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Supporting Information

An Oxygen-Tolerant PET-RAFT Polymerization for Screening Structure–Activity Relationships

Adam J. Gormley, Jonathan Yeow, Gervase Ng, Órla Conway, Cyrille Boyer, and Robert Chapman**

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Author Contributions

J.Y. Investigation: Supporting
G.N. Investigation: Supporting
Ó.C. Investigation: Supporting
R.C. co-corresponding author: Equal.

Supporting Information

Experimental Procedures

Materials:

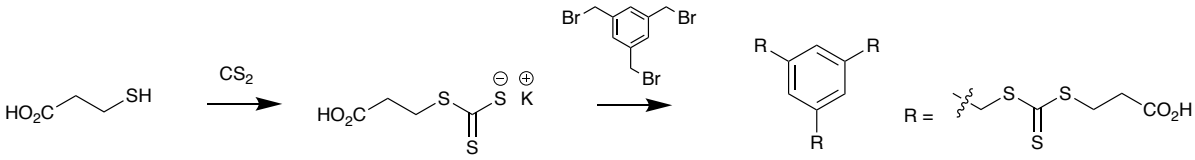
The RAFT agent 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA, **R1**) was purchased from Boron Scientific and used as supplied. *S*-benzyl *S'*-propionic acid trithiocarbonate (BSPA, **R2**), was synthesised according to literature procedures and isolated as a yellow solid.[1] With the exception of NHS acrylate (which was synthesised, see below), all monomers were purchased from Sigma Aldrich and deinhibited prior to use by passing them over MEHQ inhibitor removal resin. 1,3,4,6-tetra-O-acetyl-2-azido-2-deoxy-α-D-mannopyranose (Man(OAc)-N_3) was purchased from Carbosynth (UK). Zinc tetraphenylporphyrin and all other reagents, including the *concanavalin A – horseradish peroxidase* conjugate, were purchased from Sigma Aldrich and used as supplied.

Synthesis of N-hydroxysuccinimide (NHS) acrylate (1):

N-hydroxysuccinimide (3.0 g, 26.1 mmol) was mixed with triethylamine (2.9 g, 28.7 mmol) in anhydrous dichloromethane (50 mL) under an inert atmosphere. The solution was cooled in an ice bath and acryloyl chloride (2.6 g, 28.7 mmol) was added dropwise. After stirring overnight the mixture was washed with HCl (0.1M, 2 x 50 mL), water (1 x 50 mL) and brine (1 x 50 mL), dried with $MgSO_4$, and concentrated *in vacuo*. The crude was purified by column chromatography over silica (25-50% ethyl acetate / hexane), to yield the product as a white solid (2.75 g, 63%), ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 6.70 (dd, *J* = 17.3, 0.9 Hz, 1H), 6.32 (dd, *J* = 17.3, 10.7 Hz, 1H), 6.17 (dd, *J* = 10.7, 0.9 Hz, 1H), 2.86 (s, 4H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 169.16, 161.17, 136.33, 123.07, 25.74.

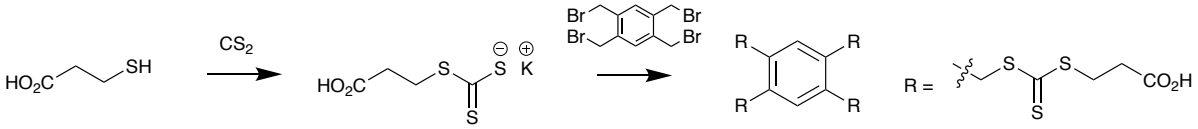
[1] M. H. Stenzel, T. P. Davis, A. G. Fane, *J. Mater. Chem.* **2003**, *13*, 2090–2097.

Synthesis of 3 arm RAFT agent, R3:



The three arm RAFT agent (**R3**) was prepared following a procedure adapted from the literature.[2] 3-mercaptopropionic acid (1.0 g, 9.4 mmol) was dissolved in acetone (20 mL) with tribasic potassium phosphate (2.0 g, 9.4 mmol). The mixture was cooled in an ice bath and Carbon disulphide (1.0 mL, 17.1 mmol) was added dropwise. After 20 min stirring at RT, 1,3,5-trisbromomethyl benzene (0.66 g, 1.9 mmol) was added and the mixture was stirred for 2 h at RT. The solution was filtered and the yellow precipitate was dissolved in water and recrystallized by dropwise acidification of the solution with HCl. After filtration the solid was washed with water to yield the product (0.961 g, 78%). ^{1}H-NMR (400 MHz, DMSO-d_6) δppm: 7.32 (s, 3H, Ph-H), 4.63 (s, 7H, Ph-CH_2-), 3.53 (t, J = 6.9 Hz, 6H, S-CH_2-), 2.67 (t, J = 6.9 Hz, 6H, -CH_2-CO_2H). ^{13}C-NMR (101 MHz, DMSO-d_6) δppm: 172.92 (CO_2H), 136.71 (Ph), 129.75 (Ph), 32.87 (S-CH_2), 32.32 (CH_2-CO_2H).

Synthesis of 4 arm RAFT agent, R4:



The four arm RAFT agent (**R4**) was prepared in following a similar methodology. 3-mercaptopropionic acid (1.0 g, 9.4 mmol) was dissolved in acetone (20 mL) with tribasic potassium phosphate (2.0 g, 9.4 mmol). The mixture was cooled in an ice bath and carbon disulphide (1.0 mL, 17.1 mmol) was added dropwise. After 20 min stirring at RT, 1,2,4,5-tetrabromomethyl benzene (0.63 g, 1.4 mmol) was added and the mixture was stirred for 2 h at RT. The solution was filtered, the yellow precipitate dissolved in isopropyl alcohol / dichloromethane (1:9 v/v, 100 mL), and the organic layers washed with HCl (0.1M, 3 x 50 mL), and then brine (1 x 50 mL). The organic fractions were dried with $MgSO_4$ and concentrated *in vacuo* to yield the product as a yellow solid (1.153 g, 97%). ^{1}H-NMR (400 MHz, DMSO-d_6) δppm: 7.50 (s, 2H, Ph-H), 4.69 (s, 8H, Ph-CH_2-), 3.52 (t, J = 6.9 Hz, 8H, S-CH_2-), 2.64 (t, J = 6.8 Hz, 8H, -CH_2-CO_2H). ^{13}C-NMR (101 MHz, DMSO-d_6)δppm: 173.09 (CO_2H), 134.39 (Ph), 133.74 (Ph), 37.97 (Ph-CH_2), 33.28 (S-CH_2), 32.70 (CH_2-CO_2H).

Measurement of polymerisation kinetics by near infrared (NIR) spectroscopy:

NIR kinetics were run on 1 mL of reaction mixture, prepared from the same solutions as above, in a 2 mm quartz cuvette. Where the sample was degassed, this was done by bubbling the sample with nitrogen through a rubber septum. The cuvette was irradiated as above, and removed from the light source at each time point to run an NIR spectrum. Conversion was determined by monitoring the decrease in area of the peak from the vinyl group at 6000-6020 cm^{-1}.

Synthesis of mannose acrylamide for enzyme linked lectin binding assay:

Sulfuric acid (98%, 3 drops) was added to a suspension of D-mannose (5.00 g, 0.028 mol) and acetic anhydride (28.39 g, 0.28 mol) over ice. After 1 h at 0 °C and then 3 h at room temperature, the clear mixture was diluted with water (100 mL), extracted with dichloromethane and washed with water (3 × 100 mL), sat. $NaHCO_3$ (1 x 100 mL), and brine (1 x 100 mL). The organic layers were dried over $MgSO_4$ and concentrated in vacuo to yield mannose (OAc) as off-white solid (9.69 g, 0.025 mol, 89.4%).

The protected mannose (5.2 g, 13.3 mmol) and N-hydroxyethyl acrylamide (1.84 g, 16.0 mmol) were then dissolved in anhydrous dichloromethane (50 mL) under a N^2 atmosphere. Anhydrous $BF_3(OEt)_2$ (8.2 mL, 9.45 g, 66.5 mmol) was added dropwise and the reaction mixture was left stirring overnight at room temperature. The resultant suspension was filtered into ice-cold water (100 mL) and extracted using dichloromethane. The extract was then washed with $NaHCO_3$ (100 mL) and water (3 × 100 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude was purified by silica chromatography using chloroform/acetone/methanol with a ratio of 7:2:1 (v/v) as the eluent, yielding the product as a pale yellow oil (2.26 g, 38%). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 6.30 (dd, J = 17.0, 1.6 Hz, 1H), 6.15 (dd, J = 17.0, 10.2 Hz, 1H), 5.67 (dd, J = 10.2, 1.6 Hz, 1H), 5.36 – 5.20 (m, 3H), 4.81 (s, 1H), 4.29 – 4.20 (m, 1H), 4.10 (dd, J = 12.2, 2.5 Hz, 1H), 3.96 (ddd, J = 9.9, 5.7, 2.5 Hz, 1H), 3.85 – 3.77 (m, 1H), 3.68 – 3.43 (m, 3H), 2.14 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ ppm: 170.65, 170.09, 169.68, 165.63, 130.53, 126.94, 97.75, 69.35, 68.99, 68.77, 67.55, 66.14, 62.50, 39.13, 20.86, 20.70.

[2] K. Belal, S. Poitras-Jolicoeur, J. Lyskaw, G. Pembouong, G. Cooke, P. Woisel, F. Stoffelbach; *Chem. Commun.*, **2016**, 52, 1847,

To remove the acetyl groups protected mannose acrylamide was dissolved in methanol and NaCO3 (0.5 eq. / mannose) was added. The mixture was stirred for 15 min, after which the solution was filtered, washed with methanol, and concentrated in vacuo to yield the product as a white solid (1.042 g, 74%). ^{1}H-NMR (400 MHz, DMSO-d_6) δ ppm: 6.24 (dd, J = 17.0, 10.1 Hz, 1H), 6.07 (dd, J = 17.1, 2.3 Hz, 1H), 5.57 (dd, J = 10.1, 2.3 Hz, 1H), 4.62 (s, 1H), 3.70 – 3.54 (m, 2H), 3.54 – 3.22 (m, 1H), 2.55 – 2.45 (m, 1H). ^{13}C-NMR (101 MHz, DMSO- d_6) δ ppm: 165.12, 132.14, 125.55, 100.45, 74.48, 71.35, 70.68, 67.43, 65.81, 61.67, 49.03.

Characterisation:

NMR spectroscopy was performed using a Bruker Advance III 400 (400.13 MHz, 1H; 75.5 MHz, 13C) or an Advance III 600 (600.13 MHz, 1H; 150 MHz, 13C) with a 5 mm BBFO probe. Spectra were processed using the Bruker TOPSPIN 3.0 and MestReNova 11.0 software.

Gel permeation chromatography (GPC) was performed using *N,N*-dimethylformamide (DMF) + 0.01 % (w/v) LiBr as the eluent on a Shimadzu modular system comprising an auto injector and a differential refractive index detector. Three phenomenex 5.0 µm bead-size columns (10^5, 10^4 and 10^3 Å) were used for separation, and all samples were filtered (0.45µm PTFE) prior to injection. Molecular weights were estimated relative to narrow molecular weight distribution poly(methyl methacrylate) (100 to 1 x 10^6 g.mol^{-1}) calibration standards without Mark-Houwink correction.

Matrix assisted laser desorption / ionisation – time of flight (MALDI-TOF) mass spectra of a crude polymer sample from a 40 µL polymerization in a 384 well plate (DMA / R2 / ZnTPP = 50 : 1 : 0.01, [DMA] = 1M, t = 5h) were taken on a Bruker ultrafleXtreme. A sample of the polymer (5 µL) was dried *in vaccuo*, redissolved in MeCN / H_2O (50 µL, 1:1 v/v) and mixed with α-cyano-4-hydroxycinnamic acid (5 mg/ml, methanol) before spotting on the MALDI target.

High performance liquid chromatography (HPLC) was used to characterise the degree of functionalization from the DBCO-NH_2 reaction and was performed on a Shimadzu modular system, with a single C-18 reverse phase silica column, using a UV detector at 280nm. Samples were prepared by diluting crude reaction mixture (5 µL) in filtered MeCN / H_2O (500 µL, 1:1 v/v). A gradient of MeCN / H_2O (10 – 95% v/v MeCN) over 10 min was used and 5 µL of sample was injected for each run. The peak at ~10 min was integrated relative to a control sample of DBCO-NH_2 at the same concentration but without polymer.

Fourier Transform Infrared (FTIR) spectroscopy was performed on a Bruker Alpha to determine coupling of the Man(OAc)-N_3 to the polymer scaffolds. In these experiments, 25 µL of crude reaction mixture was freeze dried overnight and redissolved in methanol (25 µL). 5 µL of this mixture was deposited on the ATR crystal and the methanol evaporated before recording the spectrum. The signal from the azide was compared to a control sample with the same concentration of Man(OAc)-N_3 but no polymer to give a qualitative assessment of functionalization.

Tables and Figures

Table S1. DMF-GPC data from kinetic experiments on DMA presented in Figure 2.

#	Polymer	RAFT agent	Format	[DMA] /[RAFT]	Time (min)	X (%)	M_n theo (g/mol)	M_n GPC (g/mol)	$Đ$
1	MacroR1	R1	Cuvette ($+O_2$)	50	240	30	1,759	1,830	1.13
2	Chain ext.	MacroR1	Cuvette ($+O_2$)	200	100	78	17,223	30,500	1.03
3	Kinetics	R1	Cuvette ($+O_2$)	200	200	77	15,538	20,000	1.03
4	Kinetics	R1	Cuvette ($-O_2$)	200	200	77	15,538	19,100	1.03
5	Kinetics	R1	96 well plate ($+O_2$)	200	120	76	15,147	18,900	1.07

Table S2. DMF-GPC data from other acrylamide polymerisations presented in Figure 2.

#	Monomer	RAFT agent	[DMA] /[RAFT]	Time (h)	X (%)	M_n theo (g/mol)	M_n GPC (g/mol)	$Đ$
1	Diacetone acrylamide (DAAm)	R2	200	15	94	32,100	36,900	1.11
2	*N,N*-Diethyl acrylamide (DEAm)	R2	200	15	97	24,900	24,500	1.05
3	*N*-(2-hydroxyethyl acrylamide) (HEAm)	R2	200	15	95	22,100	35,600	1.05
4	4-Acryloylmorpholine (NAM)	R2	200	15	100	28,500	32,600	1.04
5	*N*-isopropyl acrylamide (NiPAAm)	R2	200	15	92	21,110	32,500	1.04

Table S3. DMF-GPC data from NHS/DMA (1:9) libraries in 96 well plates. [M] = 0.5M, ZnTPP / RAFT = 0.01, 150µL, 16h.

#	RAFT agent	Structure	DP_{target} (Total)	M_n theo (g/mol)	M_n GPC (g/mol)	Đ
1	R2	Linear	20	2,311	2,370	1.24
2	R2	Linear	40	4,349	4,500	1.27
3	R2	Linear	80	8,427	7,700	1.23
4	R2	Linear	160	16,582	13,600	1.20
5	R2	Linear	320	32,892	23,550	1.11
6	R2	Linear	640	65,511	23,260	1.07
7	R3	3 arm	20	2,700	3,640	1.25
8	R3	3 arm	40	4,738	7,350	1.32
9	R3	3 arm	80	8,816	13,180	1.23
10	R3	3 arm	160	16,971	23,080	1.26
11	R3	3 arm	320	33,280	33,760	1.32
12	R3	3 arm	640	65,900	43,920	1.35
13	R4	4 arm	20	2,894	5,980	1.31
14	R4	4 arm	40	4,933	11,260	1.50
15	R4	4 arm	80	9,010	19,720	1.45
16	R4	4 arm	160	17,165	31,350	1.43
17	R4	4 arm	320	33,475	42,630	1.37
18	R4	4 arm	640	66,094	65,000	1.25

Note: Theoretical molecular weights (**M_n theo)** are calculated at X=100% on the assumption that NHS has completely reacted with butyl amine.

Table S4. DMF-GPC data from NHS/DMA libraries in Table S3 before and after clicking with PEG_7-N_3

#	Structure	RAFT agent	DP_{target} (Total)	Before PEG			After PEG		
				M_n theo (g/mol)	M_n GPC (g/mol)	Đ	M_n theo (g/mol)	M_n GPC (g/mol)	Đ
1	3 arm	R3	20	2700	3640	1.25	3813	6010	1.25
2	4 arm	R4	20	2894	5980	1.31	4007	11310	1.26
3	Linear	R2	40	4349	4500	1.27	6576	8620	1.08
4	3 arm	R3	40	4738	7350	1.32	6965	11590	1.22
5	4 arm	R4	40	4933	11260	1.50	7159	18800	1.29
6	Linear	R2	80	8427	7700	1.23	12880	12410	1.11
7	3 arm	R3	80	8816	13180	1.23	13269	30800	1.46
8	4 arm	R4	80	9010	19720	1.45	13464	20720	1.21

Table S5. DMF-GPC data from NHS/DMA libraries in 96 well plates. [M] = 1.0M, ZnTPP / RAFT = 0.01, 150µL, 5h.

#	RAFT agent	Structure	NHS / DMA	DP_{target} (Total)	M_n theo (g/mol)	M_n GPC (g/mol)	$Đ$
1	R2	Linear	1:9	60	6388	6500	1.16
2	R2	Linear	1:9	120	12504	10360	1.19
3	R2	Linear	1:9	240	24737	18700	1.18
4	R2	Linear	1:9	480	49201	24760	1.17
5	R2	Linear	1:9	960	98131	28500	1.22
6	R3	3-arm	1:9	60	6777	8240	1.30
7	R3	3-arm	1:9	120	12893	18720	1.44
8	R3	3-arm	1:9	240	25126	29850	1.41
9	R3	3-arm	1:9	480	49590	51490	1.36
10	R3	3-arm	1:9	960	98520	64500	1.41
11	R3	3-arm	2:8	60	6945	8810	1.24
12	R3	3-arm	2:8	120	13230	17070	1.21
13	R3	3-arm	2:8	240	25799	30730	1.15
14	R3	3-arm	2:8	480	50937	45600	1.19
15	R3	3-arm	2:8	960	101213	86550	1.17
16	R4	4-arm	1:9	60	6971	7350	1.34
17	R4	4-arm	1:9	120	13088	16650	1.51
18	R4	4-arm	1:9	240	25320	30880	1.46
19	R4	4-arm	1:9	480	49785	46310	1.54
20	R4	4-arm	1:9	960	98714	74610	1.48
21	R4	4-arm	2:8	60	7140	6260	1.30
22	R4	4-arm	2:8	120	13424	14570	1.28
23	R4	4-arm	2:8	240	25993	26480	1.25
24	R4	4-arm	2:8	480	51131	39230	1.41
25	R4	4-arm	2:8	960	101408	75360	1.30

Note: Theoretical molecular weights (**M_n theo)** are calculated at X=100% on the assumption that NHS has completely reacted with butyl amine.

Table S6. DMF-GPC data from NHS/DMA libraries in 96 well plates used to characterise the efficiency of the post-polymerisation modifications. [M] = 0.5M, ZnTPP / RAFT = 0.02, 150µL, 16h.

#	RAFT agent	Structure	NHS / DMA	DP_{target} (Total)	M_n theo (g/mol)	M_n GPC (g/mol)	*Đ*
1	R2	Linear	1:9	60	6388	18810	1.39
2	R2	Linear	1:9	120	12504	26410	1.45
3	R2	Linear	1:9	240	24737	31530	1.58
4	R2	Linear	1:9	480	49201	38540	1.43
5	R2	Linear	1:9	960	98131	48920	1.38
6	R3	3-arm	1:9	60	6777	17510	1.38
7	R4	4-arm	1:9	60	6971	16060	1.42
8	R3	3-arm	2:8	60	6945	20970	1.39
9	R4	4-arm	2:8	60	7140	13240	1.54

Note: Theoretical molecular weights (**M_n theo)** are calculated at X=100% on the assumption that NHS has completely reacted with butyl amine.

Table S7. DMF-GPC data from DBCO/DMA polymerisations in 384 well plates, conducted at 1M monomer concentration with 9:1 (mol/mol) NHS/DMA and subsequently reacted with 1 equiv / NHS DBCO-NH_2 in the presence of 1 equiv / NHS DMAP. Theoretical molecular weights are calculated at X=100%. The corresponding GPC molecular weight distributions are shown in Figure S9a

#	RAFT agent	Structure	DP_{target} (Total)	M_n theo (g/mol)	M_n GPC (g/mol)	*Đ*
1	R3	3 arm	60	6,777	3,520	1.15
2	R3	3 arm	120	12,893	8,290	1.17
3	R3	3 arm	240	25,126	15,380	1.18
4	R3	3 arm	480	49,590	28,470	1.12
5	R3	3 arm	960	98,520	41,990	1.17
6	R4	4 arm	80	9,010	7,650	1.17
7	R4	4 arm	160	17,165	13,970	1.24
8	R4	4 arm	320	33,475	20,160	1.35
9	R4	4 arm	640	66,094	31,980	1.30
10	R4	4 arm	1280	131,333	39,200	1.38

Table S8. DMF-GPC data from DBCO/DMA polymerisations in 384 well plates, conducted at 0.5M monomer concentration with 9:1 (mol/mol) NHS/DMA and subsequently reacted with 1 eq. / NHS DBCO-NH_2 in the presence of 1 eq. / NHS DMAP and then with 1 eq./NHS Man(OAc)-N_3. Theoretical molecular weights are calculated at X = 100%. The corresponding GPC molecular weight distributions are shown in Figure S9b

#	RAFT agent	Structure	DP_{target} (Total)	M_n theo (g/mol)	M_n GPC (g/mol)	$Đ$
1	R2	Linear	25	2,820	4,730	1.04
2	R2	Linear	80	8,427	9,880	1.12
3	R2	Linear	100	10,466	20,090	1.10
4	R2	Linear	200	20,659	28,610	1.15
5	R3	3 arm	80	8,816	11,280	1.17
6	R3	3 arm	100	10,855	22,260	1.17
7	R3	3 arm	200	21,048	37,410	1.22
8	R3	3 arm	400	41,435	52,020	1.28
9	R4	4 arm	80	9,010	16,110	1.22
10	R4	4 arm	100	11,049	20,570	1.22
11	R4	4 arm	200	21,242	36,330	1.33
12	R4	4 arm	400	41,630	43,980	1.38

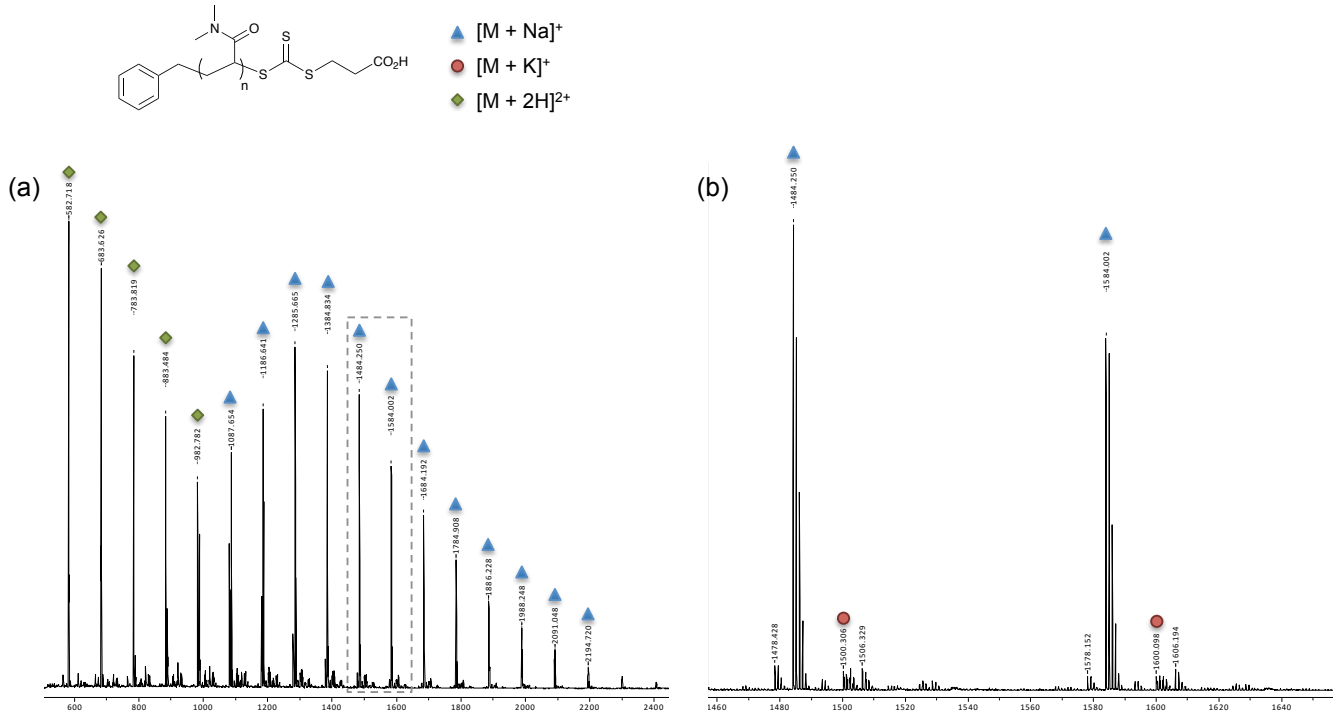


Figure S1. MALDI-TOF spectrum of pDMA synthesised in the 40 µL format by polymerising DMA / **R2** / ZnTPP (50 : 1 : 0.01) under standard conditions at a monomer concentration of 1 M for 5 h. After removal of the DMSO the crude polymer was diluted in 1:1 (v/v) H_2O / MeCN and mixed with CHCA (5 mg/mL) as a matrix before spotting on the MALDI plate. PEG monomethyl ether (M_n = 1100 Da) was used as the calibration standard.

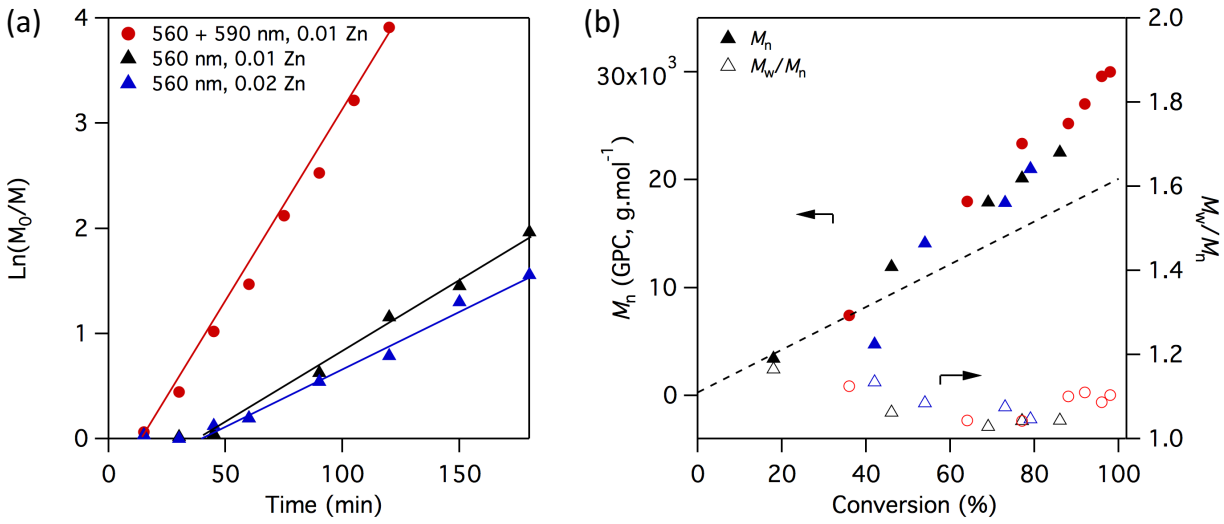


Figure S2. Comparison of a) kinetics and b) resulting molecular weights and dispersities as measured by DMF-GPC from DMA 200 polymerisations in 96 well plates. Irradiation was supplied by either the 560 nm LEDs alone or by both the 560 + 2 x 590 nm LEDs showing higher speed with the higher intensity light.

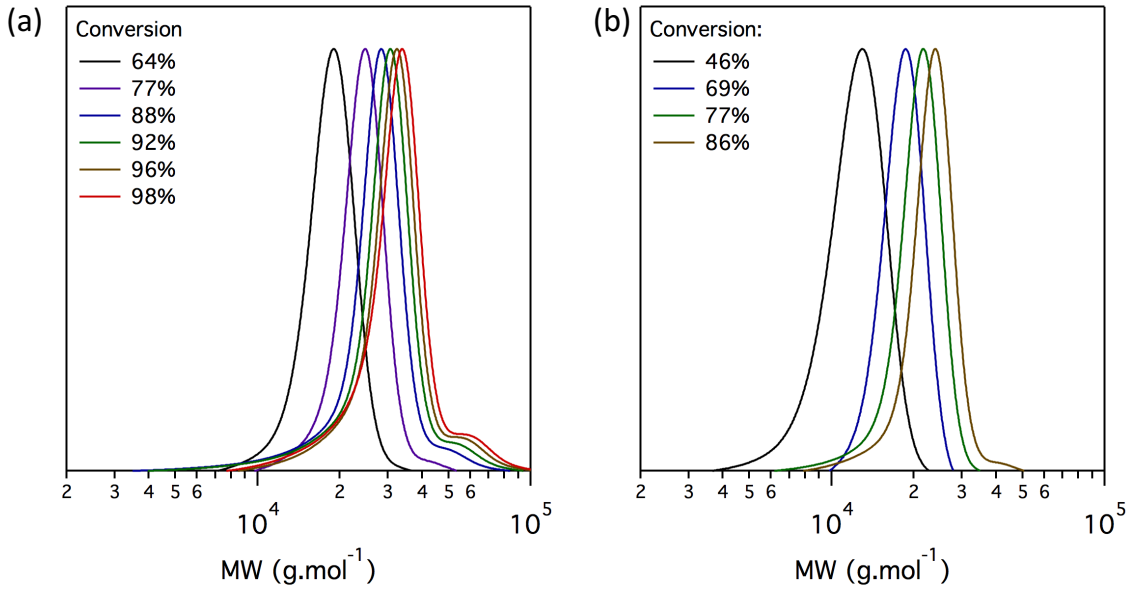


Figure S3. DMF-GPC traces from the above pDMA200 kinetic experiments showing the shoulder that forms at high conversions with the higher intensity light source. a) λ = 560 nm + 2 x 590nm LEDs, b) λ = 560 nm LEDs only.

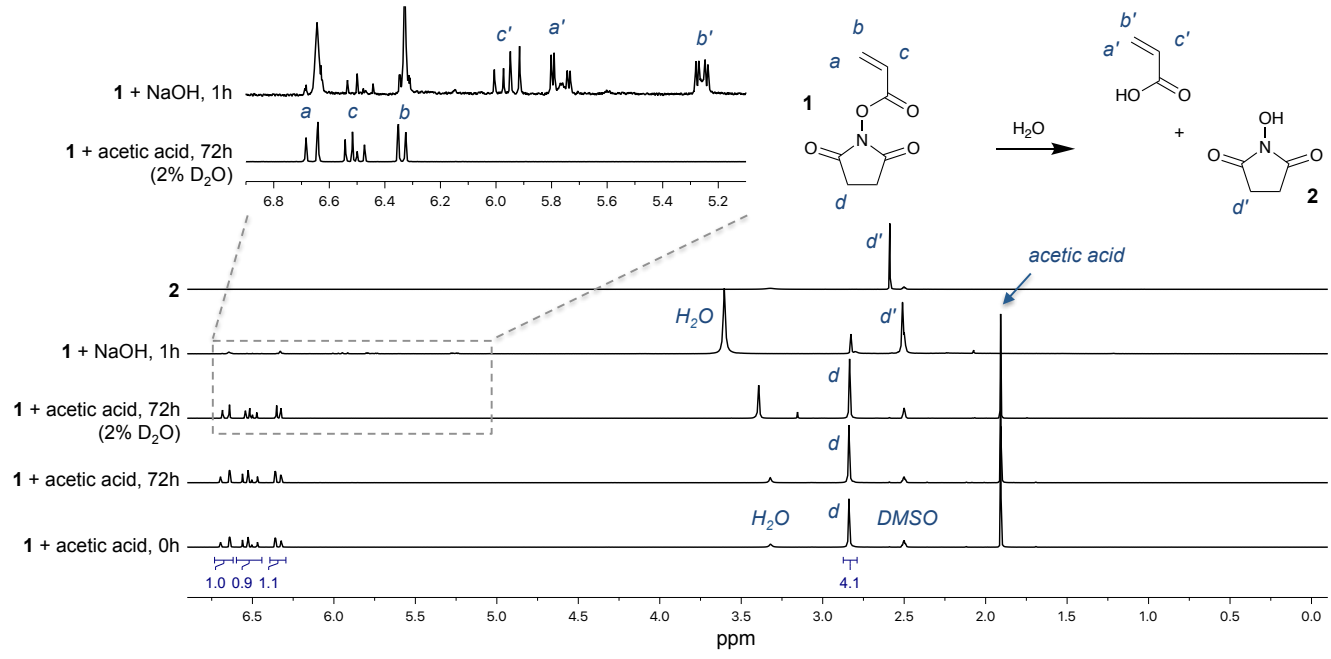


Figure S4. ^{1}H-NMR (in DMSO-d_6) of NHS acrylate (**1,** 10 mg/mL) before and after hydrolysis to acrylic acid and *N*-hydroxysuccinimide (**2**) showing no hydrolysis in the presence of acetic acid (1 equiv) and D_2O (2% v/v) after 72h, and hydrolysis with NaOH in the absence of acetic acid. Integrals are shown for the first spectrum and are representative of the first three traces.

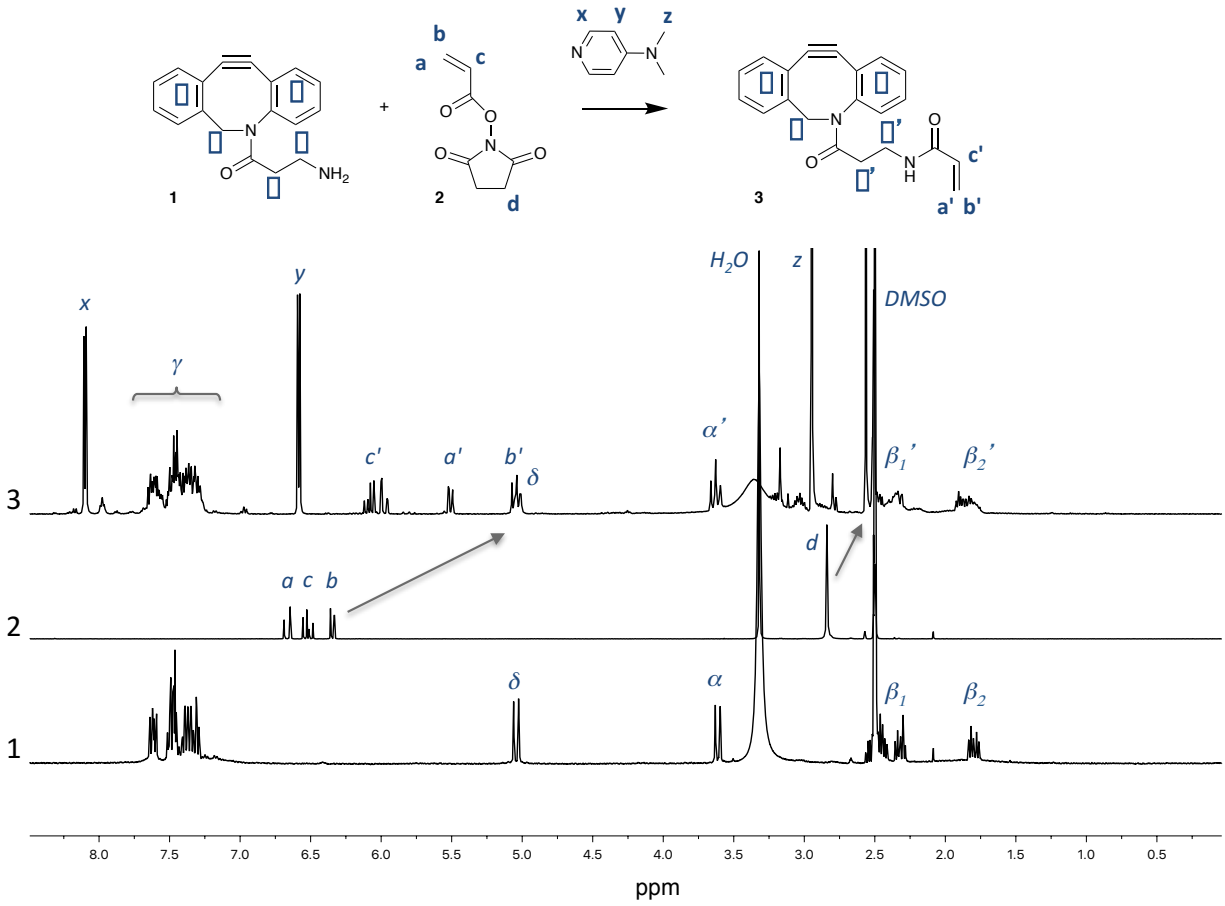


Figure S5. ^{1}H-NMR (in DMSO-d_6) of DBCO-NH_2 (**1**) and NHS acrylate (**2**) before and after mixing with dimethyl amino pyridine in a 1:1:1 molar ratio (**3**) showing click of the DBCO to the acrylate.

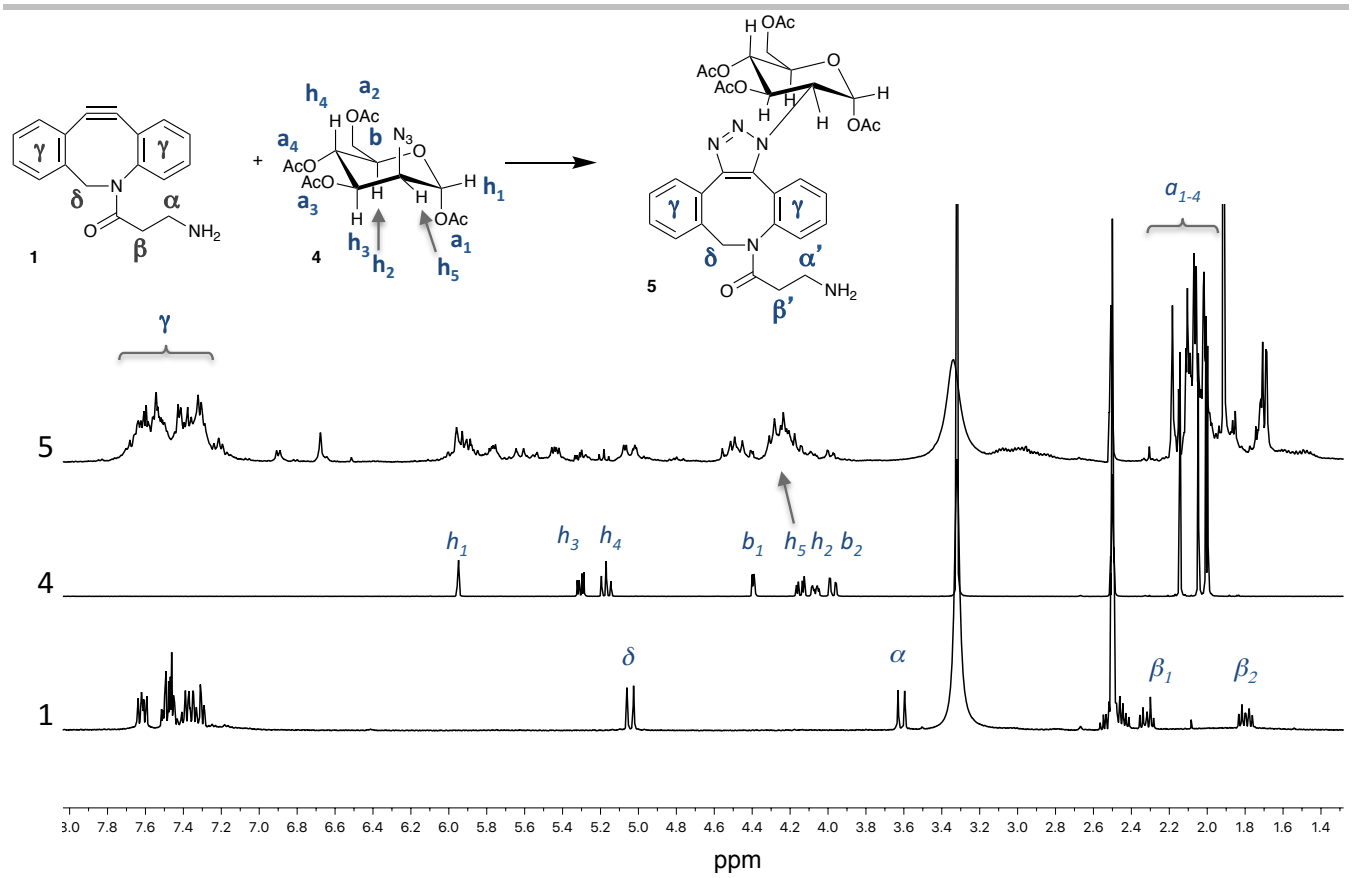


Figure S6. ^{1}H-NMR (in DMSO-d_6) of DBCO-NH_2 (**1**) and azido-mannose (OAc) (**4**) before and after mixing in a 1:1 molar ratio (**5**) showing click of the mannose to the cyclooctyne.

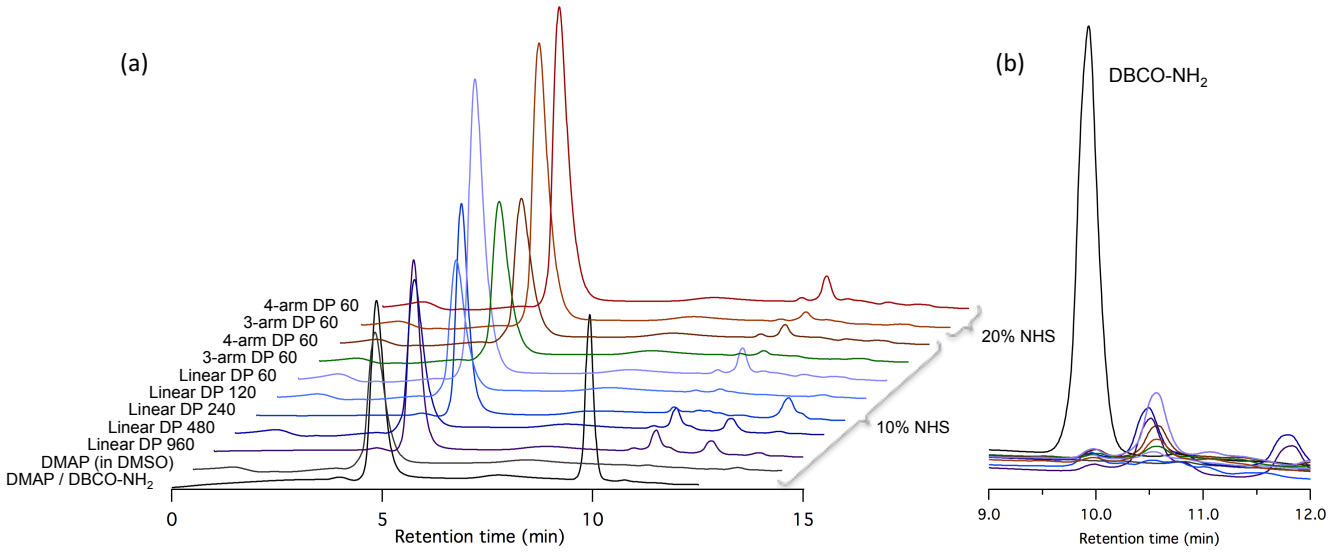


Figure S7. HPLC chromatograms of DBCO-NH_2 before and after reaction with linear polymer scaffolds (target DP = 60-960) as well as 3-arm and 4-arm scaffolds (target DP = 60) prepared with 10% and 20% (mol) NHS acrylate / DMA in a 150 µL 0.5 M well plate polymerisation. Post-polymerisation modification reactions were conducted with DBCO-NH_2 (1 equiv / NHS) in the presence of DMAP (1 equiv / NHS) for 6 h at RT. The DBCO-NH_2 trace shows the concentration of DBCO-NH_2 used in the reactions on scaffolds with 10% NHS acrylate. The HPLC was run with a linear gradient of 10-95% (v/v) MeCN / H_2O (0.1% TFA) over the first 10 min, before flushing for 2 min at 95% MeCN. a) Full chromatogram, with DMSO, polymer and DMAP eluting at ~5min. b) Zoom in on the 9-12 min region, showing the consumption of DBCO-NH_2 in all postmodification reactions.

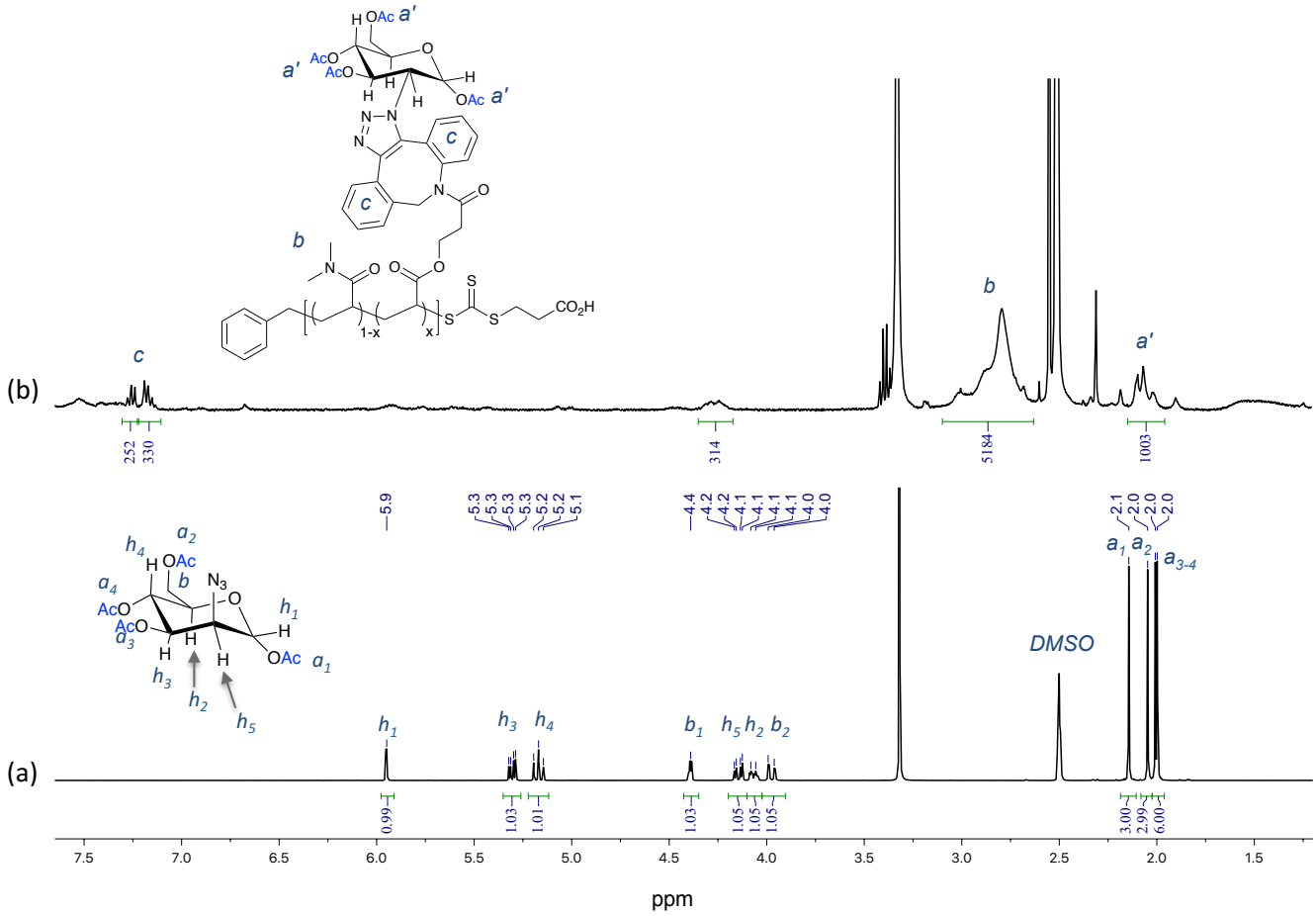


Figure S8. ^{1}H-NMR (in DMSO-d_6) of a) protected azido mannose and; b) a linear pDMA scaffold (target DP 960, polymerised overnight at 0.5M) bearing 10% (mol) NHS acrylate after post-polymerisation modification with DBCO-NH_2 and azido mannose and purification by precipitation twice in diethyl ether. The DBCO and mannose protecting groups are visible in the final polymer and integrate to approximately 10% (mol) relative to the methyl groups in the pDMA.

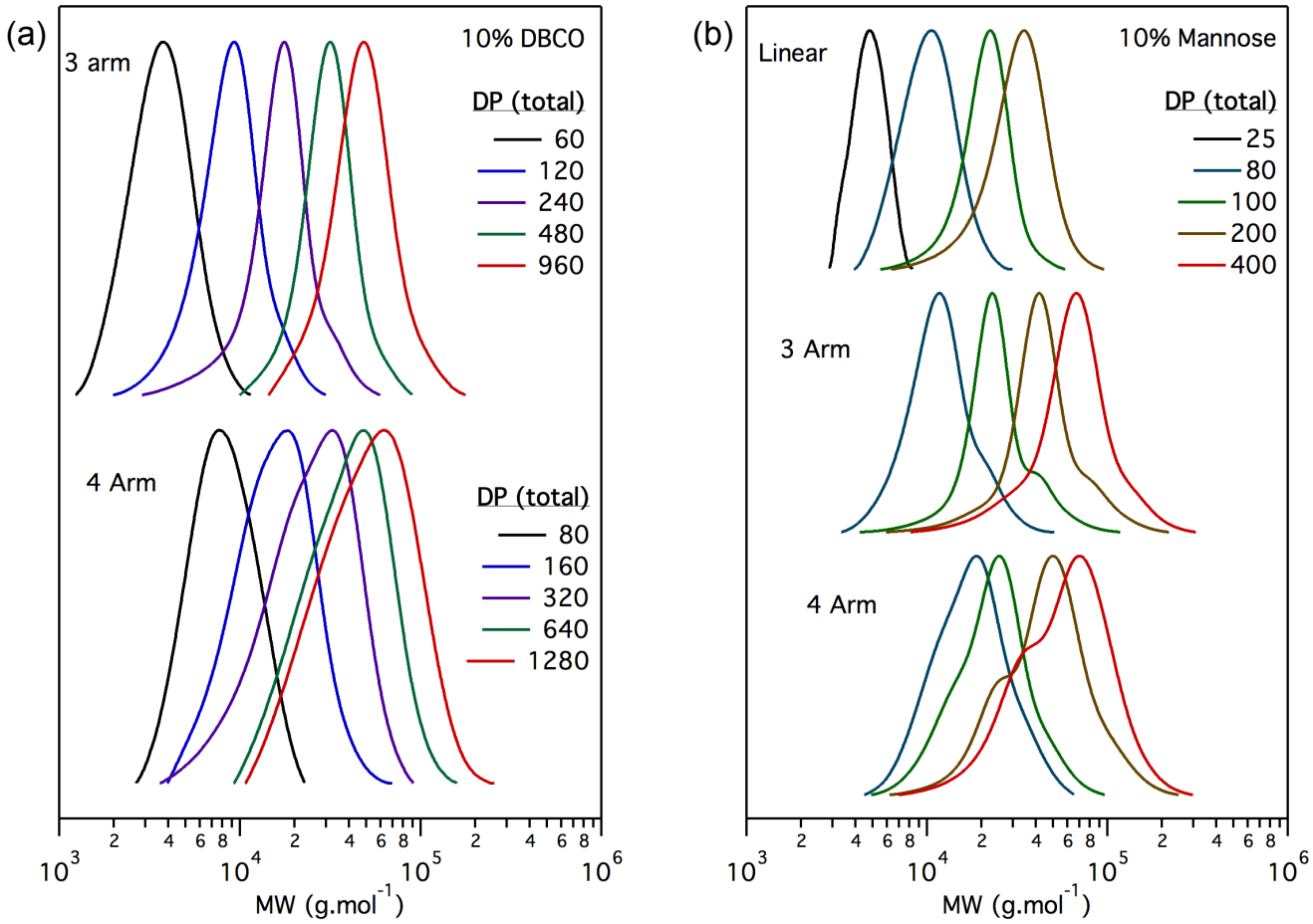


Figure S9. GPC molecular weight distributions for polymer libraries prepared in 40 µL reaction volumes on 384 well plates. a) 3-arm and 4-arm architectures, synthesised at 1M monomer concentration, after functionalization with DBCO-NH_2. b) Linear, 3-arm and 4-arm architectures synthesised at 0.5M monomer concentration, after functionalization with DBCO-NH_2 and then clicked to Man(OAc)-N_3. The corresponding GPC data are shown in Tables S7-8.

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