

Supporting Information

Optimised ‘Click’ Synthesis of Glycopolymers with mono/di and trisaccharides.

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Experimental

Materials

Copper(I) bromide, 2-chloro-1,3-dimethylimidazolium chloride (DMC), *N,N*-diisopropylethylamine (DIPEA), sodium azide, D-cellobiose, L-fucose, α -D-glucose, lactose, maltotriose, bathophenanthrolinedisulfonic acid disodium salt trihydrate (BPDS), concanavalin A and 2,2'-bipyridyl (bipyridine) were purchased from Sigma-Aldrich. Triethyl amine was purchased from Fisher Scientific. D-(+)-Galactose was purchased from Alfa-Aesar. All reagents were used as received unless otherwise specified. Copper(I) bromide was purified by the method of Keller and Wycoff.¹ Poly(propargyl methacrylate) was prepared according to previously published methods.² (SEC (DMF) $M_n = 7400$, $M_n/M_w = 1.29$ and satisfactory NMR data). The ligands *N*-ethyl-2-pyridylmethanimine³ and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)⁴ were prepared as described previously. Phosphate buffered saline solution was prepared by dissolving a pre-formulated tablet from Sigma-Aldrich in 200 mL of ultra high quality water to give a final composition of 0.01 M phosphate, 0.0027 M potassium chloride and 0.137 sodium chloride, pH 7.4.

Analytical and Physical Methods

¹H and ¹³C NMR spectra were recorded on Bruker DPX-300 and DPX-400 spectrometers using deuterated solvents obtained from Aldrich. Polymerisation kinetics were followed by ¹H NMR were recorded on a Bruker AV-400 spectrometer. Mass spectra were recorded on an Esquire2000 using electrospray ionisation (ESI) in positive mode. FTIR spectra were recorded on a Bruker Vector 22 FTIR spectrometer. SEC was conducted on a Varian 390-LC system in DMF (1 g/L LiBr) at 50°C, equipped with refractive index and viscometry detectors, 2 x PLgel 5 μ m mixed-D columns (300 x 7.5 mm), 1 x PLgel 5 μ m guard column (50 x 7.5 mm) and autosampler. Data was analysed using Cirrus 3.2 software. Molecular

weight was determined relative to narrow poly(methyl methacrylate) standards. For the turbidimetry studies absorbance was measured at 420 nm on a Perkin Elmer Lambda-35 UV/VIS spectrometer using 1 cm path length glass cuvettes.

Procedures

Click Reactions of β -Glucose Azide (Ligand Variation)

A stock solution of β -glucose azide (90 mg, 0.44 mmol), alkyne-functionalised polymer (45 mg, 0.36 mmol) and triethylamine (12 μ l, 8.7 mg, 0.088 mmol) dissolved in d_6 -DMSO (4.5 ml) was charged into a Schlenk tube, sealed with a rubber septum and deoxygenated by three freeze-pump-thaw cycles before being placed under nitrogen.

Procedure 1: Bipyridine (2 mg, 0.013 mmol) and copper(I) bromide (2 mg, 0.014 mmol) were added to a Young's tap NMR tube, followed by stock solution (0.6 ml). The reaction was quickly placed under vacuum and then nitrogen.

SEC $M_n = 19700$, $M_w = 28400$, $M_n/M_w = 1.44$

Procedure 2: BPDS (9 mg, 0.015 mmol) and copper(I) bromide (2 mg, 0.014 mmol) were added to a Young's tap NMR tube, followed by stock solution (0.6 ml). The reaction was quickly placed under vacuum and then nitrogen.

SEC $M_n = 15600$, $M_w = 18600$, $M_n/M_w = 1.19$

Procedure 3: Ethyl ligand (2 μ l, 2 mg, 0.015 mmol) and copper(I) bromide (2 mg, 0.014 mmol) were added to a Young's tap NMR tube, followed by stock solution (0.6 ml). The reaction was quickly placed under vacuum and then nitrogen.

SEC $M_n = 16500$, $M_w = 21400$, $M_n/M_w = 1.30$

Procedure 4: TBTA (8 mg, 0.015 mmol) and copper(I) bromide (2 mg, 0.014 mmol) were added to a Young's tap NMR tube, followed by stock solution (0.6 ml). The reaction was quickly placed under vacuum and then nitrogen.

SEC $M_n = 16200$, $M_w = 19300$, $M_n/M_w = 1.19$

All reactions were monitored by ^1H NMR until completion. % Conversion was determined by monitoring the disappearance of the peak at 4.46 ppm.

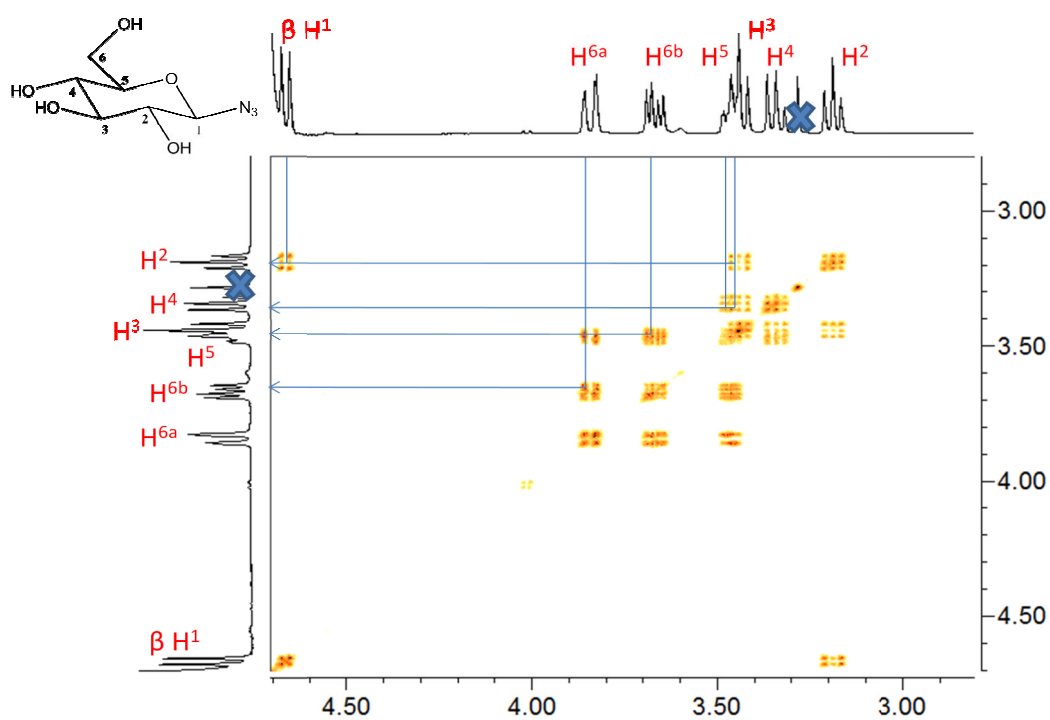


Figure S1 COSY ^1H NMR spectrum of glucose-azide in D_2O

Investigation into reaction between poly(alkyne) scaffold and glucose azide

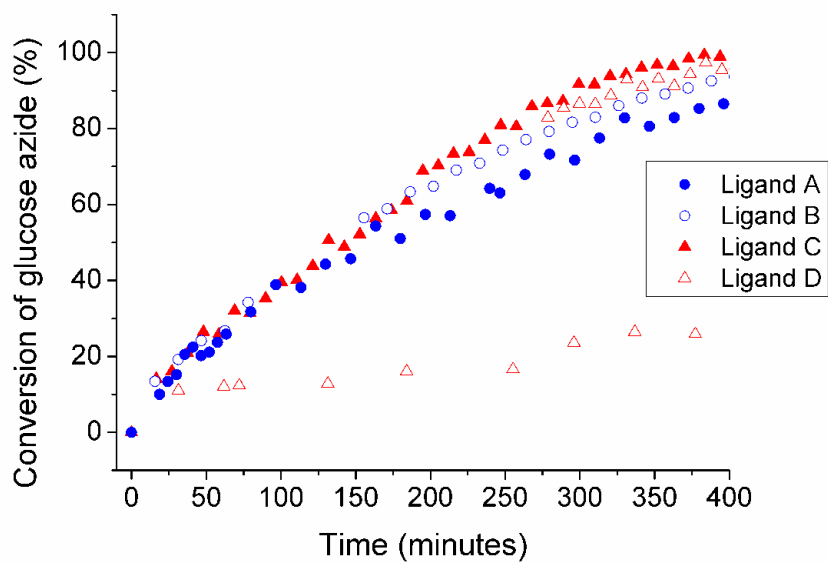


Figure S2 Conversion of glucose azide as a function of time during click reaction with **P1**.

Conversion was determined by online ^1H NMR.

Representative infrared spectra showing conversion of alkyne and azide following ‘click’ reaction.

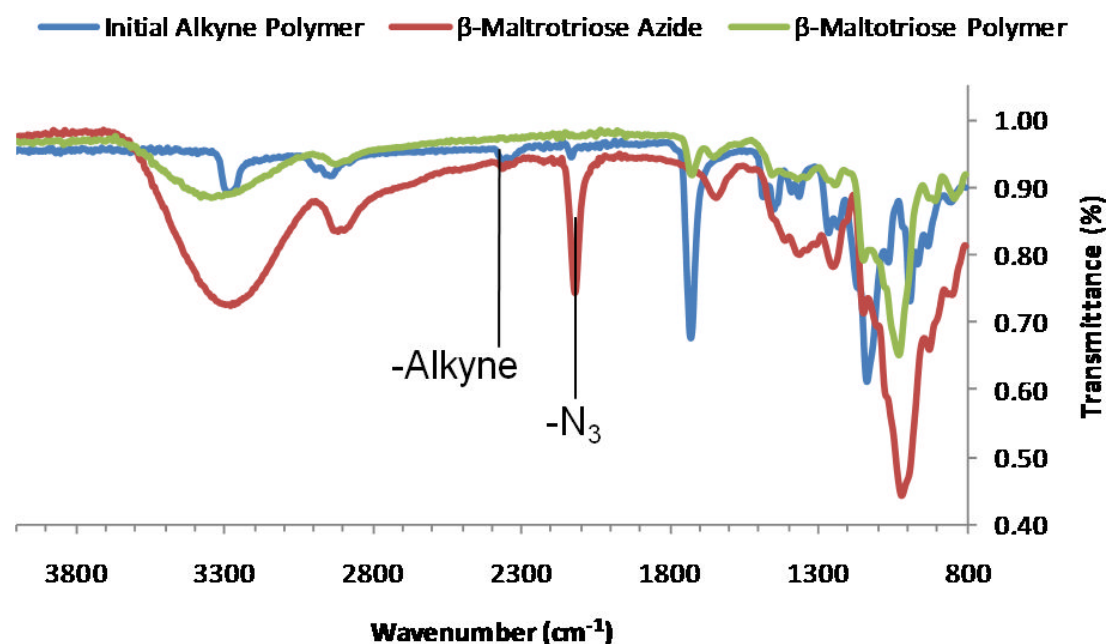


Figure S3. FTIR spectra of glycosyl azide and **P1** before and after ‘click’ reaction.

References

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