Supporting Information

Visible Light and Sunlight Photoinduced ATRP with ppm of Cu Catalyst

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Experimental:

Materials. All chemicals were purchased from commercial sources, *e.g.*, Aldrich, TCI, and used as received if not stated otherwise. Tris(2-pyridylmethyl) amine (TPMA) was purchased from ATRP Solutions. Tris((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)amine (TPMA*) was synthesized as reported in the literature.[1] Methyl methacrylate (MMA), methyl acrylate (MA) and ethyl acrylate (EA), oligo(ethylene oxide) monomethyl ether methacrylate of molecular weight 300 (OEOMA) were passed over a column filled with basic alumina to remove inhibitor prior to use.

Instrumentation.

Gel permeation chromatography (GPC): GPC was used to determine number average molecular weight (M_n) and M_w/M_n values. The GPC was conducted with a Waters 515 HPLC Pump and Waters 2414 Refractive Index Detector using PSS columns (Styrogel 10^2, 10^3, 10^5 Å) in tetrahydrofuran (THF) as an eluent at a flow rate of 1 mL/min at 35 °C. The column system was calibrated with 12 linear poly(methyl methacrylate) (PMMA, M_n = 800 ~ 2,570,000) standards. Conversion of monomer was determined by ^{1}H NMR spectroscopy. Absolute values of molecular weighs of PMA were calculated utilizing universal calibration as reported in literature.[2]

NMR: Monomer conversion was measured using ^{1}H NMR spectroscopy, using a Bruker Avance 500 MHz spectrometer at room temperature.

UV-Visible Spectroscopy: All characterizations were performed using a Varian Cary 5000 UV/Vis/NIR spectrometer. Measurements of activation rate coefficients were performed on Agilent 8453 UV-Vis Spectrometer, with measurements every 5 s at 750 nm.

Photoreactors:

The samples were illuminated in a custom designed, multi-well photoreactor: A 5 m long 24 W LED strip with 300 diodes (violet, 392 nm: superbrightleds.com WFLS-UV300; blue, 450 nm: Solid Apollo SA-LS-BL-3528-300-24V; red, 631 nm: SA-LS-RE-3528-300-24V) was mounted inside an 8 inch (203 mm) galvanized steel tube in a spiral pattern. The intensities of the three photoreactors were 0.90 ± 0.05 mW/cm^2, $1.00 \pm 0.05 \times 10^1$ mW/cm^2 and 8.9 ± 0.5 mW/cm^2 for the violet, blue, and red photoreactors respectively, with errors given by the 5% error as mentioned on the specifications. The 60 mm high illumination zone was centered on the samples, which were magnetically stirred in a Schlenk flask under nitrogen. The emission spectra of the three different photo reactors was obtained on a Horiba Jobin-Yvon Fluorolog 3, and the intensities of the photoreactors were determined using a Thor Labs PM100D light meter, with a S120VC detector.

Procedures.

Typical Polymerization of MMA:

Ethyl α-bromophenylacetate (36.5 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 75 μL of a 270 mM TPMA stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MMA (4.51 g, 45 mmol) and DMF (4.53 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor, irradiating at the desired wavelength (392, 454 or 631 nm), and monitored by taking samples periodically, analysing the polymer by both GPC and NMR.

Polymerization of MMA at 29 °C:

Ethyl α-bromophenylacetate (36.5 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 75 μL of a 270 mM TPMA stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MMA (4.51 g, 45 mmol) and DMF (4.53 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor with a water bath at 29 °C, irradiating at 392, and monitored by taking samples periodically, analysing the polymer by both GPC and NMR.

Typical Polymerization of MA:

Ethyl α-bromoisobutyrate (29.3 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 150 μL of a 135 mM TPMA* stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MA (3.87 g, 45 mmol) and DMF (3.85 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor, irradiating at the desired wavelength (392, 454 or 631 nm), and monitored by taking samples periodically, analysing the polymer by both GPC and NMR.

Polymerization of MMA under Sunlight:

Ethyl α-bromophenylacetate (36.5 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 75 μL of a 270 mM TPMA stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MMA (4.51 g, 45 mmol) and DMF (4.53 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was taken outside on a clear day and irradiated by sunlight. After 12 h of irradiation the reaction mixture was placed in the dark for 14 h, after which the reaction mixture was irradiated by sunlight again. The reaction was monitored by taking samples periodically, analysing the polymer by both GPC and NMR. The maximum temperature was 29 °C on the first day and 33 °C on the second day.

Polymerization of MA under Sunlight:

Ethyl α-bromoisobutyrate (29.3 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 150 μL of a 135 mM TPMA* stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MA (3.87 g, 45 mmol) and DMF (3.85 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was taken outside on a clear day and irradiated by sunlight, with the reaction monitored by taking samples periodically, analysing the polymer by both GPC and NMR. The maximum temperature was 29 °C.

Measurement of heating induced by Sunlight:

Ethyl α-bromophenylacetate (36.5 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 75 μL of a 270 mM TPMA stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MMA (4.51 g, 45 mmol) and DMF (4.53 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was taken outside on a clear day and irradiated by sunlight. The temperature of the reaction mixture in the sun was measured by a thermocouple in the reaction mixture and compared to the reaction mixture in the shade. Typical temperature differences between shade and sunlight were 2-4 °C.

Preparation of a PMMA macroinitiator:

Ethyl α-bromophenylacetate (36.5 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 75 μL of a 270 mM TPMA stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MMA (4.51 g, 45 mmol) and DMF (4.53 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor, irradiated at 392 nm for 23 h. The resulting conversion was 49%, and the polymer had M_n = 15000, and M_w/M_n = 1.10. The polymer was purified by precipitation into 10% water in methanol at 0 °C, followed by reprecipitation into methanol at 0 °C. The resulting macroinitiator was dried overnight, and characterized by GPC to give a macroinitiator of M_n = 15000, and M_w/M_n = 1.10.

Chain Extension of PMMA macroinitiator with EA:

PMMA macroinitiator (0.676 g, 0.045 mmol), 7.5 μL of a 180 mM $CuBr_2$ stock solution in DMF (1.35 μmol) and 45 μL of a 135 mM TPMA* stock solution in DMF (6.09 μmol) were combined in a vial. To this mixture EA (1.35 g, 13.5 mmol) and DMF (1.36 g) were added and the solution was homogenized by vigorous stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor, irradiated at 392 nm, and monitored by taking samples periodically, analysing the polymer by both GPC and NMR.

Polymerization of MMA with Dark Periods:

Ethyl α-bromophenylacetate (36.5 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 75 μL of a 270 mM TPMA stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MMA (4.51 g, 45 mmol) and DMF (4.53 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor, irradiating at 392 nm, for 5.5 h, followed by 13 hours of dark time, followed by 9 hours of irradiation at 392 nm, followed by 14.5 h of dark time, followed by 11.5 hours of irradiation at 392 nm. The reaction was monitored by taking samples periodically, analysing the polymer by both GPC and NMR.

Typical Polymerization of MA with Dark Periods:

Ethyl α-bromoisobutyrate (29.3 mg, 0.150 mmol), 25 μL of a 180 mM $CuBr_2$ stock solution in DMF (4.5 μmol) and 150 μL of a 135 mM TPMA* stock solution in DMF (20.3 μmol) were combined in a vial. To this mixture MA (3.87 g, 45 mmol) and DMF (3.85 g) were added and the solution was homogenized by stirring. The solution was transferred to a Schlenk Flask with a magnetic stirrer, and degassed by four Freeze-Pump-Thaw cycles. The reaction mixture was placed in a photoreactor, irradiating at 392 nm, for 5.5 h, followed by 13 hours of dark time, followed by 9 hours of irradiation at 392 nm, followed by 14.5 h of dark time, followed by 11.5 hours of irradiation at 392 nm. The reaction was monitored by taking samples periodically, analysing the polymer by both GPC and NMR.

Measurement of Activation Rate Coefficients:

A solution of Cu^IBr/TPMA was prepared by Freeze-Pump-Thawing acetonitrile four times, and dissolving CuBr (21.5 mg, 0.15 mmol) and TPMA(65.3 mg, 0.225 mmol) into 25 mL of acetonitrile. Similarly benzyl bromide (25.6 mg, 0.15 mmol) and TEMPO (468 mg, 3 mmol) were dissolved in 25 mL of acetonitrile and Freeze-Pump -Thawed four times. A Schlenk flask equipped with a quartz cuvette (1 cm path length) was evacuated and backfilled with nitrogen 10 times, and to this cuvette 2.5 mL of the Cu^IBr/TPMA stock solution was added. For measurement in the absence of irradiation 2.5 mL of the benzyl bromide/TEMPO solution was added and the cuvette placed in the UV-Vis spectrometer, and the spectrum was recorded over time. For the measurement in the presence of irradiation, 2.5 mL of the benzyl bromide/TEMPO solution was added, and the cuvette placed in the spectrometer, with the photoreactor sitting over the UV-Vis spectrometer.

Additional Characterization:

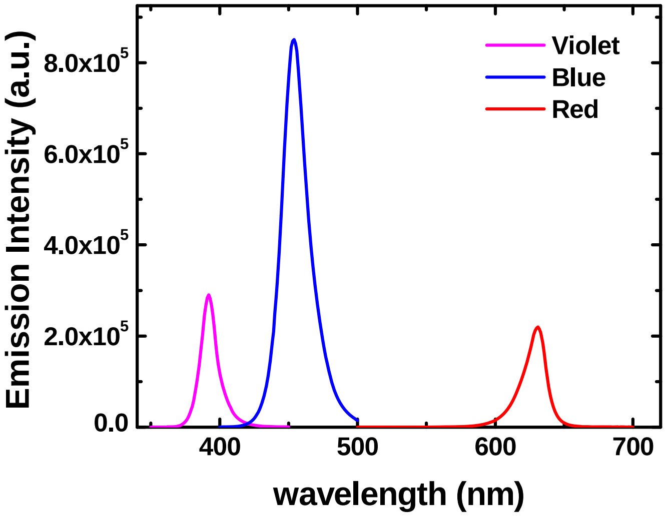

Figure S1: Emission Spectrum of LEDs. The spectra are uncorrected, but the sensitivity in the blue and violet regions is similar, and the sensitivity in the red region is greatly diminished due to the week response of the PMT. The peaks are 392 ± 7 nm for the violet LED, 450 ± 10 nm for the blue LED and 631 ± 9 nm for the red LED, with the breadths of the distribution are given by half of the full width at half maximum. The intensities of the three photoreactors were 0.90 ± 0.05 mW/cm^2, $1.00 \pm 0.05 \times 10^1$ mW/cm^2 and 8.9 ± 0.5 mW/cm^2 for the violet, blue, and red photoreactors respectively.

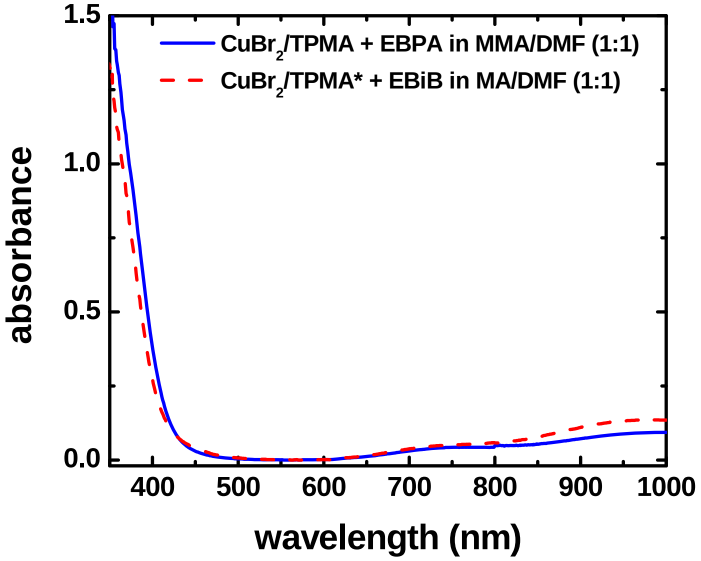

Figure S2: UV/Vis/NIR absorption spectra of $CuBr_2$/TPMA and EBPA in MMA/DMF and $CuBr_2$/TPMA* and EBiB in MA/DMF. Conditions: [MMA]:[EBPA]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.135 or [MA]:[EBiB]:[$CuBr_2$]:[TPMA*] = 300:1:0.03:0.135 both with 50 vol% DMF, and a pathlength of 1 cm.

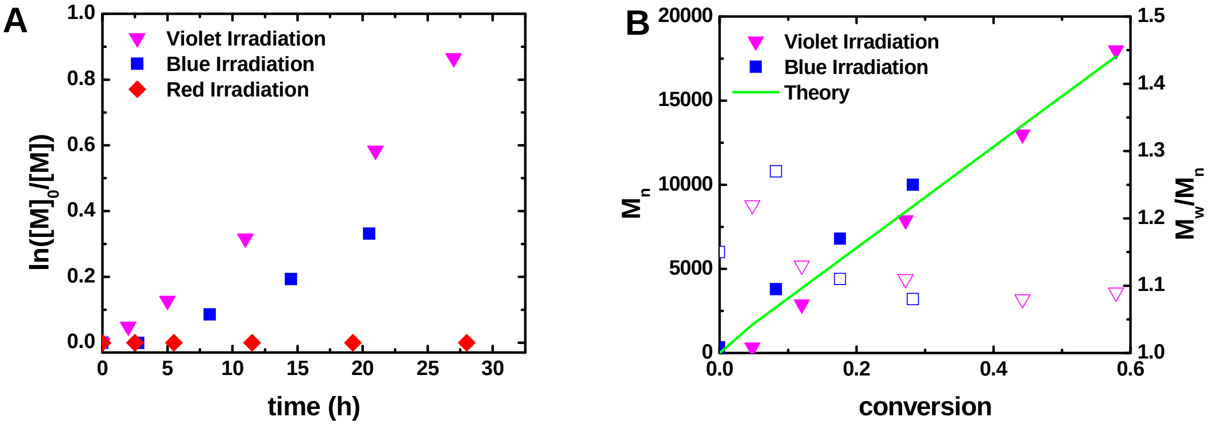

Figure S3: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MMA with $CuBr_2$/TPMA. Conditions: [MMA]:[EBPA]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature.

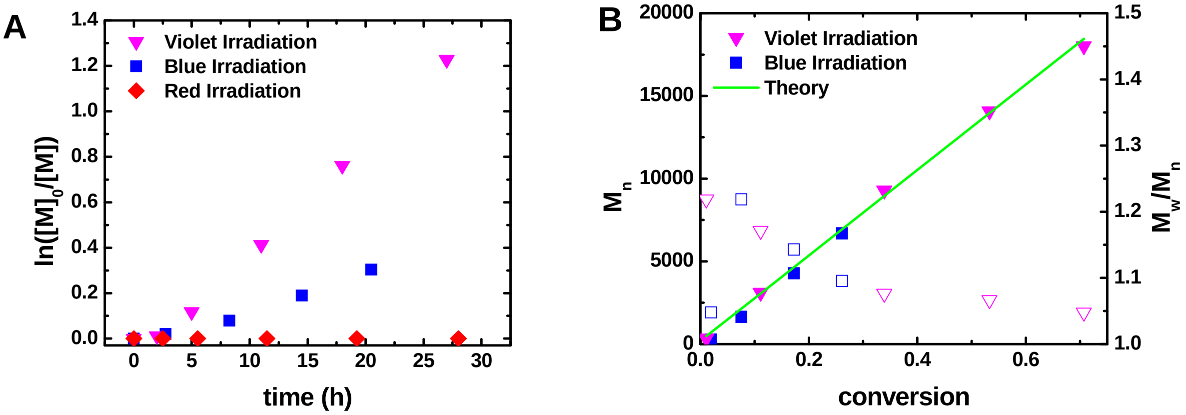

Figure S4: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MA with $CuBr_2$/TPMA*. Conditions: [MA]:[EBiB]:[$CuBr_2$]:[TPMA*] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature.

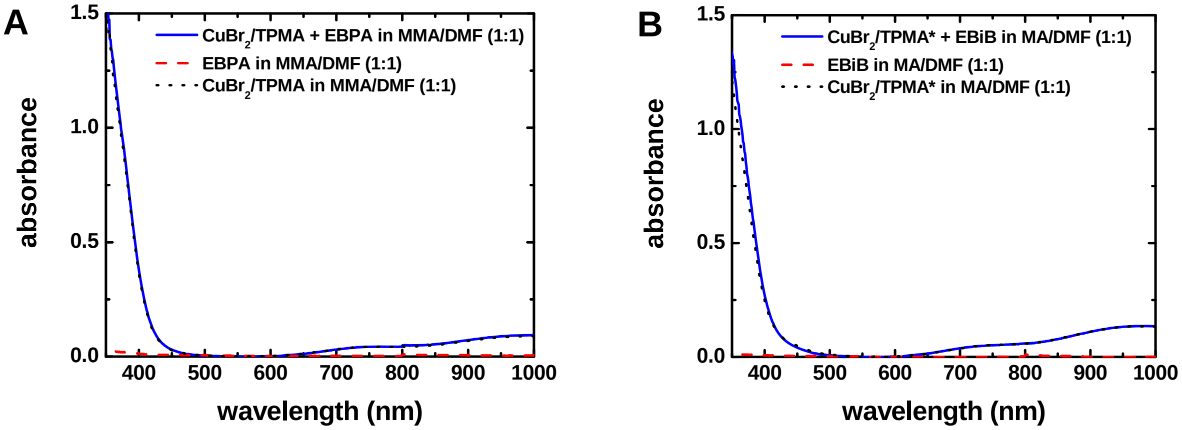

Figure S5: UV/Vis/NIR absorption spectra of: (A) $CuBr_2$/TPMA and EBPA in MMA/DMF, and (B) $CuBr_2$/TPMA* and EBiB in MA/DMF. Base conditions: [MMA]:[EBPA]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.135 or [MA]:[EBiB]:[$CuBr_2$]:[TPMA*] = 300:1:0.03:0.135 both with 50 vol% DMF, or combinations with either no initiator or no $CuBr_2$ and no ligand. In all cases a pathlength of 1 cm was used.

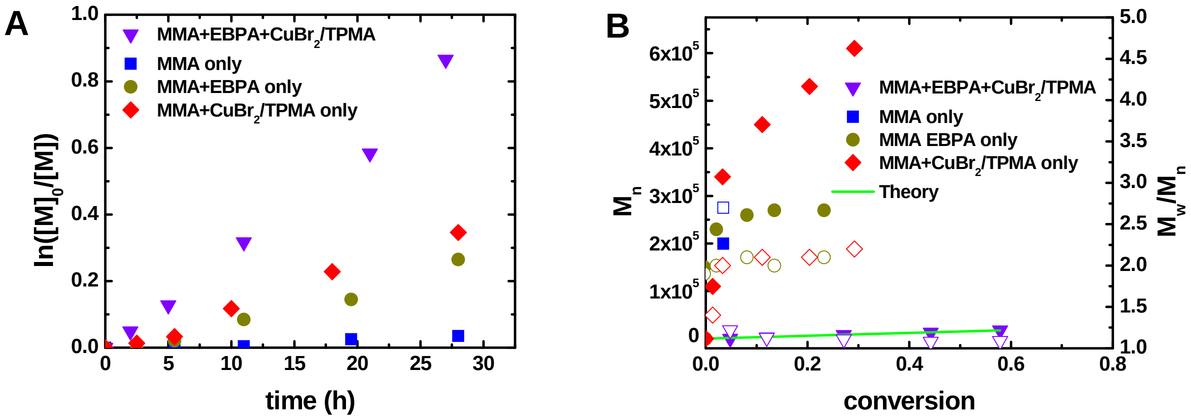

Figure S6: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MMA with $CuBr_2$/TPMA blank experiments. Base conditions: [MMA]:[EBPA]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature with violet irradiation.

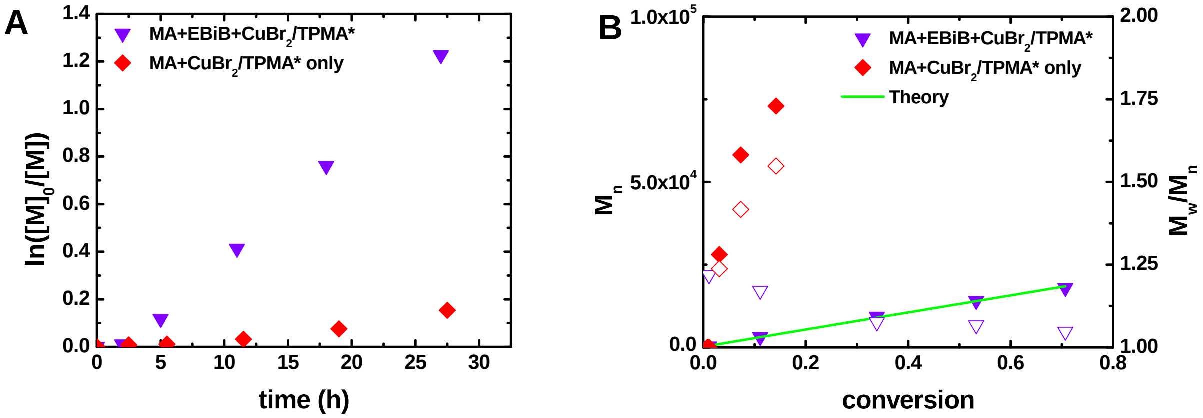

Figure S7: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MA with $CuBr_2$/TPMA* blank experiments. Base conditions: [MA]:[EBiB]:[$CuBr_2$]:[TPMA*] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature with violet irradiation.

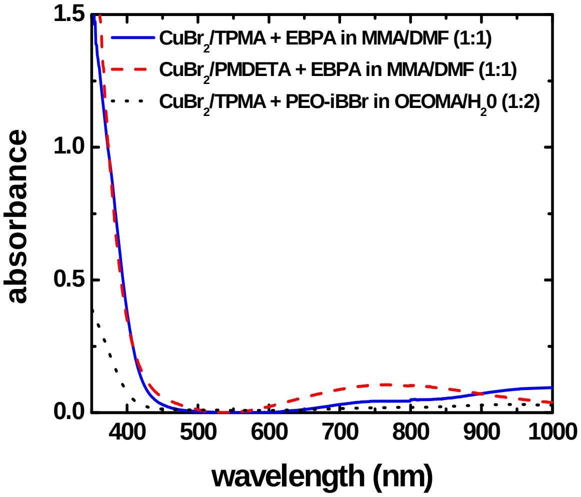

Figure S8: UV/Vis/NIR absorption spectra of $CuBr_2$/TPMA and EBPA in MMA/DMF, $CuBr_2$/PMDETA and EBPA in MMA/DMF and $CuBr_2$/TPMA and PEO-iBBr in OEOMA/H_2O. Conditions: [MMA]:[EBPA]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.135, [MMA]:[EBPA]:[$CuBr_2$]:[PMDETA] = 300:1:0.03:0.135 both in 50 vol% DMF, [OEOMA]:[PEO-iBBr]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.24 with 66 vol% H_2O with respect to monomer. In all cases a pathlength of 1 cm was used.

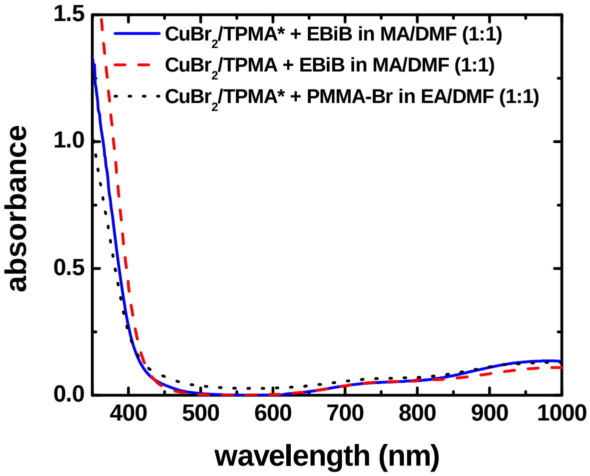

Figure S9: UV/Vis/NIR absorption spectra of $CuBr_2$/TPMA* and EBiB in MA/DMF, $CuBr_2$/TPMA and EBiB in MA/DMF, and $CuBr_2$/TPMA* and MMA-Br in EA/DMF. Conditions: [MA]:[EBiB]:[$CuBr_2$]:[TPMA*] = 300:1:0.03:0.135, [MA]:[EBiB]:[$CuBr_2$]:[TPMA*] = 300:1:0.03:0.135, [EA]:[MMA-Br]:[$CuBr_2$]:[TPMA*]= 300:1:0.03:0.135. For each system there is with 50 vol% DMF with respect to monomer. In all cases a pathlength of 1 cm was used.

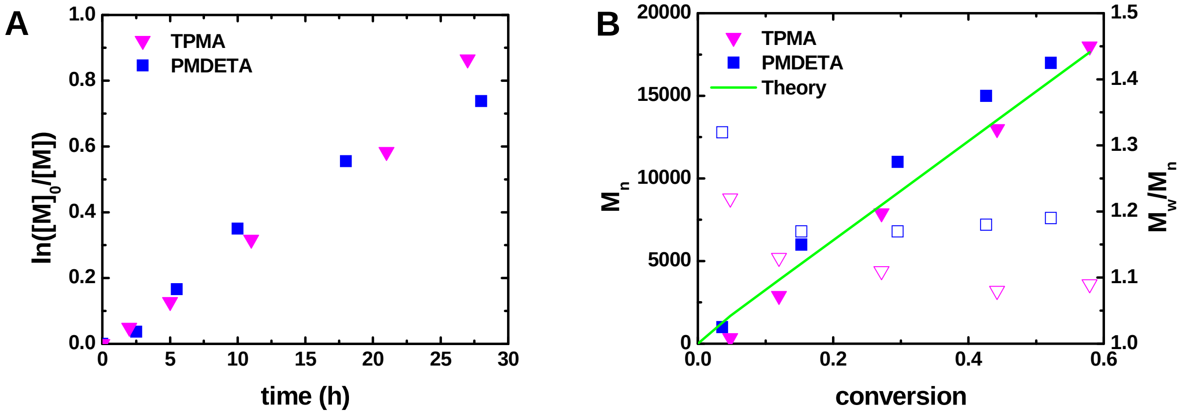

Figure S10: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MMA with $CuBr_2$/TPMA or $CuBr_2$/PMDETA. Conditions: [MMA]:[EBPA]:[$CuBr_2$]:[L] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature with violet irradiation.

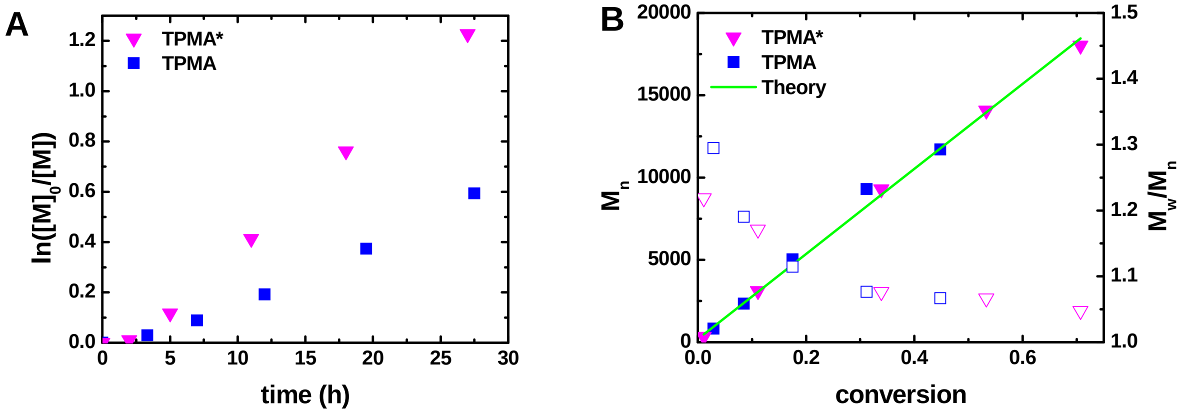

Figure S11: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MA with $CuBr_2$/TPMA* or $CuBr_2$/TPMA. Conditions: [MA]:[EBiB]:[$CuBr_2$]:[L] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature with violet irradiation.

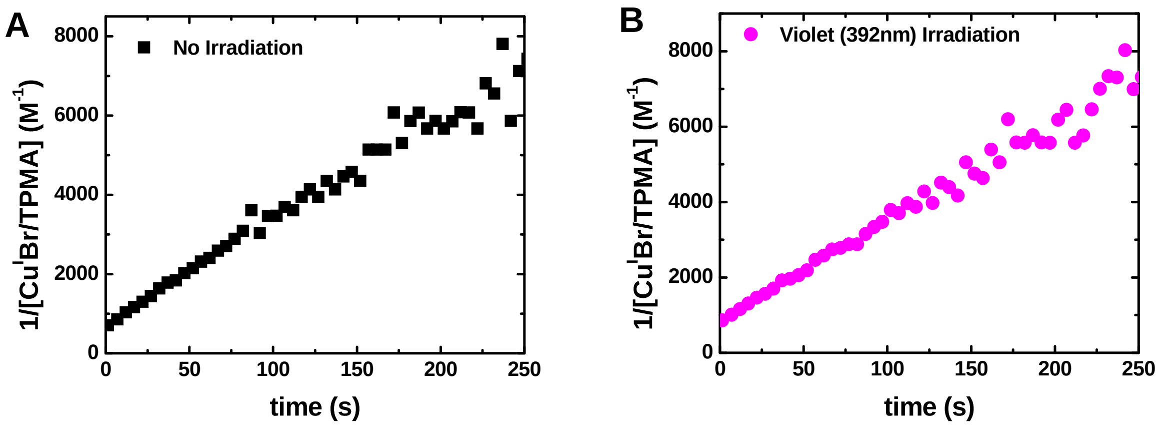

Figure S12: Second order plot of Cu^IBr/TPMA activation of benzyl bromide (BzBr) with excess TEMPO. (A) shows plot in absence of irradiation, and (B) shows plot in the presence of violet irradiation (392 nm). In both cases conditions $[CuBr]_0 = 3$ mM, $[TPMA]_0 = 4.5$ mM, [BzBr] = 3 mM, [TEMPO] = 60 mM in 5 mL of acetonitrile. The activation rate coefficient determined from the slope with no irradiation is 25.4 ± 0.6 M^{-1} s^{-1}, and the activation rate coefficient determined from the slope with violet irradiation is 25.9 ± 0.6 M^{-1} s^{-1}.

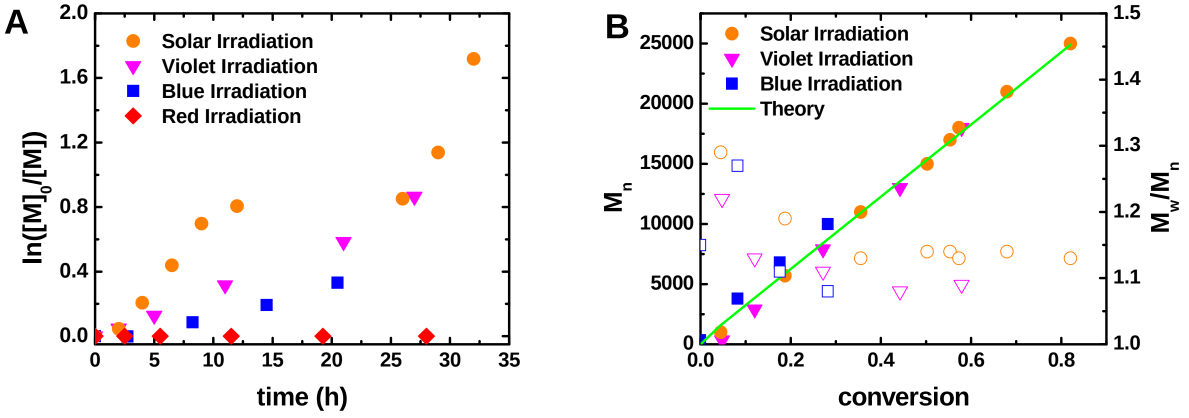

Figure S13: (A) Kinetics and (B) Evolution of M_n (solid points) and M_w/M_n (open points) for the photoinduced polymerization of MMA with $CuBr_2$/TPMA different irradiation sources. Conditions: [MMA]:[EBPA]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.135 with 50 vol% DMF at room temperature, and there is a dark period from 12 h to 26 h.

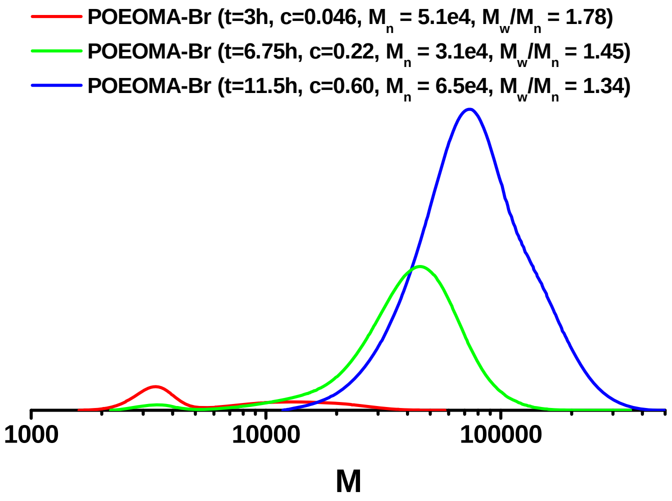

Figure S14: Evolution of the molecular weight distribution for the photoinduced polymerization of OEOMA with $CuBr_2$/TPMA. Conditions: [OEOMA]:[PEO-iBBr]:[$CuBr_2$]:[TPMA] = 300:1:0.03:0.24 with 30 mM NaBr, and 67 vol% H_2O at room temperature with violet irradiation.

Estimates of heating due to polymerization and photons and dissipation to the environment:

In order to estimate the rate of heating due to polymerization the following data were used. The heat of polymerization of MA is -78 kJ/mol,[3] and for MMA the heat of polymerization is -54 kJ/mol.[4] Therefore given a conversion of 0.71 after 27 h, with 3.87 g of MA, a total of 2500 J is released, with an average heating rate of 0.026 W. Similarly for MMA a conversion of 0.58 after 27 h, with 4.51 g leads to a total of 1400 J being released with an average heating rate of 0.015 W.

To estimate the heating rate due to irradation the energy of the source was used. For the violet light the intensity was found to be 0.90 mW/cm^2. Approximating the solution in the Schlenk flask as a half sphere of radius 1.5 cm, implies that 0.019 W are incident on the sample. Since the absorbance is quite high in the violet region, the majority of this radiation will be absorbed. In contrast, with blue and red radiation, the absorbance of the solution is lower, implying that in these cases only a small fraction of the incident energy is absorbed by the sample.

To estimate if appreciable heating due to either polymerization or due to the irradiation occurs, the rate of radiative dissipation is estimated using the Stefan-Boltzmann law. Assuming the reaction mixture is at 296 K (23 °C), and a 1.5 cm half sphere, the rate of blackbody radiation is 0.92 W.

Since the rate of black body radiation is over an order of magnitude higher than the rate of heating due to polymerization or the power of the LEDs, assuming full absorbance of the violet LEDs, no appreciable heating should occur in this system, since the rate of energy dissipation greatly exceeds the rate of heating.

References:

(1) Schröder, K.; Mathers, R. T.; Buback, J.; Konkolewicz, D.; Magenau, A. J. D.; Matyjaszewski, K. *ACS Macro Lett.* **2012**, 1037-1040.
(2) Gruendling, T.; Junkers, T.; Guilhaus, M.; Barner-Kowollik, C. *Macromol. Chem. Phys.* **2010**, *211*, 520-528.
(3) Theis, A.; Feldermann, A.; Charton, N.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Macromolecules* **2005**, *38*, 2595-2605.
(4) Horie, K.; Mita, I.; Kambe, H. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1968**, *6*, 2663-2676.