Supplementary Information

Cooperative reduction of various RAFT polymer terminals using hydrosilane and thiol via polarity reversal catalysis

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Experimental section

Materials

Vinyl acetate (VAc) (TCI, >99.0%), styrene (St) (TCI, >99.0%), methyl acrylate (MA) (TCI, >99.0%), and triethylsilane (TCI, >98.0%) were distilled over calcium hydride under reduced pressure before use. Triphenylsilane (TCI, >96.0%) and 1-dodecanethiol (TCI, >95.0%) were utilized as received. Cumyl dithiobenzoate (**3**),[1] *S*-2-cyano-2-propyl *S'*-2-ethyl trithiocarbonate (**4**),[2] and *S*,*S'*-bis(*α*,*α*'-dimethyl-*α''*-acetic acid)trithiocarbonate (**5**)[3] were synthesized according to the literature. 2,2'-Azobis(isobutyronitrile) (AIBN) (Kishida, >99%) was purified by recrystallization from methanol. Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (TCI, >98.0%) was purified by recrystallization from the mixture of *n*-hexane and acetone (8:1). Toluene (KANTO, >99.5%; H_2O <10 ppm) was dried and deoxygenized by passage through a column of Glass Contour Systems before use.

Synthesis of *S*,*S*'-(((cyclohexane-1,4-diylbis(methylene))bis(oxy))bis(ethane-1,1-diyl)) *O*,*O*'-diethyl bis(xanthate) (1)

1 was synthesized by the reaction between potassium xanthate and the HCl adduct of 1,4-cyclohexanedimethanol divinyl ether (CHDDVE) (CHDDVE-HCl). CHDDVE-HCl was prepared by adding 1.0 M Et_2O solution of hydrogen chloride (110 mL, 110 mmol) dropwise into Et_2O solution of CHDMVE (9.21 mL, 50.0 mmol) at –78 ºC. Into an Et_2O solution of potassium xanthate (19.82 g, 111 mmol) was added dropwise the CHDDVE-HCl solution (50 mmol) at 0 ºC over 30 min. After stirring for 1.0 h at 0 ºC and then 1.5 h at ambient temperature, the reaction was quenched by diluting with Et_2O. The solution was washed with 5wt% $NaHCO_3$ aqueous solution, brine, and water. The solvent was removed by the evaporation and the obtained product was purified by column chromatography on silica gel column with *n*-hexane/Et_2O (19/1) as an eluent. The difunctional xanthate was obtained as pale colorless liquid (12.3 g, 28.0 mmol, 56%yield). ^{1}H NMR ($CDCl_3$) (Fig. S1): 0.94, 1.27-1.52, and 1.78 (m, 10H, $C\mathit{H}C\mathit{H}_2C\mathit{H}_2$), 1.43(m, 6H, $OCH_2C\mathit{H}_3$), 1.67 (d, 6H, $C\mathit{H}_3CH$, J = 6.4 Hz), 3.31 and 3.51, 3.40 and 3.61 (dd, 4H, $OC\mathit{H}_2CH(CH_3))_2$, J_{vic} = 6.4 and 6.8 Hz, J_{gem} = –9.2 Hz), 4.65 (m, 4H, $C(S)OC\mathit{H}_2CH_3$), 5.57 and 5.58 (q, 2H, $CH_3C\mathit{H}$, J = 6.4 Hz). ^{13}C NMR ($CDCl_3$, r.t.): 13.8 ($OCH_2\mathit{C}H_3$), 22.8 ($\mathit{C}H_3CH$), 25.5-25.7 and 29.2 ($\mathit{C}H_2\mathit{C}H_2$), 35.2 and 37.8 ($OCH_2\mathit{C}H$), 69.5 ($C(S)O\mathit{C}H_2CH_3$), 72.5 and 74.9 ($O\mathit{C}H_2C\mathit{H}$), 88.5 ($CH_3\mathit{C}H$), 213.9 ($S\mathit{C}(S)O$).

Synthesis of *S*-(1-acetoxyethyl) *O*-ethyl xanthate (2)

2 was synthesized by the reaction between potassium xanthate and 1-acetoxyethyl iodide. 1-acetoxyethyl iodide was prepared by adding 1.0 M Et_2O solution of hydrogen chloride (110 mL, 110 mmol) and 1.1 M acetone solution of NaI (50 mL, 55 mmol) dropwise into Et_2O solution of VAc (9.21 mL, 50.0 mmol) at –78 ºC and then the solution was gradually warmed up to 0 ºC. Into an Et_2O solution of potassium xanthate (8.82 g, 55 mmol) was added dropwise the 1-acetoxyethyl iodide solution (50 mmol) at 0 ºC for more than 30 min. After stirring for 1.0 h at 0 ºC and then 1.0 h at ambient temperature, the reaction was quenched by diluting with Et_2O. The solution was washed with 5 wt% $NaHCO_3$ aqueous solution, brine, and water. The solvent was removed by the evaporation, and the obtained product was purified by column chromatography on silica gel column with *n*-hexane/Et_2O (9/1) as an eluent. The xanthate was obtained as a pale colorless liquid (7.13 g, 34.2 mmol, 68%yield). ^1H NMR ($CDCl_3$) (Fig. S5): 1.42 (t, 3H, OCH_2CH_3, $J = 6.8$ Hz), 1.62 (d, 3H, CH_3CH, $J = 6.9$ Hz), 2.08 (s, 3H, $OC(O)CH_3$), 4.64 (m, 2H, $C(S)OCH_2CH_3$), 6.66 (q, 1H, CH_3CH, $J = 6.9$ Hz). ^{13}C NMR ($CDCl_3$, r.t.): 13.6 (OCH_2CH_3), 19.9 (CH_3CH), 20.9 ($OC(O)CH_3$), 70.1 ($C(S)OCH_2CH_3$), 77.2 (CH_3CH), 169.4 ($OC(O)CH_3$), 210.3 ($SC(S)O$).

RAFT polymerization of vinyl acetate

The RAFT polymerization of VAc was performed by a syringe technique in dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is described as follows: In a 25 mL round-bottomed flask, VAc (22.4 mL, 243 mmol), **1** (3.80 mL of 362 mM in EtOAc, 1.38 mmol), AIBN solution of VAc (3.00 mL of 230 mM in VAc, AIBN: 0.69 mmol and VAc: 31.3 mmol), and EtOAc (0.76 mL) were placed at room temperature. The total volume of the reaction mixture was 30.0 mL. After mixing, the flask was immersed in thermostatic oil bath at 40 ºC. In predetermined intervals, a small aliquot of the solution was sampled and terminated by cooling to –78 ºC. The monomer conversion was determined from the concentration of residual monomer measured by the ^1H NMR with EtOAc as internal standard (13 h, Conv. 23%). The quenched reaction mixture was evaporated and purified by precipitation with *n*-hexane to give poly(VAc) (M_n=4600, M_w/M_n=1.13) (Fig. S2).

RAFT polymerization of styrene

The RAFT polymerization of St was performed by the syringe technique in dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is described as follows: In a 25 mL round-bottomed flask, St

(5.00 mL, 43.5 mmol) and **3** (0.12 g, 0.44 mmol) were placed at room temperature. The total volume of the reaction mixture was 5.12 mL. After mixing, the flask was immersed in a thermostatic oil bath at 110 ºC. In predetermined intervals, a small aliquot of the solution was sampled and terminated by cooling to –78 ºC. The monomer conversion was determined from the concentration of residual monomer measured by the ^{1}H NMR (16 h, Conv. 55%). The quenched reaction mixture was evaporated and purified by precipitation with methanol to yield polystyrene (M_n=5300, M_w/M_n=1.08) (Fig. S11).

RAFT polymerization of methyl acrylate

The RAFT polymerization of MA was performed by the syringe technique in dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the polymerization procedure is described as follows: In a 100 mL round-bottomed flask, MA (10.7 mL, 119 mmol), **4** (0.334 g, 1.18 mmol), toluene (46.9 mL), and AIBN solution of toluene (1.18 mL of 100 mM solution of toluene, 0.12 mmol) were placed at room temperature. The total volume of the reaction mixture was 59.1 mL. After mixing, the flask was immersed in thermostatic oil bath at 60 ºC. In predetermined intervals, a small aliquot of the solution was sampled and terminated by cooling to –78 ºC. The monomer conversion was determined from the concentration of residual monomer measured by the ^{1}H NMR (3 h, Conv. 52%). The quenched reaction mixture was evaporated and purified by precipitation with methanol at –78 ºC to afford poly(MA) (M_n=5400, M_w/M_n=1.06) (Fig. S14).

Reduction of RAFT chain end

The reduction of the RAFT chain end was performed by the syringe technique in dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the reduction procedure is described as follows: In a 25 mL Schlenk flask, poly(VAc) that was previously prepared (M_n = 4600, M_w/M_m = 1.13) (184 mg, 0.04 mmol), triphenylsilane (42.0 mg, 0.16 mmol), 1-dodecanethiol (0.20 mL of 200 mM in toluene, 0.04 mmol), AIBN (0.80 mL of 50 mM in toluene, 0.04 mmol), and toluene (0.77 mL) were placed at room temperature. The total volume of the reaction mixture was 2.0 mL. After mixing, the solution was charged in five glass tubes, and the tubes were sealed by flame in a nitrogen atmosphere. The tubes ware immersed in a thermostatic oil bath at 80 ºC. In predetermined intervals, the reaction was terminated by cooling of the reaction mixtures to –78 ºC. The hydride chain end ratio was determined from comparison to the residual RAFT chain end by the ^{1}H NMR. The quenched reaction mixture was evaporated and purified by preparative SEC (column: Shodex K2002 in $CHCl_3$) (hydride chain end: 97%).

Measurement

^{1}H NMR spectra were recorded on a JEOL ECS-400 spectrometer that operates at 400 MHz. MALDI-TOF-MS spectra were measured on a Shimadzu AXIMA-CFR Plus mass spectrometer (linear mode) with dithranol as the ionizing matrix and sodium trifluoroacetate as the ion source. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the product polymer were determined by size-exclusion chromatography (SEC) in THF at 40 ºC on two polystyrene gel columns [TSKgel MultiporeH$_{XL}$-M (7.8 mm i.d. x 30 cm)] that were connected to a JASCO PU-2080 precision pump and JASCO RI-2031 detector. The columns were calibrated against 10 standard polystyrene samples (Varian; M_p = 575–2783000, M_w/M_n = 1.02–1.23) and 10 standard poly(methyl methacrylate) samples (Varian; M_p = 202–1677000, M_w/M_n = 1.02–1.09). Photoreaction was conducted using blue LED lamp (CCS, LDR2-70BL2, λ_{max} = 470 nm) or UV LED lamp (CCS, LDR2-120UV365, λ_{max} = 365 nm) with a controller (CCS, PD3-5024-4-PI). The light intensity was measured by optical power meter (ADCMT 8230E Optical Power Meter).

References

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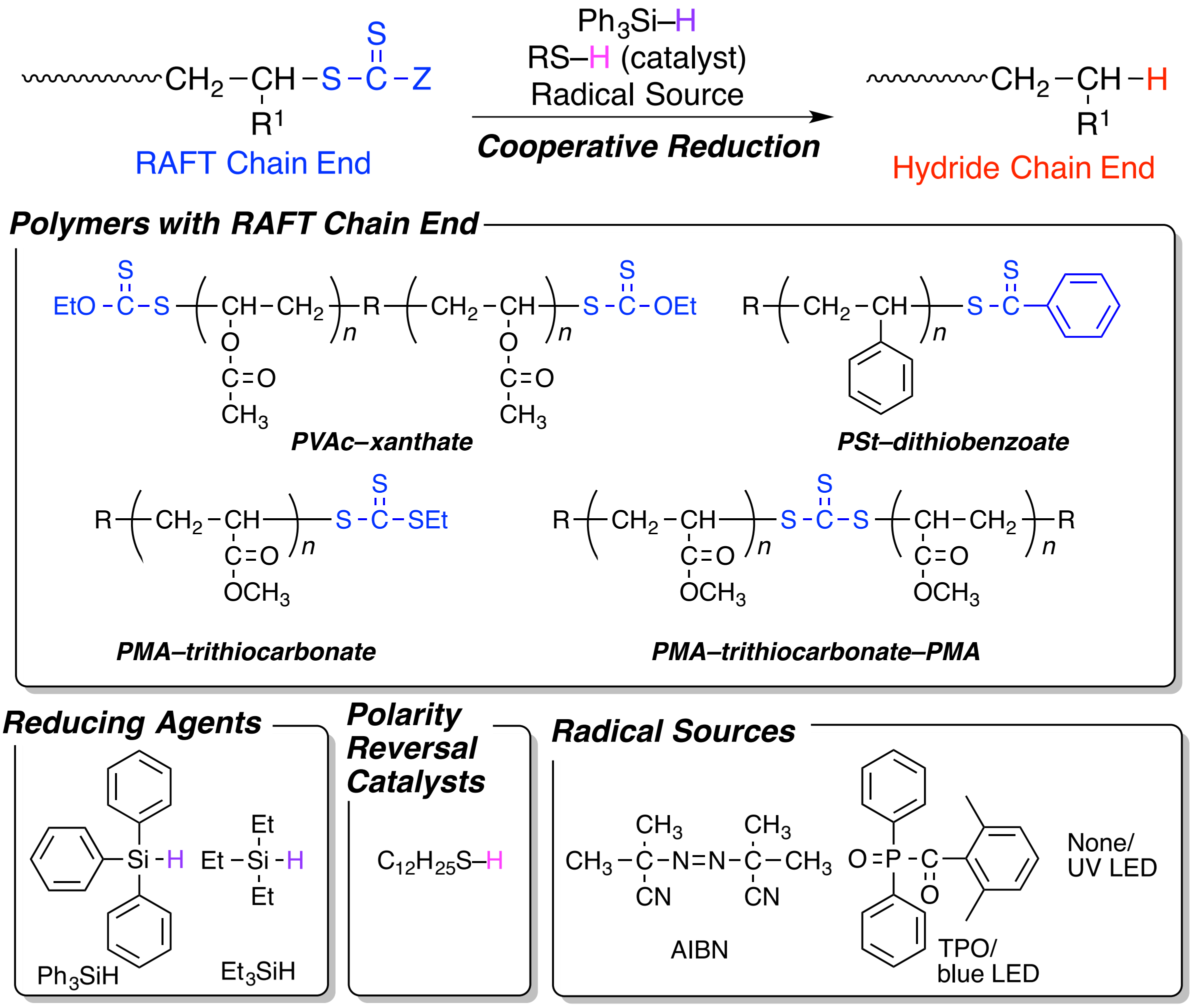
Table S1. Cooperative reduction of RAFT terminal of poly(vinyl acetate) and poly(methyl acrylate)

entry	polymer-RAFT group	radical source	$[C_{12}H_{25}SH]_0$/ $[\text{polymer}]_0$	time (h)	hydride terminal or removal of RAFT group (%)[a]	M_n(SEC)[b]	M_w/M_n[b]
1	PVAc-xanthate[c]	AIBN[d]	0.25	90	90	4600	1.14
2	PVAc-xanthate[c]	AIBN[d]	0.10	34	68	–	–
3[e]	PVAc-xanthate[c]	AIBN[d]	0.50	90	20	4300	1.13
4	PMA-trithiocarbonatete[f]	AIBN[c]	1.0	100	>99	3000	1.08
5	PMA-trithiocarbonatete[f]	TPO/blue LED[g]	1.0	120	93	2900	1.12
6	PMA-trithiocarbonatete[f]	UV LED[h]	1.0	70	>99	2800	1.09

[a] Determined by ^{1}H NMR. [b] Determined by SEC. [c] $[\text{RAFT group}]_0/[Ph_3SiH]_0$ = 40/80 mM in toluene, PVAc-xanthate: M_n = 4600, M_w/M_n = 1.13. [d] $[\text{AIBN}]_0$ = 20 mM at 80 °C. [e] Et_3SiH was used in place of Ph_3SiH. [f] $[\text{RAFT group}]_0/[Ph_3SiH]_0$ = 40/80 mM in toluene, PMA-trithiocarbonate: M_n = 2900, M_w/M_n = 1.09. [g] $[\text{TPO}]_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C. [h] UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.



Scheme S1. Cooperative reduction of RAFT chain end using hydrosilane as reducing agent and thiol as polarity reversal catalyst in radical conditions.

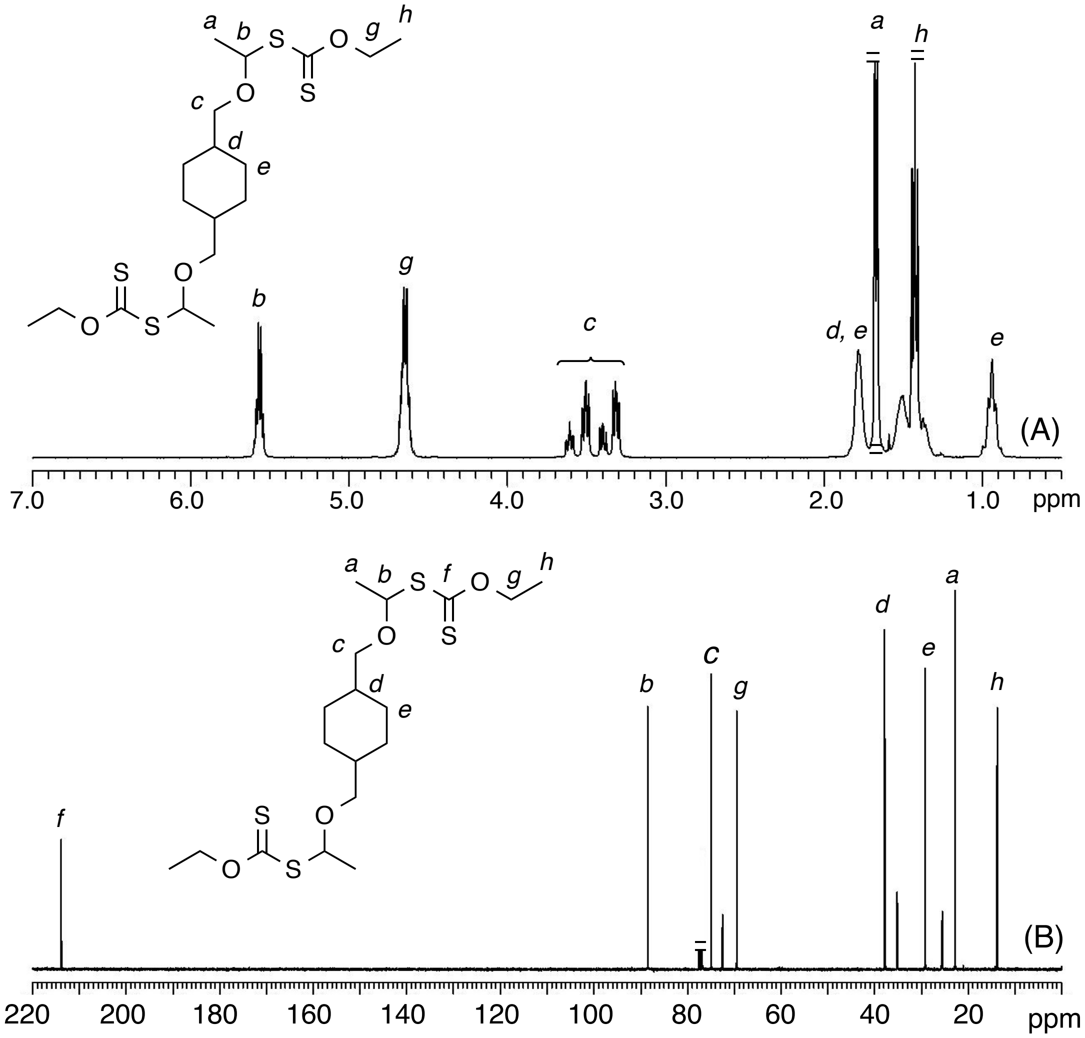


Fig. S1. ^{1}H (A) and ^{13}C (B) spectra of *S*,*S*'-(((cyclohexane-1,4-diylbis(methylene))bis(oxy))bis(ethane-1,1-diyl)) *O*,*O*'-diethyl bis(xanthate) (**1**) in CDCl$_3$ at r.t.

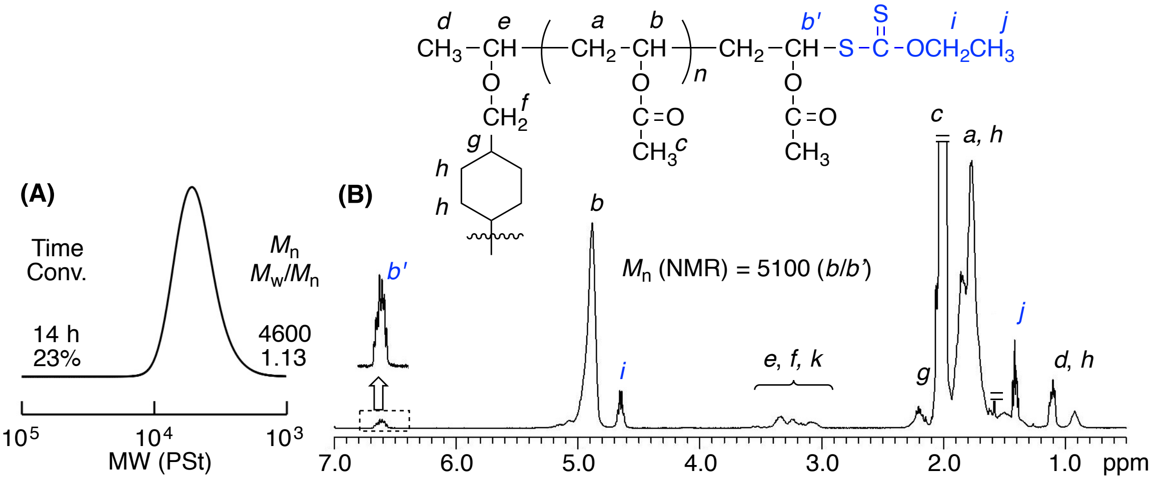


Fig. S2. SEC curve (A) and ^{1}H NMR spectrum (in CDCl$_3$ at 55 °C) (B) of PVAc-xanthate obtained by RAFT polymerization of VAc using **1** in EtOAc at 40 °C: $[\mathrm{VAc}]_0/[\mathbf{1}]_0/[\mathrm{AIBN}]_0 = 9200/46/23$ mM.

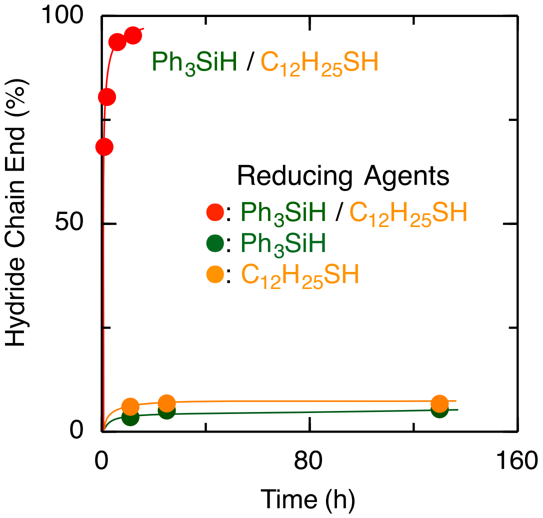


Fig. S3. Reduction of PVAc-xanthate using Ph_3SiH and/or $C_{12}H_{25}SH$ in the presence of AIBN in toluene at 80 °C: $[\text{xanthate}]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0/[\text{AIBN}]_0$ = 40/80/20/20, 40/80/0/20, or 40/0/80/20 mM.

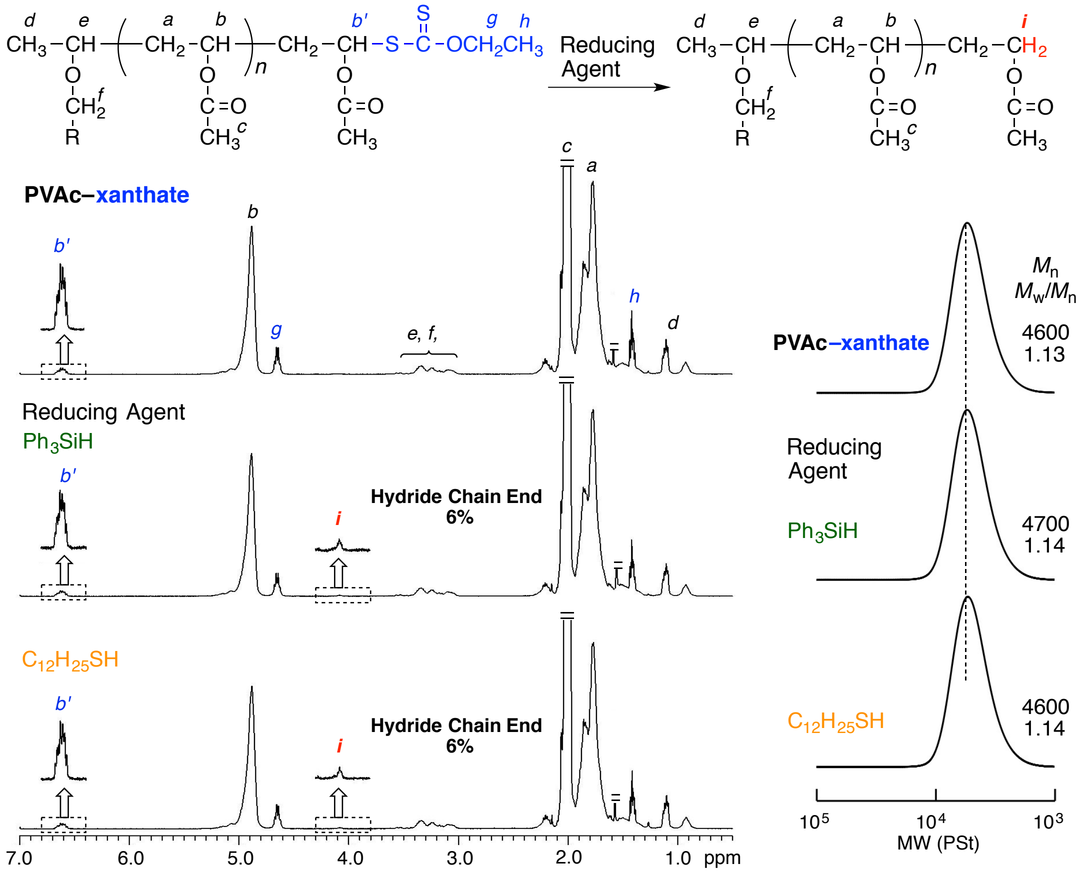


Fig. S4. ^{1}H NMR spectra (A) and SEC curves (B) for reduction of PVAc-xanthate for the same experiments as those for Fig. S3: $[\text{xanthate}]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0/[\text{AIBN}]_0$ = 40/80/0/20 or 40/0/80/20 mM.

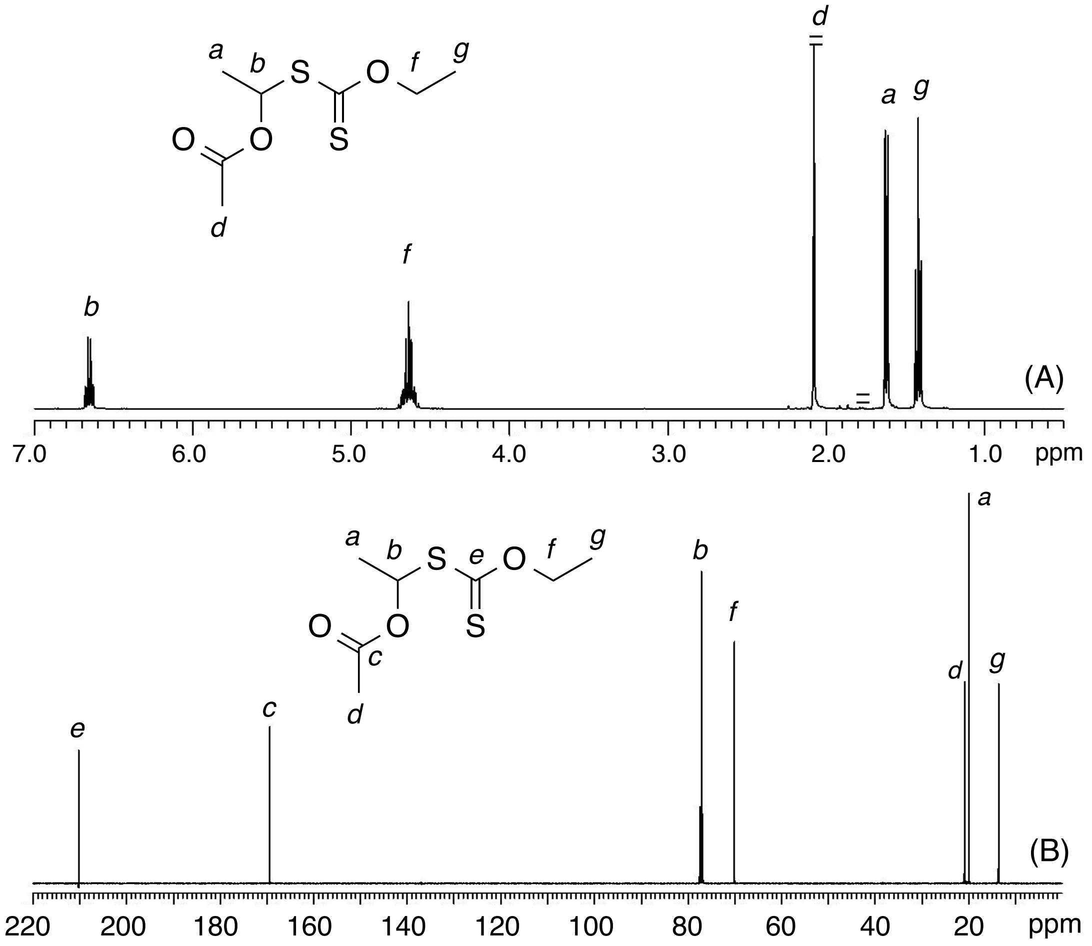


Fig. S5. ^{1}H (A) and ^{13}C (B) spectra of *S*-(1-acetoxyethyl) *O*-ethyl xanthate (**2**) in $CDCl_3$ at r.t.

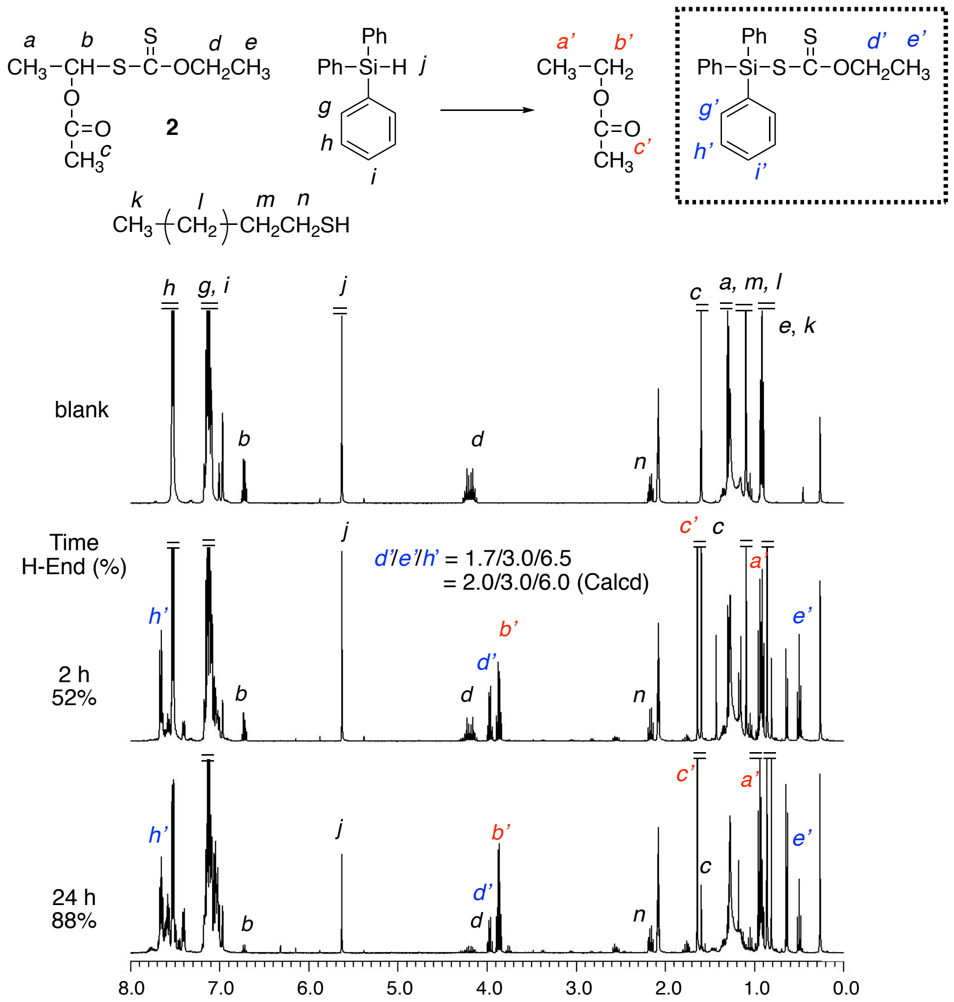


Fig. S6. ^{1}H NMR spectra of model reaction for cooperative reduction of **2** using combination of hydrosilane and thiol in toluene-d_8 at 80 °C: $[\mathbf{2}]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0/[AIBN]_0$ = 40/80/20/20 mM.

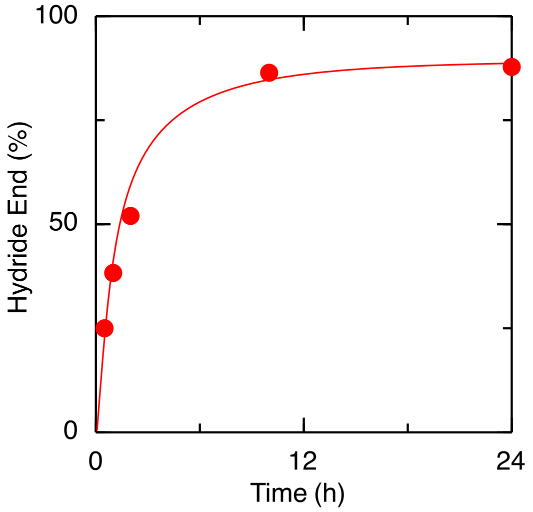


Fig. S7. Model reaction for cooperative reduction of **2** using combination of hydrosilane and thiol in toluene-d_8 at 80 °C: $[xanthate]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0/[AIBN]_0$ = 40/80/20/20 mM.

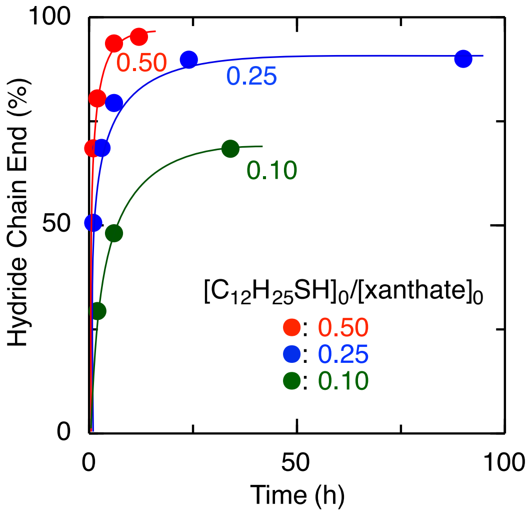


Fig. S8. Effect of $[C_{12}H_{25}SH]_0/[xanthate]_0$ on cooperative reduction of PVAc-xanthate in toluene at 80 °C: $[xanthate]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0/[AIBN]_0$ = 40/80/4–20/20 mM.

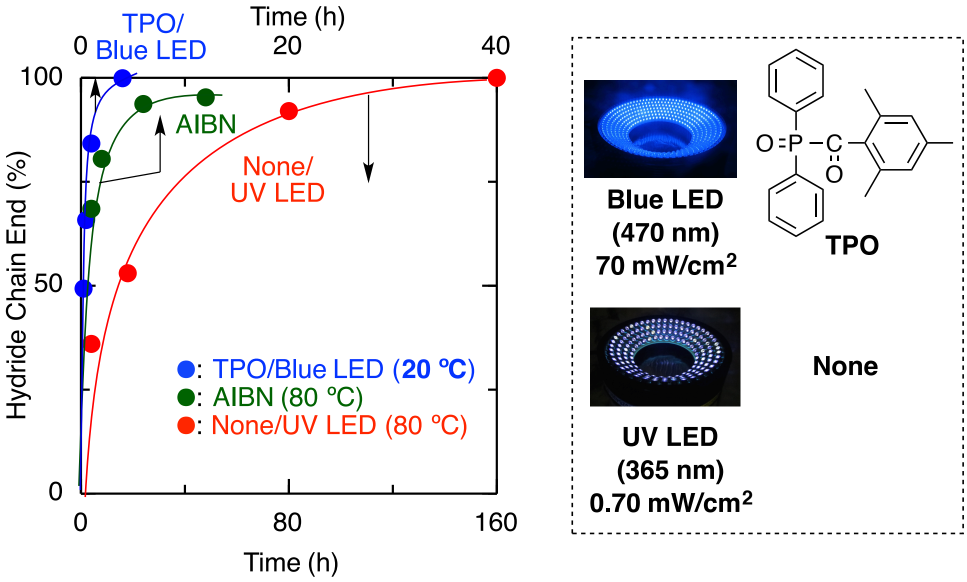


Fig. S9. Effect of radical sources on cooperative reduction of PVAc-xanthate in toluene: $[xanthate]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0$ = 40/80/20 mM, $[AIBN]_0$ = 20 mM at 80 °C, $[TPO]_0$= 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

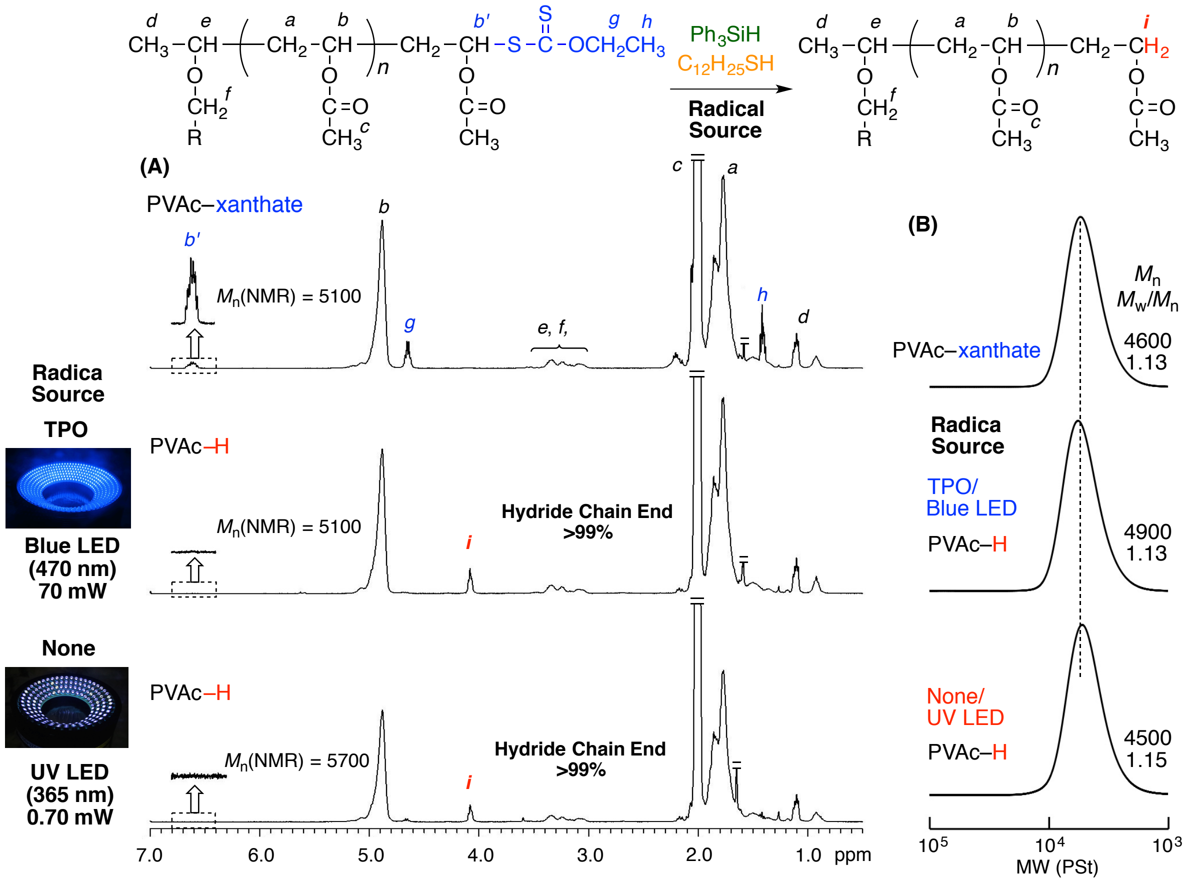


Fig. S10. ^{1}H NMR spectra (A) and SEC curves (B) for cooperative reduction of PVAc-xanthate under UV LED or using TPO under blue LED in the same experiments as Fig. S9: $[\text{xanthate}]_0/[\text{Ph}_3\text{SiH}]_0/[\text{C}_{12}\text{H}_{25}\text{SH}]_0$ = 40/80/20 mM, $[\text{TPO}]_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

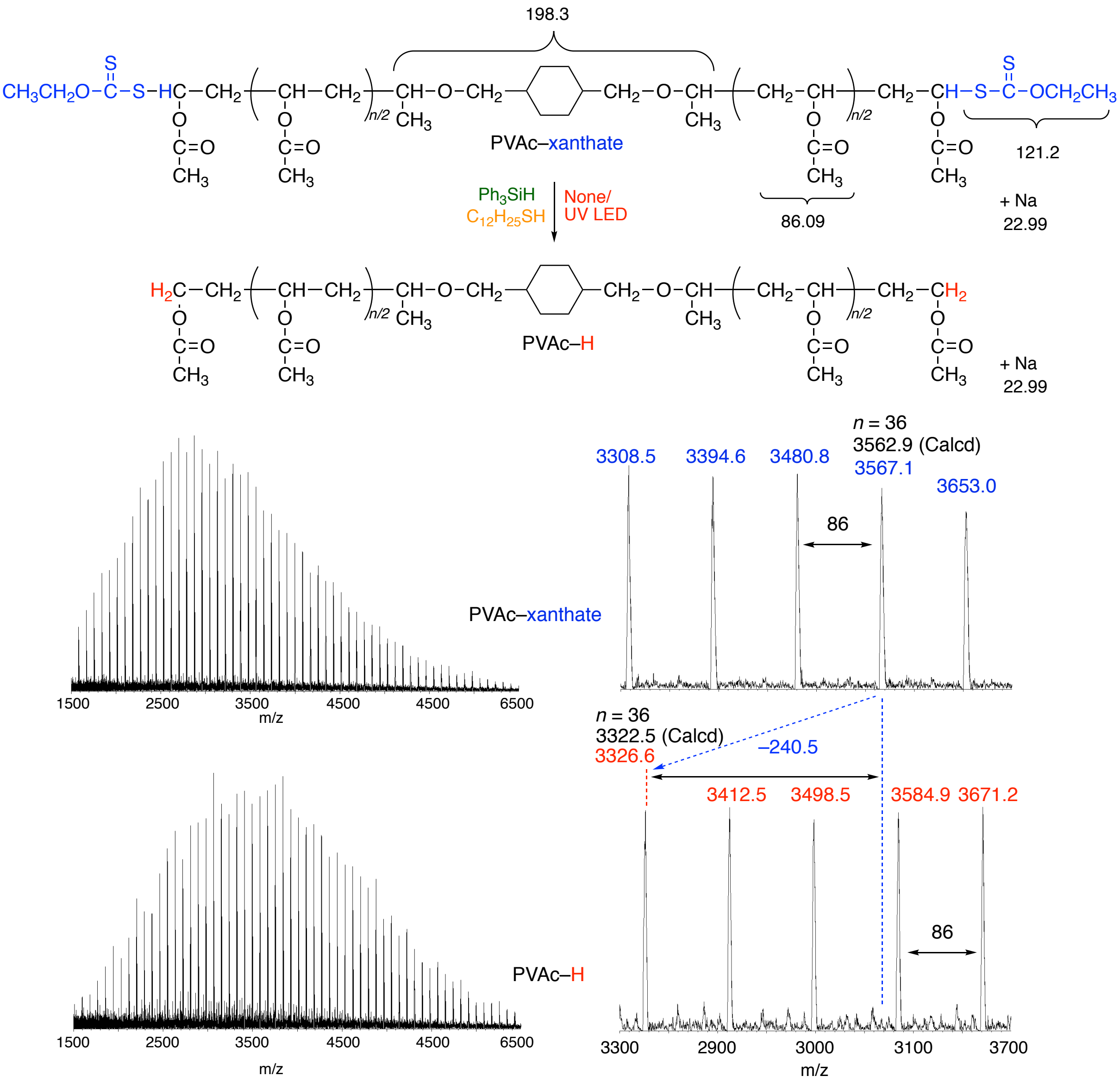


Fig. S11. MALDI-TOF-MS spectra for cooperative reduction of PVAc-xanthate under UV LED in the same experiments as Fig. S9: [xanthate]$_0$/[Ph$_3$SiH]$_0$/[C$_{12}$H$_{25}$SH]$_0$ = 40/80/20 mM, under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

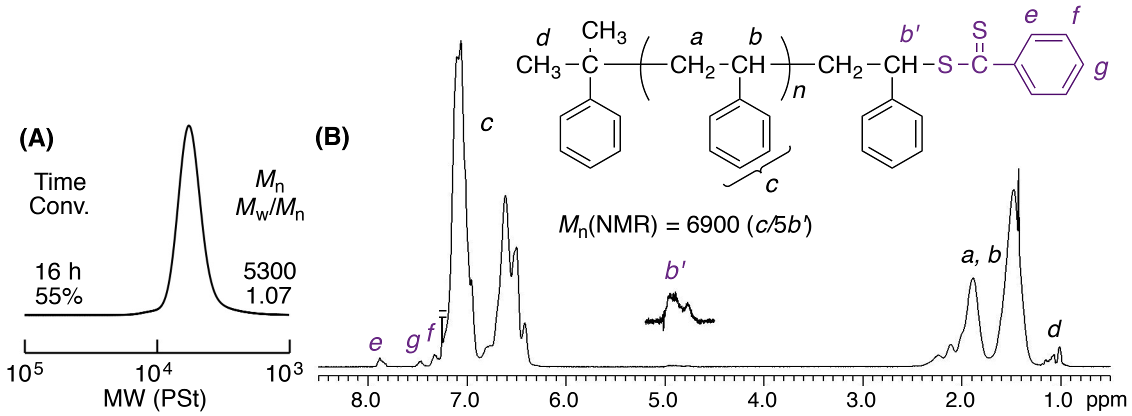


Fig. S12. SEC curve (A) and ^{1}H NMR spectrum (in $CDCl_3$ at 55 °C) (B) of PSt-dithiobenzoate obtained by RAFT polymerization of St using **3** in bulk at 110 °C: $[St]_0/[\mathbf{3}]_0$ = 8500/85 mM.

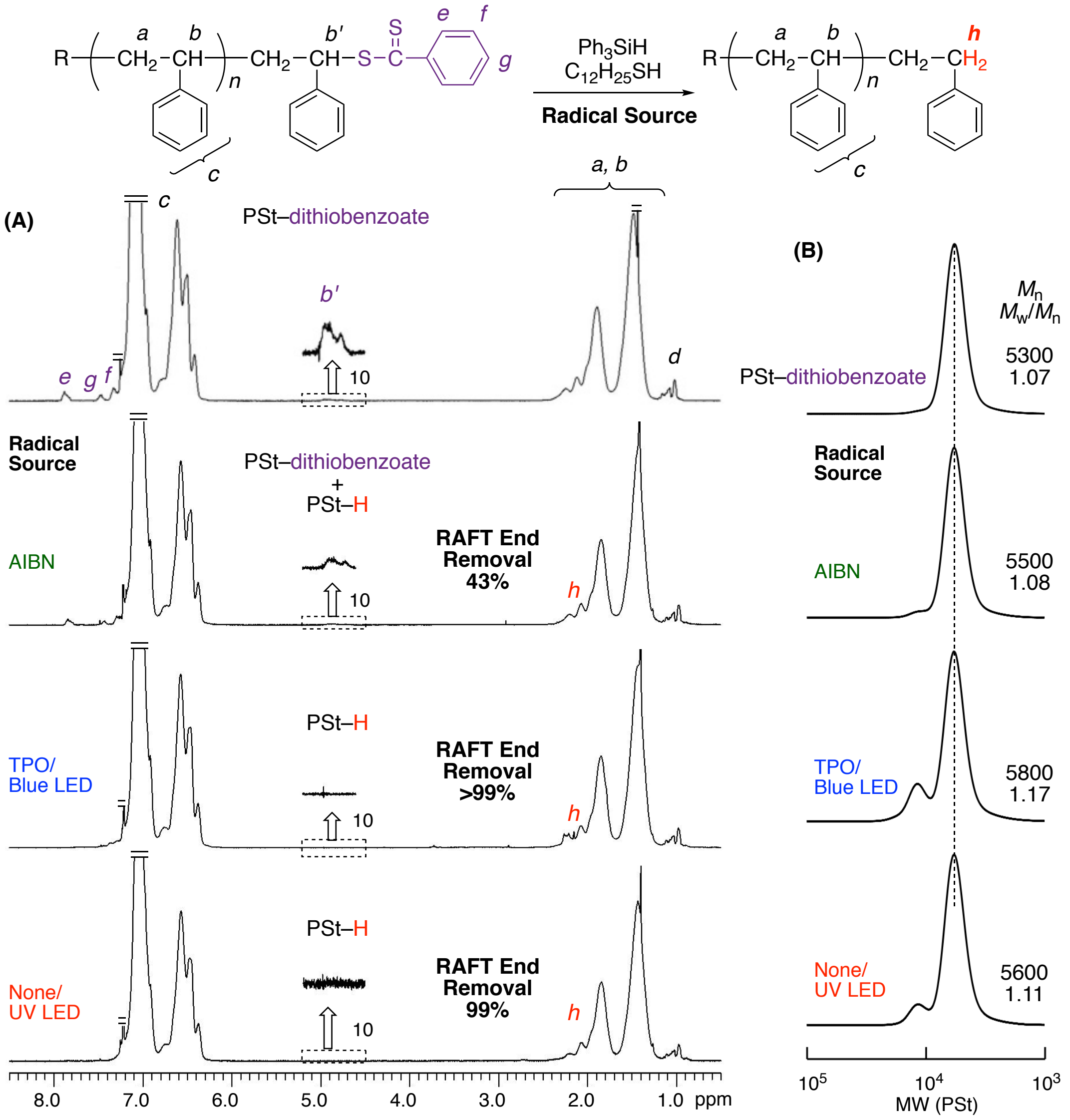


Fig. S13. ^{1}H NMR spectra (A) and SEC curves (B) for cooperative reduction of PSt-dithiobenzoate using AIBN, TPO under blue LED, or under UV LED in toluene: [dithiobenzoate]$_0$/[Ph_3SiH]$_0$/[$C_{12}H_{25}SH$]$_0$ = 20/40/10 mM, [AIBN]$_0$ = 20 mM at 80 °C, [TPO]$_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

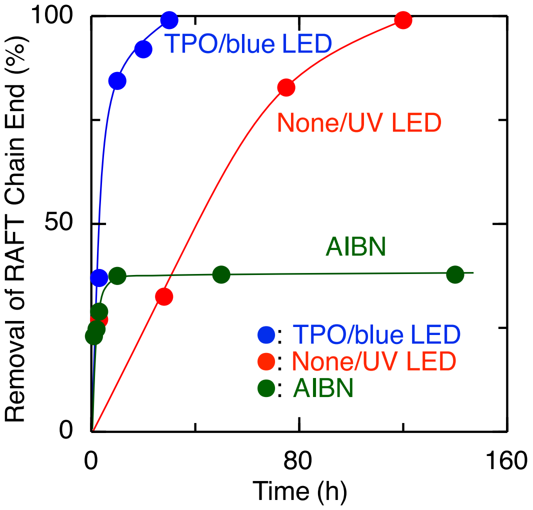


Fig. S14. Effect of radical sources on cooperative reduction of PSt-dithiobenzoate using AIBN, TPO under blue LED, or under UV LED in toluene: [dithiobenzoate]$_0$/[Ph$_3$SiH]$_0$/[C$_{12}$H$_{25}$SH]$_0$ = 20/40/10 mM, [AIBN]$_0$ = 20 mM at 80 °C, [TPO]$_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

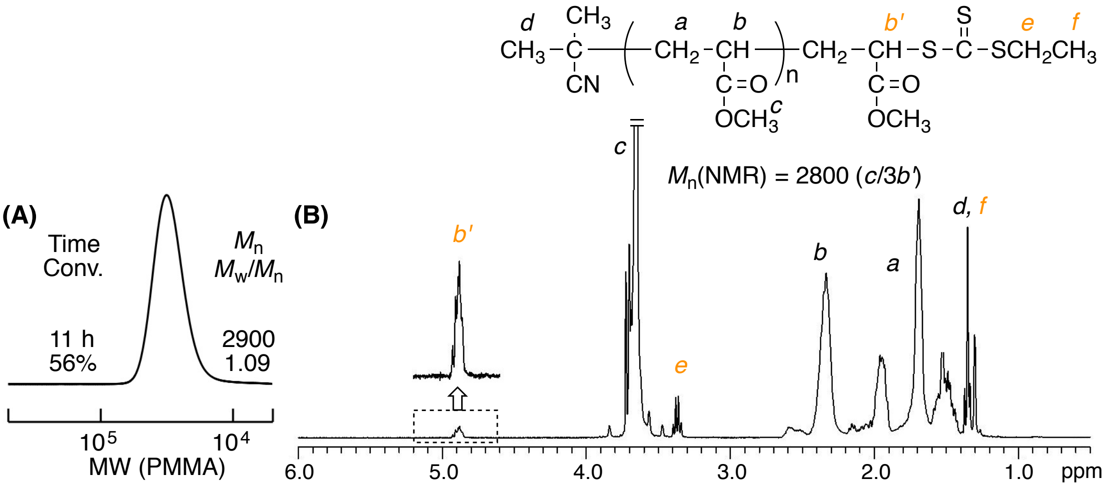


Fig. S15. SEC curve (A) and ^{1}H NMR spectrum (in CDCl$_3$ at 55 °C) (B) of PMA-trithiocarbonate by RAFT polymerization of MA using **4** in toluene at 60 °C: [MA]$_0$/[**4**]$_0$/[AIBN]$_0$ = 2000/40/2.0 mM.

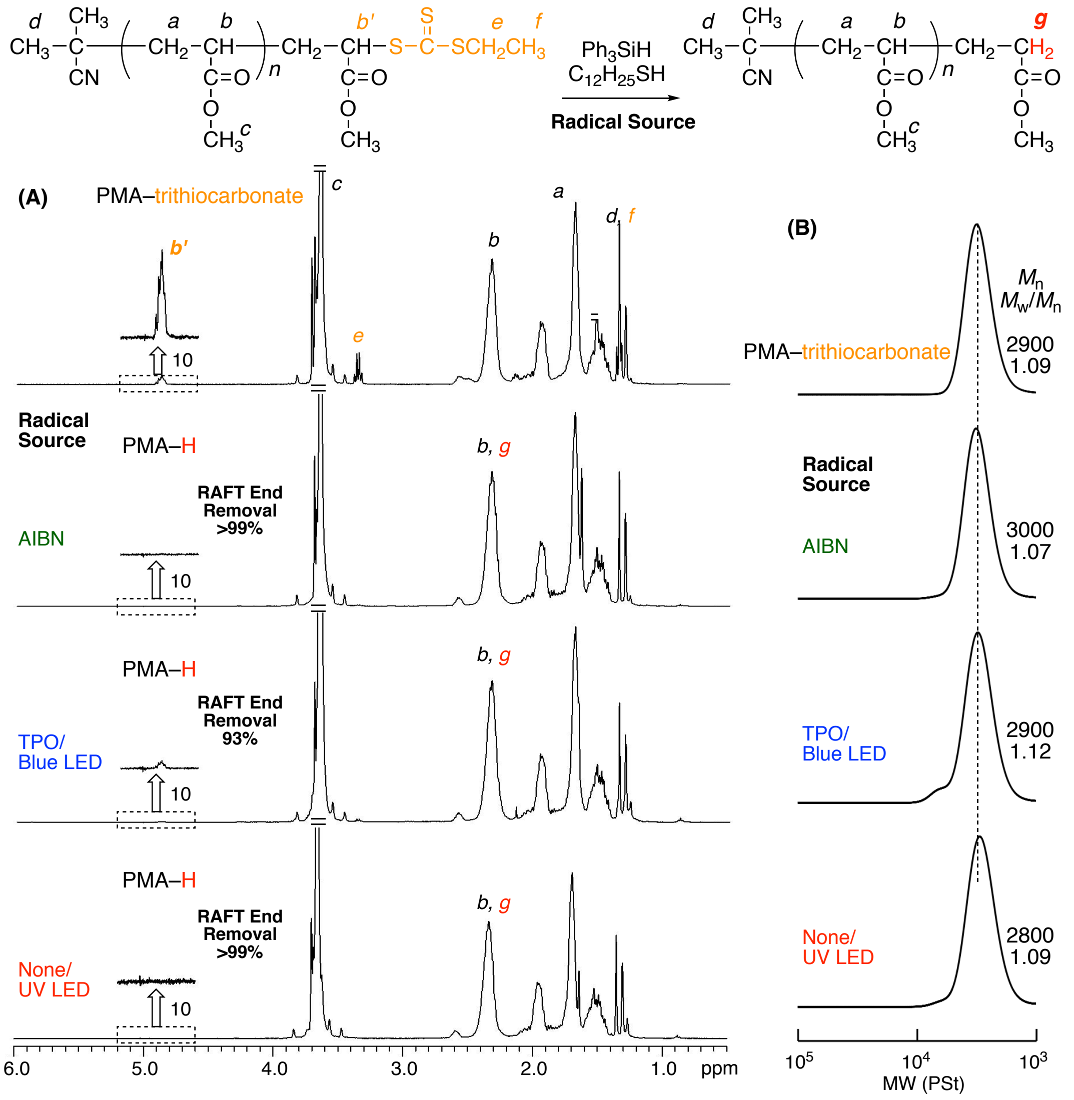


Fig. S16. ^{1}H NMR spectra (A) and SEC curves (B) for cooperative reduction of PMA-trithiocarbonate using AIBN, TPO under blue LED, or under UV LED in toluene: $[\text{trithiocarbonate}]_0/[\text{Ph}_3\text{SiH}]_0/[\text{C}_{12}\text{H}_{25}\text{SH}]_0$ = 40/80/40 mM, $[\text{AIBN}]_0$ = 20 mM at 80 °C, $[\text{TPO}]_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

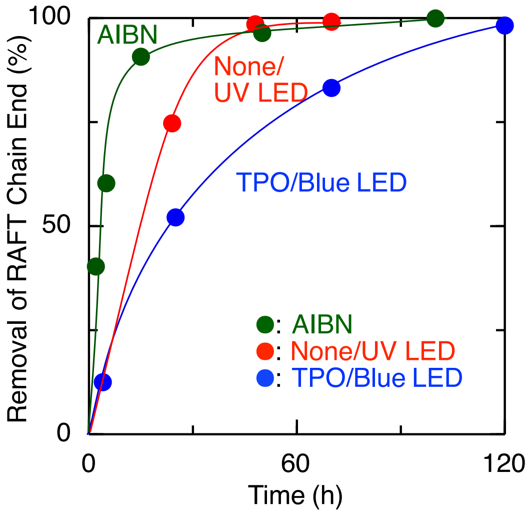


Fig. S17. Effect of radical sources on cooperative reduction of PMA-trithiocarbonate using AIBN, TPO under blue LED, or under UV LED in toluene: [trithiocarbonate]$_0$/[Ph$_3$SiH]$_0$/[C$_{12}$H$_{25}$SH]$_0$ = 40/80/40 mM, [AIBN]$_0$ = 20 mM at 80 °C, [TPO]$_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

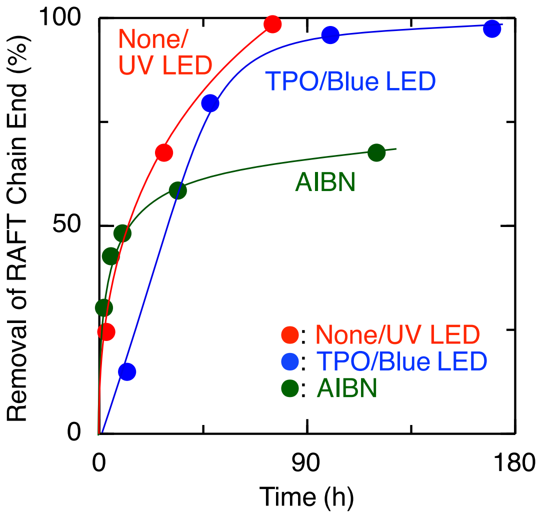


Fig. 18. Effect of radical sources on cooperative reduction of PMA-trithiocarbonate using AIBN, TPO under blue LED, or under UV LED in toluene: [trithiocarbonate]$_0$/[Ph$_3$SiH]$_0$/[C$_{12}$H$_{25}$SH]$_0$ = 40/80/20 mM, [AIBN]$_0$ = 20 mM at 80 °C, [TPO]$_0$ = 20 mM under blue LED (470 nm, 70 mW/cm^2) at 20 °C, or under UV LED (365 nm, 0.70 mW/cm^2) at 80 °C.

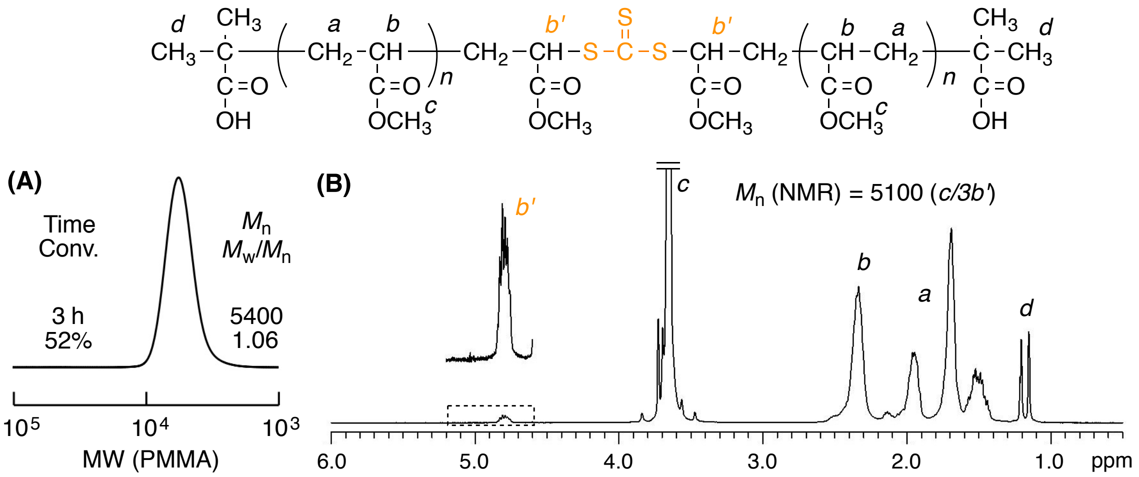


Fig. S19. SEC curve (A) and ^{1}H NMR spectrum (in $CDCl_3$ at 55 °C) (B) of PMA-trithiocarbonate-PMA by RAFT polymerization of MA using **5** in toluene at 60 °C: $[MA]_0/[\mathbf{5}]_0/[AIBN]_0 = 2000/20/2.0$ mM.

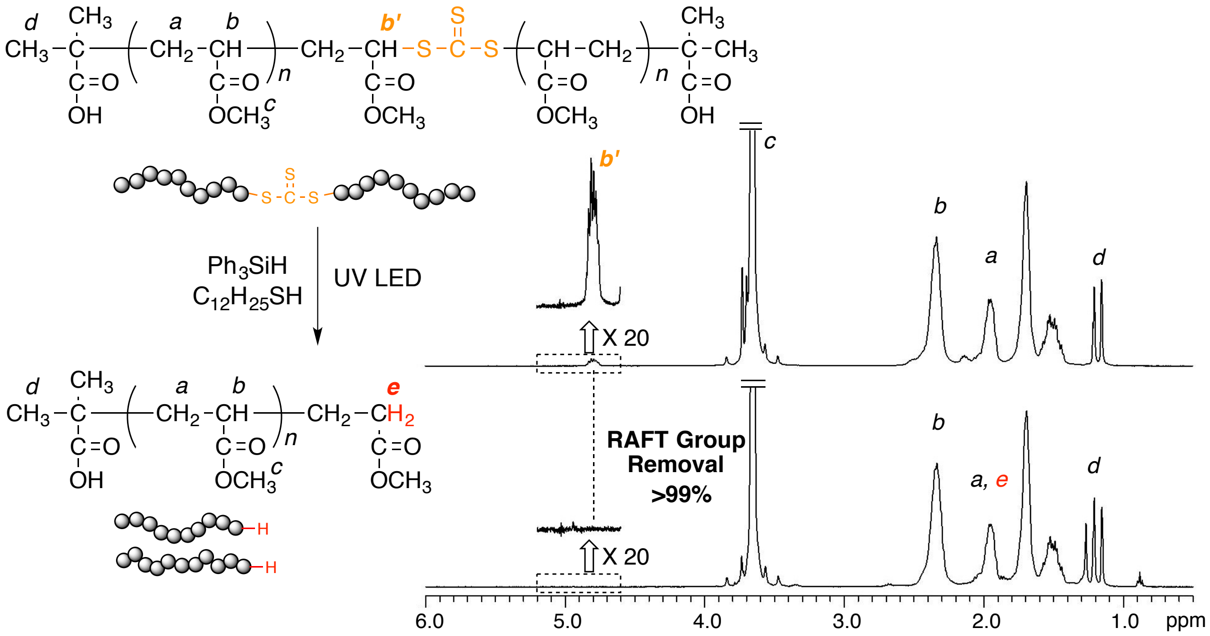


Fig. S20. ^{1}H NMR spectra for cooperative reduction of PMA-trithiocarbonate-PMA: $2[\text{trithiocarbonate}]_0/[Ph_3SiH]_0/[C_{12}H_{25}SH]_0 = 40/80/40$ mM in toluene at 80 °C under UV LED (365 nm, 0.70 mW/cm^2).