Supporting Information

Reversing RAFT Polymerization: Near-Quantitative Monomer Generation via a Catalyst-Free Depolymerization Approach

Hyun Suk Wang,¹ Nghia P. Truong,¹ Zhipeng Pei,² Michelle L. Coote,² Athina Anastasaki¹*

¹Laboratory of Polymeric Materials, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, Zurich, Switzerland

²Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory, 2601, Australia

*email: athina.anastasaki@mat.ethz.ch
Table of Contents

Methods ............................................................................................................................................... 1
  Materials ........................................................................................................................................ 1
  NMR spectroscopy .......................................................................................................................... 1
  Size-exclusion chromatography (SEC) ............................................................................................ 1
  Polymerization of MMA .................................................................................................................. 1
  Polymerization of OEGMA .............................................................................................................. 1
  Polymerization of BuMA .................................................................................................................. 2
  Polymerization of BzMA .................................................................................................................. 2
  Polymerization of TFEMA .............................................................................................................. 2
  Polymerization of HEMA ................................................................................................................ 3
  Polymerization of DMAEMA .......................................................................................................... 3
  Purification of PMMA, PBuMA, PBzMA .......................................................................................... 3
  Purification of POEGMA ................................................................................................................ 3
  Purification of PTFEMA and PDMAEMA ...................................................................................... 3
  Purification of PHEMA .................................................................................................................. 4
  Depolymerization procedure for PMMA, PBuMA, PBzMA, PTFEMA, PHEMA, PDMAEMA. ................................................................................................................................. 4
  Depolymerization procedure for POEGMA ..................................................................................... 4
  Repolymerization procedure for POEGMA ..................................................................................... 4
  Depolymerization of POEGMA for subsequent repolymerization to POEGMA hydrogel. ............ 5
  Preparation of POEGMA hydrogel from depolymerized POEGMA. ............................................. 5
  Depolymerization procedure for POEGMA hydrogel ................................................................. 5
  CTA removal of POEGMA hydrogel ............................................................................................... 5
  Addition of TEMPO to depolymerization of PMMA ...................................................................... 5
  CTA removal for PMMA .................................................................................................................. 6
  Depolymerization of CTA-removed PMMA ................................................................................... 6
  Determination of monomer conversion during polymerization .................................................... 6
  Determination of depolymerization conversion ............................................................................. 6
  Additional Data ............................................................................................................................... 7
Table of Figures

**Figure S1.** SEC trace of PMMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:120). .................................................. 8  
**Figure S2.** $^1$H-NMR spectrum of purified PMMA prior to depolymerization. .......................................................... 10  
**Figure S3.** Successful chain extension of PMMA with benzyl methacrylate at 70 °C in dioxane ([macro-CTA]:[BzMA]:[AIBN] = 1:120:0.1). ........................................................................................................ 11  
**Figure S4.** Depolymerization of PMMA macroCTA under (a) various concentrations at 120 °C and (b) under various temperatures at 5 mM. Depolymerizations were performed in dioxane after degassing via N$_2$ sparging.................................................. 12  
**Figure S5.** UV-vis of the depolymerization reaction of PMMA at 5 mM and 120 °C at 0% (black trace) and 85% (red trace) depolymerization.......................................................................................... 13  
**Figure S6.** Evolution of SEC trace of PMMA during depolymerization at 5 mM and 120 °C. Intensities are normalized to a poly(ethylene glycol) internal standard that was added at the beginning of the reaction........................................................................................................................................ 14  
**Figure S7.** Distillation setup for distillation of PMMA.......................................................... 17  
**Figure S8.** $^1$H-NMR spectra of the recovered DMSO and MMA after depolymerization of PMMA. A mixture of DMSO and MMA were distilled from the reaction solution into an aliquot in the first round, then MMA was subsequently fractionally distilled from the mixture to a second aliquot (depolymerization conversion = 40%, yield = 33%). Acetone-d$_6$ was used as the NMR solvent. 18  
**Figure S9.** SEC trace (UV detector) of PMMA before and after end group removal via reacting with excess AIBN at 70 °C ................................................................................................................... 19  
**Figure S10.** Evolution of depolymerization conversion during the depolymerization of PMMA (5 mM, 120 °C) with time in the presence or absence of TEMPO. Equivalents are relative to macroCTA. ................................................................................................................... 20  
**Figure S11.** SEC traces of the chain extension of PMMA with benzyl methacrylate at 120 °C in the presence of TEMPO. ................................................................................................................... 21  
**Figure S12.** (top) Scheme of possible autopolymerization of bulk benzyl methacrylate at 120 °C. (bottom) $^1$H-NMR of reaction after 3 h at 120 °C showing no polymerization. ..................... 22  
**Figure S13.** SEC trace of purified POEGMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 45%, $M_n$ = 18,600 g/mol, $D$ = 1.14. .................. 23  
**Figure S14.** $^1$H-NMR spectrum of purified POEGMA prior to depolymerization. .................. 24  
**Figure S15.** SEC trace of purified PBuMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 72%, $M_n$ = 4,200 g/mol, $D$ = 1.10. .................. 25  
**Figure S16.** $^1$H-NMR spectrum of purified PBuMA prior to depolymerization. .................. 26  
**Figure S17.** SEC trace of purified PBzMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 73%, $M_n$ = 4,800 g/mol, $D$ = 1.12. .................. 27  
**Figure S18.** $^1$H-NMR spectrum of purified PBzMA prior to depolymerization. .................. 28  
**Figure S19.** SEC trace of purified PTFEMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 69%, $M_n$ = 11,300 g/mol, $D$ = 1.15. .................. 29  
**Figure S20.** $^1$H-NMR spectrum of purified PTFEMA prior to depolymerization. .................. 30  
**Figure S21.** SEC trace of purified PHEMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 70%, $M_n$ = 8,900 g/mol, $D$ = 1.15. .................. 31
Figure S22. $^1$H-NMR spectrum of purified PHEMA prior to depolymerization.......................... 32
Figure S23. SEC trace of purified PDMAEMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 40%, $M_n = 3,800$ g/mol, $D = 1.13$..... 33
Figure S24. $^1$H-NMR spectrum of purified PDMAEMA prior to depolymerization..................... 34
Figure S25. NMR spectrum of supernatant of the depolymerization reaction after precipitation in diethyl ether/hexane. Inset shows the aromatic protons of the cleaved CTA responsible for the RAFT repolymerization of the depolymerization product................................................................. 35
Figure S26. Full SEC traces of the controlled repolymerization of POEGMA............................. 36
Figure S27. (a) side-by-side comparison of POEGMA hydrogels before (left) and after (right) CTA removal via reacting with excess AIBN in toluene at 70 °C. (b) Reaction mixture after removal of POEGMA hydrogel. The red color confirms cleavage of CTA from the hydrogel...... 37
Figure S28. Attempted depolymerization of CTA-removed POEGMA hydrogel at 350 mg/40 ml and 120 °C. Photos are of the hydrogel (a) in the reaction flask after 12 h and (b) after collecting the hydrogel using a filter paper. ............................................................................................................. 38
Table of Tables

**Table S1.** Gibbs free energy ($\Delta G$, kJ/mol) and equilibrium constant for depopagation, and predicted ratio of depolymerized/polymerized radical as a function of T and total starting concentration of polymer.\(^{\text{a}}\) .................................................................................................................. 7

**Table S2.** Characterization of PMMA ................................................................................................................................................. 9

**Table S3.** Characterization of PMMA during depolymerization at 5 mM and 120 °C. ............... 15

**Table S4.** Characterization of PMMA depolymerization at 70 °C......................................................... 16
Methods

Materials. All materials were purchased from either Sigma Aldrich or Fischer Scientific unless otherwise stated. Benzyl methacrylate (BzMA, >98.0%) was purchased from Tokyo Chemical Industries. Monomers were filtered through basic alumina before use.

NMR spectroscopy. $^1$H-NMR spectra were recorded on a Bruker Avance-300 spectrometer using acetone-$d_6$, dimethyl sulfoxide-$d_6$, or CDCl$_3$ as the NMR solvent. Chemical shifts are given in ppm downfield from tetramethylsilane and referenced to residual solvent proton signals.

Size-exclusion chromatography (SEC). SEC was measured on a Shimadzu equipment comprising a CBM-20A system controller, LC-20AD pump, SIL-20A automatic injector, 10.0 μm bead-size guard column (50 x 7.5 mm) followed by three KF-805L columns (300 x 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), SPD-20A ultraviolet detector, and an RID-20A differential refractive index detector. The column temperature was maintained at 40 °C using a CTO-20A oven. The flow rate was set to 1 ml/min and with N, N-dimethylacetamide (DMAc, Acros, HPLC grade, with 0.03 w/v LiBr) as the eluent. Molecular weights were determined relative poly(methyl methacrylate) standards with molecular weights ranging from 5,000 to 1.5 x 10$^6$ g/mol (Agilent Technologies). All SEC samples were dissolved in DMAc and passed through 0.45 μm filters prior to analysis.

Polymerization of MMA. Into a 25 mL round bottom flask, 184.2 mg of 2-cyanoprop-2-yl dithiobenzoate (832.3 μmol, 1 equiv) were dissolved in 7.5 mL toluene. A stock solution of AIBN (20 mg) was prepared in 2 mL toluene, and 1370 μL of this solution (13.7 mg, 83.2 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 10.6 mL of MMA (10.0 g, 99.9 mmol, 120 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for $^1$H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 48% conversion by removing the reaction from the oil bath and removing the septum.

Polymerization of OEGMA. Into a 50 mL round bottom flask, 44.3 mg of 2-cyanoprop-2-yl dithiobenzoate (200 μmol, 1 equiv) were dissolved in 10 mL toluene. A stock solution of AIBN (10 mg) was prepared in 1 mL toluene, and 328 μL of this solution (3.28 mg, 20 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 10 g of OEGMA (20 mmol, 100 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling.
for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 45% conversion by removing the reaction from the oil bath and removing the septum.

**Polymerization of BuMA.** Into a 25 mL round bottom flask, 155.7 mg of 2-cyanoprop-2-yl dithiobenzoate (703 μmol, 1 equiv) were dissolved in 3 mL toluene. A stock solution of AIBN (20 mg) was prepared in 2 mL toluene, and 1150 μL of this solution (11.5 mg, 70.3 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 4.47 mL of BuMA (4 g, 28.1 mmol, 40 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 72% conversion by removing the reaction from the oil bath and removing the septum.

**Polymerization of BzMA.** Into a 10 mL round bottom flask, 125.6 mg of 2-cyanoprop-2-yl dithiobenzoate (703 μmol, 1 equiv) were dissolved in 3 mL toluene. A stock solution of AIBN (10 mg) was prepared in 1 mL toluene, and 932 μL of this solution (9.32 mg, 56.8 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 3.85 mL of BzMA (4 g, 22.7 mmol, 40 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 73% conversion by removing the reaction from the oil bath and removing the septum.

**Polymerization of TFEMA.** Into a 10 mL round bottom flask, 131.7 mg of 2-cyanoprop-2-yl dithiobenzoate (595 μmol, 1 equiv) were dissolved in 3 mL dimethylformamide. A stock solution of AIBN (10 mg) was prepared in 1 mL dimethylformamide, and 977 μL of this solution (9.77 mg, 59.5 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 3.39 mL of TFEMA (4 g, 23.8 mmol, 40 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior
to SEC analysis. Polymerization was stopped at 69% conversion by removing the reaction from the oil bath and removing the septum.

**Polymerization of HEMA.** Into a 10 mL round bottom flask, 170.1 mg of 2-cyanoprop-2-yl dithiobenzoate (768 μmol, 1 equiv) were dissolved in 3 mL dimethylformamide. A stock solution of AIBN (20 mg) was prepared in 2 mL dimethylformamide, and 1262 μL of this solution (12.6 mg, 76.8 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 3.73 mL of HEMA (4 g, 30.7 mmol, 40 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 2 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 70% conversion by removing the reaction from the oil bath and removing the septum.

**Polymerization of DMAEMA.** Into a 10 mL round bottom flask, 70.4 mg of 2-cyanoprop-2-yl dithiobenzoate (318 μmol, 1 equiv) were dissolved in 6 mL toluene. A stock solution of AIBN (10 mg) was prepared in 1 mL toluene, and 522 μL of this solution (5.22 mg, 31.8 μmol, 0.1 equiv) was transferred to the flask. Subsequently, 4.29 mL of DMAEMA (4 g, 25.4 mmol, 80 equiv) and a stirrer bar were added, and the flask was sealed with a septum, prior to deoxygenation by nitrogen bubbling for 15 min. Polymerization was conducted in an oil bath at 70 °C for 4 h with a 400-rpm stirring rate. Samples were taken periodically under a nitrogen blanket for 1H-NMR analysis and passed through a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis. Polymerization was stopped at 40% conversion by removing the reaction from the oil bath and removing the septum.

**Purification of PMMA, PBuMA, PBzMA.** Polymers were precipitated three times in cold methanol and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.

**Purification of POEGMA.** POEGMA was precipitated in a diethyl ether/hexane solution (50% v/v) three times and blow-dried with air overnight with air before use.

**Purification of PTFEMA and PDMAEMA.** PTFEMA and PDMAEMA were precipitated in pentane three times and vacuum-filtered using a Buchner funnel. The precipitates were dried in a vacuum oven for at least 12 h before use.
Purification of PHEMA. The polymerization mixture was diluted threefold in acetone and dialyzed in acetone for 24 h during which the acetone was replaced with a fresh batch twice during this period. After 24 h, the polymer solution was concentrated using a rotavap.

Depolymerization procedure for PMMA, PBuMA, PBzMA, PTFEMA, PHEMA, PDMAEMA. PMMA will be used as the model example to describe a typical depolymerization procedure. In a 125 ml schlenk tube, 21.5 mg of PMMA was dissolved in 40 ml 1,4-dioxane (5.17 mM of MMA repeat unit). 15 mg of 35,000 g/mol poly(ethylene glycol) was added as an internal standard for SEC analysis. The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 120 °C oil bath to start the reaction. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~1 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 μM PTFE membrane).

Depolymerization procedure for POEGMA. In a 125 ml schlenk tube, 500 mg of POEGMA was dissolved in 40 ml 1,4-dioxane (25 mM of OEGMA repeat unit). The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 120 °C oil bath to start the reaction. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~1 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 μM PTFE membrane).

Repolymerization procedure for POEGMA. After depolymerization of POEGMA, the reaction mixture was concentrated via rotavap and the residual POEGMA was removed via precipitation in a diethyl ether/hexane (50% v/v) solution. The supernatant was collected and concentrated via rotavap to yield 302 mg of red liquid containing OEGMA and the recovered CTA. 14 μL of an AIBN stock solution (10 mg/ml) was added to give [CTA]:[OEGMA]:[AIBN] = 1:69:0.1. 300 μL of toluene was added and the resulting solution was transferred to a 1.5 ml vial with a magnetic stir bar and deoxygenated by nitrogen bubbling for 15 min. The reaction was placed in a 70 °C oil bath and periodically sampled under a nitrogen blanket for 1H-NMR and SEC analysis.
Depolymerization of POEGMA for subsequent repolymerization to POEGMA hydrogel. The same depolymerization procedure was used at a 2x scale (two batches of 500 mg/40 ml reactions).

Preparation of POEGMA hydrogel from depolymerized POEGMA. After the 2x scale depolymerization of POEGMA, the reaction mixture was concentrated via rotavap and the residual POEGMA was removed via precipitation in a diethyl ether/hexane (50% v/v) solution. The supernatant was collected and concentrated via rotavap to yield 613 mg of a red liquid containing OEGMA and the recovered CTA. 50 μL of an AIBN stock solution (10 mg/ml) and 121 μL of oligo(ethylene glycol) dimethacrylate (OEGDMA) was added to give [CTA]:[OEGMA]:[OEGDMA]:[AIBN] = 1:40:8:0.1. 300 μL of toluene was added and the resulting solution was transferred to a 4 ml vial and deoxygenated by nitrogen bubbling for 15 min. The reaction was placed in a 70 °C oil bath and removed after 5 h when there was visible gelation of the reaction mixture. The resulting gel was soaked in excess acetone for 36 h to remove residual monomer and toluene, then subsequently dried in a vacuum oven overnight.

Depolymerization procedure for POEGMA hydrogel. In a 125 ml schlenk tube, 350 mg of the POEGMA hydrogel was dissolved in 40 ml 1,4-dioxane. The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 120 °C oil bath to start the reaction. The schlenk tube was submerged into the oil bath until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~1 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 μM PTFE membrane).

CTA removal of POEGMA hydrogel. In a 5 ml vial, 500 mg of POEGMA hydrogel was immersed in 4 ml toluene containing 400 mg AIBN. The solution was bubbled with N₂ for 15 min and the vial was inserted into a 70 °C oil bath to start the reaction. The reaction was removed after 5. A clear discoloration of the originally red hydrogel confirmed the removal of the dithiobenzoate end group from the POEGMA hydrogel.

Addition of TEMPO to depolymerization of PMMA. In a 125 ml schlenk tube, 21.5 mg of PMMA was dissolved in 40 ml 1,4-dioxane (3.5 μmol, 1 eq macroCTA). 541 μg (3.5 μmol ,1 eq) or 54.1 (0.35 μmol ,0.1 eq) TEMPO was added using a stock solution. The schlenk tube was sealed with a rubber septum and deoxygenated by nitrogen bubbling for 20 min. The schlenk tube was then put into a 120 °C oil bath to start the reaction. The schlenk tube was submerged into the oil bath
until the surface of the solution inside was submerged ~2 cm below the surface of the oil bath. To take samples, the reaction was periodically removed from the oil bath and quickly added to an ice bath until the solution cooled to room temperature. The solution was then sampled under a nitrogen blanket. For SEC samples, ~1 ml of the sample solution was blow-dried, dissolved in DMAc, and passed through a syringe filter (0.45 μM PTFE membrane).

**CTA removal for PMMA.** To a 4 ml vial, 100 mg PMMA (16.1 μmol, 1eq macroCTA) and 53.0 mg AIBN (322 μmol, 20 eq) was dissolved in 2 ml toluene. The vial was sealed with a rubber septum and deoxygenated via nitrogen bubbling for 15 min before being put into a 70 °C oil bath. The solution was periodically sampled under a nitrogen blanket. After 3 h, the reaction was removed from the oil bath and concentrated via blow-drying with air. The polymer was precipitated in cold methanol and dried in a vacuum oven overnight.

**Depolymerization of CTA-removed PMMA.** Procedures are identical to that for the depolymerization of the parent PMMA sample.

**Determination of monomer conversion during polymerization.** Monomer conversions were determined by NMR spectroscopy. The monomer vinyl signals were compared to the combined polymer and monomer ester signals (-CH$_3$ for PMMA, -CH$_2$- for rest of the polymers used).

**Determination of depolymerization conversion.** Depolymerization conversions were determined in-situ by comparing the monomer vinyl signals to the polymer backbone -CH$_3$ signals (simply taking a sample in dioxane and re-dissolving it in deuterated acetone). In addition, an internal standard is added in each reaction to ensure accurate conversion calculation through an alternative way. Specifically, a second NMR sample was prepared by re-dissolving the dried reaction mixture (blowing the solvent with air). Conversions were then calculated by comparing the intensity of the backbone –CH$_3$ signals before and after depolymerization against a nonvolatile internal standard (methoxy-terminated polyethylene glycol). Depolymerization conversions from the two methods deviated by <5%.
Additional Data

Table S1. Gibbs free energy ($\Delta G$, kJ/mol) and equilibrium constant for depropagation, and predicted ratio of depolymerized/polymerized radical as a function of $T$ and total starting concentration of polymer.$^a$

| $T$ (K) | $\Delta G_p$ (kJ mol$^{-1}$) | $K$ (M$^{-1}$) | $\frac{[P_{n-1}]}{[P_n]}$ |
|--------|----------------------------|---------------|----------------------------|
|        |                            |               | 1 mM | 5 mM | 28 mM | 100 mM | 1 M  |
| 298    | 21.7                       | 1.59E-04      | 0.5  | 0.2  | 0.1   | 0.04   | 0.01 |
| 343    | 16.2                       | 3.46E-03      | 4.3  | 1.2  | 0.4   | 0.2    | 0.06 |
| 373    | 12.5                       | 1.78E-02      | 18.8 | 4.4  | 1.2   | 0.5    | 0.14 |
| 383    | 11.3                       | 2.91E-02      | 30.0 | 6.7  | 1.7   | 0.7    | 0.19 |
| 393    | 10.0                       | 4.63E-02      | 47.3 | 10.2 | 2.4   | 1.0    | 0.24 |
| 423    | 6.4                        | 1.64E-01      | 164.7| 33.7 | 6.7   | 2.3    | 0.49 |
| 475    | 0.0                        | 1.00E+00      | 1001.0| 201.0| 36.7  | 10.9   | 1.62 |

$^a$The Gibbs free energy change for depropagation ($\Delta G_p$) at each temperature ($T$) was calculated using Gibbs equation (i.e., $\Delta G_p = \Delta H_p - T\Delta S_p$). The value of $\Delta H_p$ was taken from the literature $^1$ ($\Delta H_p = -\Delta H_b = 58.2$ kJ mol$^{-1}$), while $\Delta S_p (122.4$ J mol$^{-1}$ K$^{-1}$) was obtained by solving $\Delta G_p = 0$ at the ceiling temperature, using the literature $^2$ value for methyl methacrylate ($T_c = 475$ K). The $\Delta G_p$ values are used to calculate the equilibrium constant at each temperature from $K_{n-p} = c^{-1} \exp \left(-\frac{\Delta G_p}{RT}\right)$, where $c$ is the standard unit of concentration (1 M) and $R$ is the universal gas constant. Noting that this equilibrium constant is related to the ratio of product to reactant concentrations, $K_{n-p} = \frac{[P_{n-1}][M]}{[P_n]}$ and that mass is conserved, we can calculate the ratio $\frac{[P_{n-1}]}{[P_n]}$ as function of the starting concentration of polymer $P_n$. To simplify the calculation, we perform this calculation for a single depropagation step only, noting that the buildup of monomer as further depropagation occurs (i.e. $P_{n-1} \rightarrow P_{n-2} + M$, $P_{n-2} \rightarrow P_{n-3} + M$, etc.) will gradually halt further depropagation, placing an upper bound to molecular weight reduction achievable at a given temperature and concentration.

$^1$ Dainton, F. S.; Ivin, K. J., Some thermodynamic and kinetic aspects of addition polymerisation. Q. Rev. Chem. Soc. 1958, 12, 61-92.

$^2$ https://polymerdatabase.com/polymer%20chemistry/Ceiling%20Temperature.html
**Figure S1.** SEC trace of PMMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate as the chain transfer agent ([CTA]:[AIBN]:[MMA] = 1:0.1:120).
| Entry | monomer [M]:[CTA]:[AIBN] | Time (h) | Conversion (%) | $M_n^{\text{theo}}$ (g/mol) | $M_n^{\text{SEC}}$ (g/mol) | $M_n^{\text{NMR}}$ (g/mol) | $D$  |
|-------|--------------------------|----------|----------------|-----------------------------|-----------------------------|-----------------------------|-----|
| 1     | MMA 120:1:0.1            | 4        | 48             | 6,000                       | 6,100                       | 6,200                       | 1.13|
Figure S2. $^1$H-NMR spectrum of purified PMMA prior to depolymerization.
Figure S3. Successful chain extension of PMMA with benzyl methacrylate at 70 °C in dioxane ([macro-CTA]:[BzMA]:[AlBN] =1:120:0.1).
**Figure S4.** Depolymerization of PMMA macroCTA under (a) various concentrations at 120 °C and (b) under various temperatures at 5 mM. Depolymerizations were performed in dioxane after degassing via N₂ sparging.
Figure S5. UV-vis of the depolymerization reaction of PMMA at 5 mM and 120 °C at 0% (black trace) and 85% (red trace) depolymerization.
Figure S6. Evolution of SEC trace of PMMA during depolymerization at 5 mM and 120 °C. Intensities are normalized to a poly(ethylene glycol) internal standard that was added at the beginning of the reaction.
Table S3. Characterization of PMMA during depolymerization at 5 mM and 120 °C.

| Time (h) | Monomer fraction (%) | $M_n^{SEC}$ (g/mol) | $D$  |
|----------|----------------------|---------------------|------|
| 0        | 0                    | 6,100               | 1.12 |
| 0.25     | 16                   | 5,600               | 1.14 |
| 0.50     | 28                   | 5,300               | 1.16 |
| 0.75     | 33                   | 4,900               | 1.16 |
| 1        | 39                   | 4,800               | 1.17 |
| 2        | 61                   | 4,700               | 1.20 |
| 8        | 86                   | 4,700               | 1.20 |
Table S4. Characterization of PMMA depolymerization at 70 °C.

| Entry | Conc. (mM) | Temp. (°C) | Depolymerization (%) |
|-------|------------|------------|----------------------|
| 1a    | 100        | 70         | 0                    |
| 1b    | 100        | 70         | 0                    |
| 2a    | 28         | 70         | 2.5                  |
| 2b    | 28         | 70         | 2.9                  |
Figure S7. Distillation setup for distillation of PMMA.
Figure S8. $^1$H-NMR spectra of the recovered DMSO and MMA after depolymerization of PMMA. A mixture of DMSO and MMA were distilled from the reaction solution into an aliquot in the first round, then MMA was subsequently fractionally distilled from the mixture to a second aliquot (depolymerization conversion = 40%, yield = 33%). Acetone-$d_6$ was used as the NMR solvent.
Figure S9. SEC trace (UV detector) of PMMA before and after end group removal via reacting with excess AIBN at 70 °C.
Figure S10. Evolution of depolymerization conversion during the depolymerization of PMMA (5 mM, 120 °C) with time in the presence or absence of TEMPO. Equivalents are relative to macroCTA.
Figure S11. SEC traces of the chain extension of PMMA with benzyl methacrylate at 120 °C in the absence of AIBN and solvent.
Figure S12. (top) Scheme of possible autopolymerization of bulk benzyl methacrylate at 120 °C. 
(bottom) $^1$H-NMR of reaction after 3 h at 120 °C showing no polymerization.
Figure S13. SEC trace of purified POEGMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 45%, $M_n = 18,600$ g/mol, $D = 1.14$. 
Figure S14. $^1$H-NMR spectrum of purified POEGMA prior to depolymerization.
Figure S15. SEC trace of purified PBuMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 72\%, M_n = 4,200 \text{ g/mol}, D = 1.10.
Figure S16. $^1$H-NMR spectrum of purified PBuMA prior to depolymerization.
Figure S17. SEC trace of purified PBzMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 73%, $M_n = 4,800$ g/mol, $D = 1.12$. 
Figure S18. $^1$H-NMR spectrum of purified PBzMA prior to depolymerization.
Figure S19. SEC trace of purified PTFEMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 69%, $M_n = 11,300$ g/mol, $D = 1.15$. 
Figure S20. $^1$H-NMR spectrum of purified PTFEMA prior to depolymerization.
Figure S21. SEC trace of purified PHEMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 70%, $M_n = 8,900$ g/mol, $D = 1.15$. 
Figure S22. $^1$H-NMR spectrum of purified PHEMA prior to depolymerization.
Figure S23. SEC trace of purified PDMAEMA synthesized via RAFT polymerization with 2-cyano-2-propyl dithiobenzoate of the CTA. Conversion = 40%, $M_n = 3,800$ g/mol, $D = 1.13$. 
Figure S24. $^1$H-NMR spectrum of purified PDMAEMA prior to depolymerization.
Figure S25. NMR spectrum of supernatant of the depolymerization reaction after precipitation in diethyl ether/hexane. Inset shows the aromatic protons of the cleaved CTA responsible for the RAFT repolymerization of the depolymerization product.
Figure S26. Full SEC traces of the controlled repolymerization of POEGMA.
Figure S27. (a) side-by-side comparison of POEGMA hydrogels before (left) and after (right) CTA removal via reacting with excess AIBN in toluene at 70 °C. (b) Reaction mixture after removal of POEGMA hydrogel. The red color confirms cleavage of CTA from the hydrogel.
Figure S28. Attempted depolymerization of CTA-removed POEGMA hydrogel at 350 mg/40 ml and 120 °C. Photos are of the hydrogel (a) in the reaction flask after 12 h and (b) after collecting the hydrogel using a filter paper.