Electronic Supplementary Material (ESI) for ChemComm.

Photo-induced living radical polymerization of acrylates utilizing a discrete copper(II)/formate complex

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Figure S2: Typical set up for **photo-induced** polymerization.

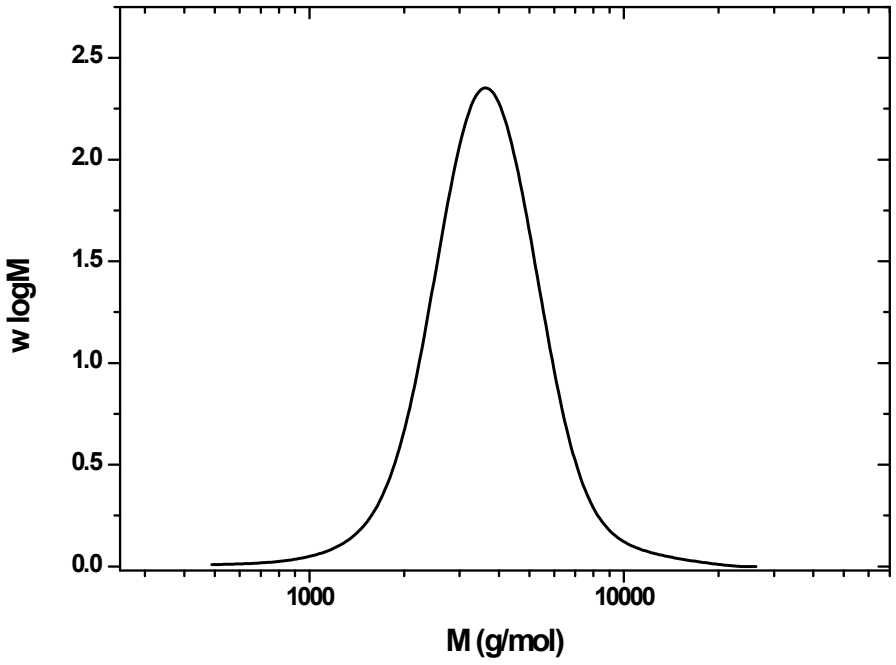
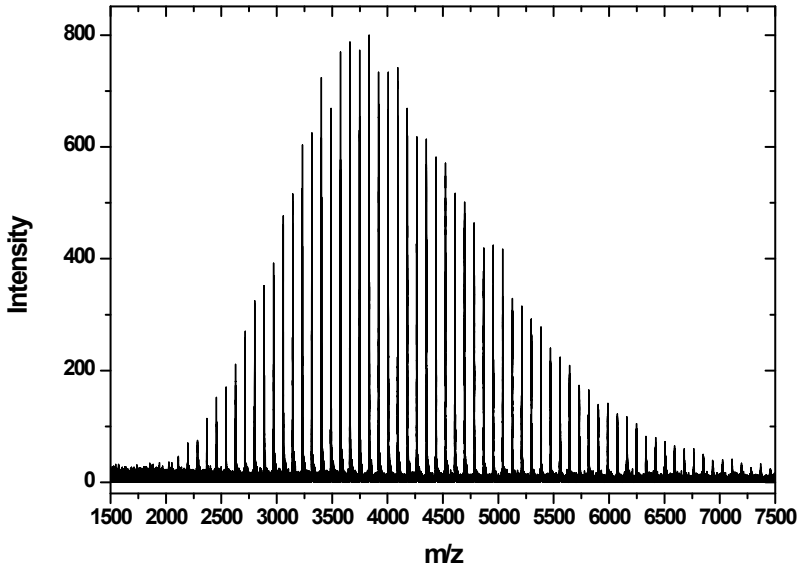


Figure S3a: Molecular weight distribution of poly(methyl acrylate), M_n= 3300g/mol; $Đ$ = 1.19; 75% conversion. [MA]:[EBiB]:**[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50]:[1]:**[0.01]** in DMSO 50% *v/v*.



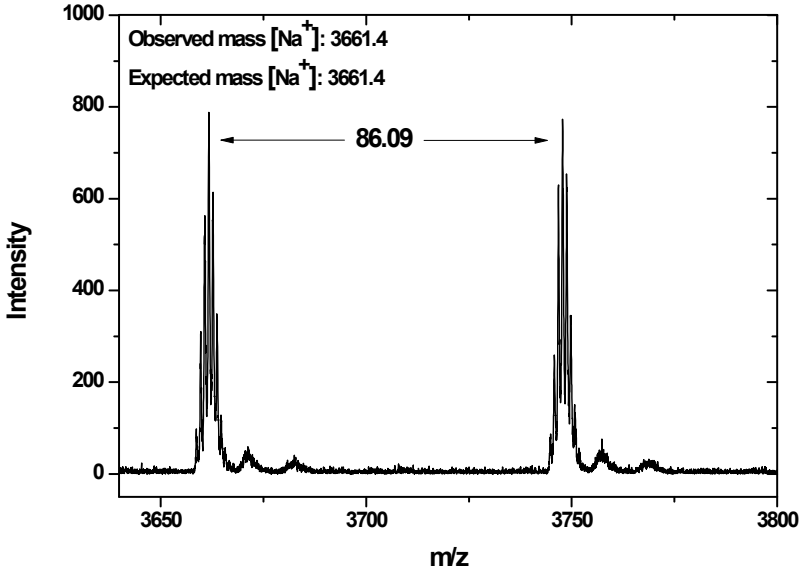


Figure S3b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate) obtained from photo-mediated polymerization: [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.01]** in DMSO 50% *v/v*.

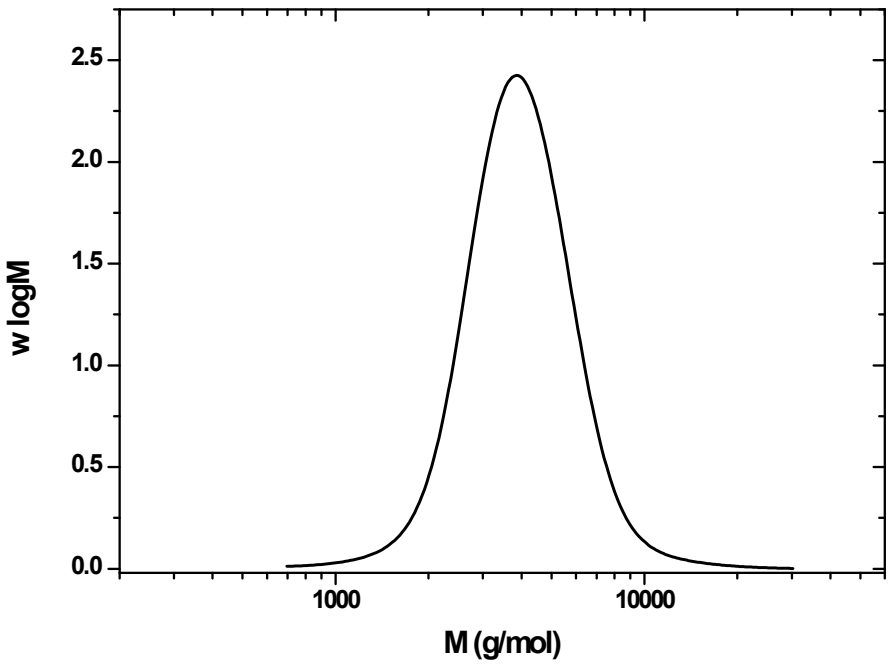


Figure S4a: Molecular weight distribution of poly(methyl acrylate), M_n= 4100g/mol; $Đ$ = 1.17; 85% conversion. [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)]** = [50] : [1] : **[0.02]** in DMSO 50% *v/v*.

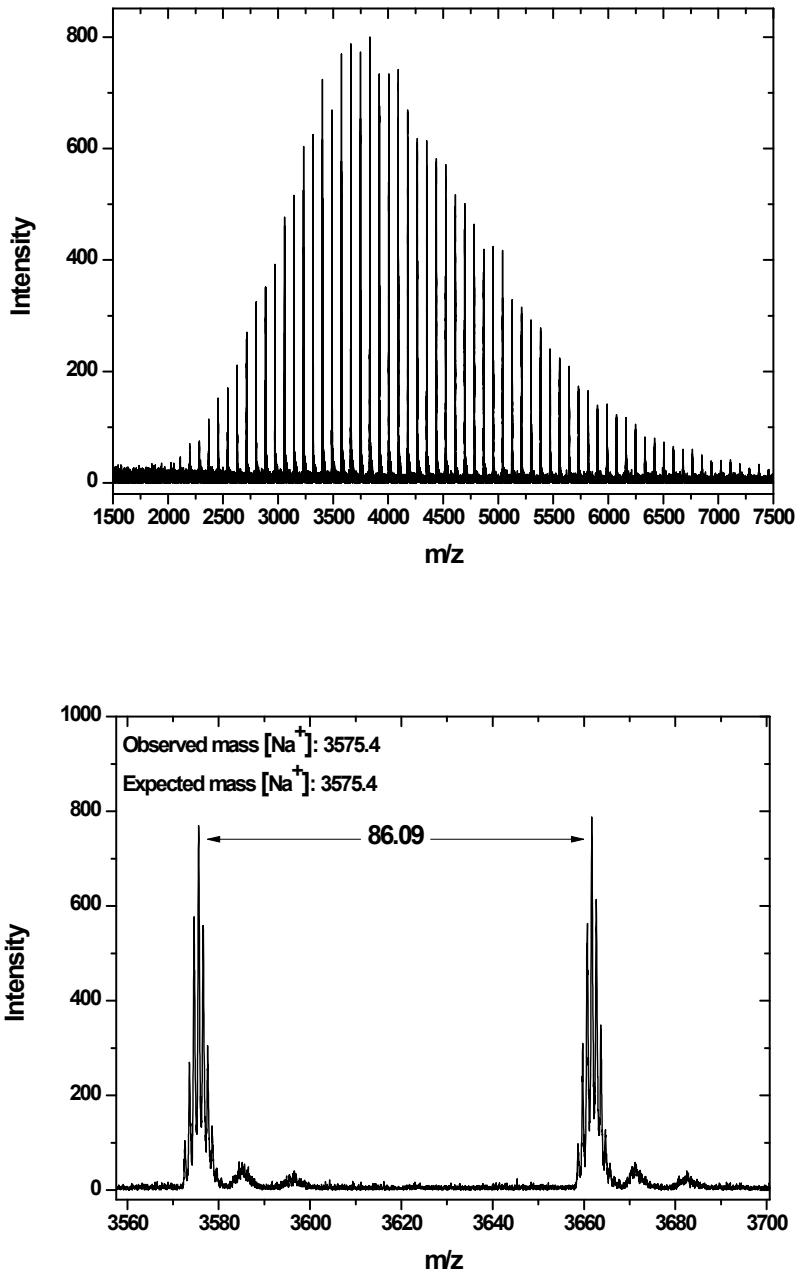


Figure S4b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate) obtained from photo-mediated polymerization: [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.02]** in DMSO 50% *v/v*.

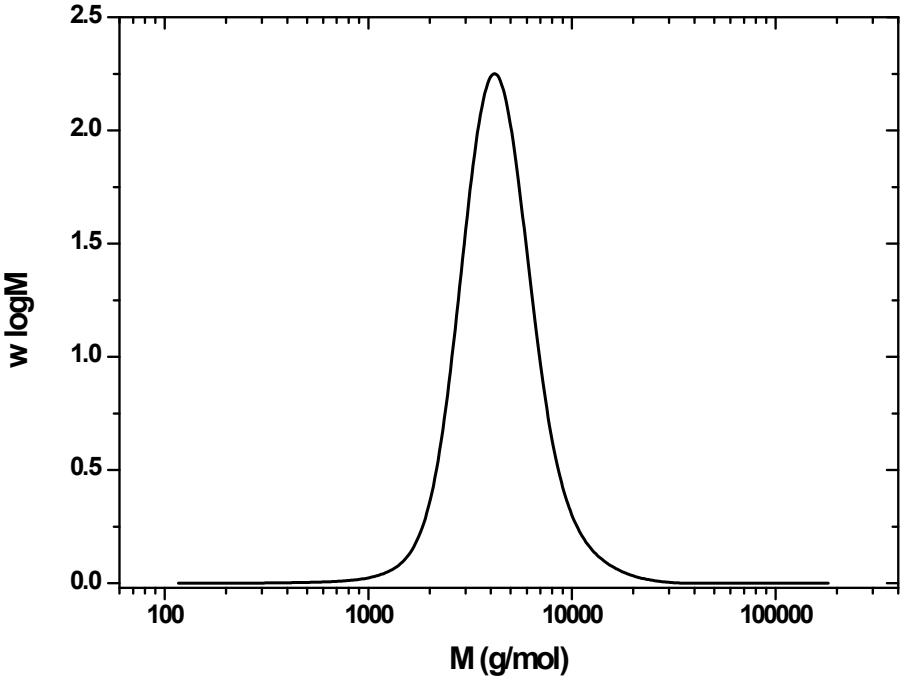
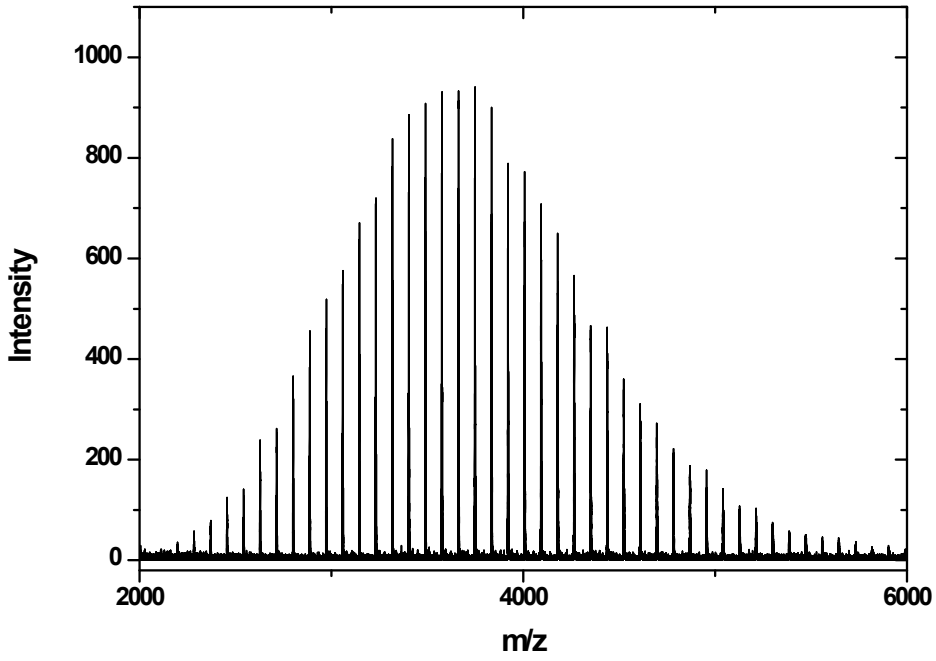


Figure S5a: Molecular weight distribution of poly(methyl acrylate), M_n= 4000g/mol; $Đ$ = 1.15; 89% conversion. [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.04]** in DMSO 50% *v/v*.



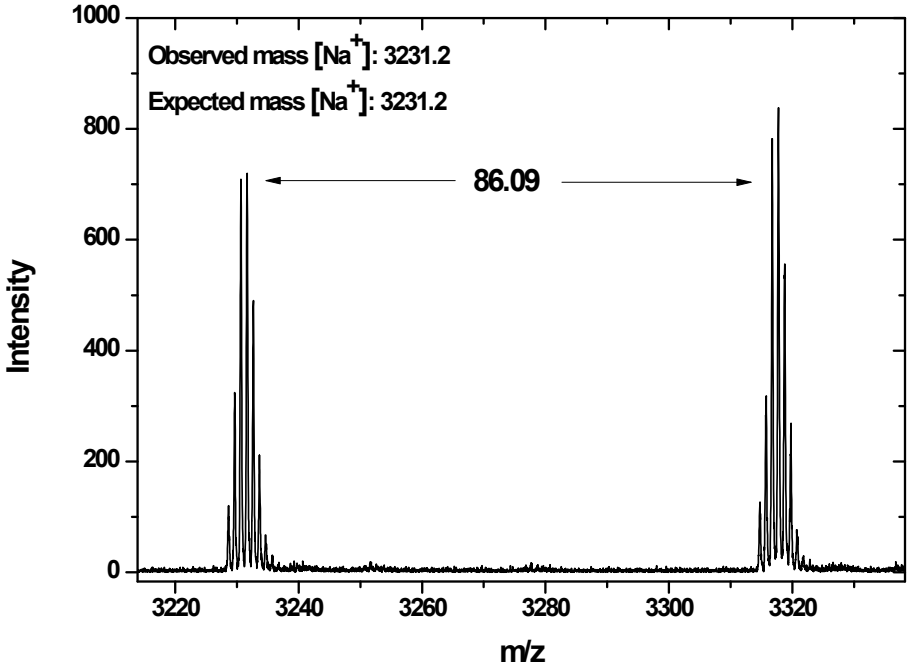


Figure S5b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate) obtained from photo-mediated polymerization: [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.04]** in DMSO 50% *v/v*.

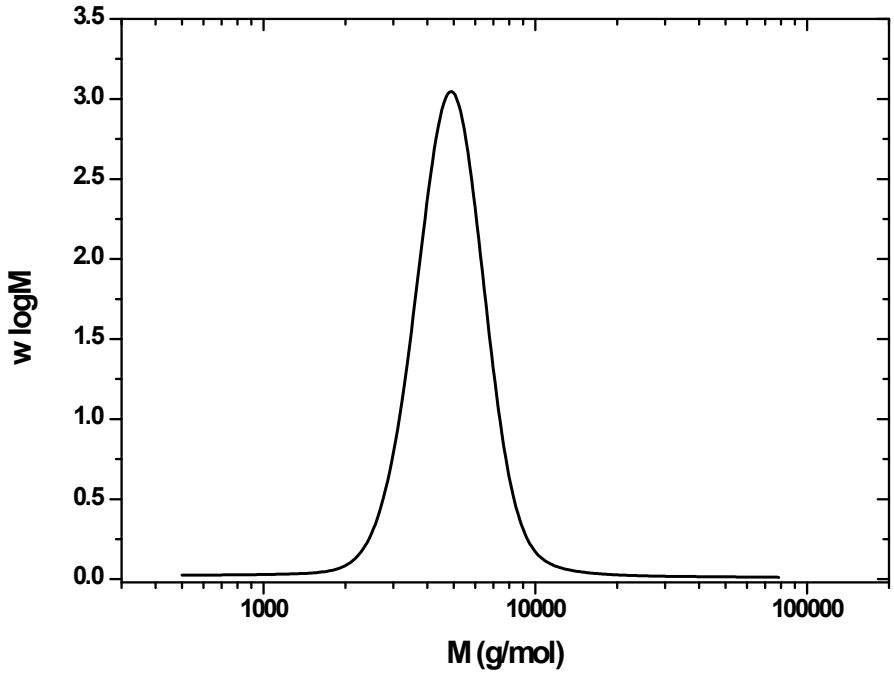
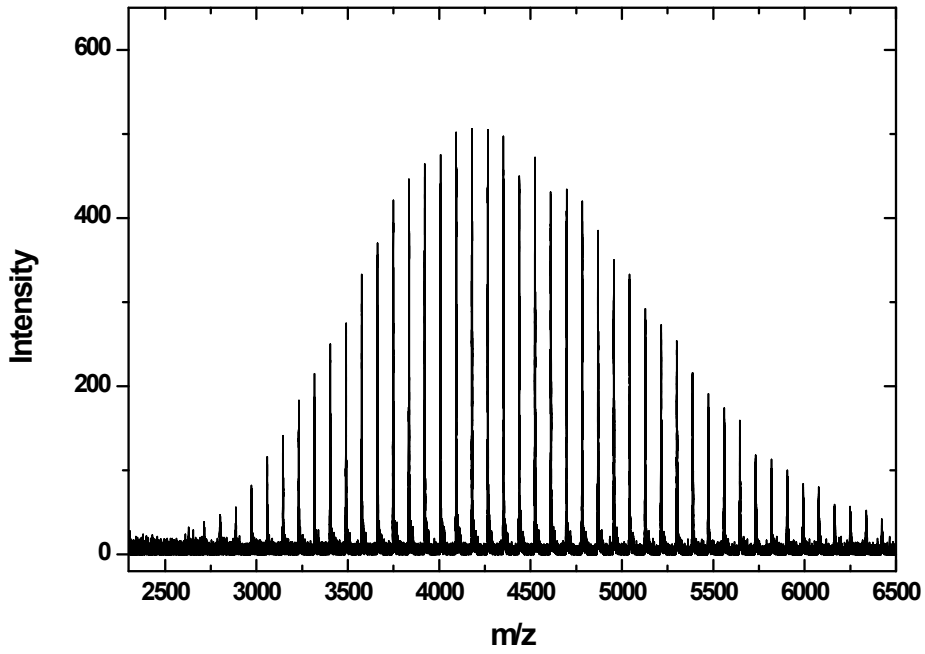


Figure S6a: Molecular weight distribution of poly(methyl acrylate), M_n= 4400g/mol; $Đ$ = 1.12; 94% conversion. [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.06]** in DMSO 50% *v/v*.



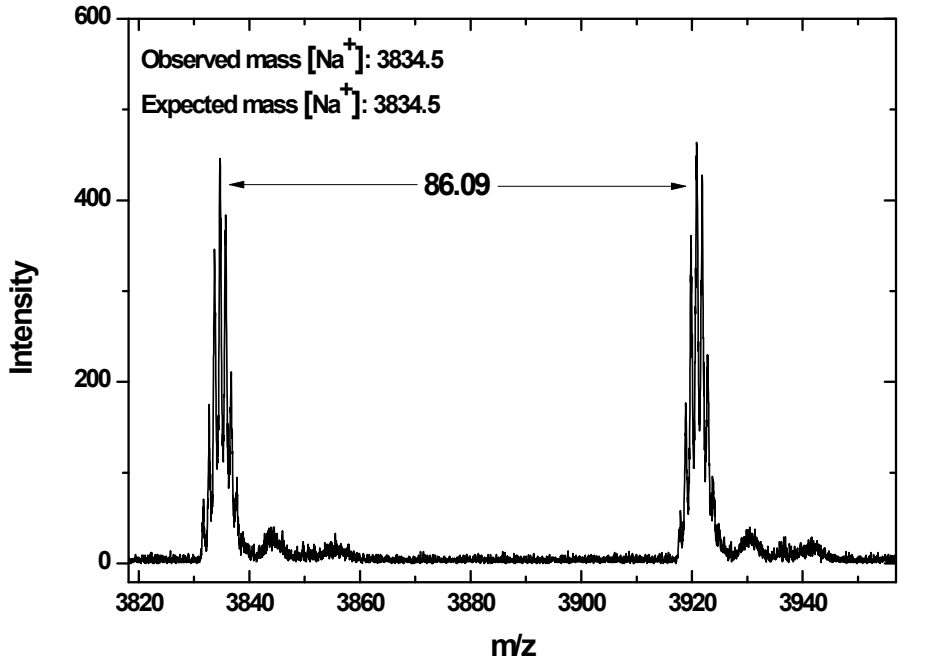


Figure S6b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate) obtained from photo-mediated polymerization: [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.06]** in DMSO 50% *v/v*.

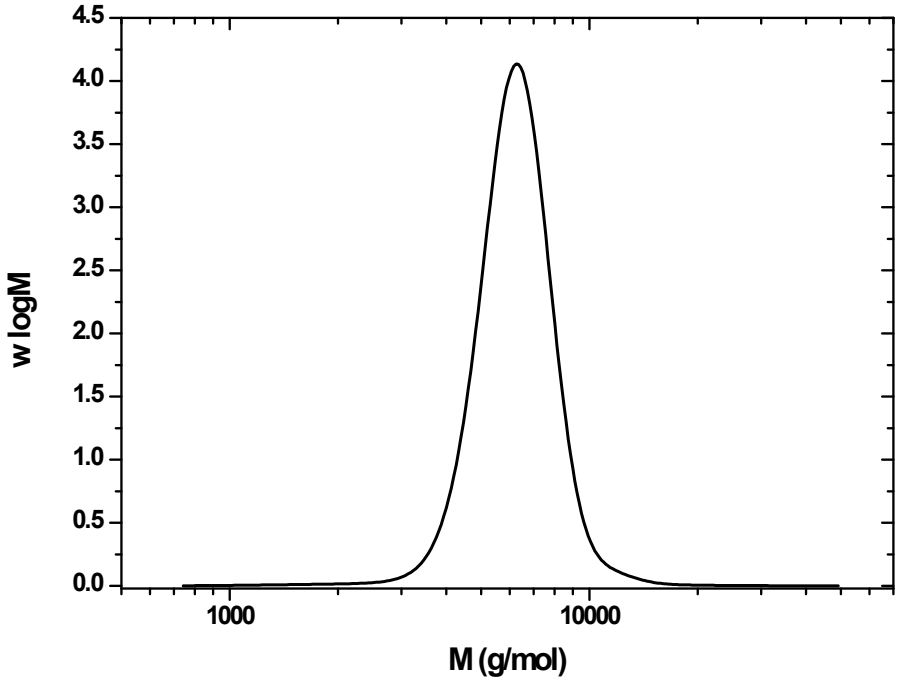
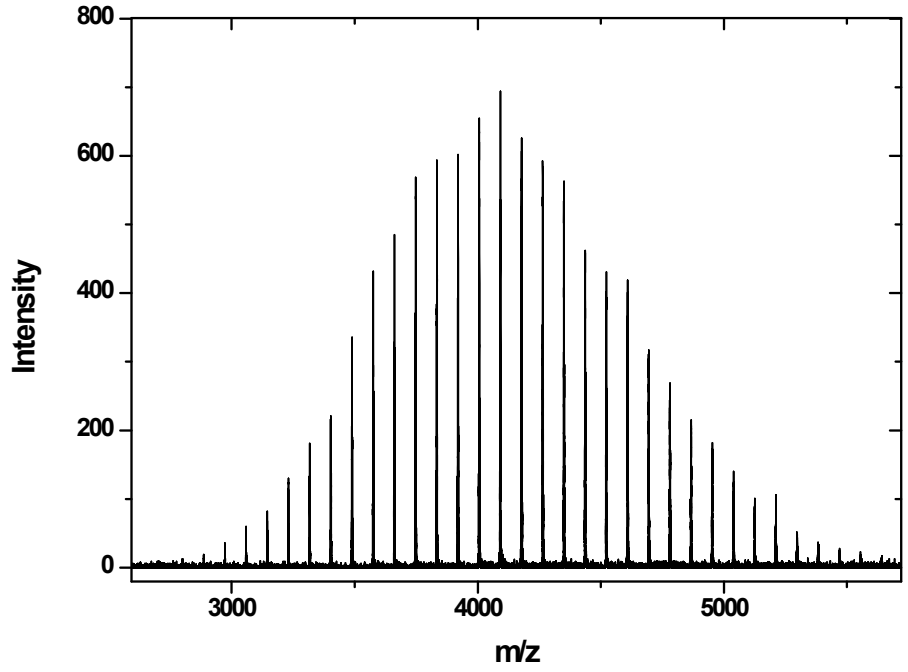
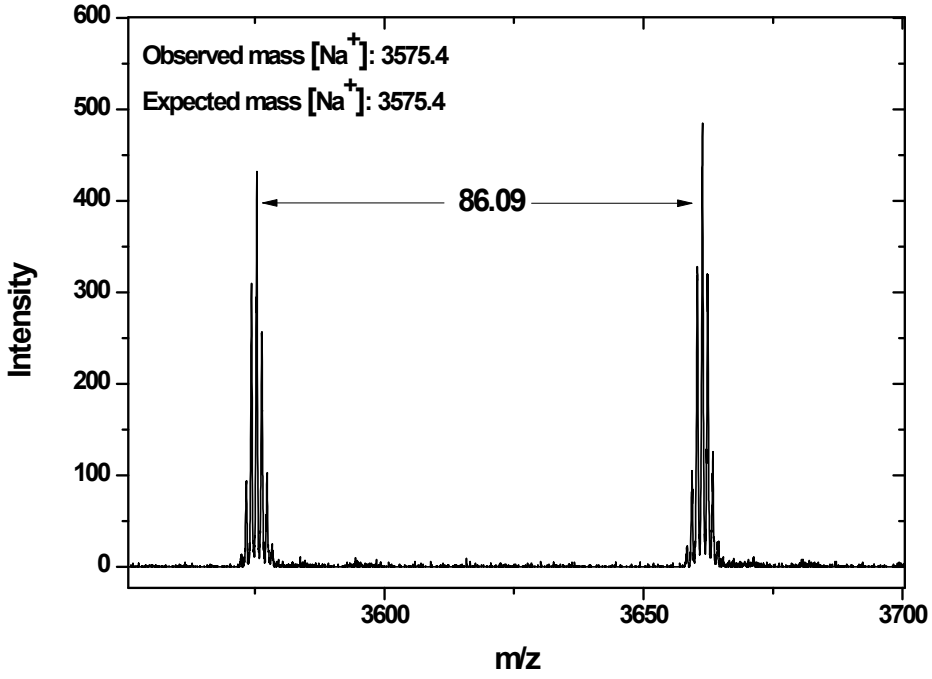


Figure S7a: Molecular weight distribution of poly(methyl acrylate), M_n= 4900g/mol; $Đ$ = 1.07; 96% conversion. [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.08]** in DMSO 50% *v/v*.


800
600
400
200
0
Intensity
3000
4000
5000
m/z


600
500
400
300
200
100
0
Intensity
Observed mass [Na+]: 3575.4
Expected mass [Na+]: 3575.4
86.09
3600
3650
3700
m/z

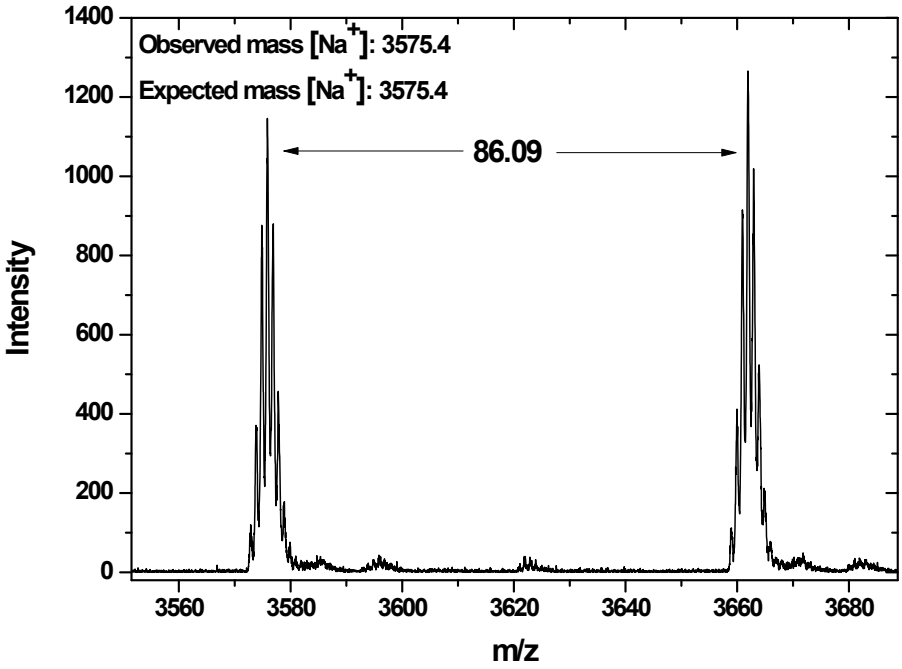


Figure S7b: MALDI-ToF-MS reflectron mode spectrum of poly(methyl acrylate) obtained from photo-mediated polymerization: [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.08]** in DMSO 50% *v/v*. Top figure **25%** laser power, bottom figure **60%** laser power (We believe the additional peaks in the last figure are due to fragmentation).

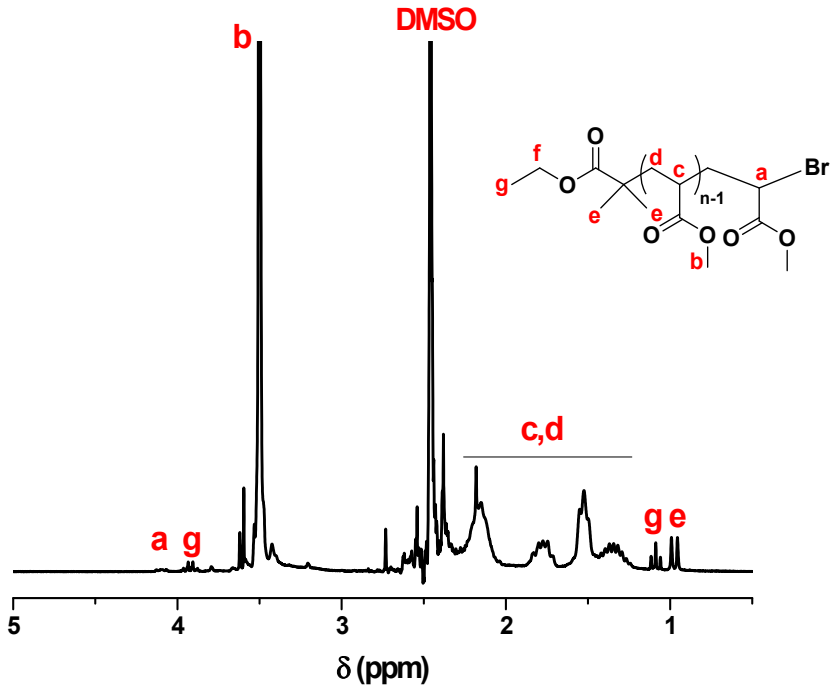


Figure S7c: ^{1}H NMR (400MHz, $CDCl_3$) of poly(methyl acrylate) obtained from UV experiment: [MA] : [EBiB] : **[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)** = [50] : [1] : **[0.08]** in DMSO 50% *v/v*.

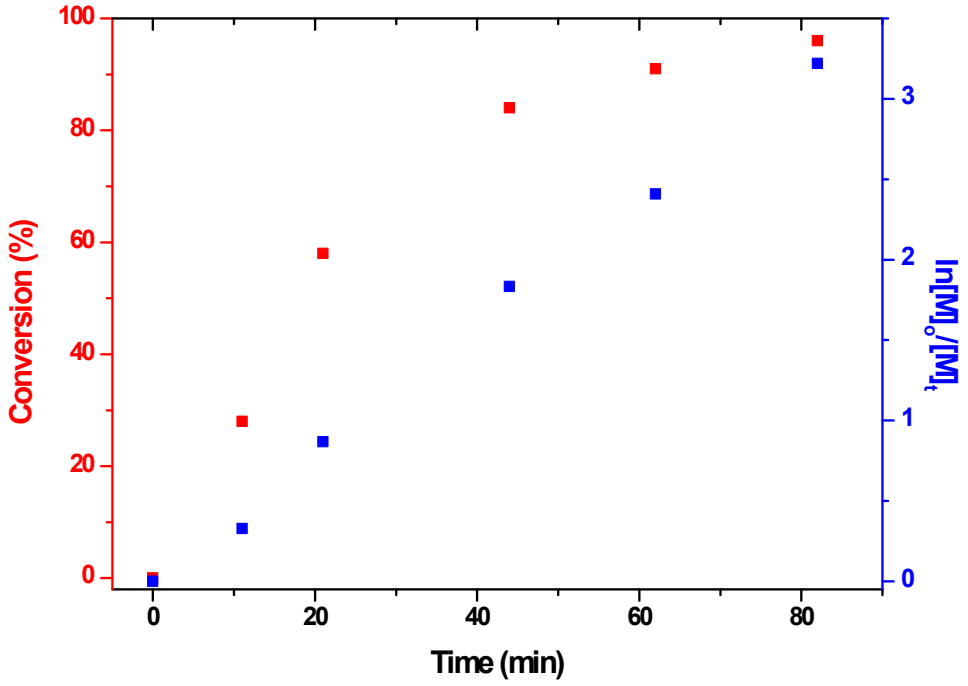


Figure S8a: Kinetic data for the polymerization of poly(methyl acrylate) under UV irradiation.

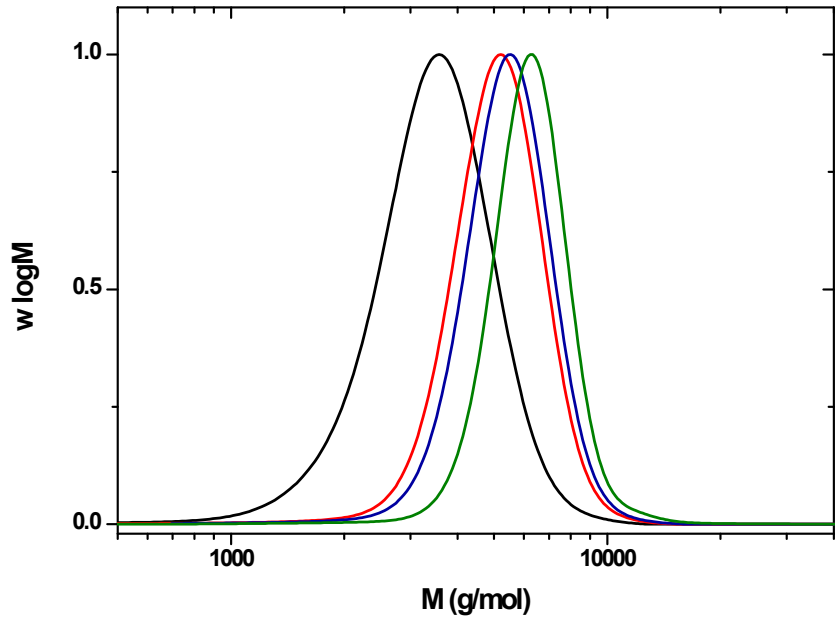


Figure S8b: SEC trace for the kinetic data shown above.

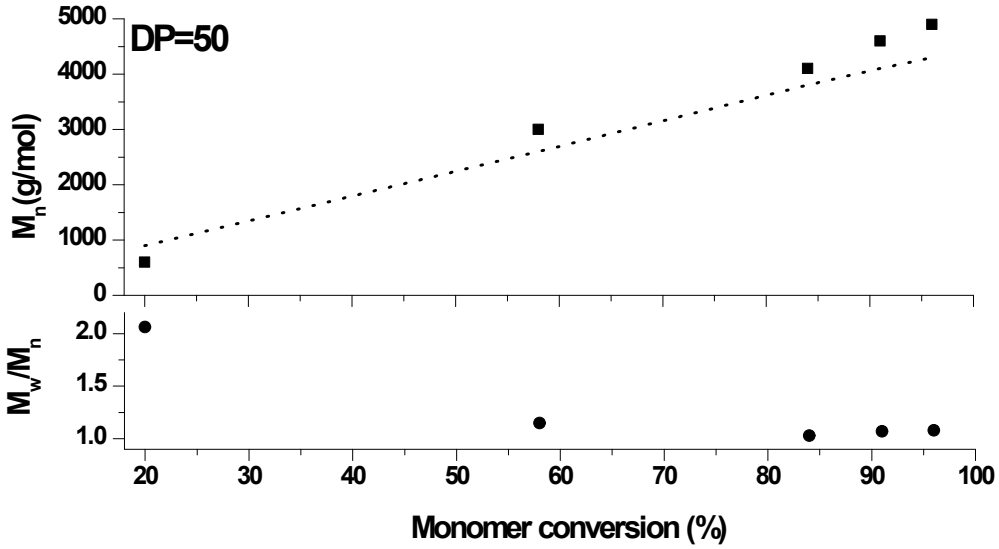


Figure S9: Molecular weight and dispersity data of the polymerization of MA under UV irradiation

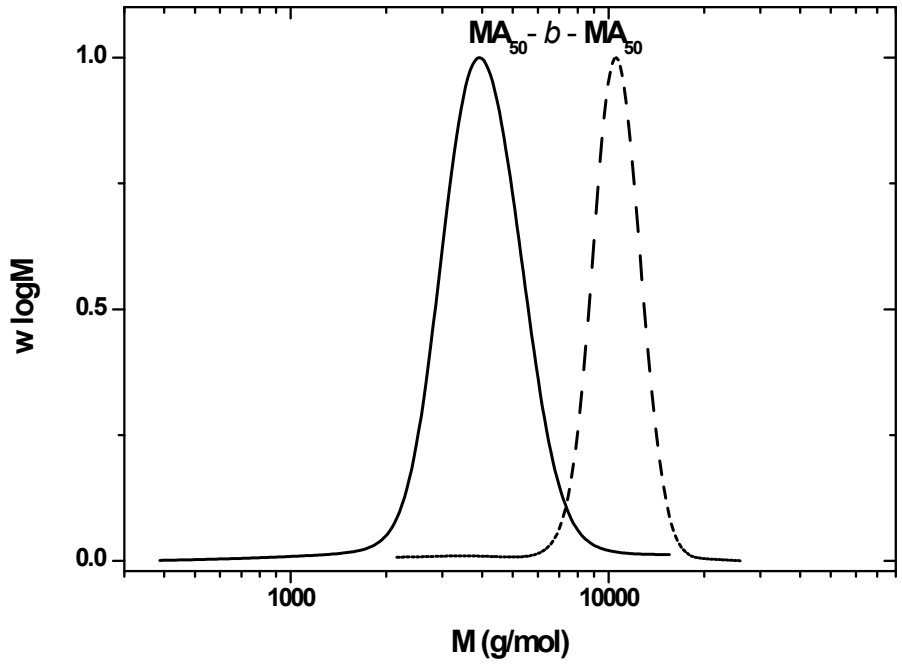


Figure S10a: In situ chain extension and block copolymerization from a PMA macroinitiator. Initial conditions: [MA] : [EBiB] : [Cu(Me_6-Tren)(O_2CH)](ClO_4) = [50] : [1] : [0.08], DMSO (50%, *v/v*). Chain extension achieved upon addition of an aliquot of MA (50 equiv.) in DMSO (33%, *v/v*).

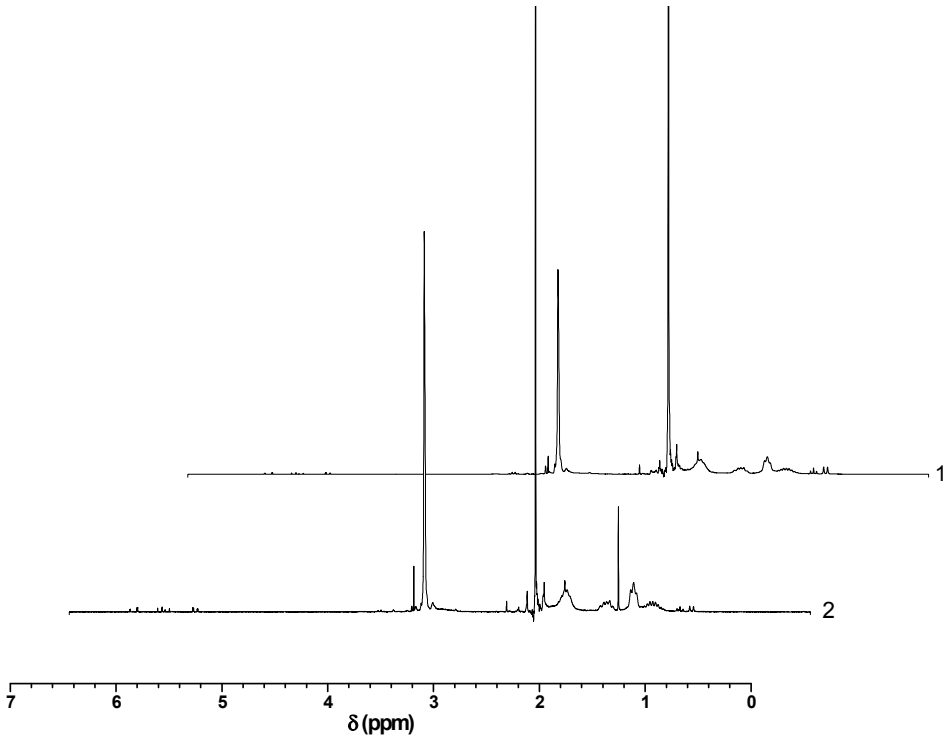


Figure S10b: ^{1}H NMR for the in situ chain extension of PMA.

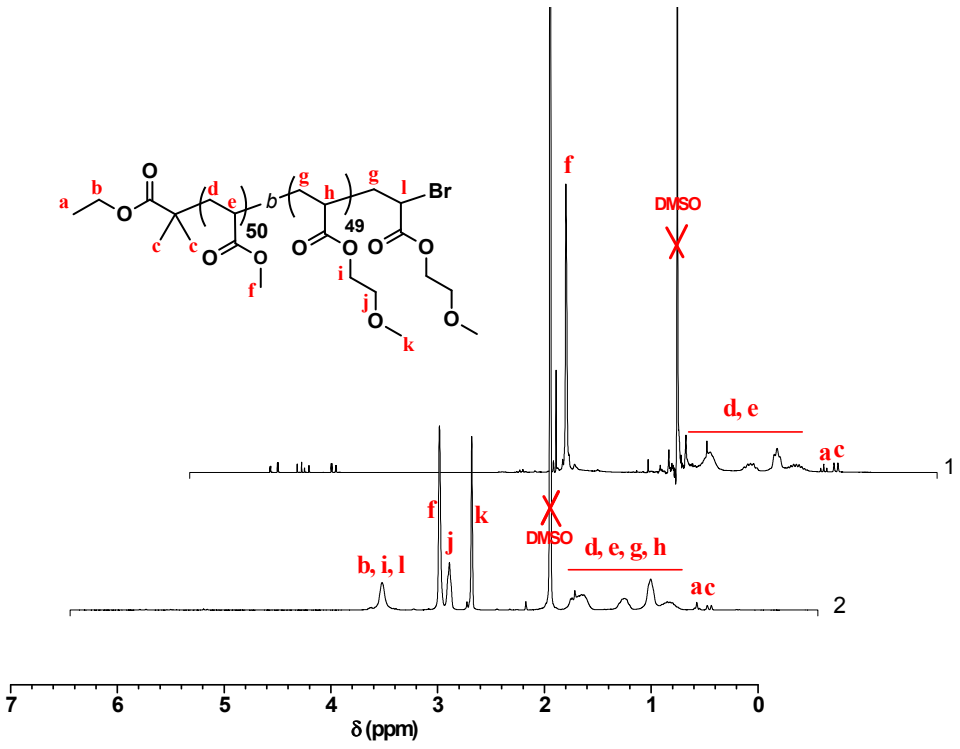


Figure S11: ^{1}H NMR (400 MHz, $CDCl_3$) of $(PMA)_{50}$-*b*-$P(EGA)_{50}$ prepared by **sequential addition of EGA to a PMA macroinitiator**. Homopolymer [MA] : [EBiB] : [Cu(Me_6-

Tren)(O_2CH)](ClO_4) = [50] : [1] : [0.08] in DMSO (50:50 *v/v* monomer/solvent). Block copolymerization achieved upon addition of EGA [EBiB] : [EGA] = [1] : [50].

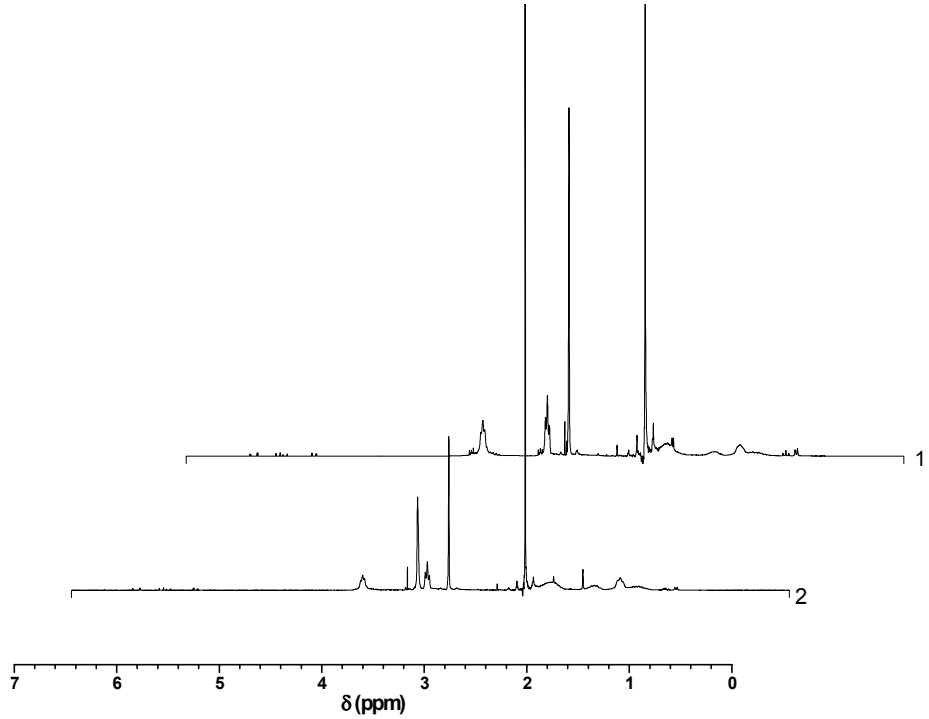


Figure S12: ^{1}H NMR (400 MHz, $CDCl_3$) of P(EGA)$_{50}$-*b*-(PMA)$_{50}$ prepared by **sequential addition of MA to a P(EGA) macroinitiator**. Homopolymer [MA] : [EBiB] : [Cu(Me$_6$-Tren)(O_2CH)](ClO_4) = [50] : [1] : [0.08] in DMSO (50:50 *v/v* monomer/solvent). Block copolymerization achieved upon addition of MA [EBiB] : [MA] = [1] : [50].

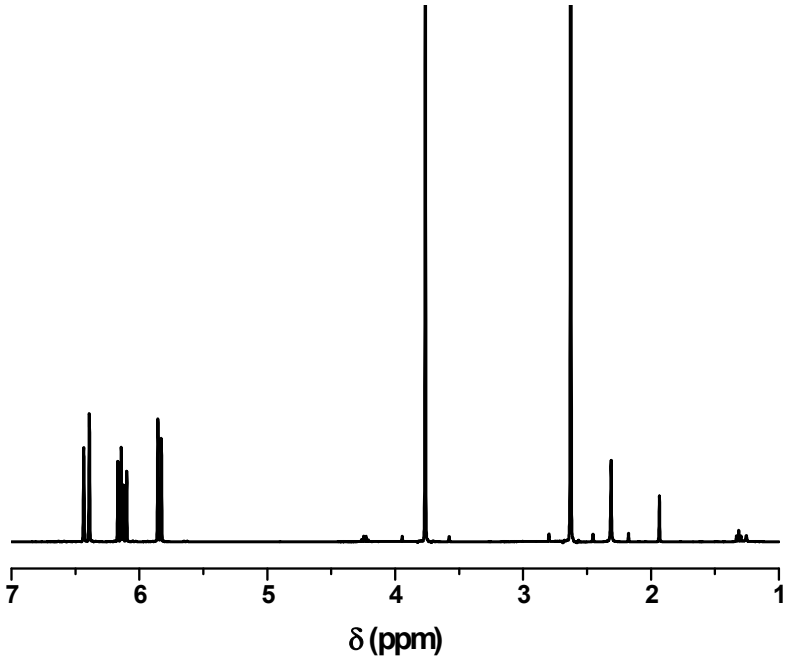


Figure S13: ^{1}H NMR (400MHz, $CDCl_3$) of poly(methyl acrylate) obtained from UV experiment: [MA] : [EBiB] : [Cu(Me_6-Tren)(O_2CH)](ClO_4) = [50] : [1] : [0.08] in DMSO 50% *v/v* under **dark conditions**.

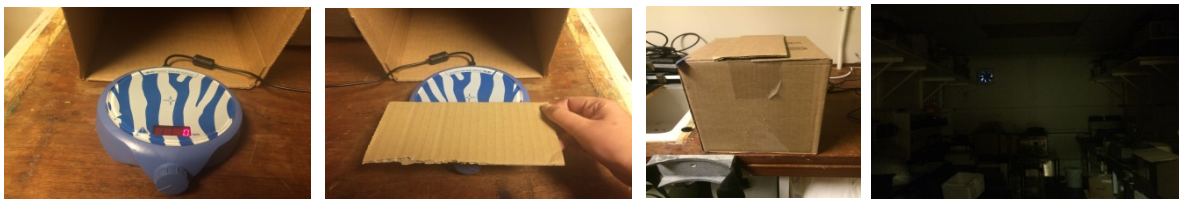


Figure S14: Typical set up for polymerization under **dark conditions**.

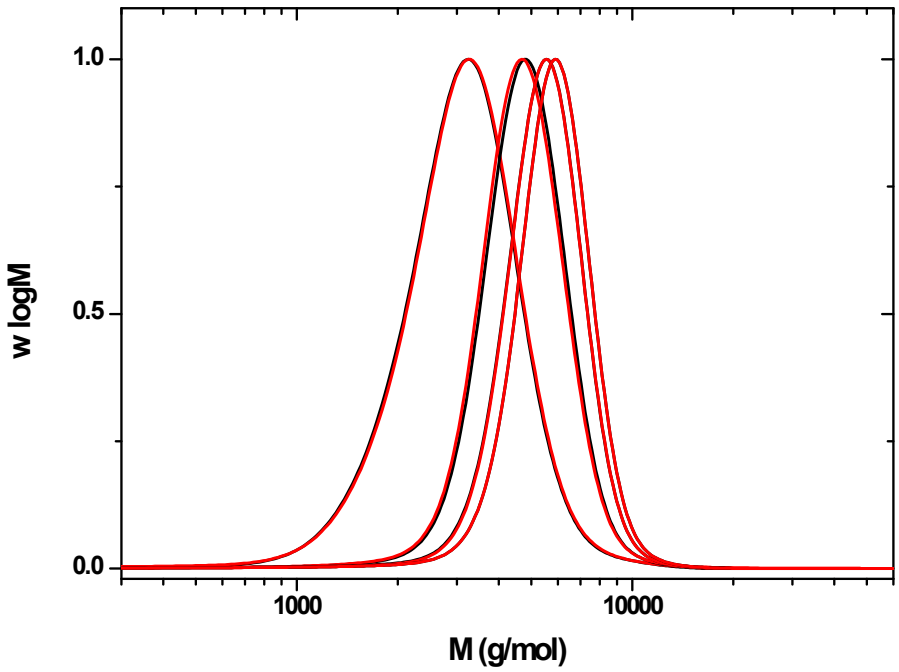


Figure S15: SEC traces of temporal control *via* consecutive light and dark exposure.

[MA] : [EBiB] : [Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$) = [50] : [1] : [0.08].

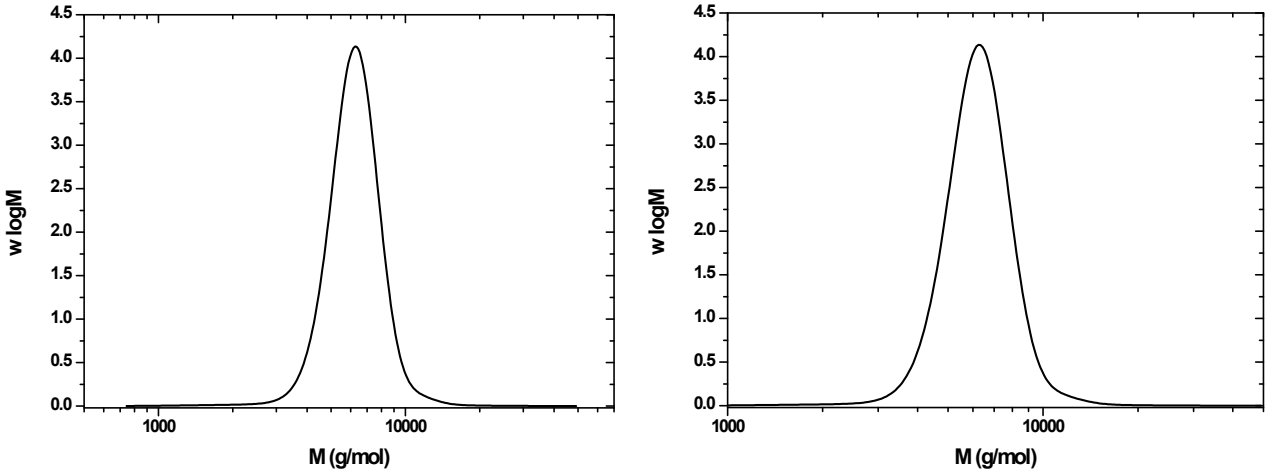


Figure S16: Molecular weight distribution of poly(methyl acrylate), M_n= 4900g/mol; $Đ$ = 1.07; 96% conversion **before** (right) **and after 6 months** M_n= 5000g/mol; $Đ$ = 1.09; 97%

conversion (left). [MA] : [EBiB] : [Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$) = [50] : [1] : [0.08] in DMSO 50% *v/v*.

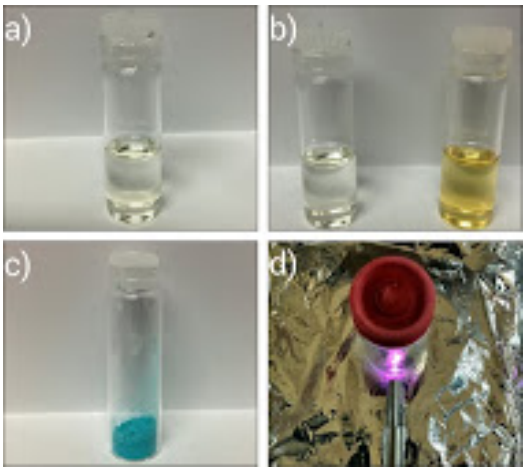


Figure S17: a) **Freshly distilled** Me$_6$-Tren b) Freshly distilled Me$_6$-Tren (left) *vs* **degraded** Me$_6$-Tren (right) after 1 month stored under nitrogen in the fridge c) [Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$) **stable after 6 months** of exposure in light/air/ambient temperature d) **Reaction vial** under UV irradiation in a homemade dark box.

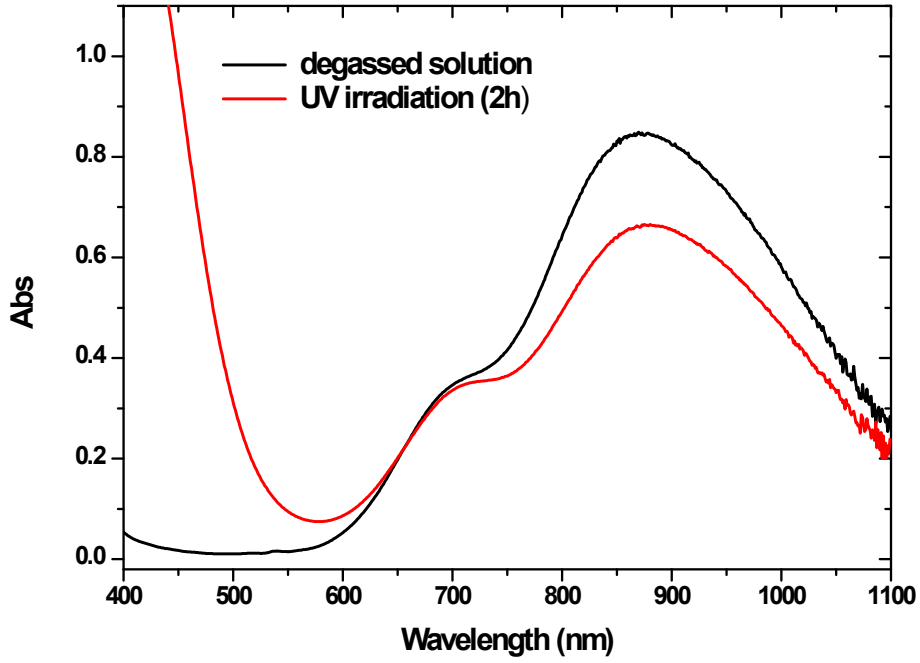


Figure S18: Monitoring effect of UV irradiation on [Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$) as a function of time by **UV−vis spectroscopy**.

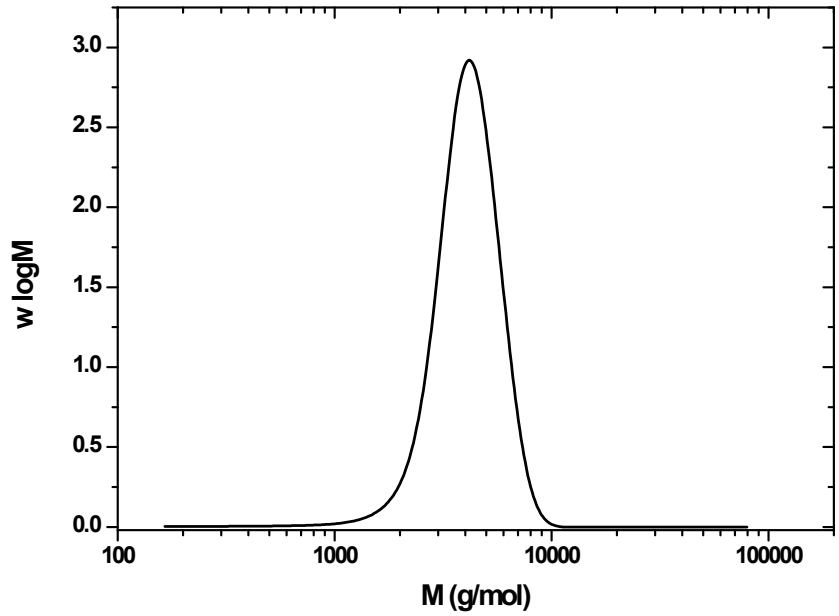


Figure S19: SEC trace of poly(methyl acrylate) M_n= 3800g/mol; $Đ$ = 1.12; 85% conversion. Obtained from UV experiment: **[MA] : [EBiB] : [$CuBr_2$] : [Me_6-Tren] : [HCOONa]** = [50] : [1] : [0.02] : [0.02] : [0.02] in DMSO 50% *v/v*.

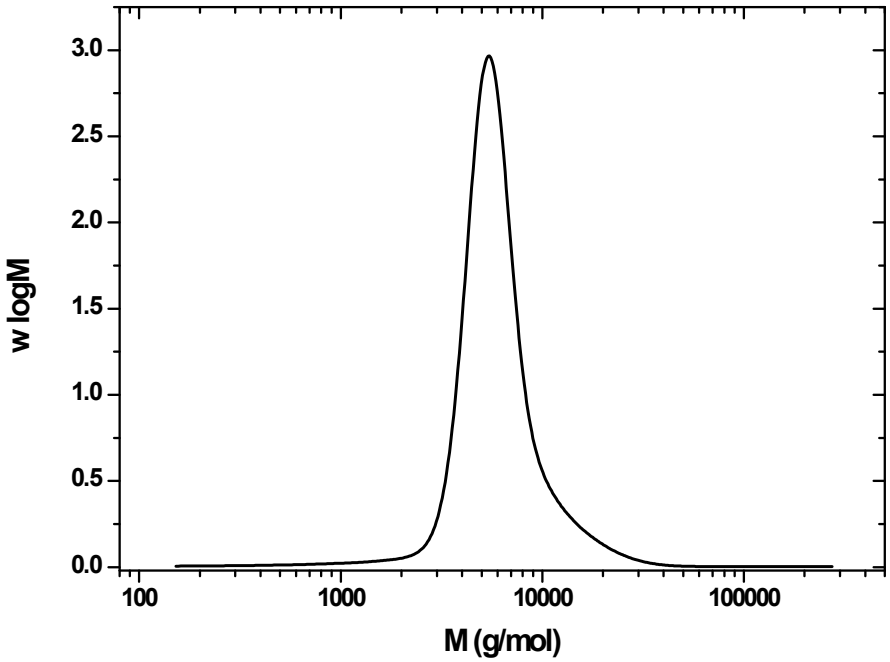


Figure S20: SEC trace of poly(methyl acrylate) M_n= 5100g/mol; $Đ$ = 1.19; 95% conversion. Obtained from UV experiment: **[MA]: [EBiB]: [$(O_2CH)_2Cu$] : [Me_6-Tren]** = [50] : [1] : [0.02] : [0.02] in DMSO 50% *v/v*.

Experimental

Materials

All materials were purchased from Sigma Aldrich or Fischer Scientific unless otherwise stated. Copper (II) bromide ($CuBr_2$) and ethyl 2-bromoisobutyrate (EBiB) were used as received. All monomers were passed through a basic Al_2O_3 chromatographic column prior to use. Tris-(2-(dimethylamino)ethyl)amine (Me_6-Tren) was synthesized according to previously reported literature.[1]

Apparatus

^1H 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 $g \cdot mol^{-1}$ 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. The source of UV light was an OmniCure® S2000 spot UV curing lamp system, 200W (λ_{max} ~ 320-390nm).

General procedure for the homopolymerization of MA

Appropriate amounts of EBiB (1 eq.), MA (DP_n eq.), [Cu(Me_6-Tren)(O_2CH)](ClO_4) (0.08 eq.) and DMSO (50% *v/v*) were placed in a polymerization 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 2h under irradiation at λ~320-390 nm. The distance of each sample from the UV source was approximately 5 cm. Samples were taken periodically for conversion and molecular weight analyses. The polymerization 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.

References

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