

Electronic Supplementary Information

Dual-functional materials *via* CCTP and selective orthogonal thio-Michael addition/Epoxide ring opening reactions

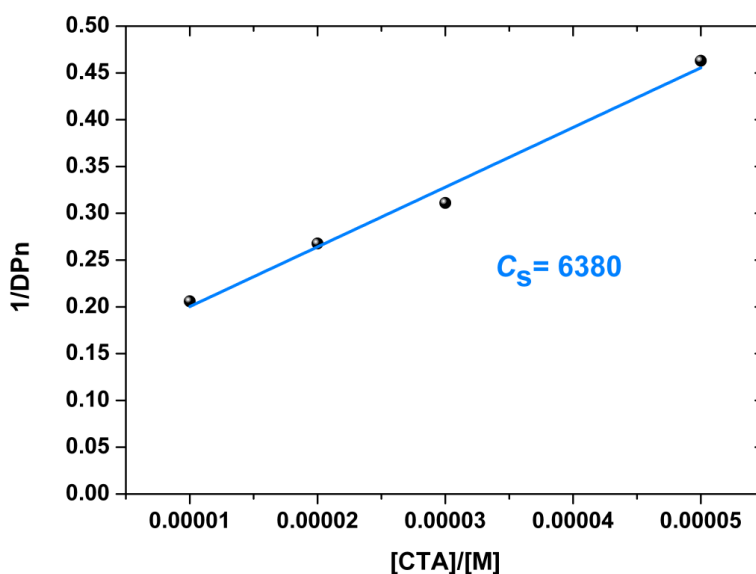
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Experimental

General

All reagents were purchased from Aldrich and used as received unless stated. AIBN was recrystallised from methanol prior to use. CoBF was synthesised according to literature (RSH).¹

Measurement of the C_s value of CoBF in GMA



The C_s value of CoBF for GMA was measured using the Mayo equation: $1/DP_n = 1/DP_{n0} + C_s [CTA]/[M]$ which when plotted the gradient of a linear Mayo plot is equal to the C_s value. Four concentrations of chain transfer agent were employed and all reactions were terminated below 5 % conversion (~20 minutes reaction time) to ensure the concentration of $[S]/[M]$ remains constant. DP_n was calculated using the M_n GPC / monomer mass. CoBF was added to a round bottomed flask equipped with stirrer bar, sealed with a suba-seal and degassed under nitrogen. Monomer, AIBN and acetonitrile were added to a second round bottomed flask equipped with stirrer bar, sealed with a suba-seal and degassed. The monomer solution was then cannulated into the CoBF flask and the solution heated to 70 °C.

[M] : [CTA] : [I]

0.07 : 0.00000035 : 0.00035

0.07 : 0.0000007 : 0.00035

0.07 : 0.0000014 : 0.00035

0.07 : 0.0000021 : 0.00035

Poly-GMA synthesis

Stock solutions of CoBF in GMA were made using 4.6 mg CoBF in 25 mL GMA. GMA was freeze pump thawed in a Schlenk tube then cannulated under nitrogen into CoBF degassed thrice *via* vacuum/nitrogen cycle. Stock solutions were stored under nitrogen in a fridge for up to one month. Degassed syringe techniques used for transferring stock solution into reaction mixtures.

A 250 mL roundbottomed flask was charged with GMA (51 mL, 0.367 mol), acetonitrile (50 mL), AIBN (400 mg, 2.44 mmol) and stirrer bar. The reaction mixture was degassed *via* nitrogen bubbler for 20 minutes prior to addition of CoBF stock solution. Degassed CoBF stock solution was added *via* degassed syringe. The round bottomed flask was immersed in an oil bath at 70 °C for 24 hours under nitrogen. Samples were taken hourly (approx 0.1 ml) *via* degassed syringe for 6 hours in order to obtain GPC, GC and ¹H NMR measurements, sample taken at 24 hours. Reaction terminated by cooling and introduction of oxygen. Solvent removed *in vacuo* for GPC analysis for the quotation of final molecular weights.

Name	CoBF Stock Sol. (mL)	CoBF (mg)	CoBF (mmol)	CoBF (mol %)
A	8	1.47	2.94×10^{-3}	7.86×10^{-6}
B	4	0.74	1.47×10^{-3}	3.94×10^{-6}
C	2	0.37	7.36×10^{-4}	1.97×10^{-6}
D	1	0.18	3.68×10^{-4}	9.84×10^{-7}

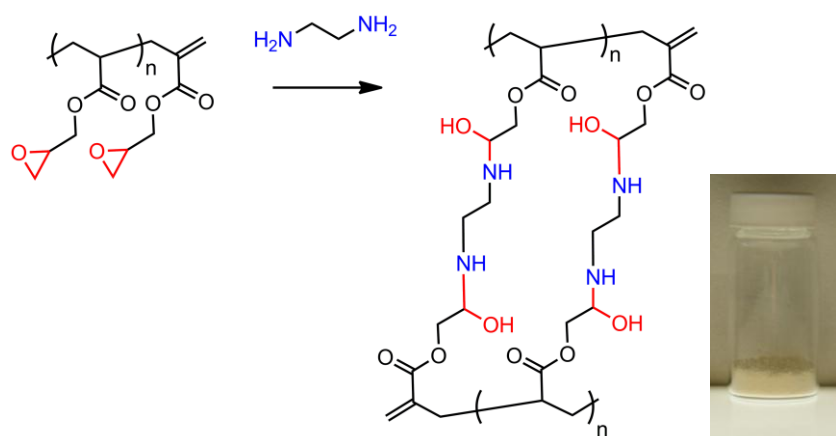
Table 1:

Concentrations of CoBF employed via stock solutions for GMA polymerisations A-D

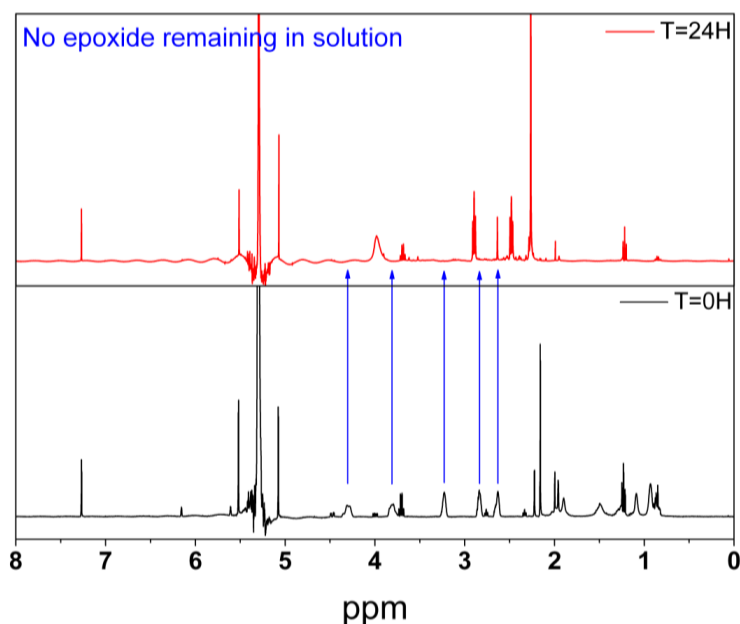
Full functionalisation of p-GMA with amine

0.5 g p-GMA (1 eq), 1.2 mol eq amine (to moles of epoxide group plus moles of double bond) in 5 mL DMSO. If the boiling point of the amine exceeded reaction temperature, reactions were carried out in 20 mL unsealed vials immersed in an oil bath at 60°C, with stirring. For amines where the boiling point was lower than reaction temperature a reflux setup was used. Solvent was removed on a Schlenk line, with gentle heating *via* heatgun. GPC's conducted prior to purification by dialysis or precipitation.

Full functionalisation of P-GMA with diamine



1 g Poly GMA ($M_{\text{wGPC}} = 4400 \text{ g}\cdot\text{mol}^{-1}$, 0.227 mM DP= 30, epoxide content= 0.775 mM) in 3 mL DCM was added to a round bottomed flask equipped with a stirrer bar and 10 equivalents of ethylenediamine (0.465 g, 7.75 mM) in 30 mL DCM was fed into the polymer solution at a rate of $13 \text{ mL}/\text{min}$ using a pump. The reaction was left stirring vigorously for 24 hours under reflux at $44 \text{ }^\circ\text{C}$.² The resultant particles were isolated by filtration and the supernatant was analysed by ^1H NMR revealing no pGMA remaining in solution. The particles were analysed by dynamic light scattering (DLS) and transmission electron microscopy (TEM) showing a particle size averaging between 10-50 nm.



Dual Functionalisation- Thiol-ene click prior to epoxide ring-opening

Dimethylphenylphosphine (DMPP) stock solutions were used. These were prepared by charging an ampoule with 8 mL d^6 -DMSO and the solution was freeze pump thawed then backfilled with nitrogen (to thaw gentle heating was required *via* heat gun), to which 0.1 mL of DMPP (previously degassed *via* freeze pump thaw) was added using a degassed syringe. Stock solutions were then stored in a fridge for up to 2 months, completely thawed prior to use using gentle heating with heat gun.

Thiol-ene click reactions were carried out on a 1 g scale in a large vial. 1:3:0.05 or 1:3:0.1 ratio of double bonds:thiol:DMPP was used. Poly-GMA dissolved in 5 mL of DMSO, then thiol added ($t=0$ ^1H NMR taken) then DMPP stock solution added *via* degassed syringe (to preserve integrity of stock solution, thiol-ene click conducted under atmospheric conditions). Reactions were checked for completion at 1 hour by ^1H NMR. No workup conducted prior to reaction with amine.

Reaction with amine uses 1.2 mol eq. amine to moles of epoxide only. Thio-functionalised polymer solution added to a roundbottomed flask fitted with a condenser (No addition of further DMSO). Amine added and reaction mixture placed in an oil bath at 60 °C for 24 hours. Solvent was removed on a Schlenk line. Polymers were precipitated in hexane or petroleum ether 40-60 °C or dialysed in methanol or water (1000 and 500-1000 MW cutoff respectively) depending on solubilities/suitability prior to IR, NMR and MALDI-TOF characterisation.

Characterisation

^1H and ^{13}C NMR

NMR was carried out on Bruker DXP-400 , Bruker AV III 600 and Bruker AV II 700 spectrometers.

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 Agilent 390-LC multi detector suites fitted with two PLgel 5 μm Mixed D columns, plus a 5 μm guard column.

For investigation of unfunctionalised p-GMA and hydrophobically functionalised p-GMA THF was used as the mobile phase, with a flow rate of 1 mL/min at an ambient operating temperature. The injection volume was 100 μ L. The GPC was equipped with a refractive index, light scattering, UV and photodiode array (PDA, Shimadzu) detectors. Data was collected and analysed using Cirrus software (Agilent) and all samples calibrated against poly(methyl methacrylate) (PMMA) EasiVial standards, purchased from Agilent.

For investigation p-GMA functionalised with hydrophilic groups (and unfunctionalised p-GMA for comparison) DMF was used as the mobile phase, with a flow rate of 1 mL/min⁻¹ at 40 °C operating temperature. The injection volume was 100 μ L. The GPC was equipped with a refractive index, UV and viscometry detectors. Data was collected and analysed using Cirrus software (Agilent) and all samples calibrated against PMMA EasiVial standards, purchased from Agilent.

For investigation of decylamine functionalised poly-GMA CHCl₃ was used as the mobile phase, with a flow rate of 1 mL/min⁻¹ at an ambient operating temperature. The injection volume was 100 μ L. The GPC was equipped with a refractive index, light scattering and viscometry detectors. Data was collected and analysed using Cirrus software (Agilent) and all samples calibrated against PMMA EasiVial standards, purchased from Agilent.

Matrix-Assisted Laser Desorption and Ionisation Time-of-Flight mass spectrometry (MALDI-ToF MS)

Mass spectra were acquired by MALDI-ToF (matrix-assisted laser desorption and ionisation 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-Dihydroxybenzoic acid (DHB) or trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) were used as an organic matrix and sodium iodide (NaI) used as the salt. Calibrations were conducted using polyethylene glycol methyl ether of average molecular weight 1,100 and 2,000. A layering method was used to spot the MALDI plate. THF or THF/water was used as the solvent for sample preparation.

Gas chromatograph – Flame ionisation detector (GC-FID)

GC-FID analysis was performed using a Varian 450. A FactorFour™ capillary column VF-1 ms, 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 Polymers

Poly-GMA

Name	CoBF (mol%)	[CoBF:GMA] (mol)	M _n (g/mol ⁻¹)	M _w (g/mol ⁻¹)	PDI	Conversion*
A	7.86x10 ⁻⁶	[1:98K]	800	1400	1.76	90.2
B	3.94x10 ⁻⁶	[1:195K]	1600	2900	1.86	91.2
C	1.97x10 ⁻⁶	[1:391K]	3100	5800	1.86	99.0
D	9.84x10 ⁻⁷	[1:783K]	5000	9100	1.84	93.4

*Conversion measured by GC-FID

Table 2: Molecular weights and conversion of polymerisations A-D with decreasing CoBF concentration

¹H NMR (400 MHz, TMS at 25 °C): δ 0.85-1.15 (m, CH₃, backbone and terminal), 1.80-2.35 (m, backbone CH₂), 2.57 (br, CH epox), 2.77 (br, CH epox), 3.16 (br, CH epox), 3.70-3.95 (m, O-CH₂-epox), 4.20-4.40 (m, O-CH₂-epox), 5.50-5.60 (m, C=CH₂), 6.20-6.25 (m, C=CH₂)

¹³C NMR (100 MHz CDCl₃ at 25 °C): δ 16.49, 21.28, 24.68, 29.62 (CH₃, backbone and terminal), 44.44 (CH₂, epoxide), 49.11 (CH, epoxide), 51.62 (C, tertiary backbone), 53.36 (CH₂, backbone), 65.73 (OCH₂), 128.74, 129.52 (vinyl CH₂), 136.62 (C, tertiary vinyl), 166.52 (C, carbonyl)

IR: ν_{max} (neat)/cm⁻¹ 2972 (m, CH sp³), 1724 (s, C=O), 1628 (m, C=C), 1485 (s), 1448 (m, CH₂), 1246 (s), 1146 (s, C-O), 992 (m), 905 (s, epoxide), 846 (m), 757 (m)

GPC (THF eluent): **A**: M_n 800, M_w 1400, PDI 1.8 **B**: M_n 1600, M_w 2900, PDI 1.8 **C**: M_n 3100, M_w 5800, PDI 1.9 **D**: M_n 5000, M_w 9100, PDI 1.8

GC-FID (conversion): **A**: 90.2% **B**: 91.2% **C**: 99.0% **D**: 93.4%

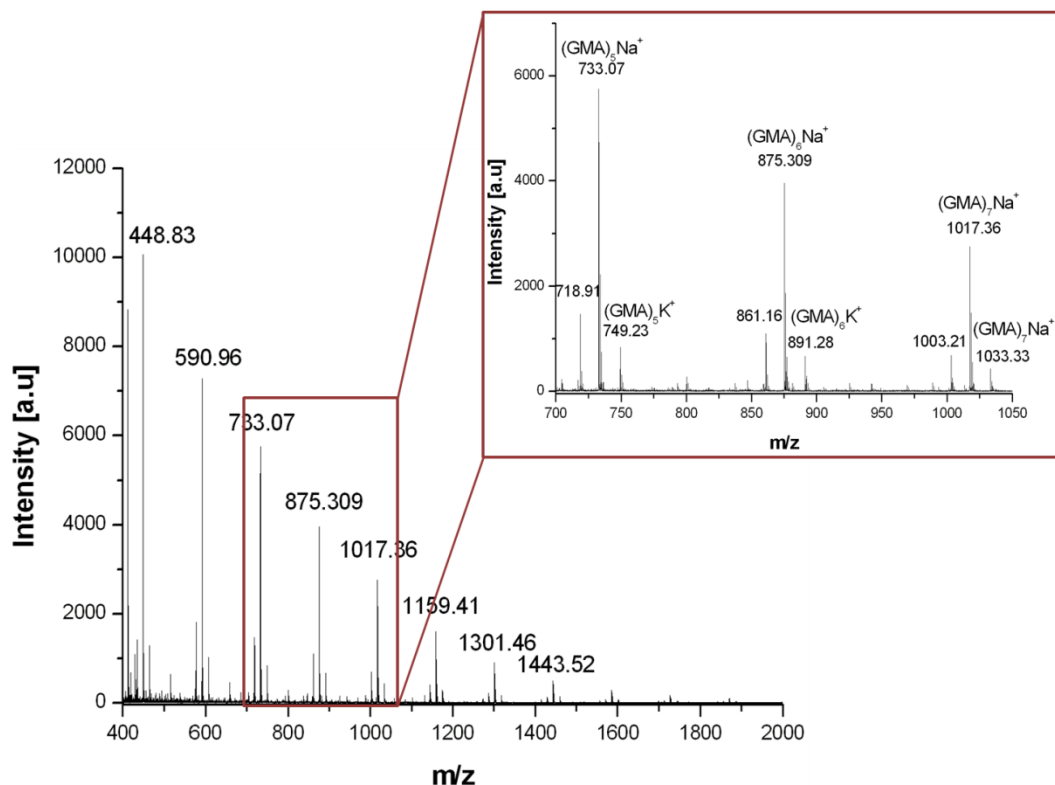


Figure 1: Typical MALDI-ToF spectrum of poly-GMA (B)

Propylamine Functionalised Poly-GMA (B)

^1H NMR (700 MHz, d^6 -acetone at 25 °C): 0.80-1.40 (m, amino CH_3 , backbone CH_3 , terminal CH_3), 1.45-1.70 (br, amino CH_2CH_3), 1.80-2.20 (m, backbone CH_2 , terminal $\text{CHC}=\text{O}$), 2.40-2.50 (m, terminal NHCH_2CH_2), 2.60-2.75 (br, CH_2NH), 2.75-2.95 (br, $\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 2.95-3.10 (br, NH/OH), 3.80-4.15 (br, OCH_2), 4.15-4.35 (br, $\text{CH}(\text{OH})$)

^{13}C NMR (175 MHz d^6 -acetone at 25 °C): 11.30 (amino CH_3), 21.10 (terminal CH_3), 22.31 (NHCH_2CH_2), 23.30 (backbone CH_3), 44.59 (backbone CH_2), 50.38 (NHCH_2), 51.73 ($\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 54.00 (terminal $\text{CH}(\text{C}=\text{O})\text{CH}_2\text{NH}$), 66.69 (OCH_2), 72.28 ($\text{CH}(\text{OH})$), 94.78 (backbone quaternary C), 177.01 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3317 (v, OH/NH), 2957 (m, CH sp^3), 1724 (s, $\text{C}=\text{O}$), 1616 (m, N-H bend), 1455 (m, CH_2), 1272 (m, C-N), 1148 (m, C-O), 1020 (m), 950 (m), 748 (m)

GPC (DMF eluent): M_n 6200, M_w 8700, PDI 1.4

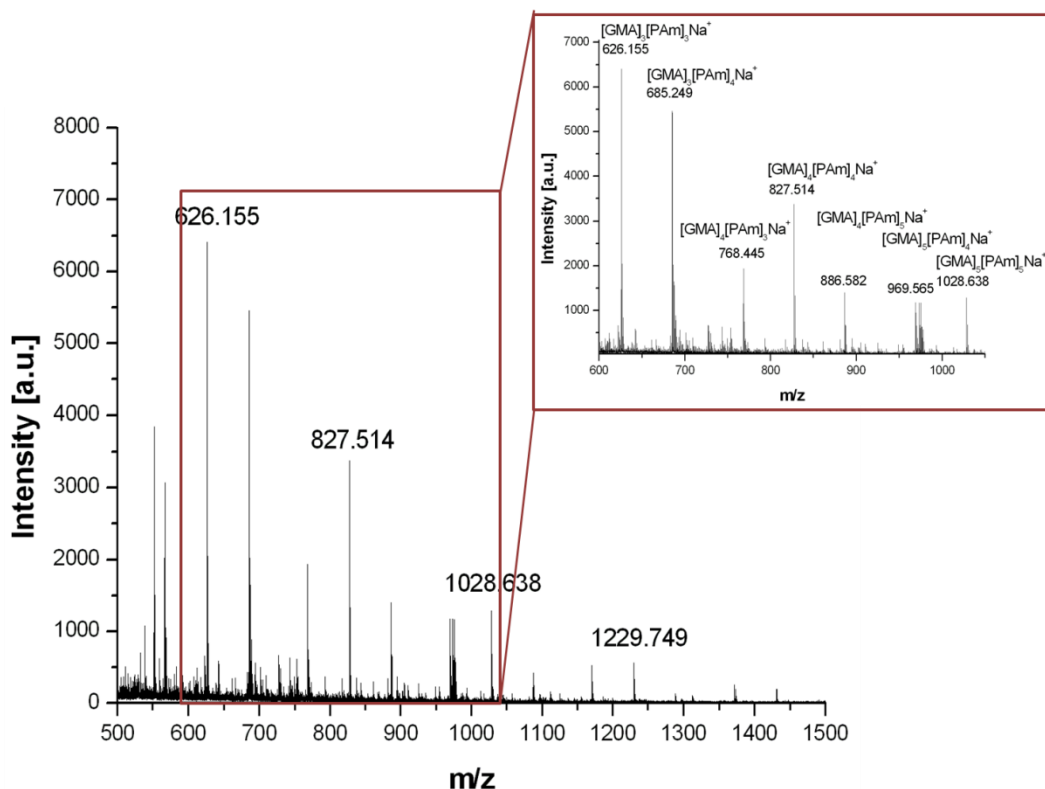


Figure 2: MALDI-TOF spectrum of Propylamine functionalised poly-GMA (B), PAm= propylamine

Benzylamine Functionalised Poly-GMA (B)

^1H NMR (700 MHz, TMS at 25 °C): 0.80-1.20 (br, backbone CH_3), 1.25-1.35 (m, terminal CH_3), 1.60-2.15 (br, backbone CH_2 , terminal $\text{CHC}=\text{O}$), 2.60-2.80 (br, CHCH_2NH), 2.80-2.90 (br, $\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 3.65-3.80 (br, CH_2 -benzyl), 2.85-4.10 (br, OCH_2), 4.15-4.25 (br, $\text{CH}(\text{OH})$), 7.10-7.40 (br, CH -benzyl)

^{13}C NMR (175 MHz CDCl_3 at 25 °C): 22.80 (terminal CH_3), 23.10 (backbone CH_3), 41.66 (terminal NHCH_2 -benzyl), 45.00 (NHCH_2 -benzyl), 51.32 ($\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 53.71 (OCH_2), 67.84 ($\text{CH}(\text{OH})$), 127.20, 128.17, 128.52, 129.01 (CH -benzyl, terminal CH -benzyl), 138.07 (terminal C -benzyl), 177.59 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3351 (v, OH/NH), 2940 (m, CH sp^3), 1721 (s, $\text{C}=\text{O}$), 1603 (m, N-H bend), 1452 (m), 1267 (m, C-N), 1149 (s, C-O), 1027 (m), 738 (m), 697 (s, $=\text{C}-\text{H}$ bend)

GPC (DMF eluent): M_n 7500, M_w 15400, PDI 2.0

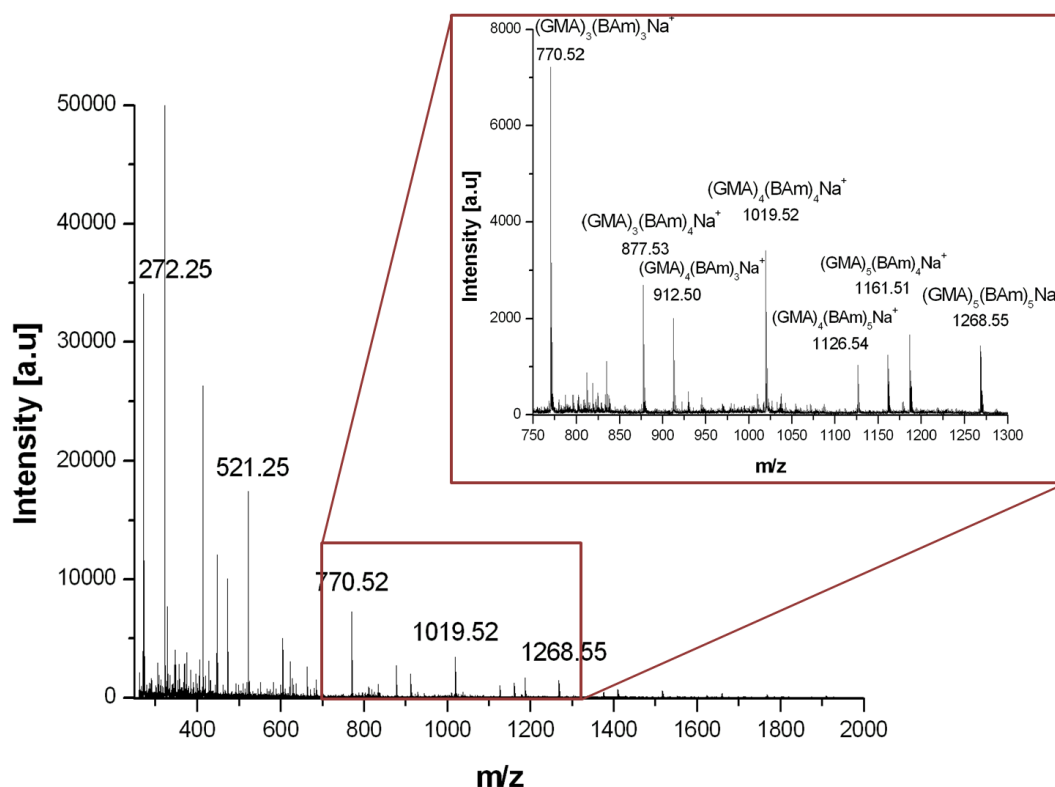


Figure 3: MALDI-ToF spectrum of benzylamine functionalised poly-GMA (B), BAm=benzylamine

Aminopropanediol Functionalised Poly-GMA (B)

^1H NMR (600 MHz, d^6 -DMSO at 25 °C): 0.60-1.00 (m, backbone CH_3), 1.00-1.25 (br, Terminal CH_3), 1.60-2.10 (br, backbone CH_2 , $\text{CH}(\text{C}=\text{O})$), 2.25-2.75 (br, terminal and side chain $\text{NHCH}_2\text{CH}(\text{OH})$), 3.15-3.40 (br, terminal $\text{CH}(\text{OH})\text{CH}_2\text{OH}$), 3.45-3.60 (m, COOCH_2), 3.60-4.30 (m, terminal and side chain $\text{CH}(\text{OH})$)

^{13}C NMR (125 MHz d^6 -DMSO at 25 °C): 15.96, 22.40 (backbone CH_3), 29.64 (terminal CH_3), 44.48 (backbone CH_2), 52.66 (terminal and side chain $\text{NHCH}_2\text{CH}(\text{OH})$), 64.37 ($\text{CH}(\text{OH})$), 67.13 (internal $\text{CH}(\text{OH})$), 70.14 (terminal $\text{CH}(\text{OH})$), 177.33 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3314 (v, OH/NH), 2931 (m, CH sp^3), 1719 (s, $\text{C}=\text{O}$), 1613 (m, N-H bend), 1450 (m), 1272 (m, C-N), 1151 (s, C-O), 1035 (m), 930 (m), 862 (m), 747 (m)

GPC (DMF eluent): M_n 5600, M_w 10600, PDI 1.9

Decylamine Functionalised Poly-GMA (B)

^1H NMR (700 MHz, TMS at 25 °C): 0.8-1.0 (br, CH_3 -decylamine, backbone CH_3), 1.0-1.15 (br, terminal CH_3), 1.40-1.65 (br, NHCH_2CH_2), 1.80-2.15 (br, backbone CH_2 , $\text{CH}(\text{C}=\text{O})$), 2.30-2.90 (br, $\text{NHCH}_2\text{CH}(\text{OH})$, CHCH_2NH), 3.70-4.20 (br, OCH_2 , $\text{CH}(\text{OH})$)

^{13}C NMR (175 MHz CDCl_3 at 25 °C): 14.07 (terminal, backbone, amino CH_3), 22.65 (CH_2CH_3), 27.00 (CH_2 decylamine, terminal), 29.33, 29.62 (decylamine CH_2), 32.15 (NHCH_2 , terminal), 34.13 (NHCH_2), 45.02 (backbone CH_2), 49.95 ($\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 51.98 (OCH_2), 177.53 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3334 (v, OH/NH), 2922 (s, CH sp^3), 1727 (s, $\text{C}=\text{O}$), 1618 (m, N-H bend), 1457 (m), 1378 (m), 1271 (m, C-N), 1149 (s, C-O), 990 (m), 934 (m), 887 (m), 748 (m)

GPC (CHCl_3 eluent): M_n 4100, M_w 6200, PDI 1.5

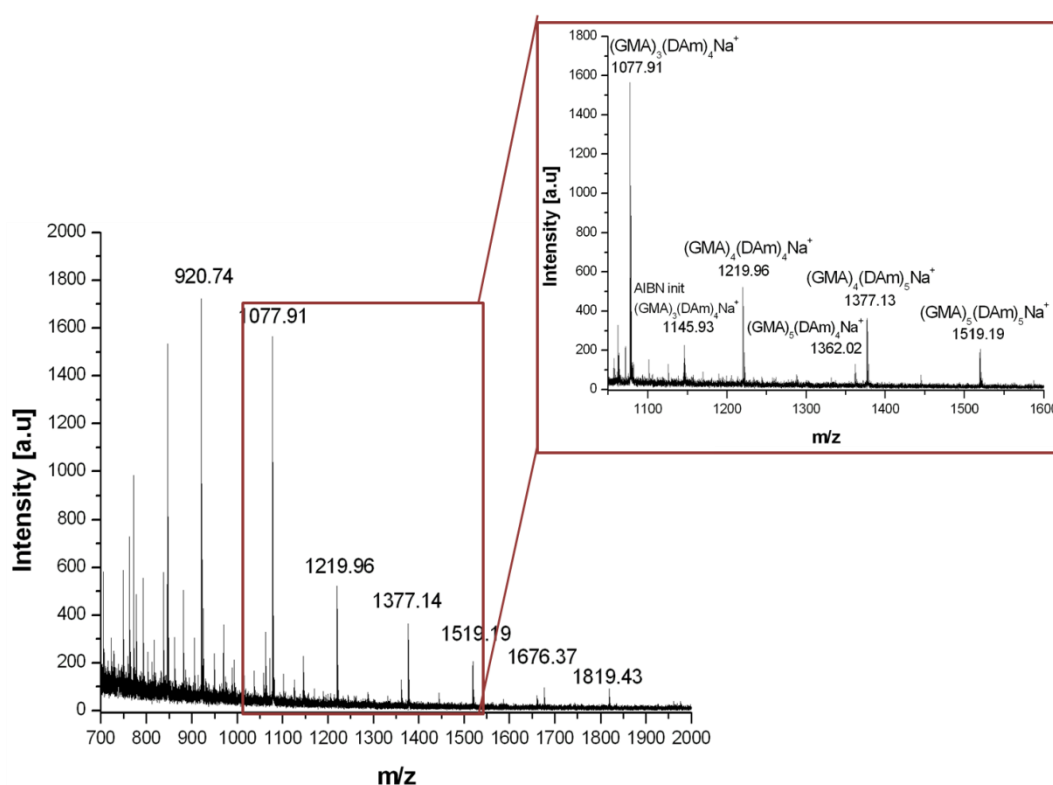


Figure 4: MALDI-ToF spectrum of decylamine functionalised poly-GMA (B), DAm=decylamine

Propargylamine Functionalised Poly-GMA (B)

^1H NMR (700 MHz, TMS at 25 °C): 0.6-1.10 (br, backbone CH_3), 1.10-1.30 (br, terminal CH_3), 1.60-2.10 (br, backbone CH_2), 2.40-2.80 (br, $\text{NHCH}_2\text{CH}(\text{OH})$), 2.90-3.05 (br, CCH), 3.05-3.60 (OCH_2 , NHCH_2C), 3.60-4.00 ($\text{CH}(\text{OH})$)

^{13}C NMR (175 MHz CDCl_3 at 25 °C): 16.42 (terminal, backbone CH_3), 18.57 (backbone CH_3), 38.06 (CH_2 , propargylamine), 44.54 (backbone CH_2), 44.98 ($\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 51.45

(OCH₂), 67.61 (CH(OH), 74.03 (OCH₂), 83.42 (quaternary C, propargylamine), 177.55 (carbonyl)

SEC (DMF eluent): M_n 12700, M_w 18100, PDI 1.4

Diethylamine Functionalised Poly-GMA (B)

¹H NMR (600 MHz, d⁶-DMSO at 25 °C): 0.70-0.90 (m, backbone CH₃), 0.90-1.05 (br, N(CH₂CH₃)₂), 1.05-1.10 (m, terminal CH₃), 1.60-2.05 (br, backbone CH₂), 2.30-2.45 (br, CH(OH)CH₂NH), 2.45-2.55 (br, N(CH₂CH₃)₂), 3.35-3.60 (br, terminal OCH₂), 3.60-3.85 (br, terminal CH(OH)), 3.85-4.05 (br, side chain OCH₂), 4.05-4.15 (br, side chain CH(OH)), 5.50-5.15 (m, vinyl CH₂), 6.10-6.20 (m, vinyl CH₂)

¹³C NMR (150 MHz, d⁶-DMSO at 25 °C): 11.82 (N(CH₂CH₃)₂), 15.92 (backbone CH₃), 17.74 (terminal CH₃), 44.48 (backbone CH₂), 47.04 (N(CH₂CH₃)₂), 55.91 (CH(OH)CH₂N), 61.15 (side chain COOCH₂), 66.59 (side chain CH(OH)), 67.32 (terminal CH(OH)), 73.01 (terminal COOCH₂), 128.25 (vinyl CH₂), 135.94 (tertiary C vinyl), 176.81 (carbonyl)

IR: ν_{max} (neat)/cm⁻¹ 3362 (m, OH/NH), 2967 (m, CH sp³), 1715 (s, C=O), 1449 (m), 1385 (m), 1270 (m, C-N), 1152 (s, C-O), 1062 (m)

GPC (DMF eluent): M_n 8600, M_w 13600, PDI 1.6

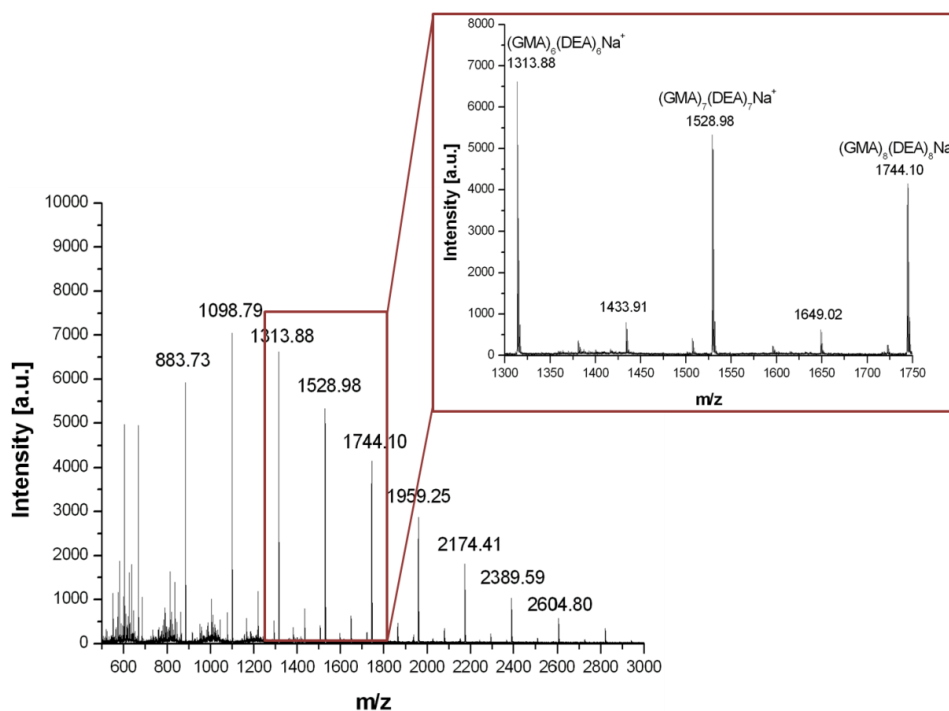


Figure 5: MALDI-ToF spectrum of diethylamine functionalised poly-GMA (B), DEA=diethylamine

Diethanolamine Functionalised Poly-GMA (B)

^1H NMR (600 MHz, d^6 -DMSO at 25 °C): 0.65-1.25 (m, backbone CH_3 , terminal CH_3), 1.65-2.10 (br, backbone CH_2), 2.50-2.70 (br, m, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.30-3.60 (br, m, $\text{NCH}_2\text{CH}_2\text{OH}$), 3.65-3.95 (br, $\text{CH}(\text{OH})$), 3.85-4.00 (br, OCH_2), 4.35-4.60 (br, amino-OH), 4.65-4.90 (br, $\text{CH}(\text{OH})$)

^{13}C NMR (150 MHz d^6 -DMSO at 25 °C): 16.36 (terminal CH_3), 18.32 (backbone CH_3), 44.56, 45.02 (backbone CH_2), 57.00 ($\text{NHCH}_2\text{CH}_2\text{OH}$), 58.74 ($\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 59.60 ($\text{NHCH}_2\text{CH}_2\text{OH}$), 66.81 ($\text{CH}(\text{OH})$), 67.73 (OCH_2), 177.74 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3346 (s, OH/NH), 2947 (m, CH sp^3), 1719 (s, $\text{C}=\text{O}$), 1450 (m), 1271 (m, C-N), 1152 (s, C-O), 1033 (s), 877 (m), 747 (m)

GPC (DMF eluent): M_n 6100, M_w 10500, PDI 1.7

Benzyl Mercaptan, Propylamine Functionalised Poly-GMA (A)

^1H NMR (400 MHz, TMS at 25 °C): 0.75-0.95 (br, $\text{NHCH}_2\text{CH}_2\text{CH}_3$), 0.95-1.10 (br, backbone CH_3), 1.10-1.20 (br, terminal CH_3), 1.35-1.65 ($\text{NHCH}_2\text{CH}_2\text{CH}_3$), 1.75-2.20 (br, backbone CH_2), 2.35-2.45 (br, $\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$), 2.45-2.65 (br, $\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 2.70-2.85 (m, $\text{NHCH}_2\text{CH}_2\text{CH}_3$), 3.30-3.45 (br, $\text{SCH}_2\text{C}_6\text{H}_5$), 3.75-4.10 (br, COOCH_2), 4.10-4.30 (br, $\text{CH}(\text{OH})$), 7.25-7.45 (m, aromatic CH), 7.55-7.65 (m, aromatic CH (DMPP)), 7.80-7.85 (m, aromatic CH (DMPP))

^{13}C NMR (100 MHz CDCl_3 at 25 °C): 11.65 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 17.91 (backbone CH_3), 22.48 ($\text{NHCH}_2\text{CH}_2\text{CH}_3$), 30.64 (terminal CH_3), 41.59 (backbone CH_2), 44.01 ($\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$), 51.18 ($\text{CH}(\text{OH})\text{CH}_2$), 52.17 ($\text{NHCH}_2\text{CH}_2\text{CH}_3$), 58.37 ($\text{SCH}_2\text{C}_6\text{H}_5$), 66.93 ($\text{CH}(\text{OH})$), 126.75 (aromatic CH (DMPP)), 128.37 (aromatic CH), 128.81 (aromatic CH), 131.27 (aromatic CH (DMPP)), 176.78 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3302 (m, OH/NH), 2958 (m, CH sp^3), 1722 (s, $\text{C}=\text{O}$), 1618 (N-H bend), 1454 (m), 1384 (m), 1261 (m, C-N), 1149 (s, C-O), 991 (m), 933 (m), 862 (m), 804 (m), 749 (m), 701 (m)

GPC: M_n 3900, M_w 4800, PDI 1.2

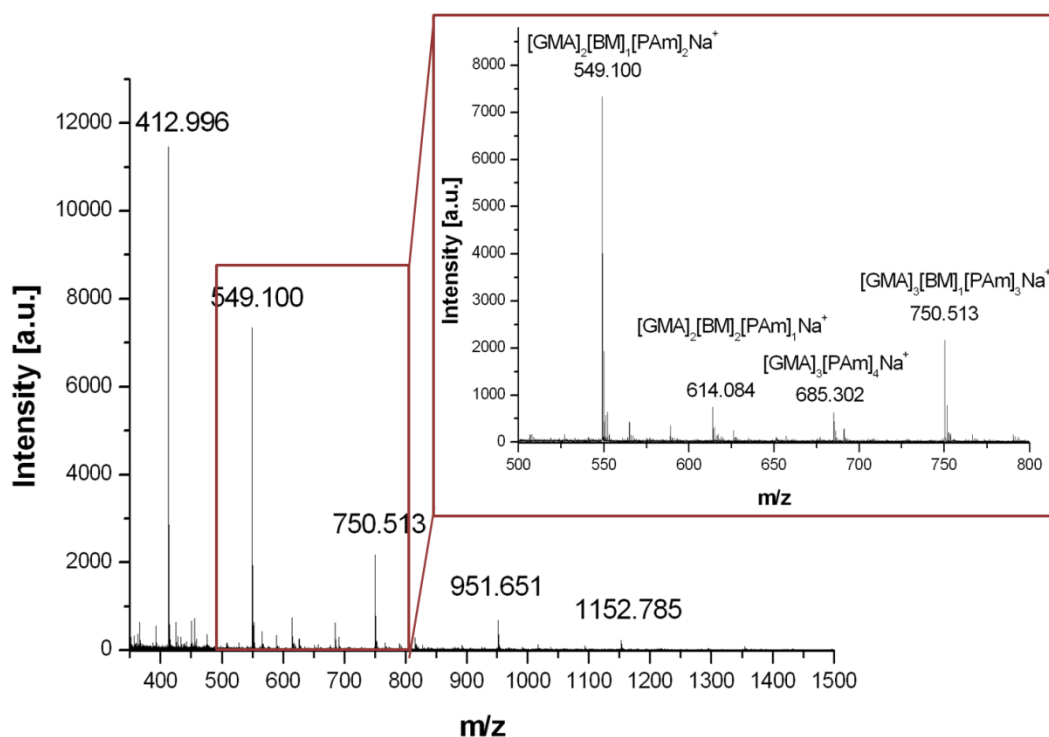


Figure 6: MALDI-ToF spectrum of dual functionalised poly-GMA (A), thio-Michael addition of benzyl mercaptan with subsequent epoxide ring-opening with propylamine, BM=benzyl mercaptan, PAm=propylamine

Benzyl Mercaptan, Diethylamine Functionalised Poly-GMA (A and B)

^1H NMR (400 MHz, TMS at 25 °C): 0.70-0.85 (br, backbone CH_3), 0.85-1.05 (br, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 1.05-1.15 (m, terminal CH_3), 1.70-2.05 (br, backbone CH_2), 2.30-2.45 (br, $\text{CH}(\text{OH})\text{CH}_2\text{NH}$, $\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$), 2.45-2.65 (br, $\text{N}(\text{CH}_2\text{CH}_3)_2$), 3.45-3.55 (br, $\text{SCH}_2\text{C}_6\text{H}_5$), 3.55-3.85 (m, COOCH_2), 3.85-4.15 (br, $\text{CH}(\text{OH})$), 7.20 (m, aromatic CH), 7.50-7.60 (m, aromatic CH (DMPP)), 7.75-7.85 (m, aromatic CH (DMPP))

^{13}C NMR (100 MHz CDCl_3 at 25 °C): 11.62 ($(\text{NCH}_2\text{CH}_3)_2$), 17.91 (backbone CH_3), 23.73 (terminal CH_3), 44.07 ($\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$), 45.13 (backbone CH_2), 47.06 ($\text{N}(\text{CH}_2\text{CH}_3)_2$), 55.88 ($\text{CH}(\text{OH})\text{CH}_2\text{NH}$), 60.63 ($\text{SCH}_2\text{C}_6\text{H}_5$), 66.23 ($\text{CH}(\text{OH})$), 67.32 (COOCH_2), 126.72 (aromatic CH (DMPP)), 128.33 (aromatic CH), 128.81 (aromatic CH), 129.58 (aromatic CH (DMPP)), 177.04 (carbonyl)

IR: ν_{max} (neat)/ cm^{-1} 3385 (m, OH/NH), 2968 (m, CH sp^3), 1724 (C=O), 1601 (N-H bend), 1453 (m), 1385 (m), 1245 (m, C-N), 1151 (s, C-O), 1063 (m), 993 (m), 934 (m), 805 (m), 767 (m), 702 (m)

GPC (DMF eluent): Thio-Michael addition to poly-GMA (A) with subsequent epoxide ring-opening: M_n 7300, M_w 11400, PDI 1.6: Epoxide ring-opening of poly-GMA (B) with subsequent thio-Michael addition: M_n 11600, M_w 18100, PDI 1.6

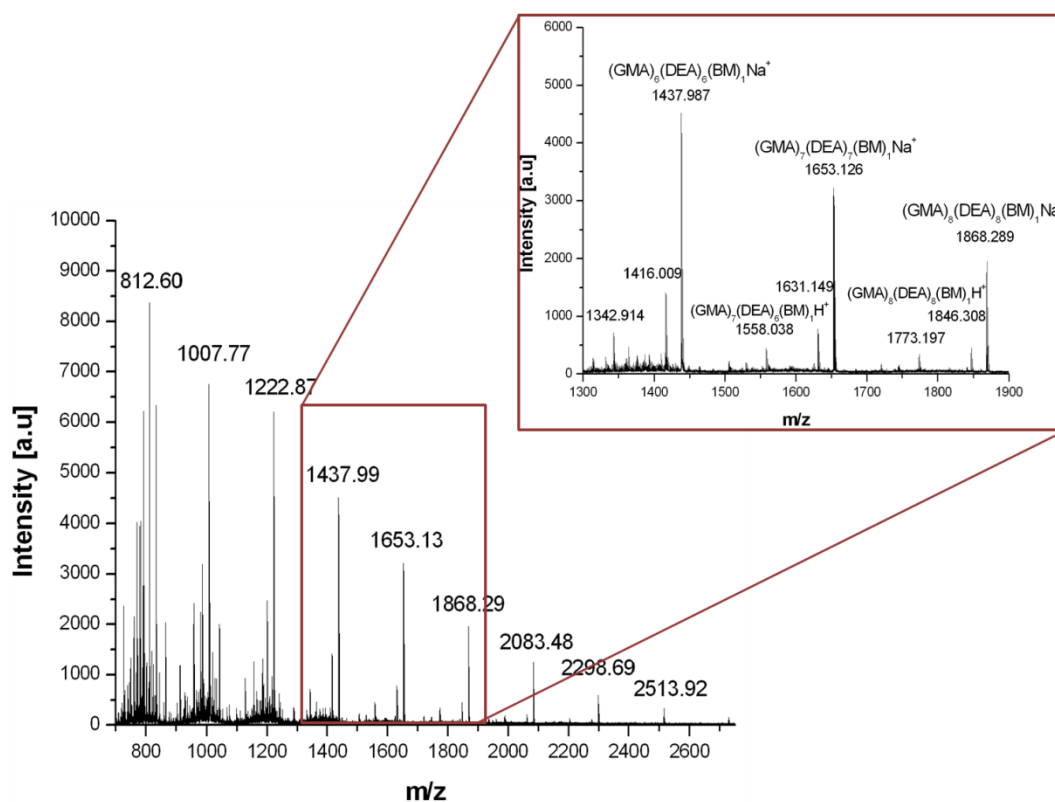


Figure 7: MALDI-TOF spectrum of dual functionalised poly-GMA (B), epoxide ring-opening with diethylamine, subsequent thio-Michael addition with benzyl mercaptan, BM=benzyl mercaptan, DEA=diethylamine

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