Supporting Information

Catalyst-Free Selective Photoactivation of RAFT Polymerization: A Facile Route for Preparation of Comb-like and Bottlebrush Polymers

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EXPERIMENTAL SECTION

Materials: Methyl methacrylate (MMA, 99%), methyl acrylate (MA, 99%), *N,N*-dimethylacrylamide (DMA, 99%), 2-hydroxyethyl methacrylate (HEMA, 98%), 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%), *N*-ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide (EDC), 4-dimethylaminopyridine (DMAP) were all purchased from Aldrich. Dichloromethane (DCM) and dimethyl sulfoxide (DMSO) were purchased from Fischer Scientific**.** De-inhibition of monomers was carried out by percolating over a basic alumina column (Ajax Chemical, AR). Thiocarbonylthiol compound: 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA) and 2-(2-(n-butyltrithiocarbonate)- propionate)ethyl methacrylate (BTPEMA) were synthesized according to literature procedures.[1, 2] 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) and 2-(dodecylthiocarbonothioylthio)propionic acid **(**DTPA) were purchased from Boron Molecular.

Synthesis of BTPA. Around 25 g of NaOH pellets were dissolved in 50 mL water (50% w/v). The pellets were slowly added into water to prevent exotherm. A 50% NaOH solution (16 mL, containing 8.00 g, 200 mmol of NaOH) was added to a stirred mixture of butanethiol (21.38 mL, 18.00 g, 200 mmol) and water (30 mL). Acetone (10 mL) was then added, and the resulting clear, colorless solution was stirred for 30 minutes then cooled to near-room temperature. Carbon disulfide (13.5 mL, 17.1 g, 225 mmol) was added resulting in clear orange solution. This was stirred for 30 minutes. The mixtures were then cooled in an ice bath to an internal temperature of 0°C. 2-Bromopropanoic acid (18.5 mL, 31.365 g, 205 mmol) was then added drop by drop with the reaction mixture in an ice bath. This was followed by 50% NaOH (16.4 mL, 8.2 g, 205 mmol) added drop by drop with the reaction mixture remaining in the ice bath. When the exotherm had stopped, the ice bath was removed and water (30 mL) was added. The reaction was stirred at ambient temperature for 24 h before diluting with water (50 mL) and stirring and cooling in an ice bath so that the reaction mixture reaches and internal temperature of 0°C. This was followed by the addition of 10 M HCl (60 mL) drop by drop over until a yellow oil separation was observed. The separated oil was continuously stirred at 0°C until the oil solidified. The solid was collected by suction filtration, pressed and washed with cold water, and dried under reduced pressure to a state of dryness. The yellow solid was recrystallized from hexane to give bright yellow microcrystals (41.3763 g, 87%). The big batch of the synthesized BTPA was kept in the freezer. A small portion (10 g) was recrystallized again from hexane for use in further experiments. ^{1}H NMR of recrystallized BTPA (**Figure S6**) is shown below.

Synthesis of BTPEMA. BTPA was further modified via EDC coupling to yield BTPEMA.[1] BTPA (2 grams, 8.4 mmol) was dissolved in 5 mL of DCM before the addition of HEMA (1.64 grams, 12.6 mmol, 1.528mL). The reaction vessel was placed in an ice bath (0 °C) before purging under nitrogen for 10 minutes. A solution of EDC (1.956 grams, 12.6 mmol) and DMAP (50 mg, 0.4 mmol) in 5 mL DCM was then added dropwise to the reaction mixture in the ice bath. The reaction mixture was degassed for additional 10 minutes followed by stirring for 48 hours at room temperature to allow esterification reaction to take place. Flash chromatography in 100% DCM was then carried out to purify the final product. DCM was removed by drying under air and a yellow viscous product was obtained. ^{1}H NMR of the final product is as shown in **Figure S12**.

Instrumentation

Gel Permeation Chromatography (GPC) was used for characterization of synthesized polymer with tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) as eluents. DMF GPC analysis with different polymer samples was conducted with a Waters 515 pump and Wyatt Optilab differential refractometer using poly(styrene sulfonate) columns (Styrogel 10^5, 10^3, and 10^2 Å) in 50 mM LiBr DMF solution as an eluent at 50 °C and at a flow rate of 1 mL min^{-1} . THF GPC analysis was carried out with Waters 515 HPLC pump and Waters 2414 refractive index detector. PSS columns (SDV 10^2, 10^3, 10^5 Å) was used with tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL min^{-1} at 35°C. Linear PMMA standards were used for GPC calibration with GPC results analyzed in WinGPC 7.0 software from PSS for the THF GPC and DMF GPC.

Nuclear Magnetic Resonance (^{1}H NMR) was carried out with Bruker Ultrashield 500 MHz operating at 500 MHz for ^{1}H using $CDCl_3$ as the solvent. Tetramethylsilane (TMS) was used as a reference with chemical shift (δ) of sample measured in ppm downfield from TMS.

Atomic Force Microscopy (AFM) images were acquired with a Veeco Dimension 3100 AFM in tapping mode. The silicon AFM probes with aluminum reflex coating used were the Tap300AI-G from BudgetSensors with a nominal resonant frequency of 300 kHz and a spring constant of approximately 40 Nm^{-1}. Images were acquired at a pixel resolution of 512 and a scan rate of 1 Hz. Polymer sample (PBTPEMA$_{480}$-*graft*-PDMA$_{38}$) was diluted in chloroform with a final concentration of 0.004 mg/mL and filtered through a 0.22 μm PTFE syringe filter using a syringe. A fresh cleaved mica substrate was used to spin coat the polymer. The images obtained were processed with ImageJ software to create a JPEG file and the length of the brushes were calculated with the JPEG image in Gwyddion software.

UV-vis Spectroscopy. UV-vis spectra were recorded using a CARY 5000 spectrophotometer (Varian).

Photopolymerization was carried out in photoreactors consisting of visible light LEDs lined around crystallization dishes (diameter of 15 cm). The narrow wavelength LEDs (green LEDs (520-525nm) and blue LEDs (465-470nm)) were purchased from aspectLED.

General procedure for thermal RAFT polymerization of methyl methacrylate (MMA) mediated by CDTPA with different concentrations of BTPA/DTPA.

A reaction stock solution consisting of DMSO (2.13 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), AIBN (0.77 mg) and CDTPA (19.7 mg, MW: 403.67) was prepared in a 10 mL round bottom flask covered with aluminum foil (MMA : CDTPA : AIBN = 200 : 1 : 0.1). The vessel was sealed with a septum before being sparged under nitrogen for 20 minutes. The reaction mixture was then placed in an oil bath at 70°C for 8 hours while still being wrapped with aluminum foil to avoid photolysis of RAFT agent. The final polymer mixture was analyzed with ^{1}H NMR to determine monomer conversion followed by THF GPC analysis to determine number average molecular weights (M_n) and dispersities (M_w/M_n). The thermal polymerization was repeated with different molar ratios of BTPA relative to CDTPA (CDTPA : BTPA = 1:1 and 1:5) with the following formulations.

MMA: CDTPA : BTPA = 1:1, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), AIBN (0.77 mg, 164.21) BTPA (11.63 mg, MW: 238.39, 0.049 mmol)

MMA: CDTPA : BTPA = 1:5, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPA (58.17 mg, MW: 238.39, 0.244 mmol)

Likewise, thermal polymerization of MMA was repeated in the presence of DTPA. These experiments were formulated as shown below.

MMA: CDTPA : DTPA = 1:0, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), AIBN (0.77 mg, 164.21)

MMA: CDTPA : DTPA = 1:1, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), AIBN (0.77 mg, 164.21), and DTPA (17.79 mg, MW: 364.63, 0.049 mmol)

MMA: CDTPA : DTPA = 1:5, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPA (58.17 mg, MW: 238.39, 0.244 mmol), and DTPA (88.97 mg, MW: 364.63, 0.244 mmol)

General procedure for kinetic studies of RAFT Photopolymerization of methyl methacrylate (MMA) mediated by CDTPA under green light irradiation with different concentrations of BTPA/DTPA.

A reaction stock solution consisting of DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67) was prepared in a glass vial covered with aluminum foil (MMA : CDTPA = 200 :1). The reaction mixture was sealed with a septum before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a green LED photoreactor (λ_{max} = 520 nm, 4.25 mW/cm^2) equipped with constant flow of cool air. Aliquots of the reaction mixture were taken at specific time points (every 30 minutes) during the reaction to determine monomer conversions through ^{1}H NMR analysis, and to determine number average molecular weights (M_n) and dispersities (M_w/M_n) through THF GPC analysis. The photopolymerization was repeated with different molar ratios of BTPA relative to CDTPA (CDTPA : BTPA = 1:1, 1:5, and 1:10) with the following formulations.

MMA: CDTPA : BTPA = 1:1, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPA (11.63 mg, MW: 238.39, 0.049 mmol)

MMA: CDTPA : BTPA = 1:5, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPA (58.17 mg, MW: 238.39, 0.244 mmol)

MMA: CDTPA : BTPA = 1:10, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPA (116.34 mg, MW: 238.39, 0.488 mmol)

Similarly, aliquots of the reaction mixture were taken at specific time points (every 30 minutes) during the reaction to determine monomer conversions through ^{1}H NMR analysis, and to determine number average molecular weights (M_n) and dispersities (M_w/M_n) through THF GPC analysis.

In the case of DTPA, a similar photopolymerization approach was applied using the formulations listed below.

MMA: CDTPA = 1:1, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67)

MMA: CDTPA : DTPA = 1:1, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), and DTPA (17.79 mg, MW: 364.63, 0.049 mmol)

MMA: CDTPA : DTPA = 1:5, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), and DTPA (88.97 mg, MW: 364.63, 0.244 mmol)

MMA: CDTPA : DTPA = 1:10, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), and DTPA (177.93 mg, MW: 364.63, 0.488 mmol)

Aliquots of the reaction mixture were taken at specific time points (every 1 hour) during the reaction to determine monomer conversions through ^{1}H NMR analysis, and to determine number average molecular weights (M_n) and dispersities (M_w/M_n) through THF GPC analysis.

The final polymer mixtures for the different concentrations of BTPA and DTPA were purified through precipitation with methanol. The supernatant and pellet obtained during precipitation were analyzed with ^{1}H NMR.

General procedure for copolymerization of methyl methacrylate (MMA) and 2-(2-(n-butyltrithiocarbonate)-propionate)ethyl methacrylate (BTPEMA) mediated by CDTPA under green light irradiation.

A reaction stock solution consisting of DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), BTPEMA (85.5 mg, MW: 350.53, 0.2439 mmol) and CDTPA (19.7 mg, MW: 403.67) was prepared in a glass vial covered with aluminum foil (MMA : CDTPA : BTPEMA = 200 : 1 : 5). The reaction mixture was sealed with a septum before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a green LED photoreactor (λ_{max} = 520 nm, 4.25 mW/cm^2) equipped with constant flow of cool air. Aliquots of the reaction mixture were taken at specific time points (every 1 hour) during the reaction to determine monomer conversions through ^{1}H NMR analysis, and to determine number average molecular weights (M_n) and dispersities (M_w/M_n) through DMF GPC analysis. The photopolymerization was repeated with different molar ratio of BTPEMA relative to CDTPA (CDTPA : BTPEMA = 1 : 10) with the following formulation. MMA: CDTPA : BTPEMA = 1:1:10, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), and BTPEMA (171 mg, MW: 350.53, 0.4878 mmol). The polymer solutions were then purified via precipitation in methanol and analyzed with ^{1}H NMR.

General procedure for chain extensions of PMMA-*rand*-PBTPEMA$_4$ and PMMA-*rand*-PBTPEMA$_7$ with methyl acrylate under blue light irradiation.

A reaction stock solution consisting of DMSO (4.1 mL), MA (0.909 mL, 0.8632 g, 10 mmol), and PMMA-*rand*-PBTPEMA$_4$ (172 mg, M_n = 17 150, 0.01 mmol) was prepared in a glass vial covered with aluminum foil. The total mole content of the chain transfer agents (CTAs) on the random copolymer is estimated to be 0.05 mmol leading to a molar ratio of MA : PMMA-*rand*-PBTPEMA$_4$ of 200 : 1. The reaction mixture was sealed with a septum before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a blue LED photoreactor (λ_{max} = 460 nm, 6.5 mW/cm^2) equipped with constant flow of cool air. Aliquots of the reaction mixture were taken at specific time points (every 1 hour) during the reaction to determine monomer conversions through ^{1}H NMR analysis, and to determine number average molecular weights (M_n) and

dispersities (M_w/M_n) through DMF GPC analysis. The chain extension was repeated for PMMA-*rand*-PBTPEMA$_7$ with DMSO (6.566 mL), MA (1.453 mL, 1.381 g, 16.041 mmol), and PMMA-*rand*-PBTPEMA$_7$ (170.5 mg, M_n = 17 000, 0.01 mmol) prepared in a glass vial covered with aluminum foil. The total mole content of the chain transfer agents (CTAs) on the random copolymer is estimated to be 0.08 mmol leading to a molar ratio of MA : PMMA-*rand*-PBTPEMA$_7$ of 200 : 1. The final polymer products were then purified via precipitation in methanol and analyzed with ^{1}H NMR.

General procedure for homopolymerization of BTPEMA under green light irradiation

A reaction stock solution consisting of dioxane (0.678 mL), BTPEMA (0.7134 g, 2.035 mmol), and CDTPA (1.369 mg, MW: 403.67) was prepared in a glass vial covered with aluminum foil (BTPEMA : CDTPA = 600:1). The reaction mixture was sealed with a septum before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a green LED photoreactor (λ_{max} = 520 nm, 4.25 mW/cm^2) equipped with constant flow of cool air. Aliquots of the reaction mixture were taken before and after the polymerization to determine monomer conversions via ^{1}H NMR analysis using dioxane as the internal standard. The number average molecular weight (M_n) and dispersity (M_w/M_n) of the final polymer product was determined via DMF GPC analysis. After 22 hours of irradiation, 80% monomer conversion was reported by ^{1}H NMR leading to an average incorporation of 480 BTPEMA repeating units ($M_{n,NMR}$ = 168 300) in each polymer chain. GPC analysis revealed a final polymer product with M_n = 97 340 and M_w/M_n = 1.38. The final polymer products were then purified via precipitation in diethyl ether and analyzed with ^{1}H NMR.

General procedure for grafting DMA from PBTPEMA$_{480}$ under blue light irradiation

A reaction stock solution consisting of dioxane (1.153 mL), DMA (1.225 mL, 1.1789 g, 11.89 mmol), and PBTPEMA (41.6 mg, M_n = 168 300, 0.247 mmol) was prepared in a glass vial covered with aluminum foil. The total mole content of the chain transfer agents (CTAs) on PBTPEMA$_{480}$ was estimated to be 0.119 mmol leading to a molar ratio of DMA : PBTPEMA$_{480}$ of 100 : 1. The reaction mixture was sealed with a septum before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a blue LED photoreactor (λ_{max} = 460 nm, 14.9 mW/cm^2) equipped with constant flow of cool air. Aliquots of the reaction mixture were taken before and during the irradiation at specific time intervals (every 1 hour) to determine monomer conversions through ^{1}H NMR analysis using dioxane as the internal standard, and to determine number average molecular weights (M_n) and dispersities (M_w/M_n) through DMF GPC analysis. The final polymer product was then purified via precipitation in diethyl ether and analyzed with ^{1}H NMR.

Table S1. Polymerization of methyl acrylate under blue or green light irradiation with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) as the primary RAFT agent in the presence or absence of 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA)/ 2-(dodecylthiocarbonothioylthio)propionic acid **(**DTPA) as the secondary RAFT agent.[a]

no.	Exp. Cond.[a] [MA] : [CDTPA] : [BTPA or DTPA]	Additives	Conditions[b]	Time (h)	α[c] (%)	$M_{n,th.}$[d]	$M_{n,GPC.}$[e]	M_w/M_n[e]
1	200 : 1 : 0	None	Green	19	< 5	-	-	-
2	200 : 1 : 1	DTPA	Green	19	< 5	-	-	-
3	200 : 0 : 1	DTPA	Green	12	< 5	-	-	-
4	200 : 0 : 1	DTPA	Blue	13	66	11 700	11 000	1.11
5	200 : 1 : 1	DTPA	Blue	13	74	13 000	6 800	1.10
6	200 : 1 : 1	BTPA	Green	12	0	-	-	-
7	200 : 0 : 1	BTPA	Blue	12	97	17 000	15 400	1.09
8	200 : 1 : 1	BTPA	Blue	4	63	10 900	5 700	1.13

Note: [a]Reactions were performed at room temperature with 50 % v/v monomer concentration in DMSO. [b]Reaction mixtures were irradiated under visible green (λ_{max} = 520 nm, intensity = 4.25 mW/cm^2) or blue (λ_{max} = 465 nm, intensity = 6.5 mW/cm^2) light LEDs. [c]Monomer conversions were determined by using ^{1}H NMR spectroscopy. [d]Theoretical molecular weights were calculated using the following equation: $M_{n,th} = [M]_o/[RAFT]_o \times MW^M \times \alpha + MW^{CDTPA}$, where $[M]_o$, $[RAFT]_o$, MW^M, α, and MW^{CDTPA} correspond to initial monomer concentration, initial CDTPA concentration, molar mass of monomer, monomer conversion determined by ^{1}H NMR, and molar mass of CDTPA. [e]Molecular weight and dispersity (M_w/M_n) values were determined by THF GPC analysis calibrated using poly(methyl methacrylate) standards.

Note: Polymerization of MA can only be promoted under blue light irradiation with CDTPA, DTPA and BTPA. Although it was possible to photolyze CDTPA under green light irradiation in the presence of MA(**Table S1**, entries 1,2 & 6), the change of R-group from tertiary carbon to secondary carbon leaving group, after the addition of MA units, prevented further reinitiation under green light. As DTPA has no absorption under green light, no polymerization of MA (**Table S1**, entry 3) was seen. Under blue light irradiation, polymerization of MA was made possible with DTPA (**Table S1**, entry 4) with good control over molecular weight and molecular weight distributions. As DTPA and CDTPA have absorptions under the blue region, this led to the photolysis of both the RAFT agents through $n \rightarrow \pi^*$ electronic transition. Polymerization of MA under blue light irradiation with equimolar CDTPA and DTPA (**Table S1**, entry 5) led to a polymer with molecular weight half of that of the theoretical value (calculated based on activation of CDTPA only) as both CDTPA and DTPA were initiated under blue light irradiation. Similar observations were also made for polymerization of MA with BTPA and mixture of BTPA and CDTPA (**Table S1**, entries 7&8).

Table S2. Polymerization of methyl methacrylate under thermal conditions with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) as the primary RAFT agent in the presence or absence of 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA)/ 2-(dodecylthiocarbonothioylthio)propionic acid **(**DTPA) as the secondary RAFT agent.[a]

no.	Exp. Cond.[a] [MMA] : [CDTPA] : [BTPA or DTPA]:[AIBN]	Additives	Time (h)	α[b] (%)	$M_{n,th.}$[c]	$M_{n,GPC.}$[d]	M_w/M_n[d]
1	200 : 1 : 0 : 0.1	None	8	51	10 600	11 200	1.14
2	200 : 1 : 1 : 0.1	DTPA	8	52	10 700	10 400	1.14
3	200 : 1 : 5 : 0.1	DTPA	8	48	10 000	10 600	1.17
4	200 : 1: 0 : 0.1	None	8	58	11 600	8 700	1.27

5	200 : 1 : 1 : 0.1	BTPA	8	57	11 400	9 500	1.20
6	200 : 1 : 5 : 0.1	BTPA	8	61	12 100	9 500	1.23

Note: [a]Reactions were carried out thermally with the use of 2,2′-Azobis(2-methylpropionitrile) (AIBN) at 70°C with monomer concentrations of 32 % v/v in DMSO. Reactions with different concentrations of DTPA/BTPA were carried out in sets: entries 1-3 as the first set and entries 4-6 as the second set. [b]Monomer conversion was determined by using ^{1}H NMR spectroscopy. [c]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_o/[RAFT]_o \times MW^M \times \alpha + MW^{CDTPA}$, where $[M]_o$, $[RAFT]_o$, MW^M, α, and MW^{CDTPA} correspond to initial monomer concentration, initial CDTPA concentration, molar mass of monomer, conversion determined by ^{1}H NMR, and molar mass of CDTPA. [d]Molecular weight and dispersity index (M_w/M_n) were determined by THF GPC analysis calibrated to poly(methyl methacrylate).

Table S3. Ab-initio calculations for propionic acid R-groups on DTPA/BTPA and PMMA initialized R-group on CDTPA performed by Coote and coworkers.[3, 4] (RSE: Radical Stablization Energy, ΔH_{CT} : chain transfer enthalpy)

RAFT Agent	R-group	Stability of RAFT Agent (kJ/mol)	RSE of R• (kJ/mol)	ΔH_{CT} (kJ/mol)
BTPA/DTPA	$CH(CH_3)COOH$	-8.4	41.3	-33.2
CDTPA-PMMA	$C(CH_3)_2COOCH_3$	-8.3	54.9	-35.9
CDTPA	$C(CH_3)_2CN$	-15.8	59.0	-56.6

Notes: (A)The R-groups described here are either similar or closest analogues of R-groups of the RAFT agents used in the experiments. The general trend provided by these analogues act as models for comparison of the different R-groups of the RAFT agents used and enable the establishment of a common trend. (B) Under green light irradiation, CDTPA undergoes photolysis and generates a radical that reacts with MMA to form PMMA radical that can either be capped to form a dormant species or react with another CDTPA to enable the cleavage of R-group. In initial stages of polymerization, although is possible for the photolyzed CDTPA R-group radical

to form adduct radical with BTPA/DTPA, the probability of this event is extremely low due to the presence of excess monomer which lead to higher probability of the CDTPA R-group radical to react with the monomer instead of BTPA/DTPA. Even if the CDTPA R-group radical reacts with BTPA/DTPA to form adduct radical, this will not result in the β-scission of the BTPA/DTPA R-group as the RSE and ΔH_{CT} is much higher for the former compared to the latter.

Table S4. Grafting of *N,N*-dimethylacrylamide (DMA) from PBTPEMA under blue light irradiation (λ_{max} = 465 nm, intensity = 14.9 mW/cm^2).[a]

Time (h)	α[b] (%)	$M_{n,th.}$[c]	$M_{n,GPC.}$[c]	M_w/M_n
0	-	168 700	97 300	1.38
1	10	577 900	165 100	1.32
2	22	1 154 600	308 500	1.21
3	38	1 923 500	434 800	1.19

Note: [a] Grafting of DMA from $PBTPEMA_{480}$, [DMA]:[$BTPEMA_{480}$] of 100 : 1 and 52% v/v monomer concentration performed in the absence of oxygen at room temperature. [b]Monomer conversion was determined by using ^{1}H NMR spectroscopy. [c]Theoretical molecular weight was calculated using the following equation: $M_{n,th} = [M]_o/[RAFT]_o \times MW^M \times \alpha + MW^{RAFT}$, where $[M]_o$, $[RAFT]_o$, MW^M, α, and MW^{RAFT} correspond to initial monomer concentration, PBTPEMA concentration, molar mass of monomer, conversion determined by ^{1}H NMR, and molar mass of PBTPEMA. [c]Molecular weight and dispersity index (M_w/M_n) were determined by DMF GPC analysis calibrated to poly(methyl methacrylate).

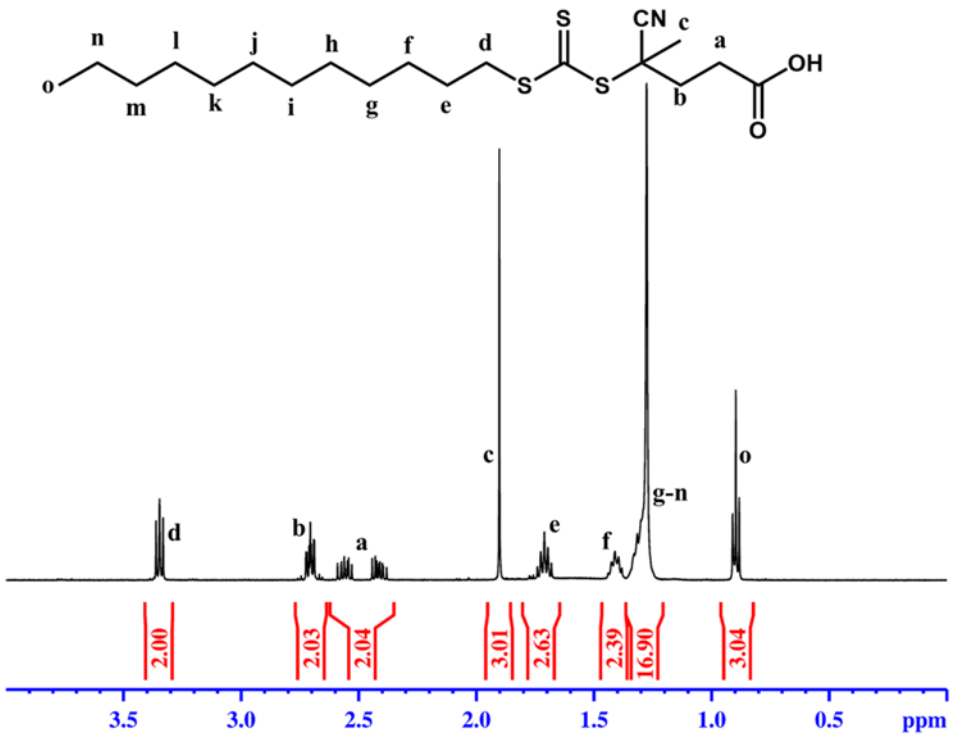

Figure S1. 500 MHz ^{1}H NMR spectrum of CDTPA RAFT agent in $CDCl_3$.

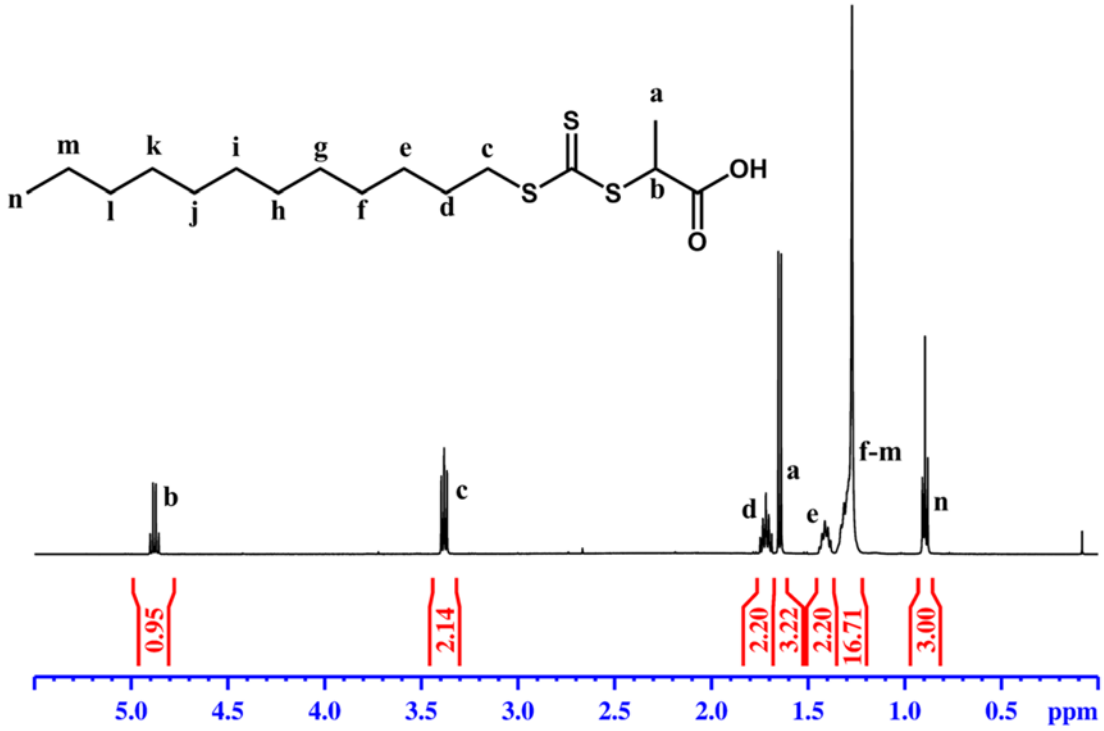

Figure S2. 500 MHz ^{1}H NMR spectrum of DTPA RAFT agent in $CDCl_3$.

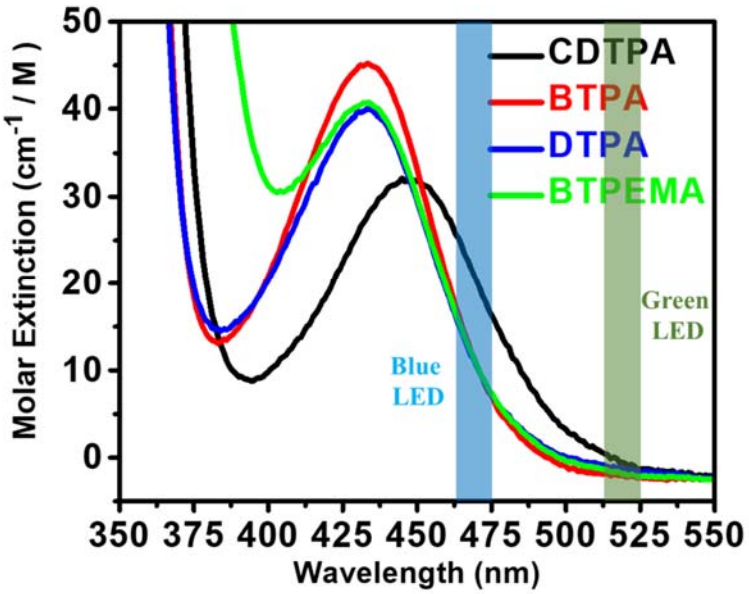

Figure S3. Optical absorption measurements of RAFT agents and emission of LEDs (λ_{max} = 520-525 nm for green and λ_{max} = 465-470) used in this study.

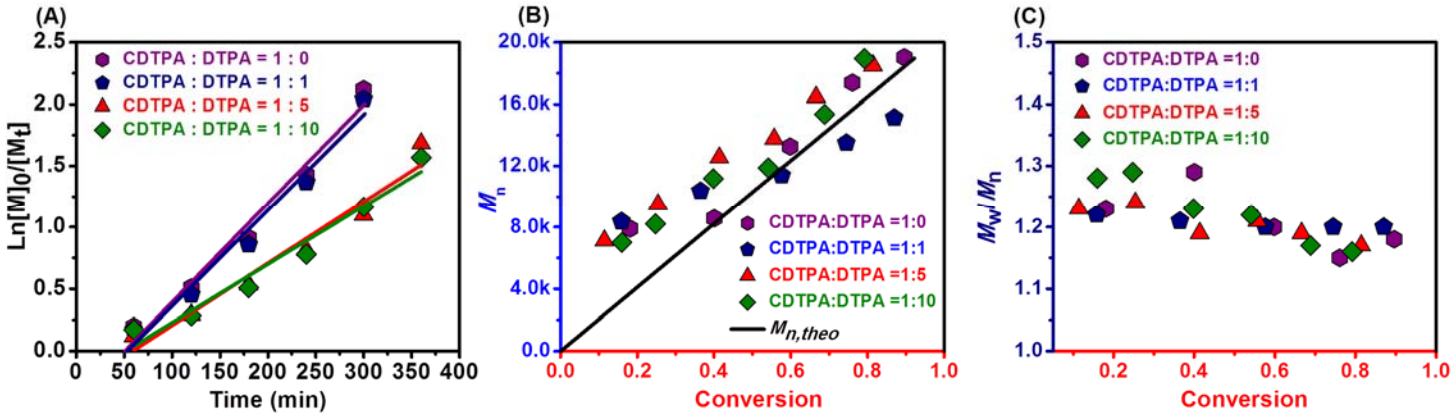

Figure S4. Polymerization of MMA mediated by CDTPA under green light irradiation performed in DMSO in the presence of different concentrations of DTPA (λ_{max} = 520 nm, intensity = 4.25 mW/cm^2) with [MMA]:[CDTPA] = 200 : 1, 50% v/v monomer concentration. (A) Plot of Ln([M$_0$]/[M]$_t$) *vs.* exposure time in the presence of different concentrations of DTPA ([CDTPA]:[DTPA] = 1:0, 1:1, 1:5, and 1:10 with k_p^{app} = 8.2 × 10^{-3} min^{-1}, 7.7 × 10^{-3} min^{-1}, 5.0 × 10^{-3} min^{-1}, 4.7 × 10^{-3} min^{-1}, respectively); (B) plot of M_n *vs.* conversion for different concentrations of DTPA; and (C) plot of M_w/M_n *vs.* conversion for different concentrations of DTPA.

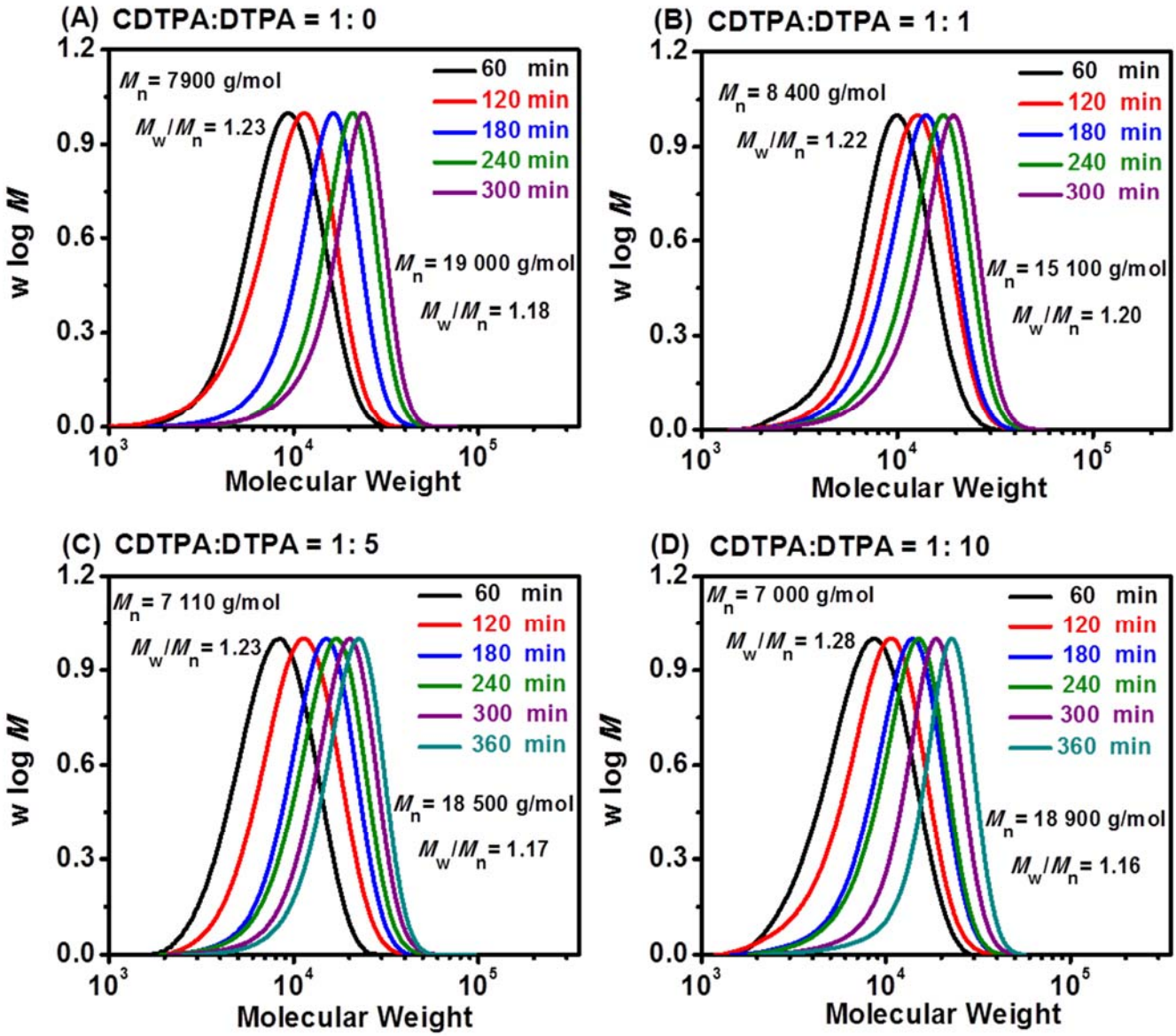

Figure S5. GPC traces for polymerization of methyl methacrylate (MMA) mediated by 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) under green light irradiation (λ_{max} = 520 nm, intensity = 4.25 mW/cm^2) in the presence of different concentrations of 2-(dodecylthiocarbonothioylthio)propionic acid **(**DTPA) ([MMA]:[CDTPA] = 200 : 1, 50% v/v monomer concentration). (A) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:DTPA = 1:0; (B) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:DTPA = 1:1; (C) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:DTPA = 1:5; and (D) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:DTPA = 1:10.

Figure S6. 500 MHz ^{1}H NMR spectrum of BTPA RAFT agent in $CDCl_3$.

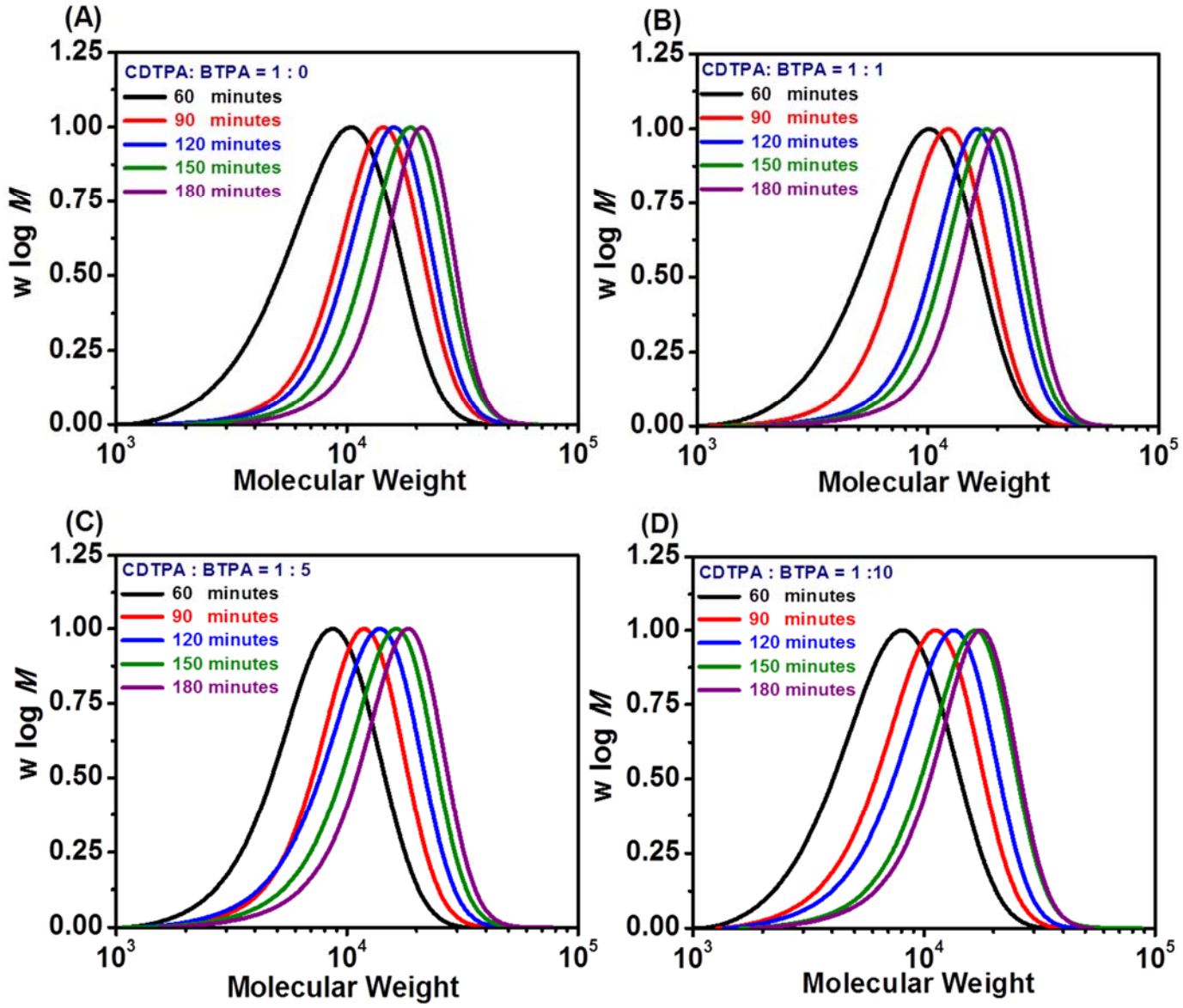

Figure S7. GPC traces for polymerization of methyl methacrylate (MMA) mediated by 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) under green light irradiation (λ_{max} = 520 nm, intensity = 4.25 mW/cm^2) in the presence of different concentrations of 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA) ([MMA]:[CDTPA] = 200 : 1, 50% v/v monomer concentration). (A) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:BTPA = 1:0; (B) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:BTPA = 1:1; (C) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:BTPA = 1:5; and (D) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:BTPA = 1:10.

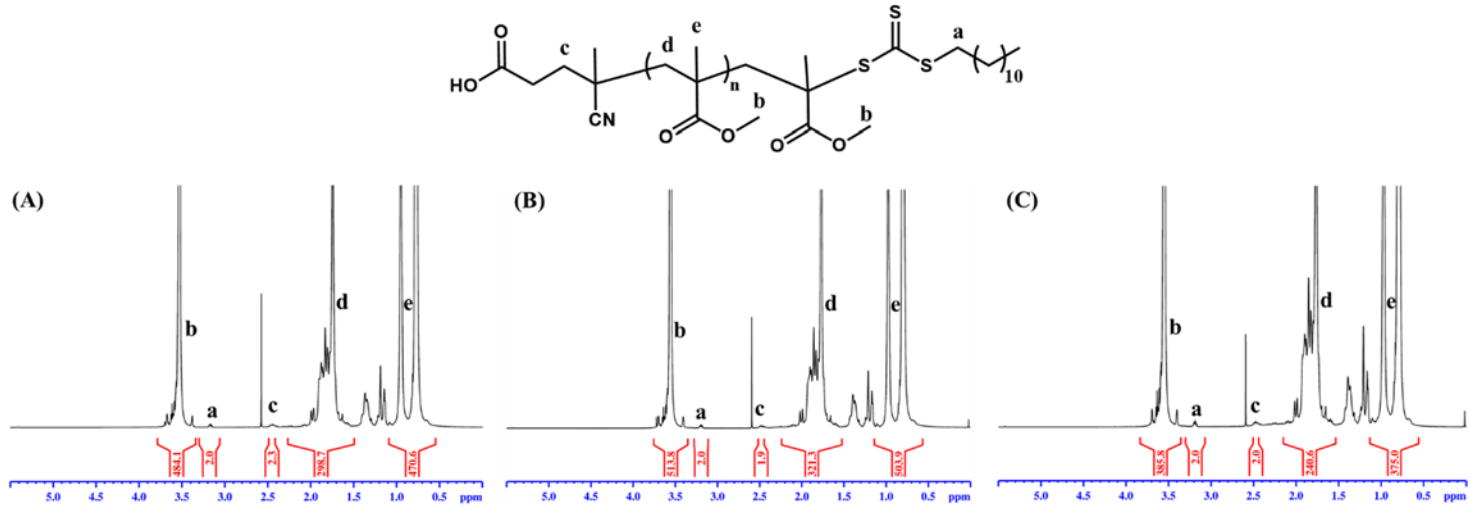

Figure S8. 500 MHz ^{1}H NMR spectrum of poly(methyl methacrylate) (PMMA, top structure) in $CDCl_3$ synthesized in the presence of different concentrations of BTPA. (A) PMMA synthesized in the presence of [CDTPA]:[BTPA] = 1 : 0 with $M_{n,NMR}$ = 16 600, $M_{n,GPC}$ = 17 400, and $M_{n,theo}$ = 15 500; (B) PMMA synthesized in the presence of [CDTPA]:[BTPA] = 1 : 1 with $M_{n,NMR}$ = 17 600, $M_{n,GPC}$ = 16 500 and $M_{n,theo}$ = 15 100; and (C) PMMA synthesized in the presence of [CDTPA]:[BTPA] = 1 : 5 with $M_{n,NMR}$ = 13 300, $M_{n,GPC}$ = 14 200 and $M_{n,theo}$ = 14 500.

* $M_{n,NMR}$ was determined using the following equation $M_{n,NMR} = (I^{3.6\ ppm}/3)/(I^{3.2\ ppm}/2) \times MW^{M} + MW^{RAFT}$ where $I^{3.6\ ppm}$ and $I^{3.2\ ppm}$ correspond to integration of proton **b** and **a**, respectively.

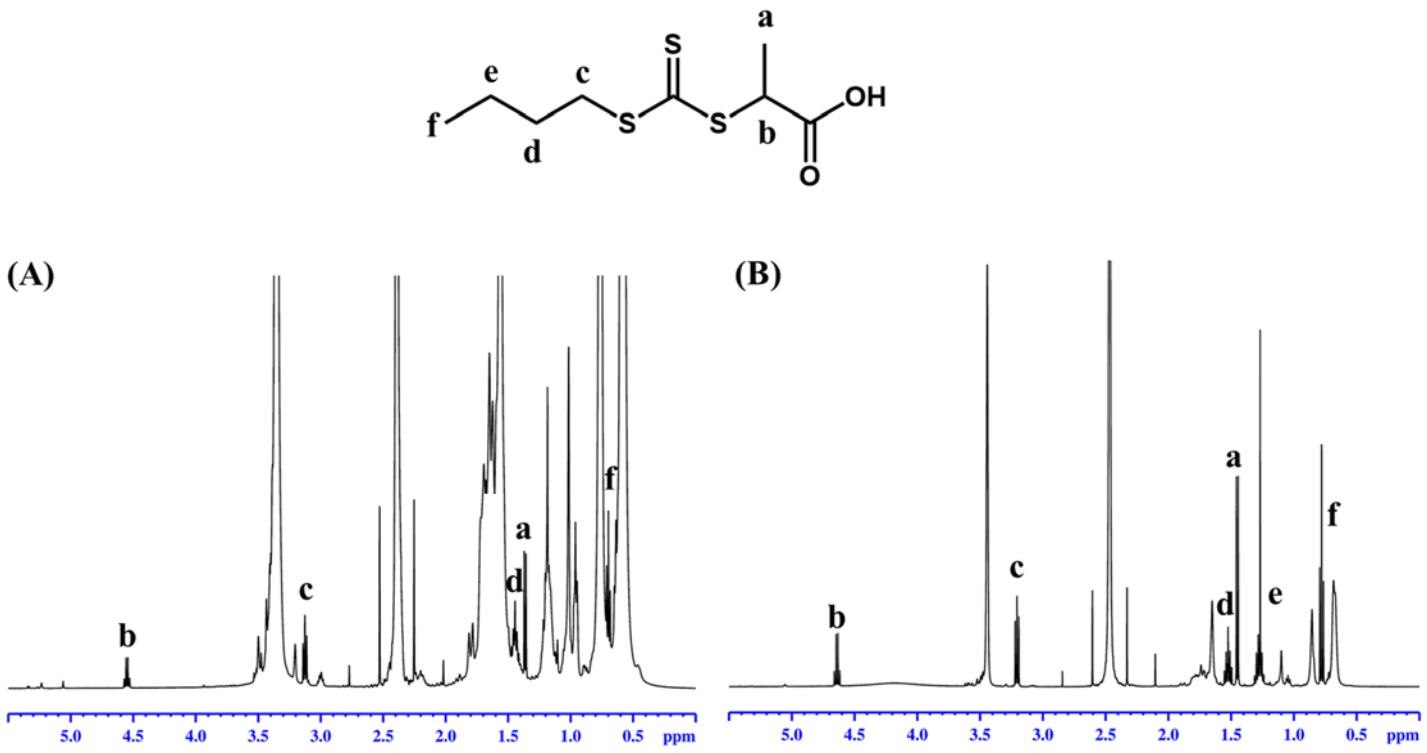

Figure S9. 500 MHz ^{1}H NMR spectrum of BTPA RAFT agent in $CDCl_3$ obtained from supernatant of PMMA purification through precipitation in methanol. (A) BTPA in supernatant obtained from PMMA synthesis with molar ratio of [CDTPA]:[BTPA] = 1 : 1 and (B)[CDTPA]:[BTPA] = 1 : 5.

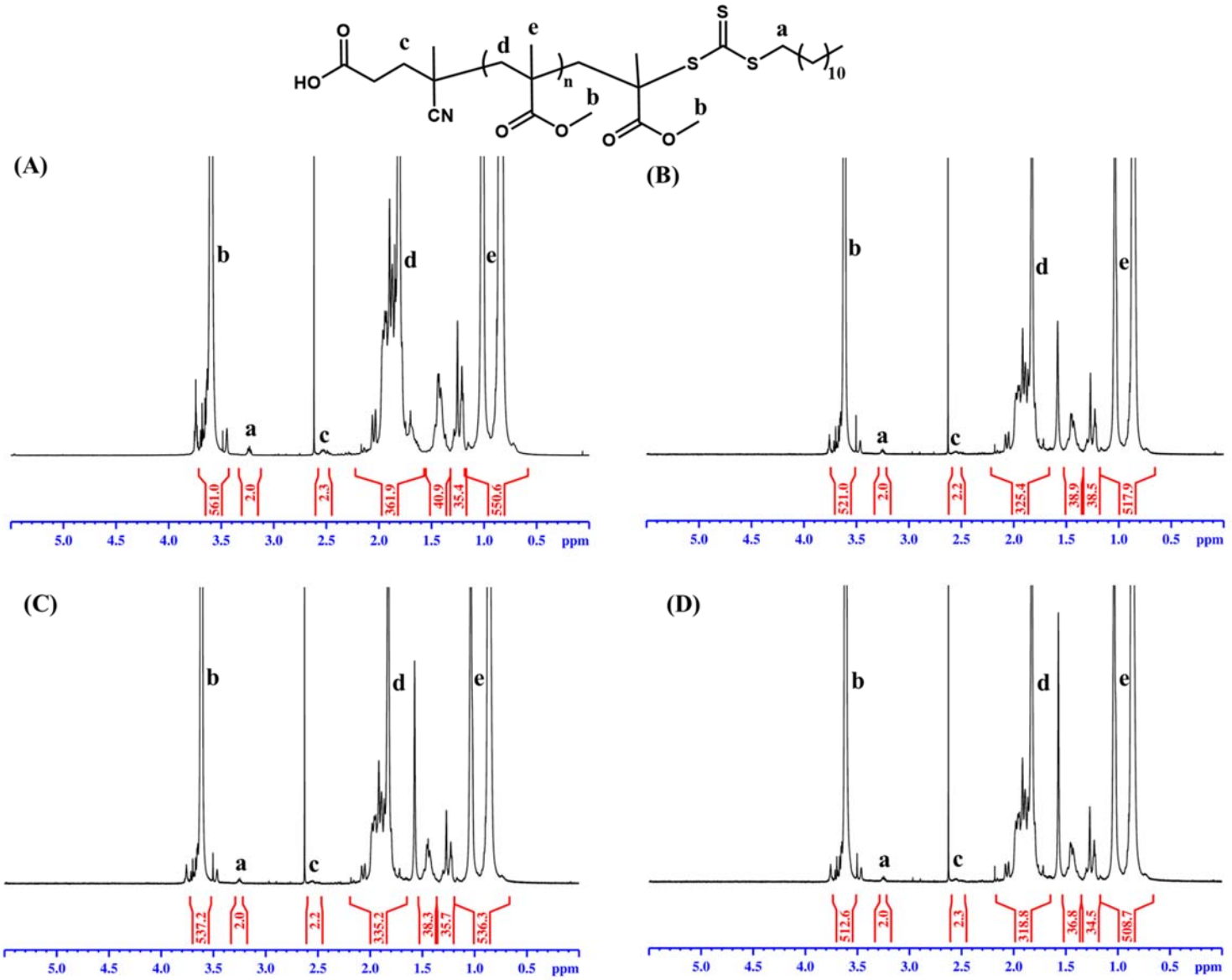

Figure S10. 500 MHz ^{1}H NMR spectrum of poly(methyl methacrylate) (PMMA, top structure) in $CDCl_3$ synthesized in the presence of different concentrations of DTPA. (A) PMMA synthesized in the presence of [CDTPA]:[DTPA] = 1 : 0 with $M_{n,NMR}$ = 19 100, $M_{n,GPC}$ = 19 000, and $M_{n,theo}$ = 18 400; (B) PMMA synthesized in the presence of [CDTPA]:[DTPA] = 1 : 1 with $M_{n,NMR}$ = 17 800, $M_{n,GPC}$ = 15 100 and $M_{n,theo}$ = 17 800; (C) PMMA synthesized in the presence of [CDTPA]:[DTPA] = 1 : 5 with $M_{n,NMR}$ = 18 300, $M_{n,GPC}$ = 18 500 and $M_{n,theo}$ = 16 700; and (D) PMMA synthesized in the presence of [CDTPA]:[DTPA] = 1 : 10 with $M_{n,NMR}$ = 17 500, $M_{n,GPC}$ = 18 900 and $M_{n,theo}$ = 16 300.

* $M_{n,NMR}$ was determined using the following equation $M_{n,NMR} = (I^{3.6\ ppm}/3)/(I^{3.2\ ppm}/2) \times MW^{M} + MW^{RAFT}$ where $I^{3.6\ ppm}$ and $I^{3.2\ ppm}$ correspond to integration of proton **b** and **a**, respectively.

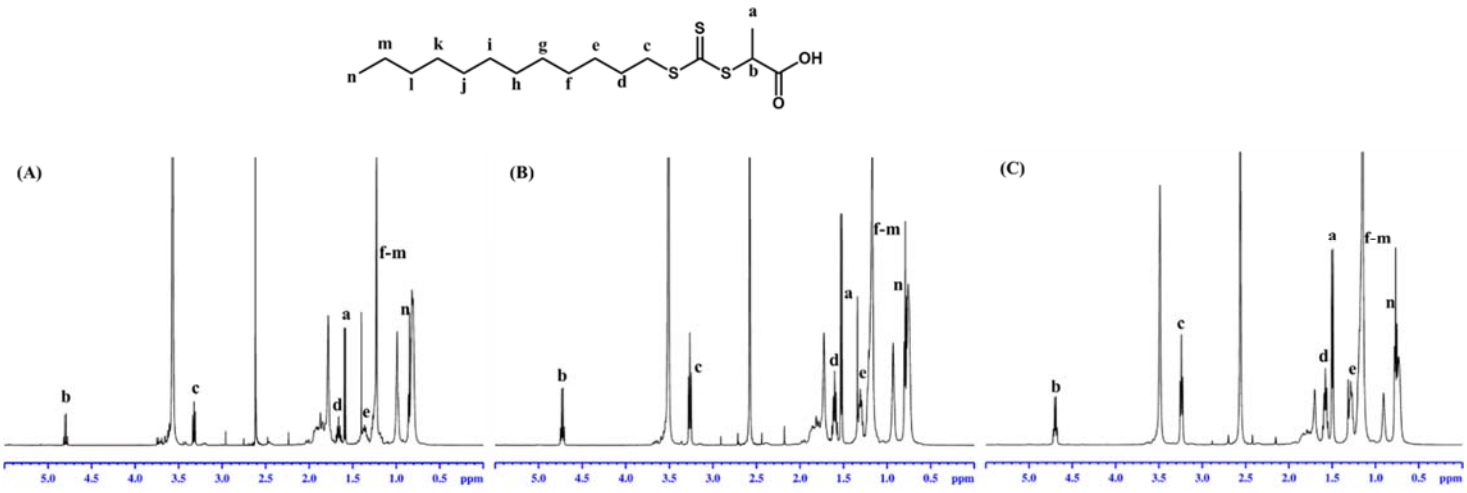

Figure S11. 500 MHz ^{1}H NMR spectrum of BTPA RAFT agent in $CDCl_3$ obtained from supernatant of PMMA purification through precipitation in methanol. (A) BTPA in supernatant obtained from PMMA synthesis with molar ratio of [CDTPA]:[DTPA] = 1 : 1, (B)[CDTPA]:[DTPA] = 1 : 5, and (C)[CDTPA]:[DTPA] = 1 : 10.

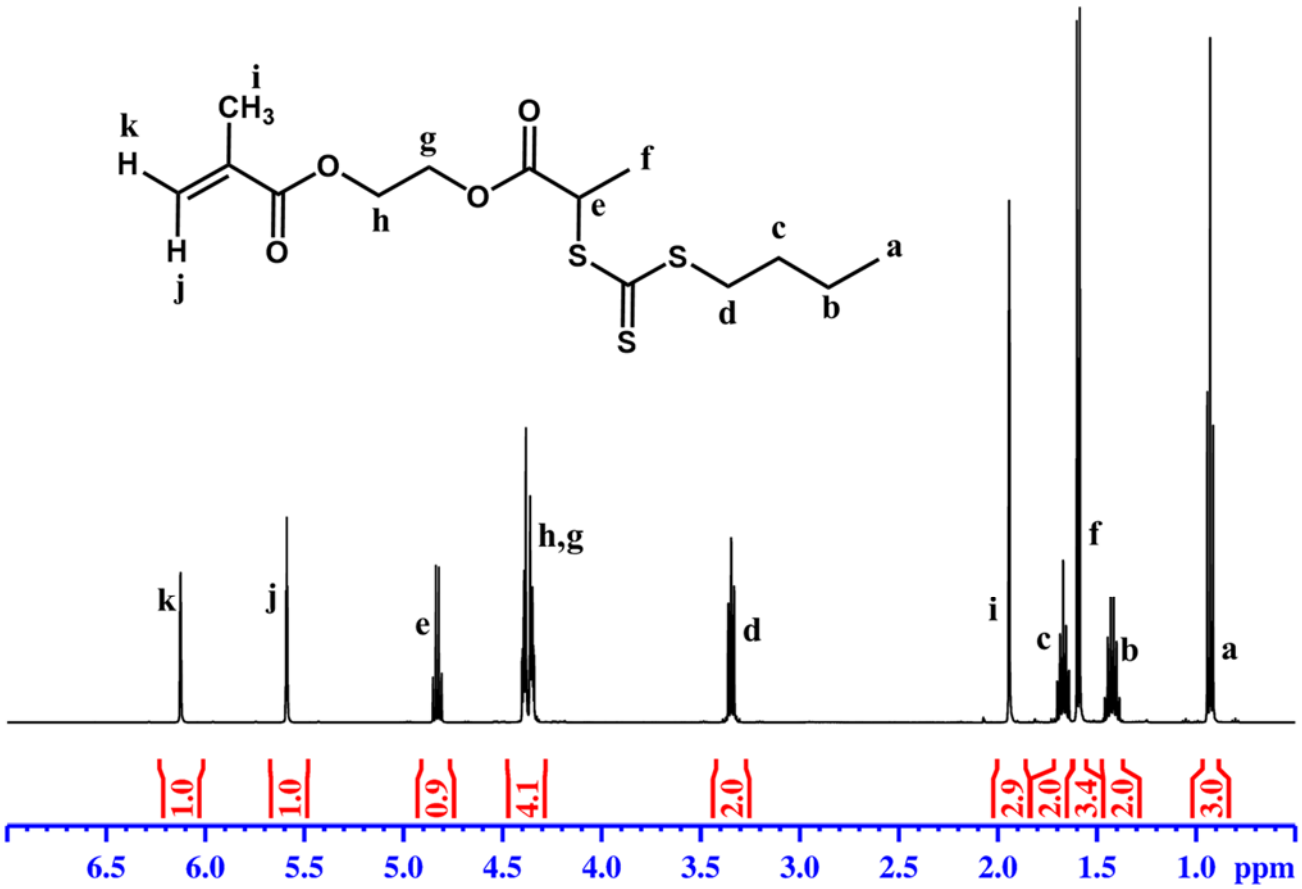

Figure S12. 500 MHz ^{1}H NMR spectrum of BTPEMA RAFT agent in $CDCl_3$.

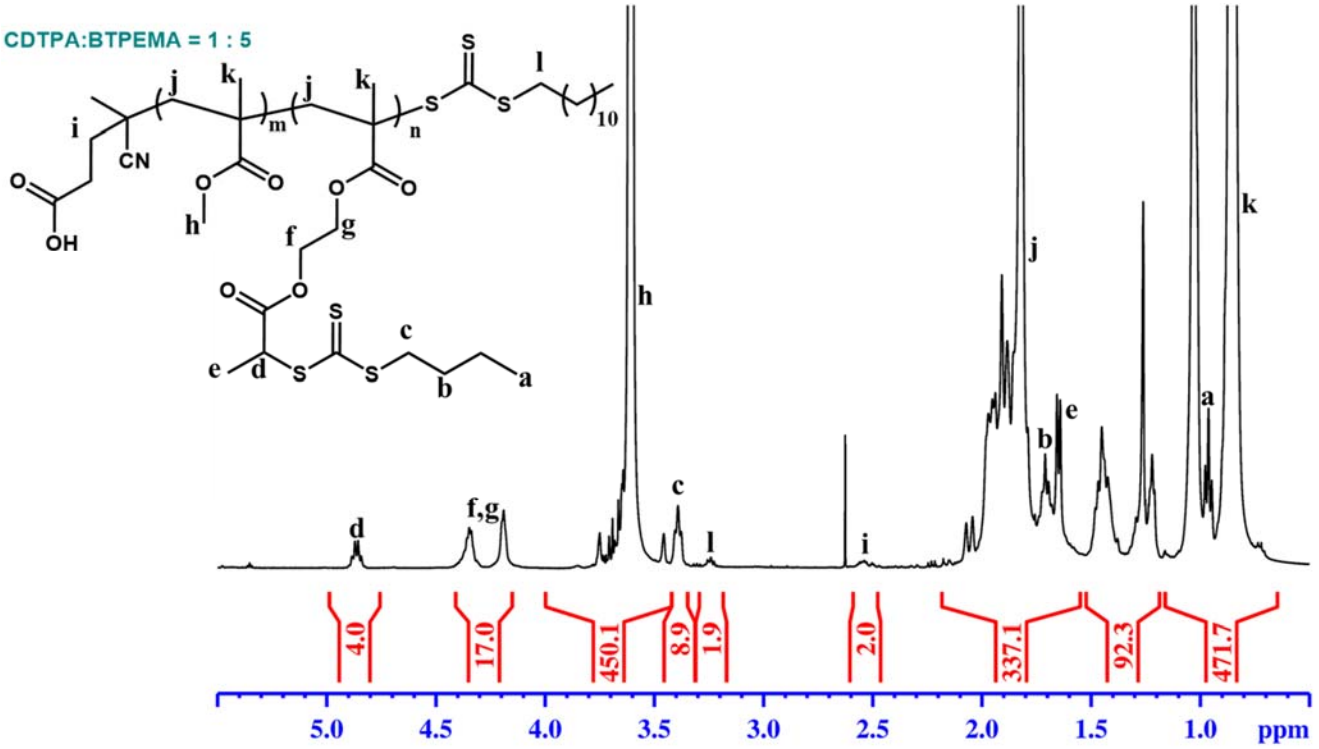

Figure S13. 500 MHz ^{1}H NMR spectrum of PMMA$_{158}$-*rand*-PBTPEMA$_{4}$ ($M_{n,NMR}$ = 17 700, $M_{n,GPC}$ = 17 800, and $M_{n,theo}$ = 18 200) in $CDCl_3$.

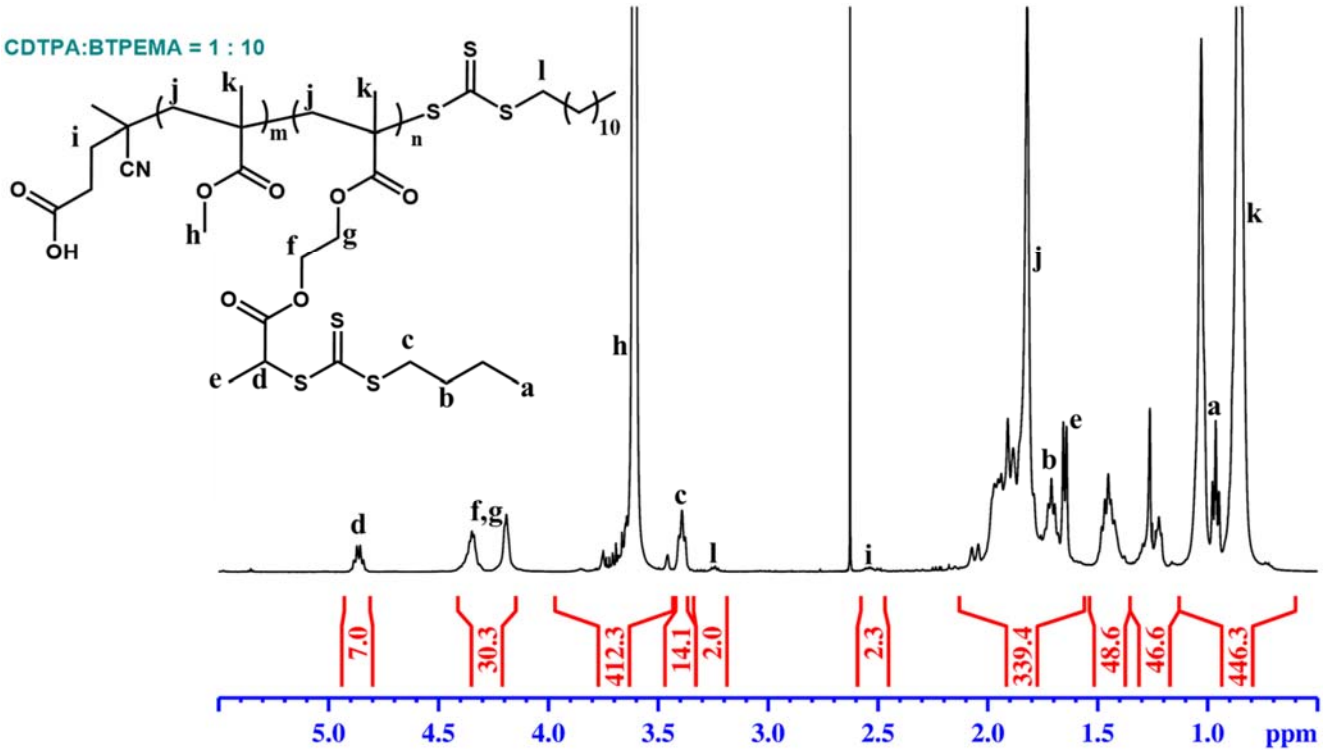

Figure S14. 500 MHz ^{1}H NMR spectrum of PMMA$_{137}$-*rand*-PBTPEMA$_{7}$ ($M_{n,NMR}$ = 16 700, $M_{n,GPC}$ = 19 160, and $M_{n,theo}$ = 18 000) in $CDCl_3$.

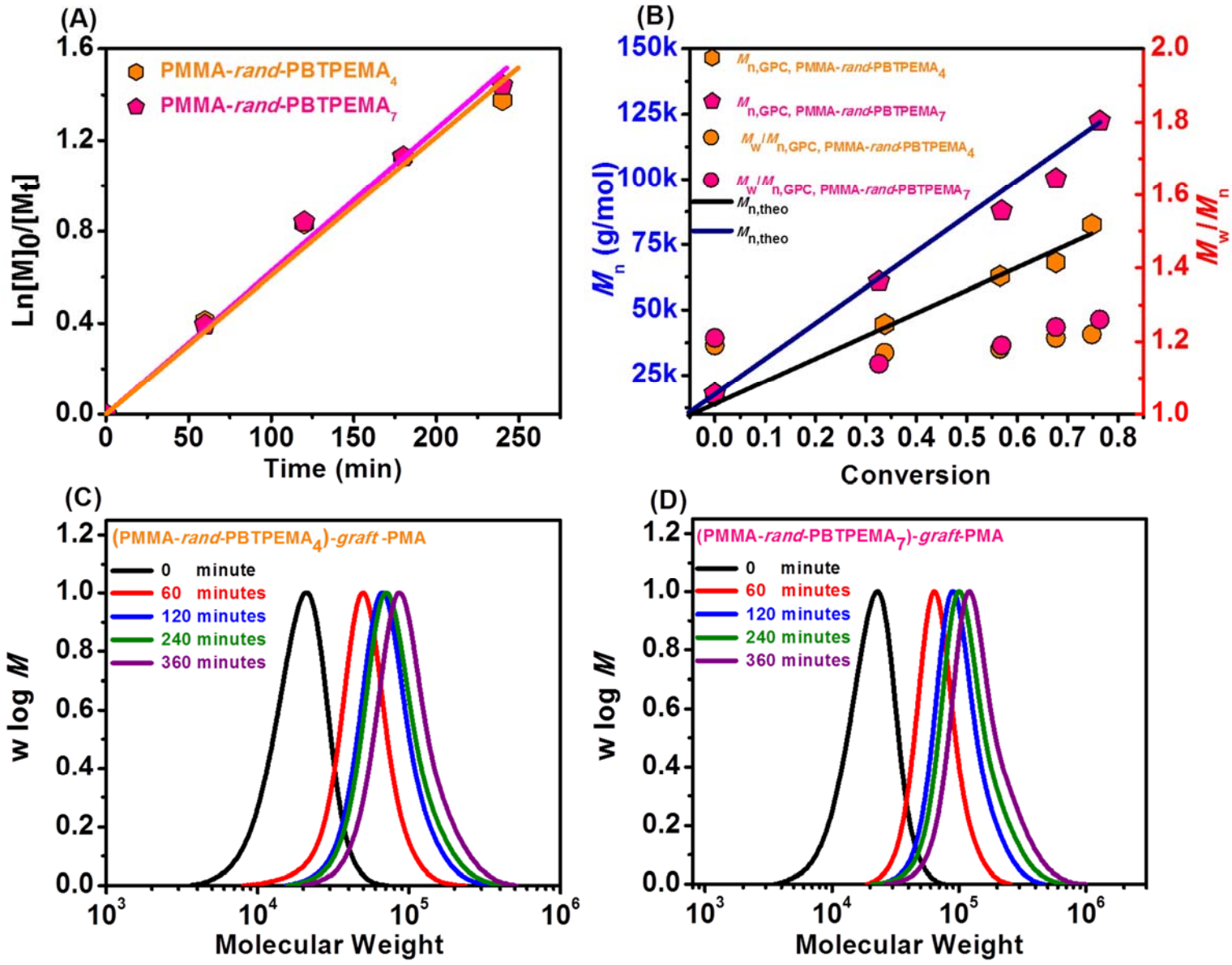

Figure S15. Grafting of MA from PMMA-*rand*-PBTPEMA$_4$ and PMMA-*rand*-PBTPEMA$_7$ in DMSO under blue light irradiation (λ_{max} = 460 nm, 6.5 mW/cm^2) with [MA]:[PMMA-*rand*-PBTPEMA$_4$ or PMMA-*rand*-PBTPEMA$_7$] = 200 : 1, 18% v/v monomer concentration. (A) Plot of Ln([M$_0$]/[M]$_t$) *vs.* exposure time for grafting of MA from PMMA$_{158}$-*rand*-PBTPEMA$_4$ and PMMA$_{137}$-*rand*-PBTPEMA$_7$; (B) plot of M_n *vs.* conversion for grafting of MA from PMMA$_{158}$-*rand*-PBTPEMA$_4$ and PMMA$_{137}$-*rand*-PBTPEMA$_7$; and (C) GPC traces mapping kinetic studies of MA grafted from PMMA$_{158}$-*rand*-PBTPEMA$_4$ and PMMA$_{137}$-*rand*-PBTPEMA$_7$.

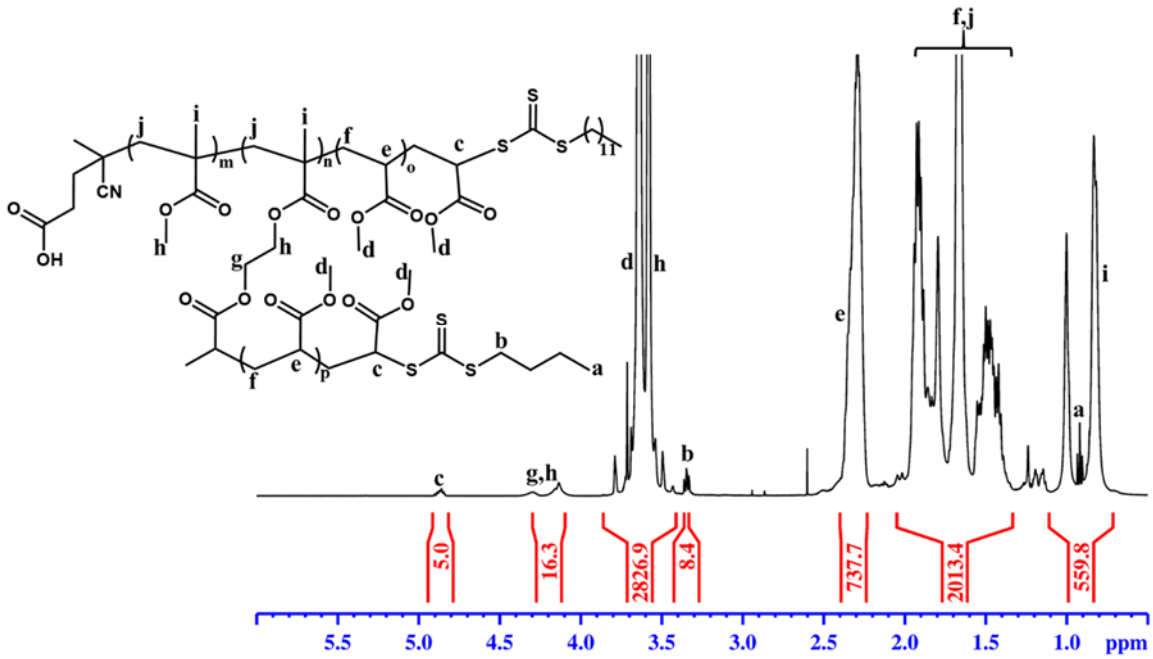

Figure S16. 500 MHz ^{1}H NMR spectrum of PMMA-*rand*-PBTPEMA$_4$ grafted with MA in $CDCl_3$ ($M_{n,NMR}$ = 81 200, $M_{n,GPC}$ = 82 530, and $M_{n,theo}$ = 83 500).

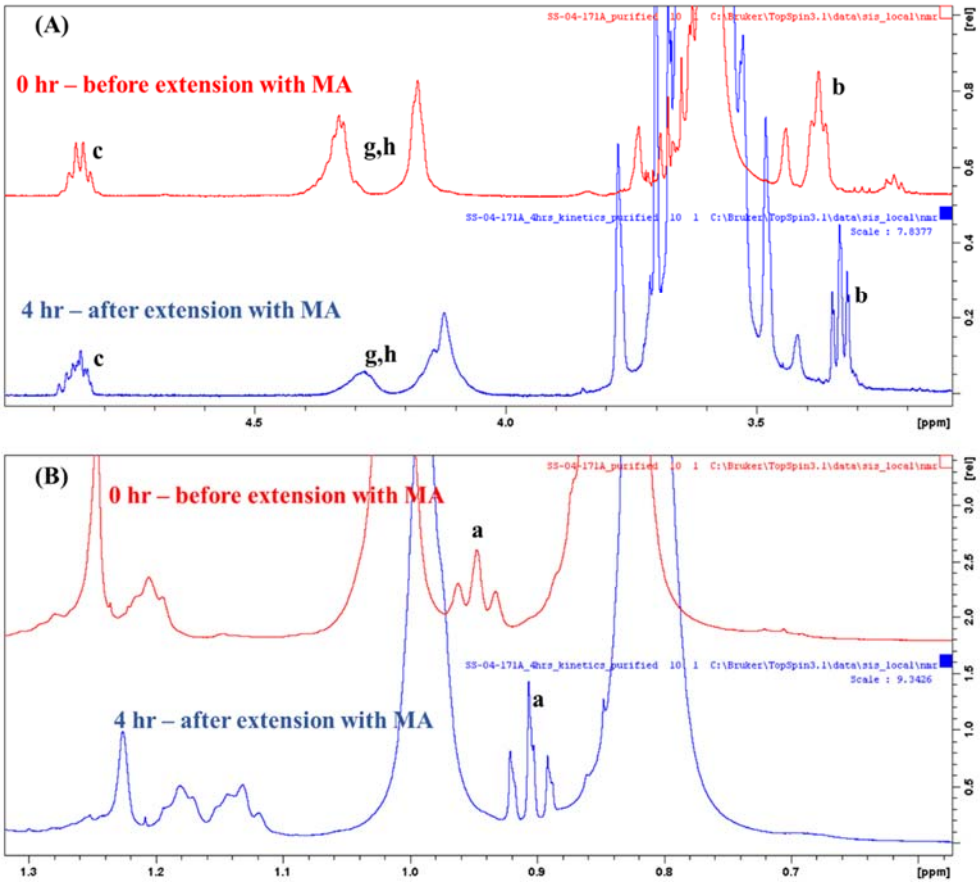

Figure S17. 500 MHz ^{1}H NMR spectrum of PMMA-*rand*-PBTPEMA$_4$ before and after grafting with MA: Regions between (A) 3.0-5.0 ppm and (B) 0.6-1.3 ppm.

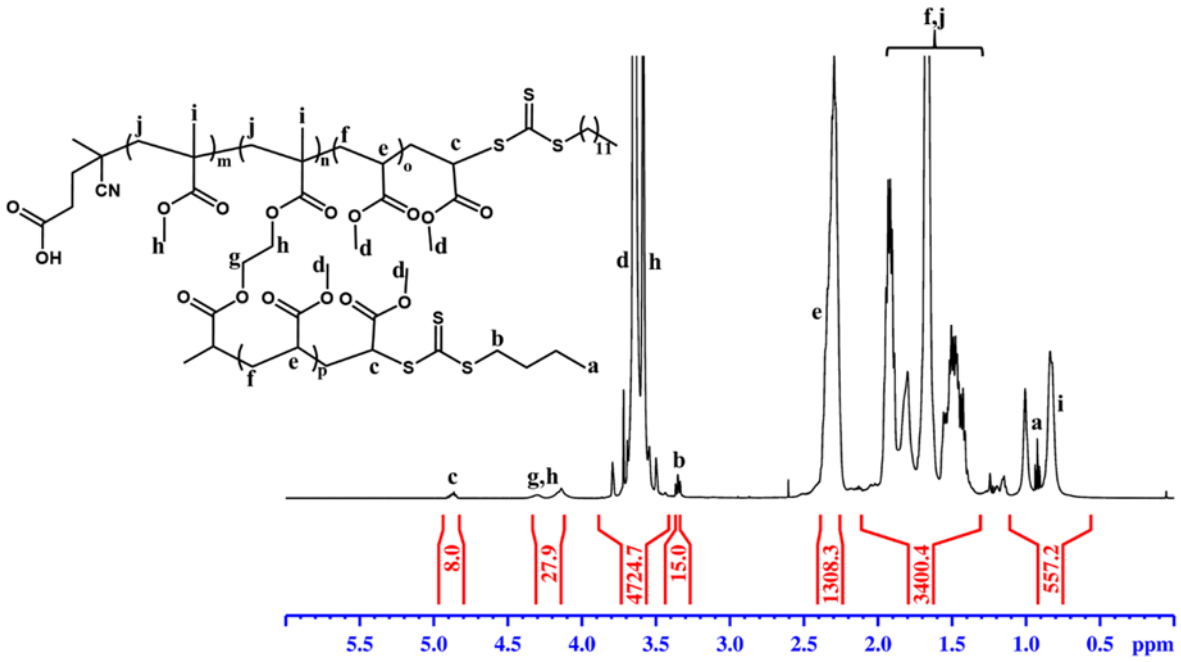

Figure S18. 500 MHz ^{1}H NMR spectrum of PMMA-*rand*-PBTPEMA$_7$ grafted with MA in $CDCl_3$ ($M_{n,NMR}$ = 129 300, $M_{n,GPC}$ = 122 500, and $M_{n,theo}$ = 122 200).

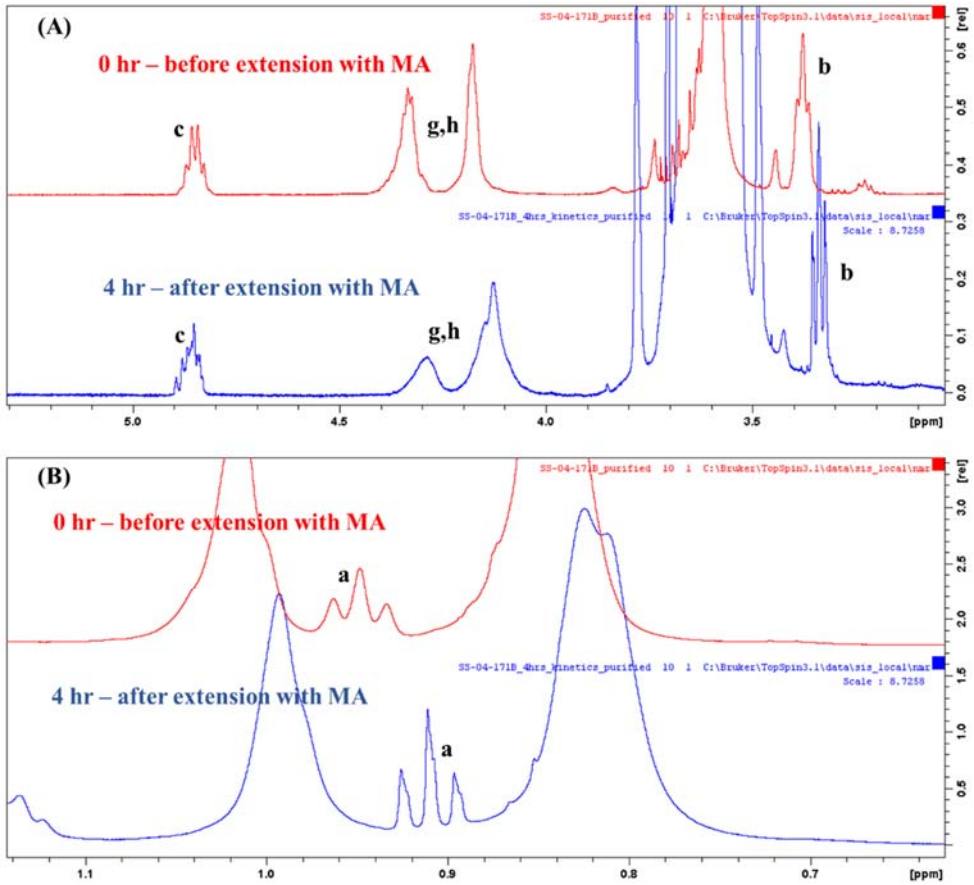

Figure S19. 500 MHz ^{1}H NMR spectrum of PMMA-*rand*-PBTPEMA$_7$ before and after grafting with MA: Regions between (A) 3.0-5.0 ppm and (B) 0.64-1.2 ppm.

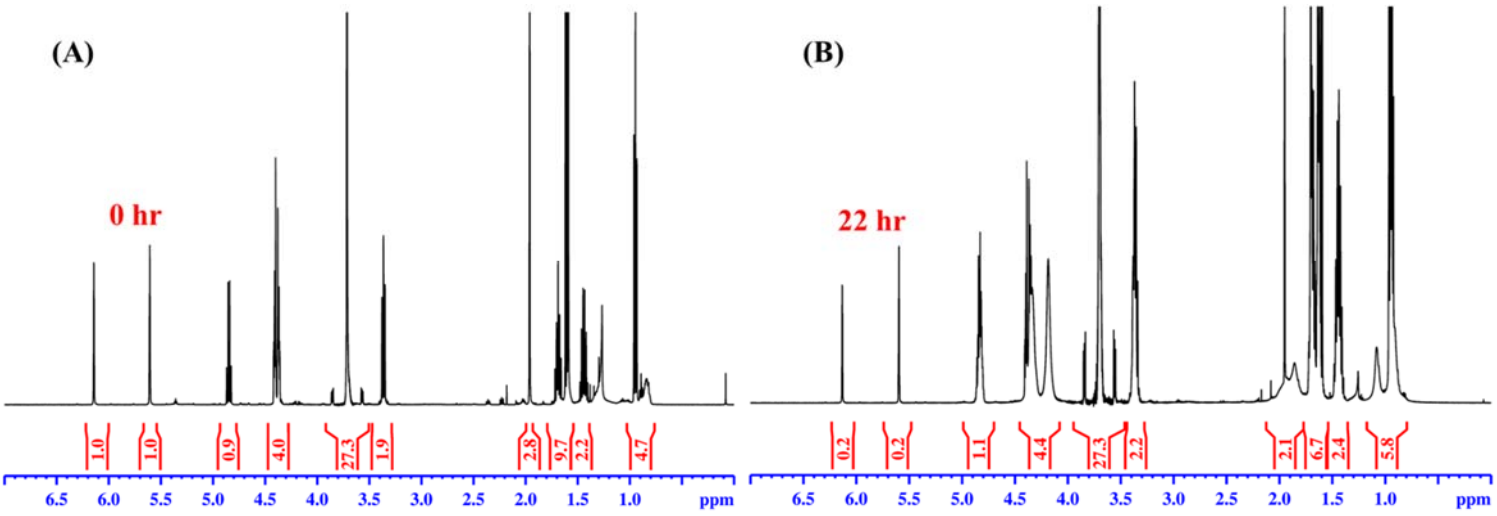

Figure S20. 500 MHz ^{1}H NMR spectrum of homopolymerization of BTPEMA in dioxane before (**A**, 0 hr) and after (**B**, 22 hr) the polymer synthesis performed in $CDCl_3$. (*Dioxane when used as the internal standard revealed BTPEMA conversion of 80% with initial ratio of BTPEMA:CDTPA = 600 : 1).

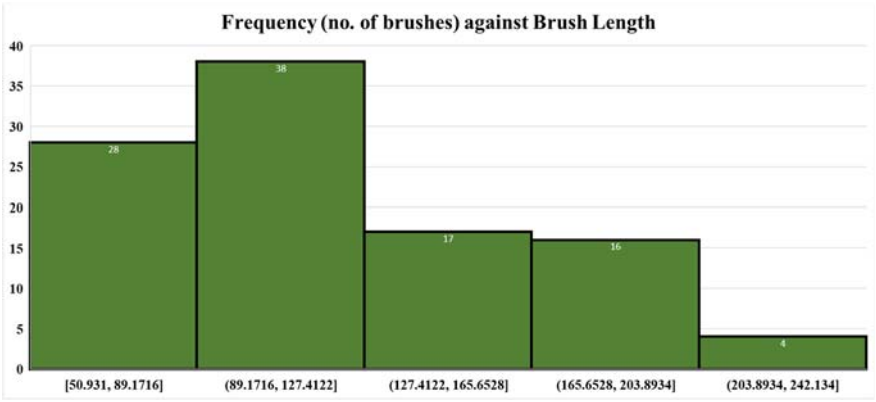

Figure S21. The length of bottlebrush polymers measured using Gwyddion software. Measuring approximately 104 brushes as seen in the histograms led to an average length of 119.9 nm. (Note: A bottlebrush with average degree of polymerization of 480 units in each polymer chain would have a contour length of 120 nm (480*0.25 nm) when fully extended. As the average length of the brushes is approximately 119.9 nm, this leads to the conclusion that the backbone is completely stretched.

Photoinitiation Mechanism of CDTPA with MMA and MA

Previous studies have shown that CDTPA can be initiated under green light irradiation to promote polymerization of methacrylates.[5-7] However, these studies only considered absorption of CDTPA before polymerization without much discussion on the absorption after initialization with methacrylate monomer units. Therefore, the absorption of CDTPA was monitored during polymerization of MMA under green light irradiation by employing UV-Vis-NIR spectrophotometer. As shown in **Figure S22A**, monomer consumption under green light irradiation led to a decrease in absorption at 1624 nm which corresponds to the absorption of =C – H.[8] The peak corresponding to the spin-forbidden n → π^* electronic transition at 448 nm shifts to 443 nm

after the polymerization (**Figure S22B**), but the absorption at the green region which coincides with the emission wavelength of the green LEDs (λ_{max} = 520 nm) was still observed. In other words, the addition of MMA units to CDTPA retains the absorption in the green region enabling continuous photolysis during the polymerization. Plot of $Ln[M]_0/[M_t]$ against time (**Figure S23A**) revealed a pseudo-first order kinetics (k_p^{app} = 1.091×10^{-2} min). The final polymer product also showed good correlation between experimental and theoretical molecular weights and narrow distributions (**Figure S23B**) with high RAFT end group fidelity (**Figure S24**).

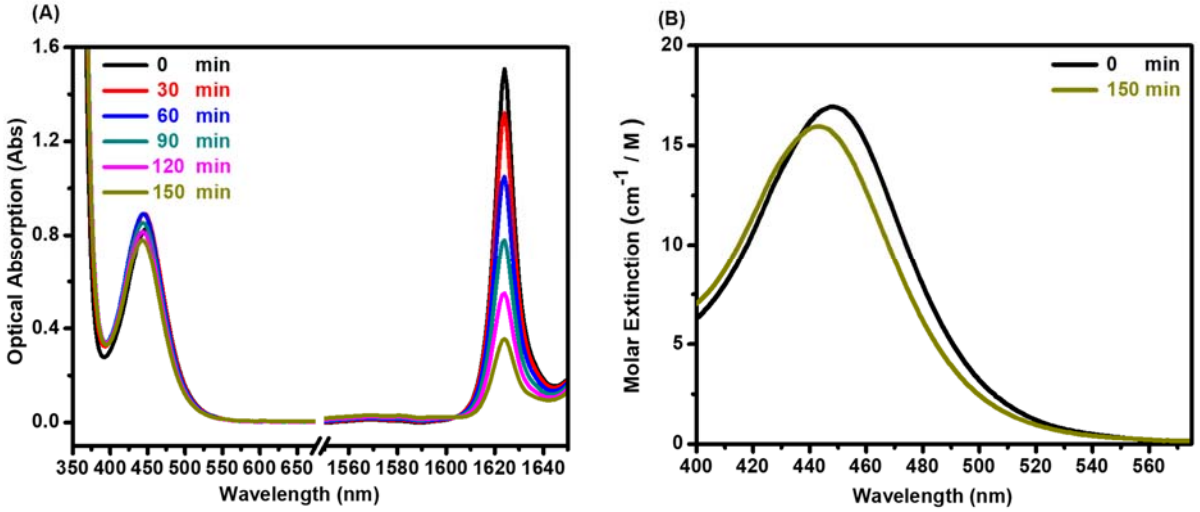

Figure S22. Optical absorption measurements of polymerization of MMA with CDTPA to determine monomer conversion (A) and changes in the spin-forbidden n → π^* electronic transition (B).

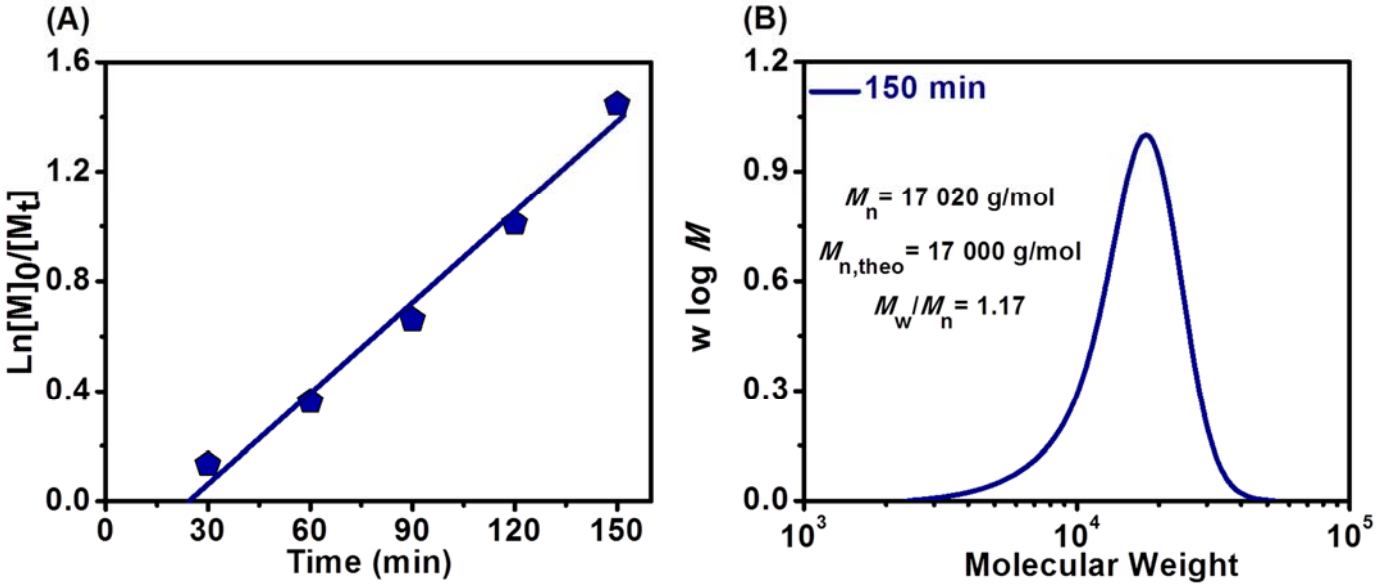

Figure S23. Polymerization of MMA mediated by CDTPA under green light irradiation (λ_{max} = 520 nm, intensity = 4.25 mW/cm^2) performed in DMSO with [MMA]:[CDTPA] = 200 : 1, 50% v/v monomer concentration. (A) Plot of $Ln([M_0]/[M]_t)$ *vs.* exposure time, and (B) GPC trace of the final polymer product.

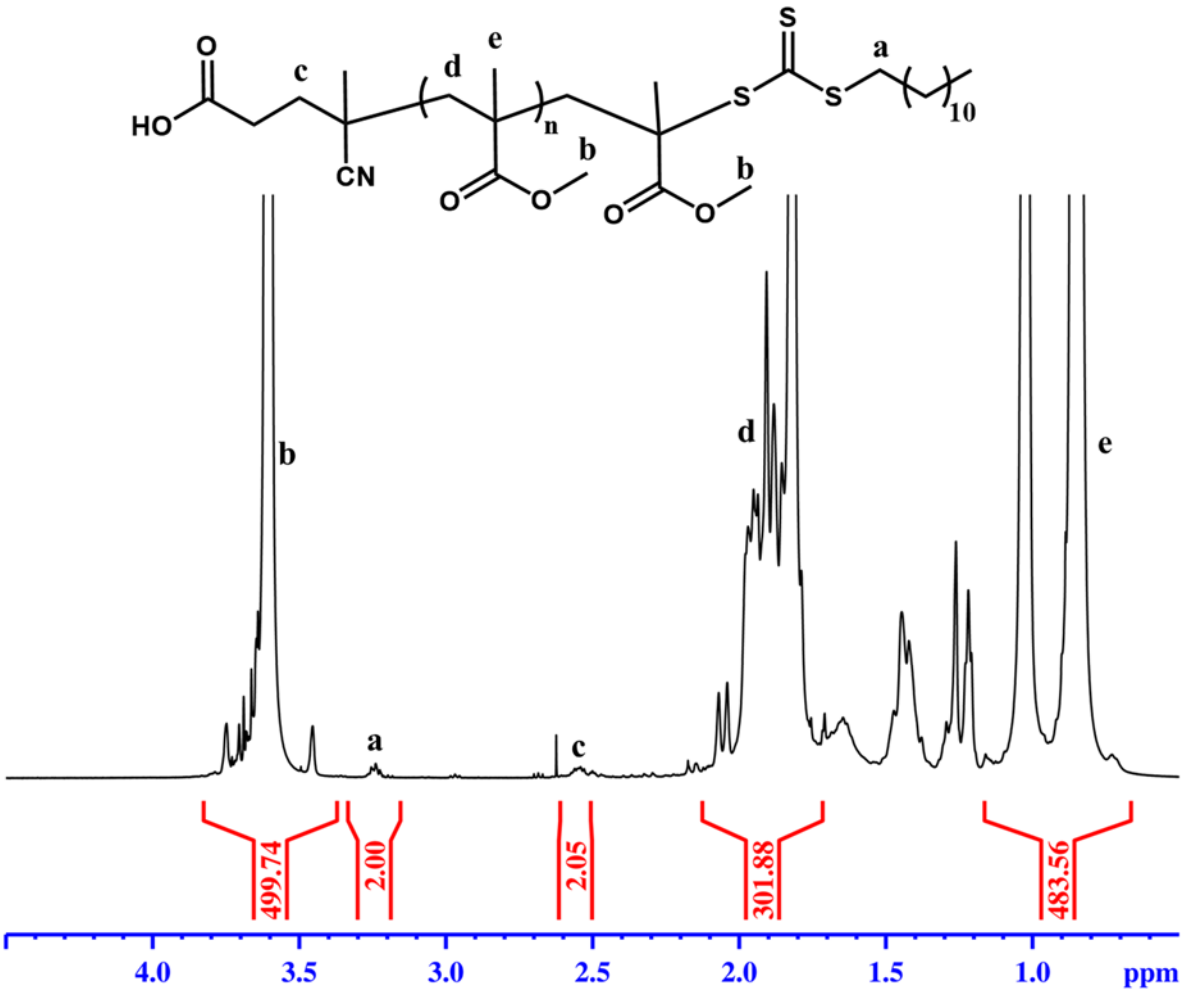

Figure S24. Characterization of PMMA via 500 MHz ^{1}H NMR. (A) The molecular weight of PMMA was found to be $M_{n,NMR}$ = 17 100 ($M_{n,NMR}$ was determined using the following equation $M_{n,NMR} = (I^{3.6\ ppm}/3)/(I^{3.2\ ppm}/2) \times MW^{M} + MW^{RAFT}$ where $I^{3.6\ ppm}$ and $I^{3.2\ ppm}$ correspond to integration of proton **b** and **a**, respectively), $M_{n,GPC}$ = 17 020, and $M_{n,theo}$ = 17 000 with end group fidelity ($f = (I^{3.2\ ppm,\ a})/(I^{2.6\ ppm,\ c})$, where $I^{3.2\ ppm}$ and $I^{2.6\ ppm}$ correspond to integration of proton **a** and **c**, respectively) close to 0.98 ± 0.05.

In the case of MA, the PMA radical that adds onto CDTPA leads to successful fragmentation of the tertiary carbon radical R-group (**Figure S25**) on CDTPA. However, the peak corresponding to the spin-forbidden n → π^* electronic transition at 448 nm of CDTPA shifts to 433 nm upon addition of PMA (**Figure S25B**) radical. As the emission wavelength of the green LEDs (λ_{max} = 520 nm) does not overlap with the n → π^* electronic transition, polymerization of MA was halted. Consequently, no changes in the absorption at 1624 nm corresponding to monomer consumption was observed (**Figure S25A**).

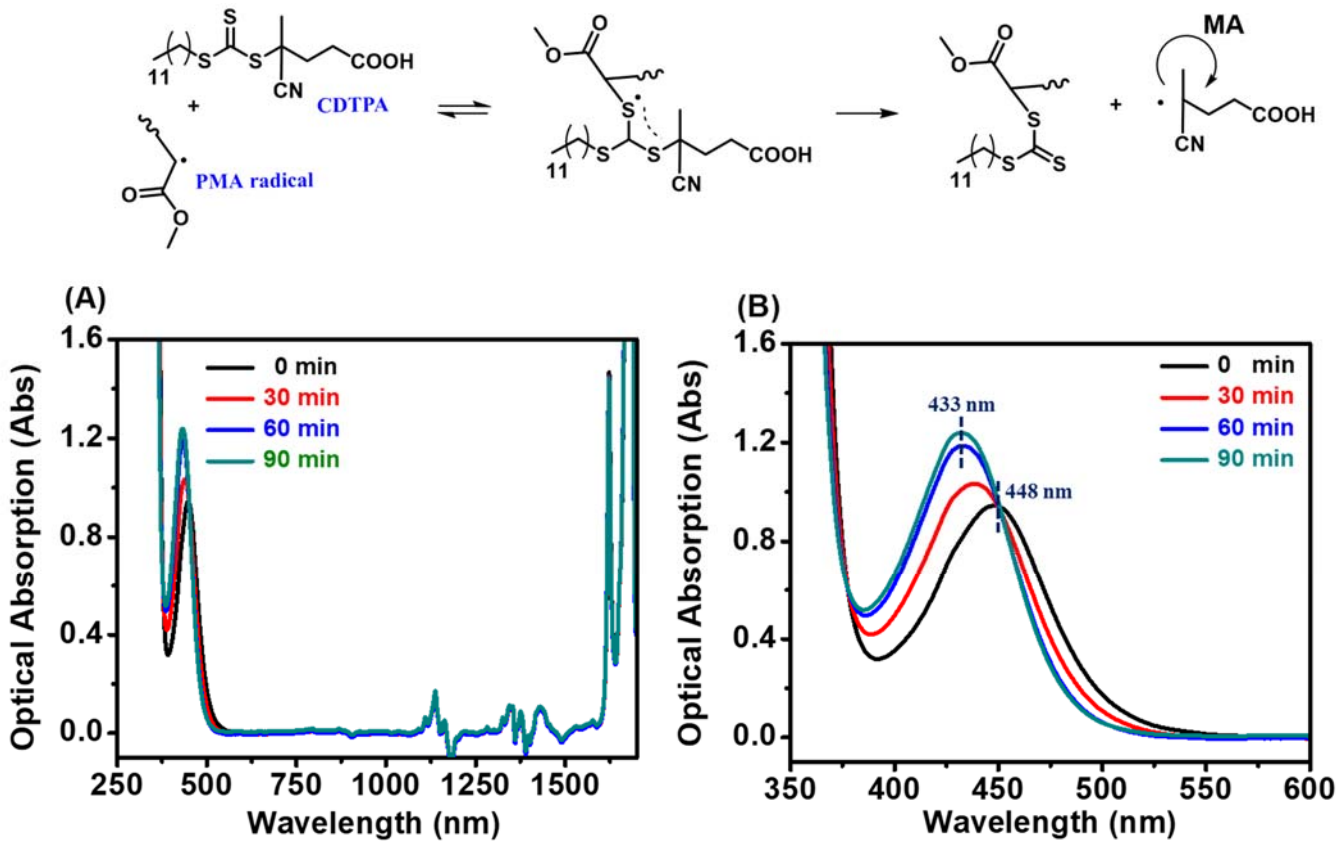

Figure S25. PMA radical addition and fragmentation of R-group on CDTPA (top), and optical absorption measurements of polymerization of MA with CDTPA to determine monomer conversion (A) and changes in the spin-forbidden n → π^* electronic transition (B) (bottom).

Additional references:

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