Supporting Information

Light-Accelerated Depolymerization Catalyzed by Eosin Y

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Materials and Methods

Materials

All materials were purchased from either Sigma Aldrich or Fischer Scientific. Monomers were filtered through basic alumina before use.

^{1}H NMR spectroscopy

^{1}H-NMR spectra were recorded on a Bruker Avance-300 spectrometer $CDCl_3$ as the NMR solvent. Chemical shifts are given in ppm downfield from tetramethylsilane and referenced to residual solvent proton signals.

Size-exclusion chromatography (SEC)

SEC was measured on Shimadzu equipment comprising a CBM-20A system controller, LC-20AD pump, SIL-20A automatic injector, 10.0 µm bead-size guard column (50 x 7.5 mm) followed by three KF-805L columns (300 x 8 mm, bead size: 10 µm, pore size maximum: 5000 Å), SPD-20A ultraviolet detector, and an RID-20Adifferential refractive index detector. The column temperature was maintained at 40 ℃ using a CTO-20A oven. The flow rate was set to 1 ml/min and with *N*, *N*-dimethylacetamide (DMAc, Acros, HPLC grade, with 0.03 w/v LiBr) as the eluent. The UV wavelength was set to 310 nm. Molecularweights were determined relative poly(methyl methacrylate) standards with molecular weights ranging from 5,000 to 1.5 x 10^6 g/mol (Agilent Technologies). All SEC samples were dissolved inDMAc and passed through 0.45 µm PTFE filters prior to analysis.

Photoreactor Characterization

The homemade photoreactor was built into a tube-like shape (diameter of 12 cm and height of 7 cm). On the inner walls of the photoreactor, an LED strip (Mxellex®) was placed inside in a spiral pattern. The final number of LEDs inside the photoreactor was 35. A silicone oil bath (diameter of 8 cm) where the reaction was heated was placed in the center of the photoreactor. Aluminum foil was used to cover the top of the reactor from external light. Photoreactor emission spectra were collected on a Varian Cary Eclipse spectrometer. The maximum emission wavelength for blue, green and red are respectively 460 nm (±17), 510 nm (±31), and 630 nm (±16) respectively. Photoreactor intensity was determined using a Thorlabs PM100D light power meter, equipped with a S170C Microscope Slide Power Sensor.

Experimental procedure

Polymerization of MMA using 2-cyano-2-propyl dithiobenzoate as a RAFT agent (PMMA-DTB).

Into a 25 mL Schlenk tube, 92.13 mg of 2-cyanoprop-2-yl dithiobenzoate (416.3 µmol, 1 equiv) and 6.85 mg AIBN (41.7 µmol, 0.1 equiv) were dissolved in 3.75 mL toluene. Subsequently, 5.32 mL of MMA (5.0 g, 49.9 mmol, 120 equiv) and a stirrer bar were added, and the tube was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in a pretreated oil bath at 70 °C for 5 h with a 400-rpm stirring rate. Polymerization was stopped at 40% conversion by removing the reaction from the oil bath and exposing to air. PMMA macroCTA was precipitated at least three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Polymerization of MMA using 2-Cyano 2-propyl dodecyltrithiocarbonate as a RAFT agent.

In a 15 mL vial, 57.5 mg of 2-Cyano 2-propyl dodecyltrithiocarbonate (166.5. µmol, 1 equiv) and 2.7 mg AIBN (16.6 µmol, 0.1 equiv) were dissolved in 1.3 mL toluene. Subsequently, 2.66 mL of MMA (2.5 g, 25 mmol, 150 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in a pretreated oil bath at 70 °C for 4.5 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 µm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 38% conversion by removing the reaction from the oil bath and exposing to air. PMMA macroCTA was precipitated at least three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Polymerization of MMA using 2-Cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1- carbodithioate as a RAFT agent.

In a 15 mL vial, 143.7 mg of 2-Cyanobutan-2-yl 4-chloro- 3,5-dimethyl-1H-pyrazole-1-carbodithioate (499.4 µmol, 1 equiv) and 8.2 mg AIBN (16.6 µmol, 0.1 equiv) were dissolved in 1.3 mL toluene. Subsequently, 2.66 mL of MMA (2.5 g, 25 mmol, 50 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in a pretreated oil bath at 70 °C for 6 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 µm PTFE membrane) prior to SEC analysis. Polymerization was stopped at 65% conversion by removing the reaction from the oil bath and exposing to air. PMMA macroCTA was precipitated at least three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Polymerization of BzMA using 2-cyano-2-propyl dithiobenzoate as a RAFT agent (PBzMA-DTB).

Into a 10 mL round bottom flask, 125.6 mg of 2-cyanoprop-2-yl dithiobenzoate (380 µmol, 1 equiv) were dissolved in 3 mL toluene. A stock solution of AIBN (10 mg) was prepared in 1 mL toluene, and 617 µL of this solution (6.17 mg, 37.6 µmol, 0.1 equiv) was transferred to the flask. Subsequently, 5.08 mL of BzMA (5.3 g, 30 mmol, 80 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Polymerization was stopped at 59% conversion by removing the reaction from the oil bath and removing the septum. PBzMA macroCTA was precipitated at least three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Polymerization of OEGMA using 2-cyano-2-propyl dithiobenzoate as a RAFT agent (POEGMA-DTB).

Into a 50 mL round bottom flask, 44.3 mg of 2-cyanoprop-2-yl dithiobenzoate (200 µmol, 1 equiv) were dissolved in 10 mL toluene. A stock solution of AIBN (10 mg) was prepared in 1 mL toluene, and 328 µL of this solution (3.28 mg, 20 µmol, 0.1 equiv) was transferred to the flask. Subsequently, 10 g of OEGMA (20 mmol, 100 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling 2 for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Polymerization was stopped at 45% conversion by removing the reaction from the oil bath and removing the septum. POEGMA macroCTA was precipitated at least three times in diethyl ether/hexane solution (50% v/v) and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

Polymerization of DMAEMA using 2-cyano-2-propyl dithiobenzoate as a RAFT agent (PDMAEMA-DTB).

Into a 10 mL round bottom flask, 70.4 mg of 2-cyanoprop-2-yl dithiobenzoate (318 µmol, 1 equiv) were dissolved in 6 mL toluene. A stock solution of AIBN (10 mg) was prepared in 1 mL toluene, and 522 µL of this solution (5.22 mg, 31.8 µmol, 0.1 equiv) was transferred to the flask. Subsequently, 4.29 mL of DMAEMA (4 g, 25.4 mmol, 80 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Polymerization was stopped at 40% conversion by removing the reaction from the oil bath and removing the septum. PDMAEMA macroCTA was precipitated at least three times in pentane and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

General thermal depolymerization procedure for PMMA

PMMA-DTB will be used as the model example to describe a typical depolymerization procedure. In a 125 ml schlenk tube, 21.5 mg of PMMA was dissolved in 40 ml 1,4-dioxane (5.17 mM of MMA repeat unit). 15 mg of 350 g/mol poly(ethylene glycol) monomethyl ether was added as an internal standard for 1H NMR analysis. The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 100 ℃ oil bath to start the reaction. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~3 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 µm PTFE membrane).

General photothermal depolymerization catalyzed by Eosin Y procedure for PMMA

PMMA-DTB will be used as the model example to describe a typical depolymerization procedure. 71.5 μL of a stock solution (0.2 mg/mL) of Eosin Y was added (100 ppm respect to the MMA repeating units) in a 125 ml schlenk tube. 21.5 mg of PMMA was dissolved in 40 ml 1,4-dioxane (5.17 mM of MMA repeat unit). 15 mg of 350 g/mol poly(ethylene glycol) monomethyl ether was added as an internal standard for 1H NMR analysis. The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 100 ℃ oil bath and the LED light strip was turned on at the selected wavelength to start the reaction. The LED lights were organized in a circular way around the oil bath whit a distance of 3 cm, the reactor was then covered by aluminum foil. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~3 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 μm PTFE membrane).

Analysis of RI/UV SEC signal during depolymerization

Relative SEC signals were analyzed by preparing the samples at the same concentration of the reaction mixture. Specifically, 3 ml of the reaction was sampled at various time points (including t0, before the reaction was put into the oil bath) and dried by air blowing. The dried polymer residue was then redissolved into 1 ml of N,N-dimethylacetamide and analyzed with SEC. The signal intensities for subsequent time points were not normalized and compared with each other. Conversion was determined by comparison of RI signal at a certain time to the one at time t_0.

Analysis of ^{1}H NMR during depolymerization

Depolymerization conversions were also determined by ^{1}H NMR, comparing the monomer vinyl signals to the polymer backbone -CH_3 signals (simply taking a sample in dioxane and re-dissolving it in deuterated chloroform). In addition, an internal standard is added in each reaction to ensure accurate conversion calculation through an alternative way. Specifically, a second NMR sample was prepared by re-dissolving the dried reaction mixture (blowing the solvent with air). Conversions were then calculated by comparing the intensity of the backbone –CH_3 signals before and after depolymerization against a nonvolatile internal standard (methoxy-terminated polyethylene glycol). Depolymerization conversions from the two methods deviated by <5%.

Supplementary Data

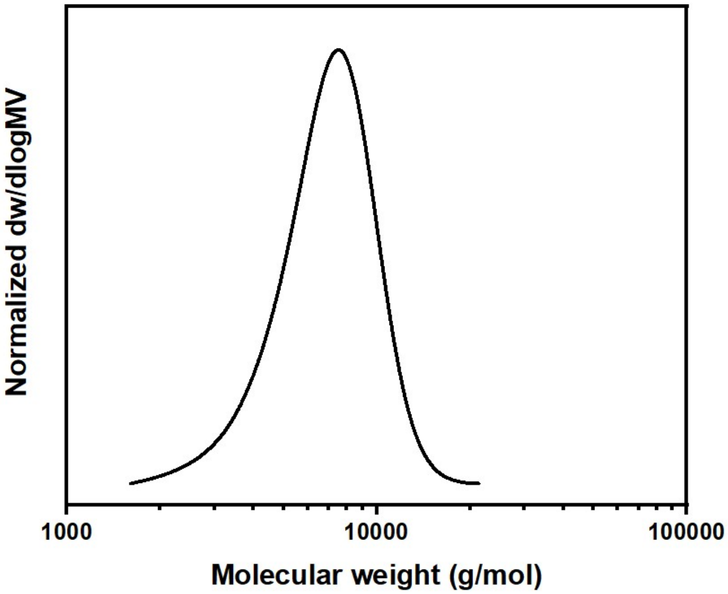

Figure S1. SEC trace of PMMA-DTB synthesized via RAFT polymerization with 2-cyano-2- propyl dithiobenzoate as a chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:120) (M_n = 6,300; $Đ$ = 1.14).

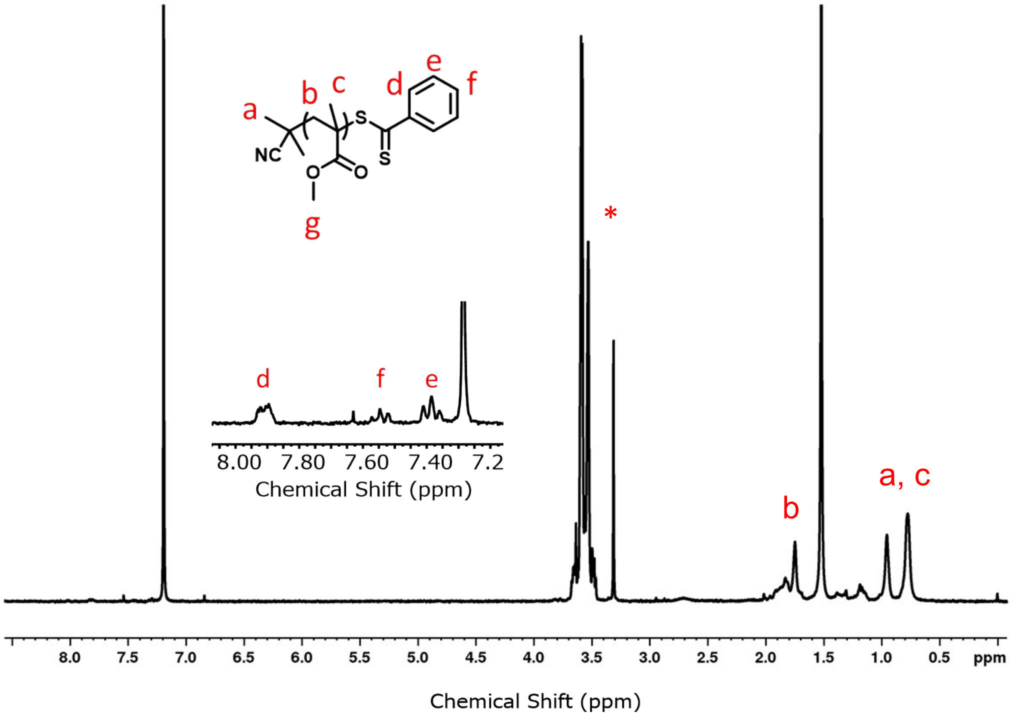

Figure S2. ^{1}H-NMR spectrum of purified PMMA-DTB prior to depolymerization. (*) Internal standard

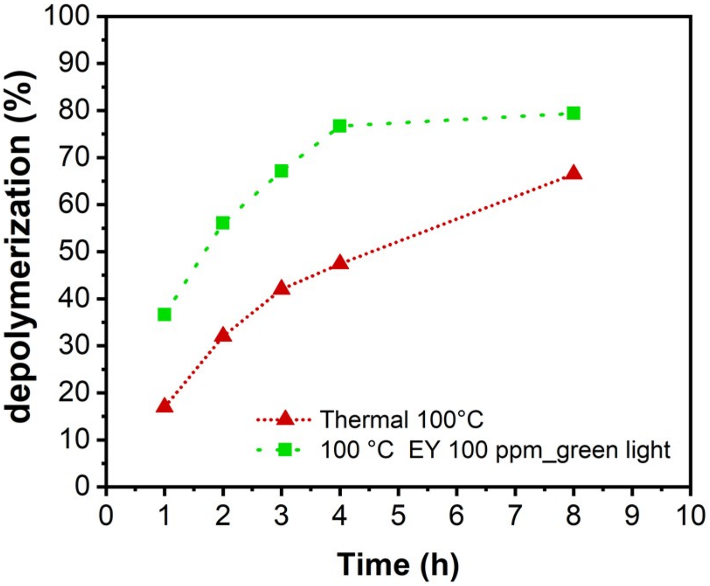

Figure S3. Depolymerization conversion versus time of PMMA-DTB thermal depolymerization (red triangle), and in the presence of 100 ppm of Eosin Y under green irradiation (green squares). Reactions were run at 100 °C, 5 mM in 1,4-dioxane.

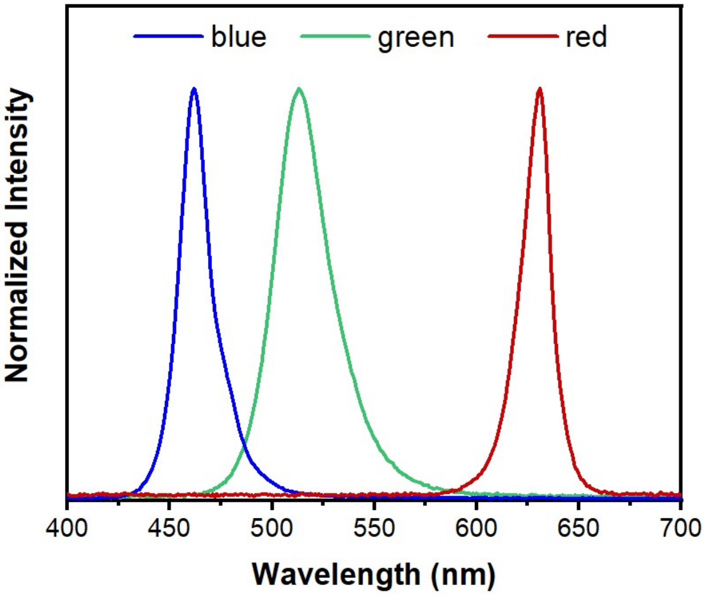

Figure S4: Normalized emission intensity of the blue, green and red RGB LED strip used for the photoreactor.

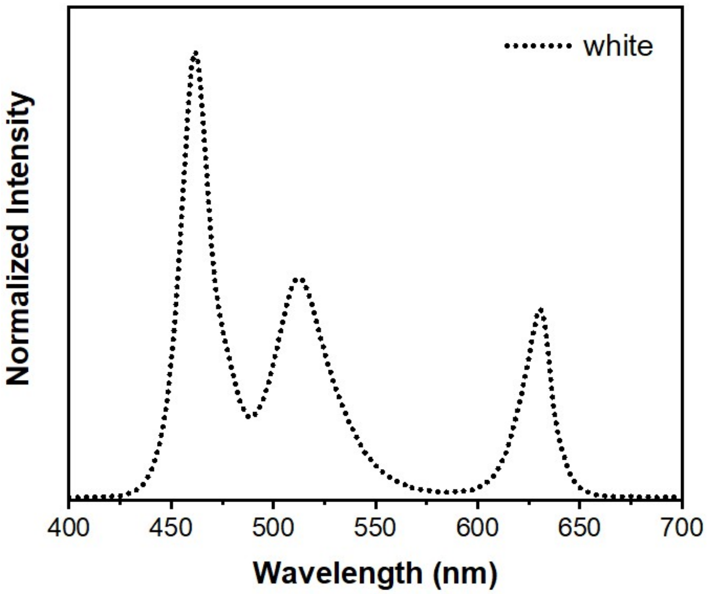

Figure S5: Normalized emission intensity of the white RGB LED used for the photoreactor.

Table S1: Characterization data of the photoreactor: Density of light has been control using a remote controller. High indicate the maxim intensity an low the minimum intensity that the LEDs strips can reach.

Reactor	Wavelength (nm)	FWHM (nm)	Density of light	Intensity (mW/cm^2)
Blue	460	17	High	3.63 ± 0.55
			Low	0.26 ± 0.03
Green	510	31	High	2.31 ± 0.14
			Low	0.18 ± 0.01
Red	630	16	High	1.14 ± 0.11
			Low	0.12 ± 0.01
White	460	17	High	8.75 ± 0.34
	520	31	High	6.04 ± 0.75
	630	16	High	5.33 ± 0.82

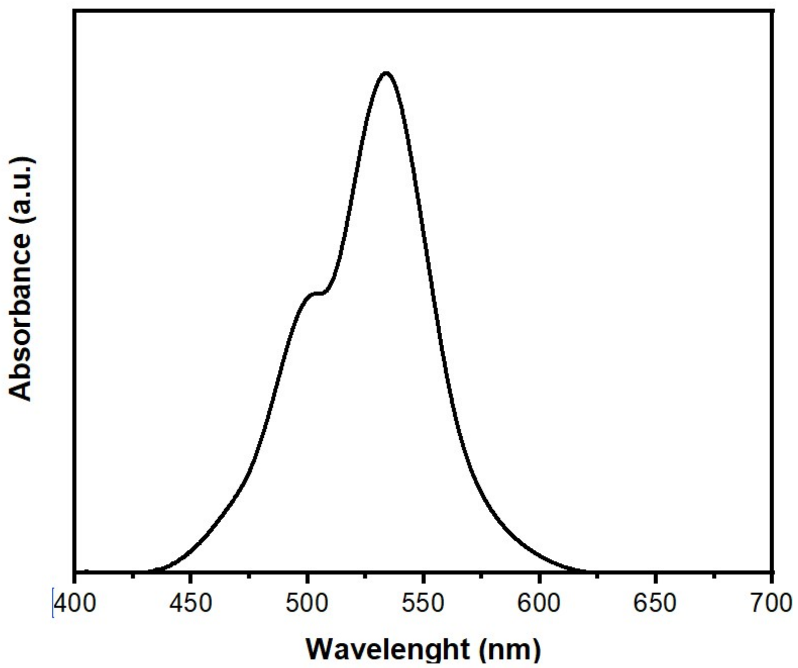

Figure S6: Absorption spectra of eosin Y in 1,4 dioxane.

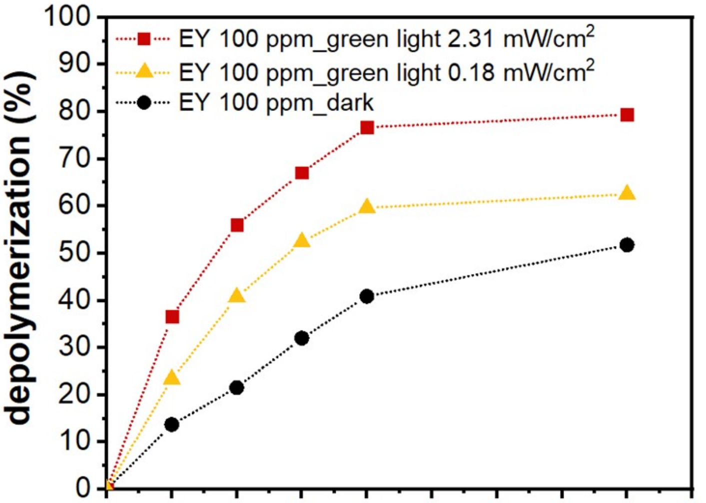

Figure S7. Depolymerization conversion versus time of PMMA-DTB in the presence of Eosin Y under green irradiation and high intensity of the photoreactor (red squares), low intensity (yellow triangles), and in the dark (black dots). Reactions were run at 100 °C, 5 mM, 100 ppm of Eosin Y, in 1,4-dioxane.

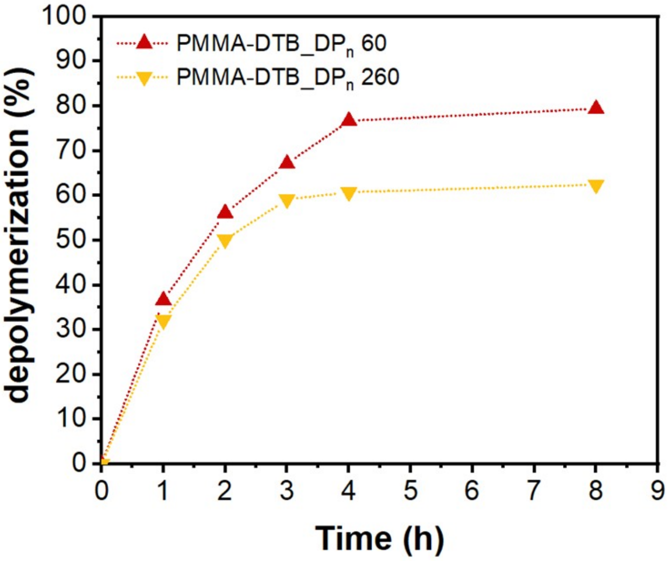

Figure S8. Depolymerization conversion versus time of PMMA-DTB with DP of 60 (red triangles), and 260 (yellow triangles). Reactions were run at 100 °C, 5 mM, 100 ppm of Eosin Y, green light, in 1,4-dioxane.

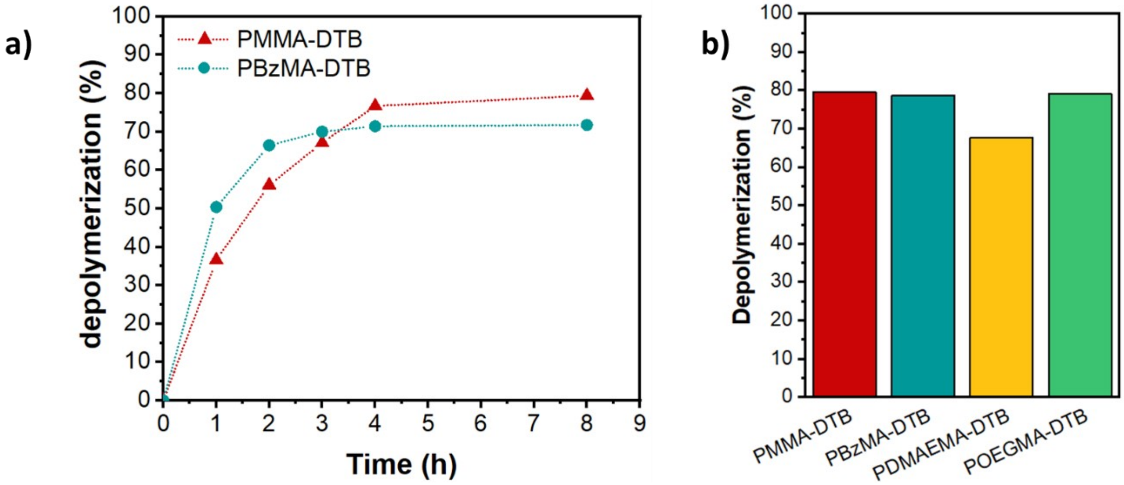

Figure S9. a) Depolymerization conversion versus time of PMMA-DTB (red triangles), and PBzMA (green dots). b) Depolymerization of PMMA, PBzMA, PDMAEMA and POEGMA after 8 hours of green irradiation. Reactions were run at 100 °C, 5 mM, 100 ppm of Eosin Y in 1,4-dioxane.

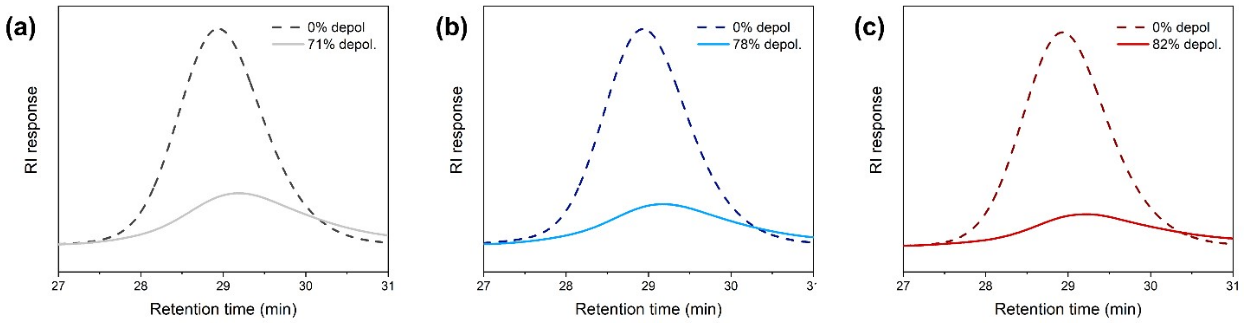

Figure S10. RI SEC traces of PMMA-DTB before and after depolymerization under (a) white, (b) blue, and (c) red light. Reactions were run at 100 °C, 5 mM in 1,4-dioxane with 100 ppm of Eosin Y for 8 h. SEC traces were obtained drying equal amount of final solution and redissolved in 1 mL of DMAC.

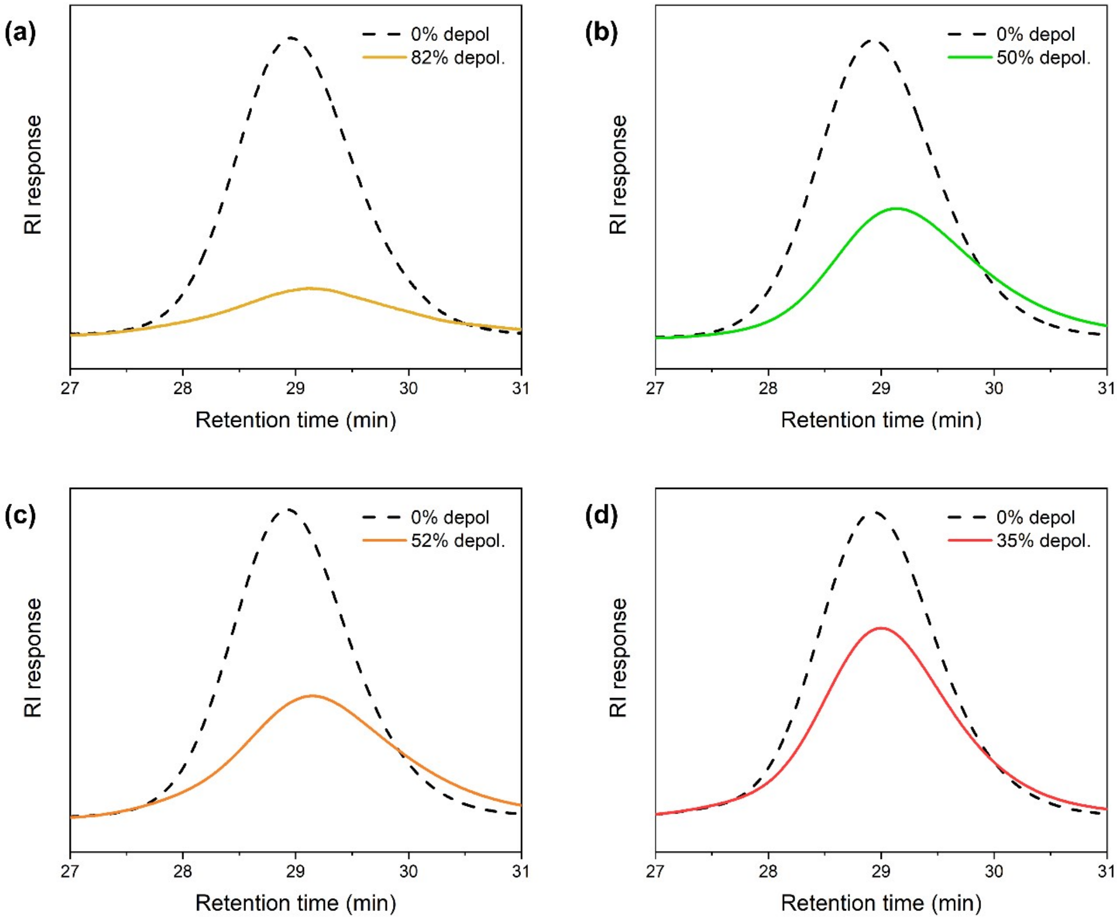

Figure S11. RI SEC traces of PMMA-DTB before and after depolymerization in (a) DMSO, (b) toluene, (c) xylene, and (d) DMF. Reactions were run at 100 °C, 5 mM in 1,4-dioxane with 100 ppm of Eosin Y under green light for 8h. SEC traces were obtained drying equal amount of final solution and redissolved in 1 mL of DMAC.

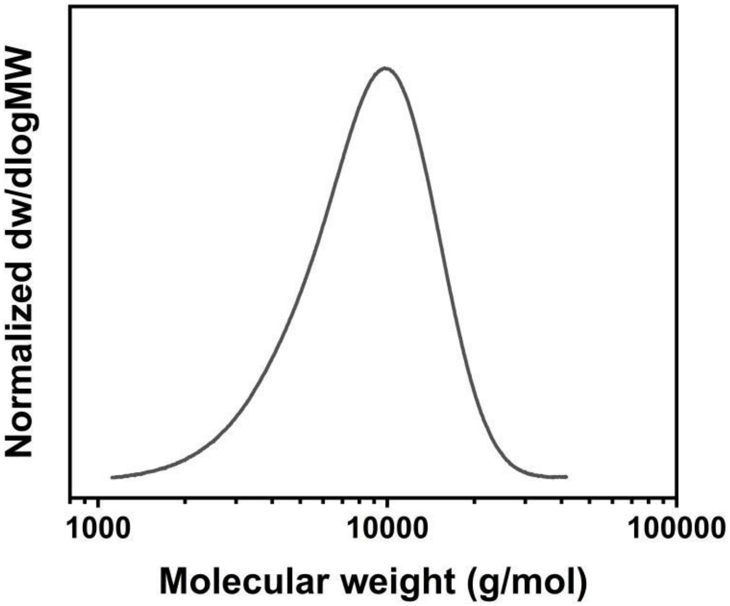

Figure S12. SEC trace of PMMA-TTC synthesized via RAFT polymerization with 2-cyano 2- propyl dodecyltrithiocarbonate as a chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:140) (M_n = 7,400; $Đ$ = 1.30).

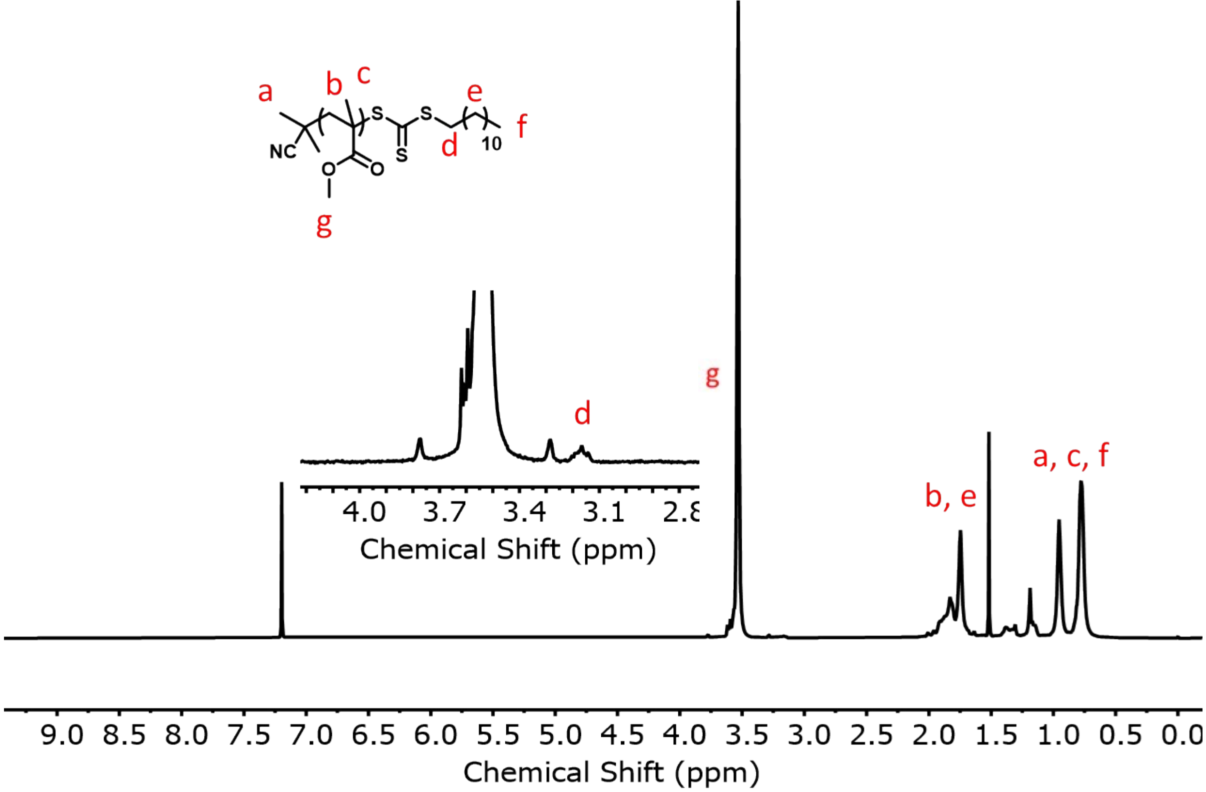

Figure S13. ^{1}H-NMR spectrum of purified PMMA-TTC prior to depolymerization.

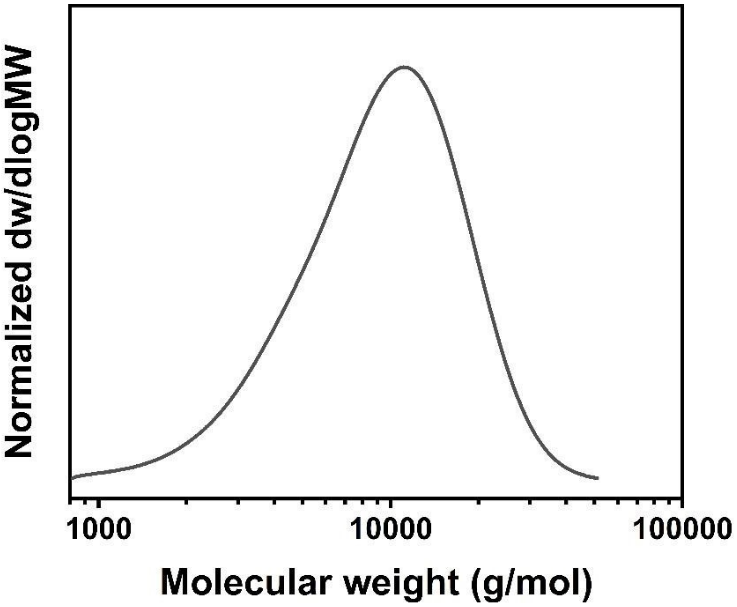

Figure S14. SEC trace of PMMA-pyrazoleCD synthesized via RAFT polymerization with cyanobutan-2-yl 4-chloro-3,5-dimethyl-1H-pyrazole-1-carbodithioate as a chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:50) (M_n = 7,400; $Đ$ = 1.50).

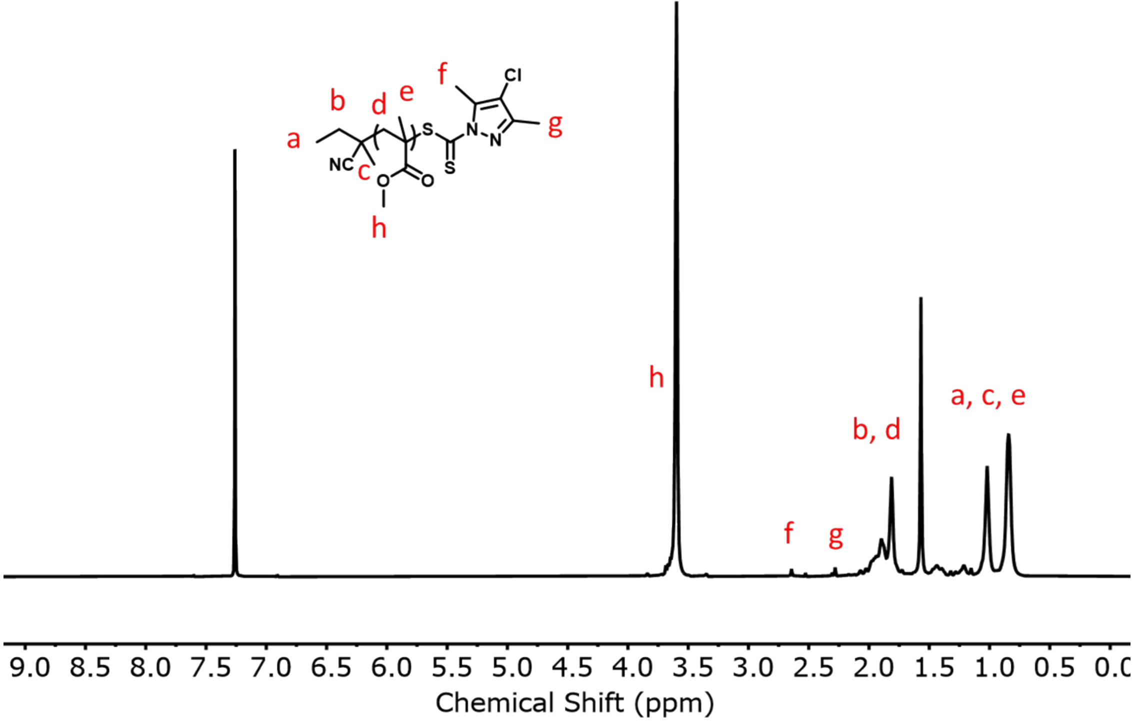

Figure S15. ^{1}H-NMR spectrum of purified PMMA-pyrazoleCD prior to depolymerization.