Electronic Supplementary Material (ESI) for Polymer Chemistry

Combining catalytic chain transfer polymerisation (CCTP) and thio-Michael addition: enabling the synthesis of peripherally functionalised branched polymers

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Experimental

General

All reagents were purchased from Aldrich and used as received unless stated. 2, 2-azobis(2,4-dimethylvaleronitrile) (V-601) was purchased from Wako and used as received. CoBF was synthesised according to literature.[1]

Polymerisation Procedure

A typical scale homopolymerisation was carried out as follows. Larger or smaller scale reactions were carried out in using the same ratios of reagents. Copolymerisations were carried out using mole equivalent amounts of comonomer to EGDMA.

A Schlenk tube was charged with monomer and dichloroethane, three cycles of freeze pump thawing was applied and the vessel backfilled with nitrogen. A separate Schlenk tube was charged with 20 mg (0.049 mol% to monomer) CoBF, 200 mg V-601, (0.8 mmol) and a stirrer bar. This was degassed using three cycles of vacuum and nitrogen, and backfilled with nitrogen. The monomer solution was cannulated into the solids and the reaction mixture stirred and left under nitrogen. The vessel was placed in an oil bath (70˚C) with stirring and left to react for between 2-6 hours. Sampling was carried out using a degassed syringe. The end product was characterised by ^{1}H NMR, ^{13}C NMR, GC-FID, GPC, IR and MALDI-ToF.

Name	Monomer	Monomer Ratio (%)	Ratio of CoBF to monomer (%)	M_n g mol^{-1}	M_w g mol^{-1}	Pdi	Conversion (%)	Duration (hr)
A	EGDMA	100	0.049	1700	4900	2.9	93	8
B	EGDMA	100	0.039	1600	5600	3.5	91	6
C	EGDMA	100	0.029	1800	8000	4.5	88	4

Table 1. Sythesis of branched products by CCTP: Effects of changing CoBF concentration.

Name	Monomer/ Solvent Ratio	M_w g mol^{-1} @ 10hr	PDi @ 10hr	Conversion @ 10hr (%)	End State of Polymer (26hr)
D	100/0	N/A	N/A	N/A	Gel
E	75/25	20,800	9	93.4	Gel
F	66.7/33.3	13,800	6.7	96	Gel
G	50/50	9,700	5	96.6	Liquid
H	33.3/66.7	6,500	3.6	96.9	Liquid
I	25/75	2,500	2.2	96	Liquid

Table 2: Effect of monomer concentration on the synthesis of branched products by CCTP.

Name	Monomer	Monomer Ratio (mol %)	CoBF/ monomer (mol %)	M_n g mol^{-1}	M_w g mol^{-1}	PDi	Conv. (%)	Reac. time (hr)
J	EGDMA/MMA	80/20	0.052	800	1800	2.2	91	6
K	EGDMA/MMA	67/33	0.066	770	1600	2.1	76	6
L	EGDMA/TMPTMA	80/20	0.052	730	1800	2.5	76	4
M	EGDMA/TMPTMA	67/33	0.066	730	1600	2.2	73	3
N	TMPTMA	100	0.043	1200	4500	3.7	78	2

Table 3: Sythesis of branched products by CCTP: tailoring the degree of branching by introduction of comonomers.

Thio-Michael addition Preparation

A 5 mL portion of polymerisation end solution was added to a vinyl bond equivalent amount of thiol to polymer (amount calculated from conversion). A mol equivalent amount of

dimethylphenyl phosphine (DMPP) to monomer was added to catalyse the reaction. The reactions were characterised by ^{1}H NMR ^{13}C NMR, GPC/ UV GPC, IR and MALDI-ToF.

Name	Thiol	Amount of Thiol (mol equiv)	Amount of DMPP (mol equiv)
A1	Benzyl mercaptan	1.5	0.2
A2	Benzyl mercaptan	1.5	0.1
A3	Benzyl mercaptan	1.5	0.05
A4	Mercaptoethanol	1	0.1
A5	Thioglycerol	1	0.1
A6	Dodecanethiol	1	0.1

Table 3: Thio-Michael addition conditions for the functionalisation reactions of **A** (EGDMA homopolymer).

Characterisation

^{1}H and ^{13}C NMR

NMR was carried out on a Bruker DXP-400 spectrometer. Chemical shifts were calibrated using TMS.

Infra Red (IR)

IR was carried out on a Bruker Vector 22 and analysed using Opus spectroscopy software

Gel Permeation Chromatography (GPC)

All GPC were performed on Varian 390-LC multi detector suites fitted with two PLgel 5 μm Mixed D columns, plus a guard column. For investigation of final molecular weights chloroform was used as the mobile phase, with a flow rate of 1mL/min at an ambient operating temperature. The injection volume was 100 μL. The GPC was equipped with a refractive index, light scattering and viscometry detectors. Data was collected and analysed using Cirrus software (Varian Inc) and all samples calibrated against poly(methyl methacrylate) (PMMA) EasiVial standards, purchased from Varian.

UV GPC results were performed using tetrahydrofuran (THF) as the mobile phase at a flow rate of 1mL/min at an ambient operating temperature. The injection volume was 100μL. The GPC was equipped with a refractive index, light scattering and UV detectors; the UV

wavelength was variable and set at λ 350 nm. Data were collected and analysed using Cirrus software (Varian Inc). RI chromatograms are calibrated against PMMA EasiVial standards, purchased from Varian; UV chromatograms are calibrated against polystyrene (PS) EasiVial standards, purchased from Varian. Universal Calibrations were setup using PMMA EasiVial standards using both the RI and viscometry detectors.

Matrix-Assisted Laser Desorption and Ionization Time-of-Flight (MALDI-ToF)

Mass spectra were acquired by MALDI-ToF (matrix-assisted laser desorption and ionization time-of-flight) mass spectrometry using a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV.

2, 5-Dihdroxybenzoic acid (DHB) was used as an organic matrix and sodium iodide (NaI) used as the salt. A layering method was used to spot the MALDI plate. THF was used as the solvent for sample preparation.

Gas chromatograph – Flame ionisation detector (GC-FID)

GC analysis was performed using a Varian 450. A FactouFour^{TM} capillary column VF-1ms, of 15 m × 0.25 mm I.D., film thickness 0.25 μm from Varian was used. The oven temperature was programmed as follows: 40 °C (hold for 1 min) at 25 °C min^{-1} to 200 °C. The injector was operated at 200 °C and the FID was operated at 220 °C. Nitrogen was used as carrier gas at a flow rate of 1 mL min^{-1} and a split ratio of 1:100 was applied. Chromatographic data were processed using Galaxie Chromatography data system, version 1.9.302.530 software.

Characterisation of Polymerisation Products

Characterisation of A, B and C (**A**: Branched PEGDMA, 0.049 mmol CoBF. **B**: Branched PEGDMA, 0.032 mmol CoBF. **C:** Branched PEGDMA, 0.024 mmol CoBF).

^{1}H NMR (400 MHz, TMS at 25˚C): δ 1.00-1.50 (backbone CH_3), 1.85-2.05 (terminal CH_3), 2.15-2.20 (backbone CH_2), 2.45-2.60 (backbone CH_2), 4.15-4.45 ($OC\underline{H_2}C\underline{H_2}O$), 5.50-5.60 (terminal $C\underline{H_a}H_b$=C + internal $C\underline{H_a}H_b$=C), 6.05-6.15 (terminal $CH_a\underline{H_b}$=C), 6.20-6.35 (internal $CH_a\underline{H_b}$=C)

^{13}C NMR (400 MHz $CDCl_3$ at 25˚C): δ 18.31 (terminal CH_3), 24.82, 27.22 and 30.37 (backbone CH_3), 40.67 (backbone CH_2), 41.58 and 43.05 (backbone quaternary carbons), 46.15 and 48.20 (backbone CH_2), 62.33 (OCH_2CH_2O), 126.04 (terminal $\underline{C}H_2$=C-), 128.63 (internal $\underline{C}H_2$=C-), 135.97 (terminal CH_2=$\underline{C}$-), 137.08 (internal CH_2=$\underline{C}$-), 167.09 (terminal ester carbonyl), 176.70 (internal ester carbonyl).

IR: υ_{max} (neat)/cm^{-1} 2972 (m, CH sp^3), 1715 (s, C=O), 1628 (m, C=C), 1451 (m, CH_2), 1391 (m, CH_3), 1367 (m), 1292 (m), 1141 (s, C-O), 1049 (m), 946 (m), 814 (m)

GPC, RI only: **A** - M_n 1700, M_w 4800, PDi 2.9

B - M_n 1600, M_w 4800, PDi 3.0

C - M_n 1700, M_w 7000, PDi 4.1

GPC, Universal Calibration: **A** - M_n 1800, M_w 6200, PDi 3.5

B - M_n 1600, M_w 6900, PDi 4.3

C - M_n 1600, M_w 11800, PDi 7.4

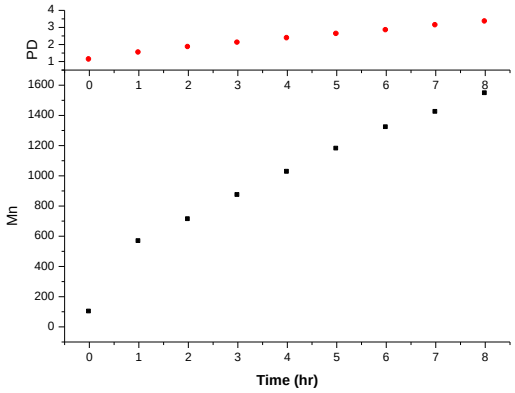

Figure S1: M_n and PDi plots for **A** (branched PEGDMA, CoBF 0.049 mol %) sampled hourly throughout the reaction.

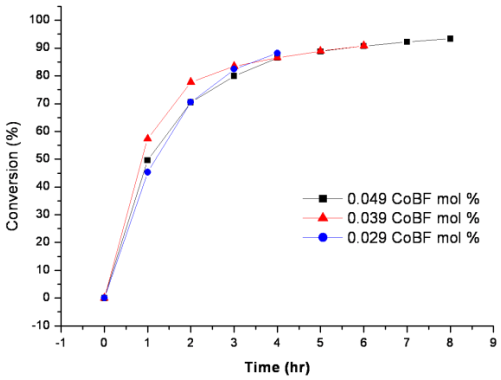

Figure S2: Conversion data comparison of reactions **A** (branched PEGDMA, CoBF 0.049 mol %), **B** (branched PEGDMA, CoBF 0.039 mol %) and **C** (branched PEGDMA, CoBF 0.029 mol %) sampled hourly throughout the reaction.

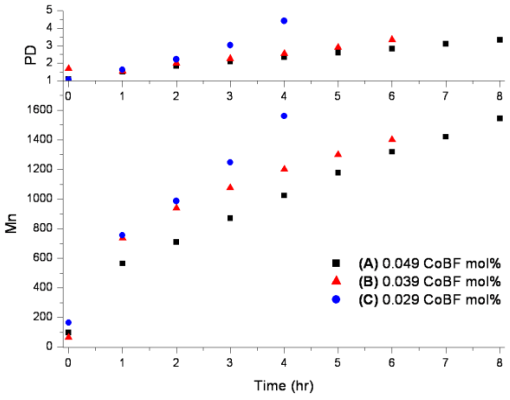

Figure S3: M_n and PDi data of reactions **A** (branched PEGDMA, CoBF 0.049 mol %), **B** (branched PEGDMA, CoBF 0.039 mol %) and **C** (branched PEGDMA, CoBF 0.029 mol %) sampled hourly throughout the reaction.

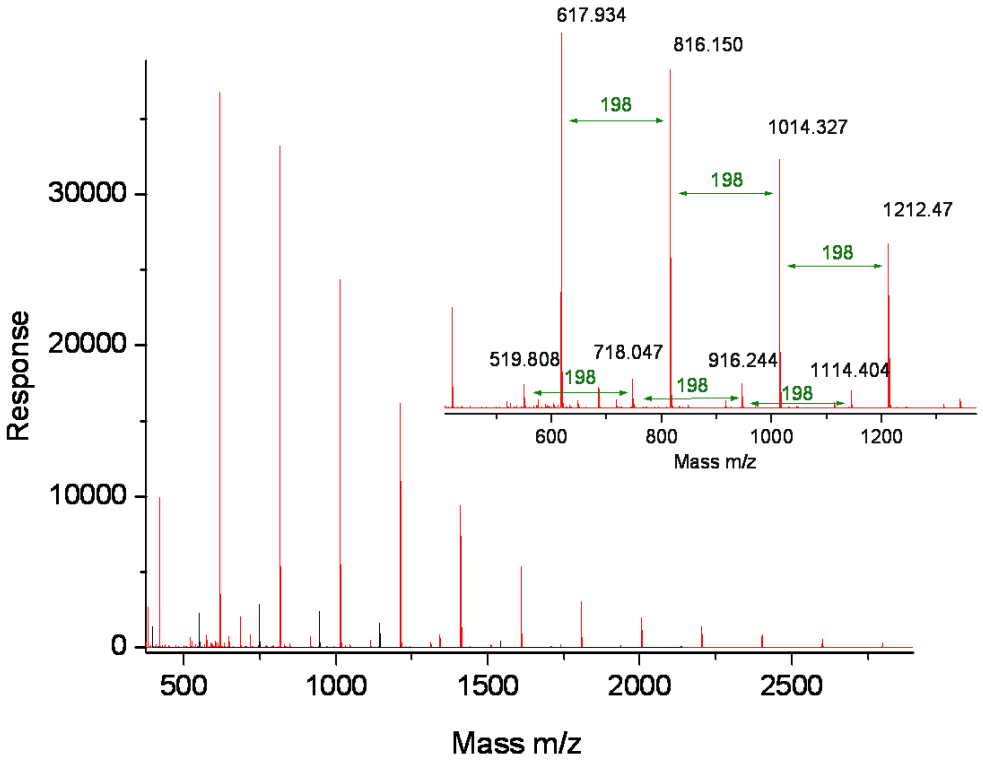

Figure S4: MALDI-TOF spectrum of **A** (branched PEGDMA, CoBF 0.049 mol %)

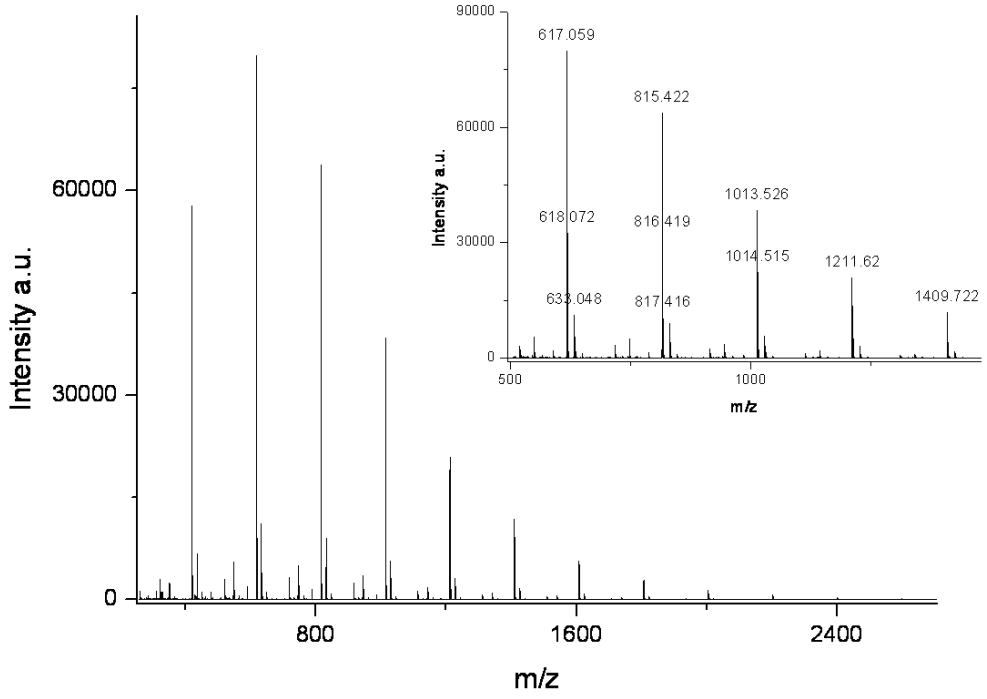

Figure S5: MALDI-TOF spectrum of **B** (branched PEGDMA, CoBF 0.039 mol %)

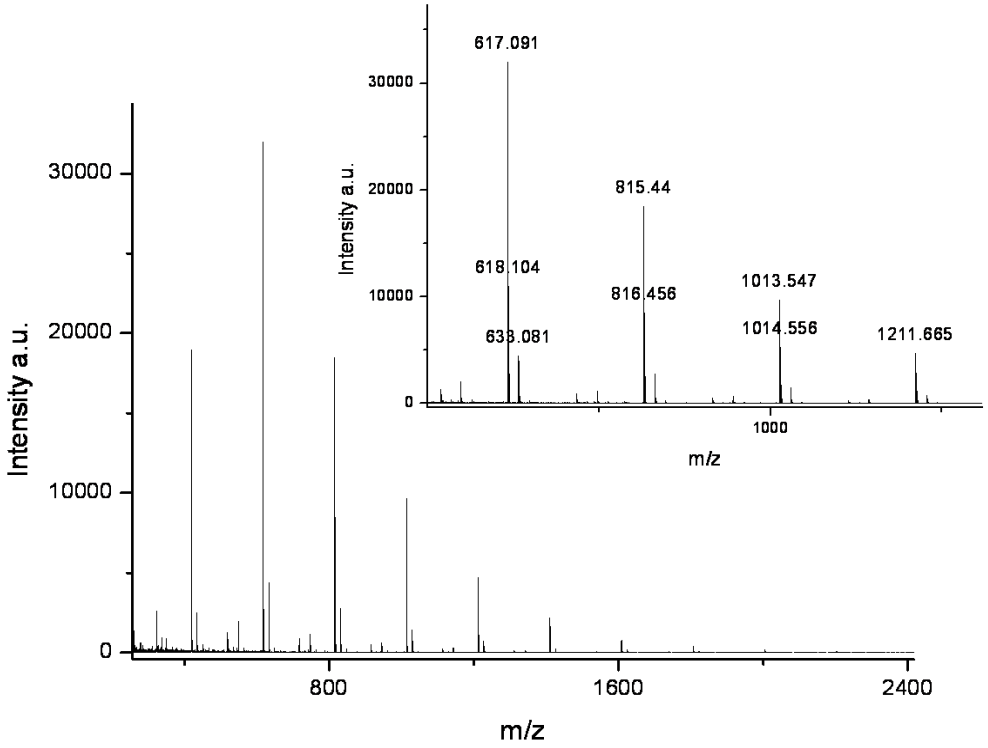

Figure S6: MALDI-TOF spectrum of **B** (branched PEGDMA, CoBF 0.029 mol %)

Characterisation of G, **H**, **I** (**G**: Branched EGDMA 50% monomer. **H**: Branched EGDMA 33% monomer. **I**: Branched EGDMA 25% monomer) (**D**, **E**, **F** gelled, no characterisation data):

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.90-1.50 (backbone CH_3), 1.85-2.00 (terminal CH_3), 2.05-2.20 (backbone CH_2), 2.45-2.65 (backbone CH_2), 4.05-4.45 ($OC\underline{H_2}C\underline{H_2}O$), 5.50-5.65 (terminal $C\underline{H_a}H_b{=}C$ + internal $C\underline{H_a}H_b{=}C$), 6.05-6.15 (terminal $CH_a\underline{H_b}{=}C$), 6.20-6.35 (internal $CH_a\underline{H_b}{=}C$)

^{13}C NMR (400 MHz $CDCl_3$ at 25˚C): δ 18.23 (terminal CH_3), 24.73, 29.74 and 30.29 (backbone CH_3), 40.61 (backbone CH_2), 41.49 and 42.91 (backbone quaternary carbons), 45.92 and 48.11 (backbone CH_2), 62.25 (OCH_2CH_2O), 126.04 (terminal $\underline{C}H_2{=}C$-), 128.63 (internal $\underline{C}H_2{=}C$-), 135.97 (terminal $CH_2{=}\underline{C}$-), 137.08 (internal $CH_2{=}\underline{C}$-), 167.09 (terminal ester carbonyl), 176.70 (internal ester carbonyl).

IR: υ_{max} (neat)/cm^{-1} 2980 (m, CH sp^3), 1716 (s, C=O), 1627 (m, C=C), 1451 (m, CH_2), 1391 (m, CH_3), 1367 (m), 1287 (m), 1141 (s, C-O), 1049 (m), 948 (m), 815 (m)

GPC RI Only: @26 hr (end)

G: M_n 3600, M_w 385300, PDi 107.9

H: M_n 2600, M_w 17900, PDi 6.9

	I: M_n 1500, M_w 4100, PDi 2.8
GPC Universal Calibration: @26 hr (end)	**G**: M_n 1296, M_w 189900, PDi 146.5
	H: M_n 1932, M_w 29400, PDi 15.2
	I: M_n 1196, M_w 6460, PDi 5.4

Characterisation of J and K (**J**: Branched PEGDMA/PMMA 80/20. **K**: Branched PEGDMA/PMMA 67/33).

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.90-1.50 (backbone CH_3), 1.85-2.00 (terminal CH_3), 2.05-2.20 (backbone CH_2), 2.45-2.7 (backbone CH_2), 3.55-3.65 (OCH_3 polymer), 3.70-3.80 (OCH_3 monomer), 4.10-4.40 ($OC\underline{H_2}C\underline{H_2}O$), 5.45-5.65 (terminal $C\underline{H_a}H_b$=C + internal $C\underline{H_a}H_b$=C), 6.05-6.15 (terminal $CH_a\underline{H_b}$=C), 6.20-6.35 (internal $CH_a\underline{H_b}$=C).

^{13}C NMR (400 MHz $CDCl_3$ at 25˚C): δ 18.21 (terminal CH_3), 24.98, 29.94 and 30.53 (backbone CH_3), 40.83 (backbone CH_2), 41.74 and 43.16 (backbone quaternary carbons), 46.06 and 48.09 (backbone CH_2), 51.90 (OCH_3), 62.54 (OCH_2CH_2O), 126.19 (terminal $\underline{C}H_2$=C-), 128.75 (internal $\underline{C}H_2$=C-), 136.19 (terminal CH_2=$\underline{C}$-), 137.25 (internal CH_2=$\underline{C}$-), 167.27 (terminal ester carbonyl), 176.87 (internal ester carbonyl).

IR: υ_{max} (neat)/cm^{-1} 2960 (m, CH sp^3), 1716 (s, C=O), 1629 (m, C=C), 1451 (m, CH_2), 1391 (m, CH_3), 1367 (m), 1293 (m), 1142 (s, C-O), 1049 (m), 945 (m), 814 (m)

GPC RI only:	**J**: M_n 1000, M_w 1900, PDi 1.9
	K: M_n 900, M_w 1600, PDi 1.7
GPC Universal Calibration:	**J**: M_n 940, M_w 2500, PDi 2.6
	K: M_n 800, M_w 2000, PDi 2.4

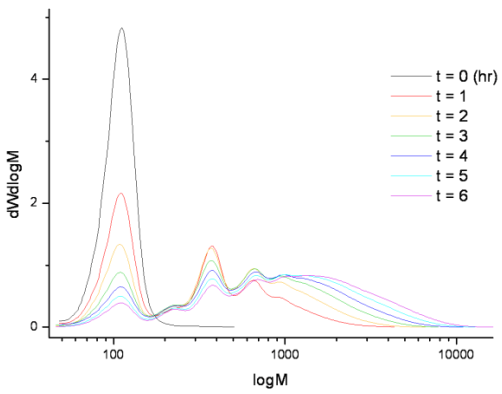

Figure S7: GPC overlay of **J** (branched PEGDMA/PMMA 80/20) sampled hourly throughout the reaction.

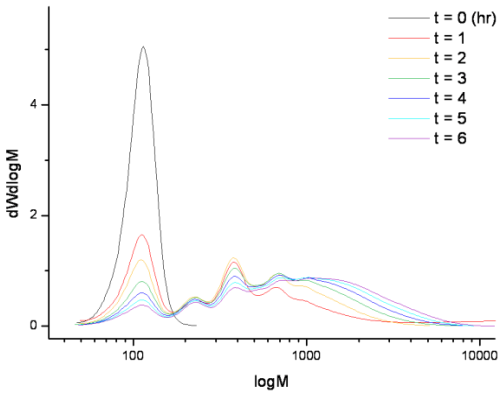

Figure S8: GPC overlay for **K** (branched PEGDMA/PMMA 67/33) sampled hourly throughout the reaction.

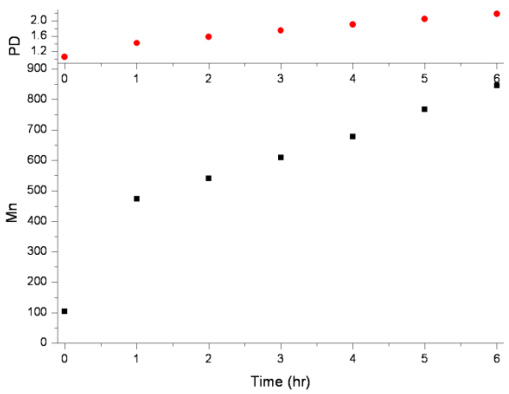

Figure S9: M_n and PDi monitoring for **J** (branched PEGDMA/PMMA 80/20) sampled hourly throughout the reaction.

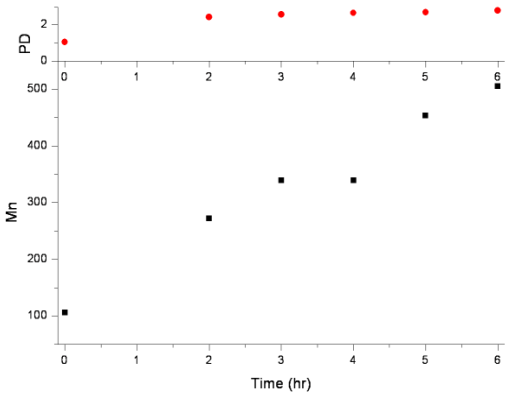

Figure S10: M_n and PDi monitoring for **K** (branched PEGDMA/PMMA 67/33) sampled hourly throughout the reaction.

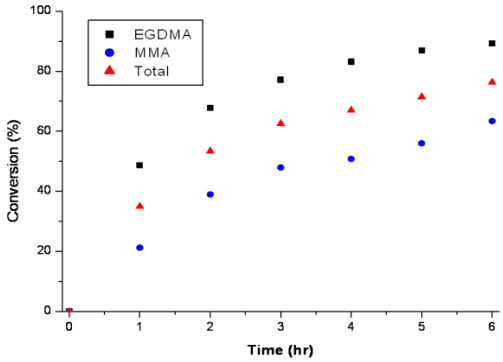

Figure S11: Conversion measured by GC-FID for **K** (branched PEGDMA/PMMA 67/33) sampled hourly throughout the reaction.

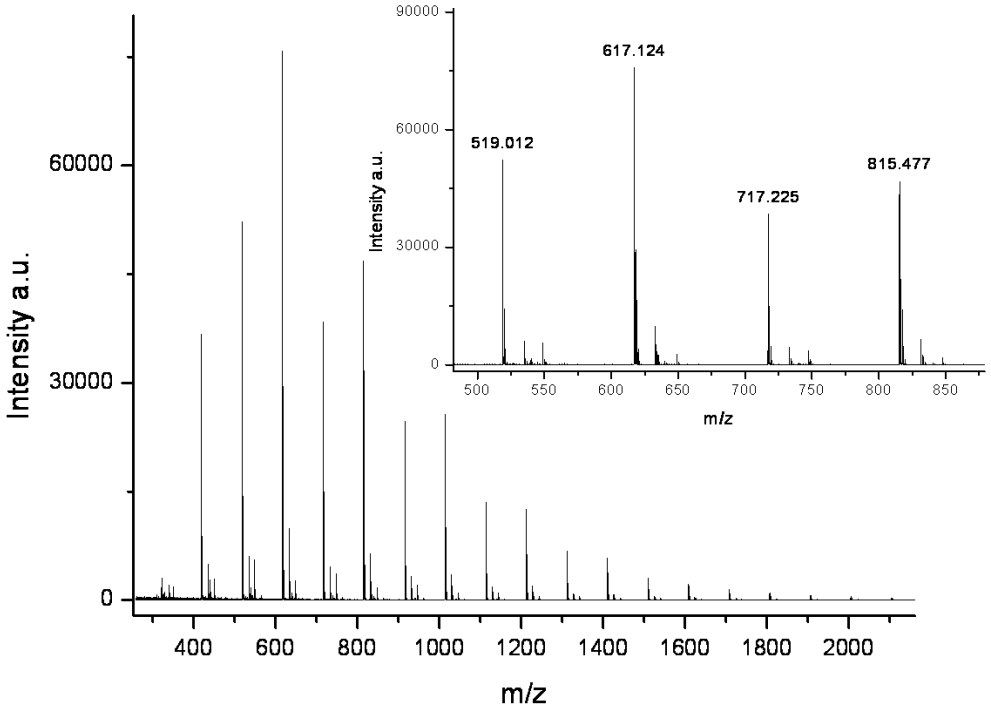

Figure S12: MALDI-ToF spectrum of **J** (branched PEGDMA/PMMA 80/20)

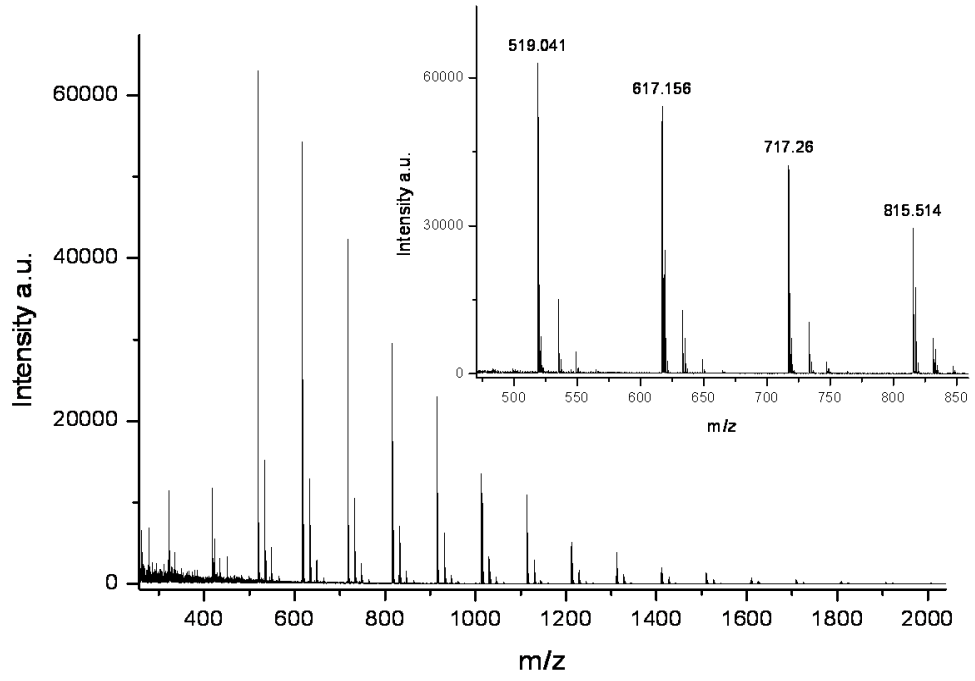

Figure S13: MALDI sprectrum for **K** (branched PEGDMA/PMMA 67/33)

Characterisation of L and M (**L**: Branched PEGDMA/PTMPTMA 80/20. **M**: Branched PEGDMA/PTMPTMA 67/33)

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.90-1.65 (backbone CH_3, $C\underline{H}_2C\underline{H}_3$), 1.85-2.05 (terminal CH_3), 2.10-2.20 (backbone CH_2), 2.40-2.70 (backbone CH_2), 3.95-4.40 (OCH_2CH_2O, OCH_2), 5.45-5.65 (terminal $C\underline{H}_aH_b$=C + internal $C\underline{H}_aH_b$=C), 6.00-6.15 (terminal $CH_a\underline{H}_b$=C), 6.20-6.35 (internal $CH_a\underline{H}_b$=C).

^{13}C NMR (400 MHz $CDCl_3$ at 25˚C): δ 7.40 ($CH_2\underline{C}H_3$), 18.14 (terminal CH_3), 23.40 (TMPTMA C=O), 24.67 (backbone CH_3), 40.55 (backbone CH_2, quaternary $\underline{C}(CH_3)_2(CH_2)_2$), 42.88 (quaternary $\underline{C}(CH_2)_2(CH_3)(C{=}O)$, $C(CH_2)_4$), 48.07 (backbone CH_2), 62.23 (OCH_2CH_2O), 66.04 (OCH_2), 125.79 (terminal $\underline{C}H_2$=C-), 128.35 (internal $\underline{C}H_2$=C-), 135.95 (terminal CH_2=$\underline{C}$-), 137.06 (internal CH_2=$\underline{C}$-), 166.85 (terminal ester carbonyl), 176.42 (internal ester carbonyl).

IR: υ_{max} (neat)/cm^{-1} 2970 (m, CH sp^3), 1729 (m, C=O), 1636 (s, C=C), 1452 (s, CH_2), 1292 (m), 1142 (m, C-O), 942 (s), 813 (s)

GPC RI only: **L**: M_n 1000, M_w 1900, PDi 2.0

M: M_n 1000, M_w 1900, PDi 2.0

GPC Universal Calibration: **L**: M_n 900, M_w 2900, PDi 3.1

M: M_n 700, M_w 2000, PDi 2.9

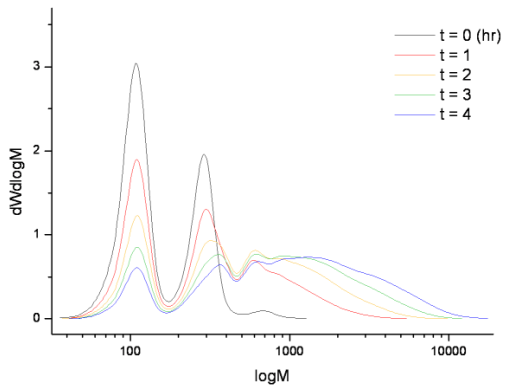

Figure S14: GPC overlay of **L** (branched PEGDMA/PTMPTMA 80/20) sampled hourly throughout the reaction.

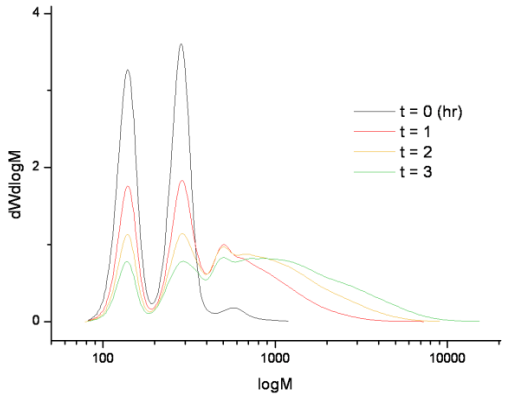

Figure S15: GPC overlay of **M** (branched PEGDMA/PTMPTMA 67/33) sampled hourly throughout the reaction.

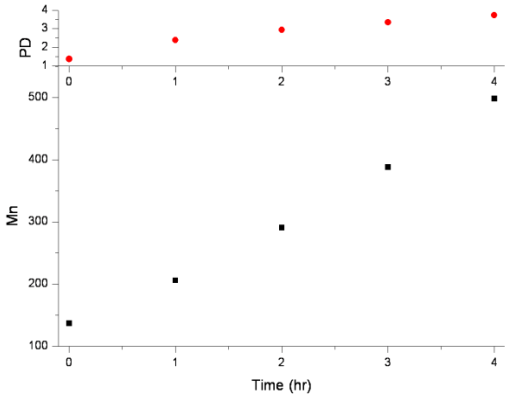

Figure S16: M_n and PDi data for **L** (branched PEGDMA/PTMPTMA 80/20) sampled hourly throughout the reaction.

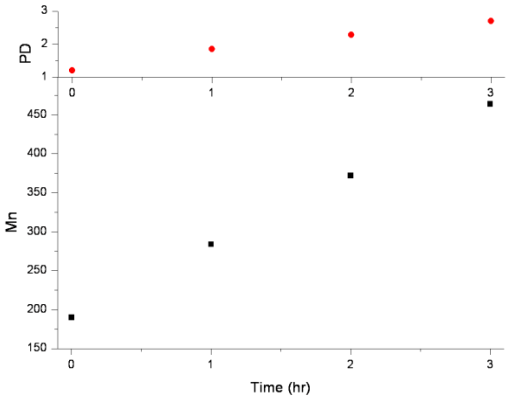

Figure S17: M_n and PDi data for **M** (branched PEGDMA/PTMPTMA 67/33) sampled hourly throughout the reaction.

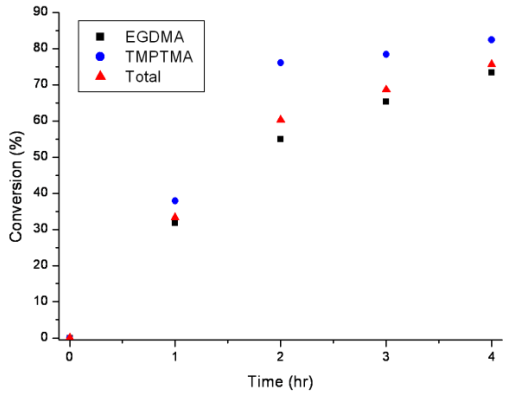

Figure S18: Conversion measured by GC-FID for **L** (branched PEGDMA/PTMPTMA 80/20) sampled hourly throughout the reaction.

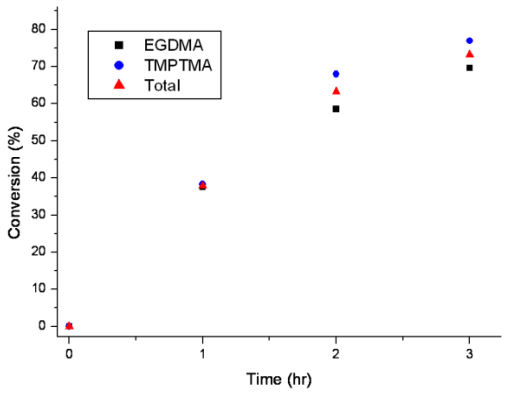

Figure S19: Conversion measured by GC-FID for **M** (branched PEGDMA/PTMPTMA 67/33) sampled hourly throughout the reaction.

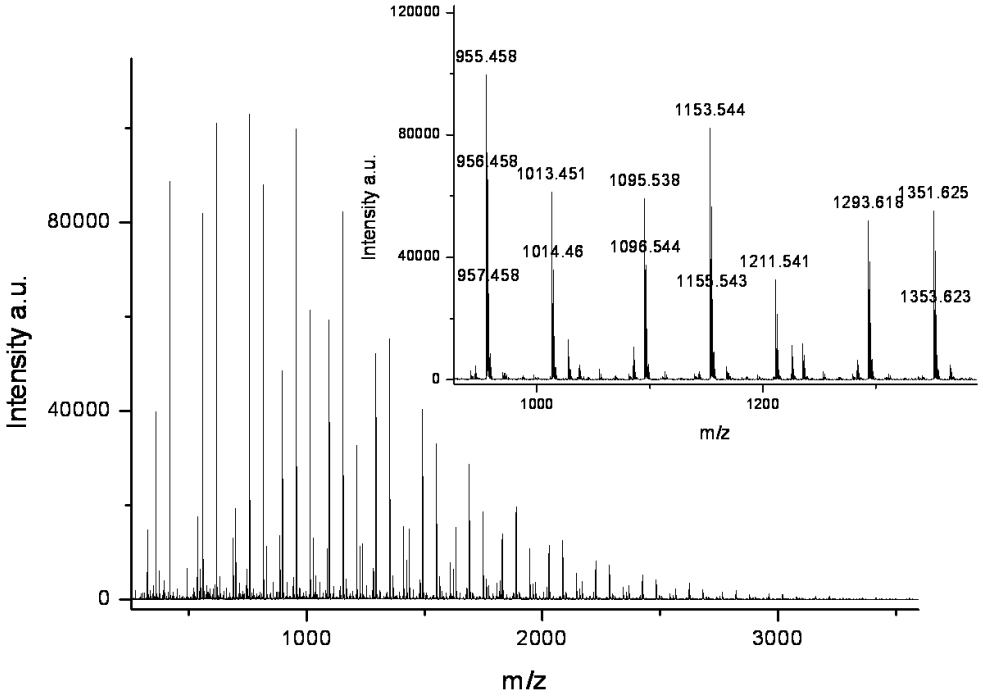

Figure S20: MALDI-TOF spectrum of **L** (branched PEGDMA/PTMPTMA 80/20)

Characterisation of N (Branched PTMPTMA)

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.70-1.10 ($CH_2C\underline{H}_3$), 1.10-1.45 ($C\underline{H}_2CH_3$), 1.85-2.10 (terminal CH_3), 3.90-4.40 (OCH_2CH_2O), 5.45-5.60 (terminal $C\underline{H}_aH_b$=C + internal $C\underline{H}_aH_b$=C), 6.00-6.35 (terminal $CH_a\underline{H}_b$=C, internal $CH_a\underline{H}_b$=C).

^{13}C NMR (400 MHz $CDCl_3$ at 25˚C): δ 7.79 ($CH_2\underline{C}H_3$), 18.59 (terminal CH_3), 23.73 ($\underline{C}H_2CH_3$), 41.48 (quaternary $\underline{C}(CH_3)_2(CH_2)_2$), 64.62 ($OCH_2CH_2O$), 125.82 (terminal $\underline{C}H_2$=C-), 136.23 (terminal CH_2=$\underline{C}$-), 137.28 (internal CH_2=$\underline{C}$-), 167.28 (terminal ester carbonyl).

IR: υ_{max} (neat)/cm^{-1} 2966 (m, CH sp^3), 1715 (m, C=O), 1637 (s, C=C), 1455 (s, CH_2), 1290 (m), 1142 (m, C-O), 940 (s), 812 (s)

GPC DRI only: M_n 1200, M_w 4500, PDi 3.7

GPC Universal: M_n 1000, M_w 9000, PDi 9.1

Characterisation of Thiol-ene Click Products

Characterisation of A1, A2, A3 (A1: Benzyl mercaptan functionalised PEGDMA 0.2 mol equiv DMPP. **A2**: Benzyl mercaptan functionalised PEGDMA 0.1 mol equiv DMPP. **A3**: Benzyl mercaptan functionalised PEGDMA 0.05 mol equiv DMPP):

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.90- 1.50 (backbone CH_3, terminal CH_3), 1.70-1.80 (DMPP CH_3), 1.90-2.10 (backbone CH_2), 2.30-2.80 (backbone CH_2, $C\underline{H_2}SC\underline{H_2}$), 3.40-3.90 (unreacted CH_2SH), 4.00- 4.40 (OCH_2CH_2O), 7.15- 7.40 (aromatic CH benzyl mercaptan), 7.45-8.05 (DMPP aromatic CH)

^{13}C NMR (400 MHz, $CDCl_3$ at 25˚C): δ 16.53 (terminal CH_3), 25.15 and 30.05 (backbone CH_3), 34.16 and 34.48 ($\underline{C}H_2SCH_2Ph$), 35.94 and 36.32 ($CH_2S\underline{C}H_2Ph$), 41.35 (backbone CH_2), 41.81 and 42.62 (backbone quaternary carbons), 61.97 (OCH_2CH_2O), 126.81 (aromatic para- CH), 128.35 (aromatic meta-CH), 128.63 (aromatic ortho-CH), 137.78 (aromatic quaternary carbon), 174.19 (terminal ester carbonyl), 177.38 (internal ester carbonyl)

IR: υ_{max} (neat)/cm^{-1} 2970 (m, CH sp^3), 1729 (m, C=O), 1493 (s), 1453 (s, CH_2), 1283 (s, CH_3), 1233 (s), 1147 (m, C-O), 1071 (s, C-S-C), 942 (s), 875 (s)

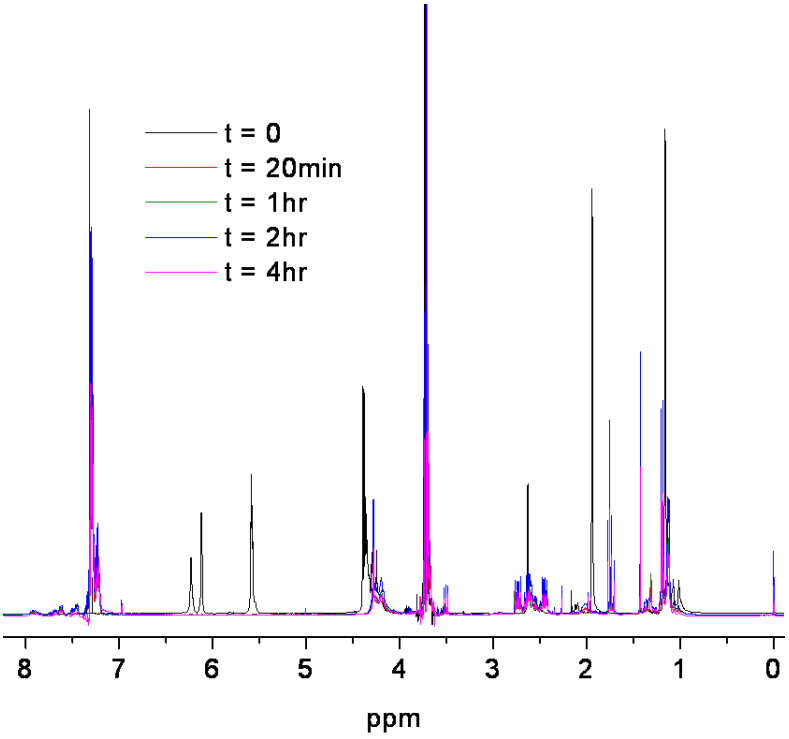

Figure S21: ^{1}H NMR monitoring of the phosphine mediated thiol-ene click reaction of benzyl mercaptan to **A** (PEGDMA, 0.049 mol% CoBF)

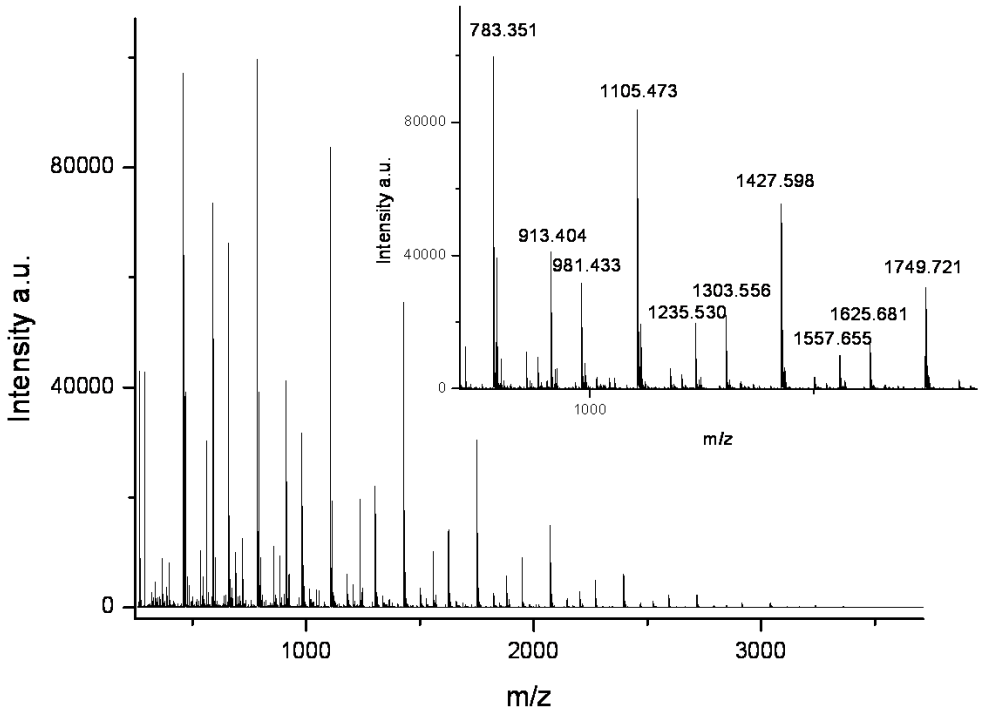

Figure S22: MALDI-TOF spectrum of **A1** (benzyl mercaptan functionalised PEGDMA 0.2 mol equiv DMPP)

Characterisation of A4 (Mercaptoethanol functionalised PEGDMA)

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.90-1.5 (terminal CH_3, backbone CH_3, DMPP CH_3), 1.70-1.90 (backbone CH_2), 1.95-2.25 (backbone CH_2), 2.30-2.60 (Terminal CH), 2.60-3.40 ($C\underline{H}_2SC\underline{H}_2CH_2O\underline{H}$), 3.60-4.05 ($C\underline{H}_2OH$), 4.10-4.60 ($OC\underline{H}_2C\underline{H}_2O$), 7.60-8.1 (DMPP aromatic CH)

^{13}C NMR (400 MHz, $CDCl_3$ at 25˚C): δ 16.87 (terminal CH_3), 25.11 (DMPP CH_3), 30.29 (backbone CH_3), 32.17 ($\underline{C}H_2SCH_2CH_2OH$), 35.17 ($S\underline{C}H_2CH_2OH$), 41.91 (backbone CH_2), 42.75 ($\underline{C}HC=O$), 60.31 ($\underline{C}H_2OH$), 61.27, 63.49 ($O\underline{C}H_2\underline{C}H_2O$), 125.43, 128.96, 130.16, 132.15, 134.55 (DMPP aromatic CH), 175.00, 177.47 (C=O)

IR: υ_{max} (neat)/cm^{-1} 3341 (br, m, OH H-bonded), 2922 (m, CH sp^3), 1721 (s, C=O), 1455 (m, CH_2), 1389 (m, CH_3), 1154 (s,C-O), 1041 (s, C-S-C), 938 (m), 875 (m)

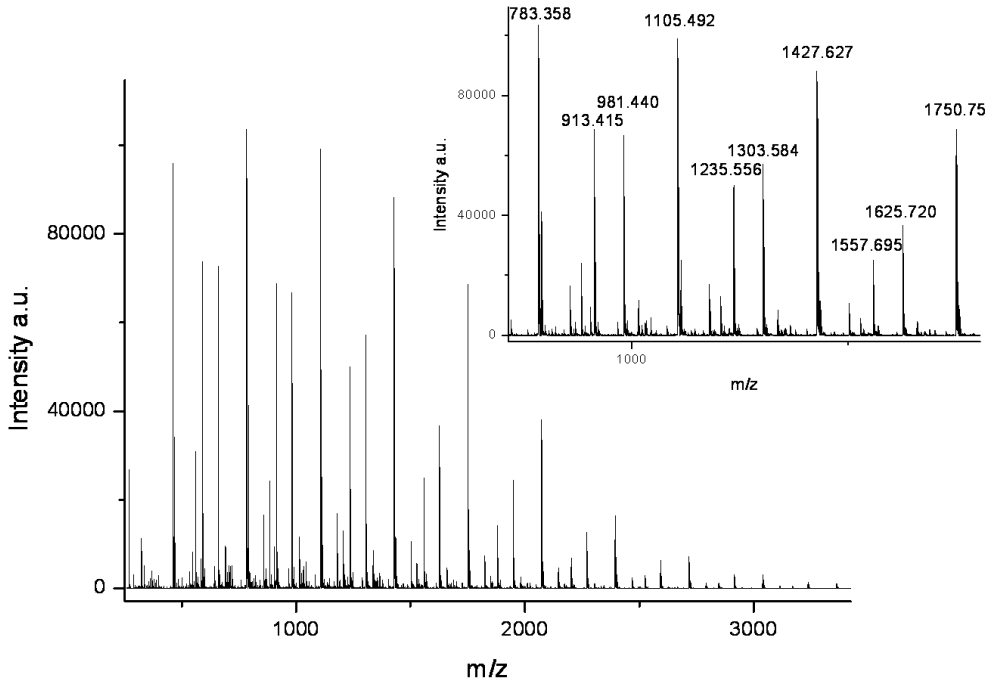

Figure S23: MALDI-TOF spectrum of **A4** (mercaptoethanol functionalised PEGDMA)

Characterisation of A5 (Thioglycerol functionalised PEGDMA)

^{1}H NMR (400 MHz, Acetone at 25˚C): δ 1.00 -1.60 (backbone CH_3, DMPP CH_3), 1.85-2.05 (terminal CH_3), 2.30-2.40 (backbone CH_2), 2.55-3.30 (CH_2, CHC$\underline{H}_2$S, SC$\underline{H}_2$CHOH), 3.60-3.90 ($CH_3\underline{C}H$), 4.05-4.60 (O$\underline{C}H_2\underline{C}H_2O, C\underline{H}OH, C\underline{H}_2$OH), 7.60-8.4 (DMPP aromatic CH)

^{13}C NMR (400 MHz, Acetone at 25˚C): δ 16.56 (terminal CH_3), 29.39 (DMPP CH_3), 29.63 (backbone CH_3), 35.95 ($\underline{C}H_2SCH_2CH_2OH$), 36.05 (S$\underline{C}H_2CH_2OH$), 40.14 (backbone CH_2), 44.78 ($\underline{C}HC{=}O$), 62.51 ($\underline{C}H_2OH$), 66.49 (O$\underline{C}H_2\underline{C}H_2$O), 68.86 ($CH_3\underline{C}H$), $\underline{C}$HOH (76.14) 130.24, 132.20, 134.60,(DMPP aromatic CH)

IR: υ_{max} (neat)/cm^{-1} 3326 (br, s, OH H-bonded), 2918 (m, CH sp^3), 1720 (s, C=O), 1391 (m, CH_2), 1155 (s, C-O), 1068 (s, C-S-C), 1028 (s) 932 (m), 876 (m)

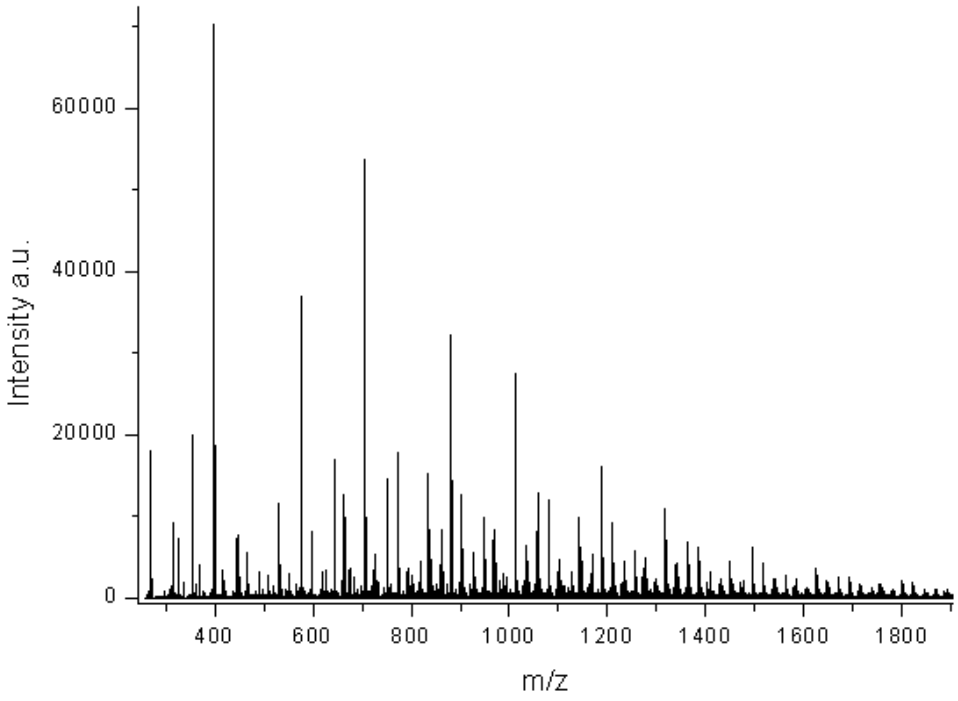

Figure S24: MALDI-ToF spectrum of **A5** (thioglycerol functionalised PEGDMA)

Characterisation of A6 (Dodecanethiol functionalised PEGDMA)

^{1}H NMR (400 MHz, TMS at 25˚C): δ 0.75-1.0 ($(CH_2)_{11}C\underline{H}_3$), 1.0-1.45 (terminal CH_3, DMPP CH_3), 1.45-1.65 ($(CH_2)_{11}$), 1.80-1.95 (backbone CH_2), 2.00- 2.20 (backbone CH_2), 2.40-2.75 ($C\underline{H}_2SC\underline{H}_2$), 2.80-2.90 (SH), 4.00-4.40 ($OC\underline{H}_2C\underline{H}_2O$), 7.45-8.00 (DMPP aromatic CH)

^{13}C NMR (400 MHz, $CDCl_3$ at 25˚C): δ 14.22 ($(CH_2)_{11}\underline{C}H_3$), 16.86 (terminal CH_3), 24.70 (DMPP CH_3), 29.73 ($C\underline{H}_2SC\underline{H}_2$), 30.39 $(CH_2)_{10}$, 32.43 (backbone CH_2), 34.17 (backbone CH_2), 41.97 ($O\underline{C}H_2\underline{C}H_2O$), 125.55, 128.84, 130.03 (DMPP aromatic CH), 174.88 (C=O)

IR: υ_{max} (neat)/cm^{-1} 2921 (s, CH sp^3), 2852 (s, CH sp^3), 1733 (s, C=O), 1457 (m, CH_2), 1376 (m, CH_3), 1247 (m), 1149 (s, C-O), 1066 (m, C-S-C), 9411 (m), 863 (m)

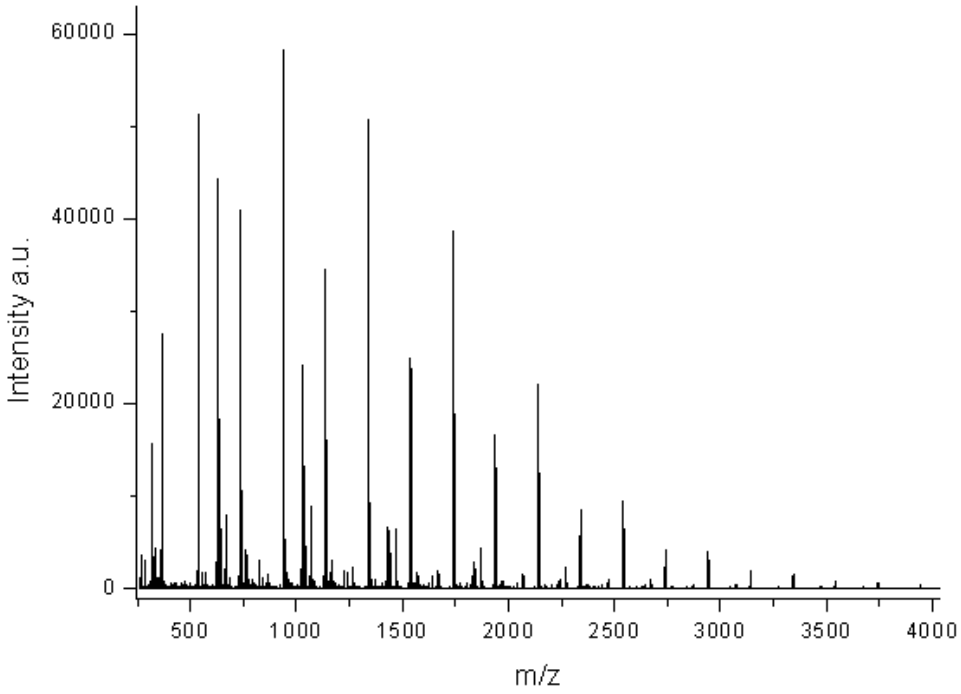

Figure S25: MALDI-ToF spectrum of **A6** (dodecanethiol functionalised PEGDMA)

References

1. A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 2002, **106**, 5197-5202.