Supplementary Information

Discrete copper(II)-formate complexes as catalytic precursors for photo-induced reversible deactivation polymerization

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Figure S1: Typical set up for photo-induced polymerization.

Materials and Methods

All materials were purchased from Sigma Aldrich or Fischer Scientific and used as received unless otherwise stated. All monomers were passed through a basic Al_2O_3 chromatographic column prior to use. $Cu(Me_6\text{-Tren})(O_2CH)](ClO_4)$ and $Cu(Me_5\text{-Dien})(O_2CH)](ClO_4)$ were synthesized according to previously reported literature and is reproduced here for completeness. [1]

Instrumentation

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

Synthesis of $[Cu(Me_6\text{-Tren})(O_2CH)](ClO_4)$ [1]

A solution of 0.463 g (2.01 mmol) of Me_6-Tren[2] in 5 mL of methanol was added dropwise to a slurry of 0.453 g (2.01 mmol) of $[Cu(OH_2)_4(O_2CH)_2]$ in 15 mL of methanol. The mixture was stirred for 10 min, and 0.246 g (2.01 mmol) of solid $NaClO_4$ was added to the light blue

solution. The mixture was stirred for 3 h and filtered, and the filtrate was taken to dryness under vacuum. The residue was dissolved in 5 mL of dichloromethane, the solution was filtered, and solvent was removed in vacuo. The residue was dissolved in a minimal amount of acetone, and several volume equivalents of ether were diffused into the solution over 24 h. The solid was collected, washed with ether, and dried under vacuum to yield the product.

Synthesis of [Cu(Me$_5$-Dien)(O$_2$CH)](ClO$_4$)[1]

A solution of 0.540 g (3.12 mmol) of Me$_5$dien in 5 mL of methanol was added dropwise to a slurry of 0.703 g (3.12 mmol) of [Cu(OH$_2$)$_4$(O$_2$CH)$_2$] in 15 mL of methanol. The resulting dark blue solution was stirred for 2 h and treated with 0.382 g (3.12 mmol) of solid NaClO$_4$, and the mixture was stirred for an additional 4 h. The precipitate was collected, washed with cold methanol and ether and dried under vacuum.

Typical procedure

EBiB (1 equiv., 4.43 x 10^{-4} mol, 65 μl), monomer (*DP* equiv., 2 ml), [Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$) or [Cu(Me$_5$-Dien)(O$_2$CH)](ClO$_4$) (0.08 equiv.) and solvent (2ml) 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 2 h under irradiation at λ ~ 320-390 nm. 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$_2$O$_3$ chromatographic column to remove the copper salts.

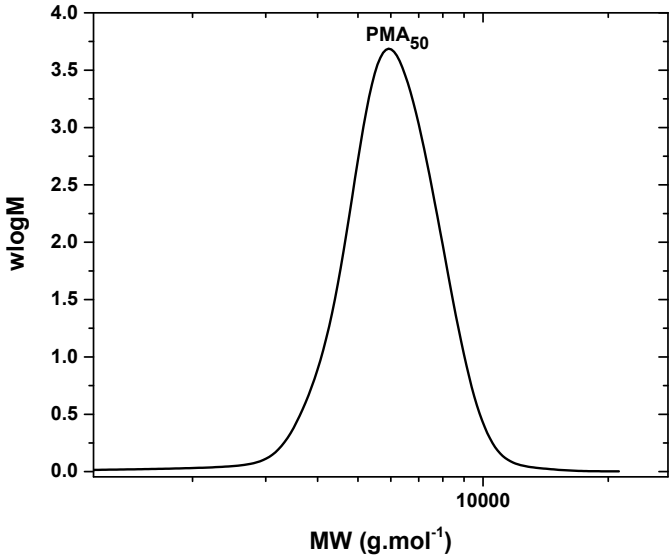


Figure S2: Molecular weight distribution of PMA *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], MeCN 50% *v/v*.

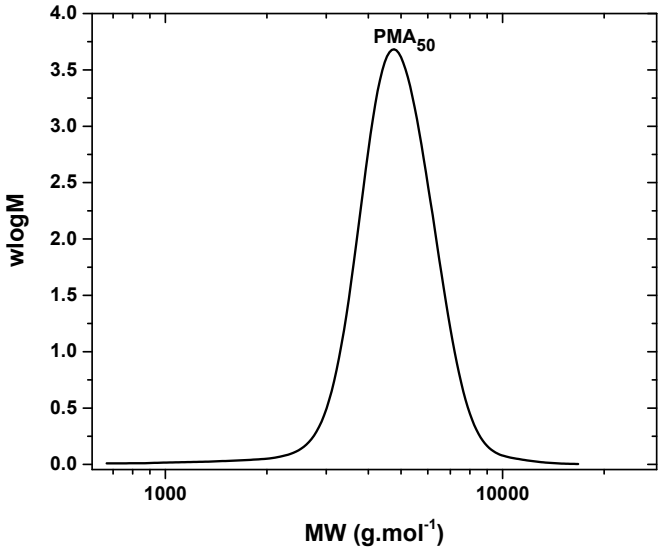


Figure S3: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMF 50% *v/v*.

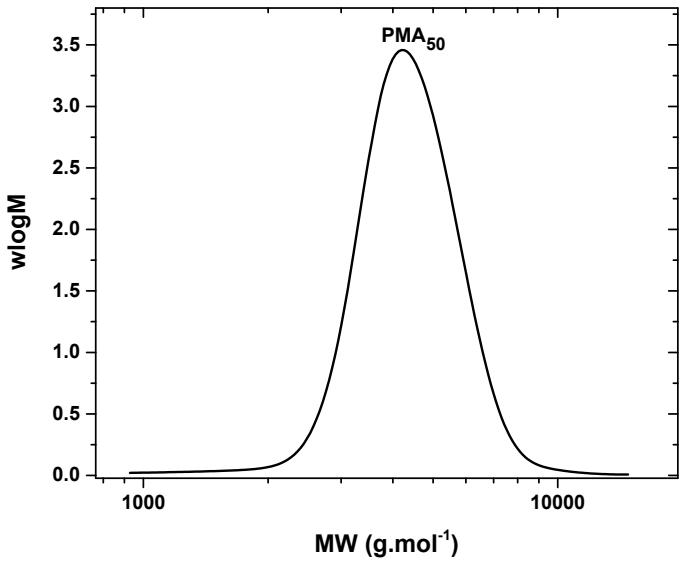


Figure S4: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], MeOH 50% *v/v*.

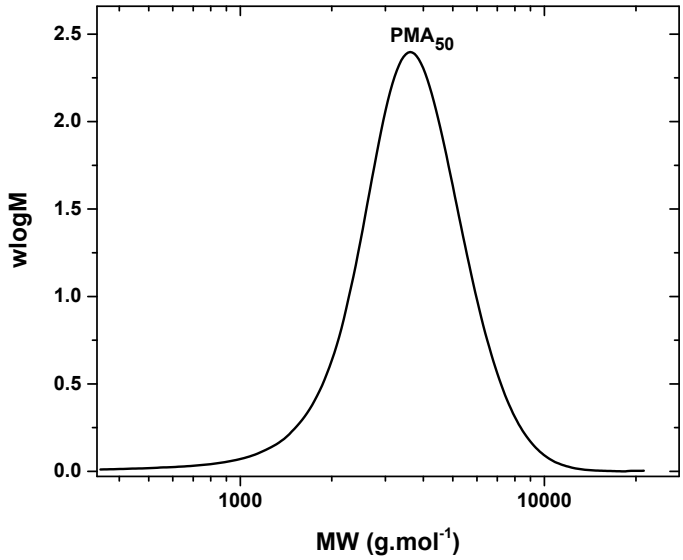


Figure S5: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], IPA 50% *v/v*.

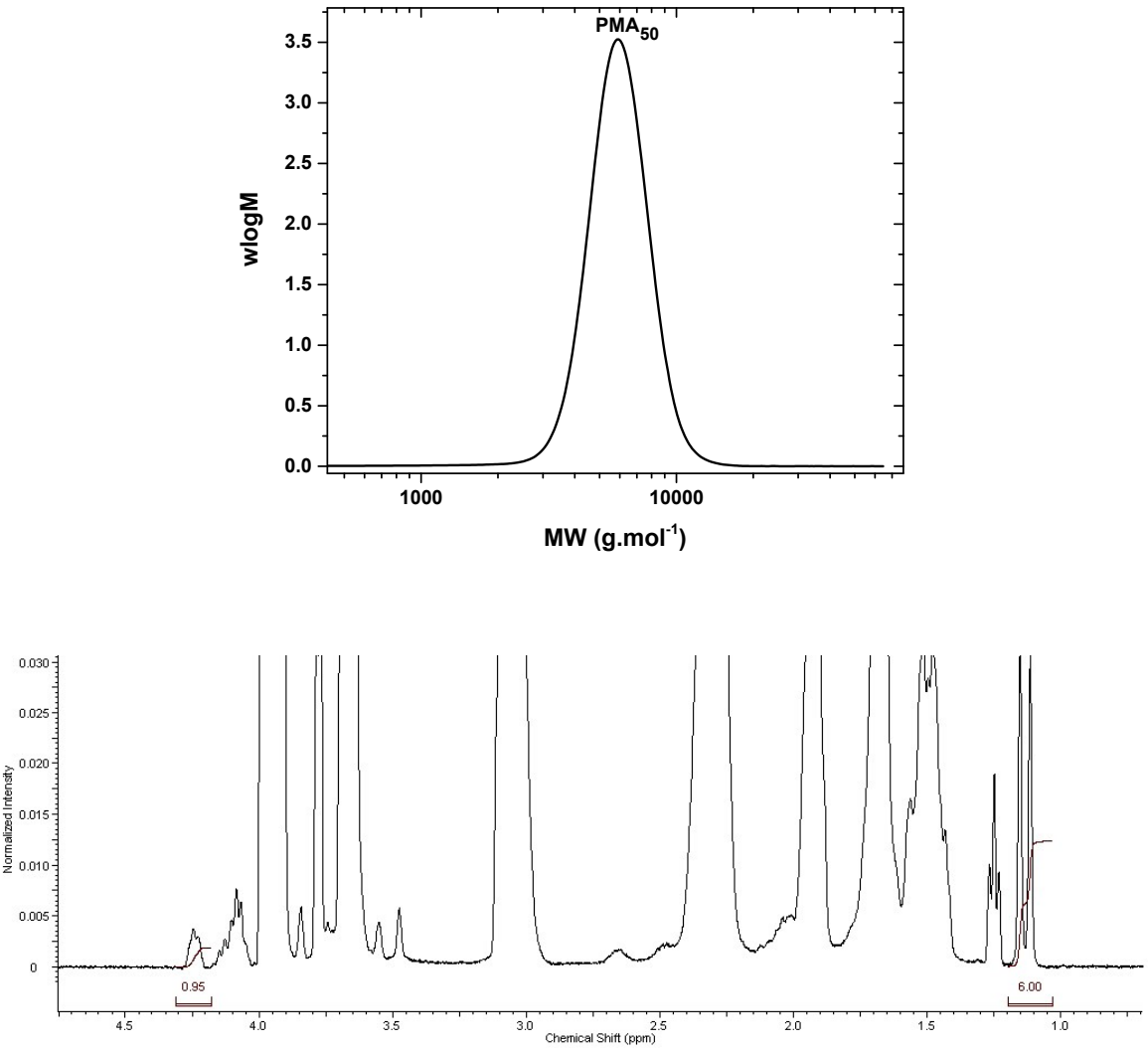


Figure S6: Molecular weight distribution (up) and ^{1}H NMR demonstrating the high end-group fidelity (down) of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], TFE 50% *v/v*

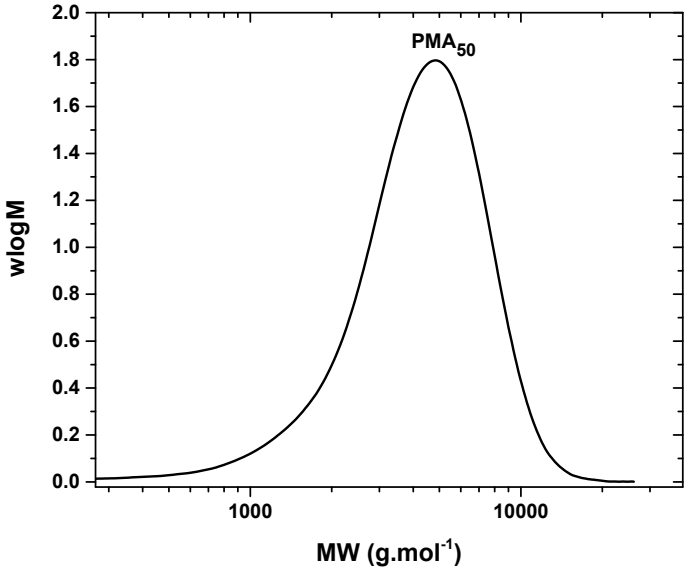


Figure S7: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], Toluene 50% *v/v*.

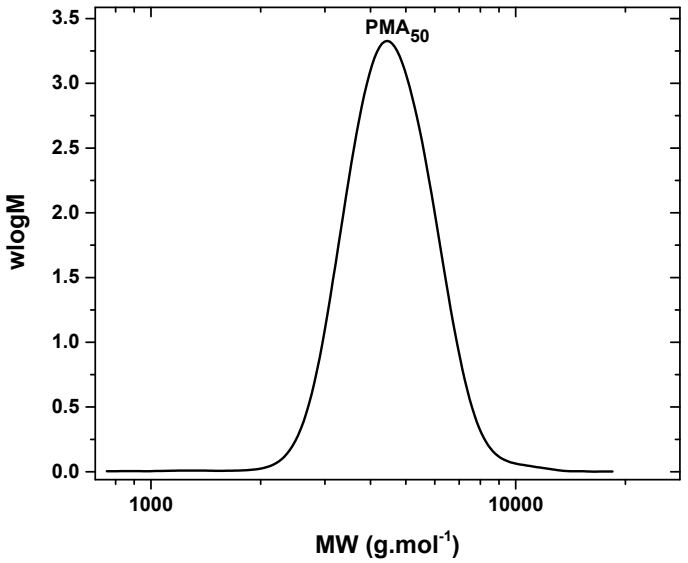


Figure S8: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], [Toluene]:[MeOH] = [4]:[1] 50% *v/v*.

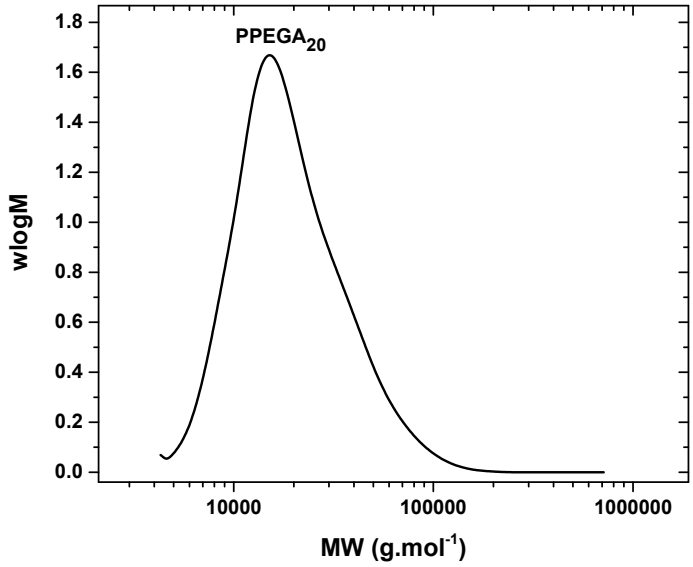
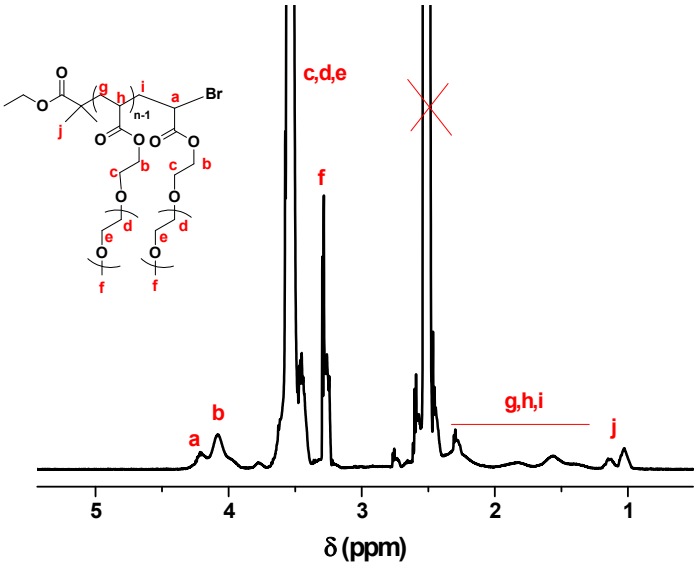


Figure S9: Molecular weight distribution of PPEGA synthesized *via* photo-induced polymerization. Initial conditions [PEGA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [20]:[1]:[0.08], H_2O 50% *v/v*.



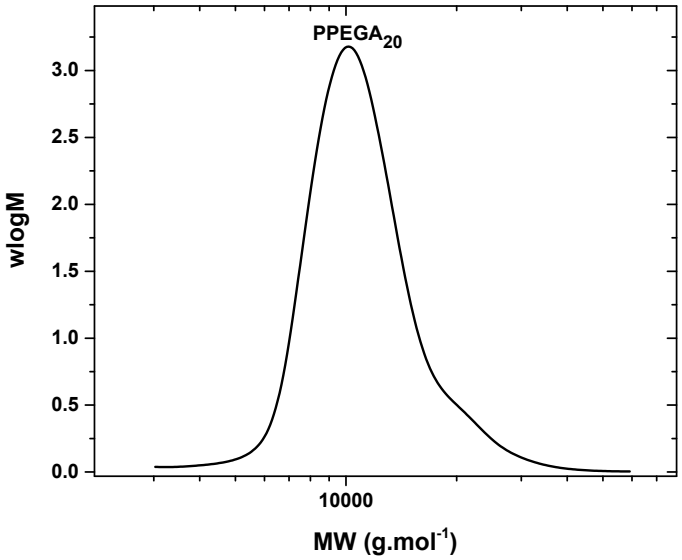
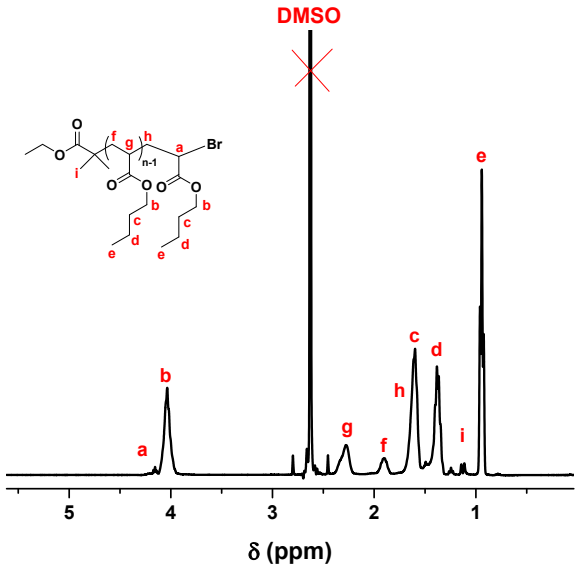


Figure S10: Molecular weight distribution of PPEGA synthesized *via* photo-induced polymerization. Initial conditions [PEGA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [20]:[1]:[0.08], DMSO 50% *v/v*.



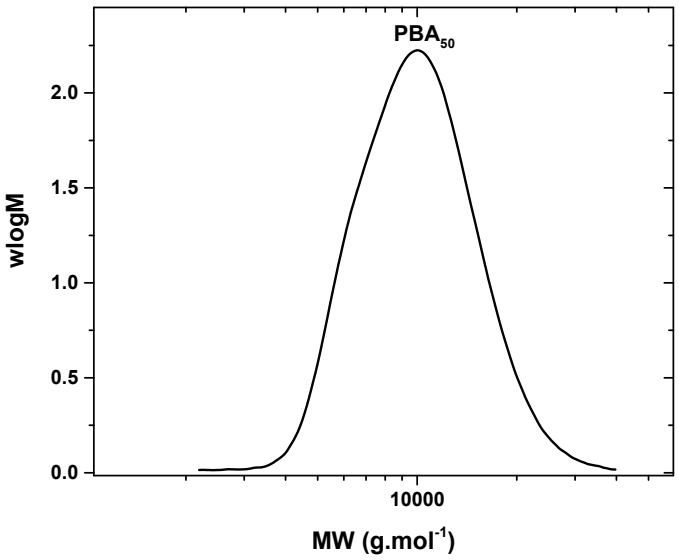
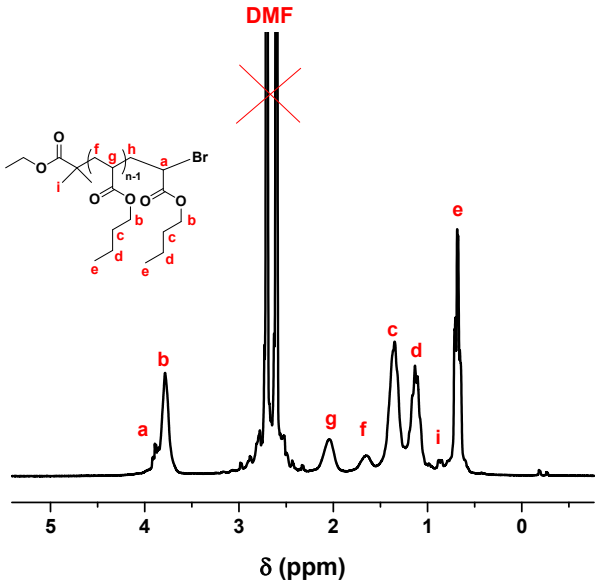


Figure S11: ^{1}H NMR and molecular weight distribution of PBA synthesized *via* photo-induced polymerization. Initial conditions [*n*-BA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.



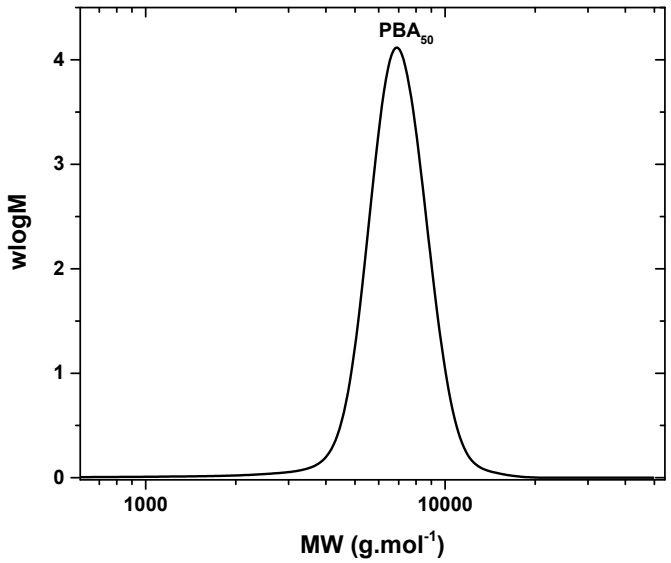
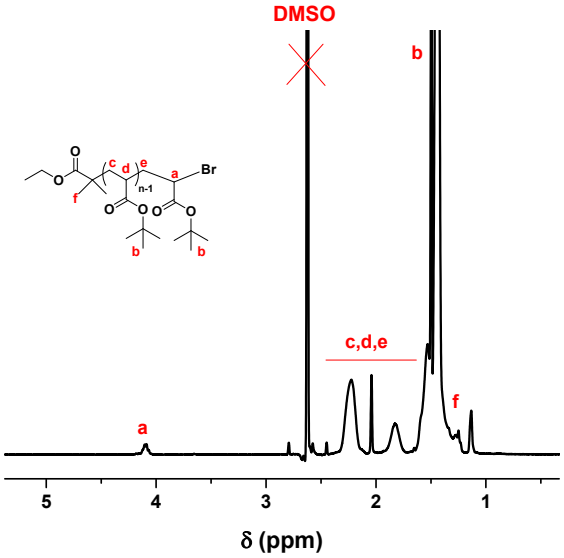


Figure S12: ^{1}H NMR and molecular weight distribution of PBA synthesized *via* photo-induced polymerization. Initial conditions [*n*-BA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMF 50% *v/v*.



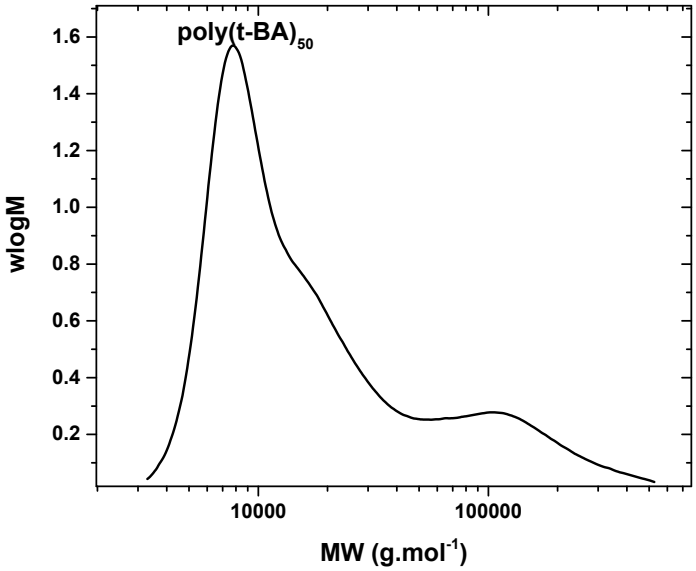
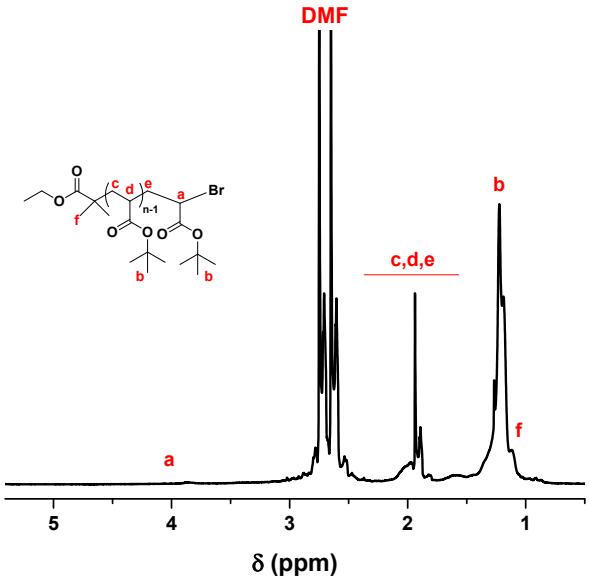


Figure S13: ^{1}H NMR and molecular weight distribution of poly(*t*-BA) synthesized *via* photo-induced polymerization. Initial conditions [*t*-BA]:[EBiB]:[[Cu(Me$_6$-Tren)(O$_2$CH)](ClO$_4$)] = [20]:[1]:[0.08], DMSO 50% *v/v*.



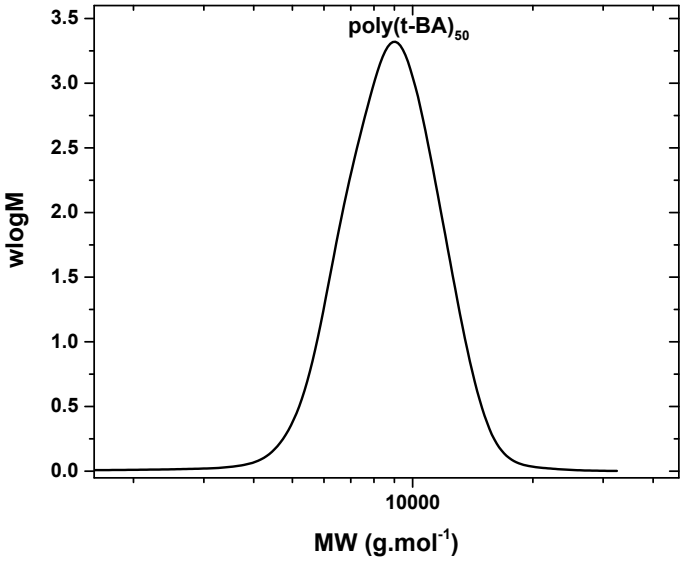
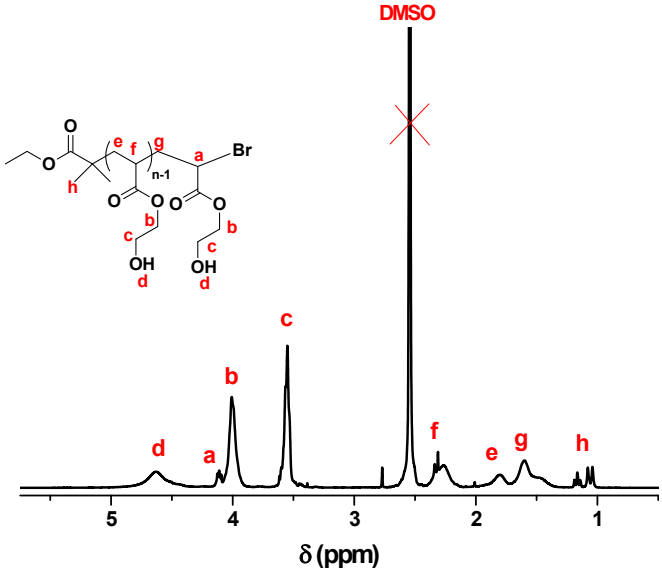


Figure S14: ^{1}H NMR and molecular weight distribution of poly(*t*-BA) synthesized *via* photo-induced polymerization. Initial conditions [*t*-BA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMF 50% *v/v*.



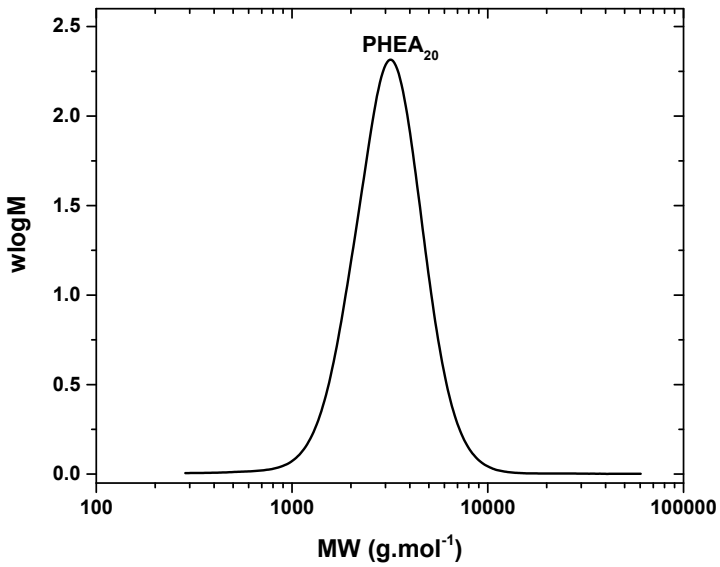
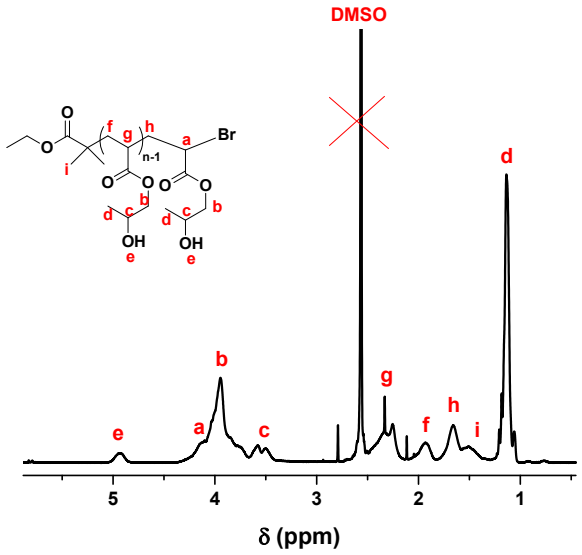


Figure S15: ^{1}H NMR and molecular weight distribution of PHEA synthesized *via* photo-induced polymerization. Initial conditions [HEA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.



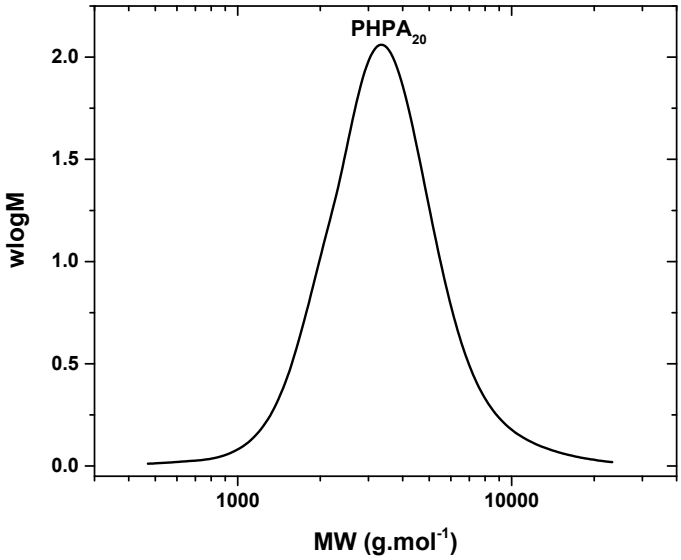
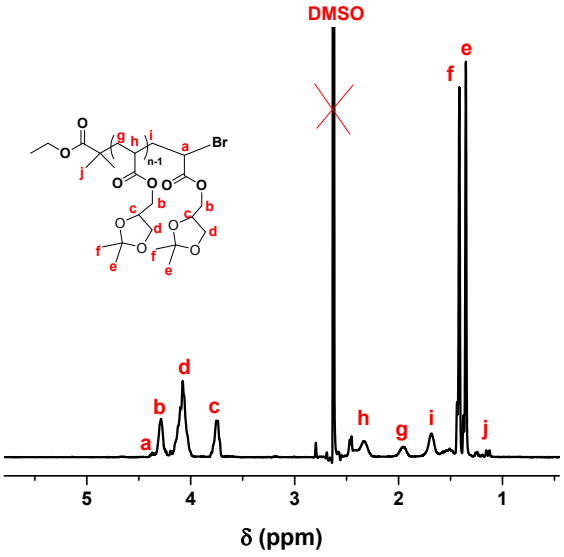


Figure S16: ^{1}H NMR and molecular weight distribution of PHPA synthesized *via* photo-induced polymerization. Initial conditions [HPA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [20]:[1]:[0.08], DMSO 50% *v/v*.



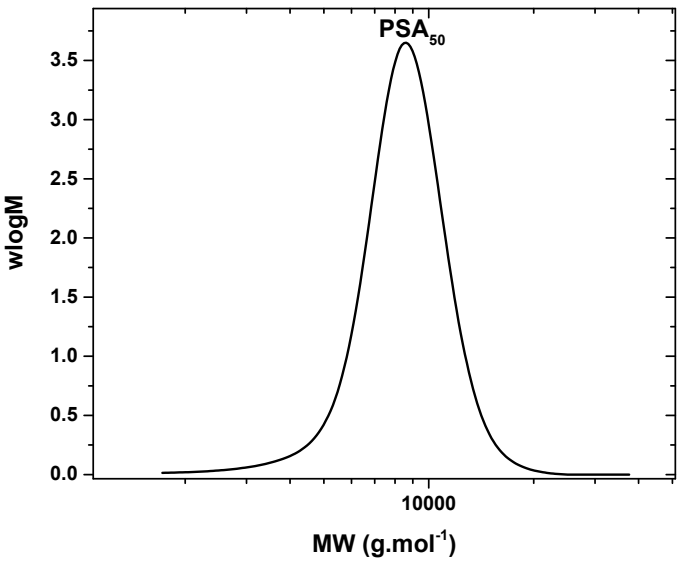
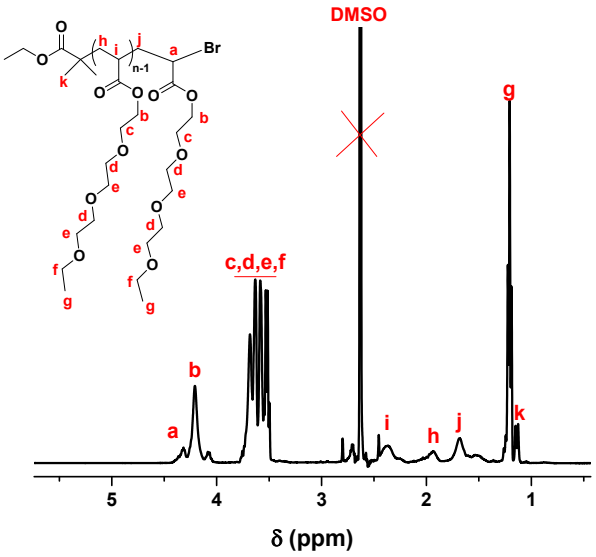


Figure S17: ^{1}H NMR and molecular weight distribution of PSA synthesized *via* photo-induced polymerization. Initial conditions [SA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.



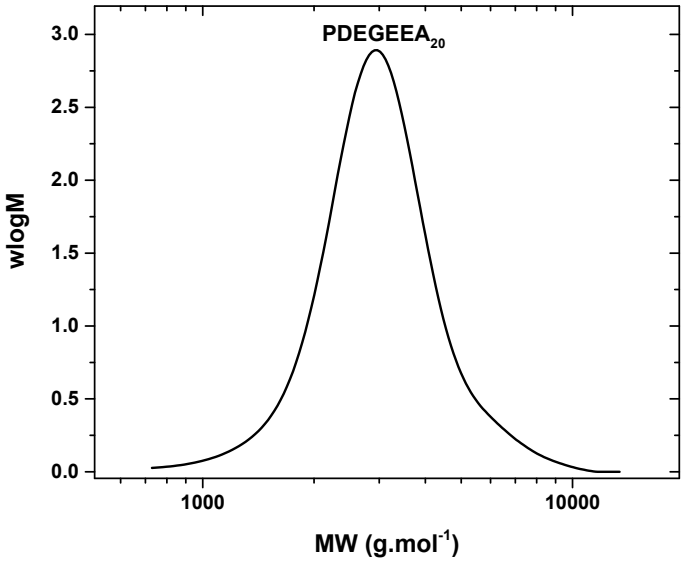
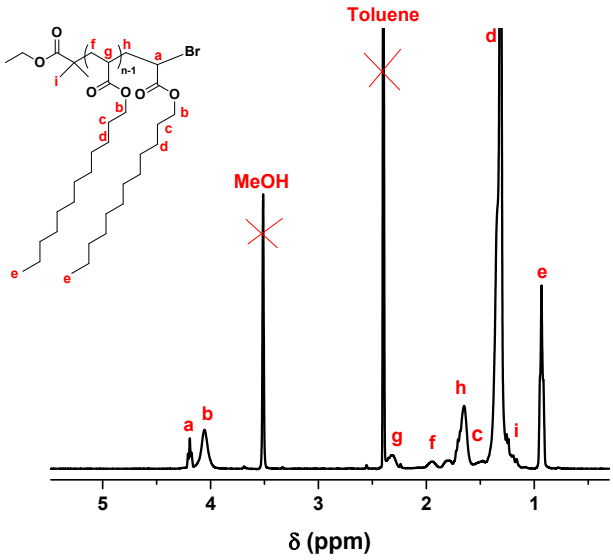


Figure S18: ^{1}H NMR and molecular weight distribution of PDEGEEA synthesized *via* photo-induced polymerization. Initial conditions [DEGEEA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.



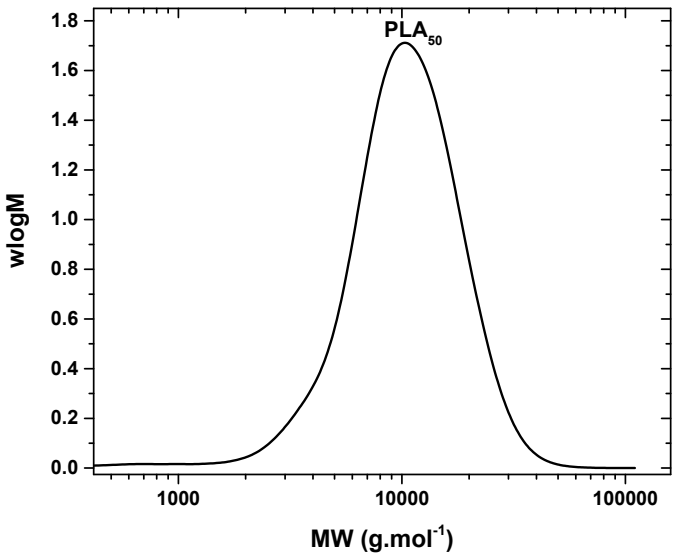
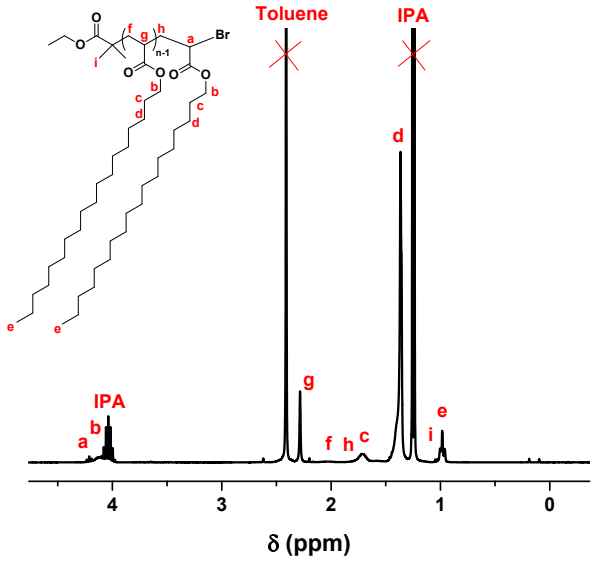


Figure S19: ^{1}H NMR and molecular weight distribution of PLA synthesized *via* photo-induced polymerization. Initial conditions [LA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], [Toluene]:[MeOH] = [4]:[1] 50% *v/v*.



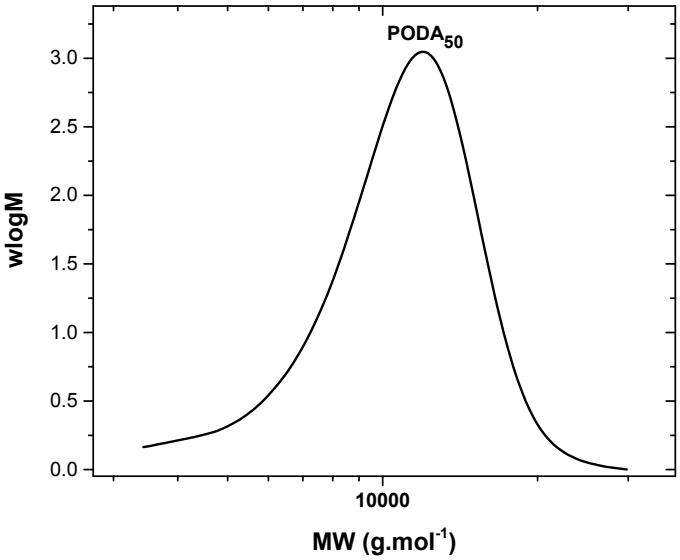
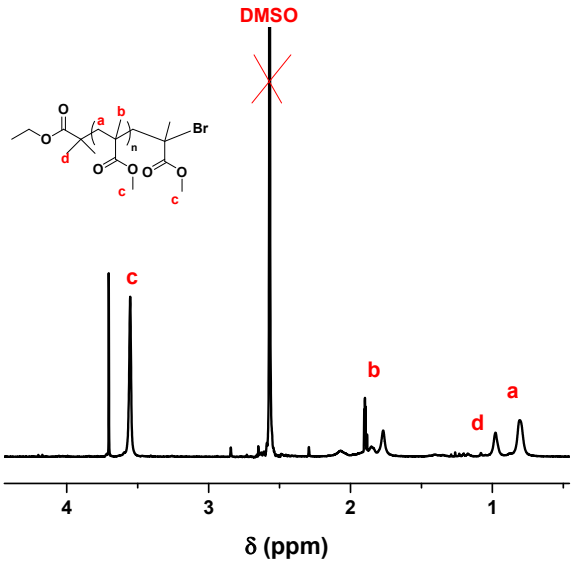


Figure S20: ^{1}H NMR and molecular weight distribution of PODA synthesized *via* photo-induced polymerization. Initial conditions [ODA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], [Toluene]:[IPA] = [4]:[1] 50% *v/v*.



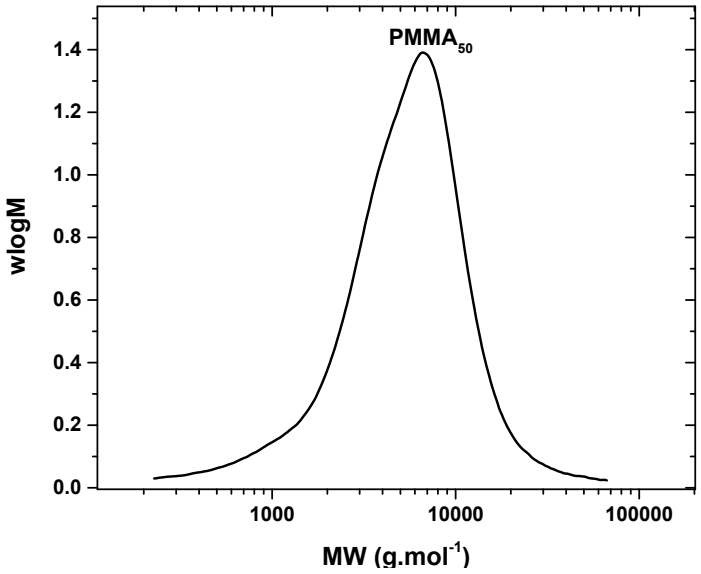


Figure S21: ^{1}H NMR and molecular weight distribution of PMMA synthesized *via* photo-induced polymerization. Initial conditions [MMA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.

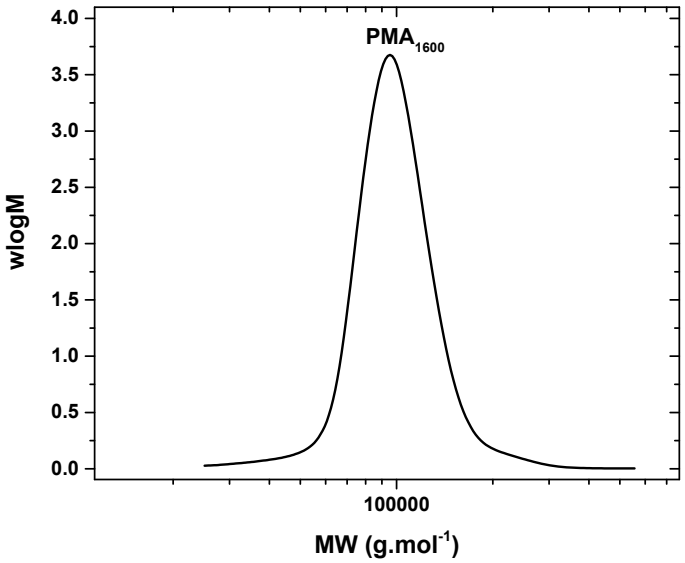


Figure S22: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [1600]:[1]:[0.08], DMSO 50% *v/v*.

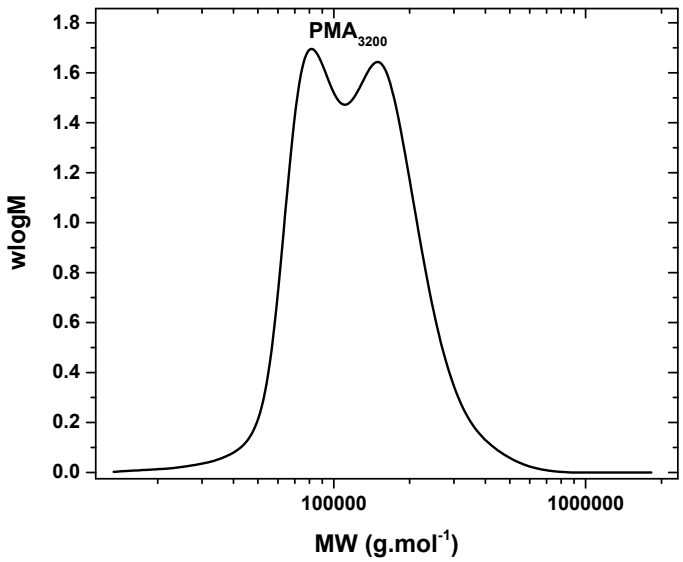


Figure S23: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [3200]:[1]:[0.16], DMSO 50% *v/v*.

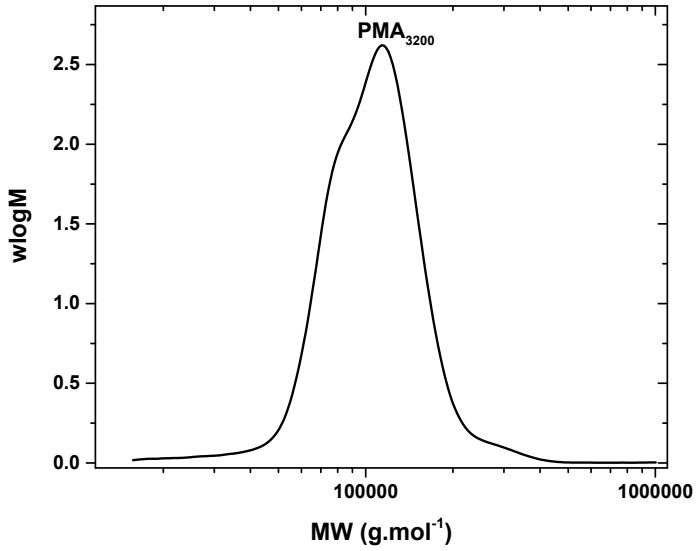


Figure S24: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)] = [3200]:[1]:[0.32], DMSO 50% *v/v*.

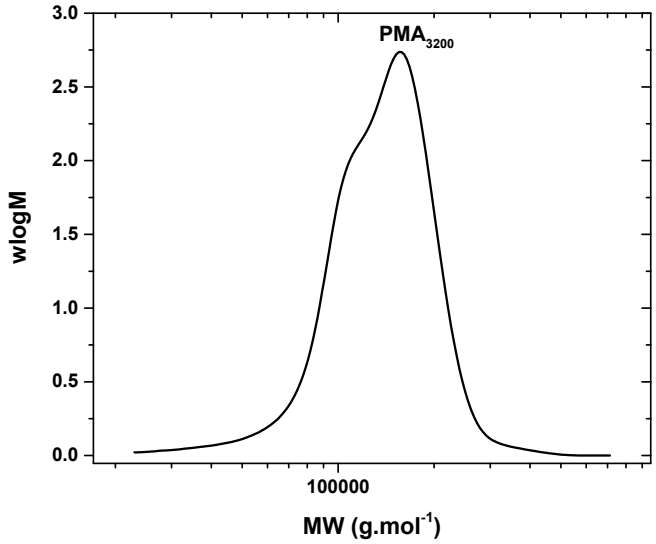


Figure S25: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_6-Tren)(O_2CH)](ClO_4)]:[NaBr] = [3200]:[1]:[0.32]:[0.32], DMSO 50% *v/v*.

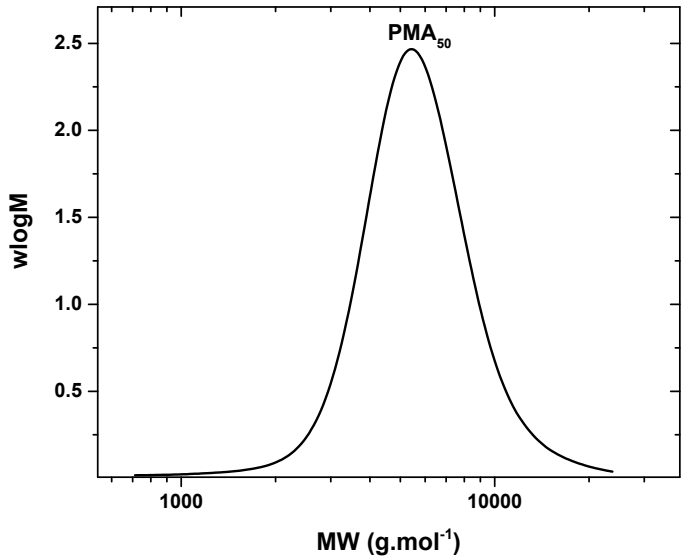


Figure S26: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.

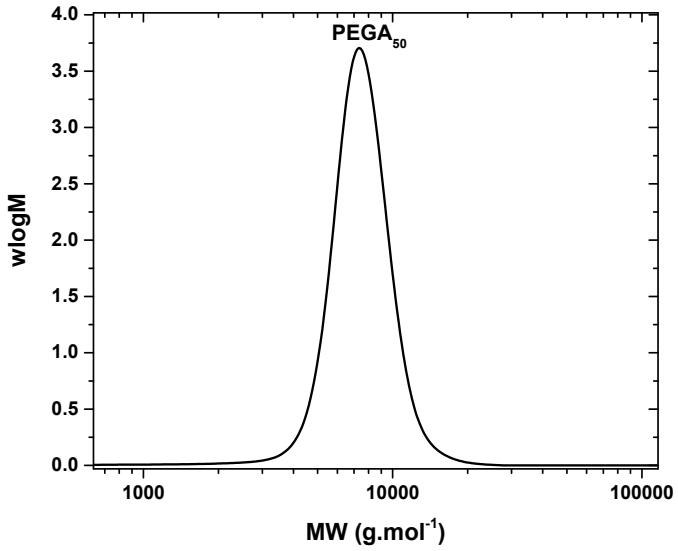


Figure S27: Molecular weight distribution of PEGA synthesized *via* photo-induced polymerization. Initial conditions [EGA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMF 50% *v/v*.

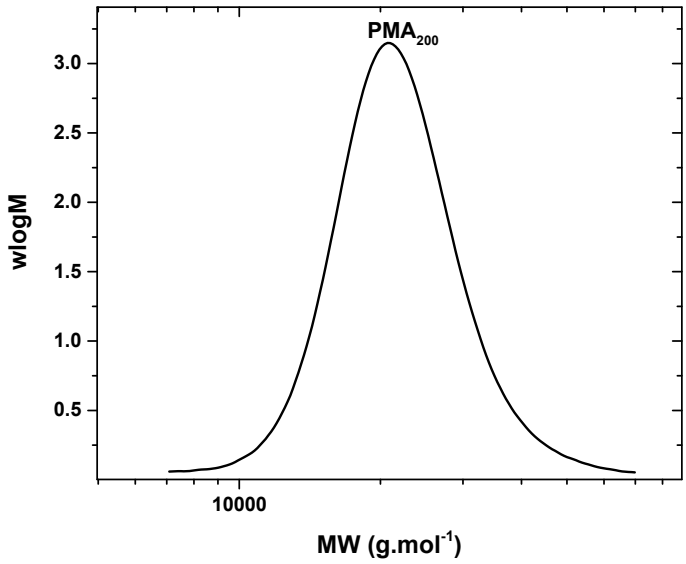


Figure S28: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [200]:[1]:[0.08], DMSO 50% *v/v*.

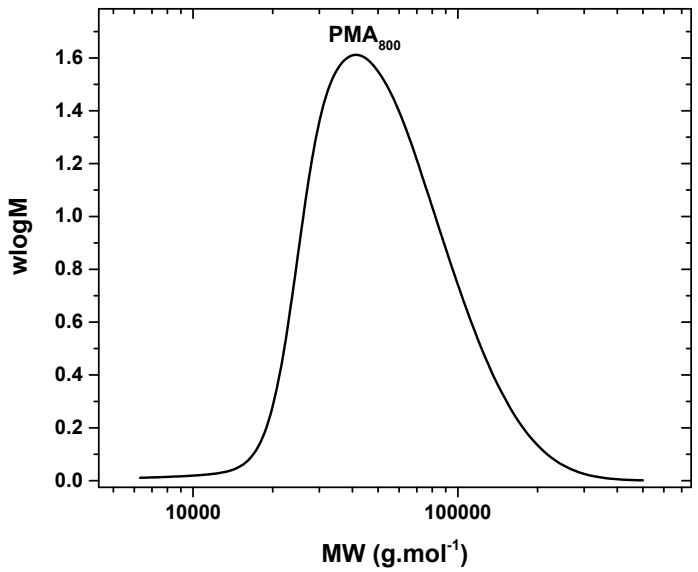


Figure S29: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [800]:[1]:[0.08], DMSO 50% *v/v*.

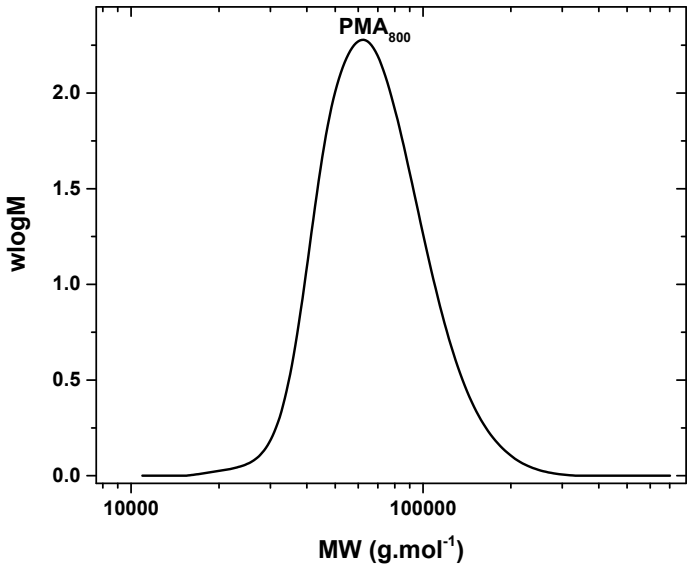


Figure S30: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [800]:[1]:[0.16], DMSO 50% *v/v*.

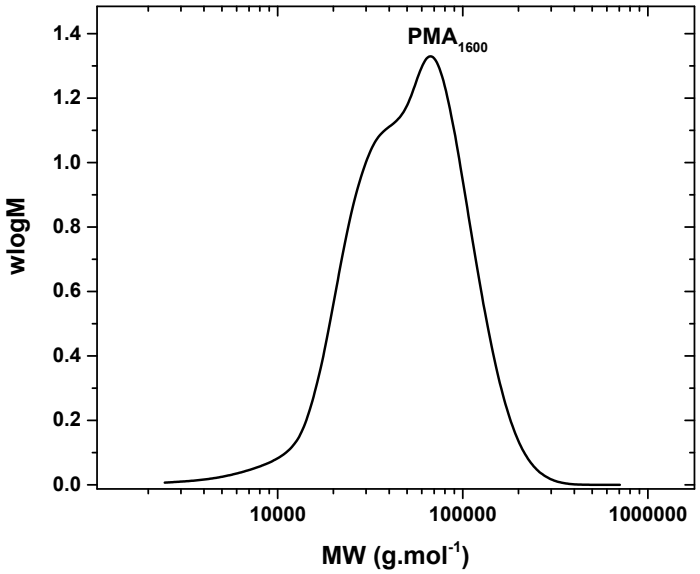


Figure S31: Molecular weight distribution of PMA synthesized *via* photo-induced polymerization. Initial conditions [MA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [1600]:[1]:[0.16], DMSO 50% *v/v*.

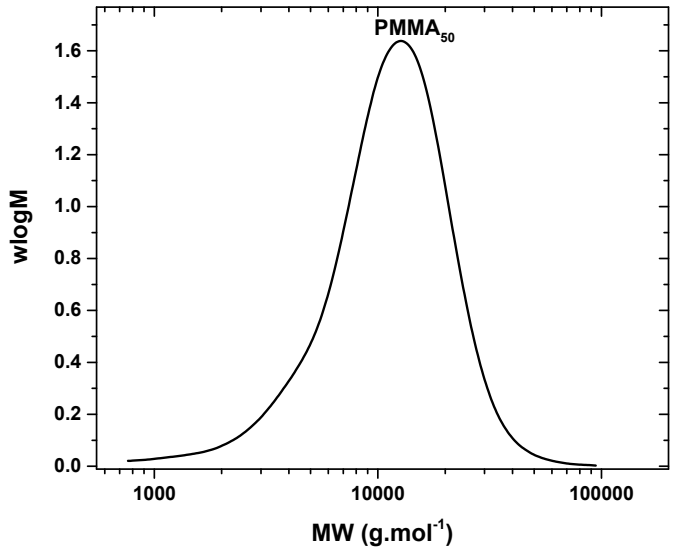


Figure S32: Molecular weight distribution of PMMA synthesized *via* photo-induced polymerization. Initial conditions [MMA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [50]:[1]:[0.08], DMSO 50% *v/v*.

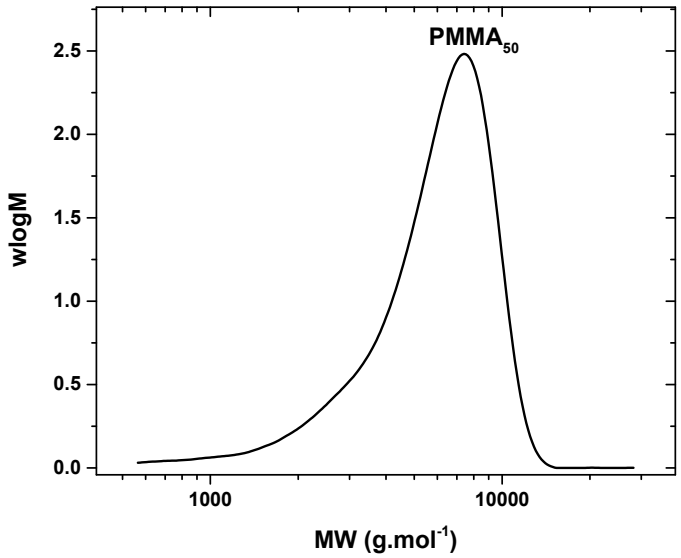


Figure S33: Molecular weight distribution of PMMA synthesized *via* photo-induced polymerization. Initial conditions [MMA]:[EBiB]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)]:[NaBr] = [50]:[1]:[0.08]:[0.08], DMSO 50% *v/v*.

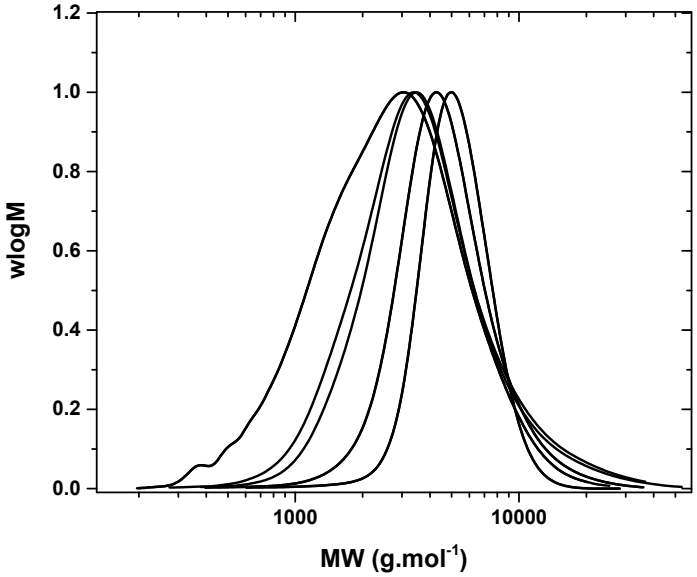


Figure S34: Molecular weight distributions for the concecutive light and dark exposures. Initial conditions: [MA]:[I]:[[Cu(Me_5-Dien)(O_2CH)](ClO_4)] = [50]:[1]:[0.08] in DMSO 50% *v/v*.

References

1. Scott, M. J.; Goddard, C. A.; Holm, R. H. *Inorganic Chemistry* **1996,** 35, (9), 2558-2567.
2. Ciampolini, M.; Nardi, N. *Inorganic Chemistry* **1966,** 5, (1), 41-44.