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Fast Track Access to Multi-Block Copolymers *via* Thiol-Bromo Click Reaction of Telechelic Dibromo Polymers

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Materials

All solvents and chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. Tris[2-(dimethylamino)ethyl]-amine (Me_6TREN) was synthesized according to a literature procedure (Ciampolini, M.; Nardi, N., Inorg. Chem. 1966, 5 (1), 41-44) and stored at 4 °C. Inhibitor/stabiliser containing monomers were filtered over a short column of basic alumina prior to use.

Instruments

Nuclear magnetic resonance. Nuclear magnetic resonance spectra were recorded on a Bruker AV-III 400 MHz for ^{1}HNMR. $CDCl_3$ was used as solvent and the resonance signal of residual $CHCl_3$ at 7.26 ppm served as reference for the chemical shift, δ. For DMSO-*d*6, the resonance signal of residual DMSO at 2.50 ppm.

Gel permeation chromatography (GPC) measurements were conducted on an Agilent 1260 infinity system operating in THF with 2% TEA and equipped with refractive index detector and variable wavelength detector, 2 PLgel 5 μm mixed-C columns (300 × 7.5 mm), a PLgel 5 mm guard column (50 × 7.5 mm) and an autosampler. The instrument was calibrated with linear narrow PMMA standards. All samples were filtered through 0.2 μm PTFE filters before analysis.

Matrix-assisted laser desorption ionisation-time of flight mass spectrometry (MALDI TOF MS) was performed on a Bruker Autoflex Speed mass spectrometer using a nitrogen laser delivering 2 ns pulses at 337 nm with positive ion ToF detection performed using an accelerating voltage of 25 kV. The matrix used was trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB) dissolved in THF. Sodium trifluoroacetate used as a cationic agent (solution in acetonitrile). The compound (diluted in THF) was applied after separate loadings of DCTB and sodium trifluoroactetate. Samples were measured in reflective or linear mode and calibrated against poly(methyl methacrylate) standards.

Experimental

Synthesis of difunctional initiator: Ethylene bis(2-bromoisobutyrate) (2f-BiB)

In a round bottom flask, ethylene glycol (1.00 equiv.) and triethylamine (5.00 equiv.) were dissolved in anhydrous dichloromethane (DCM) and cooled to 0 °C. To this, a solution of α-bromoisobutyryl bromide (5.00 equiv.) in anhydrous DCM was added via a dropping funnel. The reaction mixture was allowed to stir at ambient temperature for 15 hours, before filtration of the formed solids. The crude was washed with brine followed by saturated potassium carbonate solution (2x) and dried over magnesium sulphate. The obtained yellowish oil was purified by flash chromatography on silica (ethyl acetate/hexanes = 1:5) and recrystallised from cold acetone to receive 2f-BiBas a white crystalline solid.

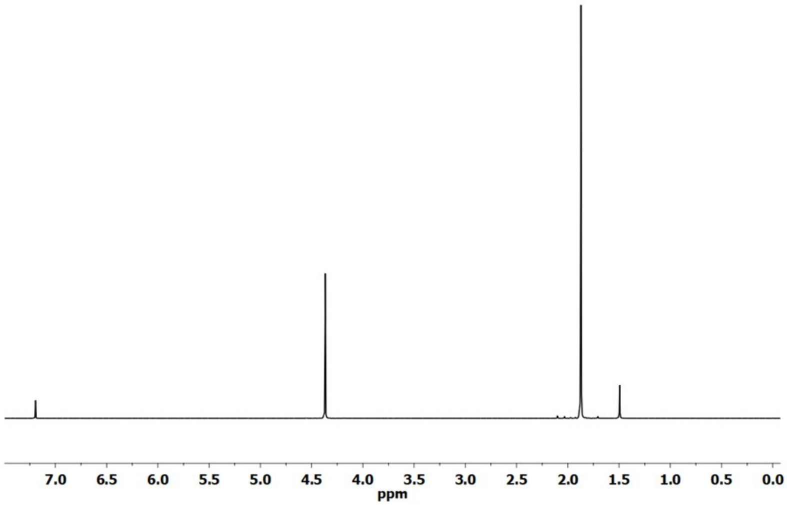


Figure S1: ^{1}H NMR spectrum of 2f-BiBbisinitiator.

General procedure for Cu(0)-mediated RDRP of acrylates and bisthiol step growth in organic solvents

Stage 1

Monomer 1 (equivalents = desired DP), 2f-BiB(1.00 equiv.), Me_6TREN (0.36 equiv.), $CuBr_2$ (0.10 equiv.) and DMSO (50% v/v) were charged to a *Schlenk* tube and sealed with a rubber septum. After degassing the reaction mixture for 30 minutes, a stirring bar wrapped with pre-activated copper wire (7 cm, diameter = 0.25 mm) was added to the reaction mixture in a countercurrent of nitrogen. The tube was sealed again and the reaction mixture stirred at 25 ^{o}C until full conversion was observed (between 4 and 12 hours). Conversion was measured by ^{1}H NMR spectroscopic analysis and SEC analysis was carried out with samples diluted in THF which were filtered over basic alumina prior to analysis to remove residual copper species. The polymerisations in TFE and IPA were carried out under the same conditions.

Stage 2

Monomer 2 in DMSO (50% v/v) and another portion of Me_6TREN (0.36 equiv.) and $CuBr_2$ (0.10 equiv.) were added into a glass vial and degassed for 30 minutes before transferring to the reaction mixture. The tube was sealed again and the reaction mixture stirred at 25 ^{o}C until full conversion was observed.

Stage 3

After full monomer conversion, a solution of bisthiol (1.00 equiv.) and triethylamine (excess) in DMF was added at ambient temperature to the reaction mixture. The mixture was then stirred overnight at room temperature before SEC analysis was carried out. The crude product was purified by filtration over basic alumina followed by precipitation from cold methanol to provide the pure polymer as a yellowish oil. The polymer obtained was characterised by ^{1}H NMR spectroscopic analysis and GPC (THF +2% TEA) equipped with RI and UV detectors.

Cu(0)-mediated RDRP of methyl methacrylate and bisthiol step growth

In a *Schlenk* tube, methyl methacrylate (20 equiv.), 2f-BiB(1.00 equiv.), *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) (0.72 equiv.) and $CuBr_2$ (0.10 equiv.) were dissolved in isopropanol (IPA) and degassed for 30 minutes. In an oilbath, the reaction mixture was heated to 40 °C before a stirring bar wrapped with pre-activated copper wire (5 cm) was added in a countercurrent of nitrogen.

After full monomer conversion (10 h), a degassed solution of 4,4′-thiobisbenzenethiol (1.00 equiv.) dissolved in DMF was added to the polymerisation mixture in a countercurrent of nitrogen and the reaction was allowed to stir for additional 8 hours. The obtained mixture was filtered over a column with basic aluminium oxide and purified by dialysis against acetone. The pure product was analysed by ^{1}H NMR spectroscopic analysis and SEC (THF+2%TEA) ($M_{\mathrm{n,GPC}}$ = 13 600, $Đ$ = 1.39).

General procedure for H_2O_2-mediated degradation of thioether-linked polymers

In a glass vial, the thioether-linked polymer (50 mg) was dissolved in 3 mL of THF. After addition of an excess of 0.75 mL H_2O_2 (30% in H_2O), the sealed reaction mixture was heated to the desired temperature 37 °C or 60 °C in an oil bath. Samples were taken at desired time points with a plastic syringe and analysed by SEC (THF + 2% TEA).

Thermal decomposition of thioether-linked polymers

In a glass vial, the thioether-linked polymer was dissolved in toluene or dodecane to obtain a 1 w% polymer solution. The reaction vial was sealed and placed in an oil bath at 120 °C. Samples were taken at desired time points with a plastic syringe and analysed by SEC (THF + 2% TEA).

General procedure for 3-chloroperbenzoic acid (MCPBA)-mediated degradation of thioether-linked polymers

In a glass vial, the thioether-linked polymer (25 mg) was dissolved in 2 mL of chloroform. After addition of an excess of 10 mg MCPBA, the sealed reaction mixture was stirred at ambient temperature. Samples were taken at desired time points with a plastic syringe and analysed by SEC (THF + 2% TEA).

MCPBA-mediated oxidative degradation of thioether-linked polymers in NMR tube

In an NMR tube, 20 mg of polymer **MB1** were placed. The thioether decomposition was induced by addition of 20 mg MCPBA dissolved in 1.5 mL deuterated chloroform. The reaction mixture was placed on a shaker and mixed at ambient temperature. ^{1}H NMR measurements were carried out at desired time points to monitor the decomposition.

Treatment of thioether-linked polymers with methyl trifluoromethanesulfonate (MeOTf)

Under a nitrogen atmosphere, 100 mg of thioether-linked polymer **MB14** were dissolved in 2 mL anhydrous dichloromethane. In a degassed syringe, 0.20 mL of MeOTf were added and the reaction mixture was stirred at room temperature. Samples were taken at desired time points with a plastic syringe and analysed by SEC (THF + 2% TEA).

SEC of MBCs derived from homopolymers

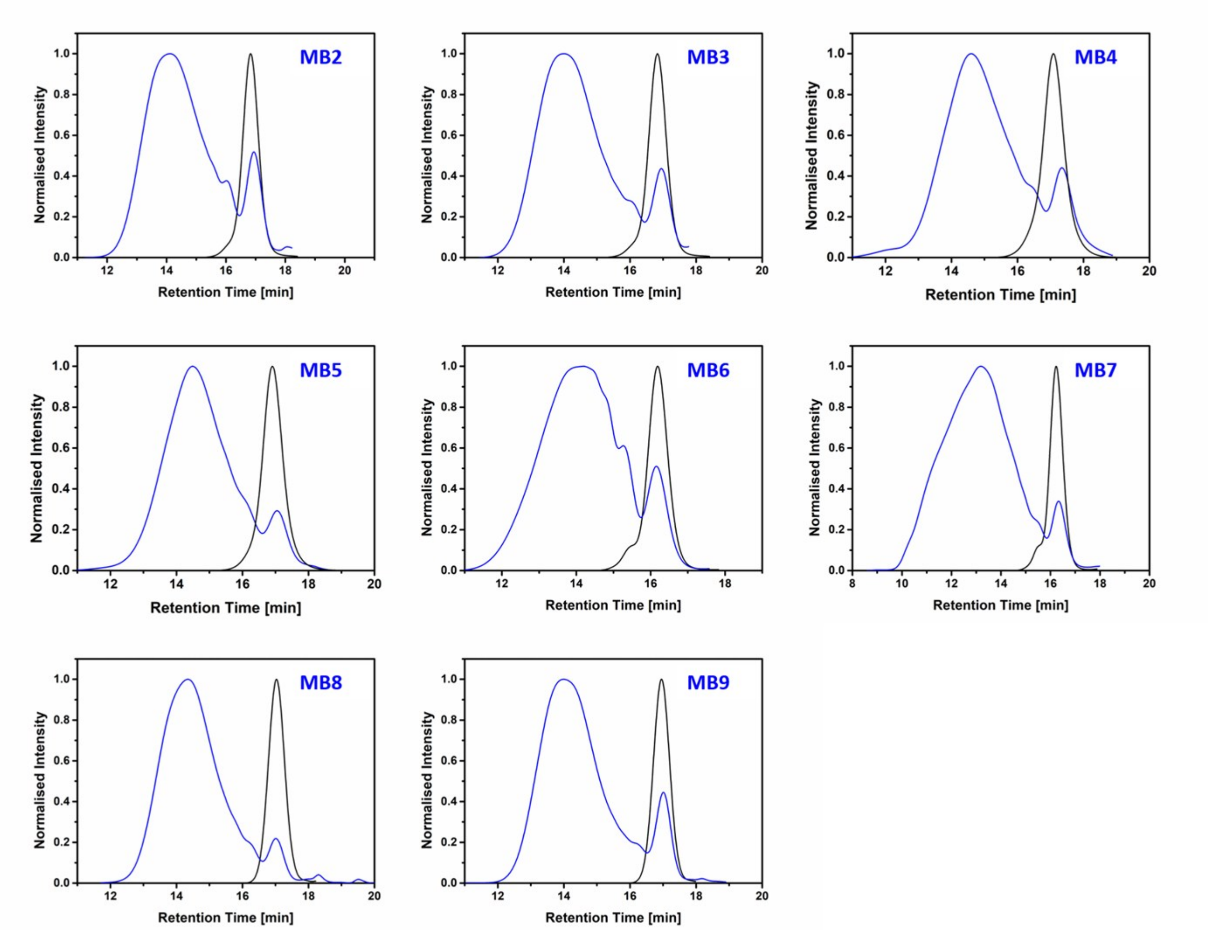


Figure S2: SEC results of step-growth polymers from PEA (**MB2-MB5**), DEGA (**MB6-MB7**) and PEHA (**MB8-MB9**) (RI detection)

SEC of MBCs derived from amphiphilic copolymers

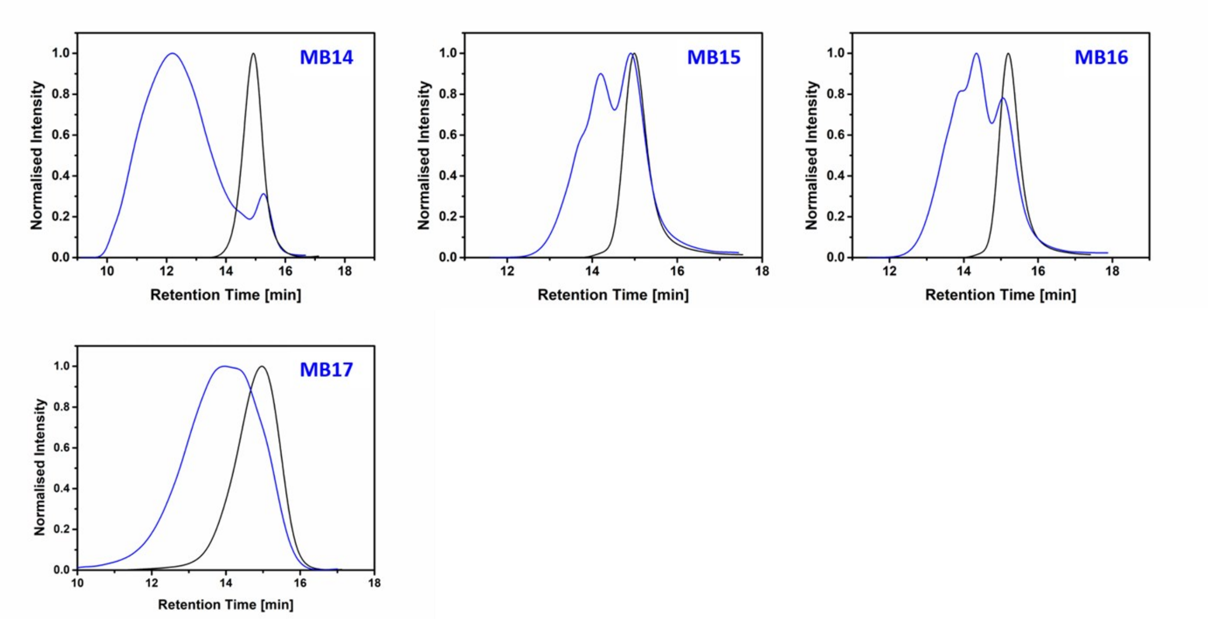


Figure S3: SEC results of step growth polymers from PEGA-EHA copolymers (**MB14-MB16**) and DEGA-EHA copolymers (**MB17**) (RI detetction).

Oxidative degradation of MB13 at 37 °C in H_2O_2 (30%)

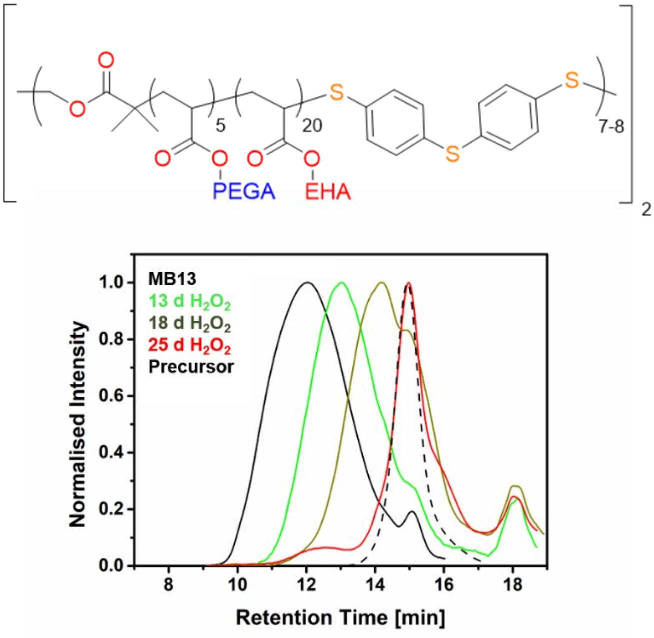
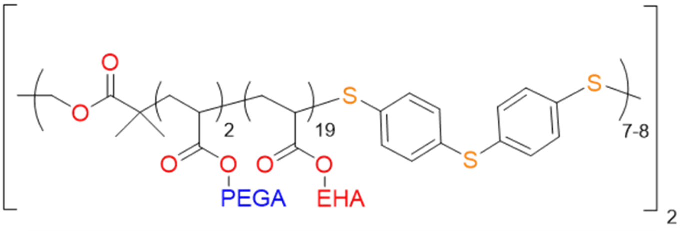


Figure S4: SEC traces of H_2O_2 induced oxidative degradation of periodic multiblock copolymer **MB13** at 37 °C linked with aromatic dithiol BPT-BT over 25 days (RI detection)

SEC analysis of MB14 upon treatment with MeOTf at ambient temperature



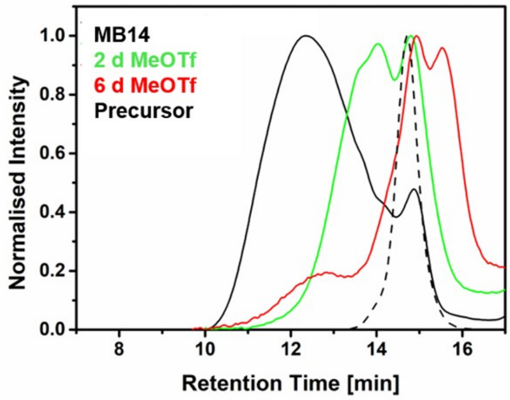


Figure S5: SEC traces of methyl triflate induced decomposition of amphiphilic multiblock copolymer **MB14** at ambient temperature (RI detection).

MALDI ToF MS studies on multiblock copolymers

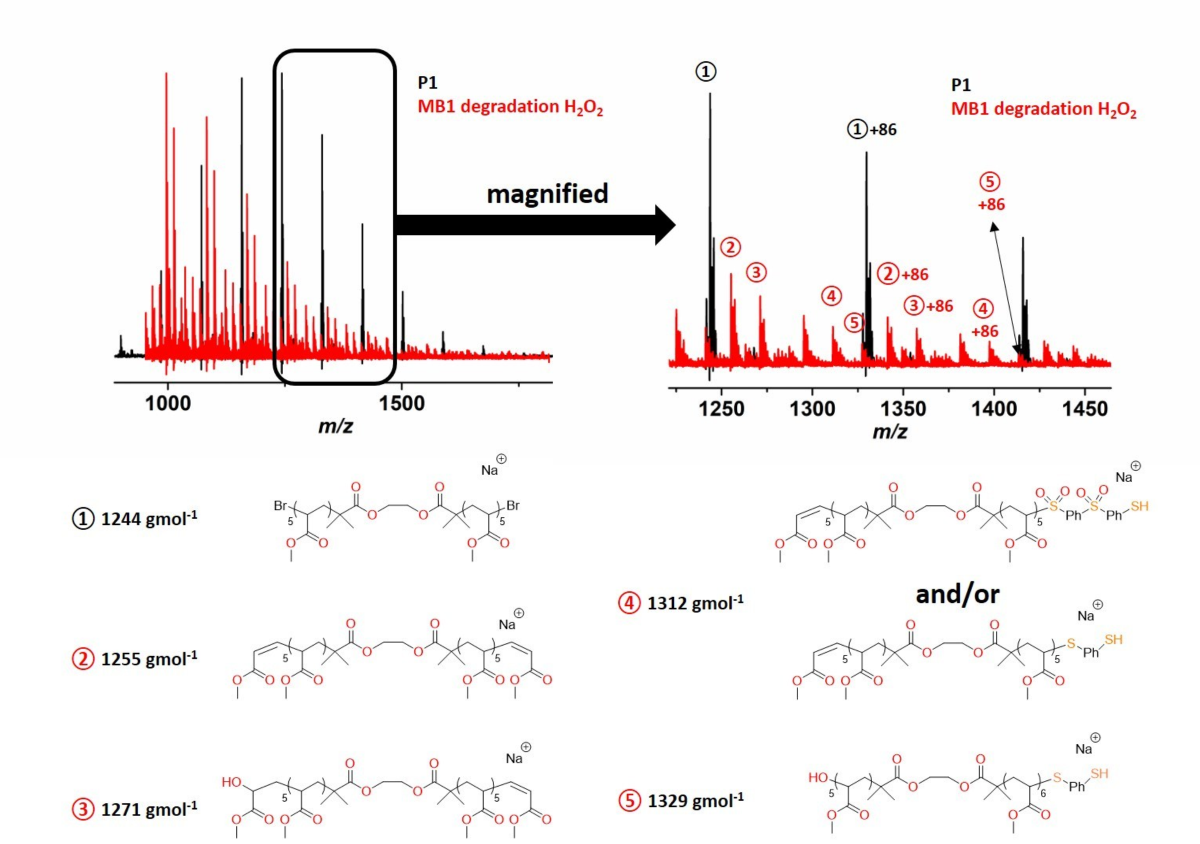


Figure S6: MALDI-ToF MS analysis of H_2O_2-induced degradation of **MB1** with proposed assignments.

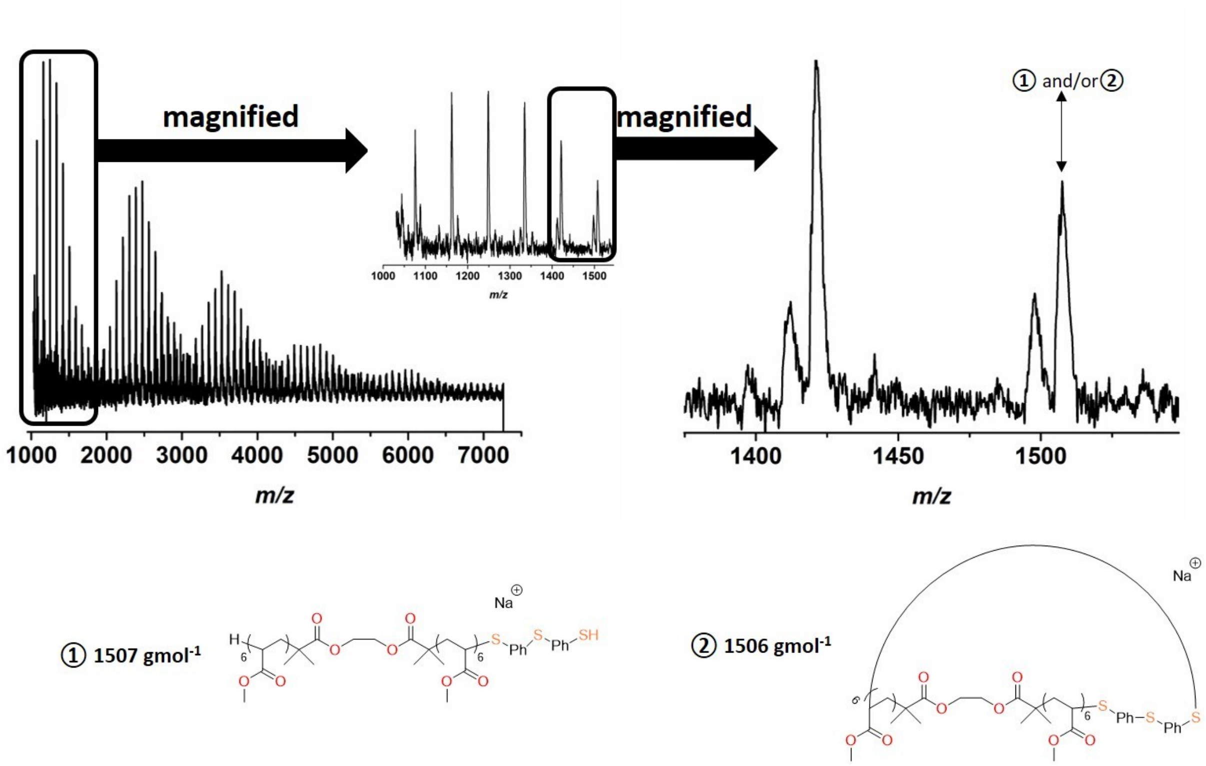


Figure S7: MALDI-ToF MS analysis of thiol-bromo step growth reaction of **P1** into **MB1** with proposed assignments.