

Supporting Information

A logic gate for external regulation of photopolymerization

Sivaprakash Shanmugam,^a Jiangtao Xu,^{a,b} and Cyrille Boyer^{a,b}*

*a- Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, UNSW
Australia, Sydney, NSW 2052, Australia*

*b- Australian Centre for NanoMedicine, School of Chemical Engineering, UNSW Australia, Sydney,
NSW 2052, Australia*

E-mail: cboyer@unsw.edu.au

EXPERIMENTAL SECTION

Materials: Oligo(ethylene glycol) methyl ether methacrylate (OEGMA, average M_n 300), *N,N*-dimethylacrylamide (DMA, 99%), and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%), poly(ethylene glycol) methyl ether (PEG₇₅₀, M_n = 750 g/mol), dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) were all purchased from Aldrich. *N,N*-diethylacrylamide (DEA, 98%) was purchased from Tokyo Chemical Industry (TCI). Dichloromethane (DCM) was purchased from Merck Millipore. Deinhibition of monomers was carried out by percolating over a basic alumina column (Ajax Chemical, AR). Milli-Q water was obtained from arium® pro Ultrapure Water Systems (Sartorius). Zn(II) meso-tetra (4-sulfonatophenyl) porphyrin (ZnTPPS⁴⁻) was purchased from Frontier Scientific and used as received. Thiocarbonylthiol compound: 4-cyanopentanoic acid dithiobenzoate (CPADB), and 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA) were synthesized according to literature procedures.¹

Synthesis of BTPA-PEG₇₅₀. BTPA was further modified through DCC coupling with PEG₇₅₀ to yield BTPA-PEG₇₅₀ according to literature procedures.² A solution of BTPA (377.4 mg, 1.58 mmol) in 10 mL of DCM was introduced in a dry Cospak bottle under nitrogen in an ice bath (0 °C) to PEG₇₅₀ (2.411 g, 3.17

mmol). A solution of DCC (360 mg, 1.74 mmol) and DMAP (20 mg, 0.164 mmol) in 5 mL DCM was then added dropwise to the reaction mixture in the ice bath. The reaction mixture was degassed for 20 minutes followed by stirring for 48 hours at room temperature to allow esterification reaction to take place. Flash chromatography (95:5, chloroform/methanol) was then carried out to purify the final product. The product was then dried at 45 °C under vacuum to obtain a yellow viscous liquid. NMR of the final product is as shown in **Figure S2**.

Instrumentation

Gel Permeation Chromatography (GPC) was used for characterization of synthesized polymer with dimethylacetamide (DMAc). The DMAc instrument consists of Shimadzu modular system with an autoinjector, a Phenomenex 5.0 μ M bead sizeguard column (50 x 7.5 mm) followed by four Phenomenex 5.0 μ M bead size columns (10^5 , 10^4 , 10^3 and 10^2 Å) and a differential refractive-index detector and a UV detector ($\lambda = 305$ nm). DMAc GPC was calibrated based on narrow molecular weight distribution of polystyrene and polymethyl methacrylate standards with molecular weights of 200 to 10^6 g mol⁻¹.

Nuclear Magnetic Resonance (NMR) spectroscopy was carried out with Bruker Avance III HD operating at 400 MHz for ¹H using CDCl₃ and DMSO-d₆ as solvent. Tetramethylsilane (TMS) was used as a reference with chemical shift (δ) of sample measured in ppm downfield from TMS.

On-line Fourier Transform Near-Infrared (FTNIR) was used to determine monomer conversion by mapping the decrease in the integration of the vinylic C-H stretching overtone of monomer at ~ 6200 cm⁻¹. A Bruker IFS 66/S Fourier transform spectrometer equipped with a tungsten halogen lamp, a CaF₂ beam splitter and liquid nitrogen cooled InSb detector was used. Polymerizations in blue or red LED lights were carried out using FT-NIR quartz cuvette (1 cm \times 2 mm). Each spectrum composed of 16 scans with a resolution of 4 cm⁻¹ was collected in the spectral region between 7000-4000 cm⁻¹ by manually placing the sample into the holder at time intervals of 5, 10, or 30 minutes. The total collection time per spectrum was about 10 seconds and analysis was carried out with OPUS software.

UV-vis Spectroscopy. UV-vis spectra were recorded using a CARY 300 spectrophotometer (Varian) equipped with a temperature controller.

Fluorescence spectroscopy. Fluorescence spectra were recorded using Agilent fluorescent spectrometer.

pH/Ion meter. pH measurements of reaction mixtures were carried out using Mettler Toledo SevenCompact pH meter calibrated to standard pH buffers.

Photopolymerization was carried out in the reaction vessel where the reaction mixtures were irradiated by RS Component PACK LAMP LED lights (5 W). The samples were irradiated at 635 nm for red light at intensity of 0.828 mW/cm². The multi-colored LED light bulb with remote control was purchased from RS Components Australia.

General Procedures for Kinetic Studies of RAFT Photopolymerization of *N,N*-dimethylacrylamide (DMA) with Online Fourier Transform Near-Infrared (FTNIR) Spectroscopy in the Absence of air

A reaction stock solution consisting of Milli-Q water (472 μ L), DMA (1.393 mL, 1.34 g, 13.52 mmol), BTPA-PEG₇₅₀ (65.6 mg, MW: 970.4 g/mol), and ZnTPPS⁴⁻ (MW: 1302.49 g/mol, 880 μ L of 0.768 mM of ZnTPPS⁴⁻ stock solution in water, 0.678 μ mol) was prepared in a glass vial covered in aluminum foil. Due to the presence of slight excess of unreacted PEG750 even after flash chromatography, ¹H NMR was carried out to determine the accurate ratio of [DMA]:[BTPA-PEG750] before proceeding with the reaction. In this case, the ratio of [DMA]:[BTPA-PEG750] was determined to be 270 : 1. All polymerizations were carried out at 50 ppm catalyst concentration which is the molar ratio between [ZnTPPS⁴⁻] : [DMA]. The reaction mixture was then sonicated for 10 minutes for homogenous mixing. Next, pH of the reaction mixture was measured using a pH meter. The initial pH of the reaction mixture without any pH adjustments was determined to be pH 8.6. Adjustments were made to the pH of the reaction mixture, if needed, through addition of 1M HCl to attain the desired pH. The reaction solution was then filtered after pH adjustments using a 0.45 μ m PTFE filter. Approximately 1.5 mL of stock solution was transferred into a 4 mL glass vial covered with aluminum foil followed by sealing with a septum. The reaction mixture was then degassed for 20 minutes under nitrogen. Concurrently, 1 mL FTNIR quartz cuvette (1 cm \times 2 mm) covered with

aluminum foil and sealed with a septum was also degassed for 20 minutes under nitrogen. The reaction mixture was then transferred from the glass vial to the cuvette completely removed of air using a syringe and needle purged under nitrogen.

The cuvette with the reaction mixture was then irradiated under red LED light (5 W, $\lambda_{\text{max}} = 635 \text{ nm}$, 0.828 mW/cm^2) at room temperature ($\sim 25^\circ\text{C}$). The cuvette was transferred to a sample holder manually for FTNIR measurements every 10 minutes. After 15 seconds of scanning, the cuvette was transferred back to the light source. Monomer conversions were calculated by taking the ratio of integrations of the wavenumber area $6250\text{-}6150 \text{ cm}^{-1}$ for all curves at different reaction times to that of 0 minutes. Aliquots of reaction samples were taken at specific time points during the reaction to be analyzed by GPC (DMAc) to determine number average molecular weights (M_n) and polydispersities (M_w/M_n).

General Procedures for Kinetic Studies of RAFT Photopolymerization of *N,N*-dimethylacrylamide (DMA) for Dual Stimuli Polymerization with Online Fourier Transform Near-Infrared (FTNIR) Spectroscopy in the Absence of air

A reaction stock solution consisting of Milli-Q water (760 μL), DMA (2.245 mL, 2.16 g, 21.77 mmol), BTPA-PEG₇₅₀ (105.7 mg, MW: 970.4 g/mol), and ZnTPPS⁴⁻ (MW: 1302.49 g/mol, 1.419 mL of 0.768 mM of ZnTPPS⁴⁻ stock solution in water, 1.090 μmol) was prepared in a glass vial covered in aluminum foil. Due to the presence of slight excess of unreacted PEG₇₅₀ even after flash chromatography, ¹H NMR was carried out to determine the accurate ratio of [DMA]:[BTPA-PEG₇₅₀] before proceeding with the reaction. In this case, the ratio of [DMA]:[BTPA-PEG₇₅₀] was determined to be 270 : 1. The reaction mixture was then sonicated for 10 minutes for homogenous mixing. Next, pH of the reaction mixture was measured using a pH meter. The initial pH of the reaction mixture without any pH adjustments was determined to be pH 8.6. The reaction solution was then filtered using a 0.45 μm PTFE filter. The stock solution was then transferred to a 4 mL glass cuvette with 1 cm path length covered with aluminum foil followed by sealing with a septum. The reaction mixture was then degassed for 20 minutes under nitrogen.

The cuvette with the reaction mixture was then irradiated under red LED light (5 W, $\lambda_{\text{max}} = 635 \text{ nm}$, 0.828 mW/cm^2) at room temperature (25 °C). The cuvette was transferred to a sample holder manually for FTNIR measurements every 10 minutes. After 15 seconds of scanning, the cuvette was transferred back to the light source. Monomer conversions were calculated by taking the ratio of integrations of the wavenumber area $6250\text{-}6150 \text{ cm}^{-1}$ for all curves at different reaction times to that of 0 minutes. For the “ON/OFF” kinetics, upon reaching 24% monomer conversion, the reaction was placed in darkness with periodical measurements taken for 30 minutes. An aliquot of the reaction sample was then taken. This is followed by adjustment of pH towards acidic conditions (pH 3-4) by adding 1M HCl with an approximate pH determined by pH paper due to viscosity issues and smaller sample volume which was inadequate for determination with a pH electrode. The sample was then degassed under nitrogen for 20 minutes. The cuvette with the reaction mixture in acidic condition was then irradiated under red LED light for 30 minutes with FTNIR measurements taken periodically. An aliquot of the reaction sample was then taken. This is followed by adjustment of pH towards slightly basic conditions (pH 7-8) by adding 2.5M NaOH with an approximate pH determined by pH paper. The sample was then degassed under nitrogen for 20 minutes. The reaction mixture was then irradiated under red LED light with FTNIR measurements taken periodically until a monomer conversion of 45% monomer was reached. The “ON/OFF” was then repeated according to the procedure described above. Aliquots of reaction samples taken at specific time points during the reaction were analyzed by GPC (DMAc) to determine number average molecular weights (M_n) and polydispersities (M_w/M_n).

Note: As we added discrete amounts of 2.5M NaOH and 1 M HCl (in the scale of less than 10 microlitres) to the final reaction mixture before polymerization, any changes to the final concentration of monomer was minimized.

General Procedures for Preparation of PDMA-*b*-PDEA Diblock Copolymers by RAFT photopolymerization in the Absence of Air under Red Light Irradiation.

In the preparation of PDMA-*b*-PDEA block copolymer, PDMA macroRAFT agent was initially prepared. A reaction stock solution consisting of Milli-Q water (350 μL), DMA (1.034 mL, 0.995 g, 10.03 mmol),

BTPA-PEG₇₅₀ (48.7 mg, MW: 970.4 g/mol), and ZnTPPS⁴⁻ (MW: 1302.49 g/mol, 654 μL of 0.768 mM of ZnTPPS⁴⁻ stock solution in water, 0.502 μmol) was prepared in a 20 mL sample vial covered in aluminum foil. Due to the presence of slight excess of unreacted PEG₇₅₀ even after flash chromatography, ¹H NMR was carried out to determine the accurate ratio of [DMA]:[BTPA-PEG₇₅₀] before proceeding with the reaction. In this case, the ratio of [DMA]:[BTPA-PEG₇₅₀] was determined to be 340 : 1. The polymerization was carried out at 50 ppm catalyst concentration which is the molar ratio between [ZnTPPS⁴⁻] : [DMA]. The reaction mixture was then sonicated for 10 minutes for homogenous mixing. The ratio of DMA: BTPA-PEG₇₅₀: ZnTPPS⁴⁻ was determined to be 340:1: 0.017. Next, pH of the reaction mixture was measured using a pH meter. The initial pH of the reaction mixture without any pH adjustments was determined to be pH 8.6. The reaction solution was then filtered after pH adjustments using a 0.45μm PTFE filter. The glass vial was then sealed with a septum and purged under nitrogen for 20 minutes.

The glass vial with the reaction mixture was then irradiated for 1 hr under red LED light (5 W, $\lambda_{\max} = 635$ nm, 0.828 mW/cm²) at room temperature (27 °C). The reaction mixture was then analyzed by ¹H NMR and GPC (DMAc) to determine monomer conversion and number average molecular weights (M_n) and polydispersities (M_w/M_n). (PDMA macroinitiator: $M_{n,theo} = 15\ 850$ g/mol, $M_{n,GPC} = 16\ 200$ g/mol, $M_w/M_n = 1.08$ and 44 % monomer conversion). The final reaction mixture was purified by precipitating in a mixture of diethyl ether/petroleum spirit (0.3/0.7, v/v) with stirring. The precipitate was collected and redissolved in minimum amount of dichloromethane before precipitating a second time in diethyl ether/petroleum spirit (0.3/0.7, v/v) mixture. The final product was then dried at 45 °C in a vacuum oven

Chain extension of PDMA macroRAFT agent to DEA was carried out in a 5 mL glass vial in the presence of Milli-Q water (404 μL), DEA (412 μL, 0.381 g, 2.99 mmol), PDMA (96.9 mg, MW: 16 200 g/mol), and ZnTPPS⁴⁻ (MW: 1302.49 g/mol, 195 μL of 0.768 mM of ZnTPPS⁴⁻ stock solution in water, 0.150 μmol) sealed with a rubber septum. Aluminum foil was used to cover the reaction mixture before degassing for 20 minutes under nitrogen. The reaction mixture was irradiated under red LED light (5 W, $\lambda_{\max} = 635$ nm (red)) at room temperature for 1.5 hour. The final reaction mixture was analyzed in ¹H NMR and GPC (DMAc) to

determine monomer conversion and number average molecular weights (M_n) and polydispersities (M_w/M_n): $M_{n,GPC} = 27\,200$ g/mol, $M_w/M_n = 1.09$ and 22 % monomer conversion.

General Procedures for UV-Vis Studies of RAFT Photopolymerization of *N,N*-dimethylacrylamide (DMA)

Samples for UV-Vis measurements were prepared in a similar fashion as the preparation of reaction mixture stock solution as described above with pH adjustments made if required. Measurements were taken without any degassing or light irradiation.

UV-Vis measurements of reaction mixtures with different pH before polymerization was carried out using Milli-Q water (503 μ L), DMA (1.480 mL, 1.423 g, 14.36 mmol), BTPA-PEG750 (69.7 mg, MW: 970.4 g/mol), and ZnTPPS4⁻ (MW: 1302.49 g/mol, 0.934 mL of 0.768 mM of ZnTPPS4⁻ stock solution in water, 0.717 μ mol). The stock solution was divided into 2 vials with one vial with pH 7.7 (no pH adjustments made) while the other vial was adjusted with 1M HCl to obtain a pH 3.3.

General Procedures for Fluorescence Studies of RAFT Photopolymerization of *N,N*-dimethylacrylamide (DMA)

Fluorescence measurement with increasing concentrations of DMA monomer was carried out in a fluorescence cuvette under conditions similar to polymerization setup. A reaction stock solution consisting of Milli-Q water (566 μ L) and ZnTPPS4⁻ (MW: 1302.49 g/mol, 1200 μ L of 0.768 mM of ZnTPPS4⁻ stock solution in water, 0.922 μ mol) was prepared in the fluorescent cuvette covered in aluminum foil. The cuvette was then sealed with a septum and degassed under nitrogen for 15 minutes. Measurements were then taken with excitation wavelength of $\lambda_{exc} = 560$ nm and emission wavelength of $\lambda_{emm} = 570 - 900$ nm. Each addition of DMA monomer to the reaction mixture was followed by degassing for 15 minutes before measurements were taken.

Fluorescence measurement with increasing concentrations of BTPA-PEG₇₅₀ was carried out in a fluorescence cuvette under conditions similar to polymerization setup. A reaction stock solution consisting of Milli-Q water (300 μ L), DMA (1.040 mL, 1.00 g, 10.09 mmol), and ZnTPPS4⁻ (MW: 1302.49 g/mol, 656

μL of 0.768 mM of ZnTPPS^{4-} stock solution in water, 0.504 μmol) was prepared in the fluorescent cuvette covered in aluminum foil. The cuvette was then sealed with a septum and degassed under nitrogen for 15 minutes. Measurements were then taken with excitation wavelength of $\lambda_{\text{exc}} = 560$ nm and emission wavelength of $\lambda_{\text{em}} = 570 - 900$ nm. A stock solution of BTPA-PEG₇₅₀ (50 mg/mL in Milli-Q water) was made. Titration of BTPA-PEG₇₅₀ to the reaction mixture was followed by degassing for 15 minutes before measurements were taken.

Supplementary Figures:

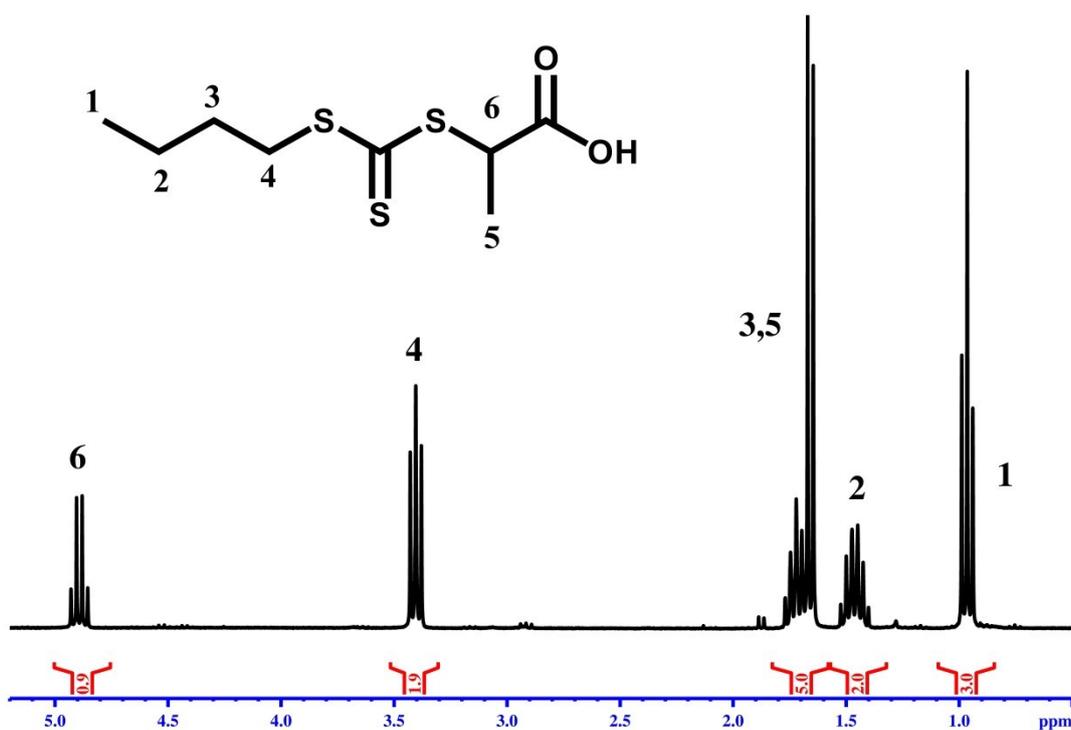


Figure S1. ¹H NMR spectrum of BTPA before conjugation to PEG₇₅₀ (recorded in CDCl₃).

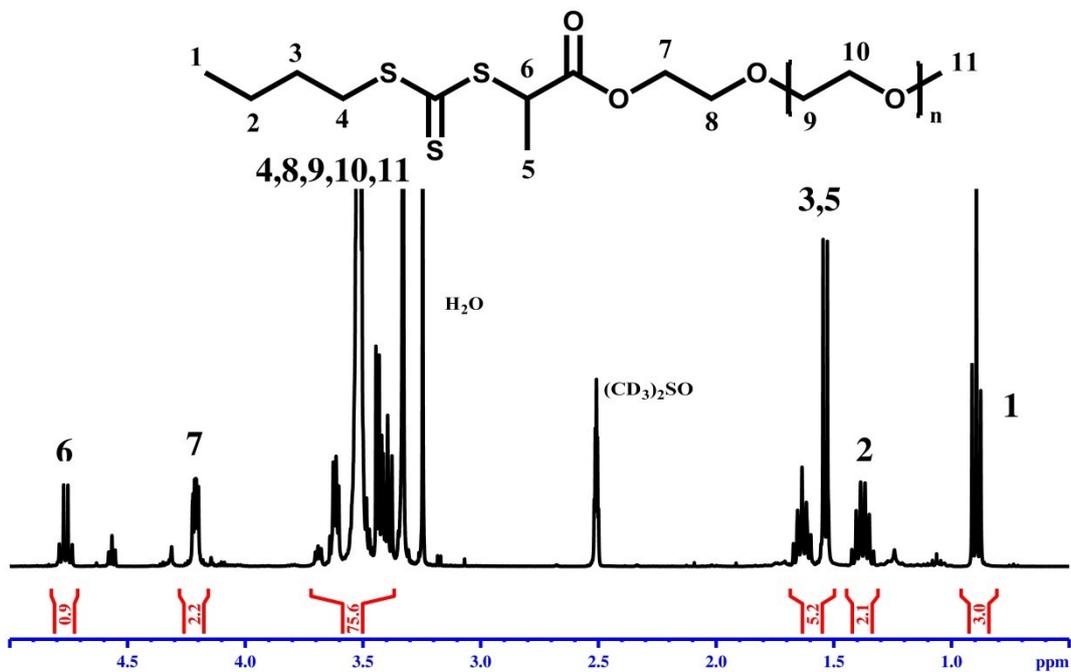


Figure S2. ^1H NMR spectrum of BTPA-PEG₇₅₀ (recorded in DMSO deuterated).

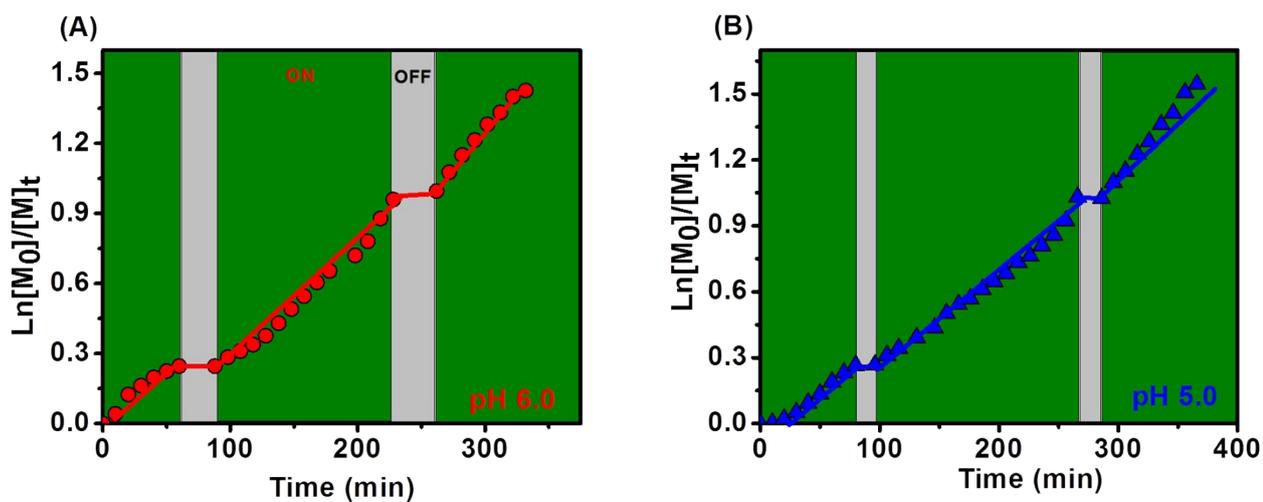


Figure S3. “ON/OFF” online FTNIR kinetics for polymerization of DMA in the absence of oxygen under red light irradiation with ZnTPPS⁴⁻ with final pH adjustments ([DMA]:[BTPA-PEG₇₅₀]:[ZnTPPS⁴⁻]= 270:1: 1.35 × 10⁻², 10 M monomer concentration and 50 ppm catalyst): pH 6.0 (A) and pH 5.0 (B).

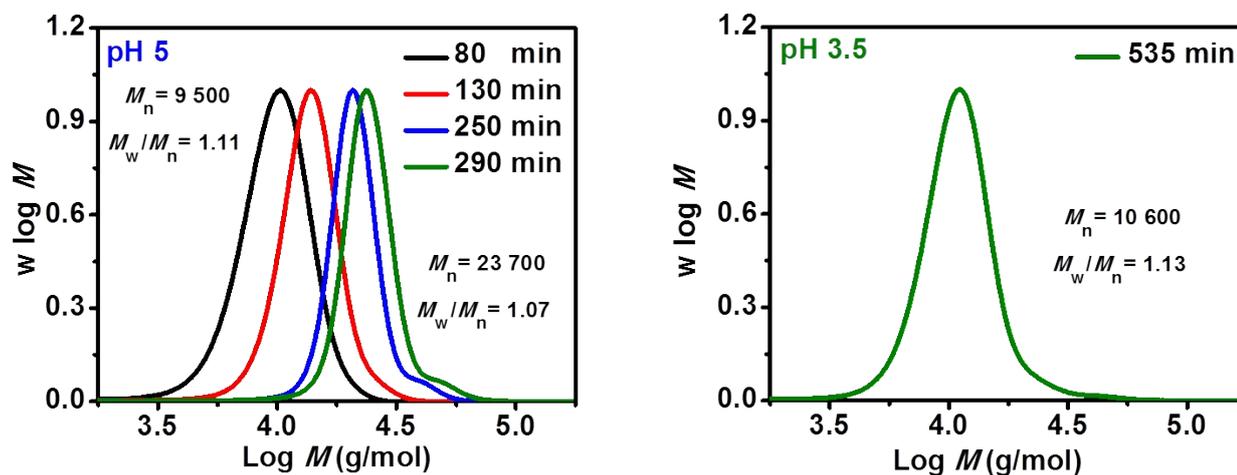


Figure S4. GPC profiles for polymerization of DMA in the absence of oxygen under red light irradiation with ZnTPPS⁴⁻ with final pH adjustments ([DMA]:[BTPA-PEG₇₅₀]:[ZnTPPS⁴⁻]= 270:1: 1.35 × 10⁻², 10 M monomer concentration and 50 ppm catalyst): pH 5.0 (A) and pH 3.5 (B).

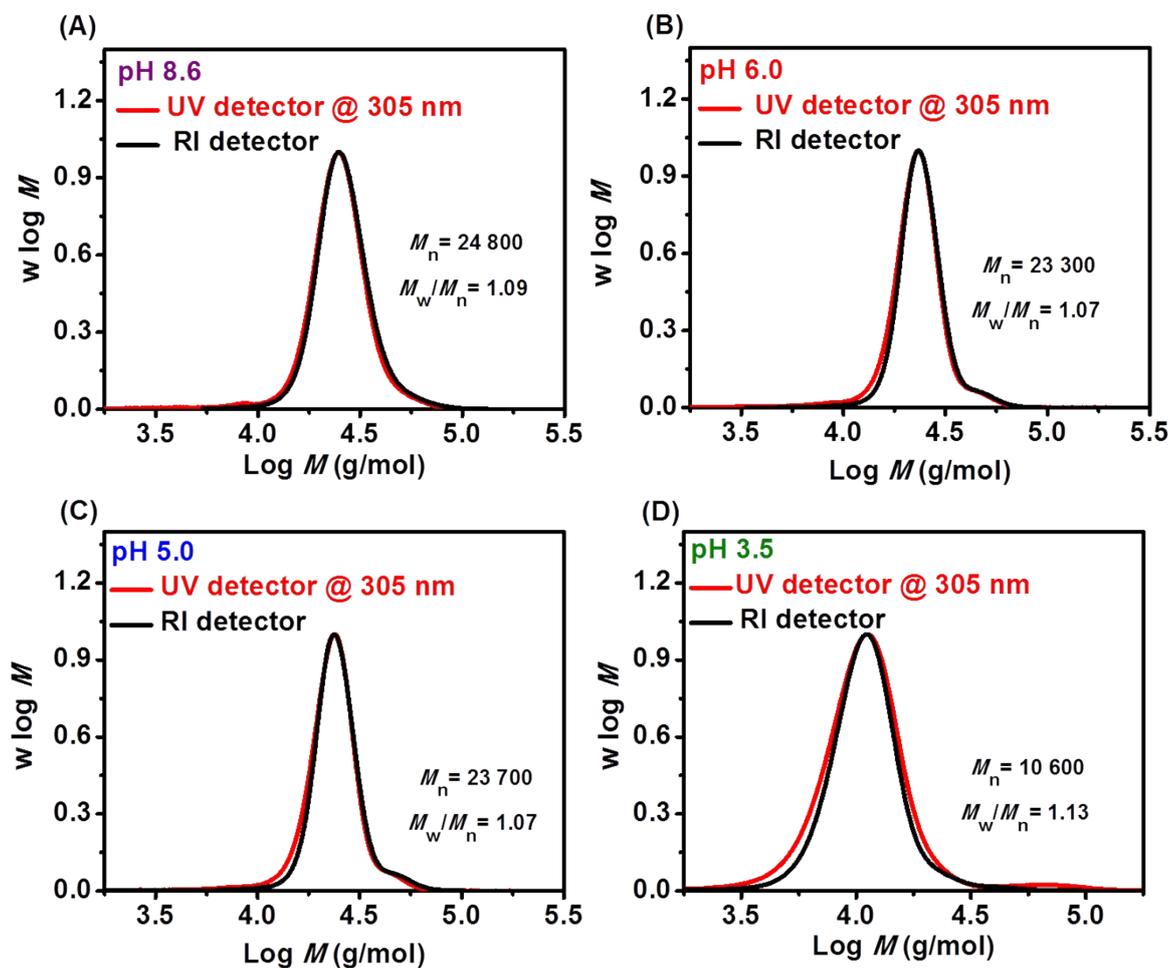


Figure S5. GPC profiles with overlaps of RI and UV traces of the final polymers for polymerization of DMA in the absence of oxygen under red light irradiation with ZnTPPS⁴⁻ with final pH adjustments ([DMA]:[BTPA-PEG₇₅₀]:[ZnTPPS⁴⁻]= 270:1: 1.35 × 10⁻², 10 M monomer concentration and 50 ppm catalyst): pH 8.6 (A), pH 6.0 (B), pH 5.0 (C) and pH 3.5 (D).

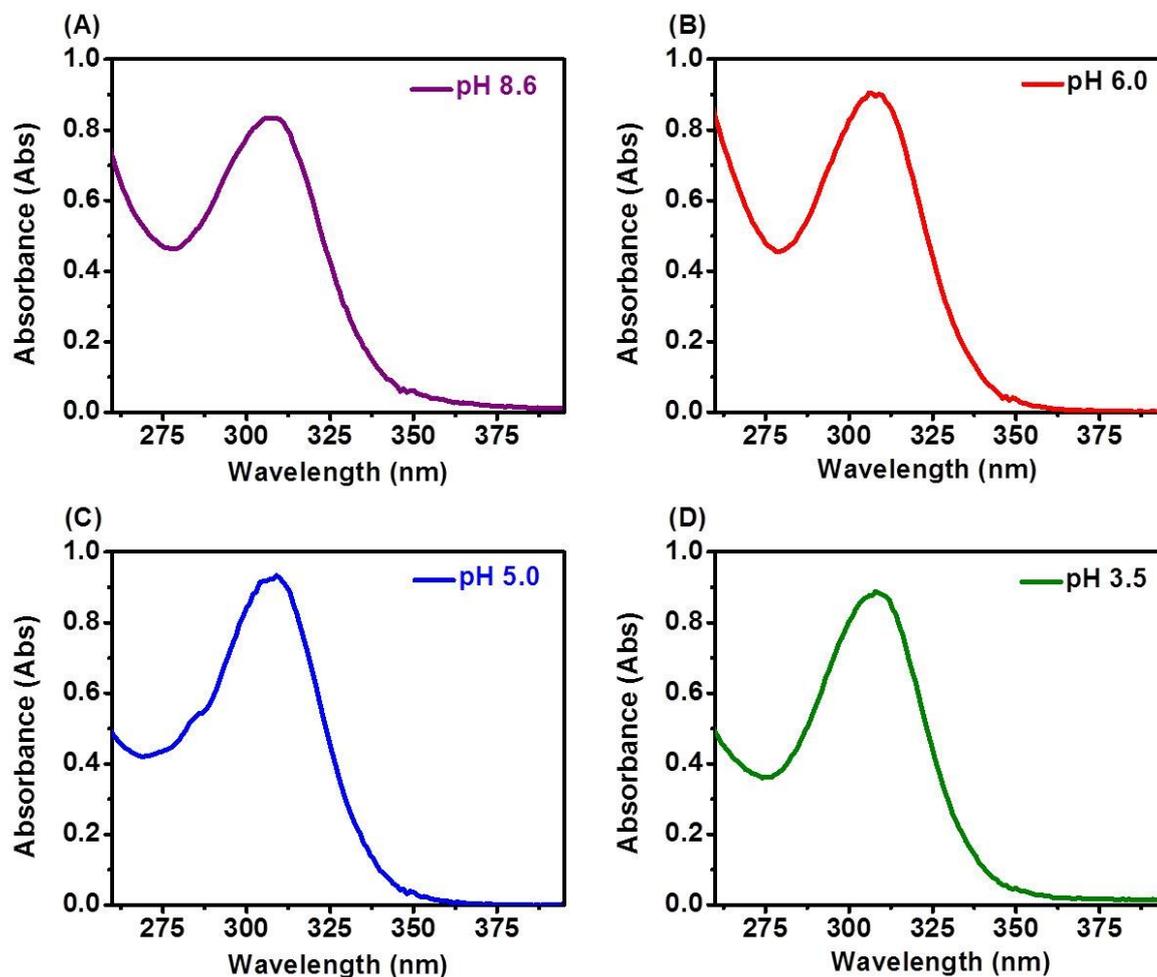


Figure S6. UV-Vis absorption profiles to determine RAFT end group integrity through detection of thiocarbonylthio bond at 305 nm of the final purified poly(*N,N*-dimethylacrylamide) polymer synthesized under different pH ranges: pH 8.6 (A), pH 6.0 (B), pH 5.0 (C), and pH 3.5 (D).

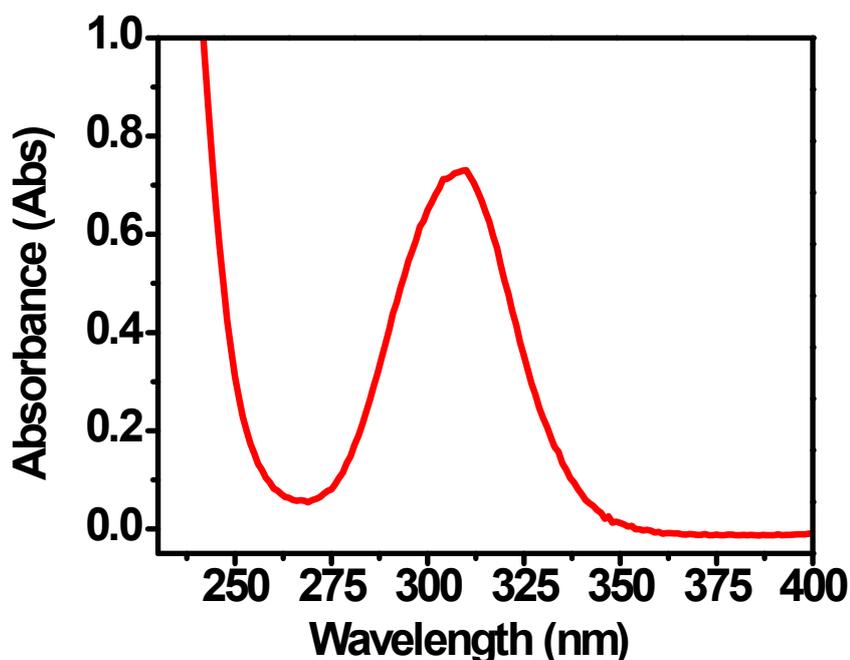


Figure S7. UV-Vis absorption profiles to determine RAFT end group integrity through detection of thiocarbonylthio bond at 305 nm of the final purified poly(*N,N*-dimethylacrylamide) polymer.

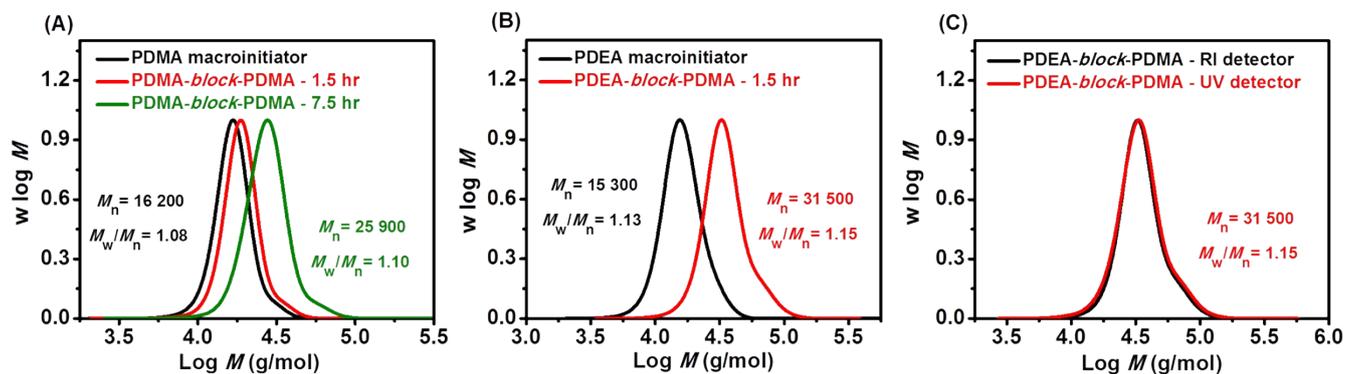


Figure S8. Chain extensions of PDMA and PDEA macroRAFT agents with DMA at room temperature using ZnTPPS⁴⁺ photocatalyst in water. (A) Molecular weight distributions of PDMA macroRAFT agent and PDMA-*block*-PDMA diblock copolymers after 1.5 h and 7.5 h irradiation under red light. (B) Molecular weight distributions of PDEA macroRAFT agent and PDEA-*block*-PDMA diblock copolymer after 1.5 h irradiation under red light. (C) Overlap of UV and RI GPC traces of PDEA-*block*-PDMA diblock copolymer obtained after 1.5 h from (B).

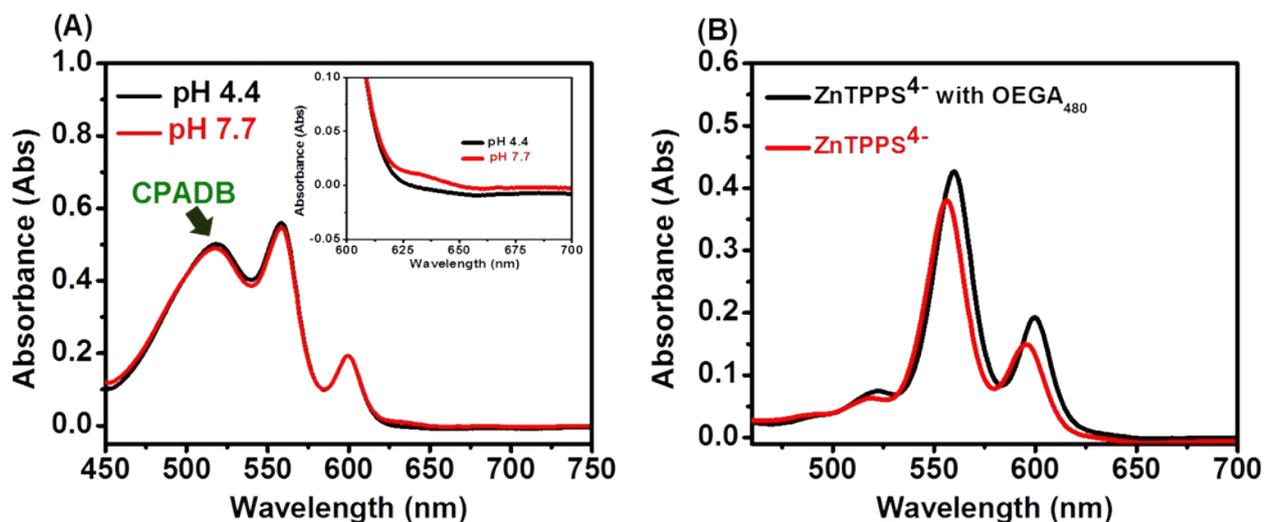


Figure S9. Understanding the interactions of ZnTPPS⁴⁻ with CPADB and OEGA with UV-Vis spectroscopy: Absorption profiles of ZnTPPS⁴⁻ after addition of CPADB and OEGA at basic (pH 7.7) and acidic (pH 4.4) conditions (A) and ZnTPPS⁴⁻ before and after addition of OEGA (A). (Note: The Q-band of ZnTPPS⁴⁻ overlaps with the absorption of CPADB and therefore leads to the unusual intense absorption at 500-525 nm of ZnTPPS⁴⁻ seen in Figure S8A).³

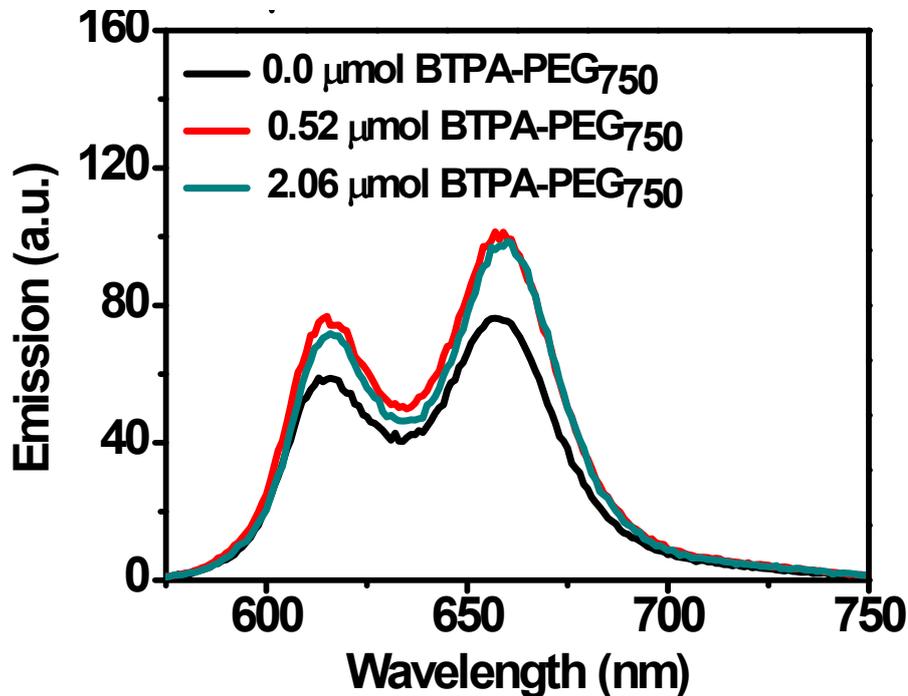


Figure S10. Fluorescence measurement studies of ZnTPPS⁴⁻ with increasing concentration of BTPA-PEG₇₅₀ in the absence of DMA.

Additional References

- (1) Shanmugam, S.; Xu, J.; Boyer, C. *Chem. Sci.* **2015**, *6*, 1341.
- (2) Tan, J.; Sun, H.; Yu, M.; Sumerlin, B. S.; Zhang, L. *ACS Macro Lett.* **2015**, *4*, 1249.
- (3) Xu, J.; Shanmugam, S.; Corrigan, N. A.; Boyer, C. In *Controlled Radical Polymerization: Mechanisms*; American Chemical Society: 2015; Vol. 1187, p 247.