Supporting Information

Dual-pathway chain-end modification of RAFT polymers using visible light and metal-free conditions

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General Reagent Information

All reactions were carried out under an argon atmosphere unless otherwise noted. All commercially obtained reagents were used as received unless otherwise noted. All reactions were performed at room temperature (ca. 23 °C), unless otherwise noted. 1-dodecanethiol, 1-adamantanethiol, 4-methoxy-α-toluenethiol, *N*-acetyl-L-cysteine methyl ester, Eosin Y, tri-*n*-butylphosphine, tris(2-carboxyethyl)phosphine, butylamine and hexylamine were purchased from Sigma-Aldrich and used as received.

General Analytical Information

Nuclear magnetic resonance spectra were recorded on a Varian 600 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise

stated. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. Gas Chromatography equipped with a mass spectrometer detector (GC-MS) was used via manual injection to obtain small molecule characterization traces. Matrix-Assisted Laser Desorption Ionization time of flight mass spectrometry (MALDI-ToF-MS) was conducted using a Bruker Microflex LRF MALDI TOF mass spectrometer, equipped with a 60 Hz nitrogen laser at 337 nm. Solutions in tetrahydrofuran of dithranol as a matrix (saturated solution, 10 µL), sodium trifluoroacetate as cationization agent (1.0 mg/ml, 2 µL) and sample (1.0 mg/ml, 10 µL) were mixed, and 0.7 µL of the mixture was applied to the target plate. Spectra were recorded in linear mode for poly(MA) and poly(DMA).

Light Source

Commercially available 465nm Blue LED strips were purchased and wrapped around a glass crystallization dish as shown below.

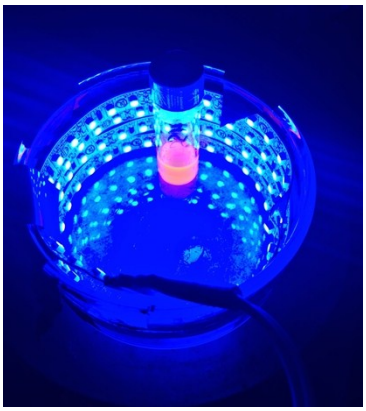


Figure S1. Representative reaction set-up comprising reaction vial surrounded by 465 nm LEDs with a tube blowing compressed air for cooling.

Desulfurization of 1-dodecanethiol:

Procedure:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, 1-dodecanethiol (20.2 mg, 0.10 mmol) and eosin Y (3.2 mg, 0.005 mmol, 0.05 eqv.) were added

and dissolved in 1 mL of DCM. Following this, hexylamine (29 µL, 0.22 mmol, 2.2 eqv.) and tri-*n*-butylphosphine (28 µL, 0.11 mmol, 1.1 eqv.) were added before sparging with argon for 5 minutes. After this time, the vial was removed and irradiated with 465 nm blue LEDs cooling to room temperature with compressed air for 1 hour. The crude mixture was analyzed by ^{1}H NMR and GC-MS.

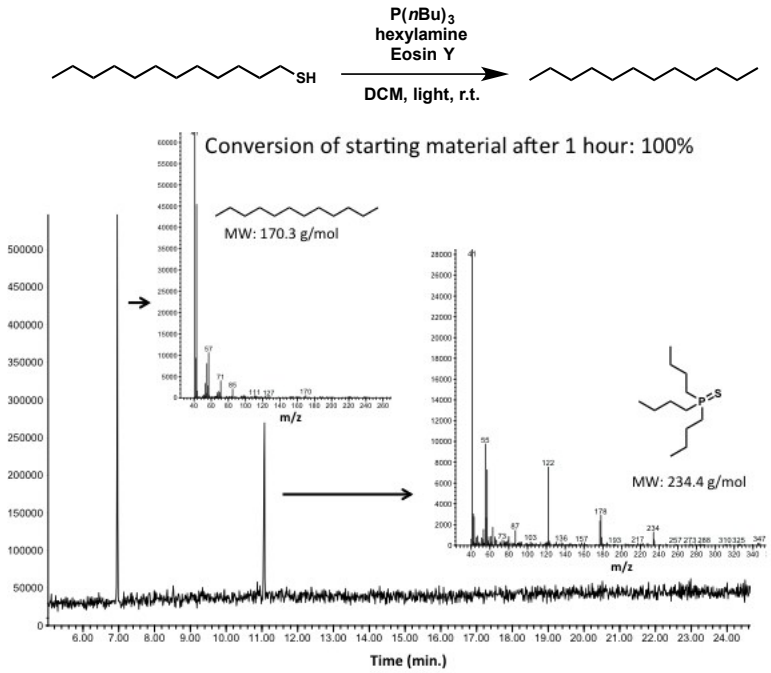


Figure S2. GC-MS data obtained for dodecanethiol

Desulfurization of methoxy-α-toluenethiol

Procedure:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, methoxy-α-toluenethiol (31 mg, 0.20 mmol) and eosin Y (6.5 mg, 0.01 mmol, 0.05 equiv.) were added and dissolved in 1 mL of DCM. Following this, hexylamine (116 µL, 0.88 mmol, 4.4 equiv.) and tri-*n*-butylphosphine (110 µL, 0.44 mmol, 2.2 equiv.) were added before sparging with argon for 5 minutes. The vial was then irradiated with 465 nm blue LEDs for 16 hours and the crude mixture was analyzed by ^{1}H NMR with quantitative conversion of starting material observed. The resulting peaks of the desired product match reported values (**Figure S3**).

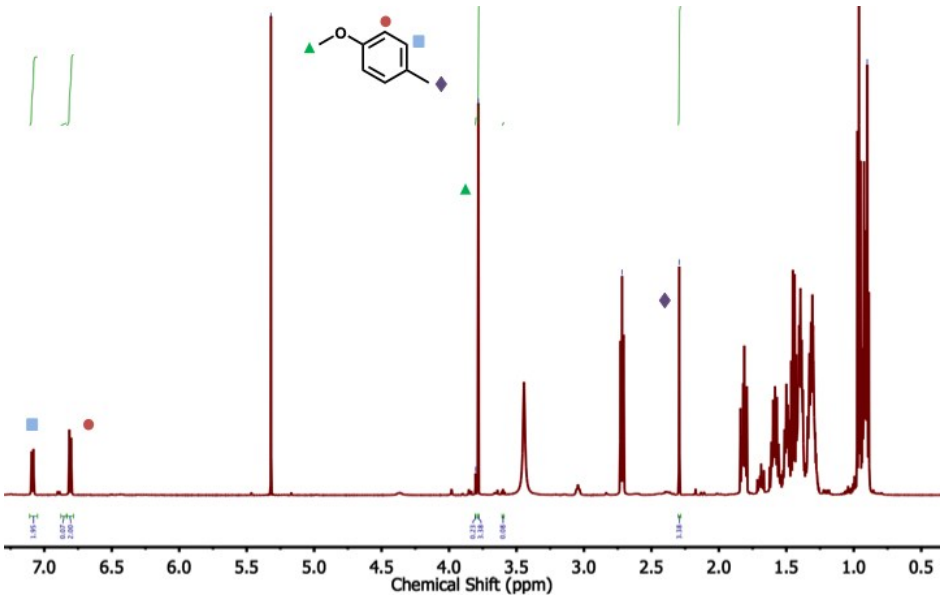


Figure S3. ^{1}H NMR of crude reaction mixture after methoxy-α-toluenethiol desulfurization showing reduction of starting material peaks and quantitative emergence of product peaks matching reported values.

Desulfurization of 1-adamantanethiol:

Procedure:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, 1-adamantanethiol (16.8 mg, 0.10 mmol) and eosin Y (3.2 mg, 0.005 mmol, 0.05 eqv.) were added and dissolved in 1 mL of DCM. Following this, hexylamine (29 µL, 0.22 mmol, 2.2 eqv.) and tri-*n*-butylphosphine (28 µL, 0.11 mmol, 1.1 eqv.) were added before sparging with argon for 5 minutes. After this time, the vial was removed and irradiated with 465 nm blue LEDs for 1 hour.

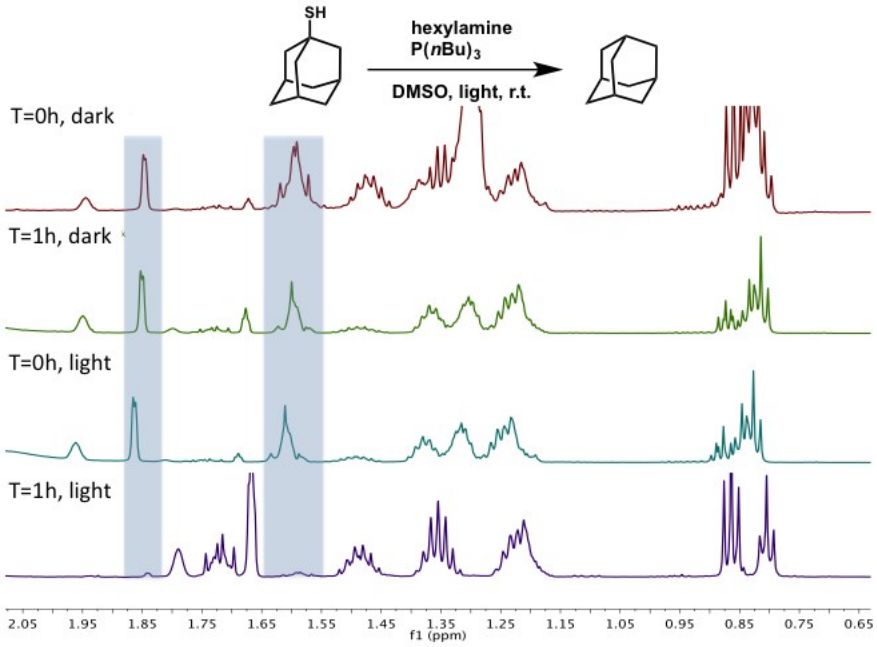
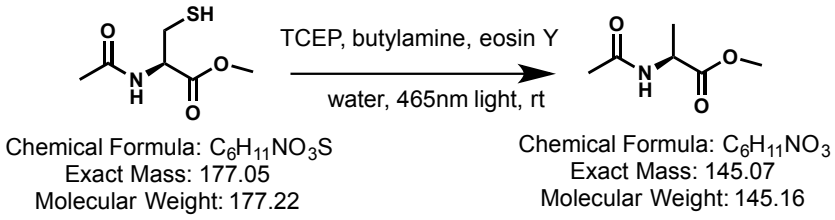


Figure S4. ^{1}H NMR of region of interest for 1-adamantanethiol desulfurization showing loss of starting material peaks

Radical Desulfurization of N-acetyl-L-cysteine ester:

Procedure:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, N-acetyl-L-cysteine ester (17.7 mg, 0.10 mmol), *tris*(2-carboxyethyl)phosphine (31.5 mg, 0.11 mmol), and eosin Y (3.2 mg, 0.0050 mmol) were weighed out and dissolved in 1 mL of water, along with butylamine (22 µL, 0.22 mmol). The vial was bubbled with argon for 10 minutes. After this time, the vial was removed and placed on a stir plate in a dish lined with 465 nm blue LED lights.



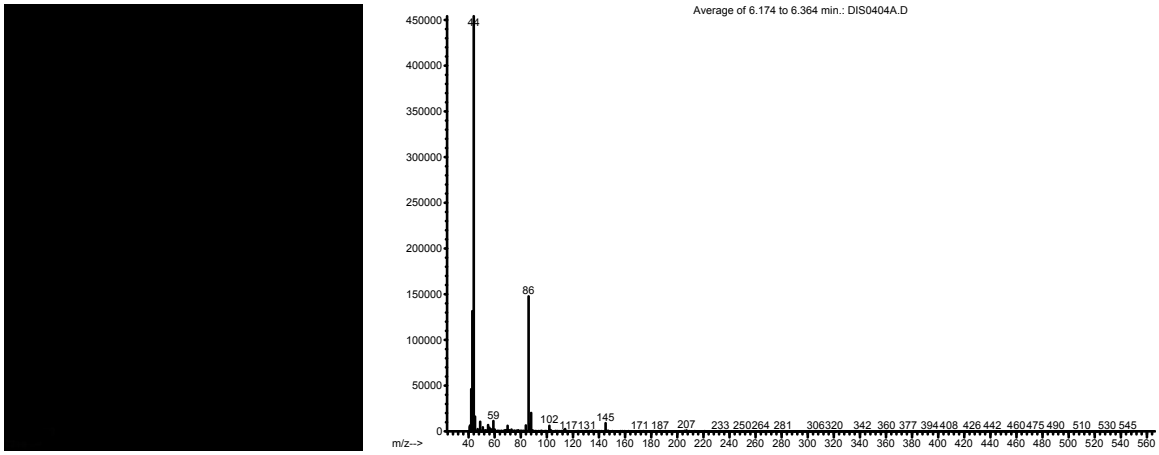


Figure S5. GC-MS data obtained for desulfurized product (alanine)

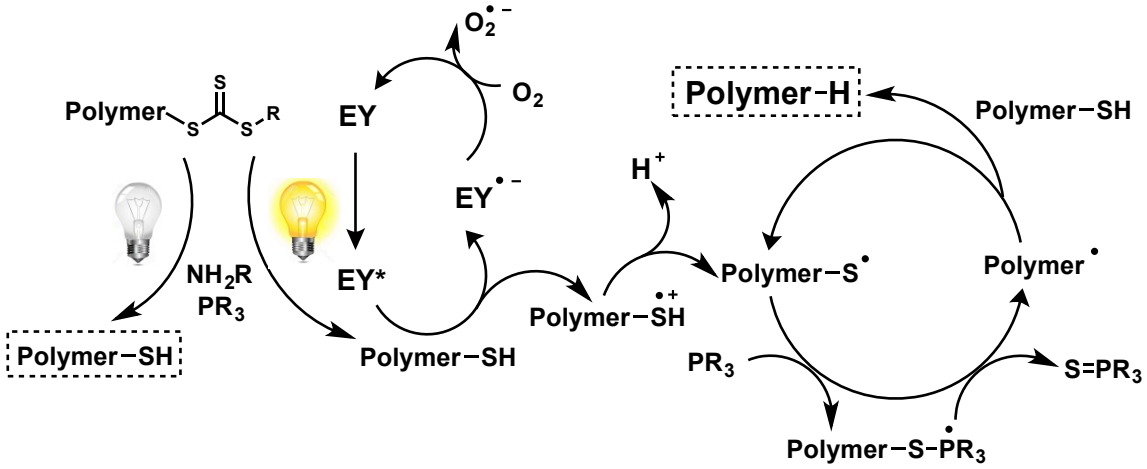


Figure S6. The above figure represents the proposed mechanistic pathway in the absence and presence of light. We hypothesize that upon *in situ* formation of –SH, EY excited by visible light is capable of generating the thiyl radical cation and the corresponding EY radical anion as previously reported in the literature.[1] The thiyl radical cation can undergo deprotonation to afford a thiyl radical, which can be subsequently trapped by a trialkylphosphine to generate a carbon-centered radical.[2] Hydrogen atom abstraction from another thiol regenerates the reactive thiyl radical, the desired hydrogen terminated chain-end and the phosphine sulfide

byproduct.[3] While EY successfully photo-initiates the cycle, possibility of regeneration of the ground state catalyst has been reported to occur in the presence of a small amount of molecular oxygen for reductive quenching catalysts such as Ruthenium and EY. This suggests the possibility of concurrent photo-initiated and catalytic cycles to drive product formation.[3-5]

Synthesis of polystyrene by RAFT:

Procedure:

To a 1-dram vial equipped with a magnetic stir bar, 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (58.3 mg, 0.16 mmol) and AIBN (8.7 mg, 0.053 mmol, 0.33 eqv.) were added and dissolved in 1 mL of deinhibited THF. At this time styrene, (640 µL, 5.6 mmol, 35 eqv.) dehinhibited by passing through basic alumina, was added to the vial. The vial was bubbled with argon for 7 minutes before placing on hot plate to stir at 70°C for 22 hours. ^{1}H NMR indicated approximately 72% conversion of styrene. Sample was further analyzed by GPC. The remaining THF was removed and the PS-CTA was redissolved in a small amount of THF before precipitating into methanol 2 times. The resulting polymer was obtained as a yellow solid (M_n=2200g/mol, Đ=1.16).

Photochemical desulfurization of CTA-terminated polystyrene:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, polystyrene (48 mg, 0.022 mmol) was added and dissolved in 1 mL of DCM. Once dissolved, eosin Y (0.7 mg, 0.001 mmol 0.05 eqv.) was added after making an appropriate stock solution. Following this, hexylamine (35 µL, 0.26 mmol, 12 eqv.) and tri-*n*-butylphosphine (17 µL, 0.066 mmol, 3 eqv.) was added. The vial was then degassed for 5 minutes with argon and irradiated with 465 nm blue LEDs for 24 hours. The polymer was dissolved in THF and precipitated twice from methanol before analyzing by NMR and GPC.

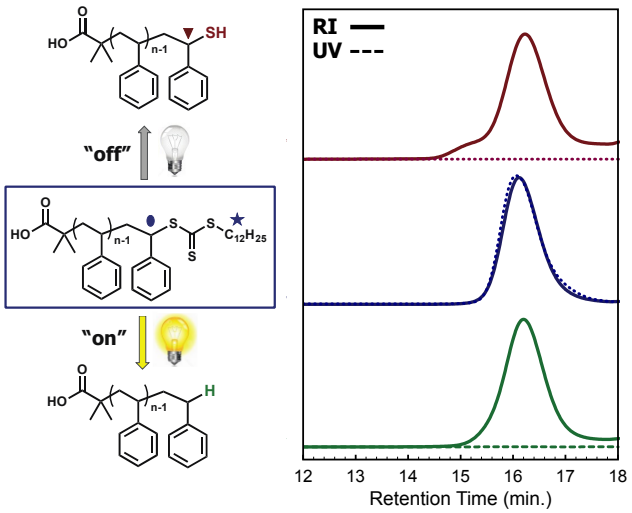
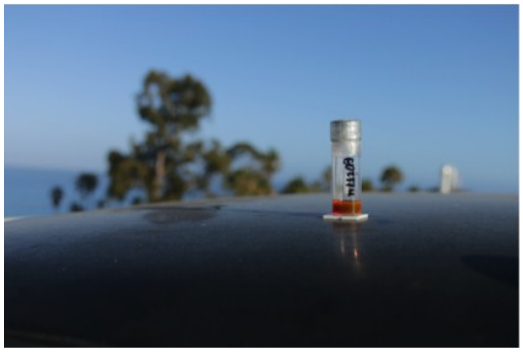


Figure S7. GPC-RI (solid lines) showing appearance of high molecular weight shoulder for thiol end-capped polymer and negligible change in hydrogen-terminated polymer. GPC-UV (dashed lines) showing removal of CTA in both cases when analyzing at 305 nm.

Photochemical desulfurization of polystyrene using natural sunlight

Procedure:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, polystyrene (38 mg, 0.015 mmol) was added and dissolved in 1 mL of DCM. Once dissolved, eosin Y (1.0 mg, 0.002 mmol 0.10 eqv.) was added after making an appropriate stock solution. Following this, hexylamine (49 µL, 0.38 mmol, 25 eqv.) and tri-*n*-butylphosphine (19 µL, 0.075 mmol, 5 eqv.) was added. The vial was then degassed for 5 minutes with argon and irradiated under natural sunlight for 9 hours. The polymer was dissolved in THF and precipitated twice from methanol before analyzing by NMR.



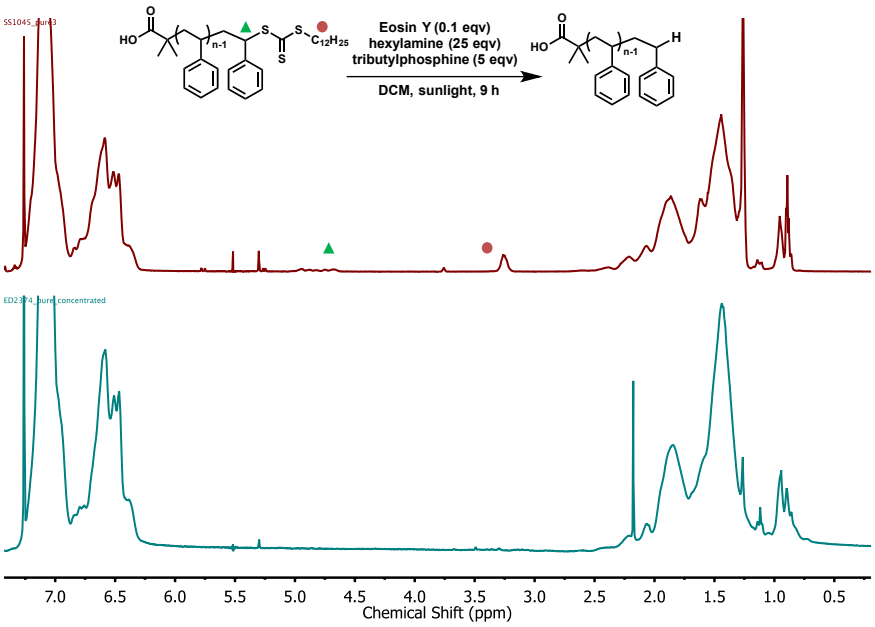


Figure S8. Photo of sunlight reaction and ^{1}H NMR of purified polystyrene before and after sunlight irradiation

Photochemical desulfurization of polystyrene control experiments:

1. PS-CTA ***with*** Eosin Y with ***NO*** irradiation
2. PS-CTA ***without*** Eosin Y ***with*** irradiation

Procedure:

Two vials were prepared for this experiment.

Vial 1: In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, polystyrene (48 mg, 0.022 mmol) was added and dissolved in 1 mL of DCM. Once dissolved, Eosin Y (0.7 mg, 0.001 mmol 0.05 eqv.) was added after making an appropriate stock solution. Following this, hexylamine (35 µL, 0.26 mmol, 12 eqv.) and tri-*n*-butylphosphine (17 µL, 0.066 mmol, 3 eqv.) was added. The vial was then degassed for 5 minutes and left to stir for 24 hours wrappen aluminum foil. The DCM was removed by rotovap before redissolving in THF and precipitating from methanol.

Vial 2: A second vial was then prepared in the same way as above but containing no Eosin Y. This vial was left to stir under 465nm lights for 24 hours. Once both reactions were stopped, the DCM was removed by rotovap before redissolving in THF and precipitating from methanol. The resulting mixtures were transferred to a centrifuge tube and centrifuged at 8000 rpm for 5

minutes to isolate the solid. This process was repeated a total of 3 times.

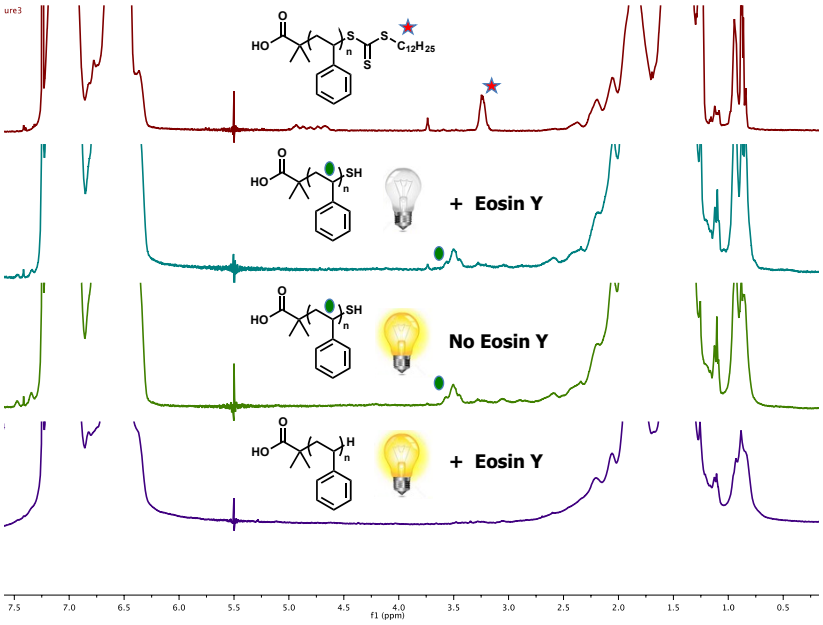


Figure S9.
NMR overlay:
1st spectrum: Starting PS-CTA showing CH_2 next to trithiocarbonate
2nd spectrum: Experiment containing Eosin Y and no light shows thiol
3rd spectrum: Experiment showing no Eosin Y but irradiated shows thiol
4th spectrum: Eosin Y and light are necessary together to get complete removal

Photochemical desulfurization of thiol end-capped polystyrene

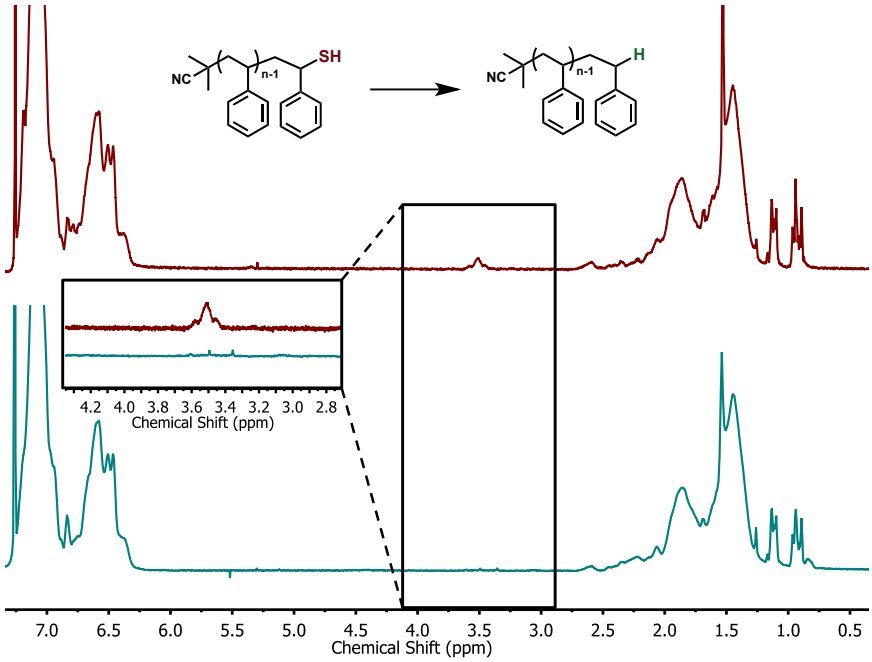


Figure S10. ^{1}H NMR overlay shows the ability to also achieve desulfurization in a sequential manner from thiol chain-end in addition to directly from the CTA-terminated system

Procedure:

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, polystyrene (25 mg, 0.010 mmol) was added and dissolved in 0.7 mL of DCM. Once dissolved, eosin Y (0.3 mg, 0.002 mmol 0.05 eqv.) was added after making an appropriate stock solution. Following this, tri-*n*-butylphosphine (25 µL, 0.100 mmol, 10 eqv.) was added. The vial was then degassed for 5 minutes with argon before placing on 465 nm LED apparatus and allowing to stir for 16 hours

Chain end analysis using *d8*-polystyrene

Procedure:

Added PS(*d8*)-CTA (50 mg) and Eosin Y (0.8 mg, 0.05 eqv.) to a 1-dram vial equipped with a magnetic stir bar. The polymer and catalyst was then dissolved in 1 mL of DCM, followed by addition of hexylamine (39 µL, 0.30 mmol, 12 eqv.), and tri-*n*-butylphosphine (19 µL, 0.075 mmol, 3 eqv.). The vial was left to bubble under argon for 5 minutes before placing on 465 nm LED apparatus and allowing to stir for 24 hours. A second vial was then prepared in the same

way but containing no Eosin Y. This vial was left to stir under ambient conditions. Once both reactions were stopped, the DCM was removed by rotovap before redissolving in THF and precipitating from methanol. The resulting mixture was transferred to a centrifuge tube and centrifuged at 8000 rpm for 5 minutes to isolate the solid. This process was repeated a total of 3 times before analyzing by ^{1}H NMR.

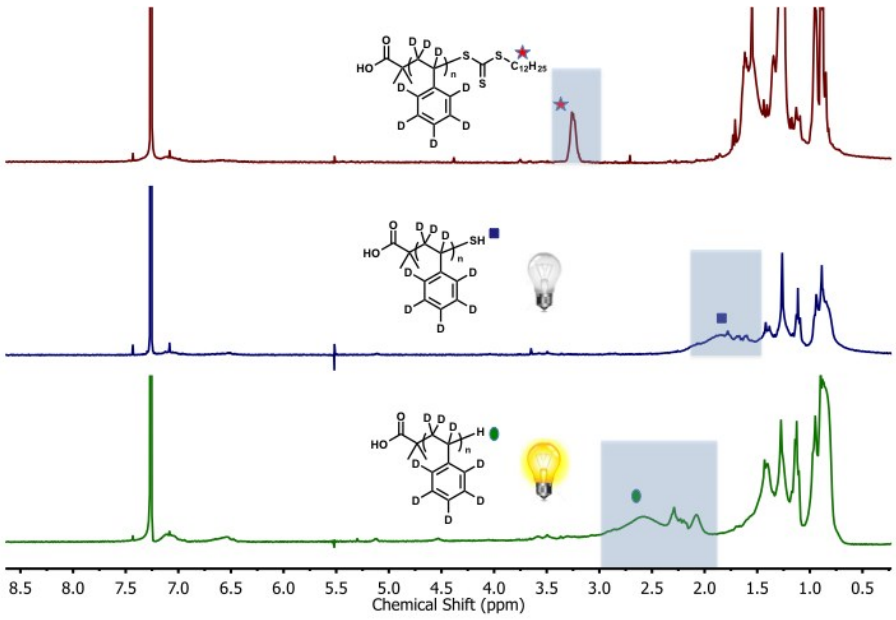


Figure S11. ^{1}H NMR of purified *d8*-polystyrene with and without light-mediated desulfurization conditions. The appearance of broad peaks in benzylic proton region is suggestive of hydrogen incorporation and supports other characterization well.

Polymerization of poly(methyl acrylate) via RAFT:

To a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, 2-cyano-2-propyl dodecyl trithiocarbonate (86.4 mg, 0.25 mmol) was added in addition to AIBN (7.0 mg, 0.043 mmol, 0.17 eqv.) and dissolved in 0.9 mL of benzene. After deinhibiting the monomer by running it through an aluminum oxide plug, methyl acrylate (906 µL, 10 mmol) was added to the reaction vial. The vial was bubbled with argon for 10 minutes before placing the vial on a stir plate in a heating block at 60°C for 24 hours. ^{1}H-NMR indicated approximately 98% conversion. Sample was further analyzed by GPC. The reaction was quenched after adding a small amount of acetone and was purified via dialysis (1k cut-off) against acetone switching several times. The resulting polymer was obtained as a yellow wax after removal of acetone.

Photochemical desulfurization of CTA-terminated poly(methyl acrylate):

In a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, poly(methyl acrylate) (48 mg, 0.012 mmol) was added and dissolved in 0.5 mL of THF. Eosin Y (0.4 mg, 0.0004 mmol, 0.05 eqv.) was added after making the appropriate stock solution to make the total volume of THF 1 mL. Following this, hexylamine (39 µL, 0.30 mmol, 25 eqv.) and tributylphosphine (15.0 µL, 0.060 mmol, 5 eqv.) was added. The vial was bubbled with argon for 5 minutes and irradiated with 465 nm blue LEDs for 24 hours. A second reaction was set up in the same way but was wrapped in foil and left to stir for 24 hours.

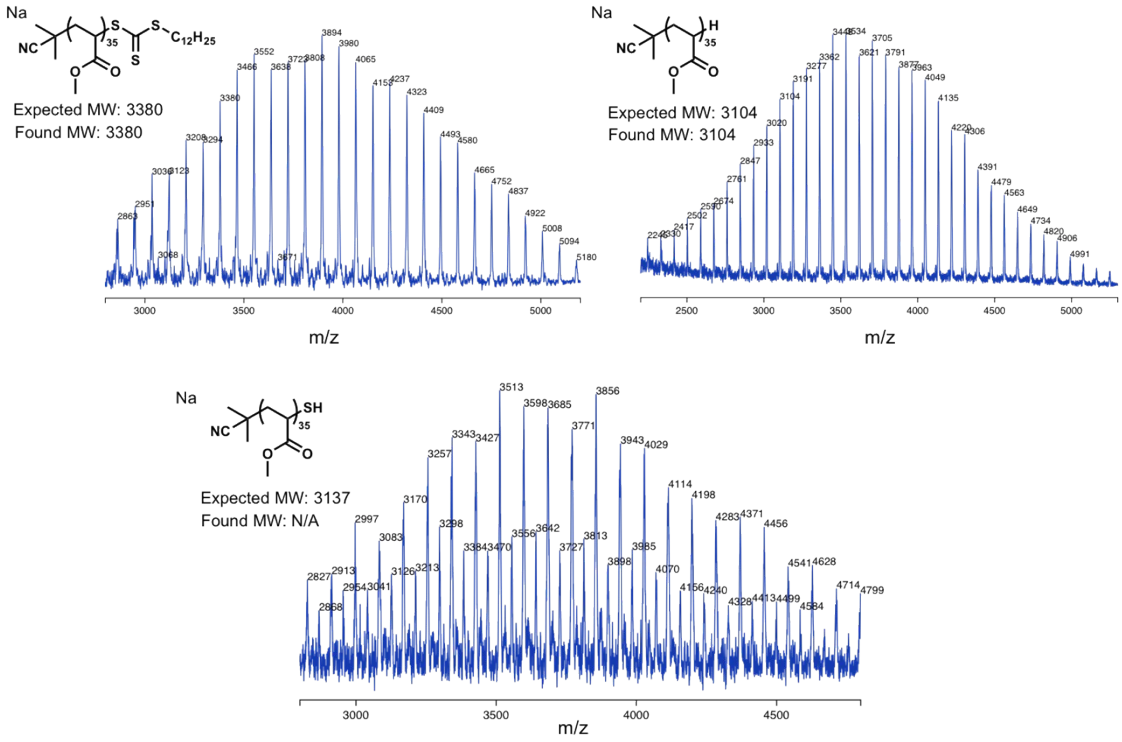


Figure S12. MALDI spectra showing expected distributions for starting CTA and H terminated polymer, but multiple distributions for thiol end-capped polymer.

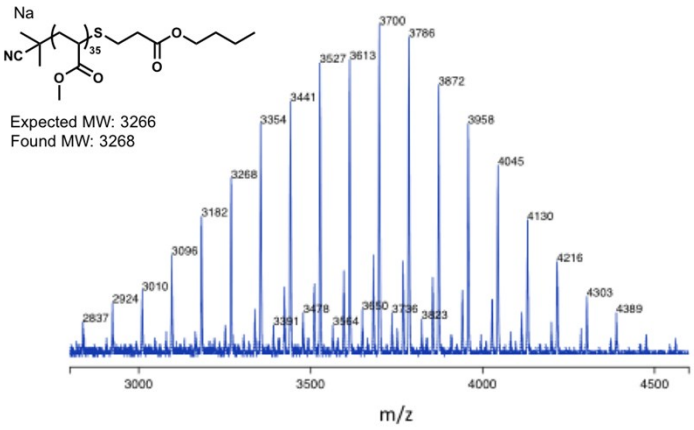


Figure S13. MALDI spectra showing expected distribution for thiol end-capped polymer end capped with butyl acrylate according to literature procedure.[6]

Photochemical desulfurization of CTA-terminated poly(methyl methacrylate) and qualitative analysis using Ellman's reagent:

Figure S14. Qualitative analysis using Ellman's reagent in DMSO provides supporting evidence that thiol is present in non-irradiated sample as indicated by emergence of a red color. Comparison with 1-dodecanethiol also results in red color.

Polymerization of poly(*N*,*N*-dimethylacrylamide) via PET-RAFT:

Using adopted literature conditions.[7] Added 4.8 mg of 2-(n-butyltrithiocarbonate)-propionic acid (BTPA) and 0.3 mg of Eosin Y to 1-dram vial equipped with stir bar before dissolving in 1 mL of DI water. At this time 330 µL of *N*,*N*-dimethylacrylamide (DMA), deinhibited by basic alumina, was added to the vial. The vial was then degassed by purging with argon for 10 minutes before placing on LED stir plate apparatus irradiating with 465 nm light. The polymerization was left to

stir for 16 hours before opening vial to air and checking conversion by ^{1}H NMR which was determined to be >95%. The polymer was further characterized by GPC (M_n=25000g/mol, Đ=1.10) and purified via dialysis against water using 3.5k cut-off tubing. The water was removed via lyophilization for 48 hours.

Photochemical desulfurization of CTA-terminated poly(N,N-dimethylacrylamide):

To a 1-dram vial equipped with a magnetic stir bar and a teflon screw cap septum, PDMA (57.0 mg, 0.0030 mmol), *tris*(2-carboxyethyl)phosphine (8 mg, 0.030 mmol, 10 eqv.), and Eosin Y (0.2 mg, 0.0003 mmol, 0.1 eqv.) were added and dissolved in 0.2 mL of water. Butylamine was added (15 µL, 0.15 mmol, 50 eqv.), with addition of an extra 10 µL to improve overall solubility. The vial was bubbled with argon for 10 minutes and irradiated with 465 nm blue LEDs. A second reaction was set up in the same way but was wrapped in foil. After allowing both reactions to stir for 24 hours, the vials were opened to air and a small amount of water was added before purification via dialysis against water using 3.5k cut-off tubing. The water was removed via lyophilization for 48 hours.

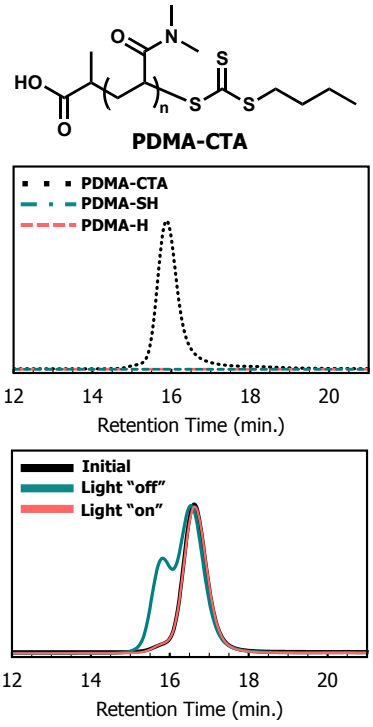


Figure S15. GPC-UV (top) analysis at 305nm showing disappearance of CTA in both "on" and "off" cases. GPC-RI (bottom) depicts overlay of purified polymer samples and clear emergence of disulfide coupled polymer in "off" case. The "on" case shows negligible change from the starting polymer.

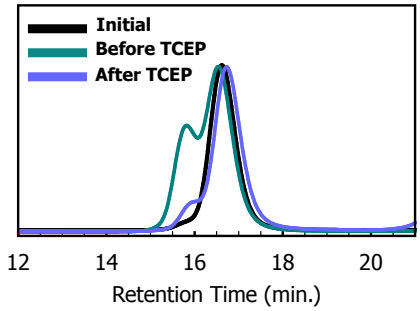


Figure S16. GPC-RI trace before and after addition of TCEP to show that high molecular weight shoulder was due to undesired disulfide coupling.

References

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