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Copper(II) gluconate (a non-toxic food supplement/dietary aid) as a precursor catalyst for effective photo-induced living radical polymerisation of acrylates

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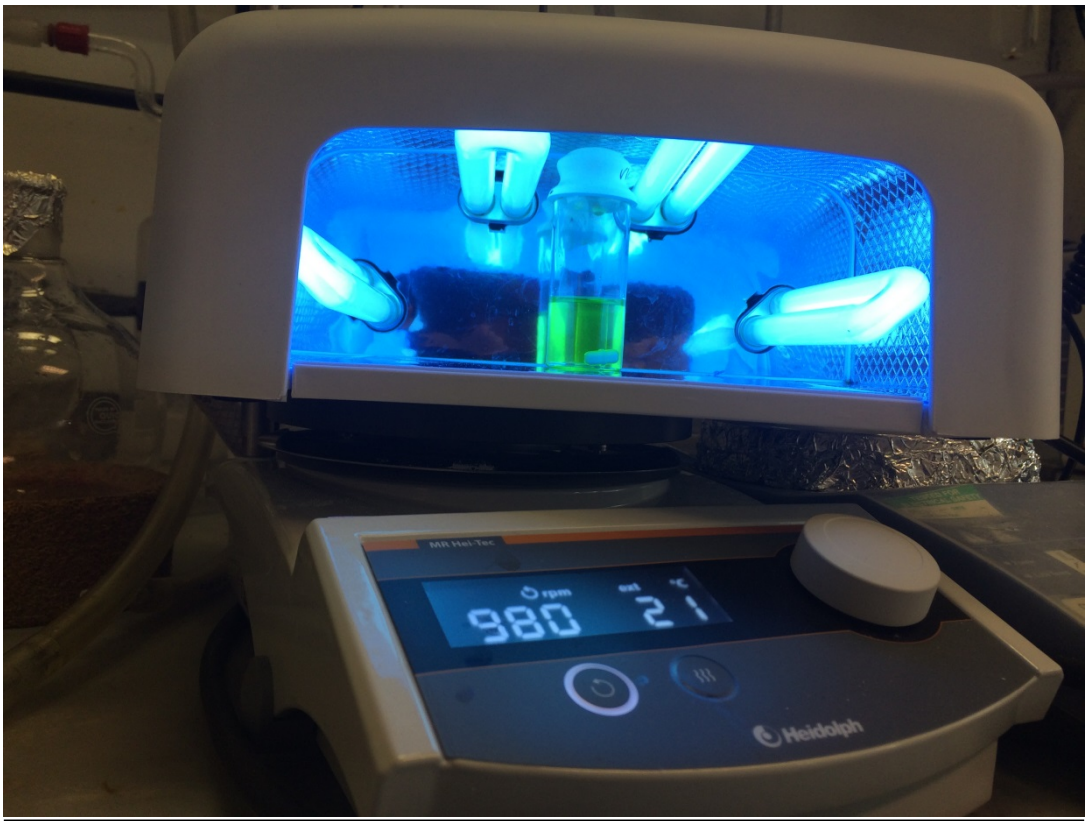


Figure S1: Typical set up for **photo-induced** polymerisation.

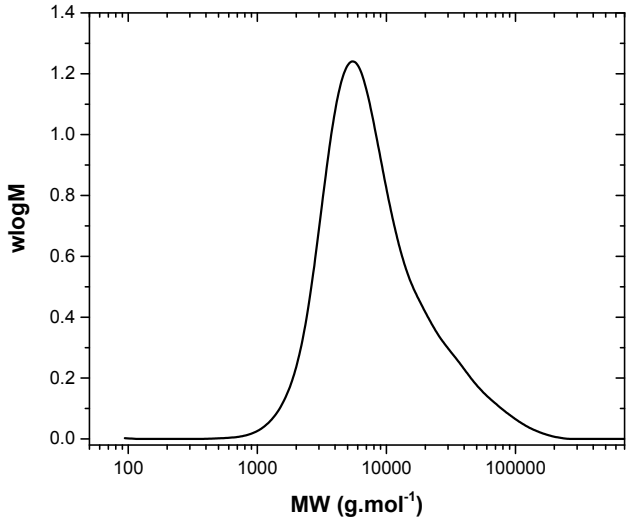


Figure S2: Molecular weight distribution of poly(methyl acrylate), M_n= 5500g/mol; $Đ$ = 2.30; 96% conversion. [MA]:[EBiB]:[**Cu$^{(II)}$ gluconate (tablet)**]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*.

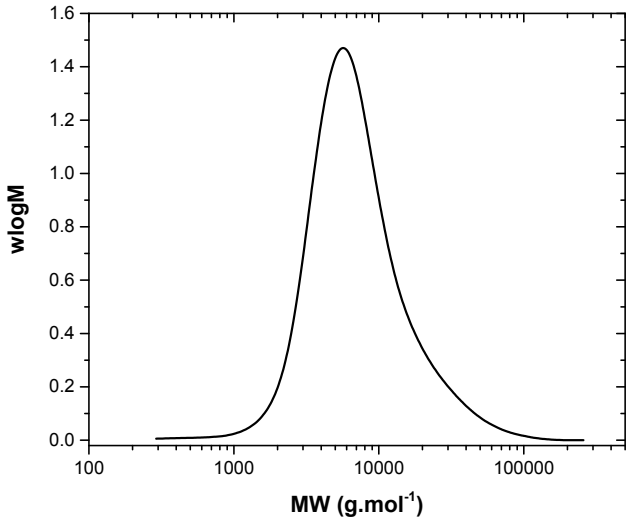


Figure S3: Molecular weight distribution of poly(methyl acrylate), M_n= 5400g/mol; $Đ$ = 1.80; 98% conversion. [MA]:[EBiB]:[**Cu$^{(II)}$ gluconate (pure)]:[**Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*.

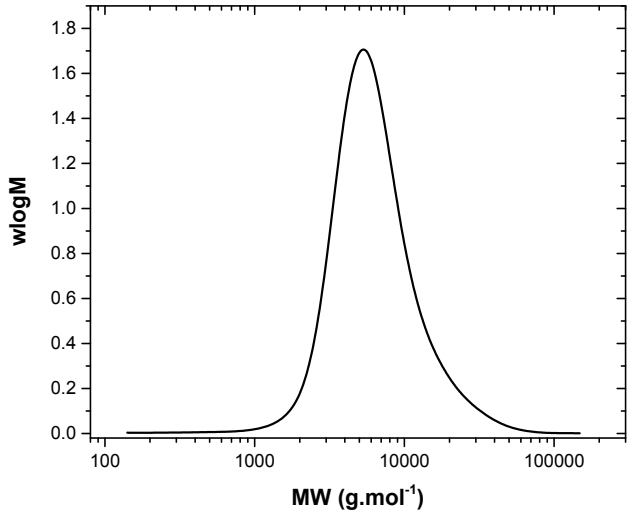


Figure S4: Molecular weight distribution of poly(methyl acrylate), M_n= 5000g/mol; $Đ$ = 1.50; 98% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h**.

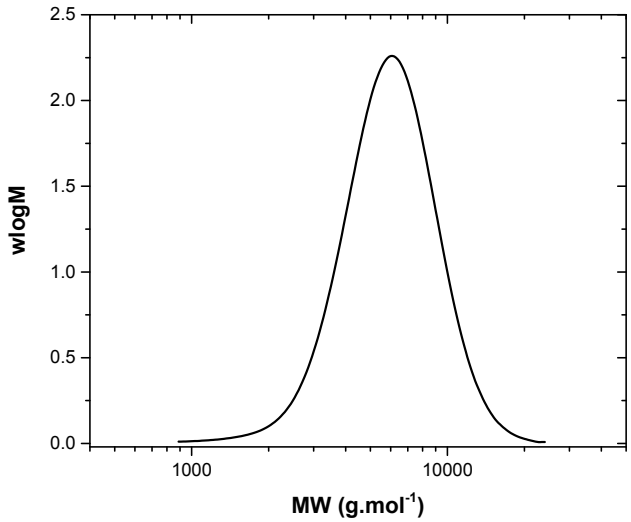


Figure S5a: Molecular weight distribution of poly(methyl acrylate), M_n= 5500g/mol; $Đ$ = 1.19; 96% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 weeks**.

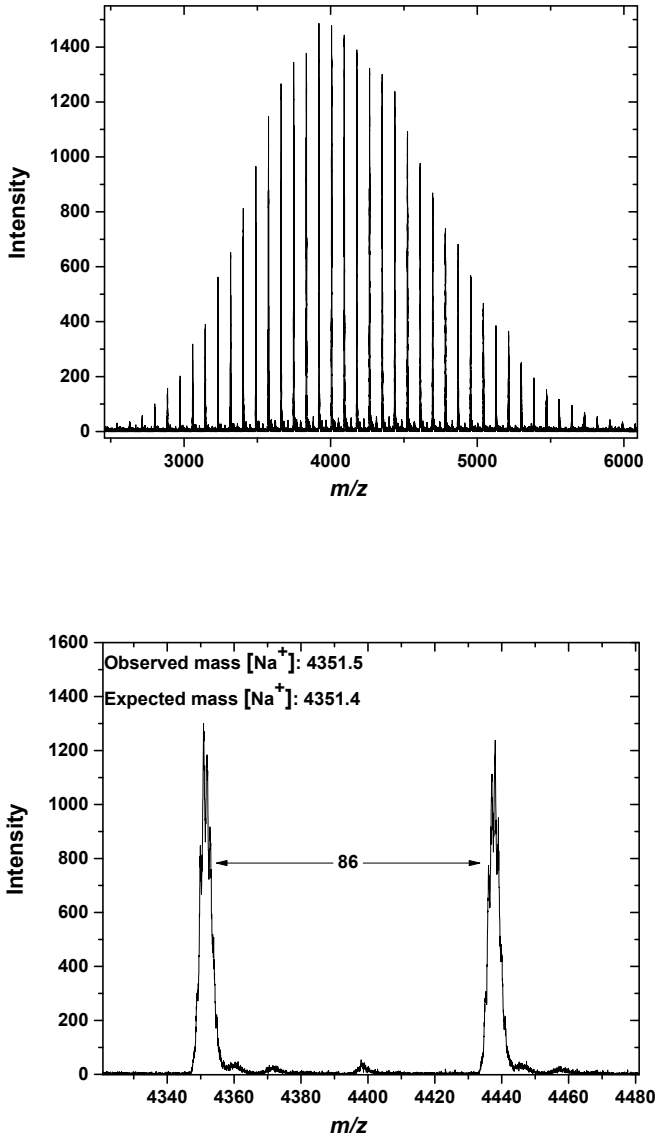


Figure S5b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate),obtained from photo-mediated polymerisation: [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 weeks**.

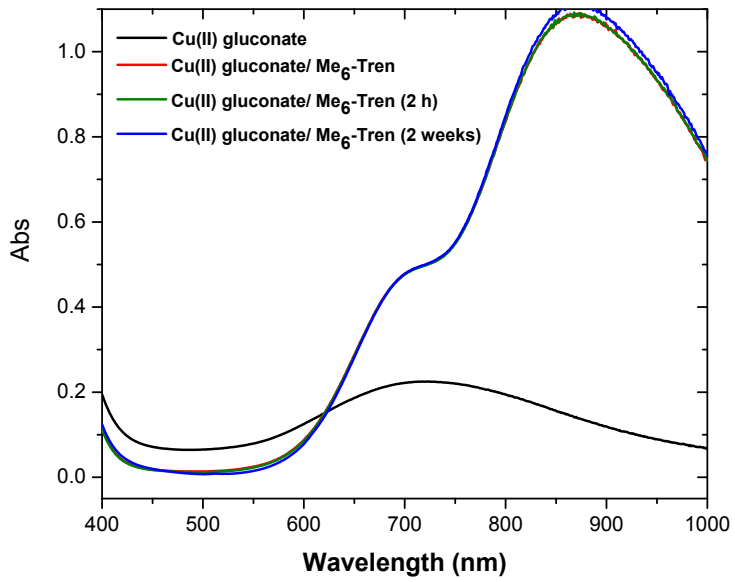


Figure S5c: Monitoring effect of UV irradiation on $Cu^{(II)}$ gluconate/Me_6-Tren in DMSO complex as a function of time by **UV−vis spectroscopy**.

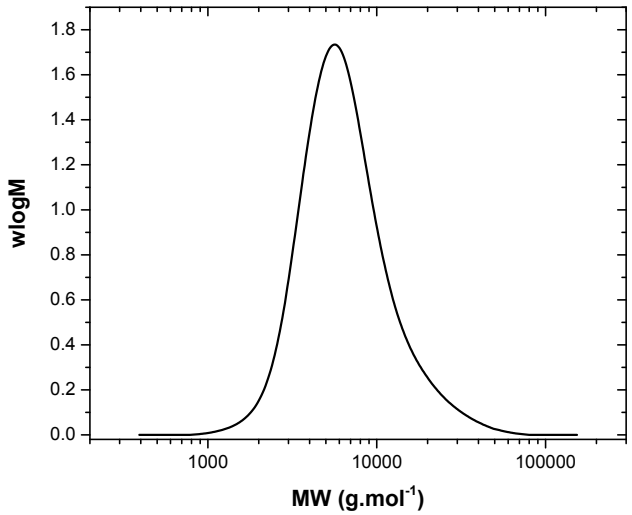


Figure S6: Molecular weight distribution of poly(methyl acrylate), M_n= 5400g/mol; $Đ$ = 1.38; 97% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 1 week**.

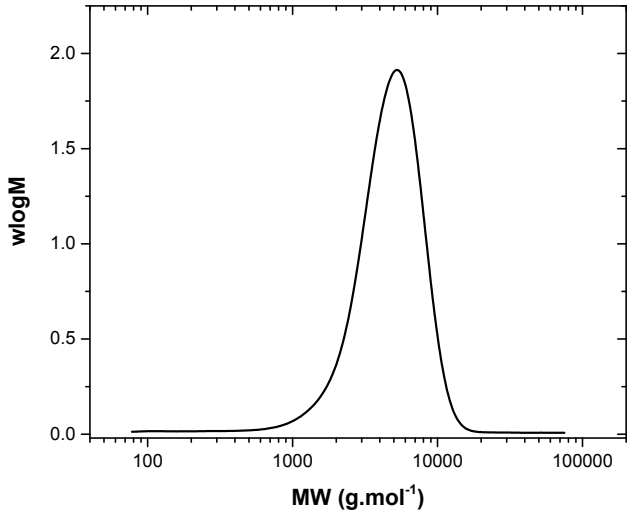
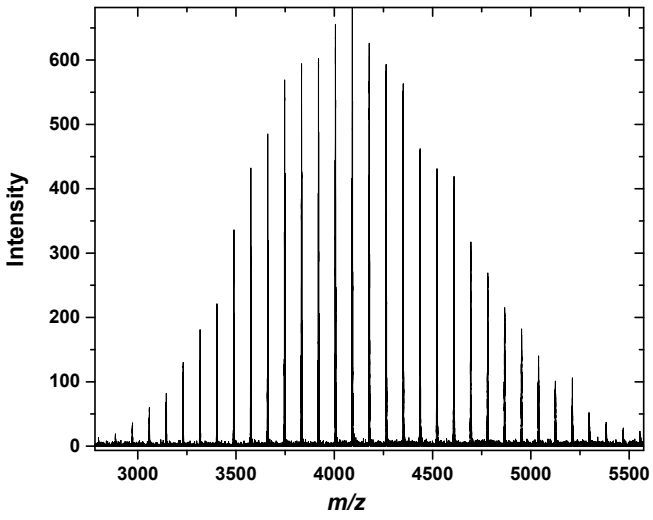


Figure S7a: Molecular weight distribution of poly(methyl acrylate), M_n= 4900g/mol; $Đ$ = 1.15; 97% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h under UV irradiation**.



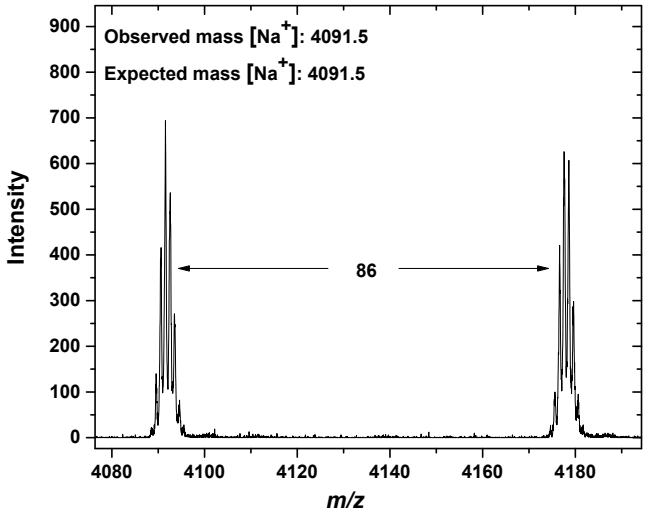


Figure S7b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate), obtained from the photo-mediated polymerisation*:* [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h under UV irradiation**.

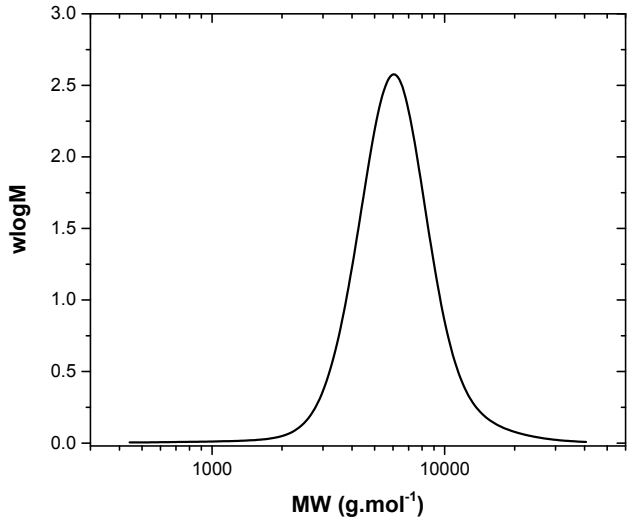


Figure S8a: Molecular weight distribution of poly(methyl acrylate), M_n= 5600g/mol; $Đ$ = 1.16; 98% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h under UV irradiation.**

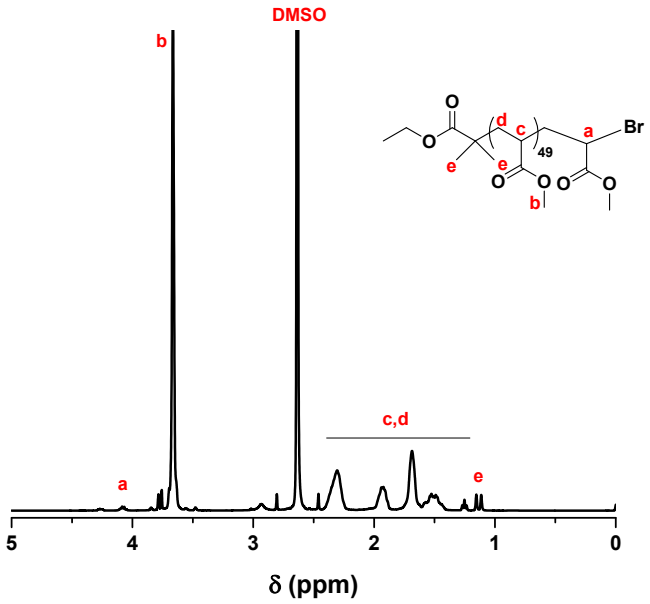


Figure S8b: ^{1}H NMR (400MHz, $CDCl_3$) of poly(methyl acrylate) obtained from UV experiment: [MA]:[EBiB]:[$Cu^{(II)}$ gluconate]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*.

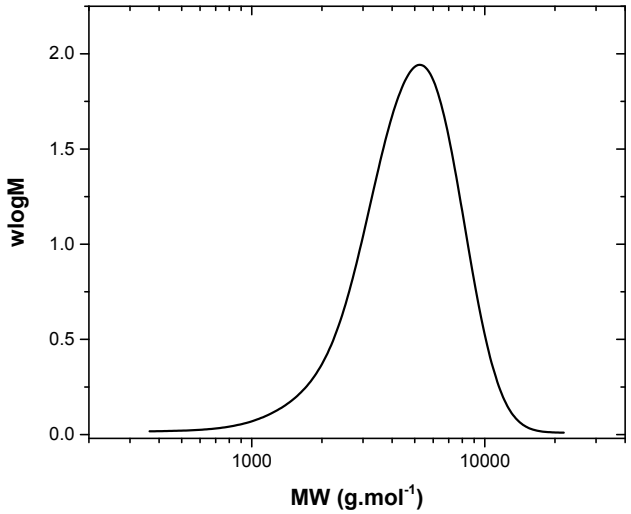


Figure S9: Molecular weight distribution of poly(methyl acrylate), M_n= 3900g/mol; $Đ$ = 1.33; 70% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h under UV irradiation at 15 °C**.

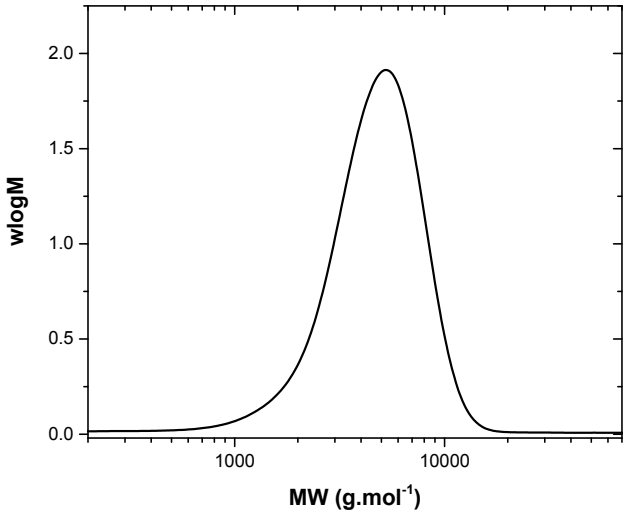


Figure S10: Molecular weight distribution of poly(methyl acrylate), M_n= 4200g/mol; $Đ$ = 1.40; 75% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h under UV irradiation at 15 °C**.

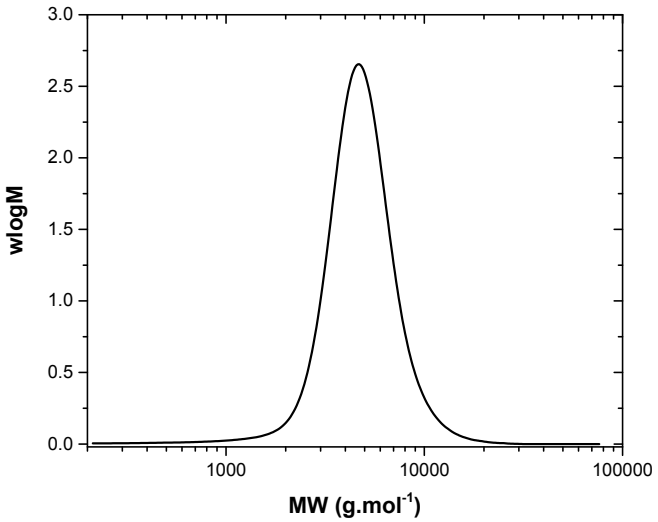


Figure S11a: Molecular weight distribution of poly(methyl acrylate), M_n= 4300g/mol; $Đ$ = 1.18; 90% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h at 60 °C**.

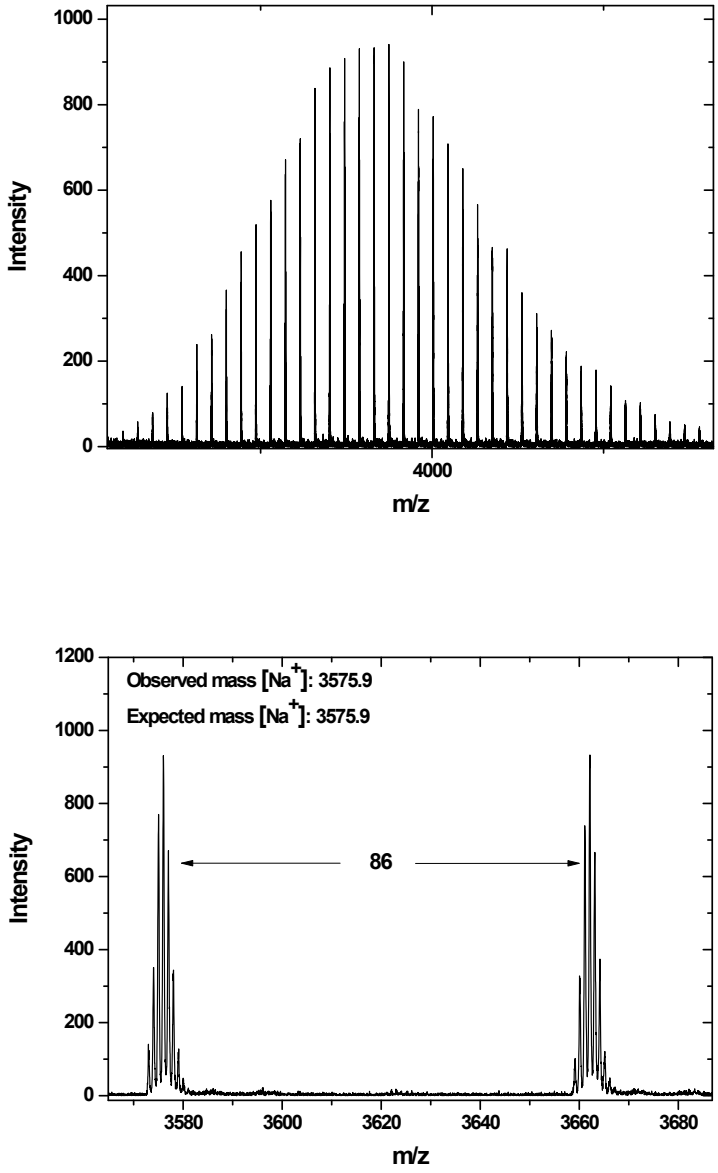


Figure S11b: MALDI-ToF-MS reflectron mode spectrum, of poly(methyl acrylate), obtained for the photo-mediated polymerisation: [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h at 60 °C**.

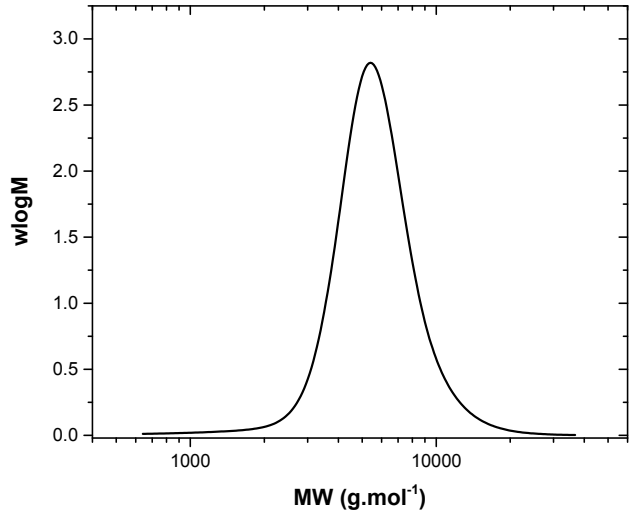
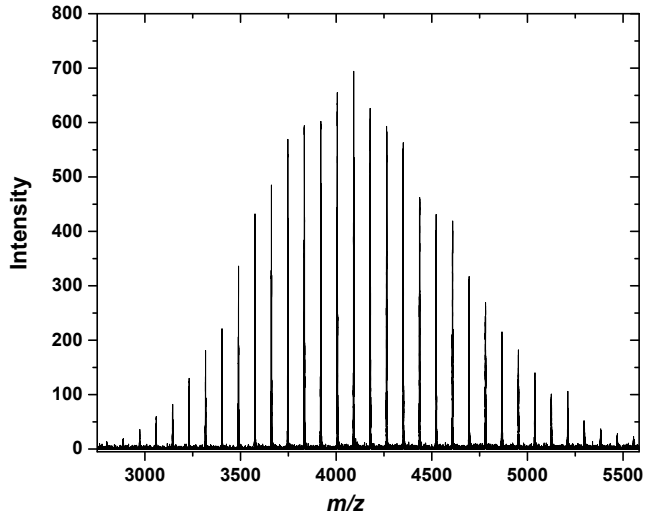


Figure S12a: Molecular weight distribution of poly(methyl acrylate), M_n= 5200g/mol; $Đ$ = 1.19; 95% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h at 60 ºC**.



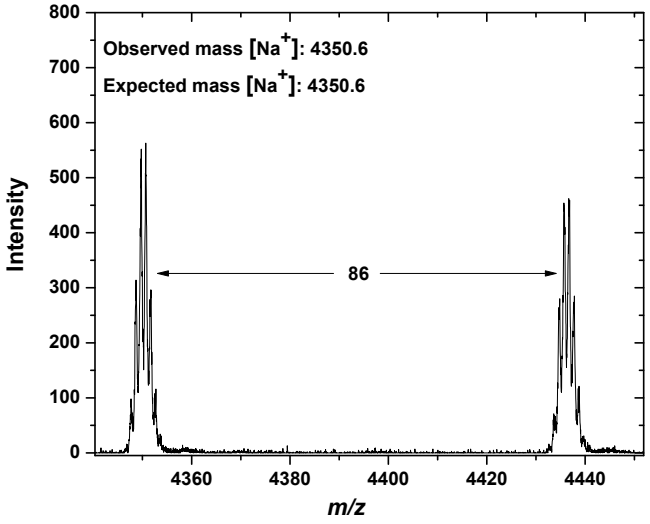


Figure S12b: MALDI-ToF-MS reflectron mode spectrum, of poly(methyl acrylate), obtained for the photo-mediated polymerisation: [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren] = [50]:[1]:[0.02]:[0.12] in DMSO 50% *v/v*, **pre-mixing of the $Cu^{(II)}$ gluconate/Me_6-Tren complex for 2 h at 60 °C**.

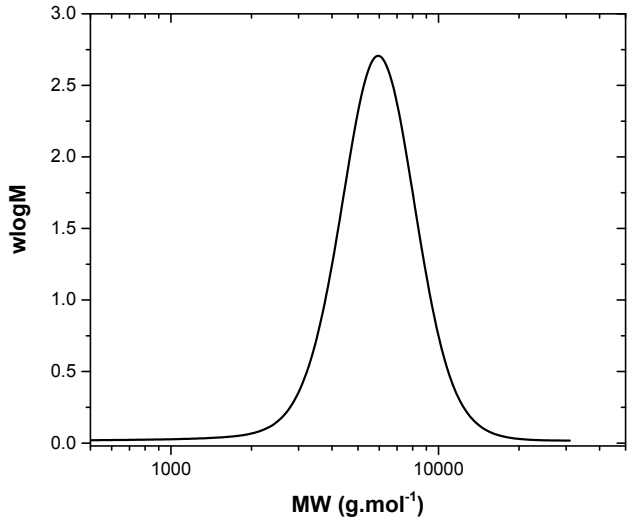


Figure S13a: Molecular weight distribution of poly(methyl acrylate), M_n= 5400g/mol; $Đ$ = 1.15; 99% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren]:[**NaBr**] = [50]:[1]:[0.02]:[0.12];[0.04] in DMSO 50% *v/v*.

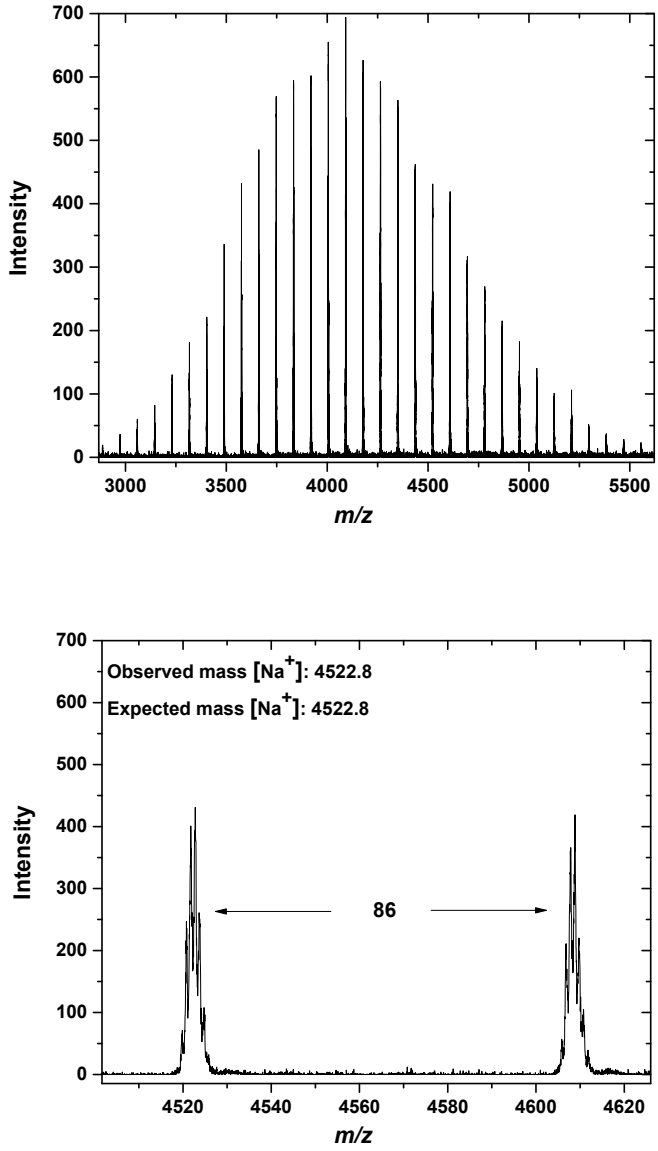


Figure S13b: MALDI-ToF-MS reflectron mode spectrum, of poly(methyl acrylate), obtained for the photo-mediated polymerisation: [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren]:[**NaBr**] = [50]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% *v/v*.

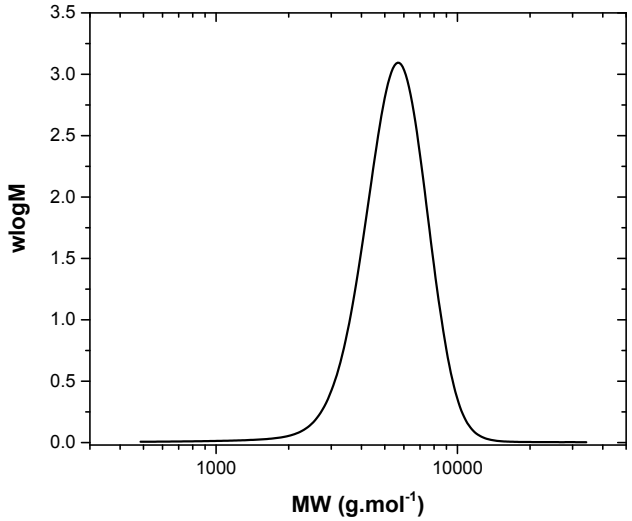
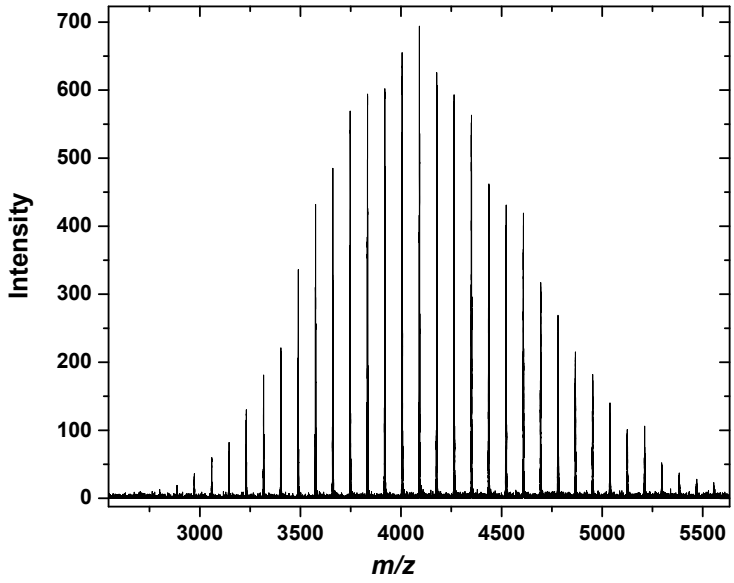


Figure S14a: Molecular weight distribution of poly(methyl acrylate), M_n= 5100g/mol; $Đ$ = 1.12; 98% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren]:[**NaBr**] = [50]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% *v/v*.



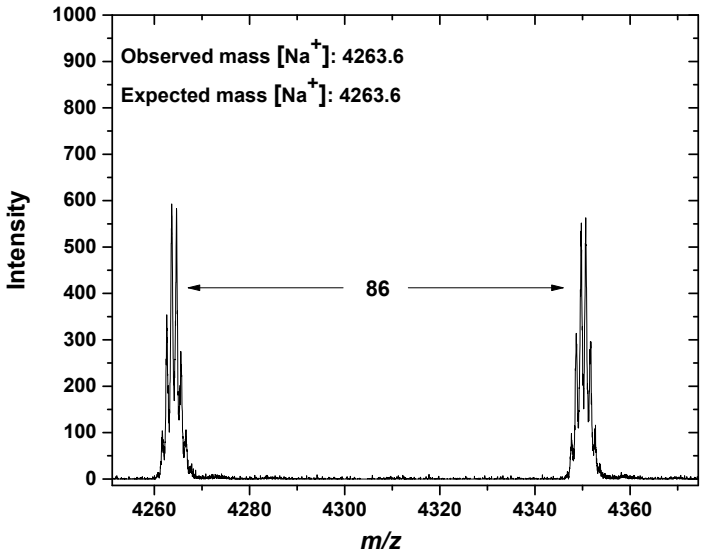


Figure S14b: MALDI-ToF-MS reflectron mode spectrum, obtained from the photo-mediated polymerisation: [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (pure)]:[Me_6-Tren]:[**NaBr**] = [50]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% *v/v*.

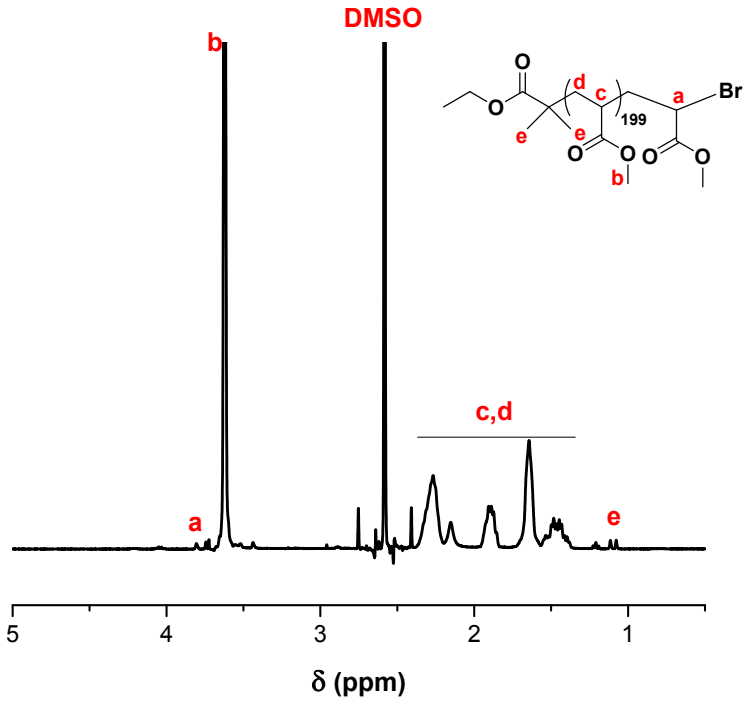


Figure S15: **^{1}H NMR** poly(methyl acrylate), 95% conversion. [MA]:[EBiB]:[$Cu^{(II)}$ gluconate (tablet)]:[Me_6-Tren]:[NaBr] = [**200**]:[1]:[0.02]:[0.12]:[0.04] in DMSO 50% *v/v*.

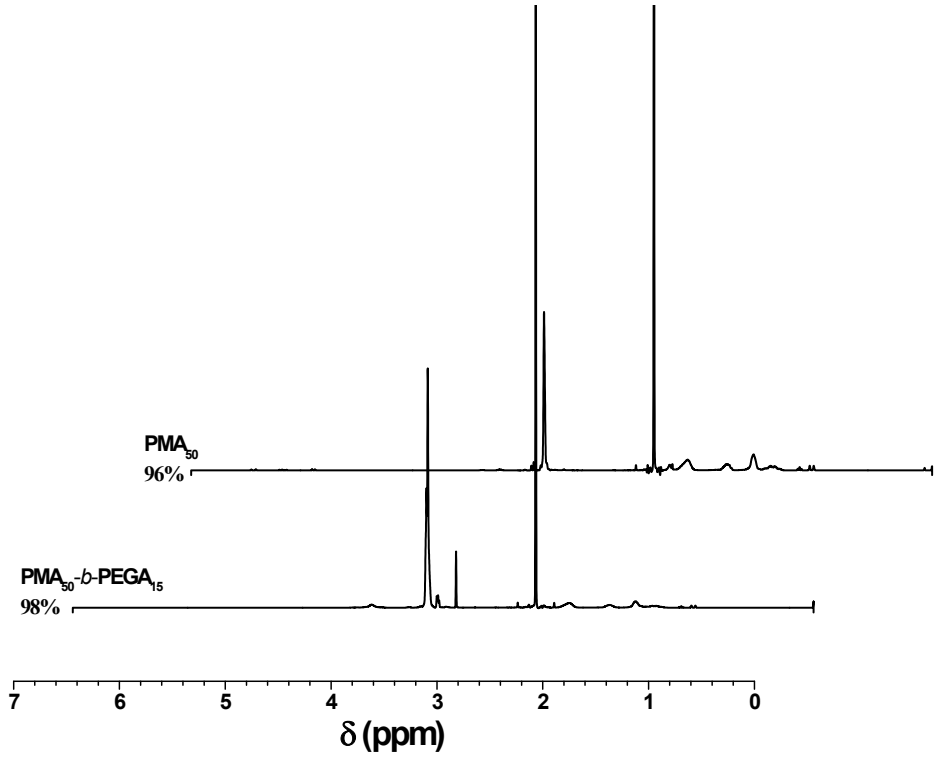


Figure S16: ^{1}H NMR for the block copolymerization from a PMA macroinitiator. Initial conditions: [MA]:[EBiB]:[Cu$^{(II)}$ gluconate (tablet)]:[Me_6-Tren]:[NaBr] = [50]:[1]:[0.02]:[0.12]:[0.04], DMSO (50%, *v/v*). Chain extension achieved upon addition of an aliquot of PEGA (15 equiv.) in DMSO (33%, *v/v*).

Experimental

Materials

All materials were purchased from Sigma Aldrich or Fisher Scientific unless otherwise stated. The dietary supplement (purchased on the internet from "BioCare" with a stated 1.1 mg Cu per poll (110% RDA)), the analytical pure copper$^{(II)}$ gluconate and ethyl 2-bromoisobutyrate (EBiB) were used as received. Methyl acrylate was passed through a basic Al_2O_3 chromatographic column prior to use. Tris-(2-(dimethylamino)ethyl)amine (Me_6-Tren) was synthesised according to previously reported literature.[1]

Apparatus

^{1}H NMR spectra were recorded on Bruker DPX-300 or DPX-400 spectrometers in $CDCl_3$ unless otherwise stated. Chemical shifts are given in ppm downfield from the internal

standard tetramethylsilane. Size exclusion chromatography (SEC) measurements were conducted using an Agilent 1260 SEC-MDS fitted with differential refractive index (DRI), light scattering (LS) and viscometry (VS) detectors equipped with 2 × PLgel 5 mm mixed-D columns (300 × 7.5 mm), 1 × PLgel 5 mm guard column (50 × 7.5 mm) and autosampler. Narrow linear poly(methyl methacrylate) standards in τηε range of 200 to 1.0 × 10^6 g·mol^{-1} were used to calibrate the system. All samples were passed through 0.45 μm PTFE filter before analysis. The mobile phase was chloroform with 2% triethylamine eluent at a flow rate of 1.0 mL/min. SEC data was analysed using Cirrus v3.3 software with calibration curves produced using Varian Polymer laboratories Easi-Vials linear poly(methyl methacrylate) standards (200-4.7×10^5 g/mol). MALDI-ToF mass spectrometry was conducted 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. Solutions in tetrahydrofuran (50 μL) of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propylidene] malonitrile (DCTB) as a matrix (saturated solution), sodium iodide as cationisation agent (1.0 mg/mL) and sample (1.0 mg/mL) were mixed, and 0.7 μL of the mixture was applied to the target plate. Spectra were recorded in reflector mode calibrating PEG-Me 1100 kDa. UV/Vis spectra were recorded on Agilent Technologies Cary 60 UV-Vis spectrophotometer in the range of 200-1100 nm using a cuvette with 10 mm path length. A nail lamp was purchased online (λ~365 nm) and used as the main UV source.

General procedure for the homopolymerisation of MA

Appropriate amounts of EBiB (1 eq.), MA (DP_n eq), $Cu^{(II)}$ gluconate (0.02 eq.), Me_6-Tren (0.12eq.) and DMSO (50% *v/v*) were placed in a polymerisation flask, which was equipped with a magnetic stir bar and fitted with a rubber septum. The reaction mixture was degassed *via* bubbling with nitrogen for 20 min. The polymerization was allowed to proceed for 2 h under irradiation at λ~365 nm. Samples were taken periodically for conversion and molecular weight analyses. The polymerisation mixture was initially dissolved in THF and then passed through a small basic Al_2O_3 chromatographic column to remove the copper salts. The resulting solution was precipitated in methanol.

In situ block copolymerisation

Filtered MA (1 mL, 11.1 mmol, 50 eq), EBiB (32 μL, 0.22 mmol, 1 eq), $Cu^{(II)}$ gluconate (tablet) (1.0 mg, 4.4μmol, 0.02 eq), Me_6-Tren (7 μL, 22.0 μmol, 0.12 eq) and DMSO (1 mL)

were added to a septum sealed vial and degassed by purging with nitrogen for 15 mins. Polymerisation commenced upon addition of the degassed reaction mixture to the UV lamp. After 90 min a 1: 0.5 mixture of degassed PEGA (15 eq) used for block copolymerization and DMSO was added to the reaction mixture *via* degassed syringe. Samples were taken periodically and conversions were measured using ^{1}H NMR and SEC analysis.

References

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41-44.