Supplementary information

The livingness of poly(methyl acrylate) under visible light photoiniferter mediated by trithiocarbonates

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Table of contents

I. Supplementary methods

A. General information

A−1. Chemicals

All chemicals and solvents were purchased commercially and used without further purification. The inhibitor in methyl acrylate monomer was removed by percolating over an aluminum oxide (Aldrich, activated, basic, Brockmann I) column. The chain transfer agent (CTA) used in this paper, 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA, Aldrich, 97%(HPLC)) was used without any further purification. Pre-prepared stock solution of the CDTPA was used for the higher reproducibility.

A−2. Photoreactor assembly

For the experiments of this work, a custom-built LED holder constructed using precisely cut PMMA plates were used. Commercial MR16 blue LEDs, along with halogen sockets, were utilized to provide illumination. The LED intensity was measured using a power meter (THORLABS PM100D optical power and energy meter) to ensure accurate light output. An external electric cooling fan was installed to avoid temperature elevation due to heat generated by LEDs. Additionally, the reaction temperature was monitored using an infrared (IR) thermometer (Daihan THE13) to track thermal variations during the experiment. All room temperature experiments were conducted at 30(±3) °C to maintain consistency across reactions.

A−3. Sample measurements

■ ***Gel-permeation chromatography (GPC)***

GPC system (Waters; Waters 1515 isocratic pump, Waters 2707 autosampler) coupled with a refractive index (RI) detector (Waters 2414 RI detector), UV/Vis detector (Waters 2489 UV/Vis detector), MALS (Wyatt DAWN 8) and three different columns (Agilent Polypore 7.5 × 300 mm, Jordi mixed bed 8.0 × 300 mm, Waters Styragel HR4 7.8 × 300 mm) was used to determine the molecular weights (MWs) and dispersity (*Đ*) of polymers synthesized. Tetrahydrofuran (THF, Samchun Chemicals, HPLC grade, stabilized, > 99.9%) was used as the eluent at 35 ℃ with a flow rate of 0.8 mL/min. Poly(methyl methacrylate) (PMMA) standards were used for calibration of RI signal. Dispersity of polymers was obtained using MALS calibrated by poly(styrene) standards.

■ ***High performance liquid chromatography (HPLC)***

HPLC analysis of synthesized poly(methyl acrylate) (PMA) samples were conducted through the LC system (Young Lin YL9100 HPLC system) connected with a refractive index (RI) detector (Young Lin YL9170 RI detector), UV/Vis detector (Young Lin YL9120 RI detector at 235 nm and 310 nm), and MALS detector (Wyatt DAWN 8) thorugh a C18 bonded silica column (Zorbax C18 250×4.6 mm, 500 Å pore, 5 μm). Acetonitrile (MeCN, Samchun Chemicals, HPLC grade, 99.9%) was used as an eluent at a flow rate of 0.6 mL/min. Column temperature were kept at 4 ℃ for optimized separation of dead chains. Every analysis was performed with injection volume of 20 μL of polymeric sample with the concentration of 3 mg/mL dissolved in eluent.

■ ***Nuclear magnetic resonance (NMR)***

The monomer conversion were determined using a ^{1}H NMR spectrometer (Brucker, AVANCE III HD (300 MHz)) with

$CDCl_3$ as the solvent. Monomer conversion of methyl acrylate was calculated utilizing the integration of vinylic hydrogens and corresponding ester hydrogens in the monomer and polymer.

B. Procedure of photoiniferter polymerization of MA

B−1. General procedure for photoiniferter polymerization of MA

Photoiniferter polymerization of methyl acrylate was carried out as described below. The inhibitor in MA was removed by percolating over an aluminum oxide column. The stock solution of CDTPA was made (100 mg/ml (0.247 mol/L), in anhydrous DMSO). For [MA]:[CDTPA] = 100:1, a 20 mL glass vial equipped with a stirring bar was charged with MA (2.0 mL, 21.8 mmol), CDTPA solution (0.910 mL, 2.18 x 10^{-1} mmol) and additional anhydrous DMSO (1.09 mL) as the solvent. The reaction vial was sealed with parafilm and then bubbled with nitrogen (99.999%) for 30 min. Polymerization was carried out under 455 nm LEDs at room temperature.

During polymerization, 0.15 mL aliquot of the reaction mixture was removed at predetermined intervals via syringe and dissolved 0.05 mL of aliquot in $CDCl_3$, 0.05 mL in THF, and 0.05 mL in dichloromethane. Without storing, the aliquots were then immediately analyzed by ^{1}H NMR for conversion and end-group analysis, GPC for MW and *Đ* analysis. The aliquot dissolved in dichloromethane was stored in a vacuum oven to remove volatiles for HPLC analysis.

C. Procedure of polymer separation by HPLC

After removing volatiles of the obtained aliquot as described in section: ***B. Procedure of photoiniferter polymerization of MA*** to complete remove of DMSO and residual MA, the sample was dissolved in MeCN. Through HPLC analysis using MeCN as the eluent under 4 ℃ with a flow rate of 0.6 mL/min, the living/dead polymer peaks can be fractionized. The "F_{dead}" (dead chains) was collected by containing the flowing eluent from 3 minutes to 5 minutes, and the "F_{living}" (living chains) was collected by containing the flowing eluent from 5 minutes to 12 minutes. The elution was left to continue until 20 minutes for removal of possible impurities. The same sample was repeatedly injected to collect more of each fraction. Depending on the fraction of dead chains, repetition up to 20 injections were performed. For the GPC analysis of the living/dead chains, MeCN was removed under reduced pressure and 100 μL HPLC grade THF was added. GPC analysis was performed using the same method as described in section: ***A-2. Sample measurements***.

D. Mechanistic interpretation of the phenomenon

The general results indicate that polymerization occurs efficiently, following first order kinetics, with loss of TCT functionality occurring continuously and essentially linearly, even after all monomer has been consumed. In the photoiniferter process, chain activation occurs through light irradiation, with radical loss due to both conventional radical termination and reversible termination with the TCT radical. The kinetics of photoiniferter process can be approximated as below:

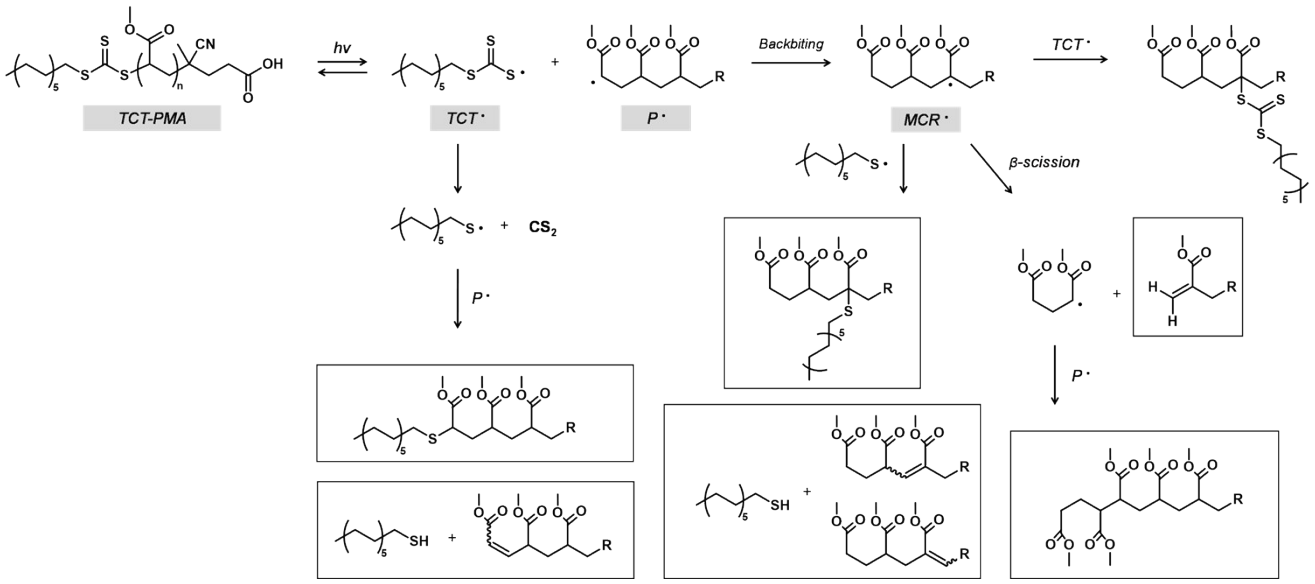
$$\frac{d[P^\bullet]}{dt} = k_a[TCT] - k_d[TCT^\bullet][P^\bullet] - k_t[P^\bullet]^2 - k_{add}[TCT][P^\bullet] - k_{frag}[PTC^\bullet TP] \quad (1)$$

Where k_a is the apparent rate coefficient of photochemical activation of the TCT groups, k_d is the rate coefficient for recombination of the TCT fragment radicals TCT• with propagating radicals P•, k_t is the conventional termination rate coefficient, k_{add} is the rate coefficient for propagating radicals to add to the TCT chains transfer agents, and k_{frag} is the rate coefficient for fragmentation of the RAFT intermediate radical, PTC•TP. Assuming the RAFT equilibrium is

established ($k_{add}[TCT][TCT^{\bullet}] = k_{frag}[PTC^{\bullet}TP]$), equation 1 can be simplified to:

$$\frac{d[P^{\bullet}]}{dt} = k_a[TCT] - k_d[TCT^{\bullet}][P^{\bullet}] - k_t[P^{\bullet}]^2 \quad (2)$$

According to Equation 2, the photoiniferter process should follow the persistent radical effect,[15, 48] with TCT• acting as the persistent radical. If the TCT• radical was consistent with other persistent radical species, for instance Cu^{II} deactivators in ATRP, over time the build-up of the persistent radical should cause the progressive decrease in propagating radical concentration. If the photoiniferter process behaved as a true PRE system, the radical concentration and therefore the rate of chain termination should substantially decrease over the course of the weeklong experiment. The near linear evolution of the dead chain fraction over the weeklong experiment suggests a near constant and steady state radical concentration. This suggests, contrary to the general principles of the PRE, that the TCT• concentration should be nearly steady, rather than increasing as is typical in systems governed by classical PRE effects.



Scheme S1. Potential pathways of thiocarbonylthio group degradation and terminations.

Near constant concentration of TCT•, rather than accumulation as in the general case of PRE, may be attributed to their degradation. Potential degradation pathways of TCT• resulting in dead chains is proposed in ***Scheme S1.*** The exact mechanism remains unclear due to the complexity of potential pathways, but we hypothesize TCT• fragmenting into a thiyl radical and CS_2.[49, 50] Trace amounts of small molecule side products at elution time near 20 minutes were observed in the HPLC chromatogram hinting the presence of side products including long alkyl chains (***Figure S9***). Previous work by Qiao et al. summarized that the photolytic stability of TCT compounds is influenced by the rate of recombination of TCT• with P•.[51] Thus, when P• is a tertiary radical as compared to secondary radical the TCT group becomes susceptible to degradation. Acrylate radicals are well known for its possibility to undergo intramolecular chain transfer yielding a tertiary midchain radical (MCR•). At high monomer conversions, MCR• cannot revert to a secondary radical via monomer propagation, allowing MCR• to remain as a tertiary radical. This stable tertiary radical may allow the decomposition of TCT• into a thiyl radical and CS_2. The remaining MCR• may then either terminate bimolecularly with other radicals[47] or fragment by β-scission forming a polymer with an unsaturated end group[52] and contribute to the

observations made in this study.

II. Supplementary Figures and Tables

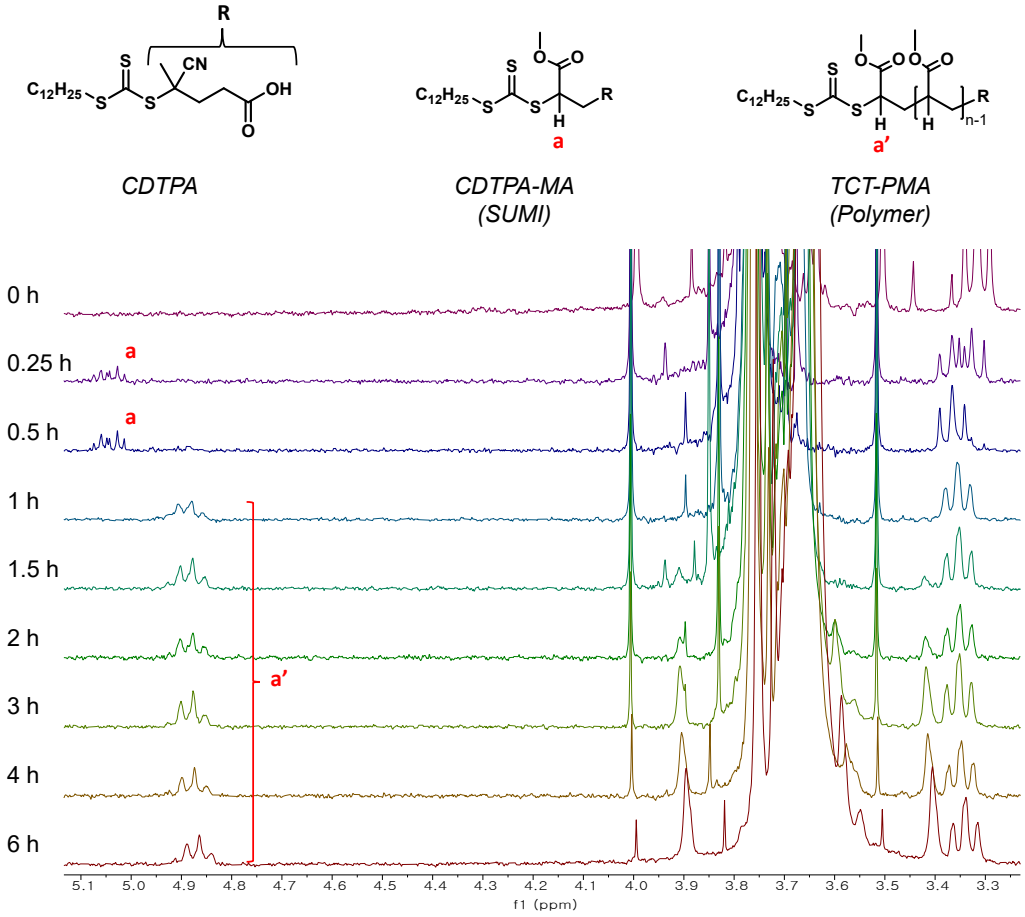


Figure S1. ^{1}H NMR spectrum change of PMA polymerization result in the presence of CDTPA under 455 nm LED (100 mW/cm^2) irradiation.

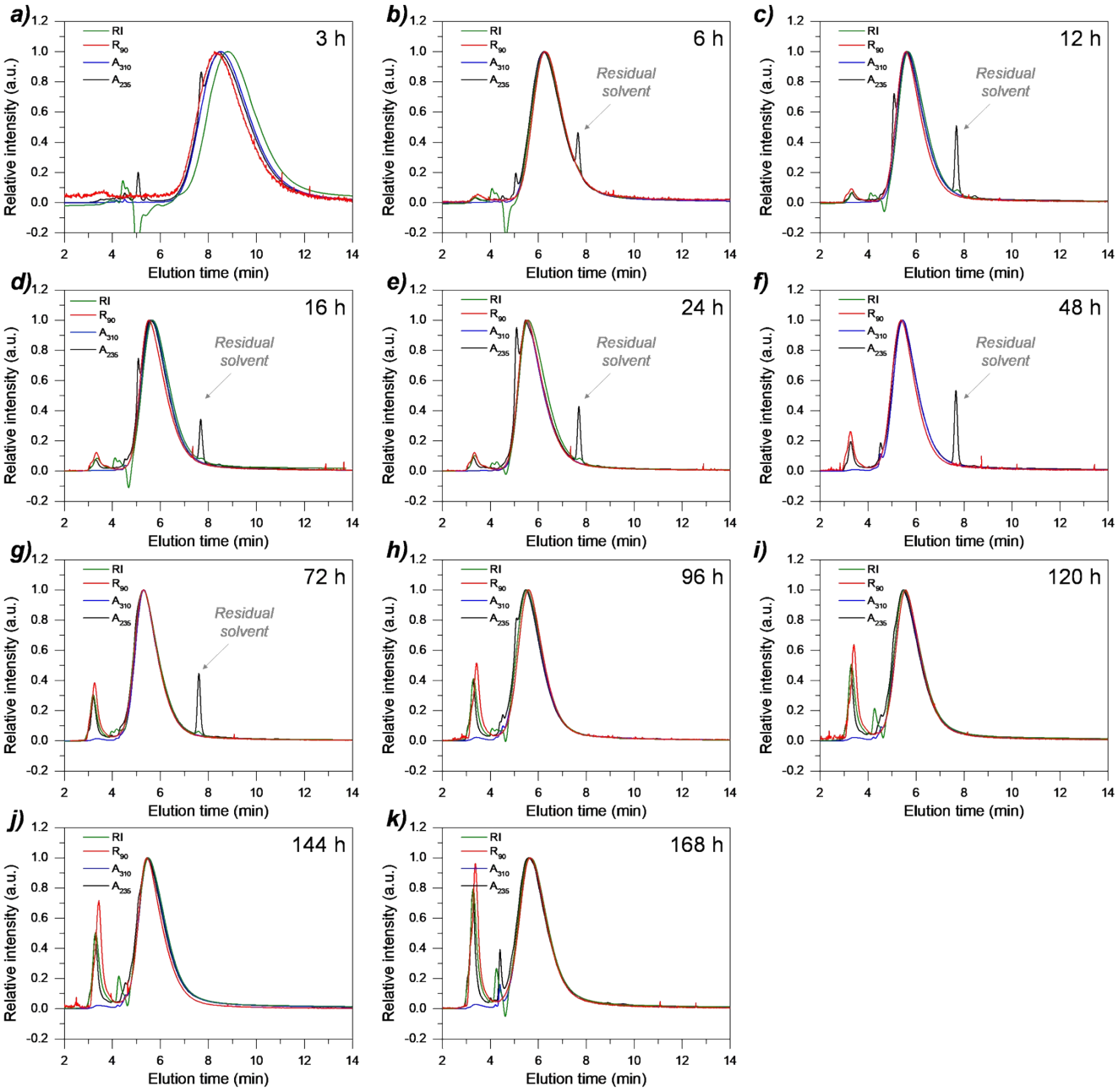


Figure S2. HPLC traces of samples depending on the irradiation time RI(green) indicates refractive index signals, R_{90}(red) indicates MALS signals, A_{310}(blue) indicates UV absorption signal at 310 nm, and A_{235}(black) indicates UV absorption signal at 235 nm: a) 3 h, b) 6 h, c) 12 h, d) 16 h, e) 24 h, f) 48 h, g) 72 h, h) 96 h, i) 120 h, j) 144 h, k) 168 h. Peak at elution time of 7.5 minutes caused by residual solvents and monomer in the sample as it does not show signals in A_{310} and R_{90} with negligible signal for RI.

Reaction time	$F_{living,int}$ [a)]	$F_{dead,int}$ [b)]	$F_{total,int}$ [c)]
3 h	0.00765	2.41164	2.41929
6 h	0.01441	1.55927	1.57368
12 h	0.02521	1.2816	1.30681
16 h	0.03004	1.30694	1.33698
24 h	0.03358	1.32575	1.35933
48 h	0.06823	1.22442	1.29265
72 h	0.10521	1.09799	1.2032
96 h	0.13722	1.23497	1.37219
120 h	0.17611	1.27975	1.45586
144 h	0.23254	1.40705	1.63959
168 h	0.27901	1.37181	1.65082

Table S1. Integrated values of normalized RI signals of HPLC traces of F_{dead} and F_{living}, a) $F_{living,int}$: integrated value of living portion between 3 min ~ 4 min,b) $F_{dead,int}$: integrated value of living portion between onset from relative intensity 0 of F_{living} to the next minimum relative intensity(between 4 min ~ 10 min), c) $F_{total,int} = F_{living,int} + F_{dead,int}$

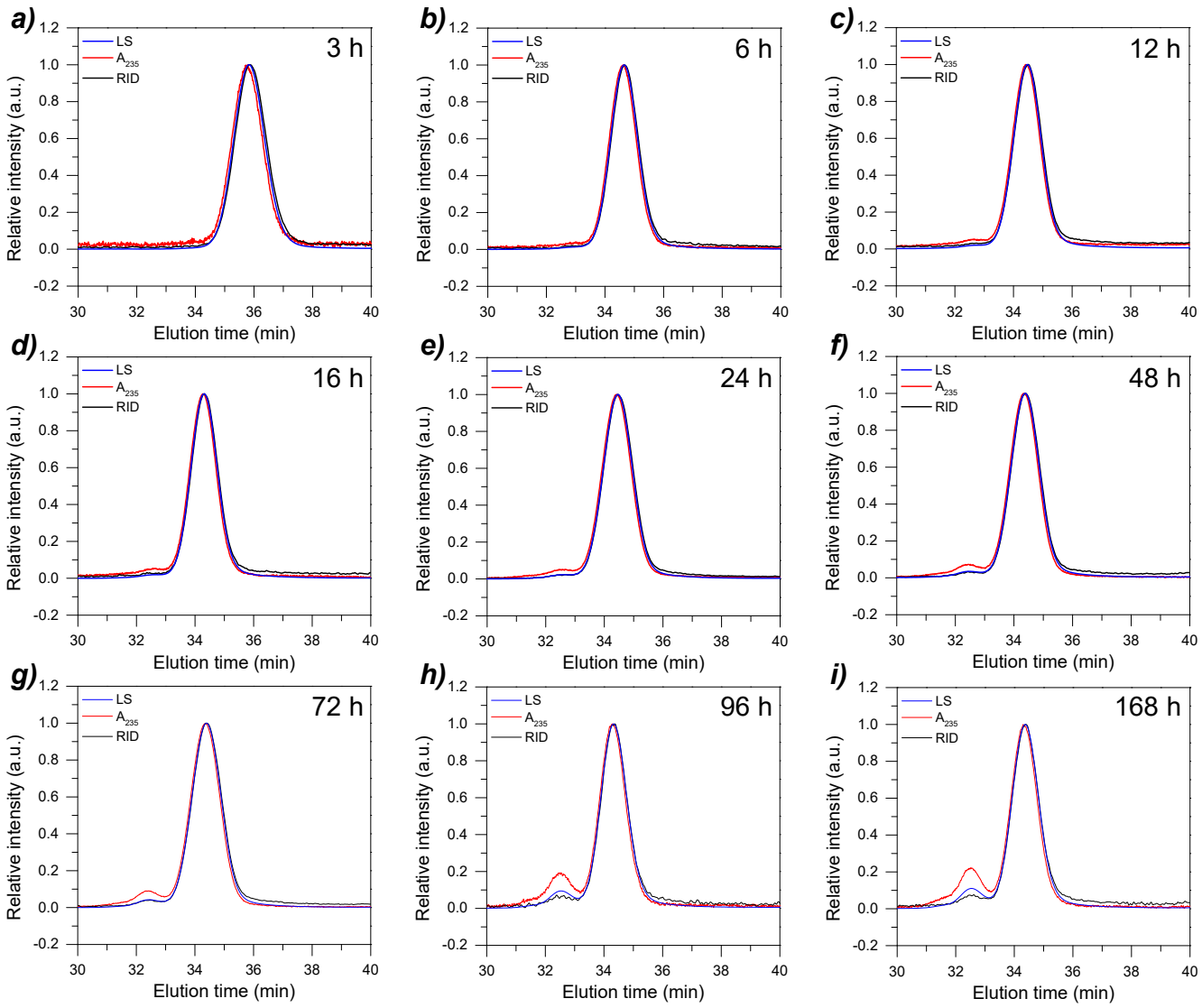


Figure S3. GPC traces of samples depending on the irradiation time : a) 3 h, b) 6 h, c) 12 h, d) 16 h, e) 24 h, f) 48 h, g) 96 h, h) 168 h.

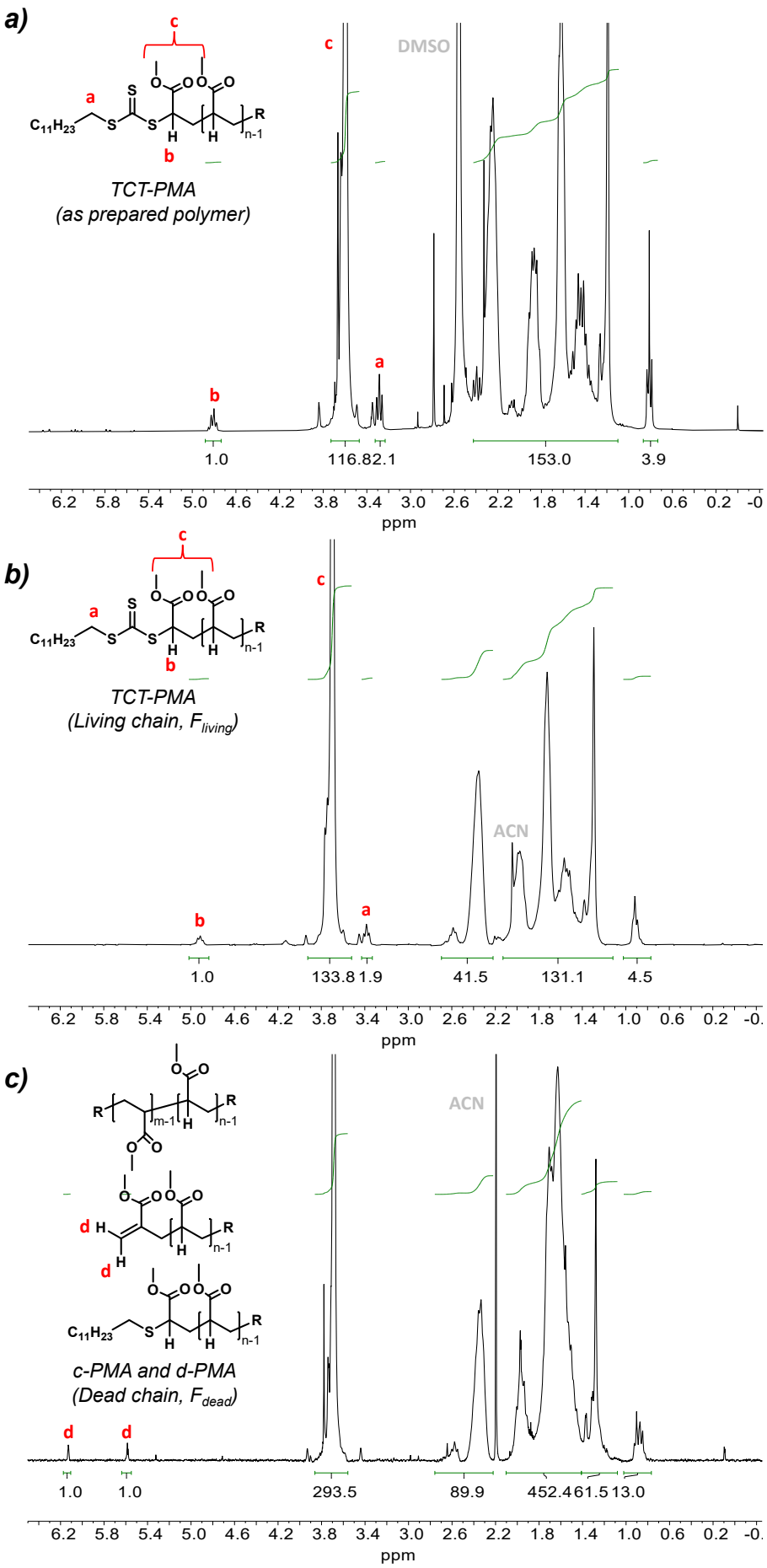


Figure S4. ^{1}H NMR spectrum of: a) PMA(DP=25, t=168 h) prepared via photoiniferter-RAFT polymerization, b) fractionized living chains, c) fractionized dead chains

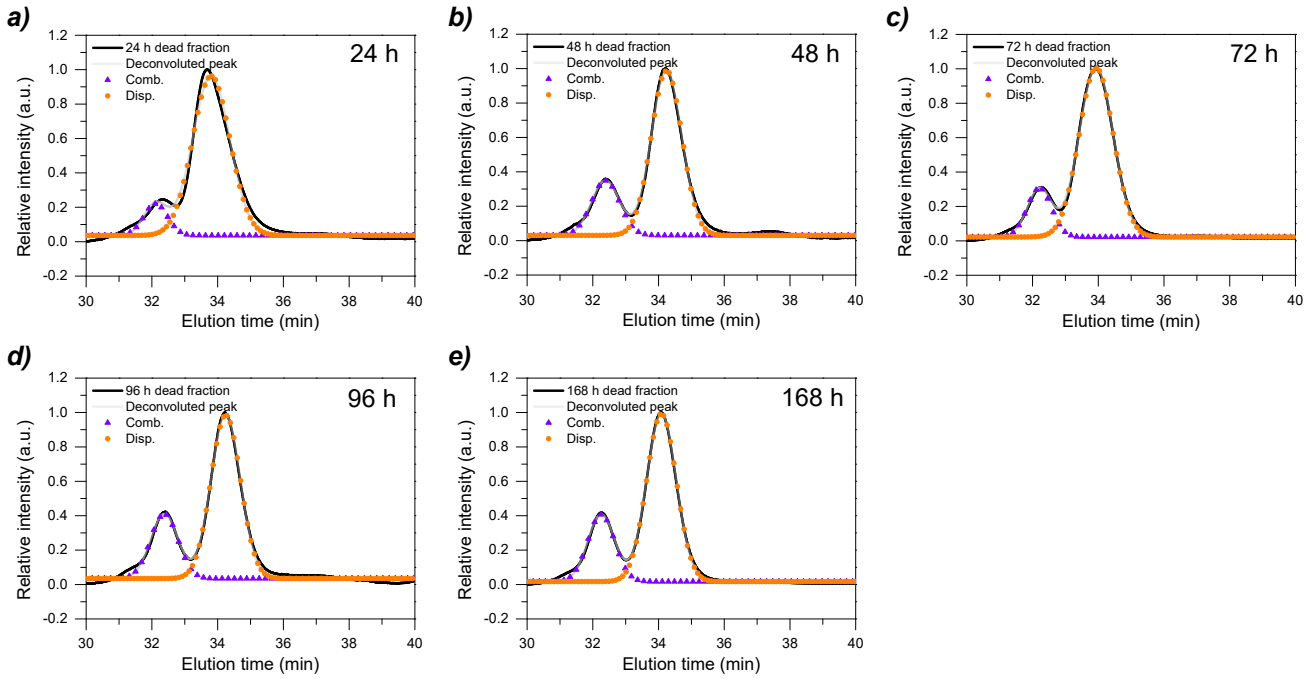


Figure S5. Deconvolution of GPC traces of fractionized chains depending on the irradiation time utilizing Origin with Gaussian peak fitting model: a) 24 h, b) 48 h, c) 72 h, d) 96 h, e) 168 h

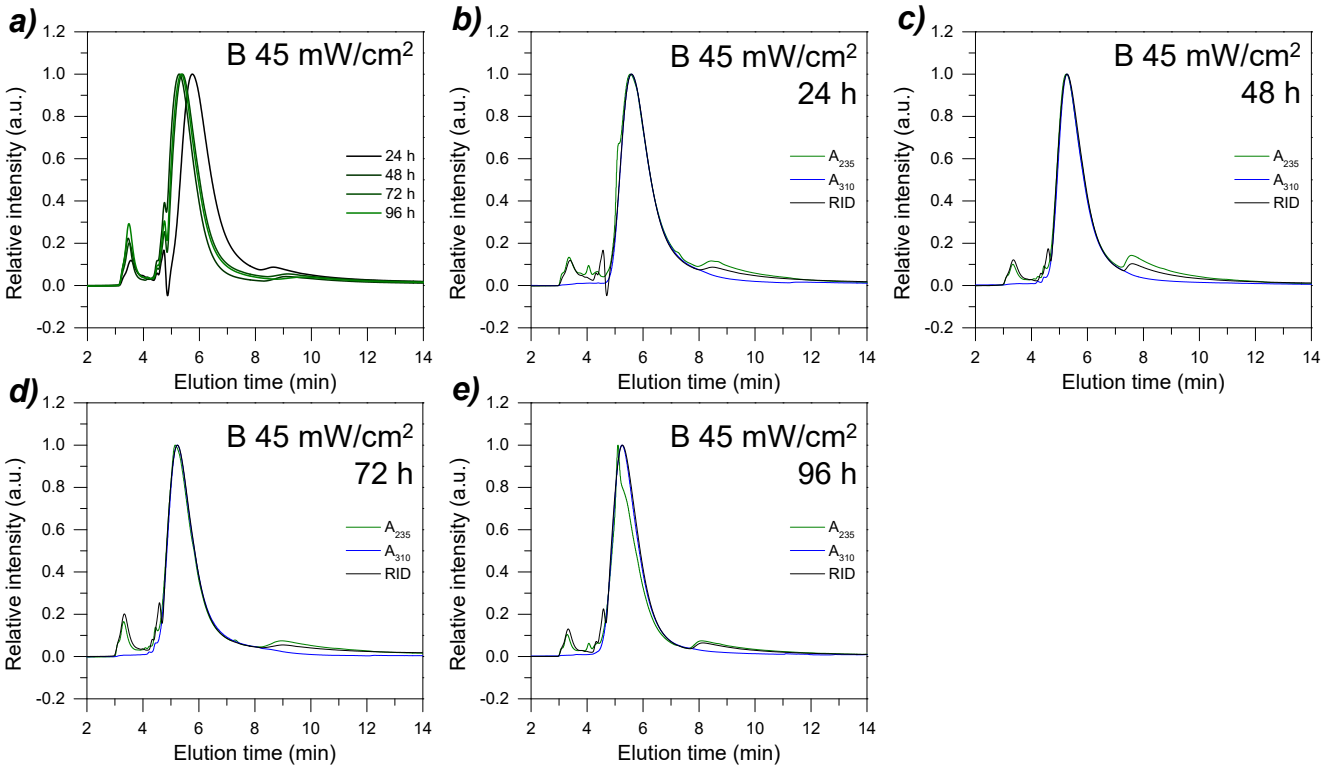


Figure S6. HPLC traces of samples depending on light intensity and irradiation time: a-e) 45 mW/cm^2

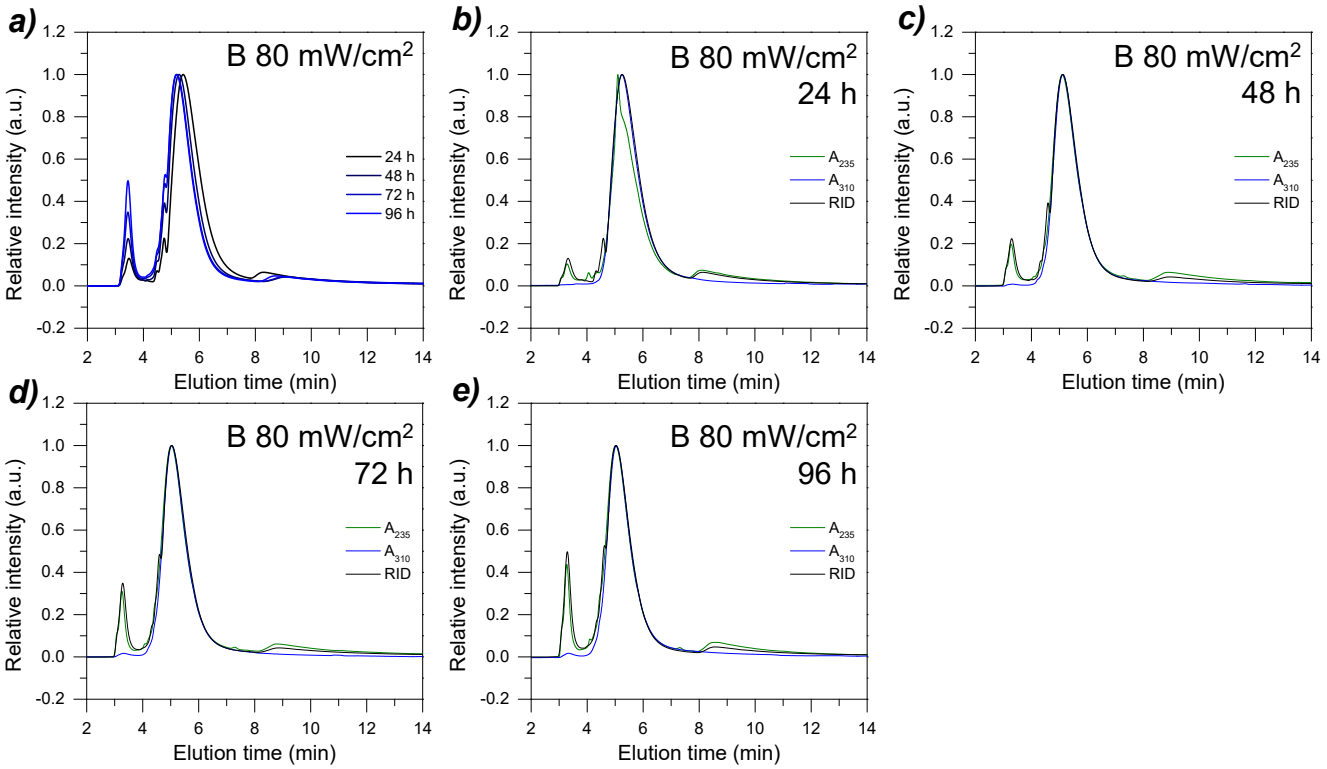


Figure S7. HPLC traces of samples depending on light intensity and irradiation time: a-e) 80 mW/cm^2

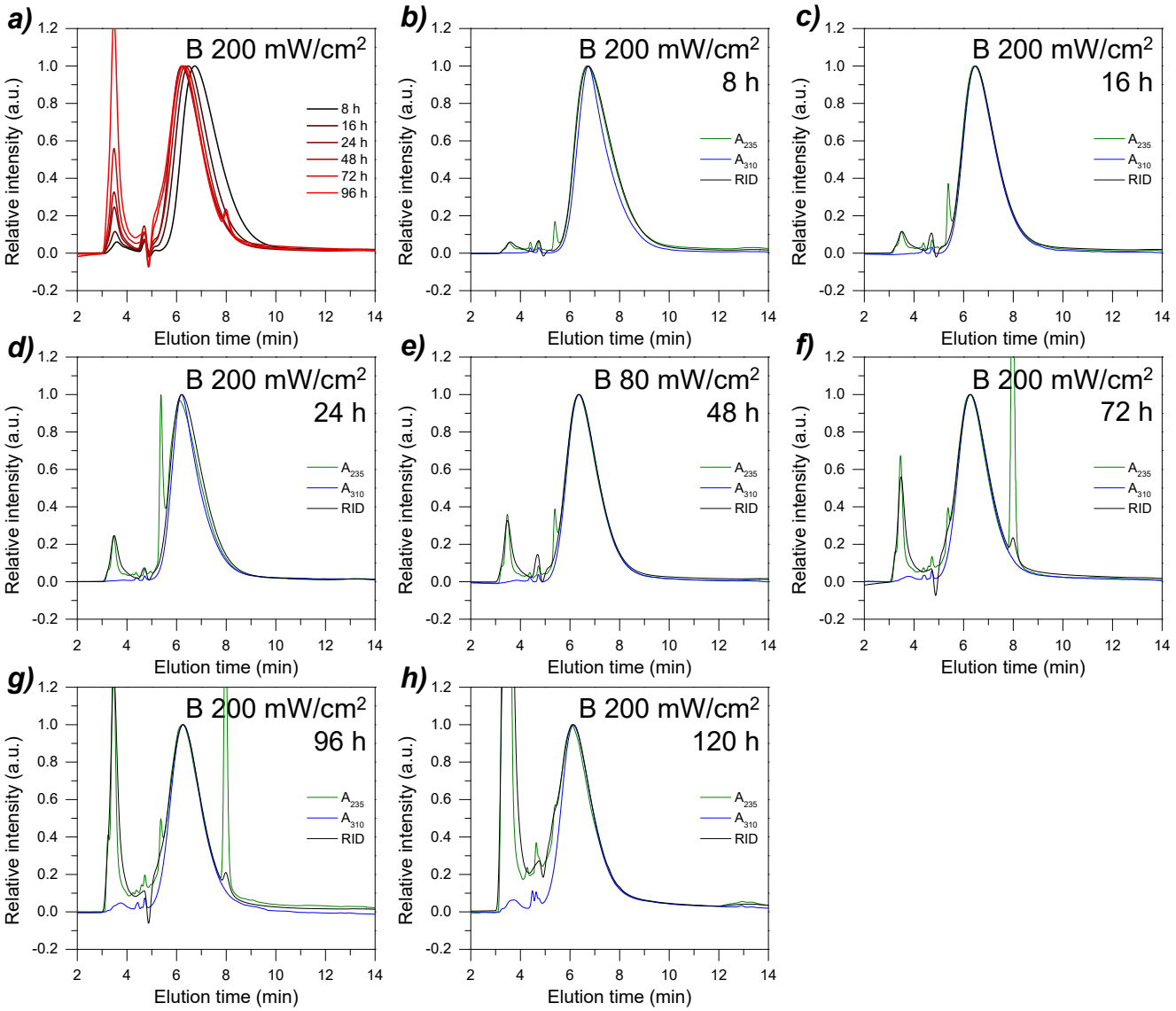


Figure S8. HPLC traces of samples depending on light intensity and irradiation time: a-h) 200 mW/cm^2

Reaction time	$F_{dead,45}$ [a)]	$F_{dead,80}$ [b)]	$F_{dead,200}$ [c)]
8 h	-	-	3.5
16 h	-	-	6.5
24 h	2.9	3.6	8.8
48 h	5.7	6.3	14.6
72 h	6.2	9.4	24.3
96 h	7.8	12.8	30.8
120 h	-	-	43.8

Table S2. a) dead fraction of samples irradiated under 45 mW/cm^2 blue LEDs, b) dead fraction of samples irradiated under 80 mW/cm^2 blue LEDs, c) dead fraction of samples irradiated under 200 mW/cm^2 blue LEDs. 200 mW/cm^2 samples were collected with longer timeframe to check if any saturation of values occur. 45 mW/cm^2 and 80 mW/cm^2 samples were collected only at 24 hours intervals from 24 hours to 96 hours.

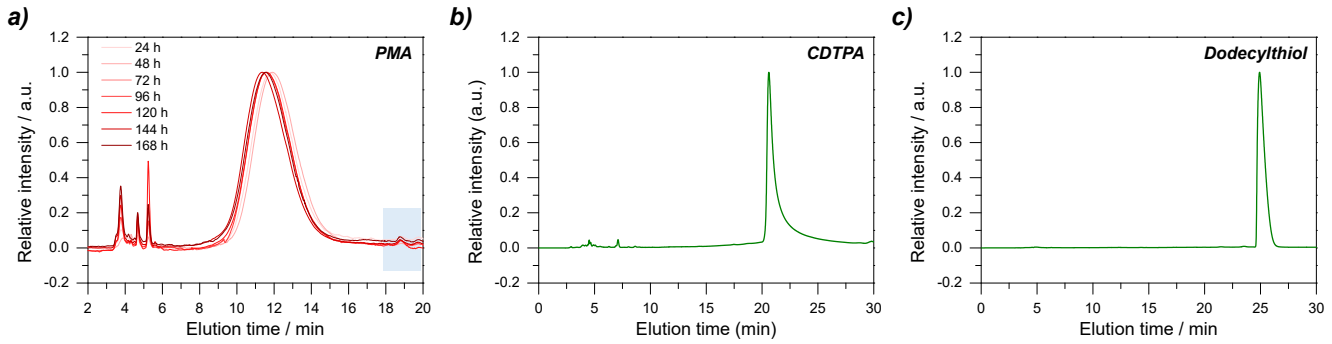
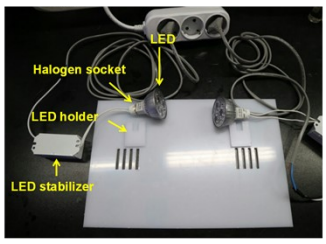
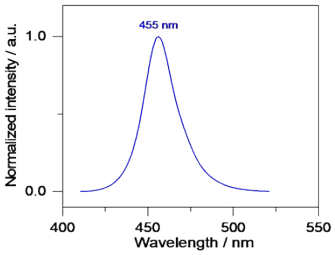


Figure S9. HPLC traces(A_{235}) of: a) PMA(DP=25) prepared via photoiniferter-RAFT polymerization. Blue box indicates small molecule side products in the sample, b) CDTPA, c) dodecylthiol

a) Photoreactor set-up

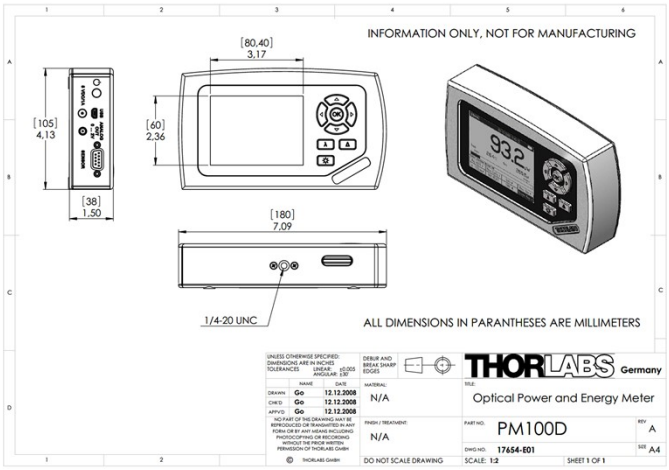


b) LED emission spectrum



d) Photoreactor for r.t. reaction

c) Optical power and energy meter (Thorlabs, PM100D)



e) Photoreactor for elevated temperature

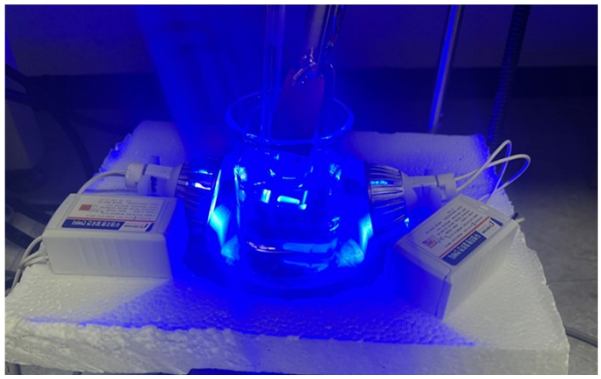


Figure S10. Experimental set-up. a-d) Photoreactor was custom built with precisely cut PMMA plates. Commercial MR16 blue LEDs and halogen sockets were used. LED intensity was measured using THORLABS PM100D optical power and energy meter. An external electric fan was installed in the surrounding to cool the heat from the LEDs. Temperature of the reaction was measured using an IR thermometer e) Photoreactor set-up for reaction at elevated temperature experiments. Temperature was measured with mercury-in-glass thermometer.

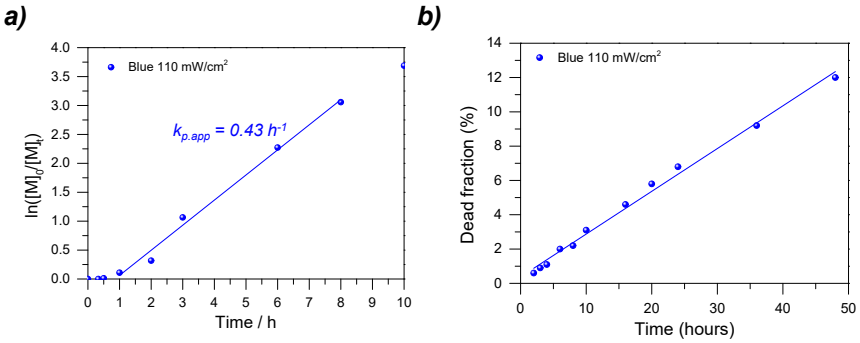


Figure S11. Reproducibility experiment of key observation. Experiment was conducted with 110 mW/cm^2 at room temperature. All the other conditions were kept the same. a) Pseudo-first order kinetics plot. b) Dead chain fraction calculated from integration of RI signals. Integration was performed up to 48 hours.