

Supporting Information

Stereo-, Temporal- and Chemical- Control through Photoactivation of Living Radical Polymerization: Synthesis of Block and Gradient Copolymers

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EXPERIMENTAL SECTION

Materials: *N,N*-dimethylacrylamide (DMA, 99%), tris[2-phenylpyridinato- C^2,N]iridium(III) (*fac*-[Ir(ppy)₃], 99%), tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate (Ru(bpy)₃Cl₂, 99.95%), Yttrium(III) trifluoromethanesulfonate (Y(OTf)₃, 98%), and Ytterbium(III) trifluoromethanesulfonate (Yb(OTf)₃, 99.99%) were all purchased from Sigma Aldrich. Monomers were deinhhibited by percolating over a basic alumina column (Ajax Chemical, AR). Dimethyl sulphoxide (DMSO, Ajax Chemical), methanol (Ajax Chemical) and toluene (Ajax Chemical), ethanol (Sigma Aldrich), isopropanol (Sigma Aldrich), n-butanol (Sigma Aldrich) were used as received. Thiocarbonylthiol compound: 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA) was synthesized according to literature procedure.¹

Instrumentation

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

Nuclear Magnetic Resonance (¹H NMR) spectroscopy was carried out with Bruker Avance III with SampleXpress operating at 300 MHz, Bruker Avance III 400 MHz, and Bruker Avance III 600 MHz with Sample Changer using DMSO-d₆ as solvent. The data was reported as chemical shift (δ) measured in ppm downfield from the tetramethylsilane reference.

On-line Fourier Transform Near-Infrared (FTNIR) was used to determine monomer conversion by mapping the decrement of the vinylic C-H stretching overtone of the monomer at $\sim 6\ 200$ cm⁻¹. A Bruker IFS 66/S Fourier transform spectrometer equipped with tungsten halogen lamp, a CaF₂ beam splitter and liquid nitrogen cooled InSb detector was used. Polymerization in blue light was 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 5-minute intervals with total collection time per spectrum was about 10 seconds. Analysis was carried out with OPUS software.

Photopolymerization was carried out in a 5 mL glass vial with RS Component PACK LAMP LED lights (5 W). The distance of the samples to the light bulb was maintained at 8 cm. The multi-colored LED light bulb with remote control was purchased from RS Components Australia.

General Procedure for the Synthesis of Isotactic Poly(*N,N*-dimethylacrylamide) (PDMAA) via PET-RAFT in the absence of air with a ratio of [DMAA]:[BTPA]:[Ir(ppy)₃]:[Y(OTf)₃] = 120: 1 : 1.2×10^{-3} :

5.75

Polymerization of (*N,N*)-dimethylacrylamide (DMAA) was carried out in a 5 mL glass vial with a rubber septum in the presence of methanol (485 μ L) /toluene (242.5 μ L) mixture (2:1), DMA (0.25 g, 259 μ L, 2.5 mmol), BTPA (5 mg, 20.97 μ mol), Ir(ppy)₃ (16.5 μ L from 1.53 mM stock solution, 0.025 μ mol), and Yttrium(III) trifluoromethanesulfonate (Y(OTf)₃) (65 mg, 120.6 μ mol). The glass vial was wrapped with aluminum foil and degassed for 25 minutes. The degassed mixture was then irradiated under blue LED light (5W, $\lambda_{\text{max}} = 460$ nm) at room temperature. After four hours of irradiation, the reaction mixture was removed from the light source. The polymer sample was purified by dialysis in water using Cellu Sep molecular porous membrane and freeze dried before analysis by ¹H NMR (DMSO-d₆) and GPC (DMAC) to determine the conversions, number average molecular weights (M_n) and dispersities (M_w/M_n).

General Procedure for Kinetic Studies of Isotactic Poly(*N,N*-dimethylacrylamide) (PDMAA) via PET-RAFT with Online Fourier Transform Near-Infrared (FTNIR) Spectroscopy

A stock solution of reaction mixture consisting of methanol (485 μ L) /toluene (242.5 μ L) mixture (2:1), DMA (0.25 g, 259 μ L, 2.5 mmol), BTPA (5 mg, 20.97 μ mol), Ir(ppy)₃ (16.5 μ L from 1.53 mM stock solution, 0.025 μ mol), and Yttrium(III) trifluoromethanesulfonate (Y(OTf)₃) (65 mg, 120.6 μ mol). Around 900 μ L of the stock solution was transferred into a 1 mL FTNIR quartz cuvette (1 cm \times 2 mm). The cuvette was covered with aluminum foil followed by degassing for 25 minutes. The cuvette was then placed under blue LED light (5W, $\lambda_{\text{max}} = 460$ nm) at room temperature. The cuvette was manually transferred to the sample holder for FTNIR measurement every 20 minutes. The cuvette was then transferred back to the irradiation source after 15 minutes of scanning. Monomer conversions were determined by taking the ratio of area of integral from 6250 cm^{-1} to 6150 cm^{-1} for all curves at different reactions times to that of 0 minutes. Sampling was carried at specific time points to analyze the aliquots of the reaction mixture with ¹H NMR (DMSO-d₆), and GPC (DMAC) to determine the conversions (α), number average molecular weights (M_n) and dispersities (M_w/M_n).

General Procedure for Stereoblock Polymers Synthesis via PET-RAFT

Atactic-*block*-isotactic PDMAA-*b*-DMAA polymers

Reaction mixture consisting of methanol (485 μL) /toluene (242.5 μL) mixture (2:1), DMA (0.25 g, 259 μL , 2.5 mmol), BTPA (5 mg, 20.97 μmol), and Ir(ppy)₃ (16.5 μL from 1.53 mM stock solution, 0.025 μmol) was prepared in a 5 mL glass vial followed by degassing under nitrogen for 30 minutes. The reaction mixture was then placed under blue LED light irradiation for 4 hours to reach a monomer conversion of 56 % (M_n : 6 890 g/mol, $M_w / M_n = 1.08$). The reaction was then removed from blue light irradiation followed by addition of Y(OTf)₃ (65 mg, 120.6 μmol). The reaction mixture was then purged under nitrogen for 25 minutes before placing it back under blue light irradiation for another 45 minutes to reach a monomer conversion of 82% (M_n : 12 380 g/mol, $M_w / M_n = 1.09$).

Isotactic-*block*-Atactic PDMAA-*b*-PDMAA polymers

Reaction mixture consisting of methanol (485 μL) /toluene (242.5 μL) mixture (2:1), DMA (0.25 g, 259 μL , 2.5 mmol), BTPA (5 mg, 20.97 μmol), Y(OTf)₃ (65 mg, 120.6 μmol), and Ir(ppy)₃ (16.5 μL from 1.53 mM stock solution, 0.025 μmol) was prepared in a 5 mL glass vial followed by degassing under nitrogen for 30 minutes. The reaction mixture was then placed under blue LED light irradiation for 1 hour to reach a monomer conversion of 46 % (M_n : 5 810 g/mol, $M_w / M_n = 1.36$). The reaction was then removed from blue light irradiation followed by addition of DMSO (259 μL , 3.51 mmol). The reaction mixture was then purged under nitrogen for 25 minutes before placing it back under blue light irradiation for another 2.5 hours to reach a monomer conversion of % (M_n : 6 990 g/mol, $M_w / M_n = 1.30$).

General Procedure for Stereogradient Synthesis via PET-RAFT by Using Online Fourier Transform Near-Infrared (FTNIR)

Reaction mixture consisting of methanol (485 μL) /toluene (242.5 μL) mixture (2:1), DMA (0.25 g, 259 μL , 2.5 mmol), BTPA (5 mg, 20.97 μmol), Y(OTf)₃ (65 mg, 120.6 μmol), and Ir(ppy)₃ (16.5 μL from 1.53 mM stock solution, 0.025 μmol) was prepared in a 5 mL glass vial followed by a transfer of 900 μL of the stock reaction mixture into a 1 mL FTNIR quartz cuvette (1 cm \times 2 mm). The reaction mixture in the cuvette was degassed under nitrogen for 25 minutes. The reaction mixture was then placed under blue LED light irradiation for 20

minutes to reach a monomer conversion of 21.5 % (M_n : 3 540 g/mol, $M_w/M_n = 1.44$). The reaction was then removed from blue light irradiation. Aliquot of the reaction mixture was taken for analysis with ^1H NMR and DMAC GPC. This is followed by addition of DMSO (20 μL , 0.28 mmol). The reaction mixture was then purged under nitrogen for 25 minutes before placing it back under blue light irradiation to reach a monomer conversion of 37% (M_n : 4 040g/mol, $M_w/M_n = 1.40$). The reaction was taken out from irradiation and sampled. Second addition of DMSO (10 μL , 0.14 mmol) was carried out before. The reaction mixture was placed back under blue LED light to target for monomer conversions of 50% and 64% where 20 μL (0.28 mmol) and 30 μL (0.42 mmol) DMSO was added after each sampling. The final monomer conversion of 71% was reached.

Supplementary Figures

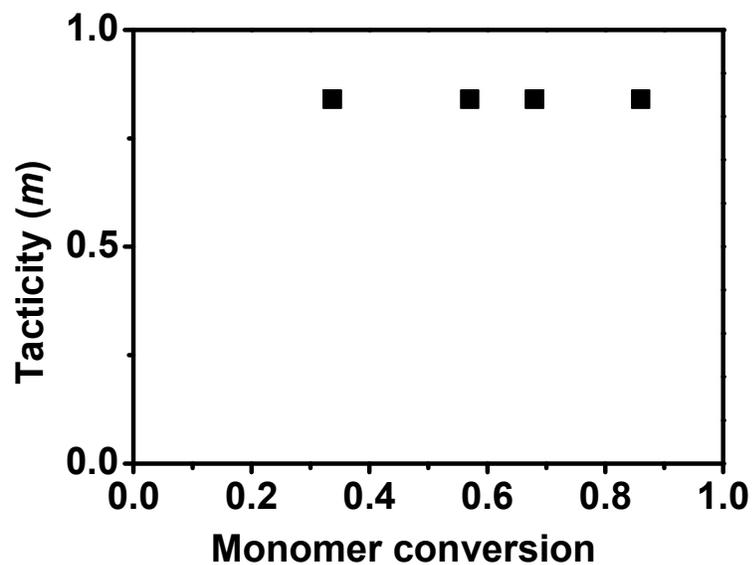


Figure S1. Tacticity (m) vs. monomer conversion determined by FTNIR measurement for kinetic study of PET-RAFT polymerization of DMAA in the absence of oxygen at room temperature with Ir(ppy)₃ as photoredox catalyst under blue light irradiation with BTPA as the chain transfer agent and initiator, using molar ratio of [MA]:[BTPA]:[Ir(ppy)₃]:[Y(OTf)₃] = 120: 1 : 1.2 × 10⁻³ : 5.75] = 120:1: 1.2 × 10⁻³.

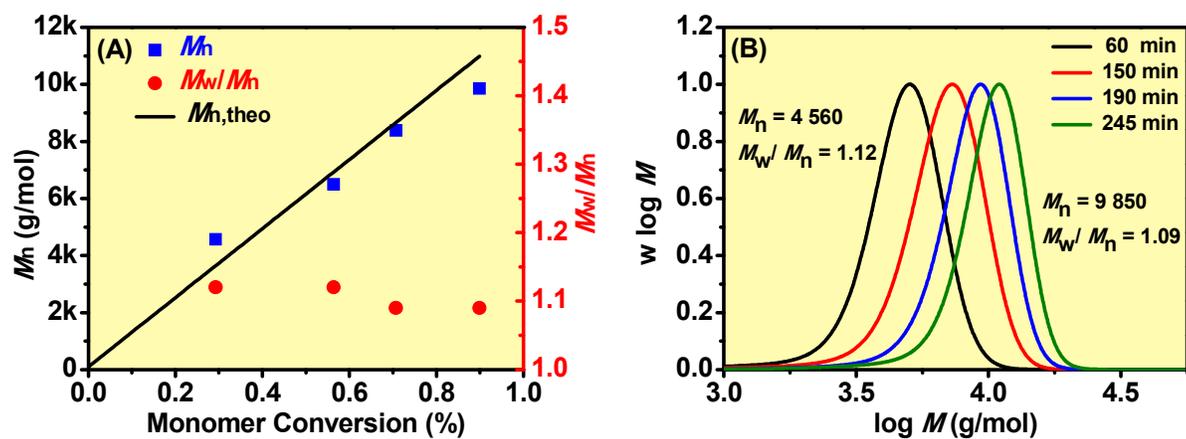


Figure S2. M_n vs. conversion in the presence of 0.014 M Y(OTf)₃ and (B) molecular weight distributions at different time points in the presence of 0.014 M Y(OTf)₃.

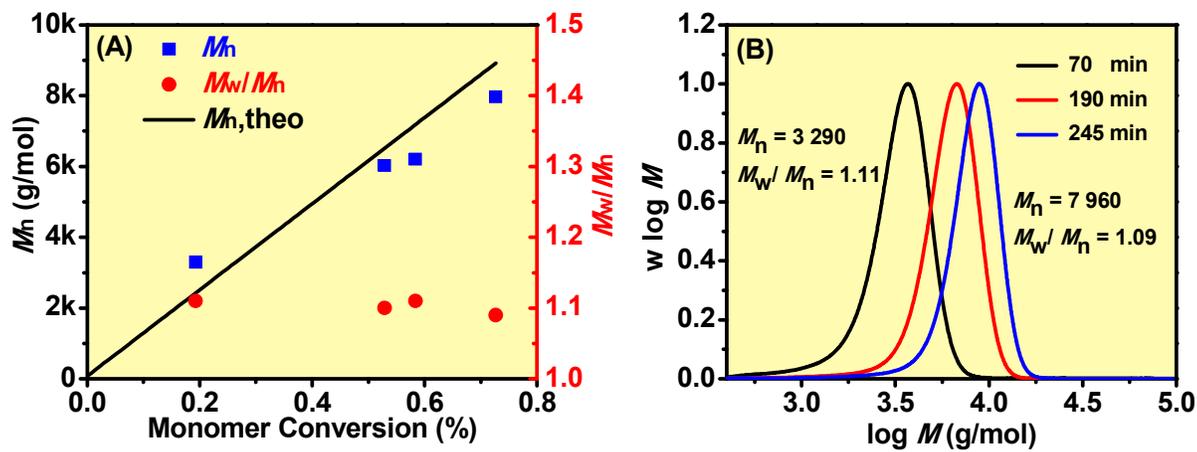


Figure S3. M_n vs. conversion in the absence of $Y(OTf)_3$ and (B) molecular weight distributions at different time points in the absence of $Y(OTf)_3$.

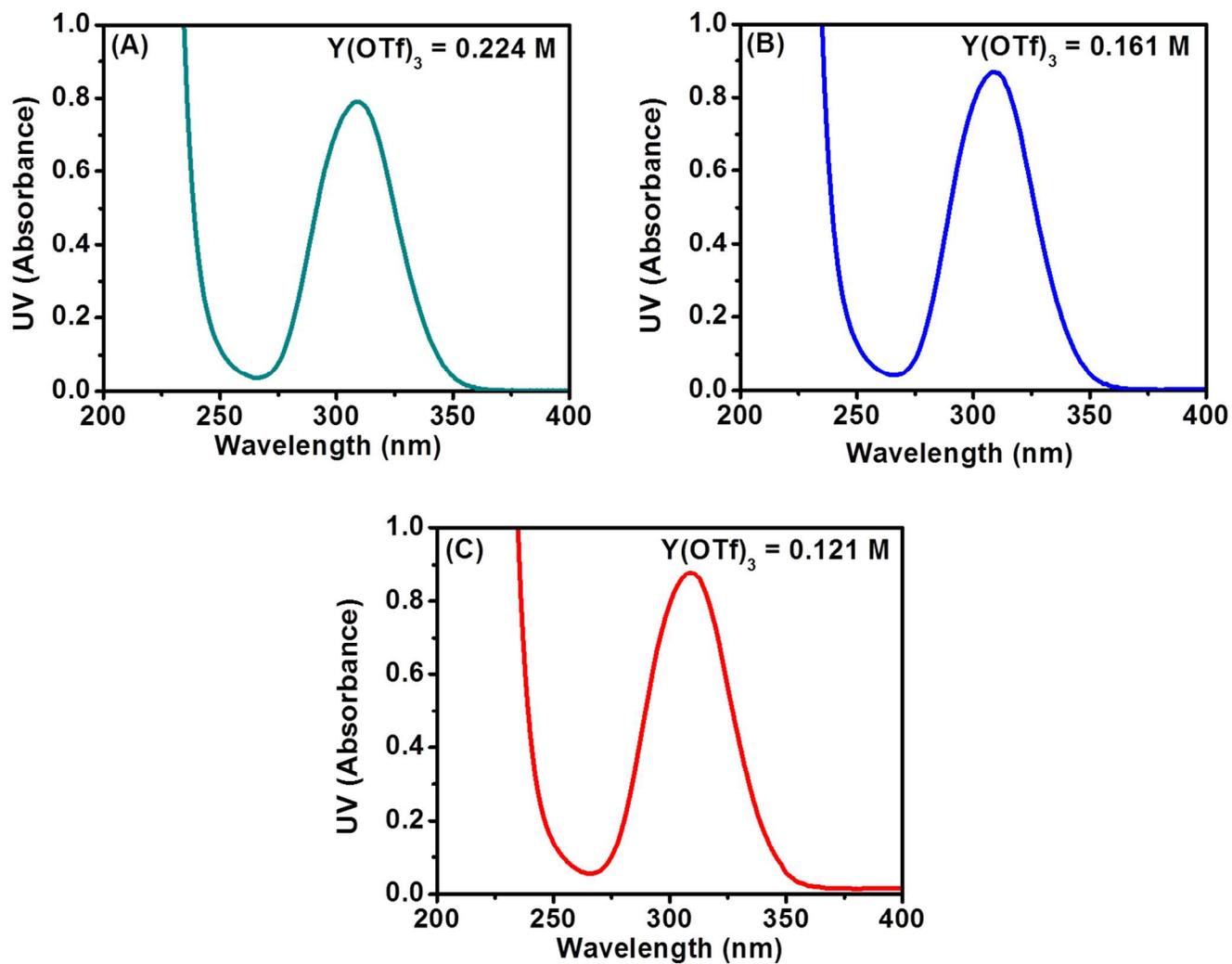


Figure S4. UV-Vis absorption studies for determination of end group fidelity of PDMAA synthesized under different concentrations of $Y(OTf)_3$: (A) 0.224 M, (B) 0.161 M and (C) 0.121 M.

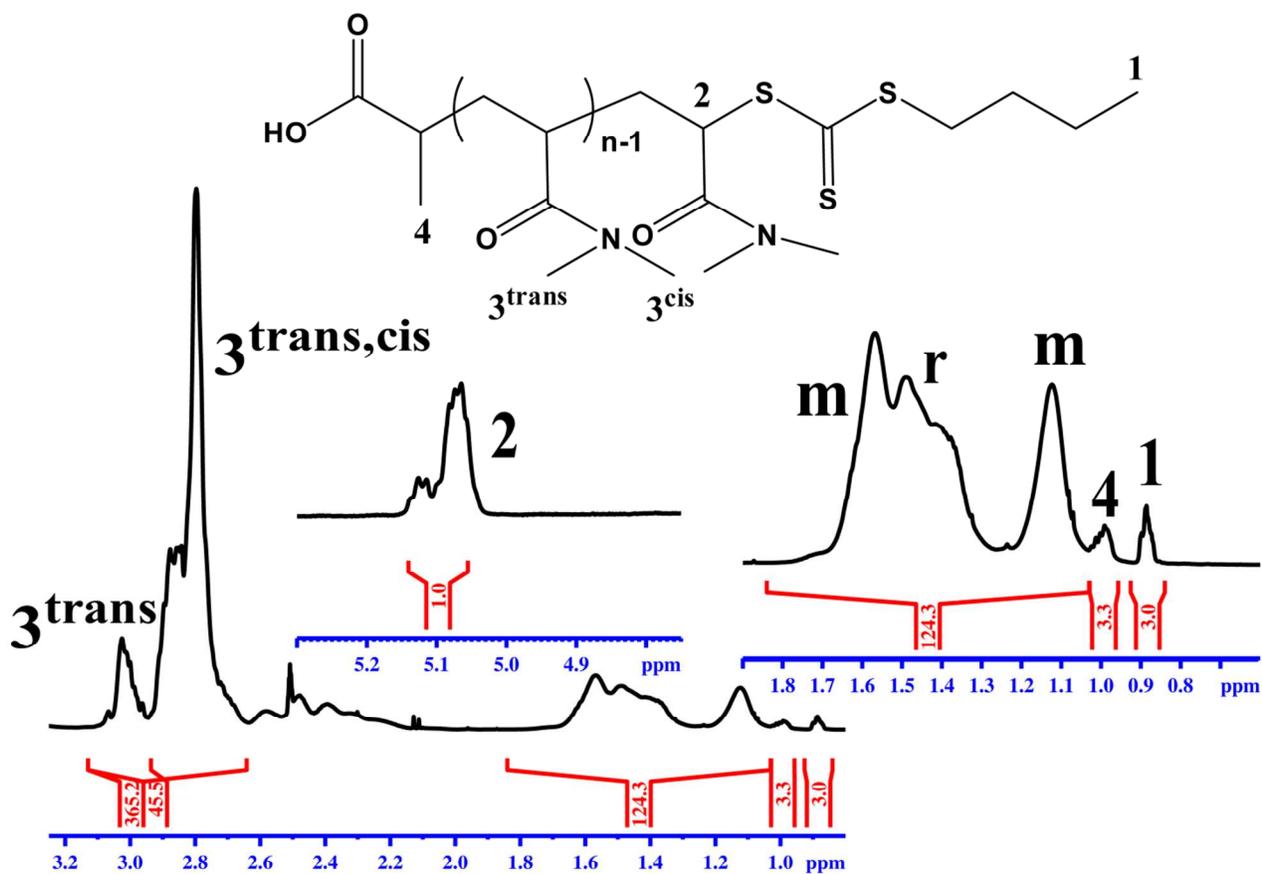


Figure S5. 600 MHz ¹H NMR for purified PDMAA synthesized under blue LED light irradiation ($M_{n,NMR} = 6400$ g/mol, $M_{n,theo} = 8800$ g/mol, $M_{n,GPC} = 7970$ g/mol, and $M_w/M_n = 1.09$; monomer conversion = 73%, m (meso content) = 0.48 ± 0.03) with $[Y(OTf)_3]_0/[DMAA]_0 = 0$.

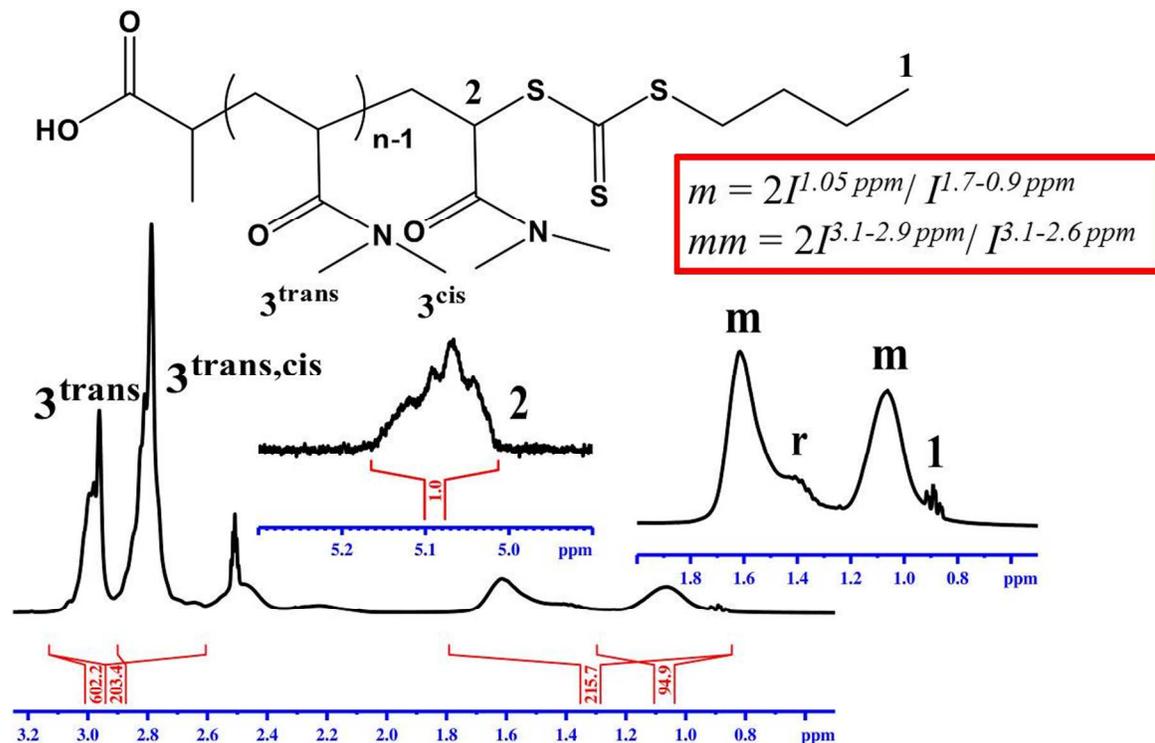


Figure S6. 300MHz ¹H NMR for purified PDMAA synthesized under blue LED light irradiation ($M_{n,NMR} = 10\ 940$ g/mol, $M_{n,theo} = 10\ 650$ g/mol, $M_{n,GPC} = 12\ 260$ g/mol, and $M_w/M_n = 1.13$; monomer conversion = 91%, m (meso content) = 0.85 ± 0.03) with $[Y(OTf)_3]_0 / [DMAA]_0 = 0.033$.

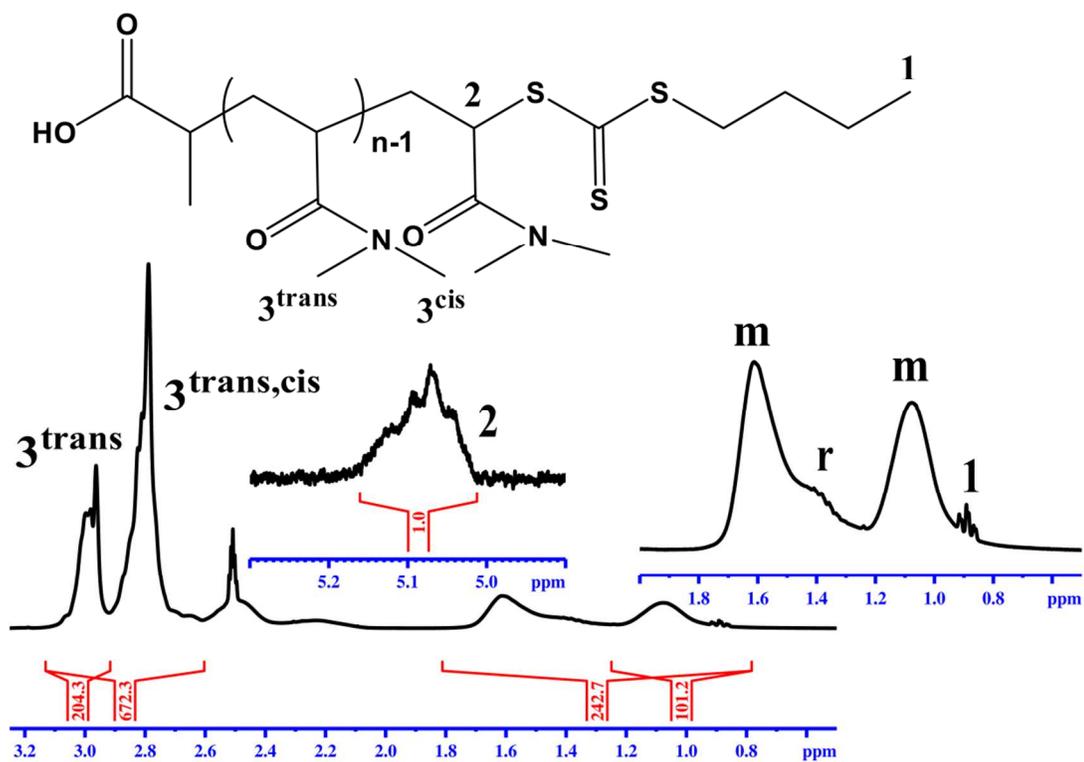


Figure S7. 300MHz ^1H NMR for purified PDMAA synthesized under blue LED light irradiation ($M_{n,NMR} = 11990$ g/mol, $M_{n,theo} = 11110$ g/mol, $M_{n,GPC} = 11570$ g/mol, and $M_w/M_n = 1.11$; monomer conversion = 91%, m (meso content) = 0.81 ± 0.03) with $[\text{Y}(\text{OTf})_3]_0 / [\text{DMAA}]_0 = 0.017$.

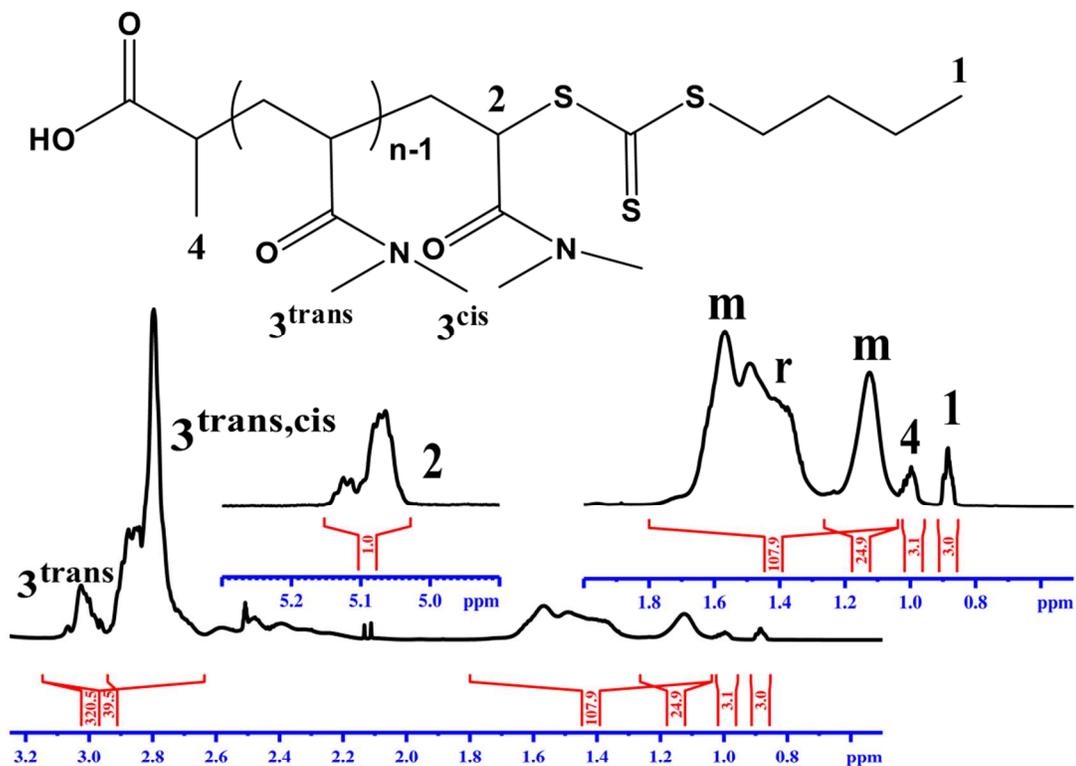


Figure S8. 600 MHz ¹H NMR for purified PDMAA synthesized under blue LED light irradiation ($M_{n,NMR} = 5600$ g/mol, $M_{n,theo} = 6900$ g/mol, $M_{n,GPC} = 6100$ g/mol, and $M_w/M_n = 1.08$; monomer conversion = 56%, m (meso content) = 0.51 ± 0.03) with $[Y(OTf)_3]_0 / [DMAA]_0 = 0$.

End group fidelity calculated by NMR: $f^{end-group} = I^{5.1ppm} / (I^{0.95ppm} / 3) \times 100$, where $I^{5.1ppm}$ and $I^{0.95ppm}$ correspond to the integration values of signals at 5.1 ppm (**2**) and 1.0 ppm (**4**), respectively.

Table S1. Poly(*N,N*-dimethylacrylamide) polymerized in the presence of different ratios of [DMSO]₀/[Y(OTf)₃]₀.^a

Entry	[DMSO] ₀ / [Y(OTf) ₃] ₀	Time (hours)	α ^b	<i>M</i> _{n,th.} (g/mol) ^c	<i>M</i> _{n,GPC} (g/mol) ^d	<i>M</i> _w / <i>M</i> _n ^d	Tacticity (<i>m/r</i>) ^e
1 ^f	0	1	88	10 710	8 690	1.25	0.83/0.17
2	2.91	7	90	10 950	12 500	1.12	0.77/0.23
3	4.25	7	90	10 950	12 000	1.12	0.74/0.26
4	5.82	7	88	10 710	12 370	1.08	0.70/0.30
5	8.73	7	83	10 110	12 900	1.06	0.65/0.35
6	11.64	7	96	11 660	13 500	1.06	0.58/0.42
7	20.37	7	83	10 110	10 990	1.06	0.52/0.48
8	29.10	7	88	10 710	11 100	1.13	0.47/0.53

^aThe reactions were performed at room temperature in methanol under blue light irradiation (5 W, λ_{max} = 460 nm) with Ir(ppy)₃ as the photocatalyst with molar ratio of [DMAA]:[BTPA]:[Ir(ppy)₃]: [Y(OTf)₃]₀ = 120: 1 : 1.2 × 10⁻³: 5.75 at room temperature. ^bMonomer conversion determined by NMR. ^cTheoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_0/[RAFT]_0 \times MW^M \times \alpha + MW^{RAFT}$, where [M]₀, [RAFT]₀, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, initial RAFT concentration, molar mass of monomer, conversion determined by ¹H NMR, and molar mass of RAFT agent. ^dMolecular weight and dispersity were determined by GPC analysis with DMAC as eluent and calibrated to PMMA standards. ^eDetermined by 300 MHz ¹H NMR.

Reference List

- (1) Shanmugam, S.; Xu, J.; Boyer, C. *Chem. Sci.* **2015**, *6*, 1341-1349.