

# Transformation of Gels via Catalyst-Free Selective RAFT Photoactivation

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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%), *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). Thiocarbonylthio compound: 2-(*n*-butyltrithiocarbonate)-propionic acid (BTPA) and 2-(2-(*n*-butyltrithiocarbonate)-propionate)ethyl methacrylate (BTPEMA), bis[(2-propionate)ethyl methacrylate] trithiocarbonate (bisPEMAT) were synthesized.<sup>[1]</sup> 4-Cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) was purchased from Boron Molecular.

**Synthesis of bis[(2-propionate)ethyl methacrylate] trithiocarbonate (bisPEMAT).** Bis(2-propionic acid) trithiocarbonate (bisPAT) was synthesized using previous reported and modified to form bisPEMAT. First, 13.2 gram of potassium hydroxide (KOH) was dissolved in 300 mL water. Carbon disulfide (CS<sub>2</sub>) (12.0 mL, 220 mmol) was then slowly added to the KOH solution. The reaction flask was placed in an ice bath to reach an internal temperature of 0 °C. 2-bromopropionic acid (9.4 mL, 100 mmol) was added slowly while stirring. The reaction mixture was stirred for 48 hours at room temperature. The reaction mixture was then washed in dichloromethane (40 mL) five times to remove excess CS<sub>2</sub>. The aqueous layer containing the product was then placed in an ice bath to reach an internal temperature of 0 °C. Concentrated hydrochloric acid (HCl) was added drop by drop to crash out the product. The bisPAT product was then dried under vacuum overnight with final yield of 30% (4 grams). The product was characterized via NMR revealing proton peaks consistent with previous synthetic approach.

BisPAT was further modified via EDC coupling to yield bisPEMAT. BisPAT (0.7508, 2.952 mmol) was dissolved in 5 mL THF before the addition of HEMA (2.305 g, 17.71 mmol, 2.144 mL). The reaction vessel was placed in an ice bath (0 °C). A solution of EDC (2.750 grams, 17.71 mmol) and DMAP (72.13 mg, 0.0590 mmol) in 10 mL DCM was then added dropwise to the reaction mixture. The reaction mixture was degassed for 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 product. To remove excess HEMA, the product was washed in water twice. As the esterification reaction may lead to the formation of monofunctionalized bisPAT as a side product, flash chromatography with hexane/ethyl acetate of 95/5 eluent was carried to obtain pure bisPEMAT with a yield of 46 % (0.6515 g). <sup>1</sup>H NMR and ESI-MS of the product are shown in **Figure S1** and **Figure S2**.

## Instrumentation

Gel Permeation Chromatography (GPC) was used for characterization of synthesized polymer with *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<sup>5</sup>, 10<sup>3</sup>, and 10<sup>2</sup> Å) in 50 mM LiBr DMF solution as an eluent at 50 °C and at a flow rate of 1 mL min<sup>-1</sup>. THF GPC analysis was carried out with Waters 515 HPLC pump and Waters 2414 refractive index detector. PSS columns (SDV 10<sup>2</sup>, 10<sup>3</sup>, 10<sup>5</sup> Å) was used with tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL min<sup>-1</sup> at 35°C. Linear PMMA standards were used for GPC calibration with GPC results analyzed in WinGPC 7.0 software from PSS for the DMF GPC.

Nuclear Magnetic Resonance (<sup>1</sup>H NMR) was carried out with Bruker Ultrashield 500 MHz operating at 500 MHz for <sup>1</sup>H using CDCl<sub>3</sub> as the solvent. Tetramethylsilane (TMS) was used as a reference with chemical shift ( $\delta$ ) of sample measured in ppm downfield from TMS.

Dynamic Mechanical Analysis- Mechanical properties of the STEM gels were assessed in the dry state using an Anton Paar MCR-302 Rheometer fitted with a parallel plate tool. Disk shaped gel samples with a thickness of 1-2 mm and diameter  $D = 12-20$  mm were subjected to periodic torsional shearing between two parallel plates under a constant normal load of 5 N in the linear viscoelastic response region. The temperature ramps were carried out at a constant ramp of 2°C/min with a constant applied shear strain of 0.1% ( $\gamma$ ) and a frequency ( $\omega$ ) of 6.28 rad/s (1 Hz).

Electrospray Ionization Mass Spectroscopy (ESI-MS) was carried out using Thermo Scientific Exactive Plus EMR. The following specifications were used: (a) flow injection analysis: 5 $\mu$ L injections (50pmol sample load) at 10  $\mu$ L/min solvent flow, (b) Polarity: positive (+) and negative (-) modes ( $m/z$  150-2000), resolution: 70,000 at  $m/z$  200, spray voltage:  $\pm 3.0$  kV, and sheath gas: 3 a.u.. The sample was diluted to 10 $\mu$ M (pmol/ $\mu$ L) in acetonitrile with the addition of 0.1% formic acid. The mass spectrum has been background subtracted.

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 kinetic studies of linear brush model with RAFT photopolymerization of methyl methacrylate (MMA) mediated by CDTPA under green light irradiation with different concentrations of BTPEMA.**

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 ( $\lambda_{\text{max}} = 520 \text{ nm}$ ,  $4.25 \text{ mW/cm}^2$ ) equipped with constant flow of cool air. Aliquots of the reaction mixture were taken at specific time points (every 60 minutes) during the reaction to determine monomer conversions through  $^1\text{H}$  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 ratios of BTPEMA (MW = 350.53 g/mol) relative to CDTPA (CDTPA : BTPEMA = 1:5, 1:10, and 1:20) with the following formulations.

MMA: CDTPA : BTPEMA = 200: 1:5, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPEMA (85.5 mg, 0.244 mmol)

MMA: CDTPA : BTPEMA = 200: 1:10, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPEMA (171 mg, 0.488 mmol)

MMA: CDTPA : BTPEMA = 200:1:20, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), BTPEMA (342 mg, 0.976 mmol)

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

The final polymer mixtures for the different concentrations of BTPEMA were purified through precipitation in diethyl ether. The final purified polymer obtained during precipitation were analyzed with  $^1\text{H}$  NMR.

**General procedure for gelation studies for RAFT photopolymerization of methyl methacrylate (MMA) mediated by CDTPA under green light irradiation with different concentrations of BTPEMA and PEGDMA<sub>750</sub> crosslinker.**

A reaction stock solution consisting of DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67 g/mol), and PEGDMA (63.5 $\mu\text{L}$ , 69.79 mg, 0.093 mmol) 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 ( $\lambda_{\text{max}} = 520 \text{ nm}$ ,  $4.25 \text{ mW/cm}^2$ ) 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  $^1\text{H}$  NMR analysis, and to determine number average molecular weights ( $M_n$ ) and dispersities ( $M_w/M_n$ ) through DMF GPC analysis. The reaction was continued until gelation was reached. Final sampling upon reaching gelation point was carried out by vortexing the sample in  $\text{CDCl}_3$  overnight to determine the monomer conversion at gelation point. However, no GPC analysis could be carried out with the gel due to poor solubility of the crosslinked polymer network in DMF. The photopolymerization was repeated with different molar ratios of BTPEMA (MW = 350.53) relative to CDTPA (CDTPA : BTPEMA = 1:5, 1:10, and 1:20) with the following formulations.

MMA: CDTPA : BTPEMA:PEGDMA<sub>750</sub> = 200:1:5:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), PEGDMA (63.5 $\mu\text{L}$ , 69.79 mg, 0.093 mmol), BTPEMA (85.5 mg, 0.244 mmol)

MMA: CDTPA : BTPEMA: PEGDMA<sub>750</sub> = 200:1:10:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), PEGDMA (63.5 $\mu\text{L}$ , 69.79 mg, 0.093 mmol), BTPEMA (171 mg, 0.488 mmol)

MMA: CDTPA : BTPEMA: PEGDMA<sub>750</sub> = 200:1:20:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), PEGDMA (63.5 $\mu\text{L}$ , 69.79 mg, 0.093 mmol), BTPEMA (342 mg, 0.976 mmol)

Similarly, aliquots of the reaction mixture were taken at specific time points (every 30 minutes) during the reaction to determine monomer conversions through  $^1\text{H}$  NMR analysis, and to determine number average molecular weights ( $M_n$ ) and dispersities ( $M_w/M_n$ ) through DMF GPC analysis. Final sampling upon reaching gelation point was carried out by vortexing the different samples in  $\text{CDCl}_3$  overnight to determine the monomer conversions at gelation point. However, no GPC analysis were carried out with the gels due to poor solubility of the crosslinked polymer network in DMF.

### **General procedure for PMMA STEM 0 gel synthesis with PEGDMA<sub>750</sub> and BTPEMA for further modification under blue light irradiation**

A reaction stock solution consisting of DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), and PEGDMA<sub>750</sub> (63.5 $\mu\text{L}$ , 69.79 mg, 0.093 mmol) was prepared in a glass vial covered with aluminum foil (MMA : CDTPA = 200 :1). For mixtures containing different concentrations of BTPEMA, the following formulations were used.

MMA: CDTPA : BTPEMA : PEGDMA<sub>750</sub> = 200:1:5:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), PEGDMA<sub>750</sub> (63.5 $\mu$ L, 69.79 mg, 0.093 mmol), BTPEMA (85.5 mg, 0.244 mmol)

MMA: CDTPA : BTPEMA : PEGDMA<sub>750</sub> = 200:1:10:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), PEGDMA<sub>750</sub> (63.5 $\mu$ L, 69.79 mg, 0.093 mmol), BTPEMA (171 mg, 0.488 mmol)

MMA: CDTPA : BTPEMA : PEGDMA<sub>750</sub> = 200:1:20:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), PEGDMA<sub>750</sub> (63.5 $\mu$ L, 69.79 mg, 0.093 mmol), BTPEMA (342 mg, 0.976 mmol)

The reaction mixtures were transferred to 3mL glass vials and sealed with septa before being sparged under nitrogen for 20 minutes. The mixtures were then irradiated in a green LED photoreactor ( $\lambda_{\text{max}} = 520 \text{ nm}$ , 4.25 mW/cm<sup>2</sup>) equipped with constant flow of cool air. Irradiation was carried out for 12 hours to ensure high monomer conversions. The resultant cylindrical gels were then removed from the glass vials. Each gel from the four different formulations was cut into 4 pieces and dried at 50 °C in a vacuum oven for a week. The gels were then dried in vacuum at room temperature in a desiccator for another 3 days.

The dried gels with different concentrations of BTPEMA were then placed in 20 mL glass vials sealed with septa and sparged with nitrogen. The gels were soaked in different nitrogen-sparged monomer (DMA or MA) solutions introduced through syringe transfer. Soaking of gels with the different monomers (formulations shown below) were carried out for a period of 24-48 hours before irradiation under blue light for 12 hours. The gels were then dried at 50 °C in a vacuum oven for a week. Monomer conversions of acrylates/acrylamides were determined through gravimetry.

For initial gel with CDTPA:BTPEMA = 1:5 with theoretical molecular weight of chains in the gel was determined to be MW= 23 680 and mass of 0.3435 g, the following formulation was used: MA: RAFT = 50:1, DMSO (0.164 mL), and MA (0.327 mL, 0.313 g, 7.252 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis and BTPEMA.

For initial gel with CDTPA:BTPEMA = 1:10 with theoretical molecular weight of chains in the gel was determined to be MW= 25 500 and mass of 0.2840 g, the following formulation was used: MA: RAFT = 50:1, DMSO (0.252 mL), and MA (0.503 mL, 0.481 g, 5.583 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis and BTPEMA.

For initial gel with CDTPA:BTPEMA = 1:20 with theoretical molecular weight of chains in the gel was determined to be MW= 28 940 and mass of 0.4175 g, the following formulation was used: MA: RAFT = 50:1,

DMSO (0.200 mL), and MA (1.3 mL, 1.243 g, 14.43 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis and BTPEMA.

For initial gel with CDTPA:BTPEMA = 1:20 with theoretical molecular weight of chains in the gel was determined to be MW= 28 940 and mass of 0.4605 g, the following formulation was used: DMA: RAFT = 50:1, DMSO (0.100 mL), and DMA (1.640 mL, 1.577 g, 15.91 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis and BTPEMA.

**General procedure for gelation studies for RAFT photopolymerization of methyl methacrylate (MMA) mediated by CDTPA under green light irradiation with bisPEMAT with/without BTPEMA.**

A reaction stock solution consisting of DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), and bisPEMAT (44.74 mg, 0.093 mmol) 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 ( $\lambda_{\max} = 520$  nm, 4.25 mW/cm<sup>2</sup>) 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 <sup>1</sup>H NMR analysis, and to determine number average molecular weights ( $M_n$ ) and dispersities ( $M_w/M_n$ ) through DMF GPC analysis. The reaction was continued until gelation was reached. Final sampling upon reaching gelation point was carried out by vortexing the sample in CDCl<sub>3</sub> overnight to determine the monomer conversion at gelation point. However, no GPC analysis could be carried out with the gel due to poor solubility of the crosslinked polymer network in DMF. The photopolymerization was repeated with different molar ratios of BTPEMA (MW = 350.53) relative to CDTPA (CDTPA : BTPEMA =1:10, and 1:20) with the following formulations.

MMA: CDTPA : BTPEMA: bisPEMAT = 200:1:10:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), bisPEMAT (44.74 mg, 0.093 mmol), BTPEMA (171 mg, 0.488 mmol)

MMA: CDTPA : BTPEMA: bisPEMAT = 200:1:20:2, DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), and CDTPA (19.7 mg, MW: 403.67), bisPEMAT (44.74 mg, 0.093 mmol), BTPEMA (342 mg, 0.976 mmol)

Similarly, aliquots of the reaction mixture were taken at specific time points (every 30 minutes) during the reaction to determine monomer conversions through <sup>1</sup>H NMR analysis, and to determine number average molecular weights ( $M_n$ ) and dispersities ( $M_w/M_n$ ) through DMF GPC analysis. Final sampling upon reaching gelation point was carried out by vortexing the different samples in CDCl<sub>3</sub> overnight to determine the monomer conversions at gelation point. However, no GPC analysis were carried out with the gels due to poor solubility of the crosslinked polymer network in DMF.

## **General procedure for PMMA STEM 0 gel synthesis with bisPEMAT crosslinker with/without BTPEMA for further modification under blue light irradiation**

### **(A) PMMA STEM 0 gel synthesized with bisPEMAT crosslinker without BTPEMA for further modification with MA and DMA**

A reaction stock solution consisting of DMSO (2.088 mL), MMA (2.088 mL, 2.009 g, 20.26 mmol), CDTPA (39.39 mg, MW: 403.67), and bisPEMAT (93.4 mg, 0.195 mmol) was prepared in a glass vial covered with aluminum foil (MMA : CDTPA = 200 :1). The stock solution was transferred to 8 glass vials under nitrogen with each vial having 0.5 mL of the reaction mixtures. The mixtures were then irradiated in a green LED photoreactor ( $\lambda_{\text{max}} = 520 \text{ nm}$ ,  $4.25 \text{ mW/cm}^2$ ) equipped with constant flow of cool air. Irradiation was carried out for 12 hours to ensure high monomer conversions. The resultant cylindrical gels were then removed from the glass vials. The gels were dried at  $50 \text{ }^\circ\text{C}$  in a vacuum oven for a week. The gels were then dried in vacuum at room temperature in a desiccator for another 3 days.

The dried gels were then placed in 20 mL glass vials sealed with septa and sparged with nitrogen. The gels were soaked in different nitrogen-sparged monomer (DMA or MA) solutions introduced through syringe transfer. Soaking of gels with the different monomers (formulations shown below) were carried out for a period of 24-48 hours before irradiation under blue light for 12 hours. The gels were then dried at  $50 \text{ }^\circ\text{C}$  in a vacuum oven for a week. Monomer conversions of acrylates/acrylamides were determined through gravimetry.

Formulation: For PMMA gel modified with MA, the theoretical molecular weight of chains in the gel was determined to be MW= 21 400 and mass of 0.2727 g. The following formulation was used: MA: RAFT = 200:1, DMSO (0.308 mL), and MA (0.692 mL, 0.661 g, 7.678 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis and the crosslinker bisPEMAT.

Formulation: For PMMA gel modified with DMA, the theoretical molecular weight of chains in the gel was determined to be MW= 21 400 and mass of 0.2351 g. The following formulation was used: DMA: RAFT = 200:1, DMSO (0.220 mL), and DMA (0.680 mL, 0.654 g, 6.596 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis and the crosslinker bisPEMAT.

### **(B) PMMA STEM 0 gel synthesized with bisPEMAT crosslinker with BTPEMA for further modification with MA**

For PMMA STEM 0 gel synthesized with bisPEMAT crosslinker with BTPEMA ([MMA]:[CDTPA]:[BTPEMA]:[bisPEMAT] = 200:1:2:20), a reaction stock solution consisting of DMSO (1 mL), MMA (1.044 mL, 0.9772 g, 9.76 mmol), CDTPA (19.7 mg, MW: 403.67), BTPEMA (0.342 g, 0.9757 mmol) and bisPEMAT (44.74 mg, 0.093 mmol) was prepared in a glass vial covered with aluminum foil (MMA : CDTPA = 200 :1). The reaction mixture was transferred to 3mL glass vials and sealed with septa before being sparged under nitrogen for 20 minutes. The mixtures were then irradiated in a green LED photoreactor ( $\lambda_{\max} = 520$  nm, 4.25 mW/cm<sup>2</sup>) equipped with constant flow of cool air. Irradiation was carried out for 12 hours to ensure high monomer conversions. The resultant cylindrical gel was then removed from the glass vials. The gel was cut into 4 pieces and dried at 50 °C in a vacuum oven for a week. The gels were then dried in vacuum at room temperature in a desiccator for another 3 days.

One of the dried gels was then placed in 20 mL glass vials sealed with septa and sparged with nitrogen. The gel was soaked in nitrogen-sparged MA solution introduced through syringe transfer. Soaking of gel with the formulation shown below was carried out for a period of 24-48 hours before irradiation under blue light for 12 hours. The gel was then dried at 50 °C in a vacuum oven for a week. Monomer conversion of MA was determined through gravimetry.

Formulation: The theoretical molecular weight of chains in the gel was determined to be MW= 28 400 and mass of 0.4324 g. The following formulation was used: MA: RAFT = 25:1, DMSO (0.200 mL), and MA (0.800 mL, 0.7648 g, 8.884 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis, the crosslinker bisPEMAT and BTPEMA.

### **(C) PMMA STEM 0 gel synthesized with bisPEMAT crosslinker with BTPEMA for further modification with DMA**

For PMMA STEM 0 gel synthesized with bisPEMAT crosslinker with BTPEMA ([MMA]:[CDTPA]:[BTPEMA]:[bisPEMAT] = 200:1:2:20), a reaction stock solution consisting of DMSO (0.753 mL), MMA (0.753 mL, 0.7048 g, 7.040 mmol), CDTPA (14.2 mg, MW: 403.67), BTPEMA (0.247 g, 0.7046 mmol) and bisPEMAT (33.7 mg, 0.070 mmol) was prepared in a glass vial covered with aluminum foil (MMA : CDTPA = 200 :1). The reaction mixture was transferred to 3mL glass vials and sealed with septa before being sparged under nitrogen for 20 minutes. The mixture was then irradiated in a green LED photoreactor ( $\lambda_{\max} = 520$  nm, 4.25 mW/cm<sup>2</sup>) equipped with constant flow of cool air. Irradiation was carried out for 12 hours to ensure high monomer conversions. The resultant cylindrical gel was then removed from the glass vials. The gel was cut into 3 pieces and dried at 50 °C in a vacuum oven for a week. The gels were then dried in vacuum at room temperature in a desiccator for another 3 days.

One of the dried gels was then placed in 20 mL glass vials sealed with septa and sparged with nitrogen. The gel was soaked in nitrogen-sparged DMA solution introduced through syringe transfer. Soaking of gel with the formulation shown below was carried out for a period of 24-48 hours before irradiation under blue light for 12 hours. The gel was then dried at 50 °C in a vacuum oven for a week. Monomer conversion of DMA was determined through gravimetry.

Formulation: The theoretical molecular weight of chains in the gel was determined to be MW= 28 400 and mass of 0.2961 g. The following formulation was used: DMA: RAFT = 33:1, DMSO (0.200 mL), and DMA (0.800 mL, 0.7696 g, 7.764 mmol). RAFT agent in this context refers to total number of moles of CDTPA initialized with MMA units in the first step of gel synthesis, the crosslinker bisPEMAT and BTPEMA.

Determination of degrees of polymerizations of side chains and blocks

The theoretical molecular weight (MW) of STEM-0 gel was determined to be MW of polymer chain without crosslinking.

$$M_{n,th, STEM-0} = ([MMA]_o/[CDTPA]_o \times MW^{MMA}) + MW^{CDTPA} + ([BTPEMA]_o/[CDTPA]_o \times MW^{BTPEMA}) + ([X-linker]_o/[CDTPA]_o \times MW^{X-linker})$$

where  $[MMA]_o$ ,  $[CDTPA]_o$ ,  $MW^{MMA}$ ,  $MW^{CDTPA}$ ,  $[BTPEMA]_o$ ,  $MW^{BTPEMA}$ ,  $[X-linker]_o$ ,  $MW^{X-linker}$ , correspond to initial MMA monomer concentration, initial CDTPA concentration, molar mass of MMA, molar mass of CDTPA, initial BTPEMA concentration, molar mass of BTPEMA, initial crosslinker concentration, molar mass of crosslinker. The crosslinker used was either PEGDMA<sub>750</sub> for the D-STEM-0 gels or bisPEMAT for E-STEM-0 gels and D/E-STEM-0 gels. As linear model experiments and gelation kinetics were shown to yield gels with almost complete monomer conversions, we assume all monomers were consumed in all the STEM-0 gels synthesized.

The moles of STEM-0 gels and moles of RAFT inimer used for post-modification to yield STEM 1A/1B gels was determined as shown in the equation below.

$$\text{moles of STEM-0 gel} = (\text{mass of STEM-0 gel}) / (M_{n,th, STEM-0})$$

$$\text{moles of RAFT inimer} = (\text{total number of RAFT agents per polymer chain}) \times (\text{moles of STEM-0 gel})$$

The total number of RAFT agents per polymer chain is the sum of BTPEMA, CDTPA initialized by MMA, and bisPEMAT.

Assuming that all the RAFT agents in the second step is initiated, the degree of polymerization of side chains (chains grown from BTPEMA) and block copolymers (chains extended from CDTPA initialized by MMA and chains extended from bisPEMAT). In the case of bisPEMAT and CDTPA in the second step, it was assumed

that same average number of monomers polymerized from every RAFT R group. Therefore, when polymerizing with bisPEMAT, there are two R groups.

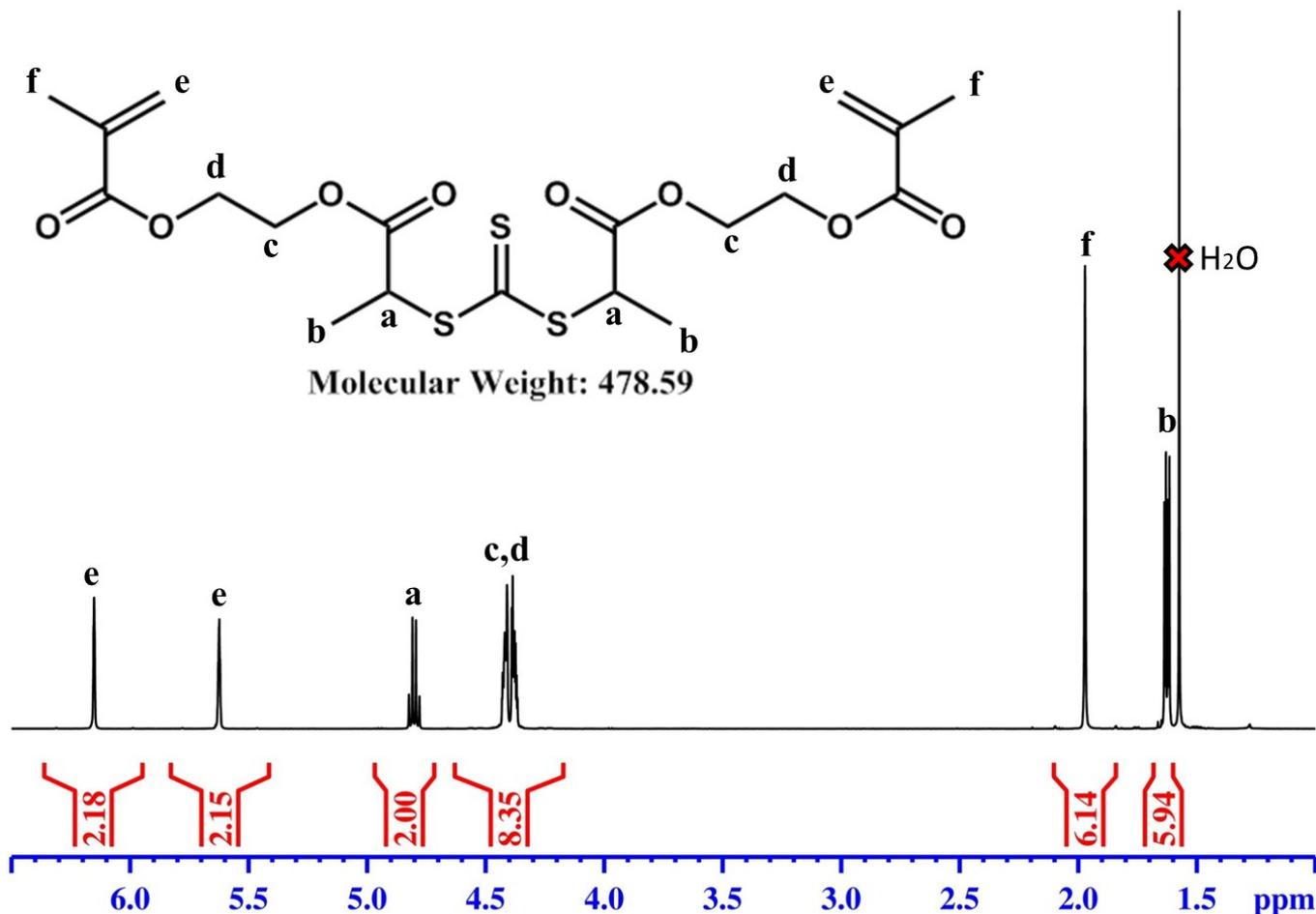
### General procedure for the Determination of Swelling Ratios in DMSO and Water

The STEM-0 and STEM-1 gels were thoroughly dried as described previously. Samples were weighted (mass ranging from 225-575 mg) were immersed in excess solvent (DMSO or Water) at room temperature (22°C).

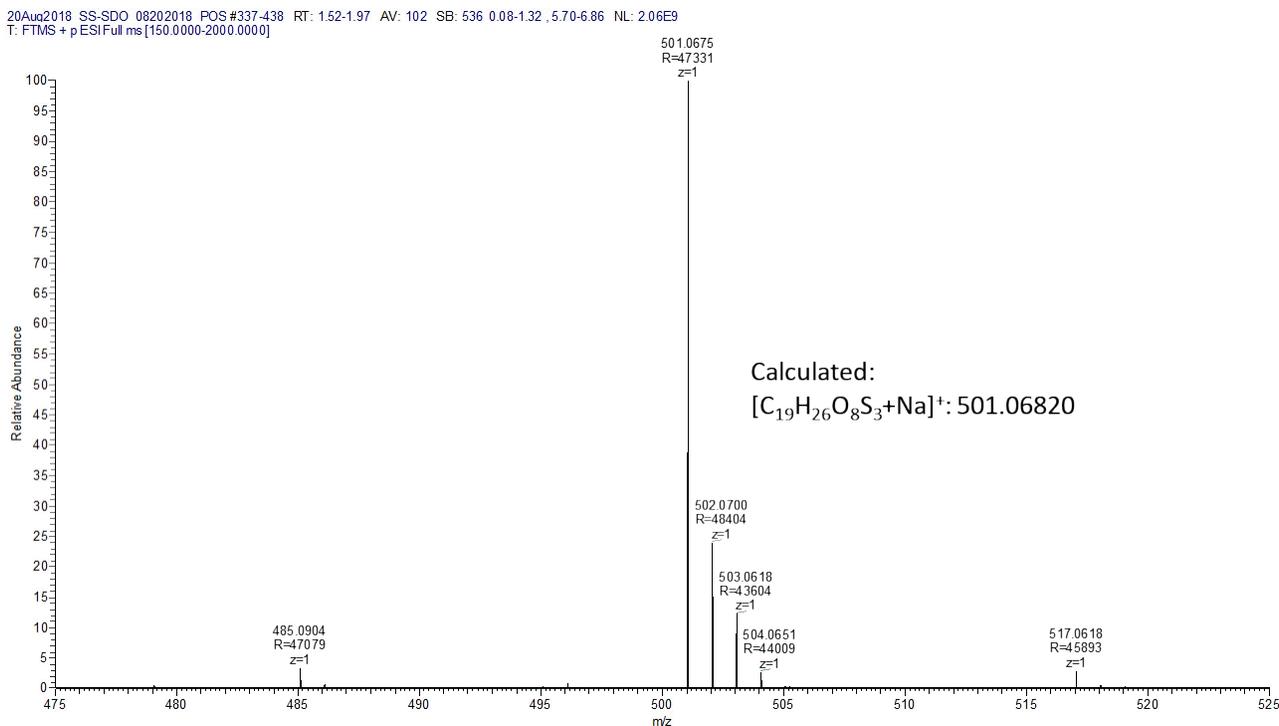
After 48 h, the samples were weighed. The swelling ratio was calculated as:

$$\text{Swelling ratio} = \frac{W_S - W_D}{W_D}$$

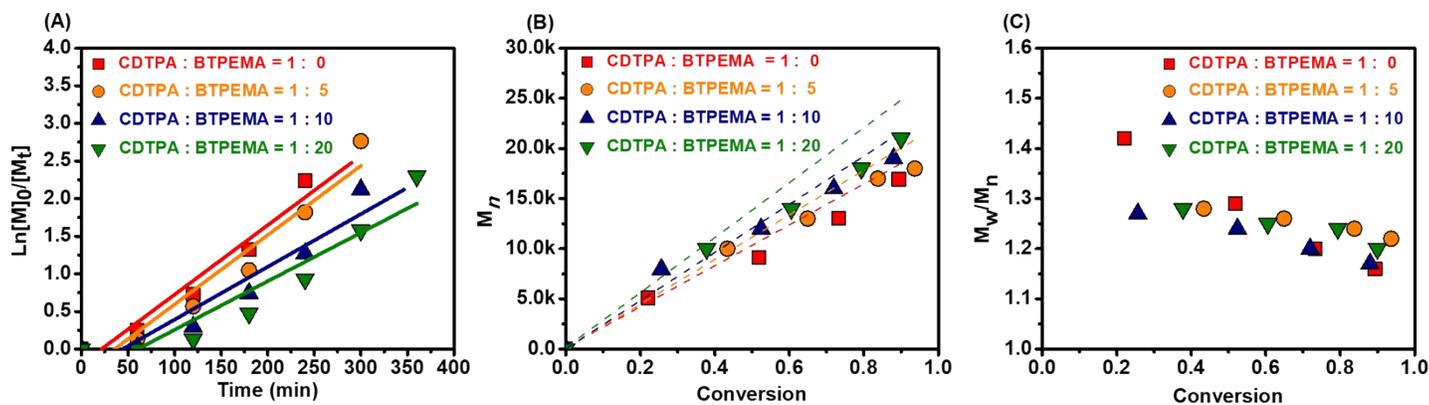
where  $W_S$  and  $W_D$  are the weights of the swollen and dry gels respectively.



**Figure S1.** 500 MHz  $^1\text{H}$  NMR spectrum of bisPEMAT RAFT agent in  $\text{CDCl}_3$ .



**Figure S2.** ESI-MS spectrum of bisPEMAT RAFT agent.



**Figure S3.** Polymerization of MMA mediated by CDTPA under green light irradiation performed in DMSO in the presence of different concentrations of BTPEMA ( $\lambda_{\text{max}} = 520$  nm, intensity =  $4.25$  mW/cm $^2$ ) with  $[\text{MMA}]:[\text{CDTPA}] = 200 : 1$ , 50% v/v monomer concentration. (A) Plot of  $\text{Ln}([M]_0/[M]_t)$  vs. exposure time in the presence of different concentrations of BTPEMA ( $[\text{CDTPA}]:[\text{BTPEMA}] = 1:0, 1:5, 1:10,$  and  $1:20$  with  $k_p^{\text{app}} = 9.25 \times 10^{-3} \text{ min}^{-1}, 9.21 \times 10^{-3} \text{ min}^{-1}, 7.05 \times 10^{-3} \text{ min}^{-1},$  and  $6.46 \times 10^{-3} \text{ min}^{-1}$ , respectively); (B) plot of  $M_n$  vs. conversion for different concentrations of BTPEMA (solids represent molecular weights determined by DMF GPC while dotted lines represent theoretical molecular weights); and (C) plot of  $M_w/M_n$  vs. conversion for different concentrations of BTPEMA.

**Table S1.** Polymerization of methyl methacrylate under green light irradiation with 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) as the RAFT agent in the presence of different concentrations of BTPEMA.<sup>a</sup>

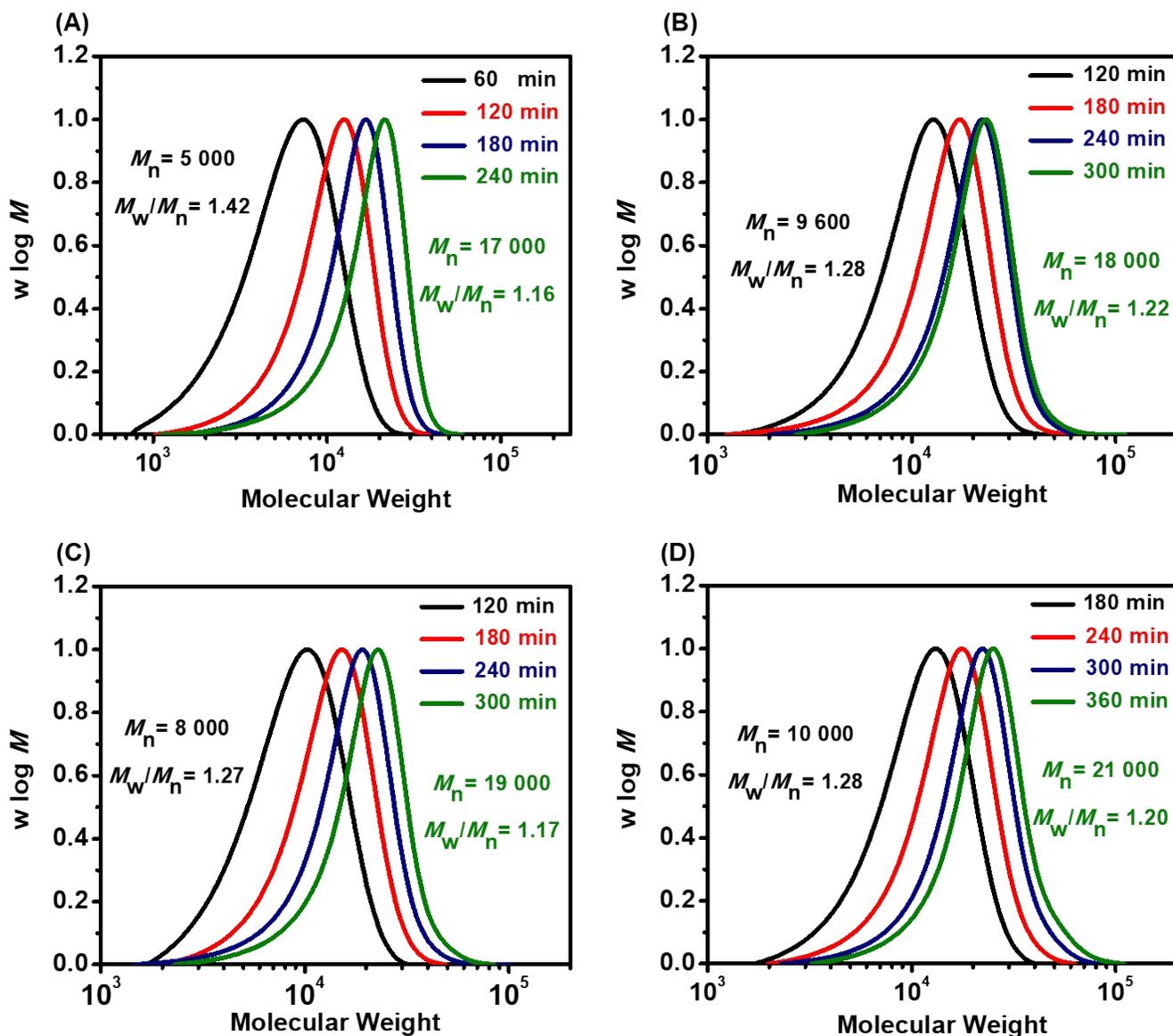
no.	Exp. Cond. <sup>a</sup> [MMA] : [CDTPA] : [BTPEMA]	Time (hr)	$\alpha^c$ (%)	$M_{n,th}^d$	$M_{n,GPC}^e$	$M_w/M_n^e$
1	200 : 1 : 0	4	90	18 300	17 000	1.16
2	200 : 1 : 5	5	94	22 300	18 000	1.22
3	200 : 1 : 10	5	90	21 500	19 000	1.17
4	200 : 1 : 20	6	90	24 800	21 000	1.20

Note: <sup>a</sup>Reactions were performed at room temperature with 50 % v/v monomer concentration in DMSO.

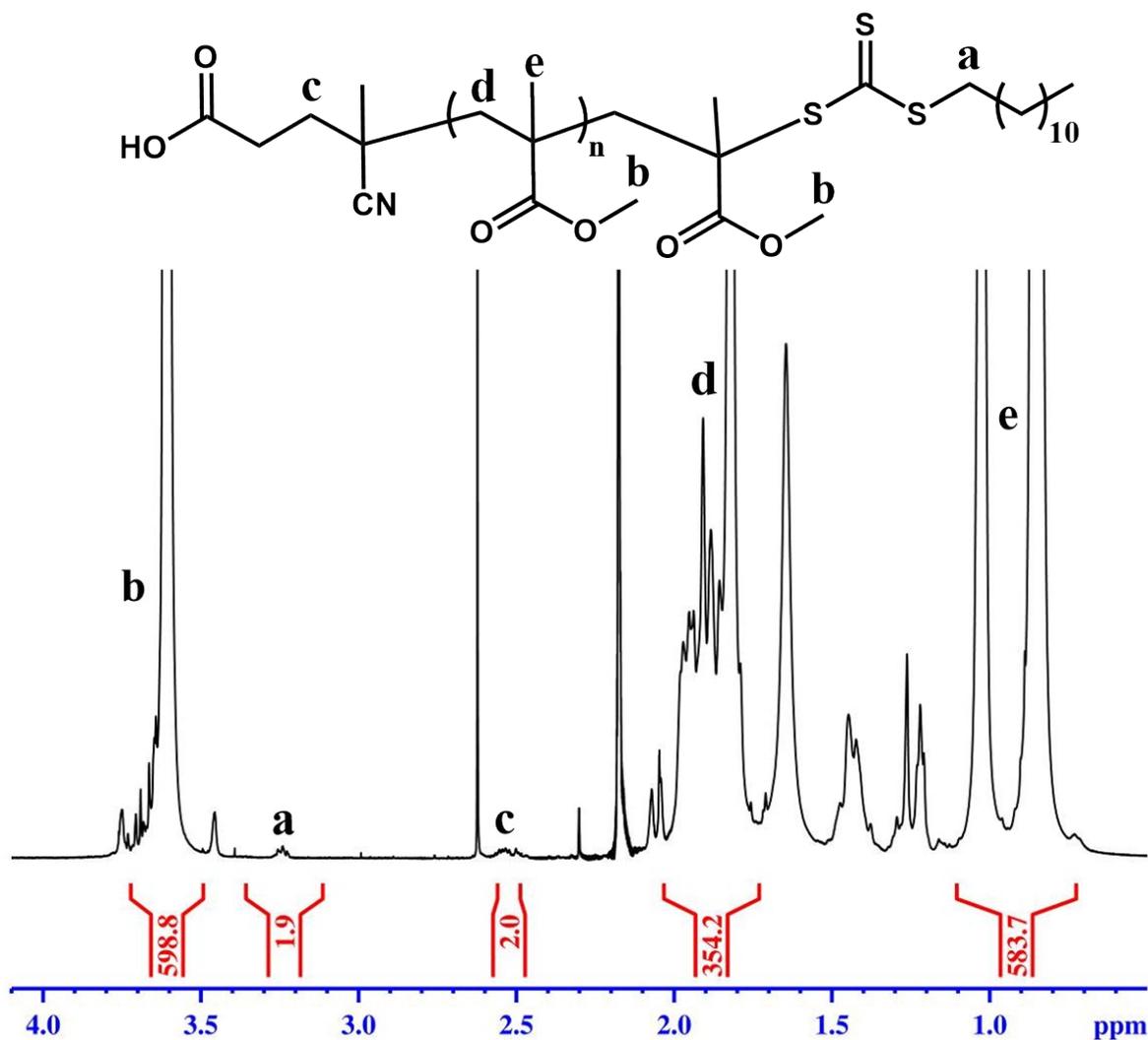
<sup>b</sup>Reaction mixtures were irradiated under visible green light LEDs ( $\lambda_{max} = 520$  nm, intensity = 4.25 mW/cm<sup>2</sup>).

<sup>c</sup>Monomer conversions were determined by using <sup>1</sup>H NMR spectroscopy. <sup>d</sup>Theoretical molecular weights were calculated using the following equation:  $M_{n,th} = [MMA]_0/[CDTPA]_0 \times MW^{MMA} \times \alpha^{MMA} + MW^{CDTPA} + [BTPEMA]_0/[CDTPA]_0 \times MW^{BTPEMA} \times \alpha^{BTPEMA}$ , where  $[MMA]_0$ ,  $[CDTPA]_0$ ,  $MW^{MMA}$ ,  $\alpha^{MMA}$ ,  $MW^{CDTPA}$ ,  $[BTPEMA]_0$ ,  $MW^{BTPEMA}$ ,  $\alpha^{BTPEMA}$  correspond to initial MMA monomer concentration, initial CDTPA concentration, molar mass of MMA, MMA conversion determined by <sup>1</sup>H NMR, molar mass of CDTPA, initial BTPEMA concentration, molar mass of BTPEMA, and BTPEMA conversion determined by <sup>1</sup>H NMR.

<sup>e</sup>Molecular weight and dispersity ( $M_w/M_n$ ) values were determined by THF GPC analysis calibrated using poly(methyl methacrylate) standards.

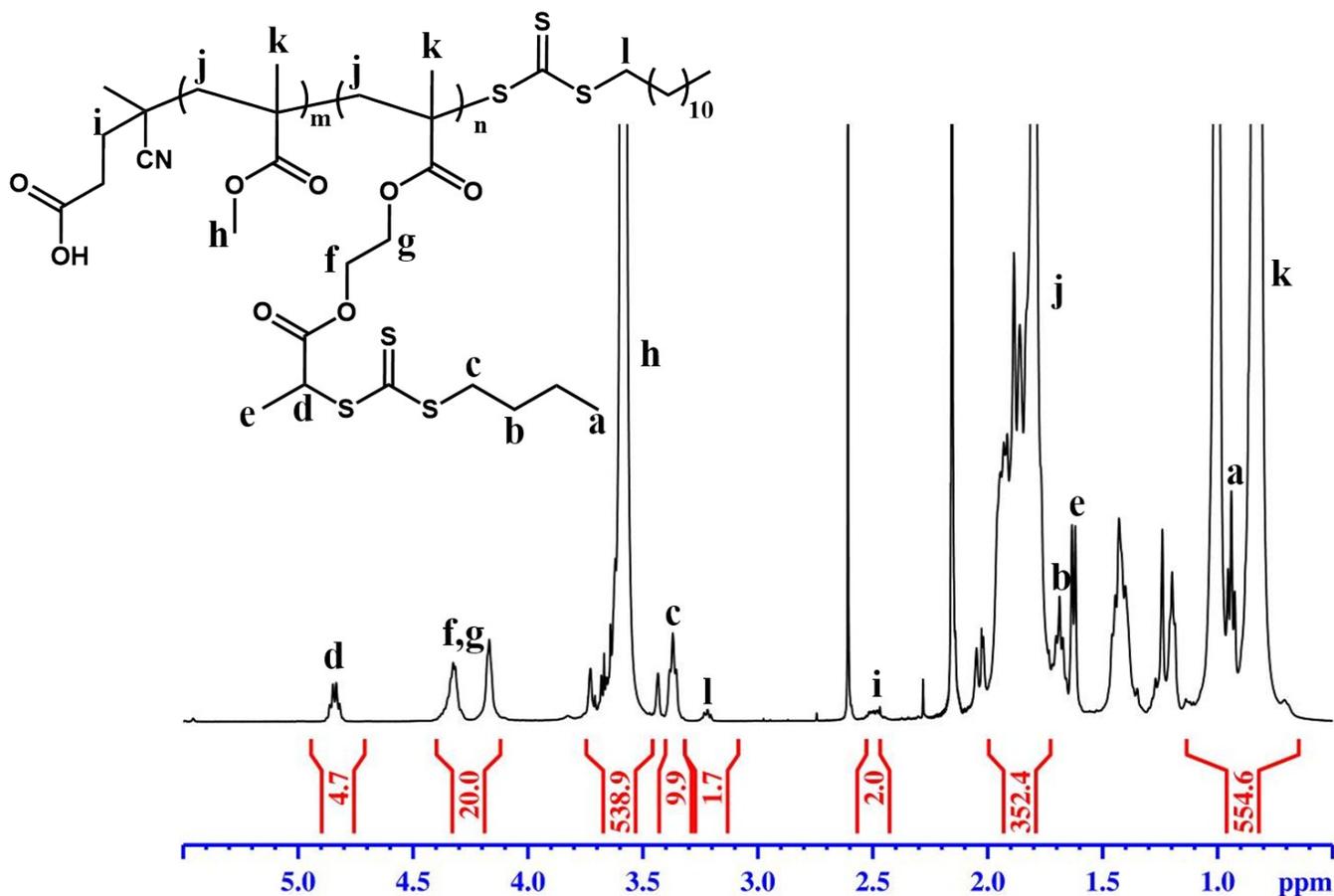


**Figure S4.** GPC traces for polymerization of methyl methacrylate (MMA) mediated by 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA) under green light irradiation ( $\lambda_{\max} = 520$  nm, intensity = 4.25 mW/cm<sup>2</sup>) in the presence of different concentrations of BTPEMA ([MMA]:[CDTPA] = 200 : 1, 50% v/v monomer concentration). (A) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA:BTPEMA = 1:0; (B) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA: BTPEMA = 1:5; (C) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA: BTPEMA = 1:10; and (D) GPC traces mapping kinetic studies of polymerization of MMA with CDTPA: BTPEMA = 1:20.



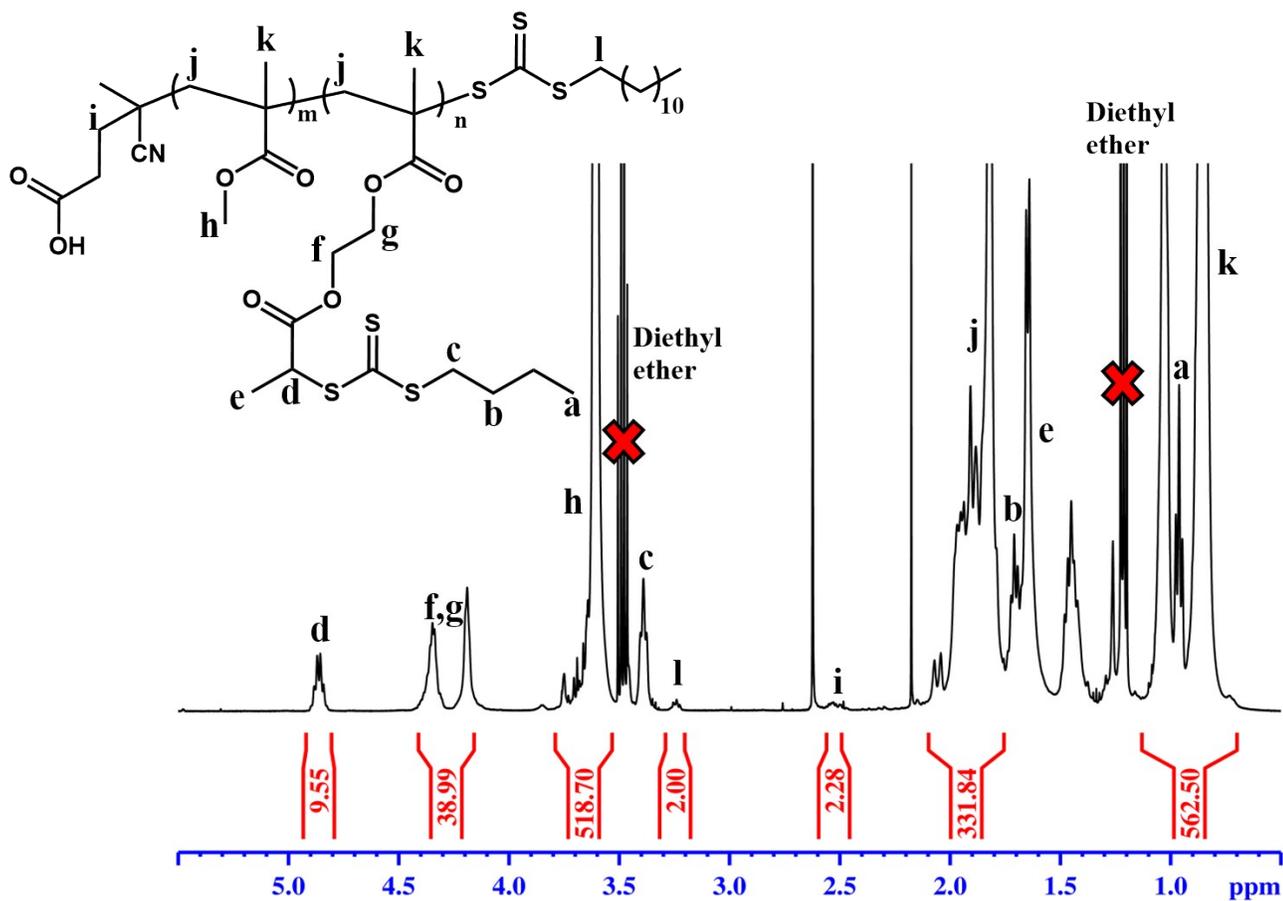
**Figure S5.** 500 MHz <sup>1</sup>H NMR spectrum of poly(methyl methacrylate) (top structure) in CDCl<sub>3</sub> with  $M_{n,NMR} = 18\,200$ ,  $M_{n,GPC} = 17\,000$ , and  $M_{n,theo} = 18\,300$  in the presence of [CDTPA]:[BTPEMA] = 1 : 0.

\*  $M_{n,NMR}$  was determined using the following equation  $M_{n,NMR} = (I^{1.7-2.0\text{ ppm}}/2)/(I^{3.2\text{ ppm}}/2) \times MW^M + MW^{RAFT}$  where  $I^{1.7-2.0\text{ ppm}}$  and  $I^{3.2\text{ ppm}}$  correspond to integration of proton **d** and **a**, respectively.



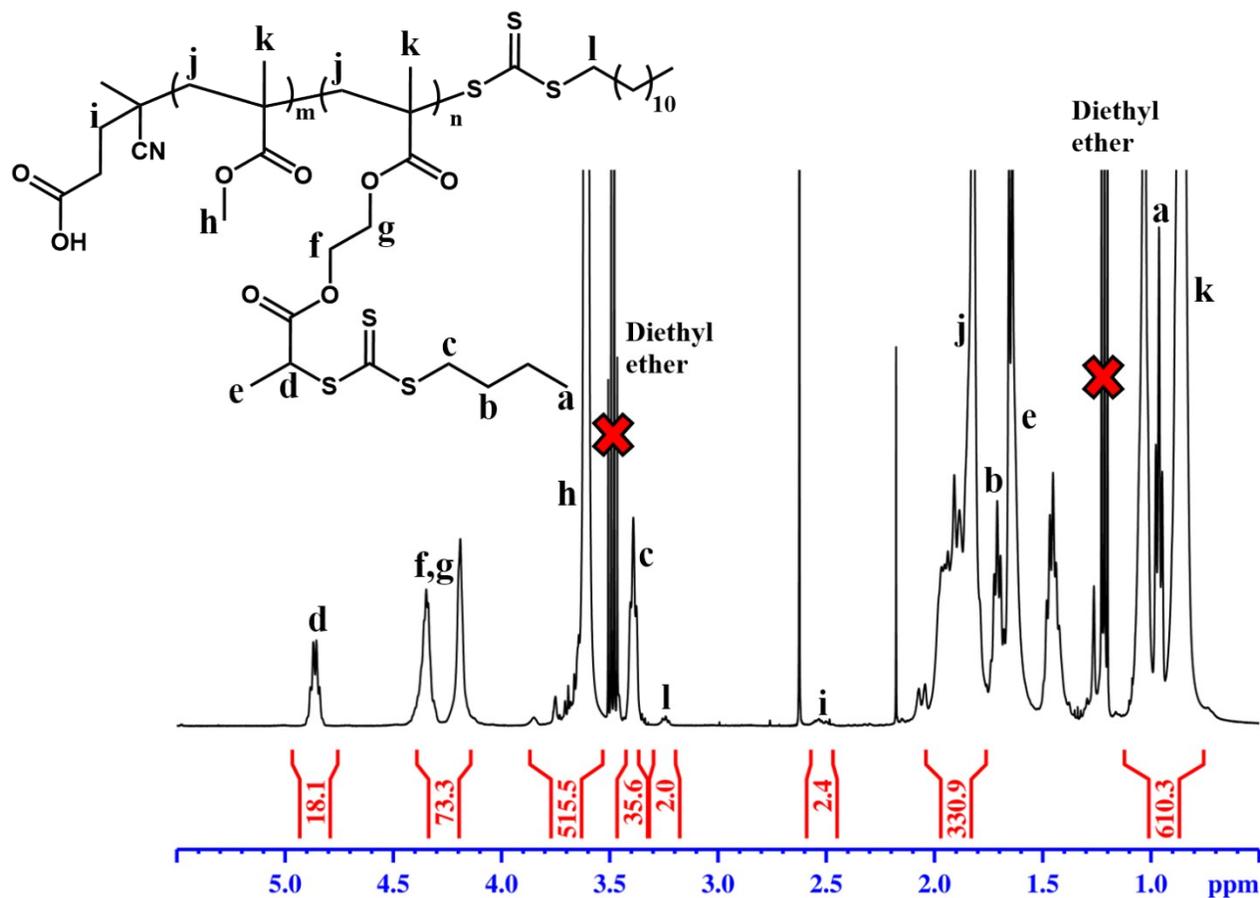
**Figure S6.** 500 MHz <sup>1</sup>H NMR spectrum of PMMA-*rand*-P(BTPEMA) (top structure) in CDCl<sub>3</sub> with  $M_{n,NMR} = 20\ 000$ ,  $M_{n,GPC} = 18\ 000$ , and  $M_{n,theo} = 22\ 300$  in the presence of [CDTPA]:[BTPEMA] = 1 : 5.

\* $M_{n,NMR}$  was determined using the following equation  $M_{n,NMR} = (I^{3.6-3.7\text{ ppm}}/2)/(I^{3.2\text{ ppm}}/2) \times MW^M + MW^{RAFT}$  where  $I^{3.6-3.7\text{ ppm}}$  and  $I^{3.2\text{ ppm}}$  correspond to integration of proton **h** and **a**, respectively.



**Figure S7.** 500 MHz <sup>1</sup>H NMR spectrum of PMMA-*rand*-P(BTPEMA) (top structure) in CDCl<sub>3</sub> with  $M_{n,NMR} = 21\,200$ ,  $M_{n,GPC} = 19\,000$ , and  $M_{n,theo} = 21\,500$  in the presence of [CDTPA]:[BTPEMA] = 1 : 10.

\* $M_{n,NMR}$  was determined using the following equation  $M_{n,NMR} = (I^{3.6-3.7\text{ ppm}}/2)/(I^{3.2\text{ ppm}}/2) \times MW^M + MW^{RAFT}$  where  $I^{3.6-3.7\text{ ppm}}$  and  $I^{3.2\text{ ppm}}$  correspond to integration of proton **h** and **a**, respectively.



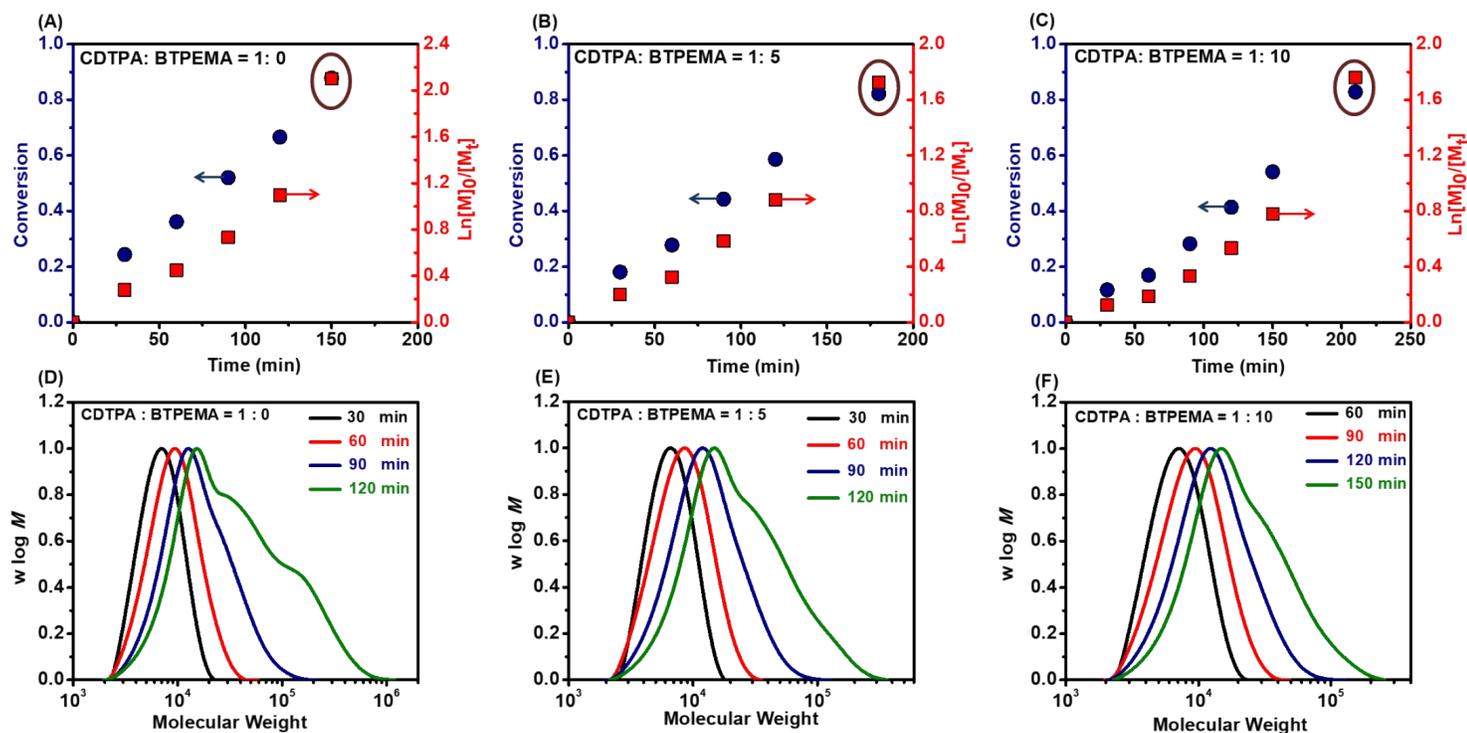
**Figure S8.** 500 MHz <sup>1</sup>H NMR spectrum of PMMA-*rand*-P(BTPEMA) (top structure) in CDCl<sub>3</sub> with  $M_{n,NMR} = 24\,000$ ,  $M_{n,GPC} = 21\,000$ , and  $M_{n,theo} = 24\,800$  in the presence of [CDTPA]:[BTPEMA] = 1 : 20.

\* $M_{n,NMR}$  was determined using the following equation  $M_{n,NMR} = (I^{3.6-3.7\text{ ppm}}/2)/(I^{3.2\text{ ppm}}/2) \times MW^M + MW^{RAFT}$  where  $I^{3.6-3.7\text{ ppm}}$  and  $I^{3.2\text{ ppm}}$  correspond to integration of proton **h** and **a**, respectively.

**Table S2.** D-STEM-0 network synthesis under green light irradiation ( $\lambda_{\max} = 520$  nm, intensity = 4.25 mW/cm<sup>2</sup>) with [MMA]:[CDTPA]:[PEGDMA<sub>750</sub>] of 200 : 1 : 2.<sup>a</sup>

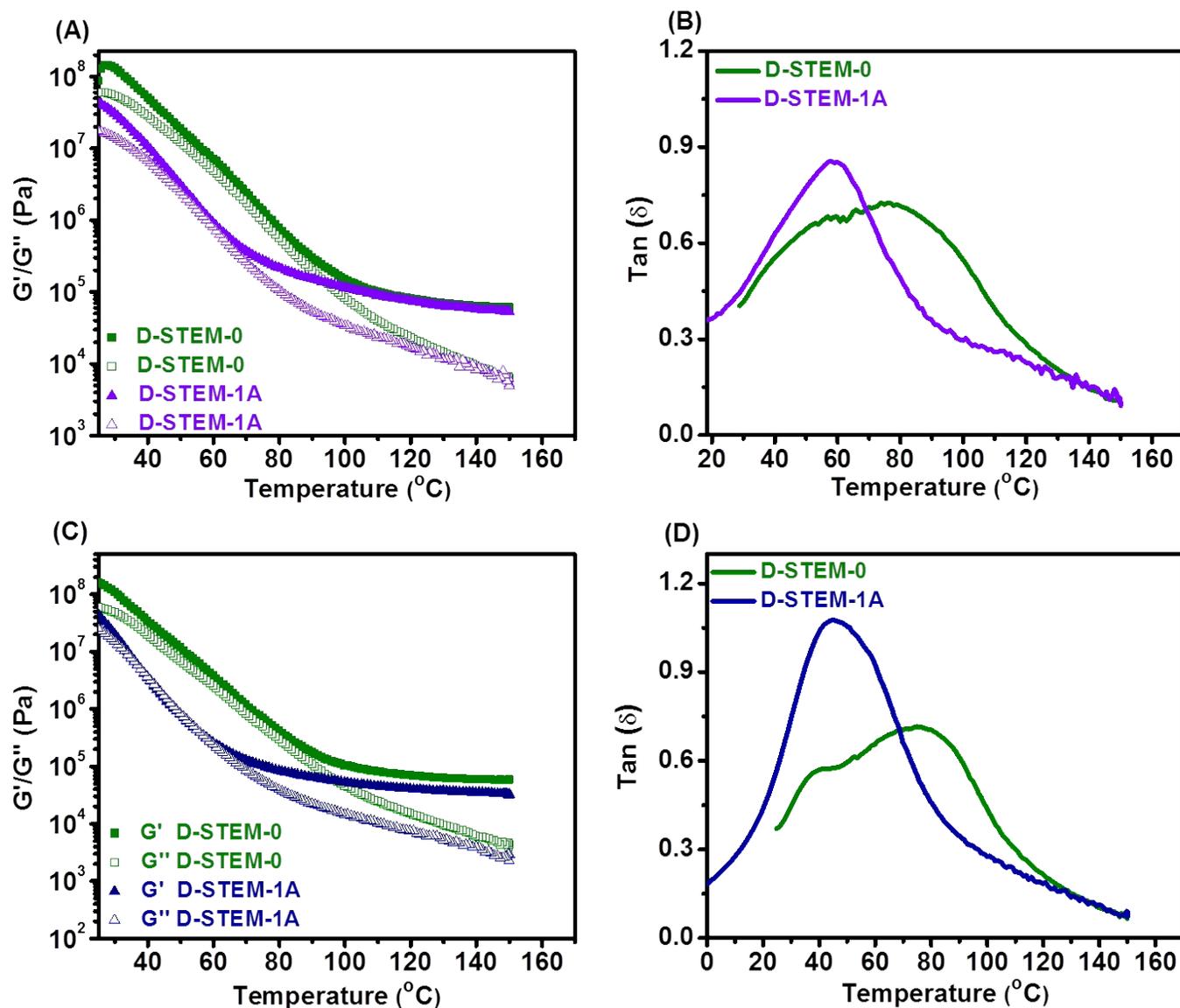
no.	Exp. Cond. <sup>a</sup> [MMA] : [CDTPA] : [BTPEMA]	Time (hr)	$\alpha^b$ (%)
1	200 : 1 : 0	2.5	88
2	200 : 1 : 5	3	82
3	200 : 1 : 10	3.5	83
4	200 : 1 : 20	4	80

Note: <sup>a</sup>Reactions were performed at room temperature with 50 % v/v monomer concentration in DMSO. <sup>b</sup>Monomer conversions were determined by using <sup>1</sup>H NMR spectroscopy and correspond to the monomer conversion at gelation point.

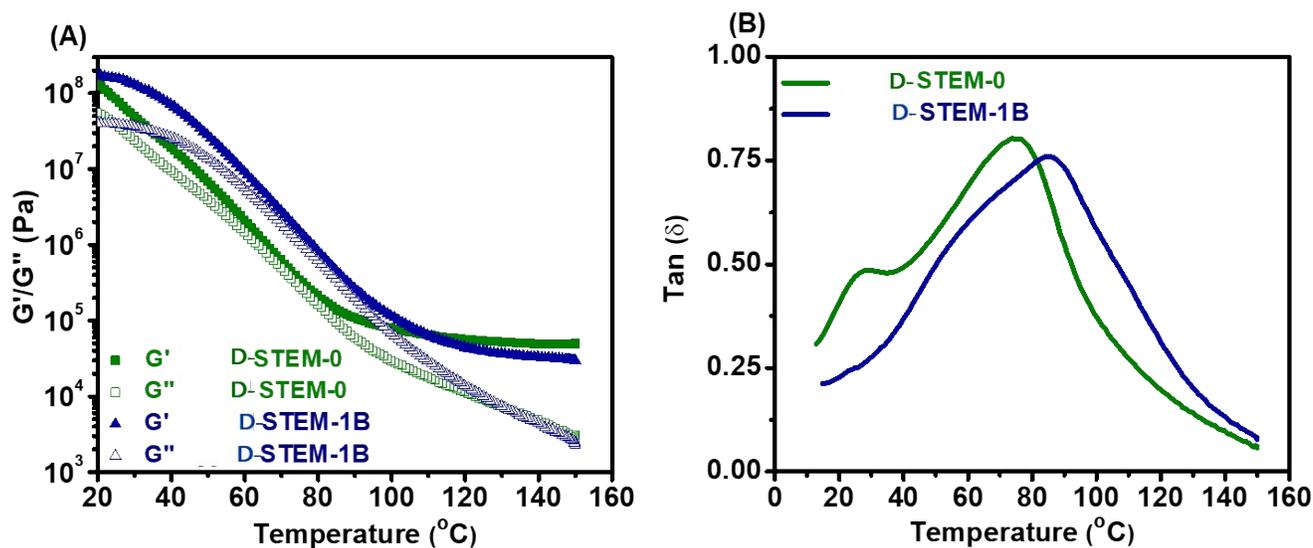


**Figure S9.** Polymerization of MMA mediated by CDTPA to determine gelation point of polymer under green light irradiation ( $\lambda_{\max} = 520$  nm, intensity = 4.25 mW/cm<sup>2</sup>) performed in DMSO and PEGDMA<sub>750</sub> crosslinker in the presence of different concentrations of BTPEMA with [MMA]:[CDTPA]:[PEGDMA<sub>750</sub>] = 200 : 1 : 2, 50% v/v monomer concentration. (A,B,C) Plots of conversion and  $\ln([M]_0/[M]_t)$  vs. exposure time in the presence of different concentrations of BTPEMA ([CDTPA]:[BTPEMA] = 1:0, 1:5, and 1:10, respectively) with brown circles representing monomer conversions upon reaching gelation point; and (D,E,F) GPC traces mapping kinetic studies of gelation of PMMA with CDTPA:BTPEMA = 1:0, 1:5, and 1:10, respectively.

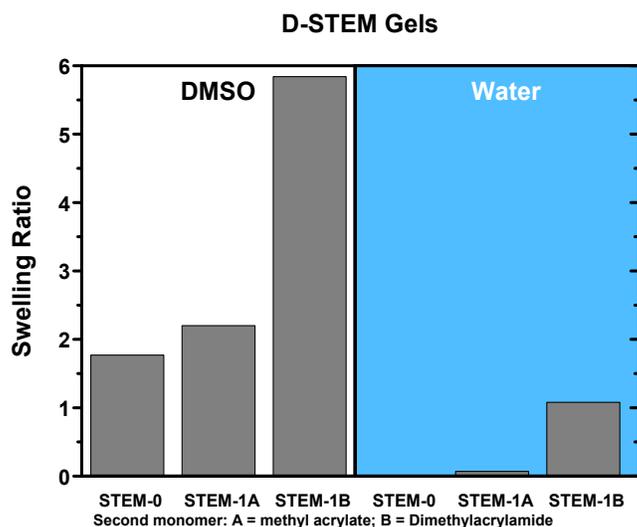
Note: Gelation point was determined visually as the time at which the gel did not flow upon inverting the vial.



**Figure S10.** Temperature dependence on the storage ( $G'$ ) and loss moduli ( $G''$ ) and  $\tan(\delta)$  before and after growing PMA side chains in STEM networks with different concentrations of BTPEMA. (A,B) D-STEM-0 network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{BTPEMA})_5$  while D-STEM-1A network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{BTPEMA-graft-PMA}_{18})_5\text{-block-PMA}_{18}$ ; and (C,D) D-STEM-0 network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{BTPEMA})_{10}$  while D-STEM-1A network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{BTPEMA-graft-PMA}_7)_{10}\text{-block-PMA}_7$ .



**Figure S11.** Temperature dependence on the storage ( $G'$ ) and loss moduli ( $G''$ ) and  $\tan(\delta)$  before and after growing PDMA side chains in STEM networks with D-STEM-0 network is composed of  $\text{PMMA}_{200}\text{-rand-P(BTPEMA)}_{20}$  while D-STEM-1B network is composed of  $\text{PMMA}_{200}\text{-rand-P(BTPEMA-graft-PDMA}_{15})_{20}\text{-block-PDMA}_{15}$ .

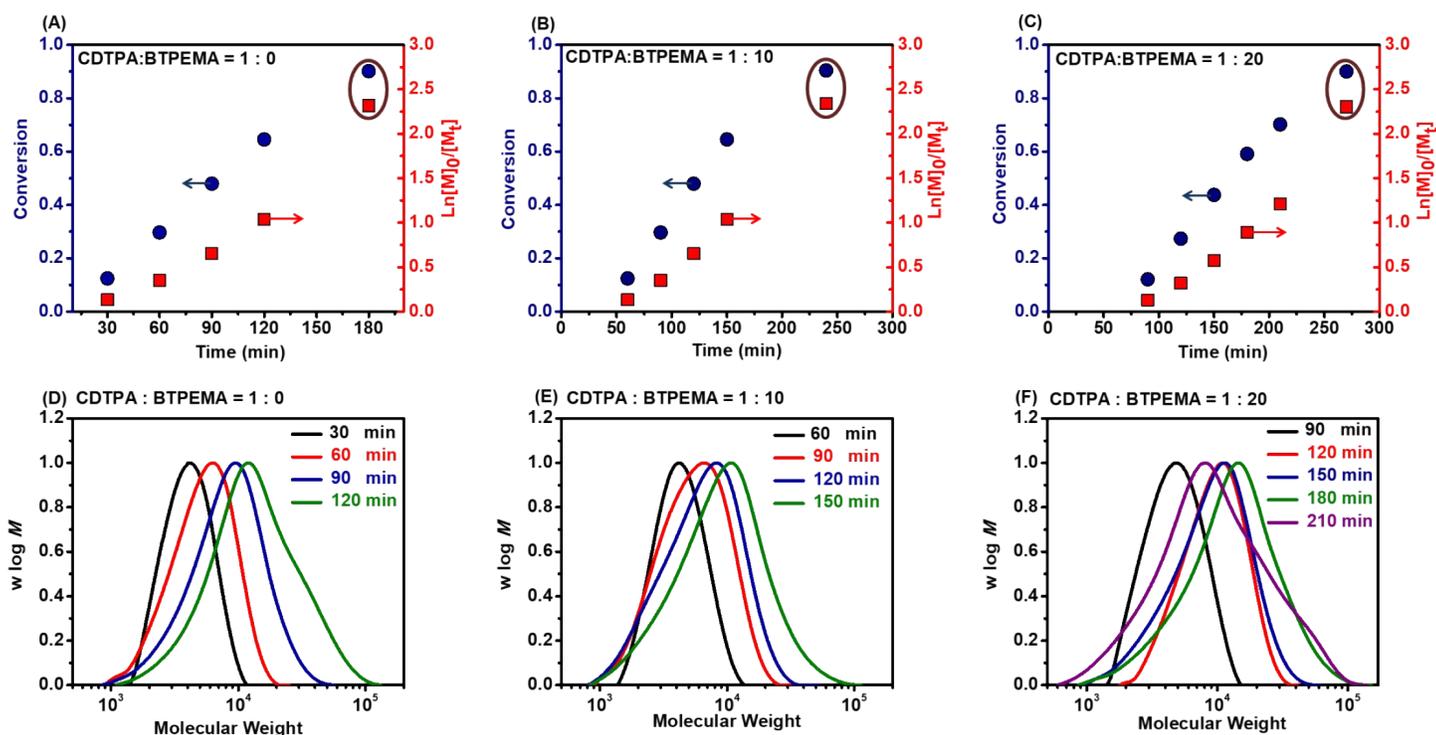


**Figure S12.** The swelling ratios of the D-STEM gels (Figure 1 and Figure S11) in DMSO and water.

**Table S3.** E-STEM-0 network synthesis under green light irradiation ( $\lambda_{\text{max}} = 520 \text{ nm}$ , intensity =  $4.25 \text{ mW/cm}^2$ ) with  $[\text{MMA}]:[\text{CDTPA}]:[\text{bisPEMAT}]$  of  $200 : 1 : 2$ .<sup>a</sup>

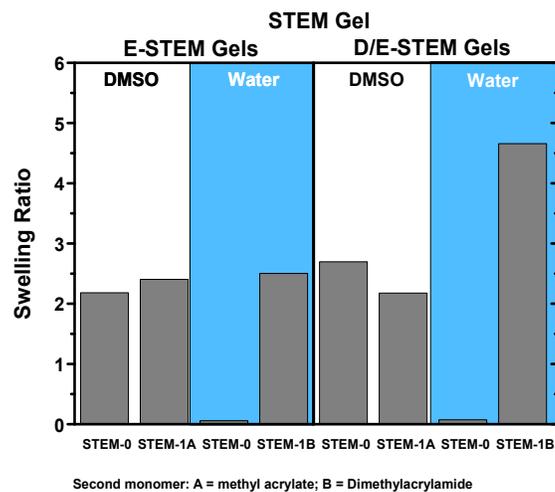
no.	Exp. Cond. <sup>a</sup>	Time	$\alpha^b$
	[MMA] : [CDTPA] : [BTPEMA]	(hr)	(%)
1	200 : 1 : 0	3	90
2	200 : 1 : 10	4	91
3	200 : 1 : 20	4.5	90

Note: <sup>a</sup>Reactions were performed at room temperature with 50 % v/v monomer concentration in DMSO. <sup>b</sup>Monomer conversions were determined by using <sup>1</sup>H NMR spectroscopy and correspond to the monomer conversion at gelation point.

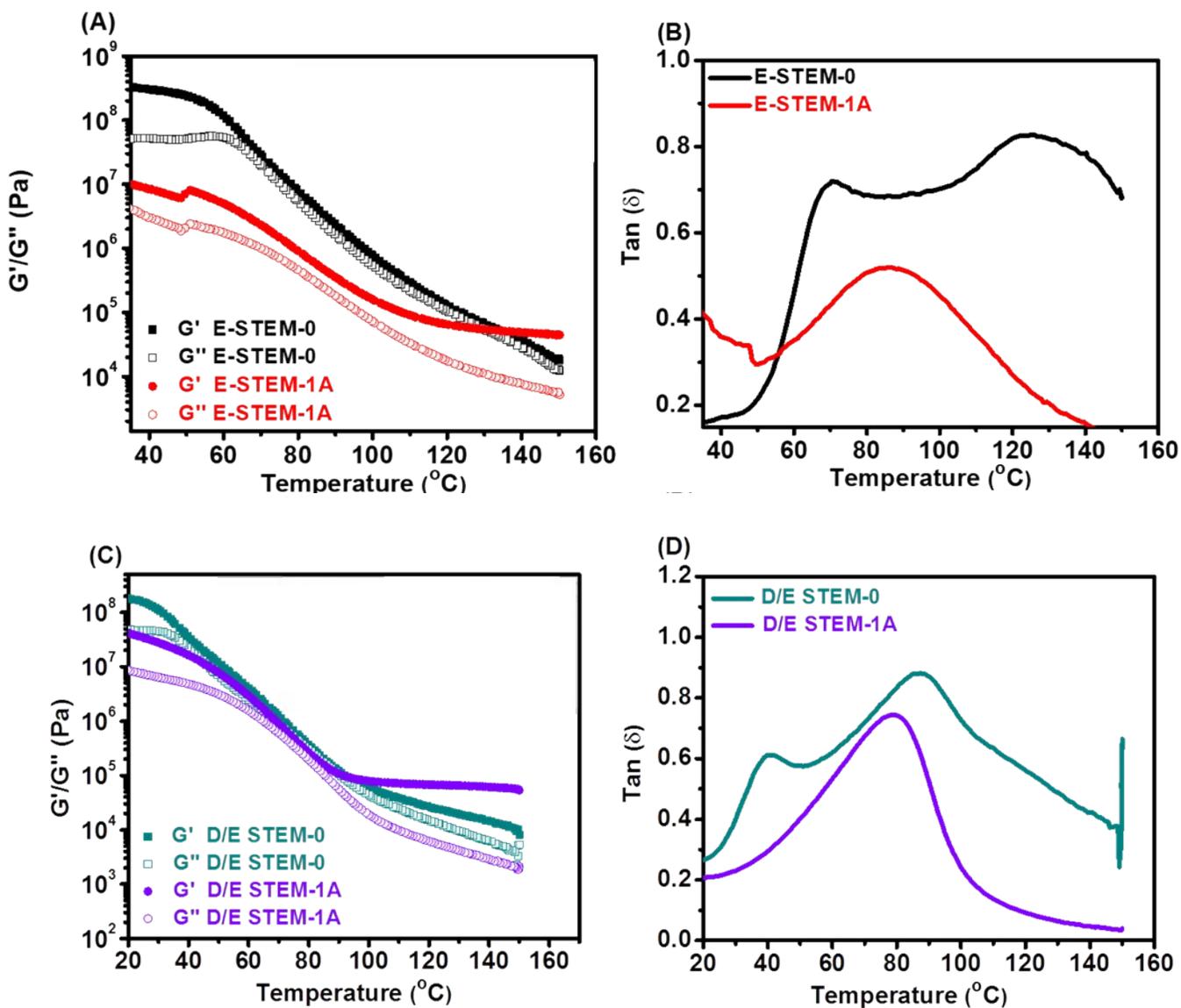


**Figure S13.** Kinetic studies of MMA mediated by CDTPA to determine gelation point of polymer under green light irradiation ( $\lambda_{\text{max}} = 520 \text{ nm}$ , intensity =  $4.25 \text{ mW/cm}^2$ ) performed in DMSO and bisPEMAT crosslinker in the presence of different concentrations of BTPEMA with [MMA]:[CDTPA]:[bisPEMAT] = 200 : 1 : 2, 50% v/v monomer concentration. (A,B,C) Plots of conversion and  $\text{Ln}([M]_0/[M]_t)$  vs. exposure time in the presence of different concentrations of BTPEMA ([CDTPA]:[BTPEMA] = 1:0, 1:10, and 1:20, respectively) with brown circles representing monomer conversions upon reaching gelation point; and (D,E,F) GPC traces mapping kinetic studies of gelation of PMMA with CDTPA:BTPEMA = 1:0, 1:10, and 1:20, respectively.

Note: Gelation point was determined visually as the time at which the gel did not flow upon inverting the vial.



**Figure S14.** The swelling ratios of the E- and D/E-STEM gels (Figure 2 and Figure S15) in DMSO and water.



**Figure S15.** Temperature dependence on the storage ( $G'$ ) and loss moduli ( $G''$ ) and  $\tan(\delta)$  before and after growing PMA side chains in STEM networks crosslinked with bisPEMAT in the absence (A,B) and presence (C, D) of BTPEMA. (A,B) D-STEM-0 network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{bisPEMAT})_2$  while E-STEM-1A network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{bisPEMAT-block-PMA}_{90})_2\text{-block-PMA}_{45}$ ; and (C,D) D/E-STEM-0 network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{bisPEMAT})_2\text{-rand-PBTPEMA}_{20}$  while D/E-STEM-1A network is composed of  $\text{PMMA}_{200}\text{-rand-P}(\text{bisPEMAT-block-PMA}_{16})_2\text{-rand-P}(\text{BTPEMA-graft-PMA}_8)_{20}\text{-block-PMA}_8$ .

### References:

[1] S. Shanmugam, J. Cuthbert, T. Kowalewski, C. Boyer, K. Matyjaszewski, *Macromolecules* **2018**, *51*, 7776.