Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Self-Catalyzing Photoredox Polymerization for Recyclable Polymer Catalysts

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Supporting Information:

Materials and Instrumentation:

Materials:

All chemicals were used as received from commercial vendors unless otherwise noted. Methyl methacrylate (MMA), benzyl methacrylate (BzMA), and hexyl methacrylate (HMA) were passed through a column of basic alumina to remove inhibitors prior to polymerization. 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]petanoic acid (CDP, RAFT agent) and the PEG-CDP macroRAFT agent (5,400 g/mol) were synthesized according to previous literature.[1-2] Dry *N,N*-dimethylformamide (DMF) was obtained by passing the solvent through two sequential activated alumina columns in a MBRAUN solvent purification system.

Instrumentation:

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR spectra were recorded on an Inova 500 MHz spectrometer or on a Varian Mercury 300 MHz spectrometer. ^{1}H NMR chemical shifts in DMSO-d_6 or $CDCl_3$ were referenced to CHD_2SOCD_3 (2.50 ppm) or $CHCl_3$ (7.26 ppm).

Size-Exclusion Chromatography (SEC). SEC was performed in DMAc with 50 mM LiCl at 50 °C and a flow rate of 1.0 mL/min (Agilent isocratic pump, degasser, and autosampler; columns: Viscogel I-series 5 µm guard + two ViscoGel I-series G3078 mixed bed columns, molecular weight range $0-20 \times 10^3$ and $0-100 \times 10^4$ g/mol). Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm, a Wyatt miniDAWN Treos light scattering detector operating at 659 nm, and a Viscotek VE 3210 UV/vis detector operating at 532 nm. Absolute molecular weights and molecular weight distributions were calculated using the Wyatt ASTRA software or from conventional calibration using PMMA standards.

UV-Vis Spectroscopy. All measurements were taken using a Molecular Devices SpectraMax M2 Multimode Microplate Reader at 25 °C. Absorbance measurements were conducted with 200 µL of sample on clear 96-well polypropylene microplates (Greiner Bio-One).

High Resolution Mass Spectrometry (HRMS). HRMS was conducted on an Agilent 6220 TOF spectrometer with electro spray ionization (ESI).

Transmission Electron Microscopy (TEM). TEM was conducted on a Tecnai G2 Spirit TWIN TEM from Field Electron and Ion Company (FEI Company, Hillsboro, OR, USA) operating at an accelerating voltage of 120 kV. Digital images were acquired with a Gatan Ultrascan 1000 2k × 2k CCD camera and DigitalMicrograph 1.93 image acquisition software (Gatan Inc., Pleasanton, CA, USA.) Electron Microscopy Sciences Formvar Carbon Film on 400 mesh nickel grids (FCF400-Ni) were used for all trials. For unstained samples, 5 µL purified nanoparticle solution (0.1 mg/mL) was spotted on the grid for 20 s. The excess solvent was wicked off. The grid was gently rinsed with 5 drops of ultrapure water and air-dried after wicking off excess solvent.

Dynamic Light Scattering (DLS). DLS was performed with a non-invasive backscatter system (Malvern Zetasizer Nano ZS) with a measuring angle at 173˚ and adjustable focus. was performed at 25 ˚C at 0.1 wt%. The size distributions reported were averaged over five runs.

Synthesis and Characterization of EYMA and EYMe:

Synthetic Procedures:

Eosin Y (0.500 g, 0.772 mmol), DMAP (0.028 g, 0.23 mmol), and ethylcarbodiimide hydrochloride (EDC·HCl) were combined in a flame dried round bottom flask under Argon (Ar). At 0 ˚C, dry DMF (4 mL) was added together with the hydroxy nucleophile (2-hydroxyethyl methacrylate for EYMA, 0.422 g, 3.24 mmol; methanol for EYMe, 0.148 g, 4.63 mmol) and TEA (0.078 g, 0.77 mmol). The reaction was stirred overnight and warmed up to room temperature. Upon dilution with DCM, the crude mixture was washed with aqueous HCl (1 M), $NaHCO_3$ (saturated), water and brine. After drying the organic extract with $MgSO_4$, the solvent was evaporated, and the compound was purified by flash column chromatography on silica gel with DCM/AcOH (97/3 v/v).

EYMA

0.420 g (0.553 mmol; 72% yield)

R_f ~ 0.29 in DCM/AcOH (97/3; v/v)

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.91 (m, 1H), 7.84 (m, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.10 (s, 2H), 5.77 (s, 1H), 5.52 (s, 1H), 4.29 (m, 2H), 4.03 (m, 2H), 1.73 (s, 3H)

^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 166.2, 164,7, 152.1, 151.0, 135.2, 133.7, 132.6, 131.2, 130.9, 130.8, 130.2, 129.3, 126.0, 117.3, 115.6, 100.3, 63.2, 62.5, 18.0

HRMS (ESI-TOF): Calculated for $[M+H]^+$ requires 760.7664; found 760.7674.

EYMe

0.317 g (0.469 mmol; 62% yield)

R_f ~ 0.36 in DCM/AcOH (97/3; v/v)

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.91 (m, 1H), 7.83 (m, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.13 (s, 2H), 3.61 (s, 3H), 5.52 (s, 1H), 4.29 (m, 2H), 4.03 (m, 2H), 1.73 (s, 3H)

^{13}C NMR (125 MHz, DMSO-*d*$_6$) δ 165.1, 164.5, 152.1, 151.2, 133.4, 132.6, 131.0, 130.73, 130.69, 130.1, 129.4, 117.1, 115.5, 100.2, 52.2

HRMS (ESI-TOF): Calculated for $[M+H]^+$ requires 662.7295; found 662.7311

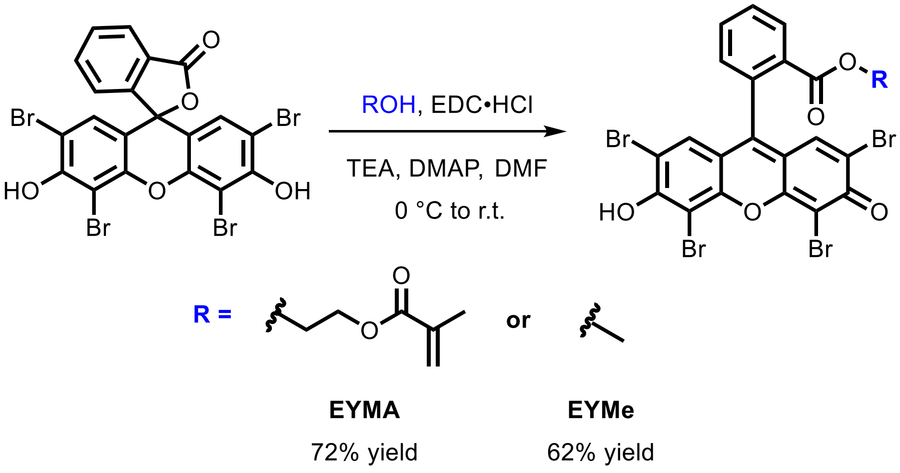


Figure S1. Reaction scheme for the synthesis of eosin Y methacrylate (EYMA) and eosin Y methyl ester (EYMe).

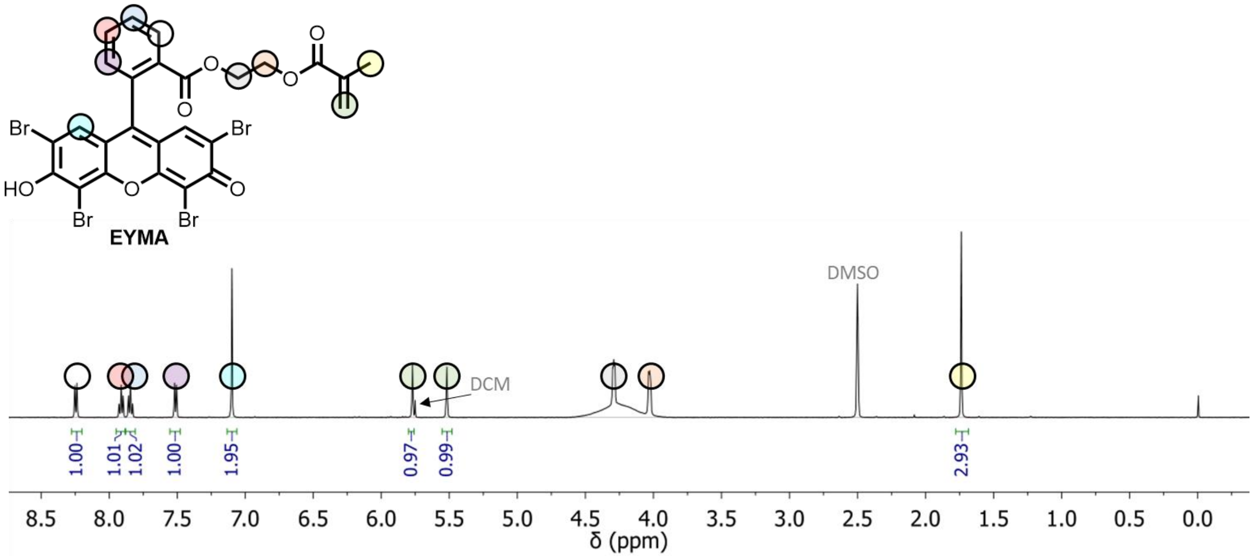


Figure S2. ^{1}H NMR spectrum of eosin Y methacrylate (EYMA) in DMSO-d_6.[3]

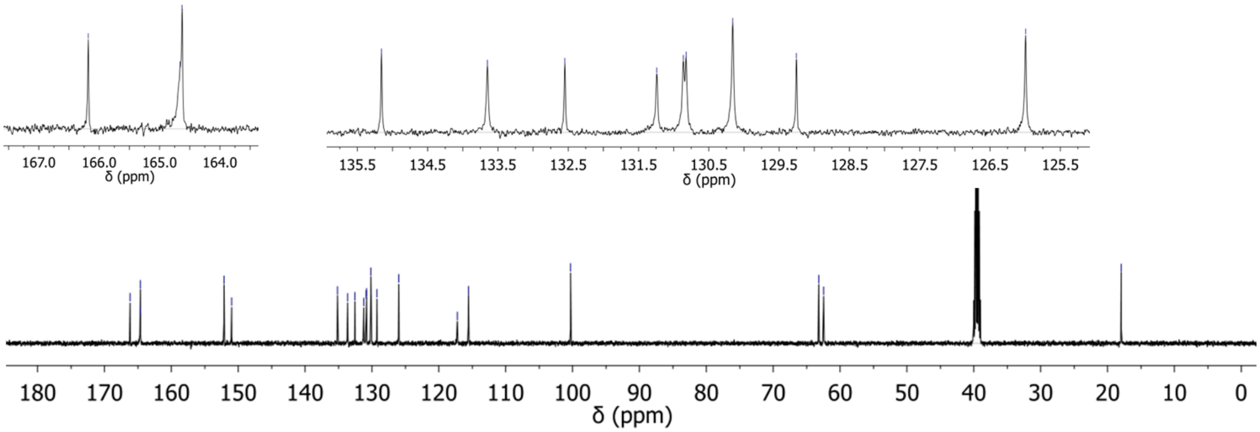


Figure S3. ^{13}C NMR spectrum of eosin Y methacrylate (EYMA) in DMSO-*d$_6$*.

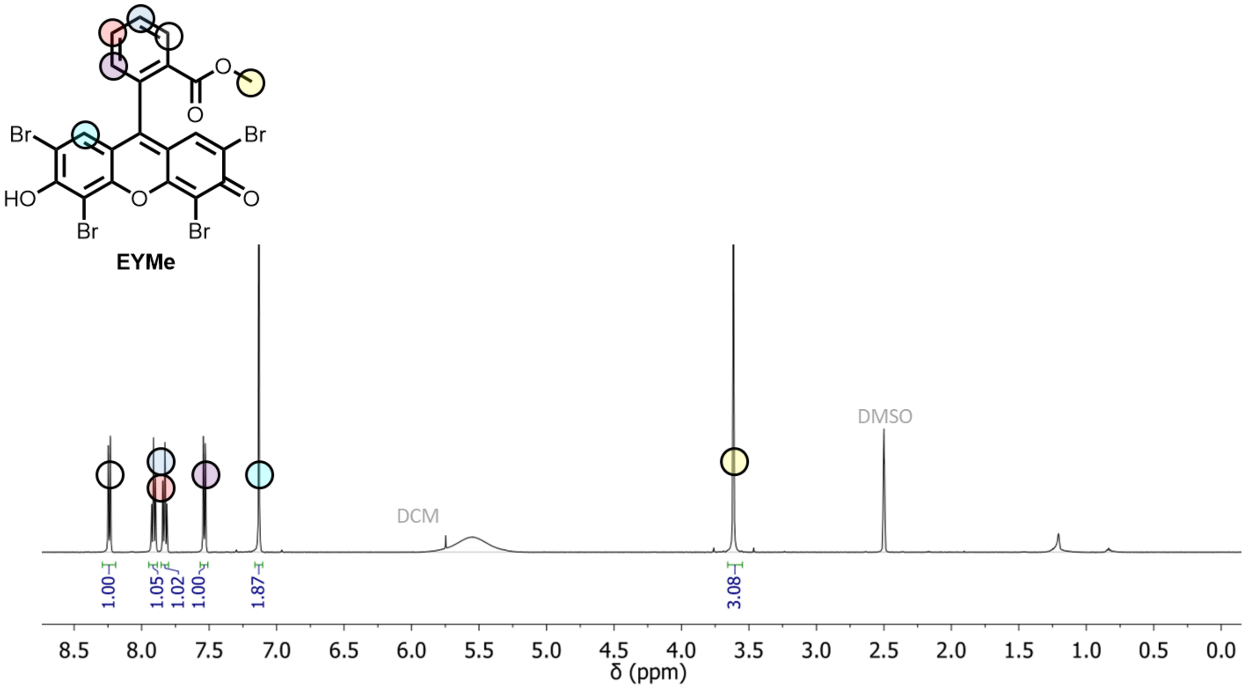


Figure S4. ^{1}H NMR spectrum of eosin Y methyl ester (EYMe) in DMSO-*d$_6$*.

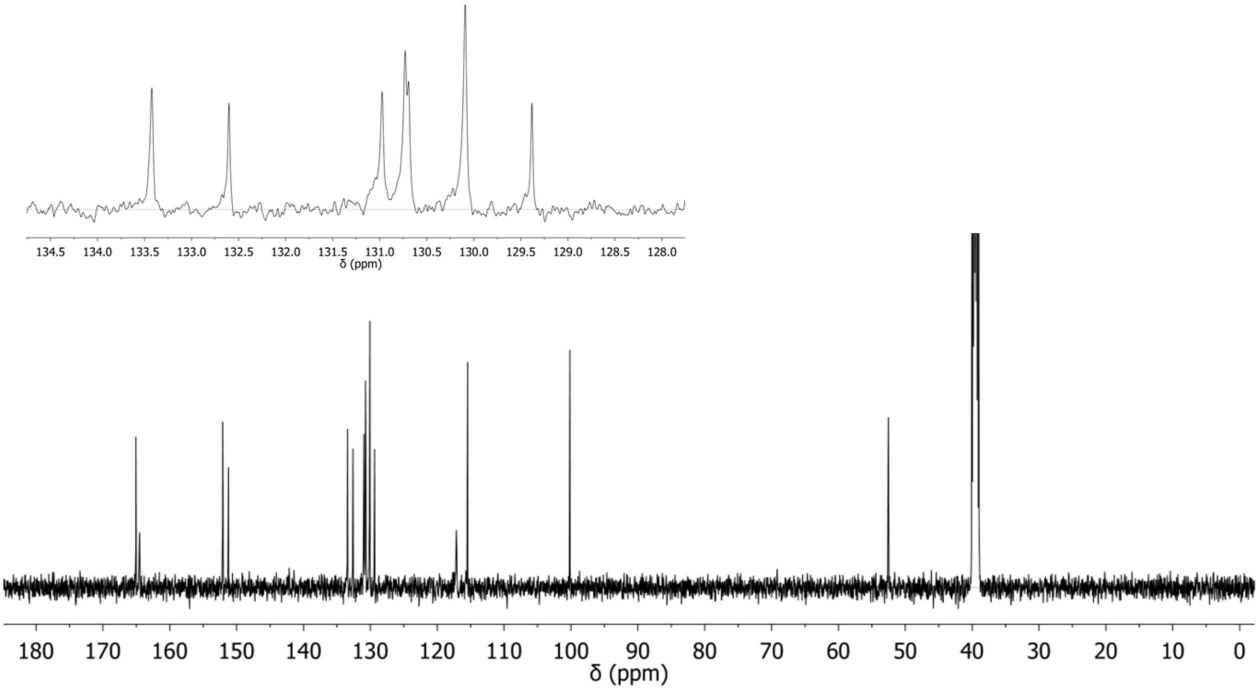
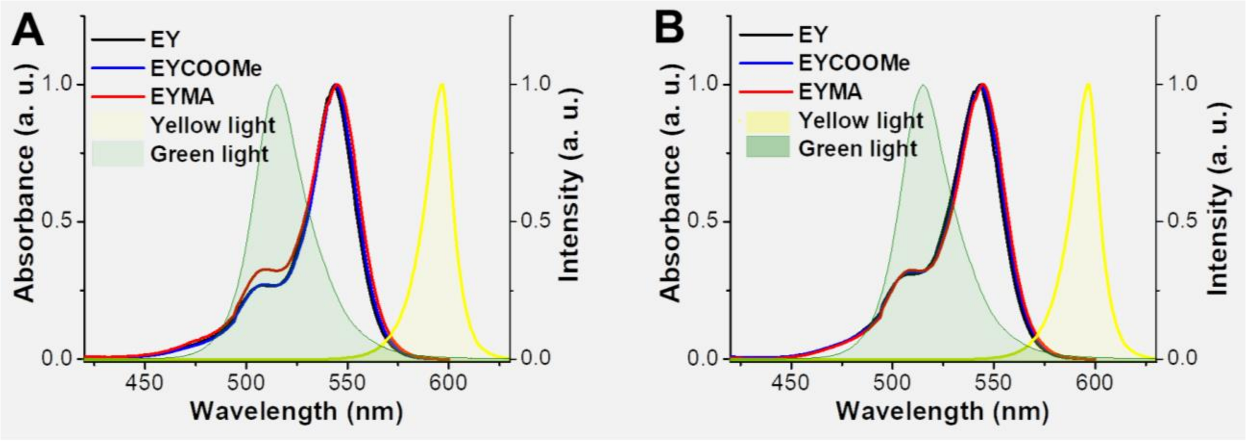


Figure S5. ^{13}C NMR spectrum of eosin Y methyl ester (EYMe) in DMSO-*d*$_6$.

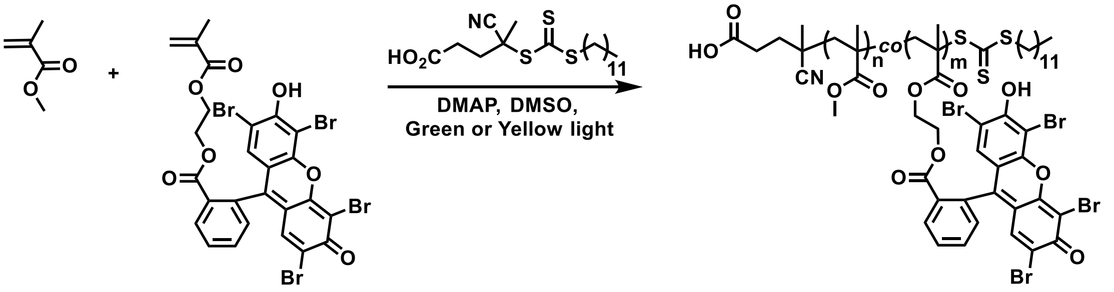


0.025 mg/mL DMSO

0.025 mg/mL DMSO + 2 equiv. DMAP

Figure S6. Normalized UV-vis absorption of eosin Y (EY), eosin Y methyl ester (EYMe), and eosin Y methacrylate (EYMA) overlaid with the normalized emission profile for the green and yellow light. (A) Absorption at 0.025 mg/mL sample concentration in DMSO. (B) Absorption at 0.025 mg/mL sample concentration and 2 equiv of DMAP mimicking the photoredox polymerization conditions. No significant change of the absorption was observed upon adding DMAP.

P(EYMA-*co*-MMA) Polymerizations and Characterization:



Synthetic Procedures:

0.001 equiv EYMA:

MMA (1.06 mL, 400 equiv), EYMA (0.019 mg, 0.0010 equiv, from a 1 mg/mL stock solution in DMSO), DMAP (3.1 mg, 1.0 equiv, from a 30 mg/mL stock solution in DMSO), CDP (10.1 mg, 1.00 equiv), and DMF (0.106 mL, as an internal standard) were added to a Schlenk flask containing DMSO (0.814 mL). The solution was purged with Ar prior to the irradiation with green light. Reaction aliquots were withdrawn in regular time intervals and analyzed by SEC and ^{1}H NMR. EY-PMMA was precipitated into diethyl ether yielding in a pink solid.

0.01 equiv EYMA:

MMA (1.06 mL, 400 equiv), EYMA (0.19 mg, 0.010 equiv, from a 10 mg/mL stock solution in DMSO), DMAP (3.1 mg, 1.0 equiv, from a 30 mg/mL stock solution in DMSO) and CDP (10.1 mg, 1.00 equiv) were added to a Schlenk flask containing DMSO (0.814 mL) and DMF (0.106 mL, as an internal standard). The solution was purged with Ar prior to the irradiation with green or yellow light. Reaction aliquots were withdrawn in regular time intervals and analyzed by SEC and ^{1}H NMR. EY-PMMA was into ether resulting in a pink solid.

0.1 equiv EYMA:

MMA (1.06 mL, 400 equiv), EYMA (1.9 mg, 0.10 equiv, from a 10 mg/mL stock solution in DMSO), DMAP (3.1 mg, 1.0 equiv, from a 30 mg/mL stock solution in DMSO) and CDP (10.1 mg, 1.00 equiv) were added to a Schlenk flask containing DMSO (0.643 mL) and DMF (0.106 mL, as an internal standard). The solution was purged with Ar prior to the irradiation with green or yellow light. Reaction aliquots were withdrawn in regular time intervals and analyzed by SEC and ^{1}H NMR. EY-PMMA was precipitated into ether resulting in a pink solid.

1 equiv EYMA (EY-PMMA-1):

MMA (1.06 mL, 400 equiv), EYMA (19 mg, 1.0 equiv), DMAP (3.1 mg, 1.0 equiv, from a 30 mg/mL stock solution in DMSO) and CDP (10.1 mg, 1.00 equiv) were added to a Schlenk flask containing DMSO (0.822 mL) and DMF (0.106 mL, as an internal standard). The solution was purged with Ar prior to the irradiation with yellow light. Reaction aliquots were withdrawn in regular time intervals and analyzed by SEC and ^{1}H NMR. EY-PMMA was precipitated into ether resulting in a pink solid.

0.1 equiv EY:

MMA (1.06 mL, 400 equiv), EY (1.62 mg, 0.100 equiv), DMAP (3.1 mg, 1.0 equiv, from a 30 mg/mL stock solution in DMSO) and CDP (10.1 mg, 1.00 equiv) were added to a Schlenk flask containing DMSO (0.814 mL) and DMF (0.106 mL, as an internal standard). The solution was purged with Ar prior to the irradiation with yellow light. Reaction aliquots were withdrawn in regular time intervals and analyzed by SEC and ^{1}H NMR. PMMA was precipitated into ether resulting in a pink solid.

0.1 equiv EYMe:

MMA (1.06 mL, 400 equiv), EYMe (1.65 mg, 0.100 equiv), DMAP (3.1 mg, 1.0 equiv, from a 30 mg/mL stock solution in DMSO) and CDP (10.1 mg, 1.00 equiv) were added to a Schlenk flask containing DMSO (0.837 mL) and DMF (0.106 mL, as an internal standard). The solution was purged with Ar prior to the irradiation with yellow light. Reaction aliquots were withdrawn in regular time intervals and analyzed by SEC and ^{1}H NMR. PMMA was precipitated into ether resulting in a pink solid.

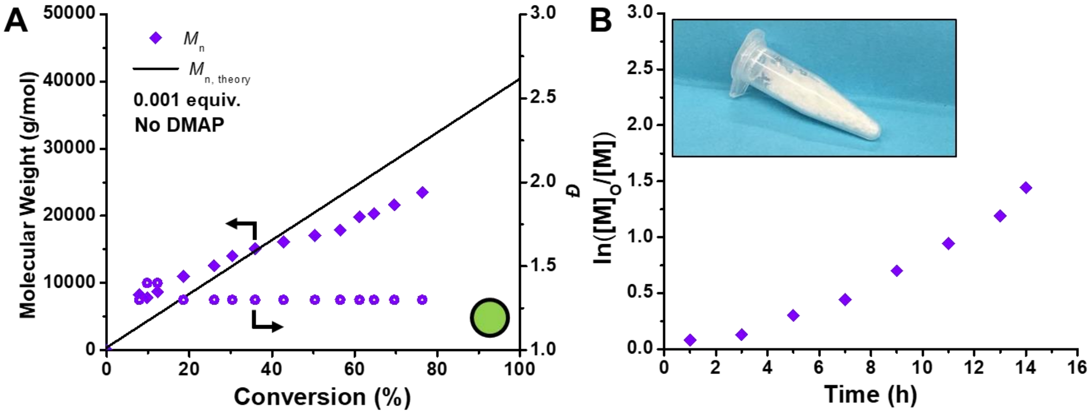


Figure S7. The self-catalyzed photoredox polymerization of MMA (400 equiv to RAFT agent) in DMSO using EYMA (0.001 equiv) under green light irradiation without DMAP showed substantial photobleaching. A) Number-average molecular weight (M_n, left axis) and dispersity ($Đ$, right axis) versus conversion and (B) pseudo-first-order rate plot and picture of the photobleached polymer.

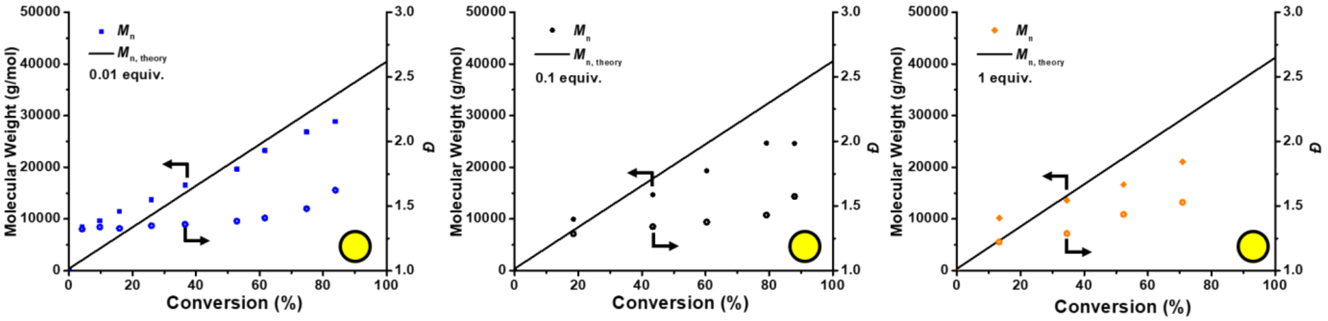


Figure S8. M_n and *Đ* versus conversion of the self-catalyzed photoredox copolymerization of EYMA at 0.01 (blue), 0.1 (black), and 1 (orange) equiv with respect to RAFT agent and MMA (400 equiv to CTA) under yellow light irradiation with 1 equiv of DMAP. M_n was obtained via conventional calibration relative to poly(methyl methacrylate) (PMMA) standards.

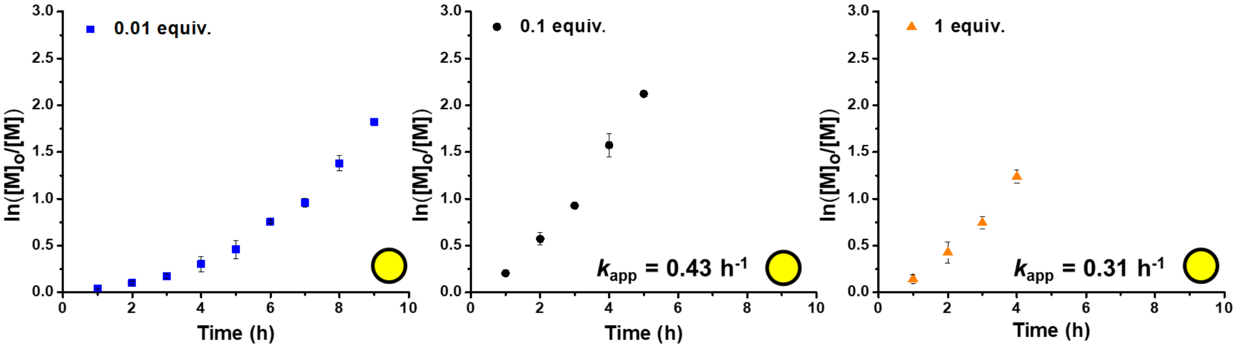


Figure S9. Pseudo-first-order rate plot of the self-catalyzed photoredox copolymerization of EYMA at 0.01 (blue), 0.1 (black), and 1 (orange) equiv with respect to RAFT agent and MMA (400 equiv to RAFT agent) under yellow light irradiation with 1 equiv of DMAP. Curvature of 0.01 equiv was attributed to viscous acceleration of the reaction.

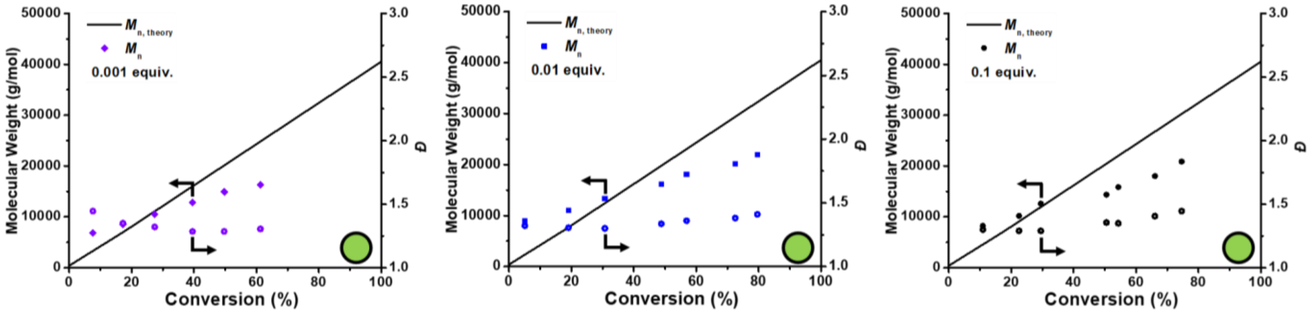


Figure S10. M_n and *Đ* versus conversion of the self-catalyzed photoredox copolymerization of EYMA at 0.001 (purple), 0.01 (blue), and 0.1 (black) equiv with respect to RAFT agent and MMA (400 equiv to CTA) under green light irradiation with 1 equiv of DMAP. M_n was obtained via conventional calibration relative to poly(methyl methacrylate) (PMMA) standards.

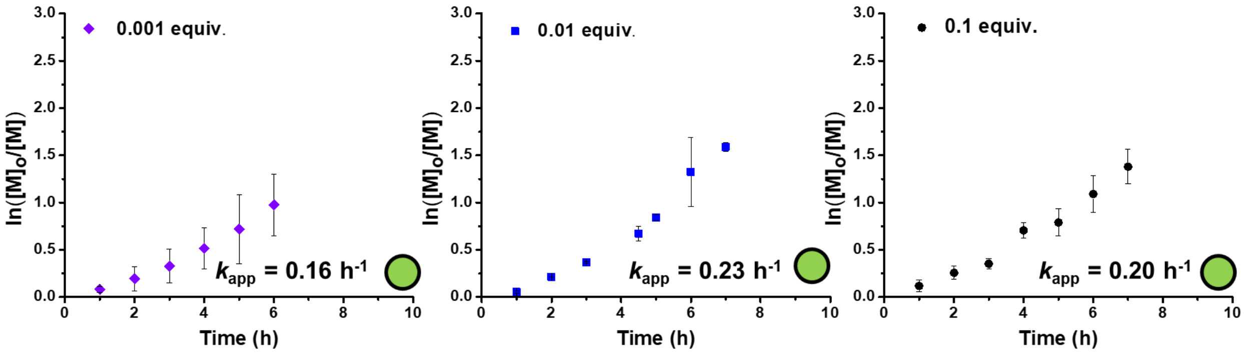


Figure S11. Pseudo-first-order rate plot of the self-catalyzed photoredox copolymerization of EYMA at 0.001 (purple), 0.01 (blue), and 0.1 (black) equiv with respect to RAFT agent and MMA (400 equiv to CTA) under green light irradiation with 1 equiv of DMAP.

Table S1. Conversion, theoretical number-average molecular weight ($M_{n,theo}$), M_n obtained from size-exclusion chromatography using conventional calibration, and dispersity ($Đ$) for EY-PMMA polymers generated at varying EYMA feed ratios after purification (relative to RAFT agent).

Green Light Irradiated

Feed Equiv	Conversion (%)	$M_{n,\ theory}$ (g/mol)	M_n (g/mol)	$Đ$
0.1	71	29,000	29,000	1.34
0.01	79	32,000	25,800	1.36
0.001	61	24,800	18,400	1.28

Yellow Light Irradiated

Feed Equiv.	Conversion (%)	$M_{n,\ theory}$ (g/mol)	M_n (g/mol)	$Đ$
1	72	29,300	27,100	1.52
0.1	88	35,600	27,600	1.50
0.01	76	30,900	24,000	1.36

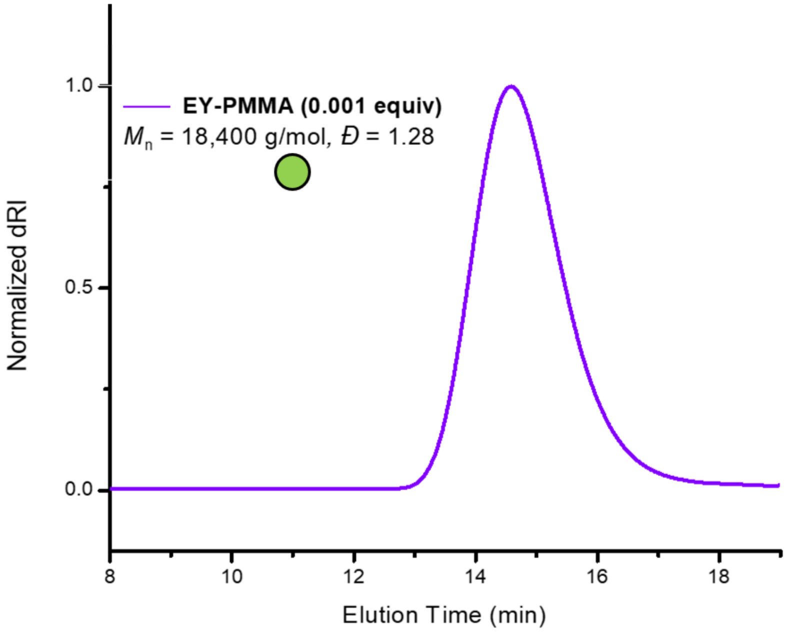


Figure S12. SEC analysis of EY-PMMA (0.001 equiv to RAFT agent) after green light irradiation. M_n and $Đ$ were determined by relative to PMMA standards.

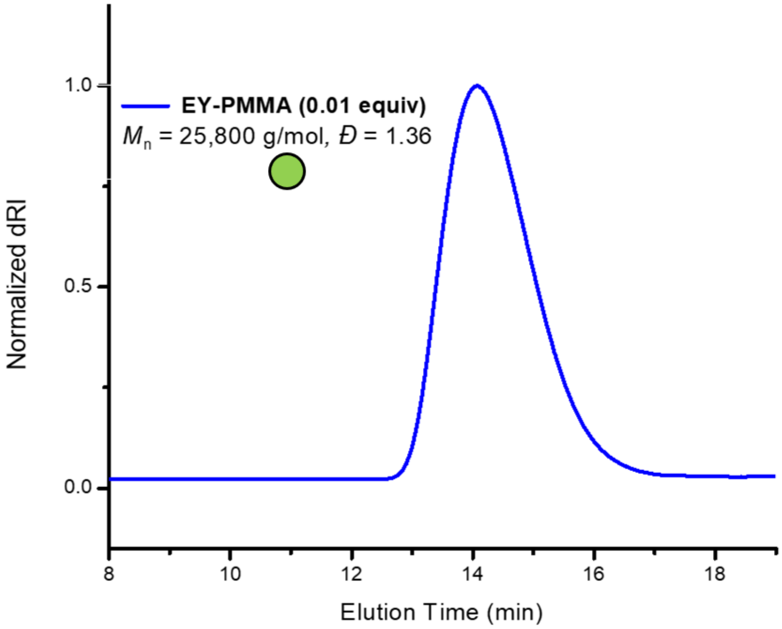


Figure S13. SEC analysis of EY-PMMA (0.01 equiv to RAFT agent) after green light irradiation. M_n and $Đ$ were determined by relative to PMMA standards.

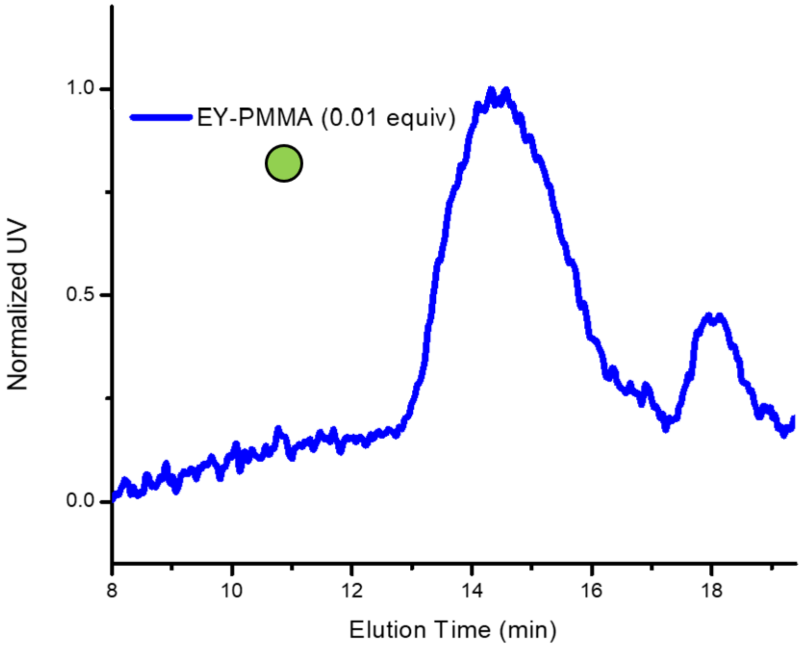


Figure S14. SEC coupled with UV-vis absorbance detection (532 nm) of EY-PMMA (0.01 equiv to RAFT agent) showing EY absorption across the whole polymer elution time. The second smaller peak around 18.5 min corresponds to residual EYMA.

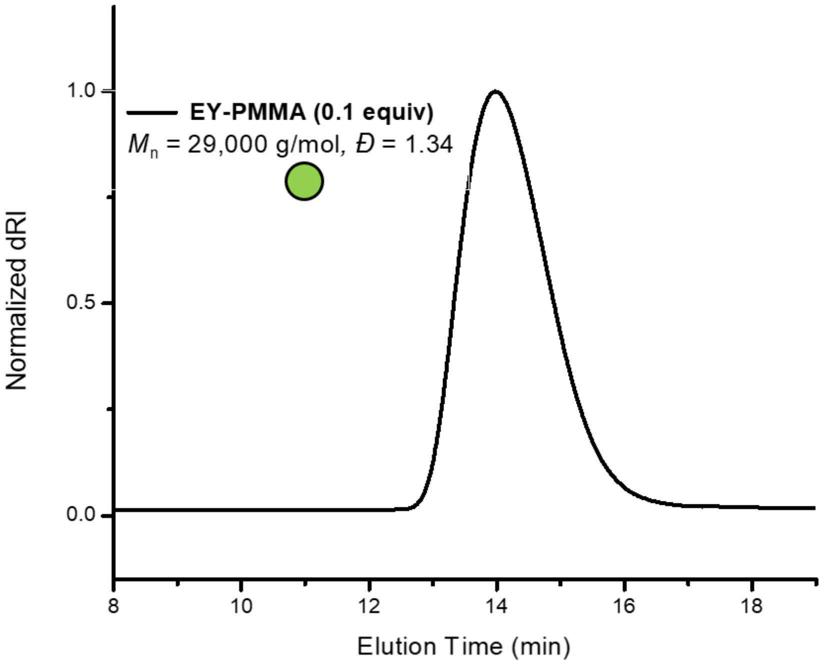


Figure S15. SEC analysis of EY-PMMA (0.1 equiv to RAFT agent) after green light irradiation. M_n and $Đ$ were determined by relative to PMMA standards.

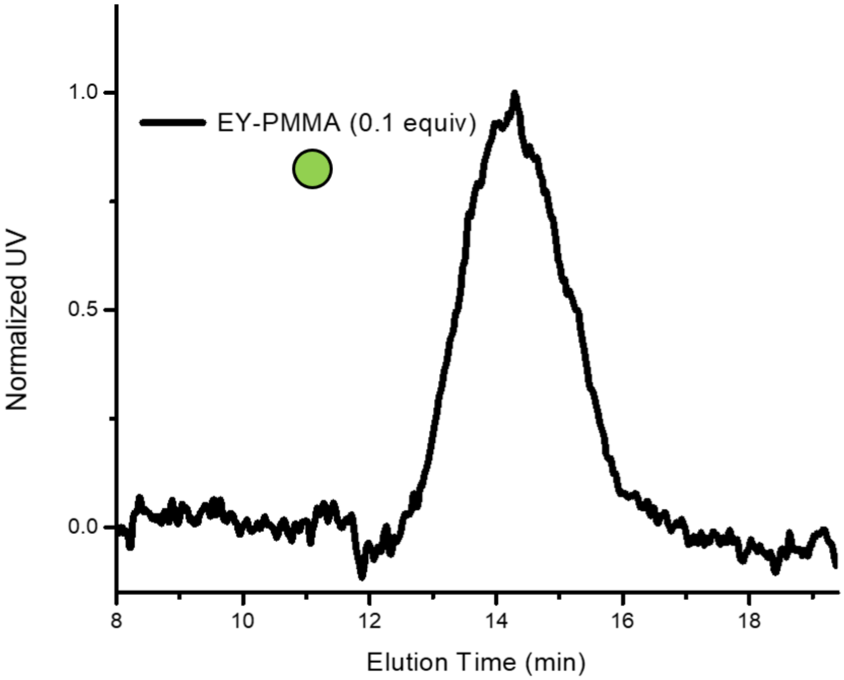


Figure S16. SEC coupled with UV-vis absorbance detection (532 nm) of EY-PMMA (0.1 equiv to RAFT agent) showing EY absorption across the whole polymer elution time.

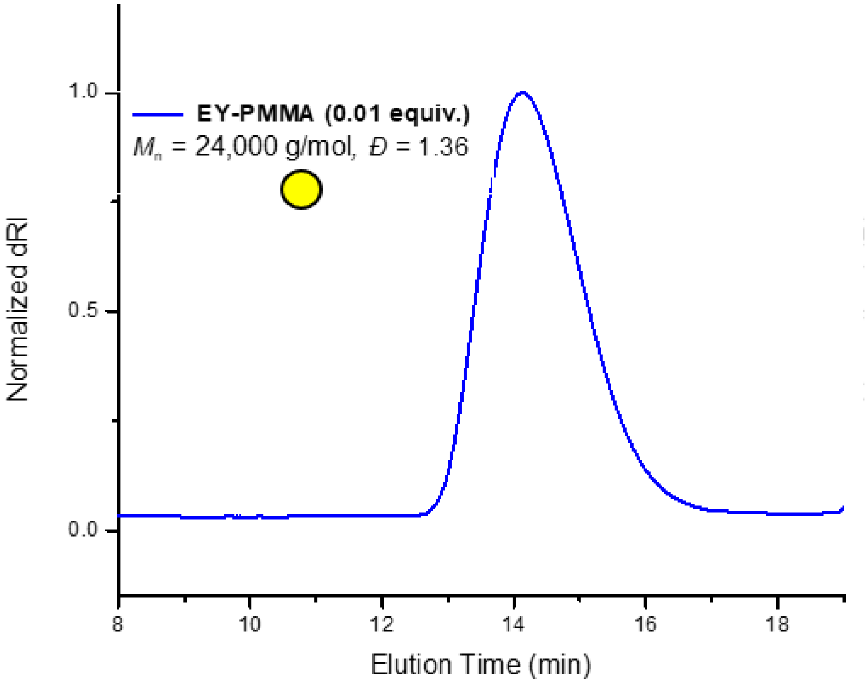


Figure S17. SEC analysis of EY-PMMA (0.01 equiv to RAFT agent) after yellow light irradiation. M_n and $Đ$ were determined by relative to PMMA standards.

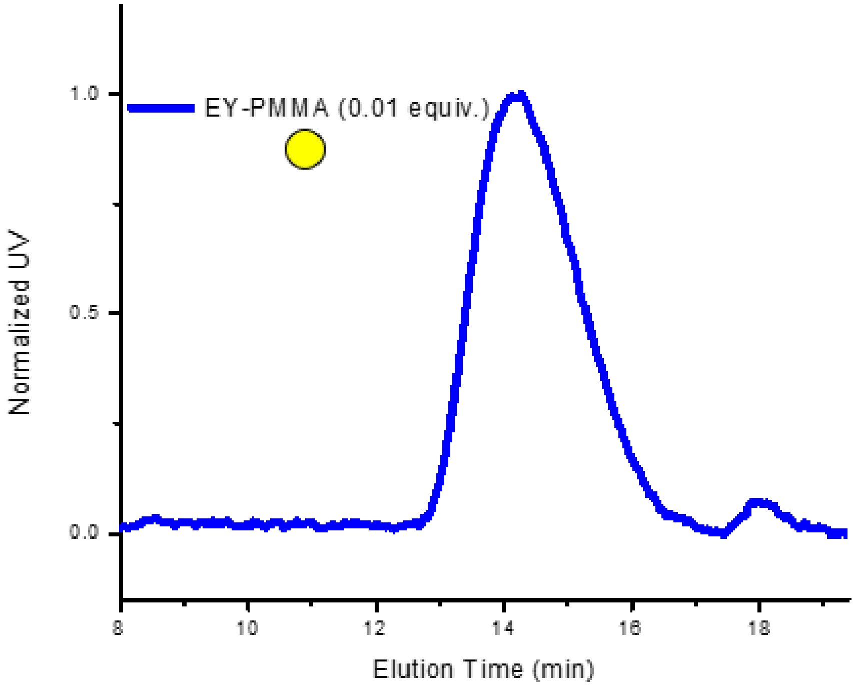


Figure S18. SEC coupled with UV-vis absorbance detection (532 nm) of EY-PMMA (0.01 equiv to RAFT agent) showing EY absorption across the whole polymer elution time.

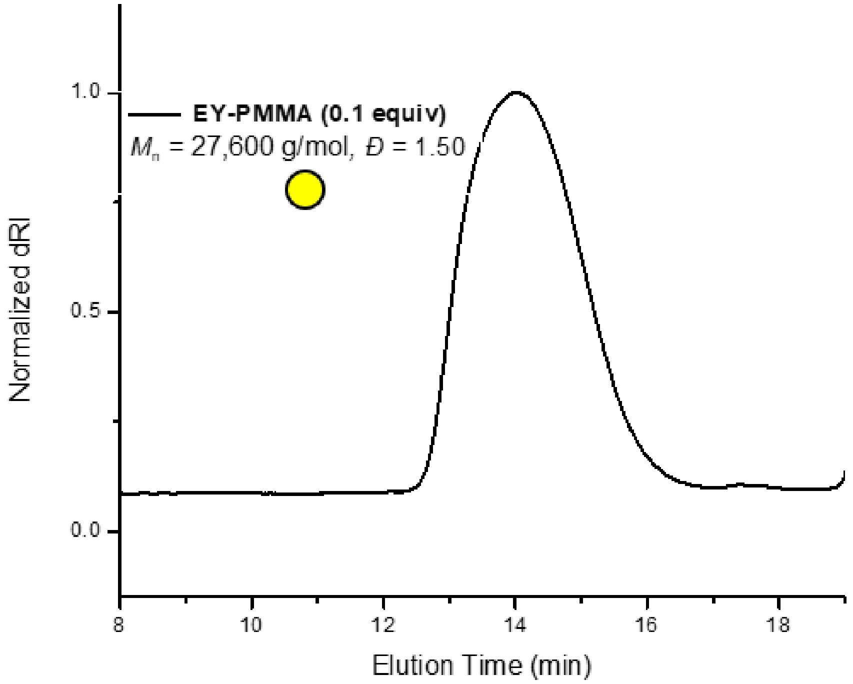


Figure S19. SEC analysis of EY-PMMA (0.1 equiv to RAFT agent) after yellow light irradiation. M_n and $Đ$ were determined by relative to PMMA standards.

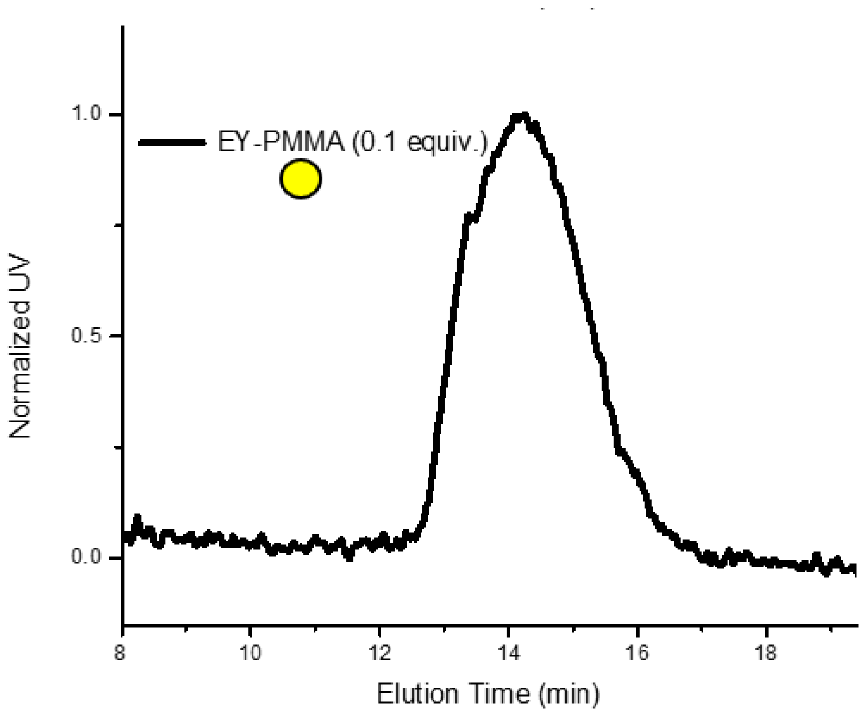


Figure S20. SEC coupled with UV-vis absorbance detection (532 nm) of EY-PMMA (0.1 equiv to RAFT agent) showing EY absorption across the whole polymer elution time.

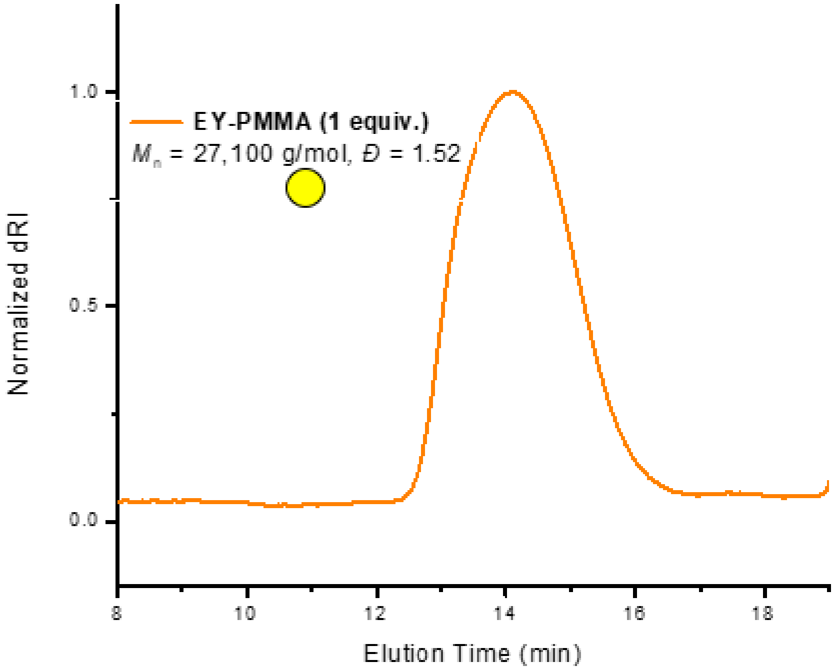


Figure S21. SEC analysis of EY-PMMA (1 equiv to RAFT agent) after yellow light irradiation. M_n and *Đ* were determined by relative to PMMA standards.

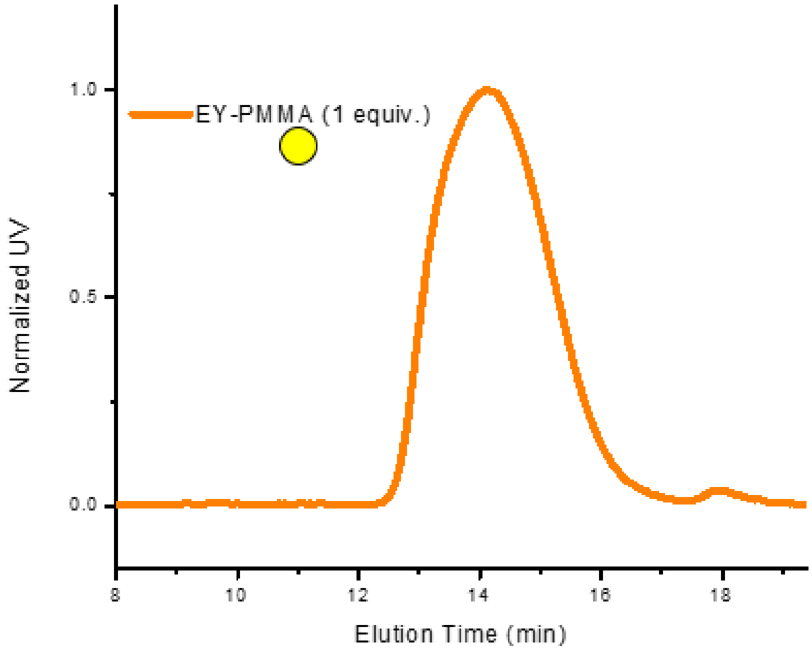


Figure S22. SEC coupled with UV-vis absorbance detection (532 nm) of EY-PMMA (1 equiv to CTA) showing EY absorption across the whole polymer elution time.

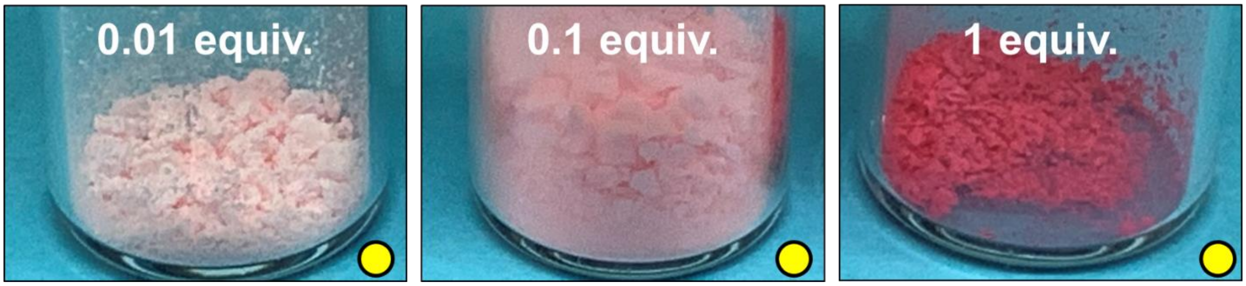


Figure S23. Image of the photoredox polymer catalyst EY-PMMA with 0.01, 0.1, and 1 equiv of EYMA after purification.

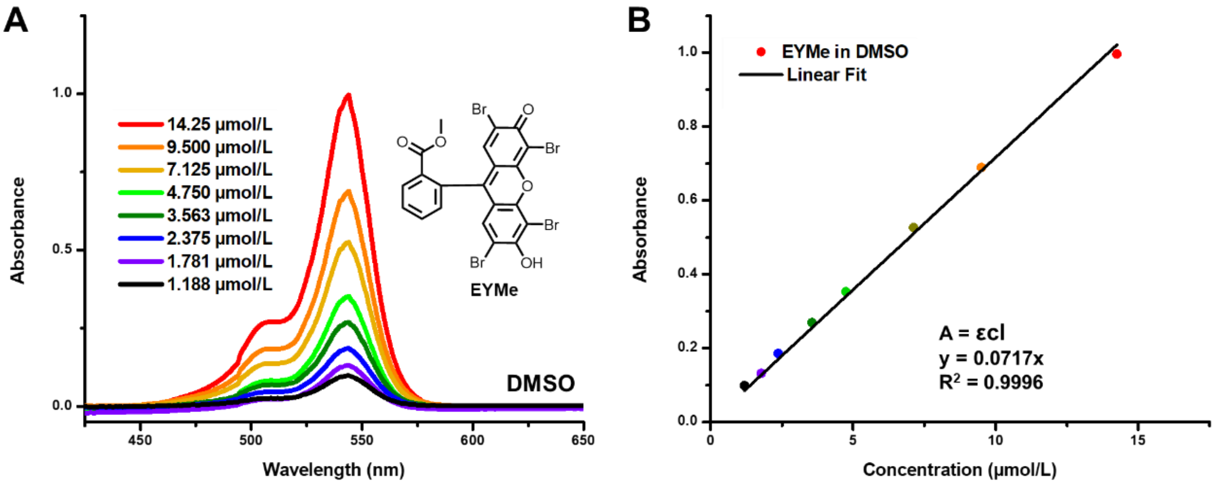


Figure S24. (A) UV-vis spectroscopy concentration assay of EYMe in DMSO. (B) Calibration curve from the absorbance at 537 nm at different concentrations used for calculating the concentration of EYMA in polymers.

Table S2. EYMA incorporations determined via UV-vis spectroscopy of purified EY-PMMA after green and yellow light polymerizations (“n.d." indicates absorbance below the limit of quantification). Photographs of EY-PMMA generated from 0.1 equiv and 1 equiv feed ratio under green and yellow light, respectively.

Green Light Irradiated

Feed Equiv	mg EYMA / 1 g polymer	Units per polymer
0.1	1.06	0.03
0.01	0.082	0.002
0.001	n.d.	n.d.

0.1 equiv.

Yellow Light Irradiated

Feed Equiv	mg EYMA / 1 g polymer	Units per polymer
1	16.0	0.44
0.1	0.82	0.03
0.01	0.072	0.003

1 equiv.

P(EYMA-*co*-MMA) Reactions and Characterization:

Synthetic Procedures:

Oxidative hydroxylation of 4-methoxyboronic acid

4-Methoxyphenylboronic acid (0.018 g, 0.12 mmol), EY-PMMA-1 (0.10 g, corresponding to 1.6 mg and 0.0025 mmol of EYMA) were combined in a round bottom flask. Diisopropylethylamine (0.080 g, 0.62 mmol), H_2O (0.4 mL), and MeCN (1.5 mL) were added, and the reaction was stirred open to air for 10 h. The mixture was precipitated into diethyl ether, and the organic supernatant was washed with water and brine, followed by drying over $MgSO_4$. After solvent evaporation, the crude product was analyzed by ^1H NMR (Figures S25–S26).

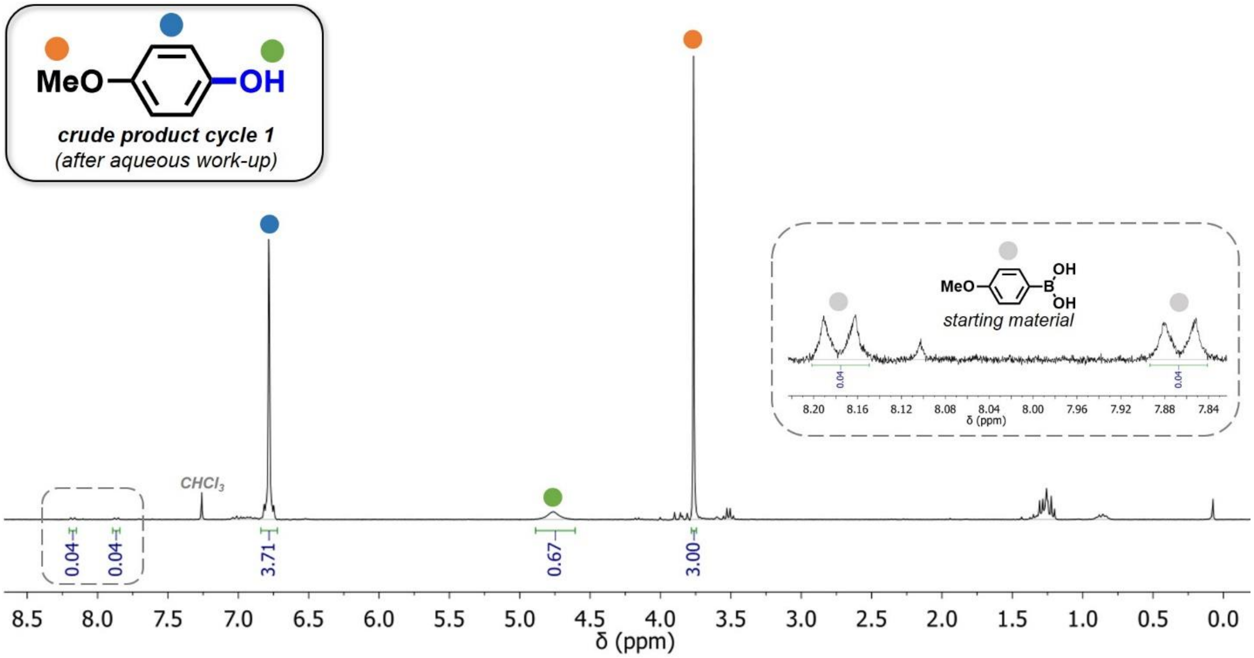


Figure S25. ^1H NMR spectrum of 4-methoxyphenol in $CDCl_3$ after cycle 1. The grey inset shows proton resonances of remaining 4-methoxyphenylboronic acid starting material, yielding a total conversion of 97%. The spectrum was obtained from the crude reaction mixture after aqueous work-up to remove boronic acid and diisopropylethylamine and evaporation of the solvent, showing that no major unwanted by-products were formed during the reaction.

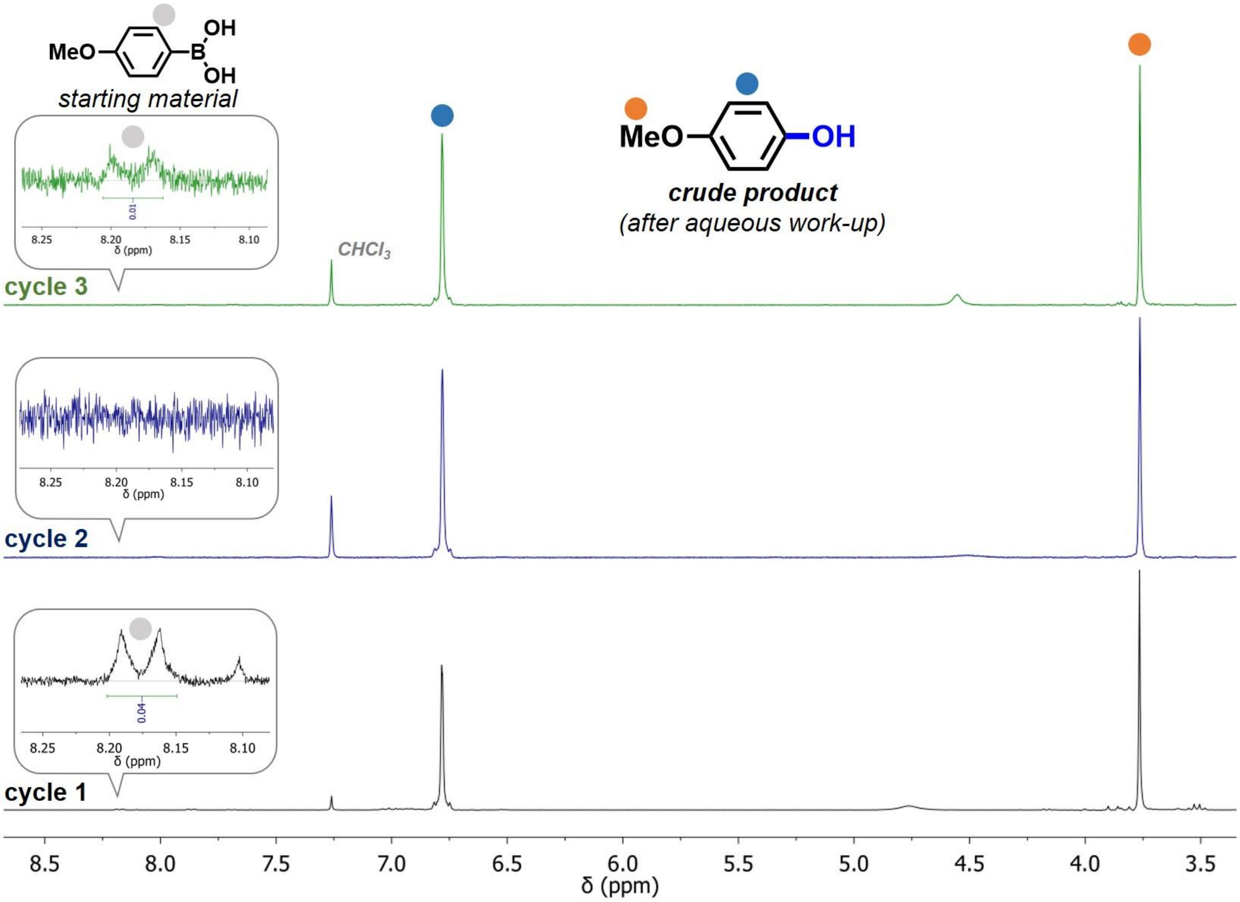


Figure S26. Stacked ^{1}H NMR spectra of the reaction product in $CDCl_3$ after cycle 1–3. The insets show the presence of small amounts of unreacted starting material.

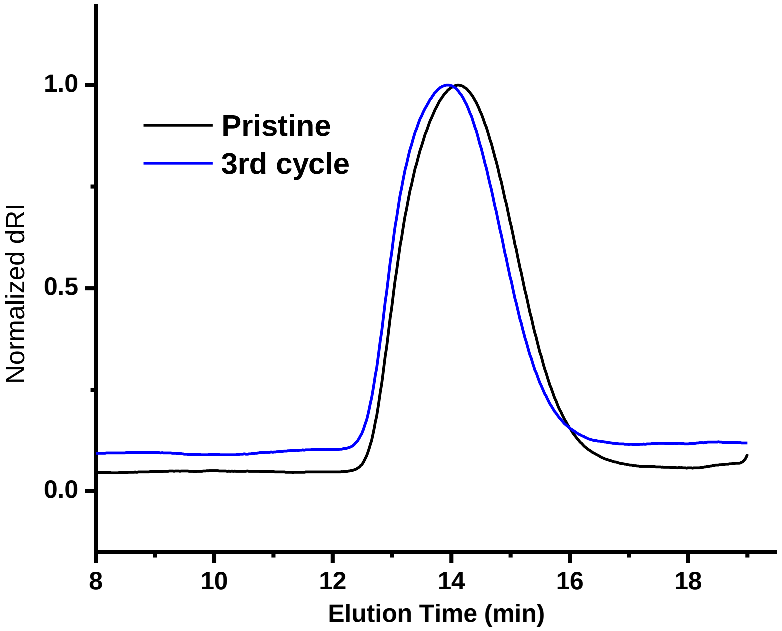


Figure S27. SEC analysis of EY-PMMA (1 equiv to RAFT agent) before and after three cycles in the oxidative hydroxylation of 4-methoxyphenylboronic acid.

Figure S28. Image of reaction mixture after purification showing no visual trace of EY.

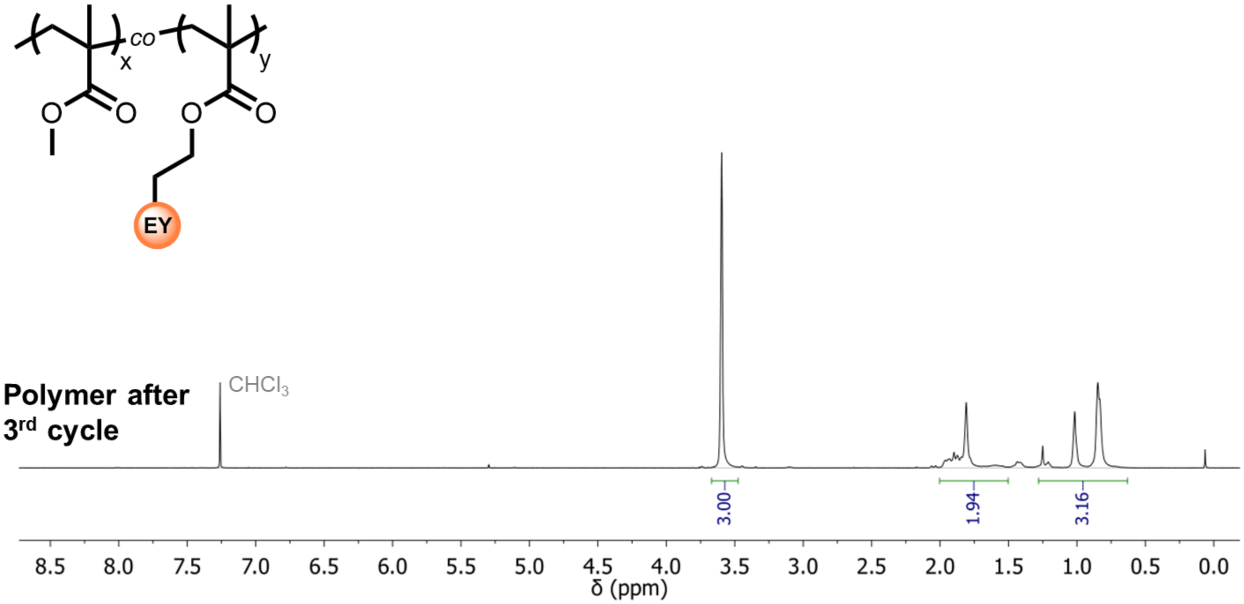
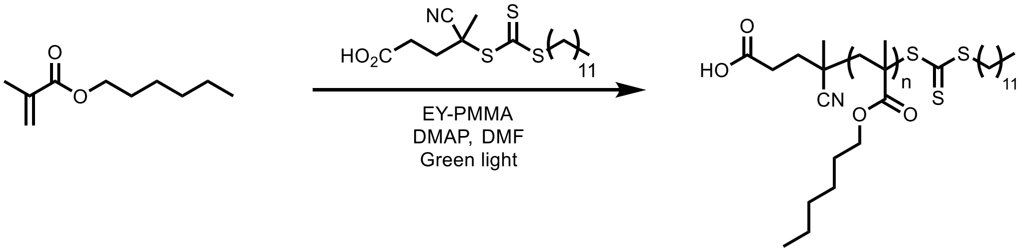


Figure S29. ^{1}H NMR spectrum of EY-PMMA in $CDCl_3$ after three consecutive reaction-precipitation cycles in the oxidative hydroxylation of 4-methoxyphenylboronic acid.

Polymerization of Hexyl methacrylate (HMA):



Synthetic Procedure:

HMA (1.085 mL, 100.0 equiv), EY-PMMA (0.026 mg polymer, corresponding to 0.41 mg and 0.01 equiv EYMA), DMAP (6.7 mg, 1.0 equiv) and CDP (22.2 mg, 1.00 equiv) were added to a Schlenk flask containing DMF (1.665 mL). The solution was sparged with Ar prior to the irradiation with green light. After 18 h of irradiation, EY-PMMA was removed by precipitation into cold hexanes resulting in a pink solid (11.3 mg, 43.6% catalyst recovery). Then, poly(hexyl methacrylate) (PHMA) in hexanes was precipitated into cold methanol resulting in a yellow solid (0.2419 g, 76% conversion, $M_{\text{n, theory}}$ = 13,400 g/mol, $M_{\text{n,SEC MALS}}$ = 13,600 g/mol, M_w = 14,000 g/mol; $Đ$ = 1.03)

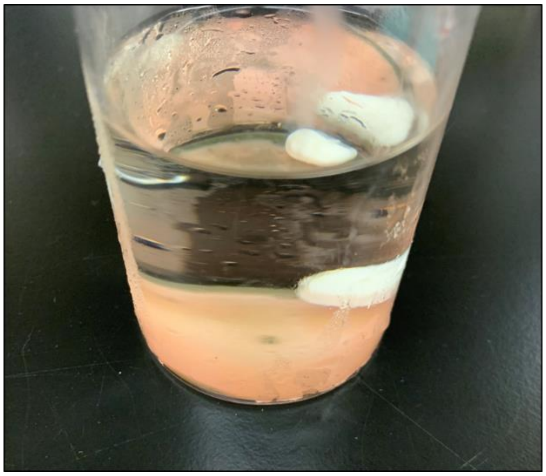


Figure S30. Image of the EY-PMMA catalyst removal via the selective precipitation in hexanes after photoredox polymerization of HMA.

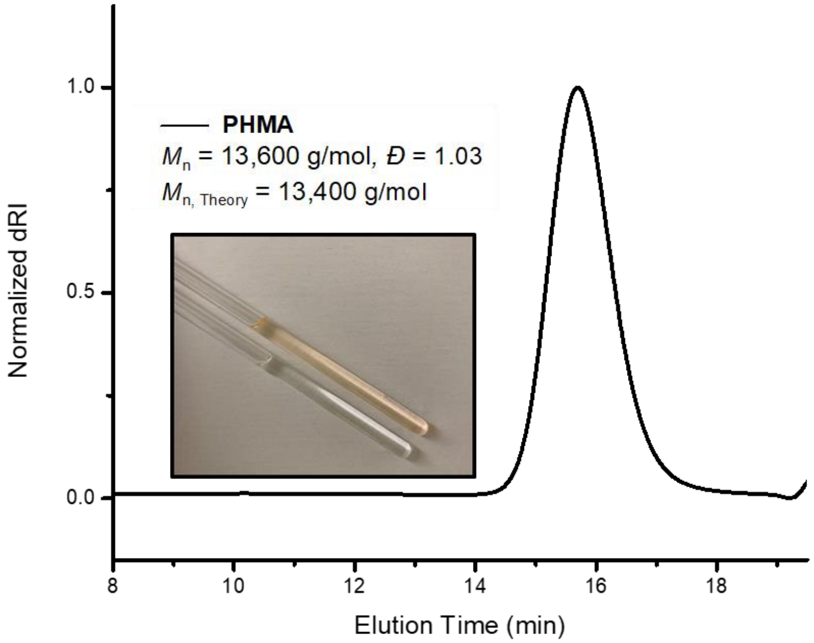


Figure S31. SEC of purified PHMA with M_n and $Đ$ determined by multi-angle light scattering detection. Inset image is a solution of the reaction mixture (top) and the purified polymer (bottom) dissolved in deuterated chloroform showing removal of EY-PMMA from PHMA.

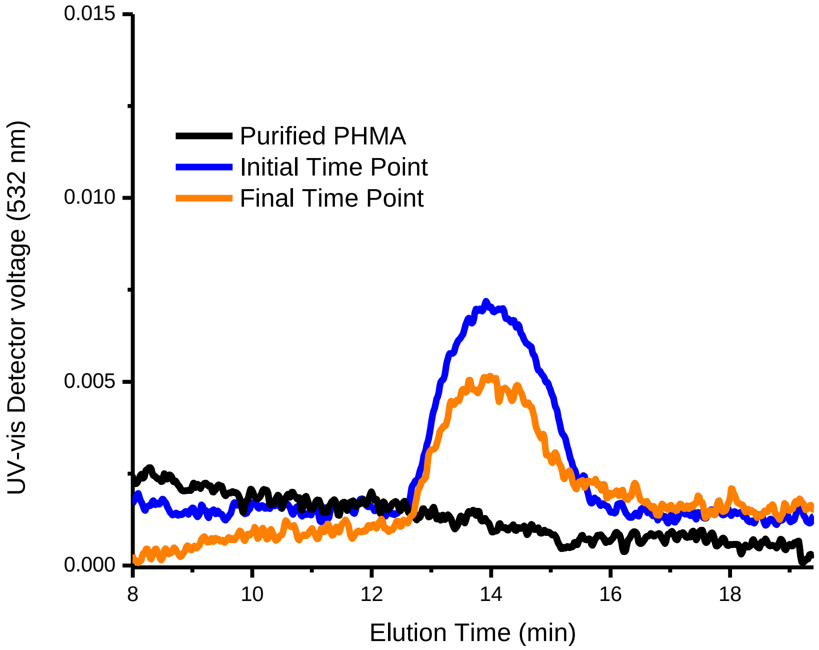
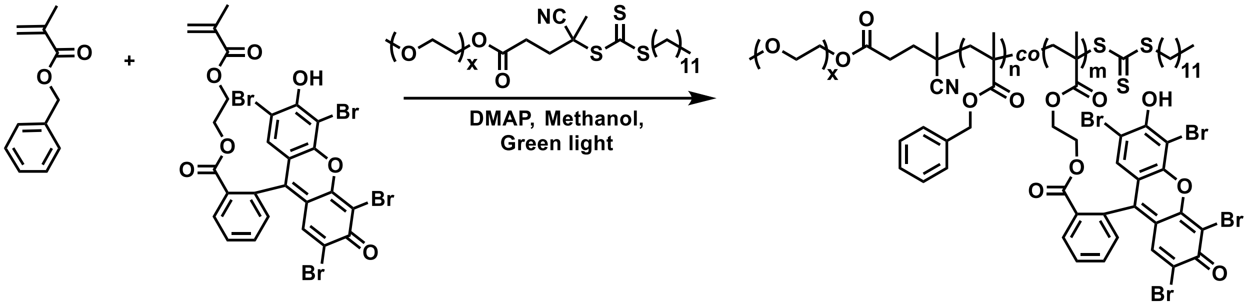


Figure S32. SEC coupled with UV-vis absorbance detection at 532 nm showing complete removal of EY-PMMA from the PHMA.

Self-catalyzed polymerization-induced self-assembly (PISA):



Synthetic Procedure:

BzMA (0.0769 mL, 250 equiv), EYMA (1.4 mg, 1.0 equiv), DMAP (0.226 mg, 1.00 equiv, from a stock solution in water), PEG macroCTA (5,400 g/mol, 10 mg, 1.0 equiv), were added to a vial containing methanol (0.609 mL). The solution was purged with Ar prior to the irradiation with green light overnight. The resulting solution was analyzed using TEM and DLS (**Figure S33-34**).

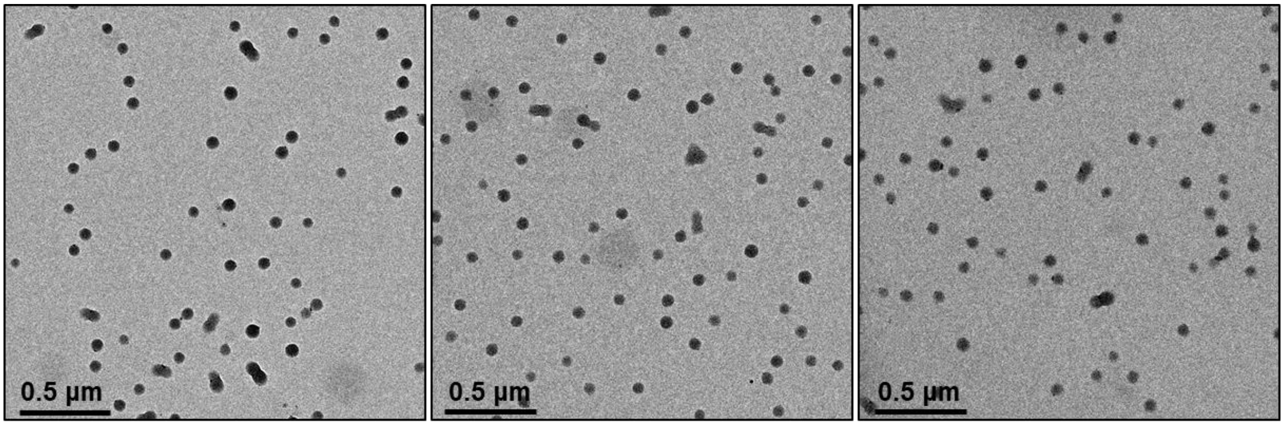


Figure S33. Transmission electron microscopy images of micelles after photoredox polymerization in methanol.

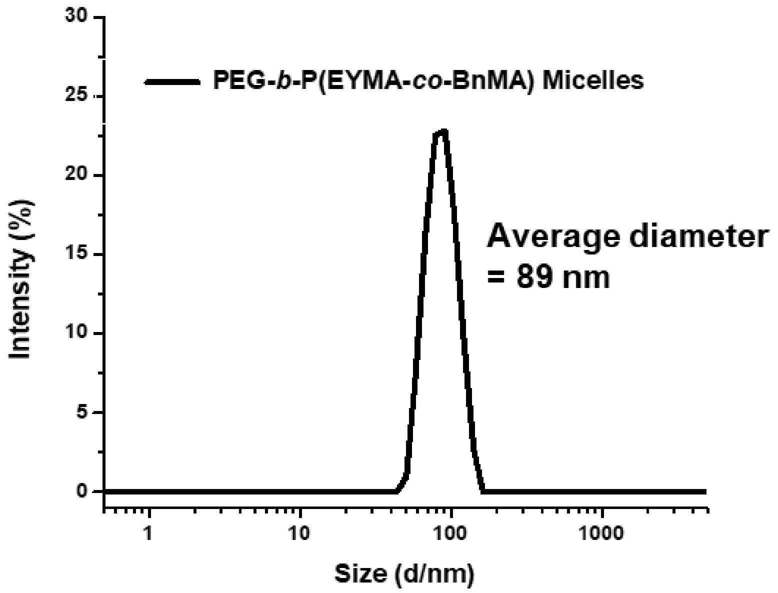


Figure S34. Dynamic light scattering intensity of micelles after photoredox polymerization in methanol showing an average hydrodynamic diameter of 89 nm in methanol.

References

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