments highlighted by circled numbers for protons that appear from installation of the PEG_{2k} chain upon post-polymerization modification.

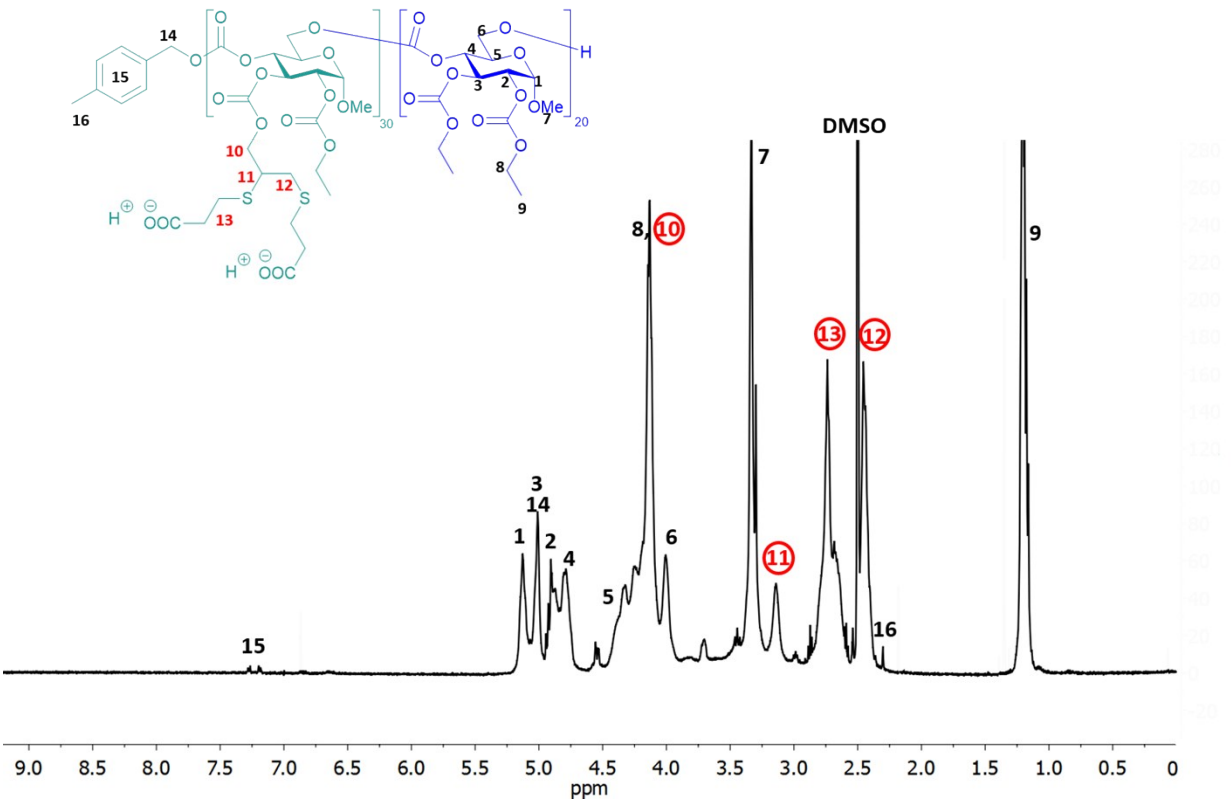

Figure S14. ^{1}H NMR spectrum of **10** in DMSO-d_6 with proton assignments highlighted by circled numbers for protons that appear from installation of 3-mercaptopropionic acid upon post-polymerization modification.

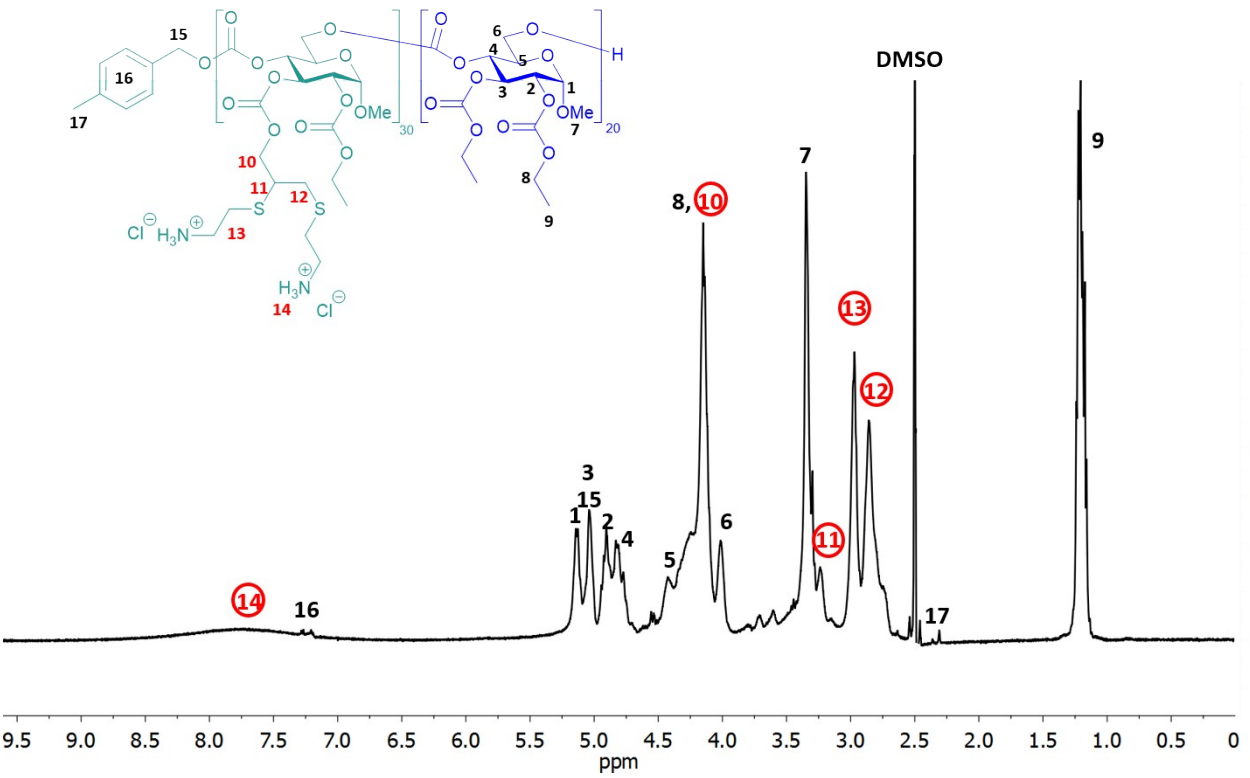

Figure S15. ^{1}H NMR spectrum of **11** in DMSO-d_6 with proton assignments highlighted by circled numbers for protons that appear from installation of cysteamine hydrochloride upon post-polymerization modification.

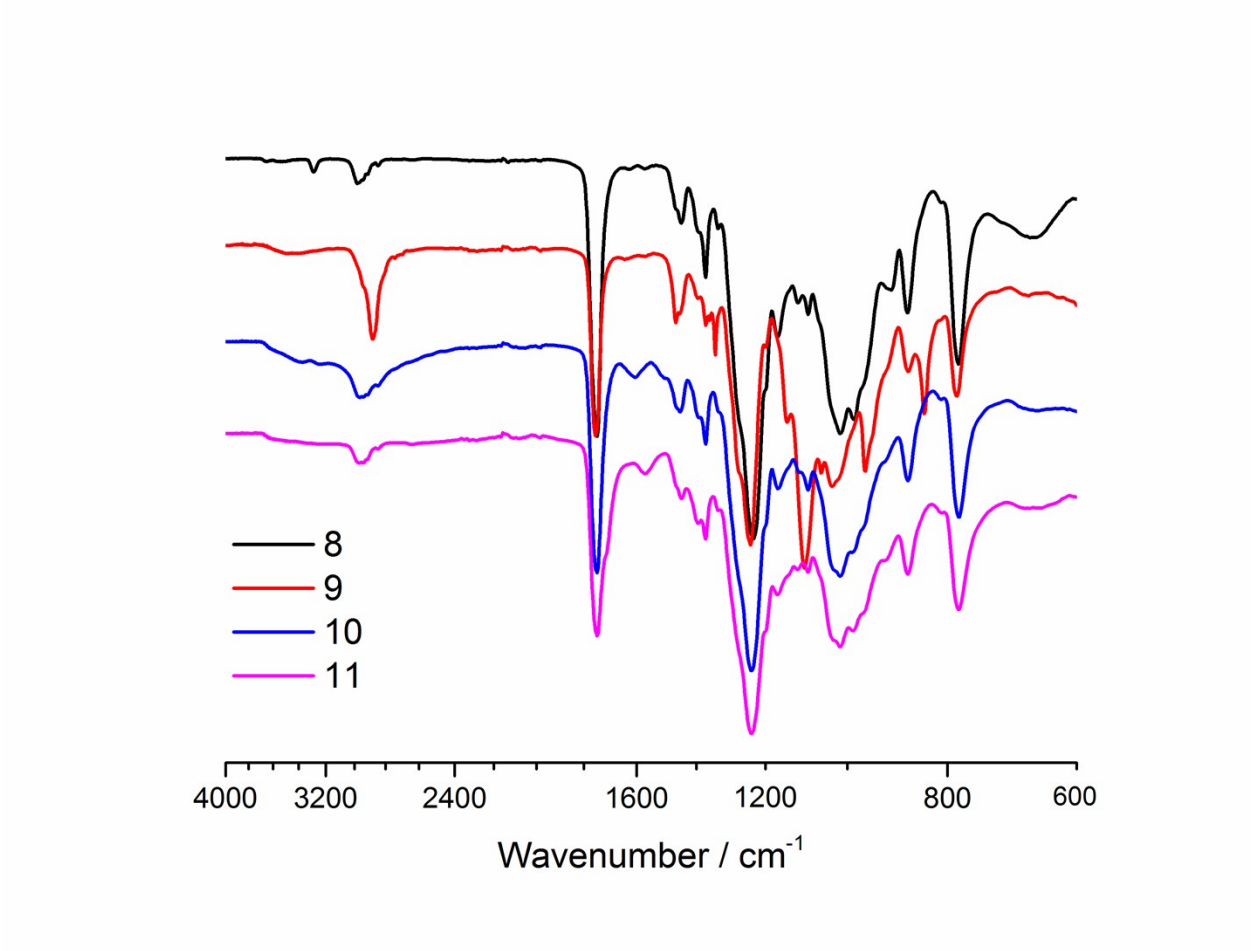

Figure S16. FT-IR spectra of **8**, **9**, **10**, **11**.

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H1 H 0.9514 0.7384 0.6557 0.070 Uiso 1 1 calc R . .

C2 C 0.90505(12) 0.6859(5) 0.4599(4) 0.0554(9) Uani 1 1 d . . .

H2 H 0.9237 0.7779 0.4135 0.067 Uiso 1 1 calc R . .

C3 C 0.85182(10) 0.7054(5) 0.3872(3) 0.0443(7) Uani 1 1 d . . .

H3 H 0.8328 0.6040 0.4254 0.053 Uiso 1 1 calc R . .

C7 C 0.9100(2) 0.5998(10) 0.8272(5) 0.1004(16) Uani 1 1 d . . .

H7A H 0.8937 0.4923 0.8655 0.151 Uiso 1 1 calc R . .

H7B H 0.9017 0.7320 0.8598 0.151 Uiso 1 1 calc R . .

H7C H 0.9449 0.5796 0.8589 0.151 Uiso 1 1 calc R . .

C8 C 0.94923(14) 0.4439(8) 0.3690(5) 0.0764(12) Uani 1 1 d . . .

C9 C 0.9889(2) 0.1759(14) 0.2900(8) 0.1368(14) Uani 1 1 d . . .

H9A H 1.0111 0.2876 0.2829 0.164 Uiso 1 1 calc R . .

H9B H 1.0082 0.0670 0.3472 0.164 Uiso 1 1 calc R . .

C10 C 0.9691(2) 0.1048(14) 0.1635(8) 0.1368(14) Uani 1 1 d . . .

H10A H 0.9944 0.0603 0.1208 0.205 Uiso 1 1 calc R . .

H10B H 0.9499 0.2116 0.1059 0.205 Uiso 1 1 calc R . .

H10C H 0.9483 -0.0105 0.1698 0.205 Uiso 1 1 calc R . .

C11 C 0.82099(12) 0.5072(5) 0.1854(4) 0.0518(8) Uani 1 1 d . . .

C12 C 0.78814(18) 0.3573(8) -0.0342(5) 0.0833(13) Uani 1 1 d . . .

H12A H 0.7777 0.4021 -0.1330 0.100 Uiso 1 1 calc R . .

H12B H 0.7590 0.3372 -0.0010 0.100 Uiso 1 1 calc R . .

C13 C 0.8131(2) 0.1662(8) -0.0273(5) 0.0808(12) Uani 1 1 d . . .

C14 C 0.8299(3) 0.0111(11) -0.0270(8) 0.134(3) Uani 1 1 d . . .

H14 H 0.8439 -0.1192 -0.0268 0.161 Uiso 1 1 calc R . .

loop_

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_atom_site_aniso_U_11

_atom_site_aniso_U_22

_atom_site_aniso_U_33

_atom_site_aniso_U_23

_atom_site_aniso_U_13

_atom_site_aniso_U_12

O2 0.0669(15) 0.0593(16) 0.0864(18) -0.0154(15) 0.0298(13) 0.0148(13)

O4 0.0521(15) 0.0702(19) 0.110(2) -0.0048(17) 0.0237(14) 0.0176(14)

O3 0.0451(11) 0.0437(12) 0.0687(14) -0.0022(11) 0.0167(10) 0.0037(10)

O5 0.0634(14) 0.0558(15) 0.0702(16) 0.0068(13) 0.0189(12) 0.0017(12)

O6 0.0556(14) 0.0549(16) 0.0978(19) -0.0016(14) 0.0357(13) 0.0124(12)

O7 0.115(2) 0.155(3) 0.165(3) -0.043(3) 0.079(2) 0.008(2)

O8 0.091(2) 0.097(3) 0.160(4) -0.039(3) 0.045(2) 0.040(2)

O9 0.0662(14) 0.0392(12) 0.0608(13) -0.0028(10) 0.0299(11) -0.0050(10)

O10 0.106(2) 0.0605(18) 0.0760(18) -0.0062(14) 0.0350(16) -0.0318(16)

O11 0.098(2) 0.0509(15) 0.0558(15) -0.0043(12) 0.0149(13) 0.0030(14)

C6 0.073(2) 0.047(2) 0.073(2) -0.0126(18) 0.0266(18) -0.0013(17)

C15 0.0511(19) 0.0445(18) 0.082(2) -0.0003(18) 0.0316(18) 0.0098(16)

C4 0.0399(15) 0.0340(15) 0.0610(18) 0.0003(14) 0.0221(13) -0.0007(13)

C5 0.0443(15) 0.0398(17) 0.0612(19) -0.0014(15) 0.0209(13) -0.0033(14)

O1 0.0471(12) 0.0511(14) 0.0740(15) -0.0088(12) 0.0159(11) -0.0079(11)

C1 0.0396(16) 0.058(2) 0.077(2) -0.0014(19) 0.0138(15) -0.0029(16)

C2 0.0457(17) 0.046(2) 0.082(2) -0.0007(18) 0.0299(16) 0.0056(15)

C3 0.0441(16) 0.0386(17) 0.0554(17) -0.0010(14) 0.0223(13) -0.0023(13)

C7 0.117(4) 0.110(4) 0.072(3) 0.009(3) 0.022(3) 0.011(4)

C8 0.048(2) 0.083(3) 0.103(3) -0.008(3) 0.028(2) 0.005(2)

C9 0.115(2) 0.155(3) 0.165(3) -0.043(3) 0.079(2) 0.008(2)

C10 0.115(2) 0.155(3) 0.165(3) -0.043(3) 0.079(2) 0.008(2)

C11 0.0547(18) 0.0378(18) 0.064(2) 0.0011(16) 0.0173(15) 0.0056(15)

C12 0.089(3) 0.072(3) 0.075(3) -0.014(2) -0.001(2) 0.000(2)

C13 0.115(4) 0.053(3) 0.087(3) -0.009(2) 0.049(3) -0.010(2)

C14 0.189(7) 0.074(4) 0.179(7) 0.004(4) 0.117(6) 0.008(4)

_geom_special_details

;

All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell s.u.'s are taken

into account individually in the estimation of s.u.'s in distances, angles

and torsion angles; correlations between s.u.'s in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

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loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_geom_bond_publ_flag

O2 C15 1.321(5) . ?

O2 C6 1.451(5) . ?

O4 C15 1.193(4) . ?

O3 C15 1.344(4) . ?

O3 C4 1.434(3) . ?

O5 C1 1.387(5) . ?

O5 C7 1.405(5) . ?

O6 C8 1.317(5) . ?

O6 C2 1.436(4) . ?

O7 C8 1.188(7) . ?

O8 C8 1.301(7) . ?

O8 C9 1.424(6) . ?

O9 C11 1.338(4) . ?

O9 C3 1.430(4) . ?

O10 C11 1.177(4) . ?

O11 C11 1.334(4) . ?

O11 C12 1.443(5) . ?

C6 C5 1.508(5) . ?

C6 H6A 0.9900 . ?

C6 H6B 0.9900 . ?

C4 C5 1.495(4) . ?

C4 C3 1.502(4) . ?

C4 H4 1.0000 . ?

C5 O1 1.432(4) . ?

C5 H5 1.0000 . ?

O1 C1 1.421(5) . ?

C1 C2 1.523(5) . ?

C1 H1 1.0000 . ?

C2 C3 1.519(4) . ?

C2 H2 1.0000 . ?

C3 H3 1.0000 . ?

C7 H7A 0.9800 . ?

C7 H7B 0.9800 . ?

C7 H7C 0.9800 . ?

C9 C10 1.318(9) . ?

C9 H9A 0.9900 . ?

C9 H9B 0.9900 . ?

C10 H10A 0.9800 . ?

C10 H10B 0.9800 . ?

C10 H10C 0.9800 . ?

C12 C13 1.444(7) . ?

C12 H12A 0.9900 . ?

C12 H12B 0.9900 . ?

C13 C14 1.131(8) . ?

C14 H14 0.9500 . ?

loop_

_geom_angle_atom_site_label_1

_geom_angle_atom_site_label_2

_geom_angle_atom_site_label_3

_geom_angle

_geom_angle_site_symmetry_1

_geom_angle_site_symmetry_3

_geom_angle_publ_flag

C15 O2 C6 124.3(3) . . ?

C15 O3 C4 120.0(3) . . ?

C1 O5 C7 114.6(4) . . ?

C8 O6 C2 118.2(4) . . ?

C8 O8 C9 119.0(6) . . ?

C11 O9 C3 116.7(2) . . ?

C11 O11 C12 115.4(3) . . ?

O2 C6 C5 108.5(3) . . ?

O2 C6 H6A 110.0 . . ?

C5 C6 H6A 110.0 . . ?

O2 C6 H6B 110.0 . . ?

C5 C6 H6B 110.0 . . ?

H6A C6 H6B 108.4 . . ?

O4 C15 O2 120.8(3) . . ?

O4 C15 O3 119.1(4) . . ?

O2 C15 O3 120.0(3) . . ?

O3 C4 C5 109.9(2) . . ?

O3 C4 C3 108.6(2) . . ?

C5 C4 C3 109.5(3) . . ?

O3 C4 H4 109.6 . . ?

C5 C4 H4 109.6 . . ?

C3 C4 H4 109.6 . . ?

O1 C5 C4 109.6(2) . . ?

O1 C5 C6 109.1(3) . . ?

C4 C5 C6 107.7(3) . . ?

O1 C5 H5 110.1 . . ?

C4 C5 H5 110.1 . . ?

C6 C5 H5 110.1 . . ?

C1 O1 C5 111.6(2) . . ?

O5 C1 O1 113.3(3) . . ?

O5 C1 C2 108.1(3) . . ?

O1 C1 C2 109.4(3) . . ?

O5 C1 H1 108.7 . . ?

O1 C1 H1 108.7 . . ?

C2 C1 H1 108.7 . . ?

O6 C2 C3 107.8(3) . . ?

O6 C2 C1 109.8(3) . . ?

C3 C2 C1 111.5(2) . . ?

O6 C2 H2 109.2 . . ?

C3 C2 H2 109.2 . . ?

C1 C2 H2 109.2 . . ?

O9 C3 C4 109.9(3) . . ?

O9 C3 C2 108.3(2) . . ?

C4 C3 C2 107.2(2) . . ?

O9 C3 H3 110.4 . . ?

C4 C3 H3 110.4 . . ?

C2 C3 H3 110.4 . . ?

O5 C7 H7A 109.5 . . ?

O5 C7 H7B 109.5 . . ?

H7A C7 H7B 109.5 . . ?

O5 C7 H7C 109.5 . . ?

H7A C7 H7C 109.5 . . ?

H7B C7 H7C 109.5 . . ?

O7 C8 O8 126.0(5) . . ?

O7 C8 O6 124.6(5) . . ?

O8 C8 O6 109.4(5) . . ?

C10 C9 O8 113.9(6) . . ?

C10 C9 H9A 108.8 . . ?

O8 C9 H9A 108.8 . . ?

C10 C9 H9B 108.8 . . ?

O8 C9 H9B 108.8 . . ?

H9A C9 H9B 107.7 . . ?

C9 C10 H10A 109.5 . . ?

C9 C10 H10B 109.5 . . ?

H10A C10 H10B 109.5 . . ?

C9 C10 H10C 109.5 . . ?

H10A C10 H10C 109.5 . . ?

H10B C10 H10C 109.5 . . ?

O10 C11 O11 126.7(3) . . ?

O10 C11 O9 127.1(3) . . ?

O11 C11 O9 106.2(3) . . ?

O11 C12 C13 113.2(4) . . ?

O11 C12 H12A 108.9 . . ?

C13 C12 H12A 108.9 . . ?

O11 C12 H12B 108.9 . . ?

C13 C12 H12B 108.9 . . ?

H12A C12 H12B 107.8 . . ?

C14 C13 C12 175.4(7) . . ?

C13 C14 H14 180.0 . . ?

loop_

_geom_torsion_atom_site_label_1

_geom_torsion_atom_site_label_2

_geom_torsion_atom_site_label_3

_geom_torsion_atom_site_label_4

_geom_torsion

_geom_torsion_site_symmetry_1

_geom_torsion_site_symmetry_2

_geom_torsion_site_symmetry_3

_geom_torsion_site_symmetry_4

_geom_torsion_publ_flag

C15 O2 C6 C5 -26.1(5) . . . . ?

C6 O2 C15 O4 179.8(3) . . . . ?

C6 O2 C15 O3 2.1(6) . . . . ?

C4 O3 C15 O4 174.3(3) . . . . ?

C4 O3 C15 O2 -8.0(5) . . . . ?

C15 O3 C4 C5 37.8(4) . . . . ?

C15 O3 C4 C3 157.6(3) . . . . ?

O3 C4 C5 O1 -178.4(2) . . . . ?

C3 C4 C5 O1 62.4(3) . . . . ?

O3 C4 C5 C6 -59.8(3) . . . . ?

C3 C4 C5 C6 -179.0(3) . . . . ?

O2 C6 C5 O1 171.9(3) . . . . ?

O2 C6 C5 C4 53.0(3) . . . . ?

C4 C5 O1 C1 -63.5(3) . . . . ?

C6 C5 O1 C1 178.7(3) . . . . ?

C7 O5 C1 O1 -70.9(4) . . . . ?

C7 O5 C1 C2 167.7(4) . . . . ?

C5 O1 C1 O5 -61.1(4) . . . . ?

C5 O1 C1 C2 59.5(3) . . . . ?

C8 O6 C2 C3 113.8(4) . . . . ?

C8 O6 C2 C1 -124.5(4) . . . . ?

O5 C1 C2 O6 -51.8(3) . . . . ?

O1 C1 C2 O6 -175.6(2) . . . . ?

O5 C1 C2 C3 67.6(4) . . . . ?

O1 C1 C2 C3 -56.1(4) . . . . ?

C11 O9 C3 C4 -129.7(3) . . . . ?

C11 O9 C3 C2 113.4(3) . . . . ?

O3 C4 C3 O9 64.7(3) . . . . ?

C5 C4 C3 O9 -175.3(2) . . . . ?

O3 C4 C3 C2 -177.8(2) . . . . ?

C5 C4 C3 C2 -57.8(3) . . . . ?

O6 C2 C3 O9 -65.6(3) . . . . ?

C1 C2 C3 O9 173.8(3) . . . . ?

O6 C2 C3 C4 175.8(3) . . . . ?

C1 C2 C3 C4 55.2(3) . . . . ?

C9 O8 C8 O7 3.5(9) . . . . ?

C9 O8 C8 O6 -175.8(5) . . . . ?

C2 O6 C8 O7 5.0(7) . . . . ?

C2 O6 C8 O8 -175.8(4) . . . . ?

C8 O8 C9 C10 -103.7(8) . . . . ?

C12 O11 C11 O10 6.6(5) . . . . ?

C12 O11 C11 O9 -174.6(3) . . . . ?

C3 O9 C11 O10 -4.4(5) . . . . ?

C3 O9 C11 O11 176.8(3) . . . . ?

C11 O11 C12 C13 -79.3(5) . . . . ?

O11 C12 C13 C14 175(7) . . . . ?

_diffrn_measured_fraction_theta_max 0.997

_diffrn_reflns_theta_full 25.03

_diffrn_measured_fraction_theta_full 0.997

_refine_diff_density_max 0.559

_refine_diff_density_min -0.574

_refine_diff_density_rms 0.042