Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supporting Information for Reversible-addition fragmentation chain transfer (RAFT) mediated depolymerization of brush polymers

Michael J. Flanders and William M. Gramlich*

Department of Chemistry, University of Maine

156 Aubert Hall, Orono, ME 04469

*corresponding author: william.gramlich@maine.edu

Materials and General Methods

All solvents used were of reagent grade, and were purchased from Sigma-Aldrich unless otherwise noted. Monomers used were a supplier reported molecular weight of 500 g/mol variant of the monomer oligo-ethyleneglycol methylmethacrylate (OEGMA, Sigma Aldrich), a 600-800 molecular weight variant of monomethacryloxypropyl terminated oligo(dimethylsiloxane) (ODMSMA7, Gelest product ID MCR-M07), ODMSMA70 monomer (Gelest product id MCR-M17), and methyl methacrylate (MMA, Sigma Aldrich). Inhibitor was removed immediately prior to use by passing the monomers through a column of basic alumina. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich and was recrystallized by dissolving in methanol at room temperature followed by cooling over 10 days at -20 °C. Product crystals were obtained by vacuum filtration. 4-cyano-4-[(dodecylsulfanyl)carbono thioylsulfanyl]pentanoic acid (CDTP) was synthesized according to a previously published procedure.[1]

For ^{1}H NMR spectroscopic analysis, all samples were first dried of organic solvents by sparging with nitrogen. Samples were dissolved in 0.7 mL of deuterated chloroform ($CDCl_3$) and analyzed on an Oxford Instruments Varian Unity 400 MHz NMR spectrometer. Data was obtained and processed with MestReNova11 ^{1}H-NMR spectroscopy software utilizing a sin^2 apodization. Size exclusion chromatography was performed 1 mg/mL concentration of polymer in solvent. Solutions were passed through a 0.2 µm PTFE syringe filter prior to injection on an Agilent 1260 Infinity Size Exclusion Chromatograph equipped with a temperature controlled refractive index array. To analyze PODMSMA polymers, HPLC grade THF was used as the eluent at a 1 mL/min flow rate and operating temperature of 35 ºC. To analyze POEGMA polymers, HPLC grade DMF was used as the eluent at a 1 mL/min flow rate and operating temperature of 50 °C. The SEC was equipped with three Phenogel columns with different pore sizes (Phenomenex Organic columns, 50A, 10E3A, 10E6A) and calibrated prior to use with polystyrene standards. UV-Vis was performed on a Beckman Du 7400 UV-Vis spectrometer using quartz cuvettes and blanks of the analysis solvent.

General RAFT Polymerization Procedure

Each macromonomer was combined with CDTP and recrystallized AIBN at a molar ratio of 25:1:0.2 (macromonomer:CDTP:AIBN) and dissolved in air-free uninhibited 1,4-dioxane (Sigma Aldrich). This solution was then transferred into a Wheaton brand gold band ampule with a small bar magnet, degassed by 3 freeze-pump-thaw (FPT) cycles, and the ampule was sealed under vacuum by melting the neck with a torch. The sealed ampules were placed in an oil bath and heated at the desired reaction temperature for the desired time. Following the reaction period, the vessel was opened and a crude sample was obtained for ^{1}H-NMR spectroscopy. The remaining crude solution was then purified by 3 rounds of precipitation into dry ice chilled 10X excess 200 proof ethanol (PODMSMA) or diethyl ether (POEGMA). The excess solvent was decanted off the polymer product and the purified homopolymers were obtained by evaporating any remaining solvent with nitrogen. Samples were stored in a -20 °C freezer until further reactions were run. Monomer conversion was calculated from the ^{1}H-NMR spectrum of crude sample by comparing monomer to polymer integrations. To synthesize RAFT polymers for degradation studies, the concentration of macromonomer in solvent was 0.67 g/mL and the reaction was run in 20 mL ampules. Using the procedure above, the polymerizations were run at 70 °C for 8 h before quenching the reaction.

General RAFT Depolymerization Procedure

Either PODMSMA7 or POEGMA homopolymer was dissolved in enough 1,4-dioxane to bring the RU concentration to 0.1 M. For PODMSMA7, the solution was a cloudy white emulsion, which was heated in a warm water bath to 35 ºC to create a uniform solution. To study inhibition of PODMSMA7 depolymerization, butylated hydroxytoluene (BHT) also was added to the vial at a 0.2 molar ratio of BHT to the RAFT CTA present on the PODMSMA7. For all depolymerizations, the solutions were aliquoted into 10 mL Wheaton gold band ampules. A small bar magnet was added, the ampules were stored at -20 ºC prior to degassing with 3 FPT cycles, and then stored at -20 °C until used. Sealed ampules were placed in a 70 ºC oil bath, removed at specific time points (4 at each time point), and placed into a water bath to quickly cool. The ampules were opened and the contents recovered with addition of 1 mL of reagent grade dichloromethane. Solvent was removed by purging nitrogen yielding a semi-viscous polymer and monomer solution. ^{1}H NMR spectroscopy was then performed to compute monomer concentration of each sample assuming no monomer volatility. In selected cases, SEC was also performed to aid in characterization of the depolymerization process under study.

Kinetic and Thermodynamic Study RAFT Polymerization Procedures

For the kinetic and equilibrium monomer measurement studies of polymerization, the reaction stock solution was prepared at 0.1 M concentration of macromonomer in 1,4-dioxane at a 25:1:0.2 macromonomer:CDTP:AIBN ratio and split into ampules following the procedure for the general RAFT polymerization. The ampules were stored in a -20 °C freezer until being placed in the 70 °C oil bath and heated for various times. At least 4 ampules were run for each time point. To solubilize the ODMSMA70 stock solution prior to splitting it into ampules, the solution was heated to 35 °C in a water bath, creating a homogenous solution. Monomer conversion was calculated from the ^{1}H-NMR spectrum of each crude sample by comparing monomer to polymer integrations. For the MMA polymerizations, due to the volatility of MMA the conversion of monomer to polymer was calculated from the mass of the recovered polymer by evaporating solvent from the crude with nitrogen and pulling vacuum until the mass stopped changing (13 days).

Polymerization thermodynamic studies were performed by using the same concentrations and ratios of reagents for the kinetic RAFT polymerization procedure for each macromonomer. Instead of measuring time points, polymerizations were run at 60, 70, 80, 90, and 100 °C for 56 – 96 h. The equilibrium monomer concentration was measured by ^{1}H NMR spectroscopic analysis of the nitrogen dried crude reaction mixtures using the total monomer and RU concentration as an internal standard to calculate the monomer concentration.

Controlled RAFT Depolymerization and Reinitiation of Polymerization Procedure

For depolymerization, a 22 RU PODMSMA7 homopolymer was dissolved in 1,4-dioxanes to 0.1 M RU concentration. The sample was prepared in an ampule as described above and heated in an oil bath set to 70 ºC for a depolymerization reaction period of 56 hours. Following the reaction, the ampule was opened, recovered with 1 mL of reagent grade dichloromethane, and dried with purging nitrogen. ^{1}H-NMR spectroscopy, SEC, and UV-Vis spectroscopy analysis were then performed. Following these analyses, the sample was dissolved in 1,4-dioxane and ODMSMA7 was added to give a 0.5 M solution of monomer. AIBN was added to give a 1:0.2 CTA:AIBN. This solution was placed in an ampule and polymerization proceeded as described above at 70 ºC and for 16 h. Following this reaction period, the ampule was opened and the new sample was recovered with 1 mL of reagent grade dichloromethane. The solvent was evaporated with nitrogen and the sample was analyzed with ^{1}H NMR spectroscopy, SEC, and UV-Vis spectroscopy.

Controlled RAFT Polymerization and Subsequent AIBN Re-addition Procedure

ODMSMA7 was combined with CDTP and recrystallized AIBN at a molar ratio of 25:1:0.2 (macromonomer:CDTP:AIBN) and dissolved in air-free uninhibited 1,4-dioxane (Sigma Aldrich). This reaction solution was aliquoted in 2 mL portions into 3 Wheaton brand gold band ampules. Each ampule was prepared as described above and heated in an oil bath set to 70 ºC for a polymerization reaction period of 56 hours before being quenched in an ice water bath. Following the initial reaction period, each ampule was opened, and the contents were thoroughly mixed with a magnetic stir plate before a 1 mL aliquot of the crude solutions were removed for ^{1}H-NMR spectroscopy and SEC analysis. Next, the remaining 1 mL of crude PODMSMA7 solutions were removed from the 3 initial ampules, and placed into 3 new Wheaton brand gold band ampules. For AIBN re-initiation, the number of moles of CDTP agent in the crude solutions were computed, and the appropriate amount of AIBN to yield a 1:0.2 molar ratio of CDTP:AIBN was placed into each. Again, the ampules were degassed and sealed as described above, and heated in an oil bath set to 70 ºC for an additional polymerization reaction period of 24 hours, bringing the total polymerization time for these solutions to 80 hours. Following the second reaction period, all 3 ampules were opened, and fully recovered with a quantitative transfer using 1 mL of reagent grade dichloromethane, before being dried with purging nitrogen. ^{1}H-NMR spectroscopy and SEC analysis were then performed on these 3 samples.

Derivation of Equation 1

For a RAFT polymerization the rate of polymerization is equal to

$$R_p = k_p[P^{\cdot}][M] \tag{S1}$$

where R_p is the rate of polymerization, k_p is the polymerization rate constant, $[P^{\cdot}]$ is the concentration of propagating radicals, and $[M]$ is the instantaneous monomer concentration. Assuming steady state, the quantity $k_p[P^{\cdot}]$ is assumed to be constant for RAFT polymerizations at short polymerization times,[2] yielding k_{app}. For RAFT polymerization the rate of depolymerization is equal to

$$R_d = k_d[P^{\cdot}] \tag{S2}$$

where k_d is the rate constant for depolymerization. With these definitions we can define the change monomer concentration as equation 3 below by combining equations S1 and S2.

$$\frac{d[M]}{dt} = k_d[P^{\cdot}] - k_p[P^{\cdot}][M] \tag{S3}$$

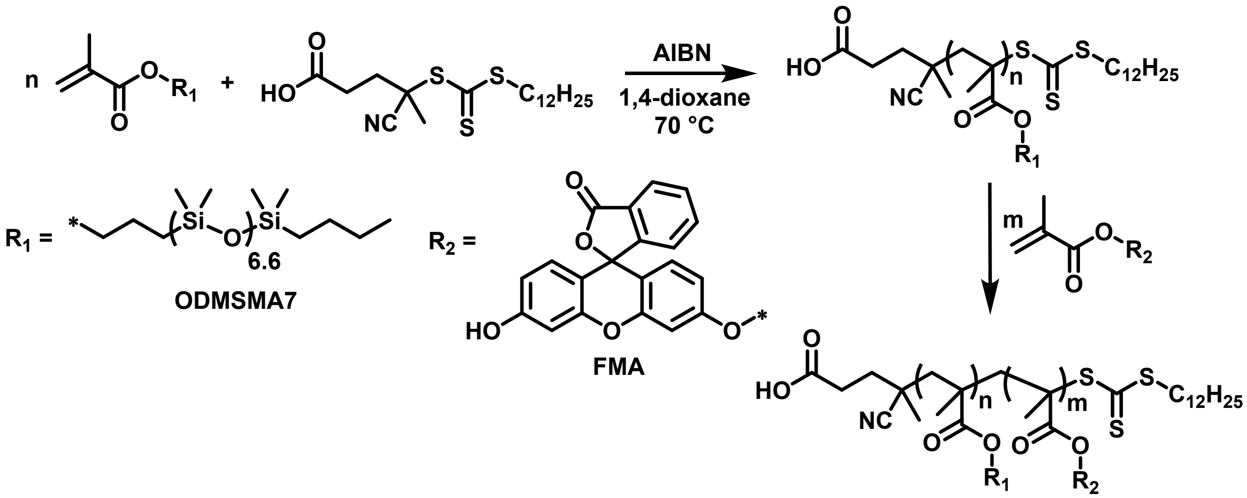
At equilibrium $\frac{d[M]}{dt} = 0$ and $[M] = [M]_{eq}$, yielding equation S4 below.

$$k_d = k_p[M]_{eq} \tag{S4}$$

Substituting equation S4 into equation S3 and including our assumption for k_{app} we obtain equation S5 below.

$$\frac{d[M]}{dt} = k_{app}([M]_{eq} - [M]) \tag{S5}$$

Integration of equation S5 from initial time and monomer concentration to final time and concentration yields equation 1 in the manuscript.



Scheme S1: Attempted block polymerization of ODMSMA7 and FMA using RAFT polymerization.

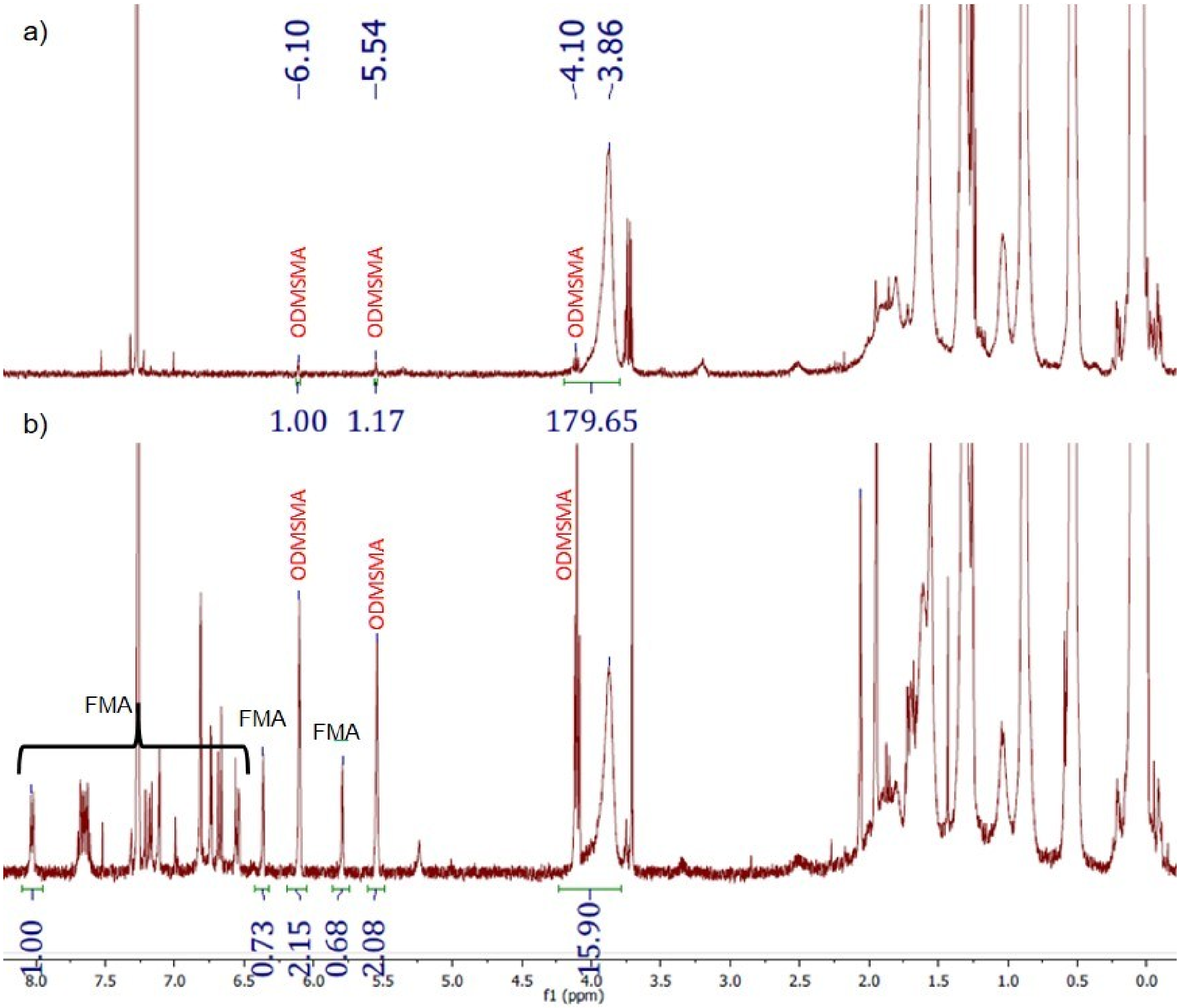


Figure S1. A) ^{1}H NMR spectrum of 23 RU PODMSMA7 after precipitation with trace levels of ODMSMA7 monomer present. B) ^{1}H NMR spectrum of crude reaction mixture after heating at 70 °C for 12 h in THF. Reaction conditions of 5:1:0.2 molar ratio of FMA to macroCTA (PODMSMA7) to AIBN at 0.1 g of PODMSMA7 in 1.5 mL of THF. Depolymerization resulted in a loss of 6 RU from the 23 RU PODMSMA7 polymer.

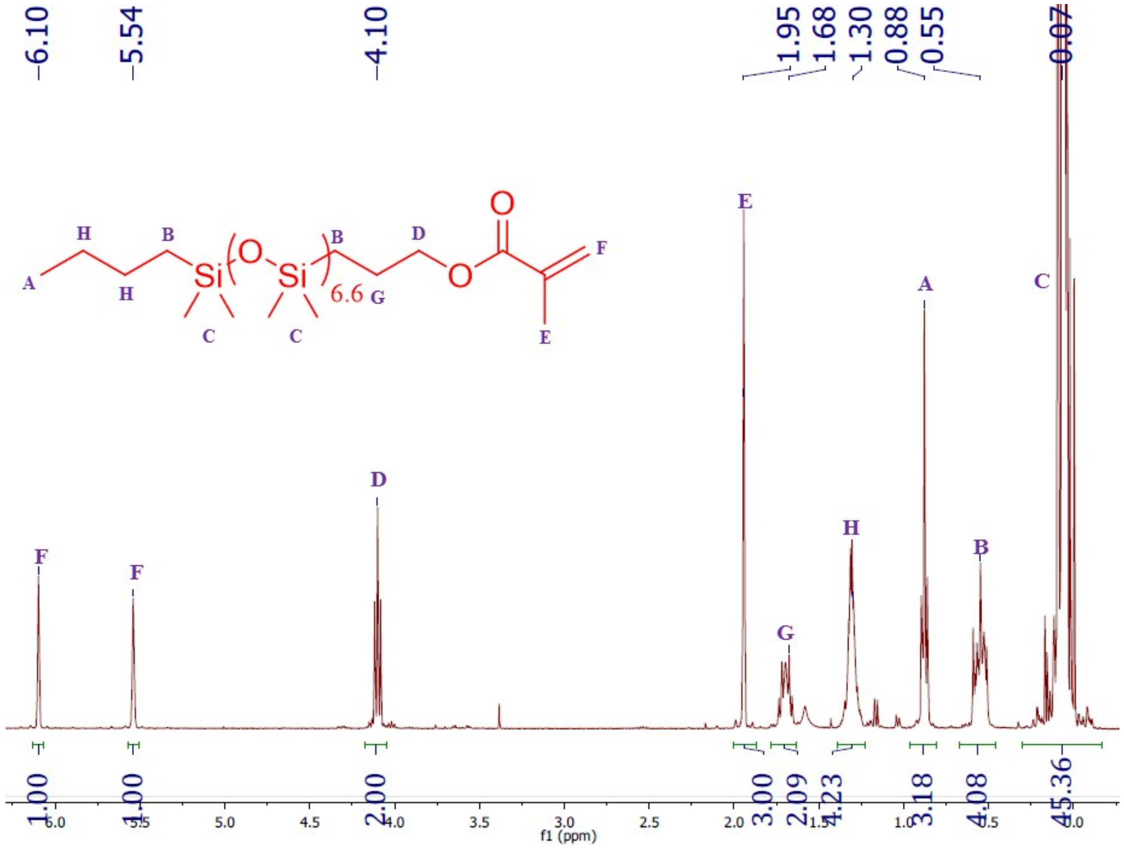


Figure S2. ^{1}H NMR spectrum of ODMSMA7 monomer with peak assignments in $CDCl_3$.

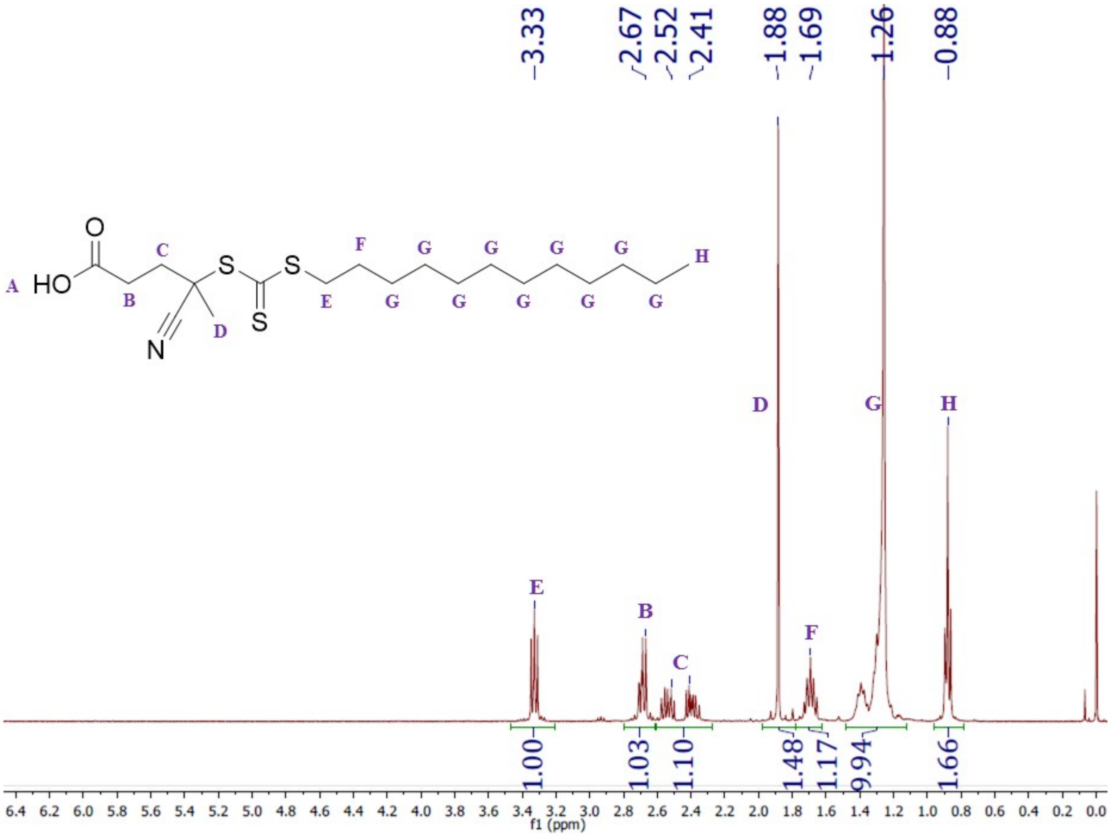


Figure S3. ^{1}H NMR spectrum of CDTP CTA with peak assignments in $CDCl_3$.

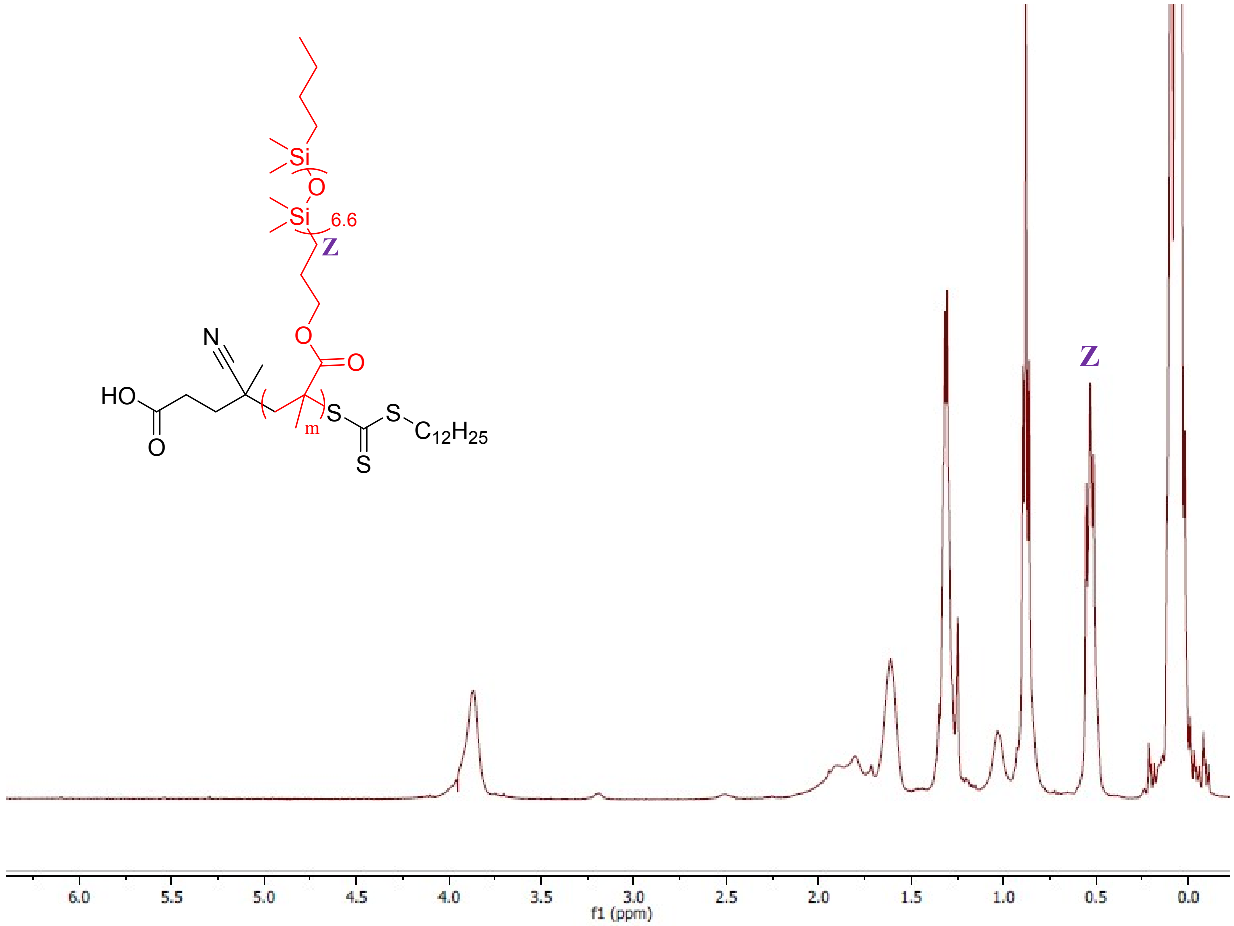


Figure S4. ^{1}H NMR spectrum of PODMSMA7 in $CDCl_3$ with peak labeled that was used to track monomer conversion into polymer.

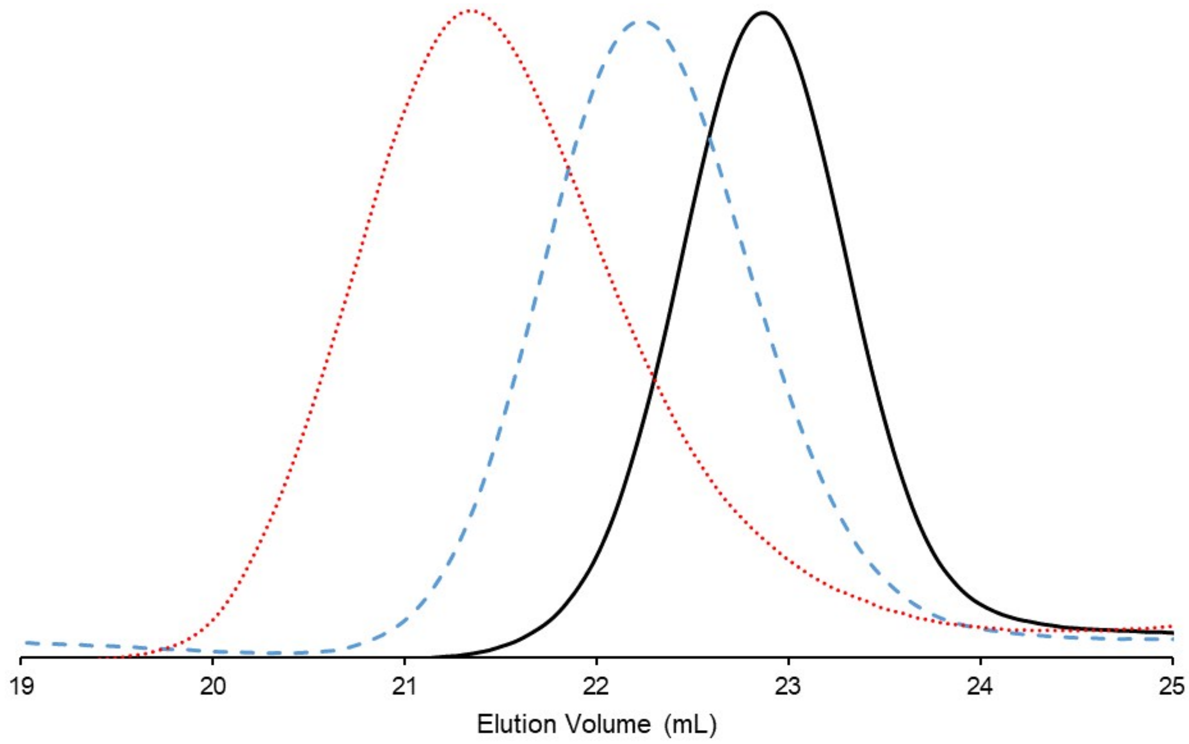


Figure S5. SEC elution curves of PODMSMA7 with 22 (solid black), 48 (blue dashed), and 89 (red dotted) RU of macromonomer. SEC run in THF with polystyrene standards and a refractive index detector. For 22 RU polymer M_n = 19.7 kg/mol. Đ = 1.14, 48 RU polymer M_n = 30.3 kg/mol. Đ = 1.22, and 89 RU polymer M_n = 54.6 kg/mol. Đ = 1.37.

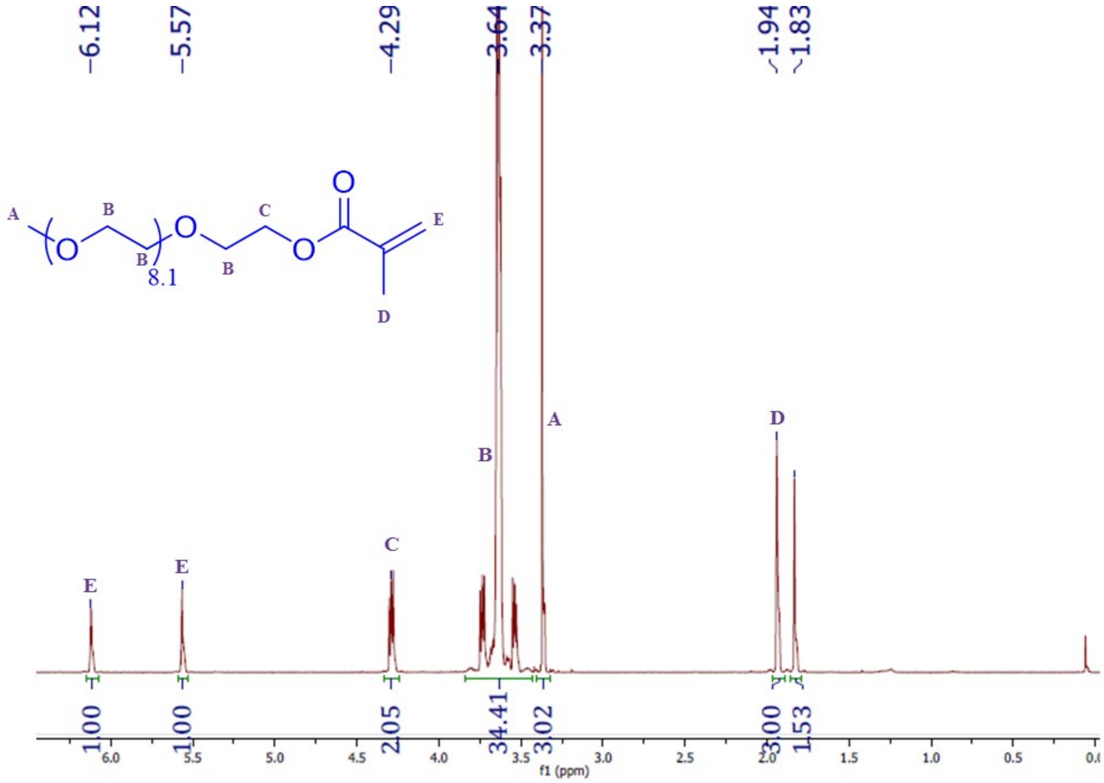


Figure S6. ^{1}H NMR spectrum of OEGMA monomer with peak assignments in $CDCl_3$.

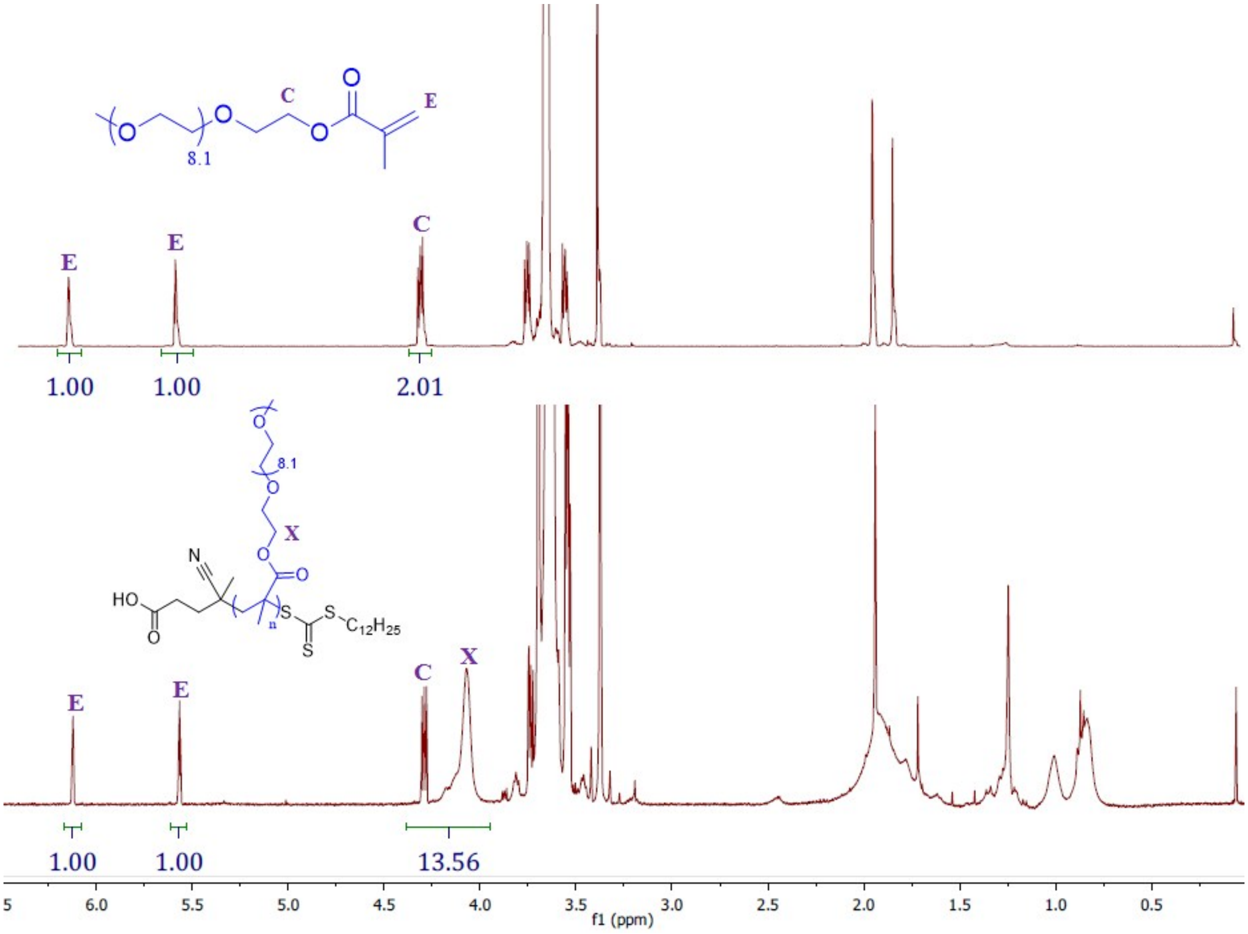


Figure S7. Top: ^{1}H NMR spectrum of OEGMA monomer with peak assignments in $CDCl_3$. Bottom: ^{1}H NMR spectrum of crude reaction mixture of POEGMA.

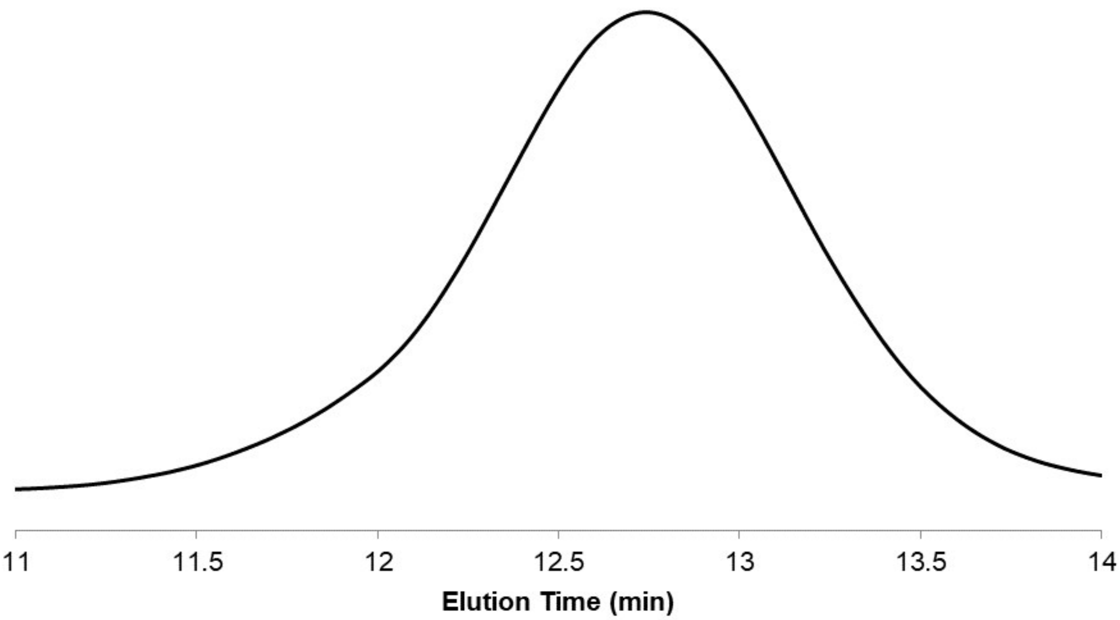


Figure S8. SEC elution curve of POEGMA with 21 RU of macromonomer. SEC run in DMF with polystyrene standards and a refractive index detector. M_n = 23 kg/mol. Đ = 1.08.

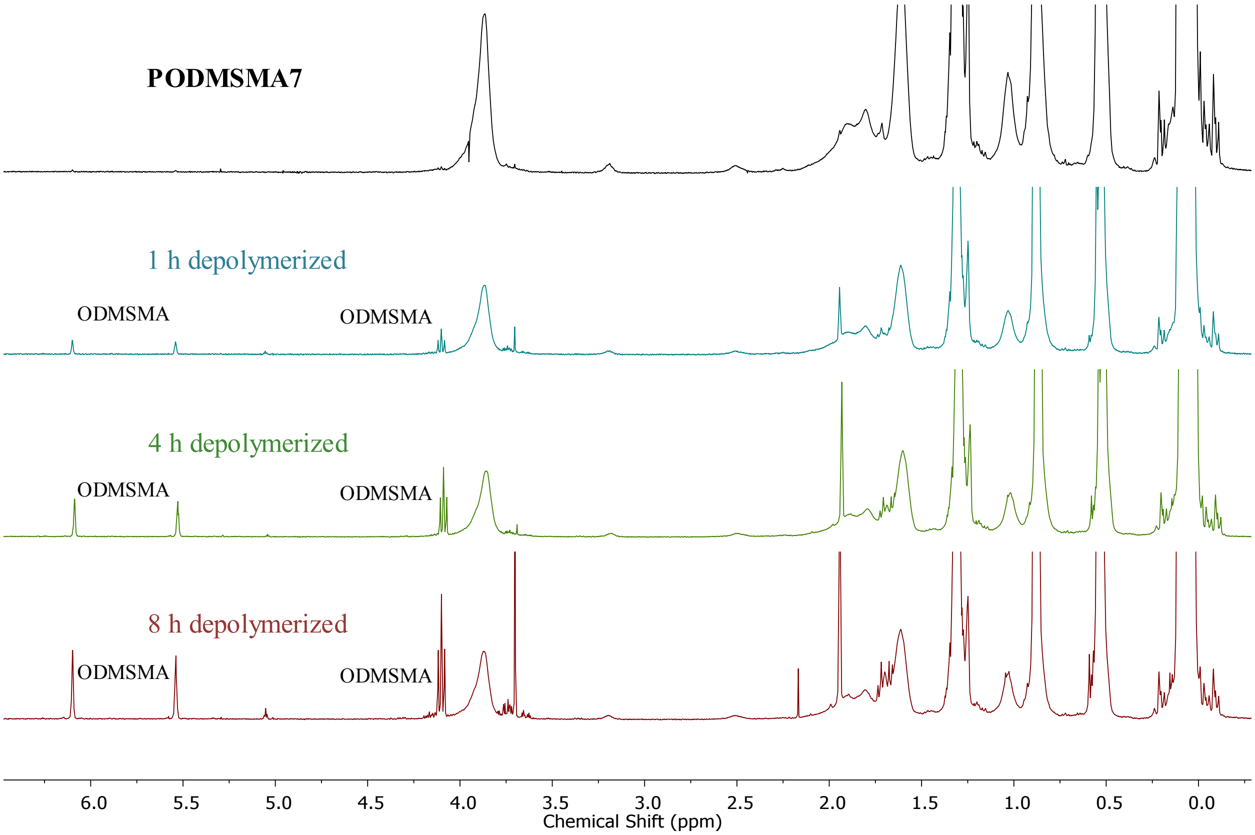


Figure S9. ^{1}H NMR spectra of crude reaction solution (solvent removed by evaporation) time points taken during the depolymerization of PODMSMA7 at 70 °C in 1,4-dioxane. Removal of the solvent by evaporation concentrated impurities in the 1,4-dioxane, namely 1,4-dioxan-2-ol which has a peak at 5.1 ppm that can be observed in some ^{1}H NMR spectra, including the ones above.[3,4]

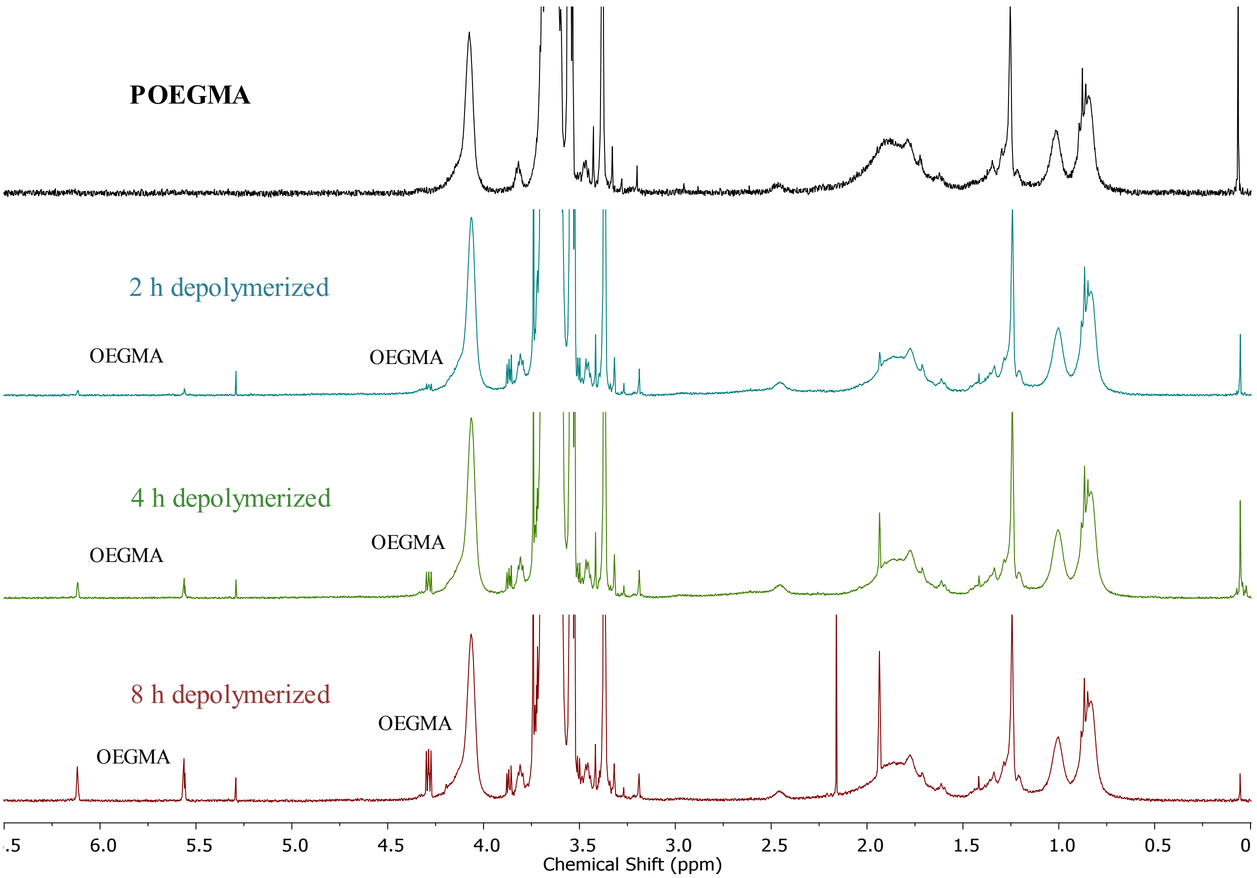


Figure S10. ^{1}H NMR spectra of crude reaction solution (solvent removed by evaporation) time points taken during the depolymerization of POEGMA at 70 °C in 1,4-dioxane.

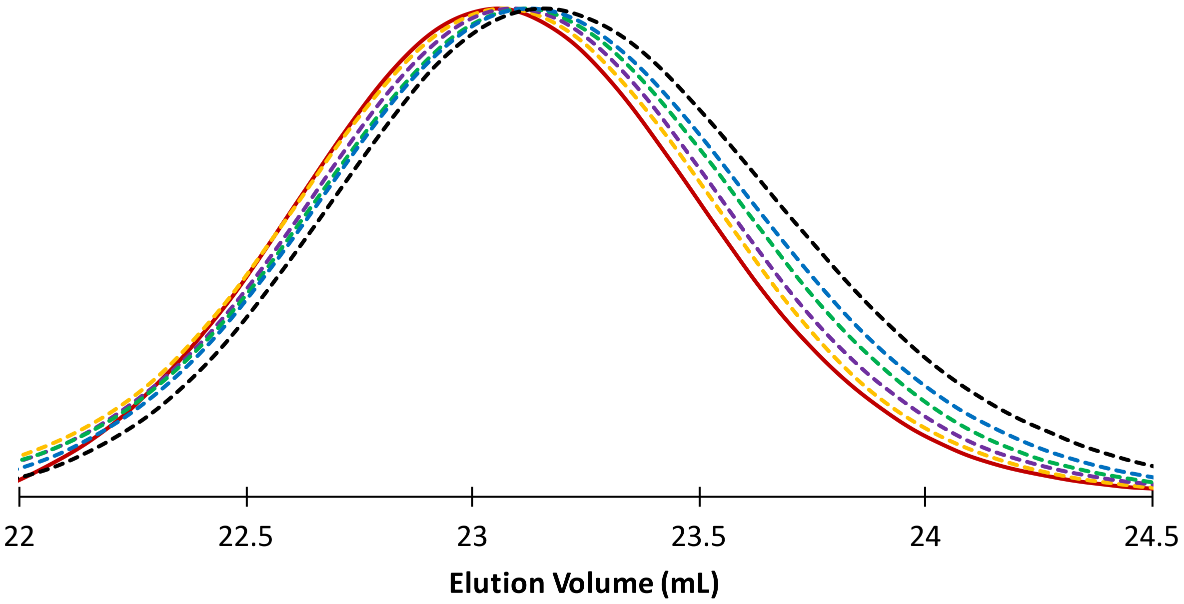


Figure S11. SEC elution curves for the depolymerization of 22 RU PODMSMA7 at 0.1 M initial starting condition of polymerized monomer and at 70 °C in 1,4-dioxane (red line, M_n = 16.9 kg/mol, Đ = 1.16) at 1 h (orange line, M_n = 16.9 kg/mol, Đ = 1.17), at 2 h (purple line, M_n = 16.5 kg/mol, Đ = 1.16), at 4 h (green line, M_n = 16.1 kg/mol, Đ = 1.19) , at 8 h (blue line, M_n = 16.0 kg/mol, Đ = 1.20) , and at 32 h (black line, M_n = 15.0 kg/mol, Đ = 1.17).

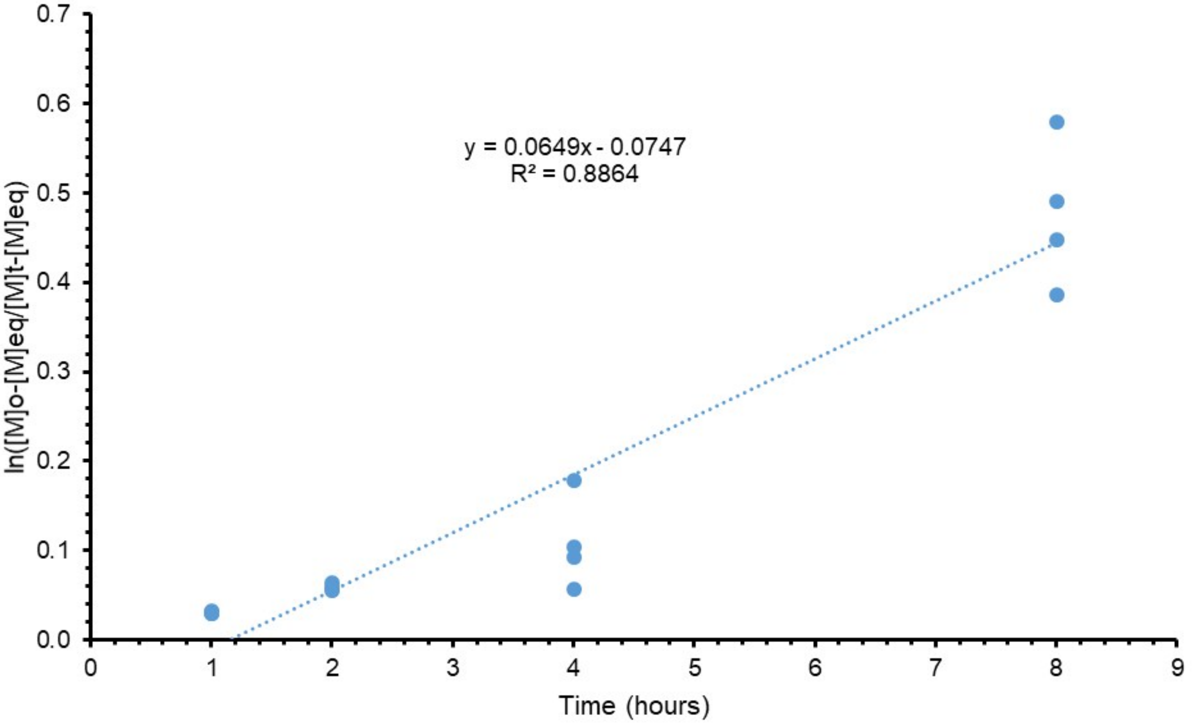


Figure S12: Linearized average kinetic data for the first 8 h of depolymerization of 21 RU POEGMA assuming equilibrium kinetics and a $[M]_{eq} = 2.74 \times 10^{-2}$ M from the average of four depolymerizations.

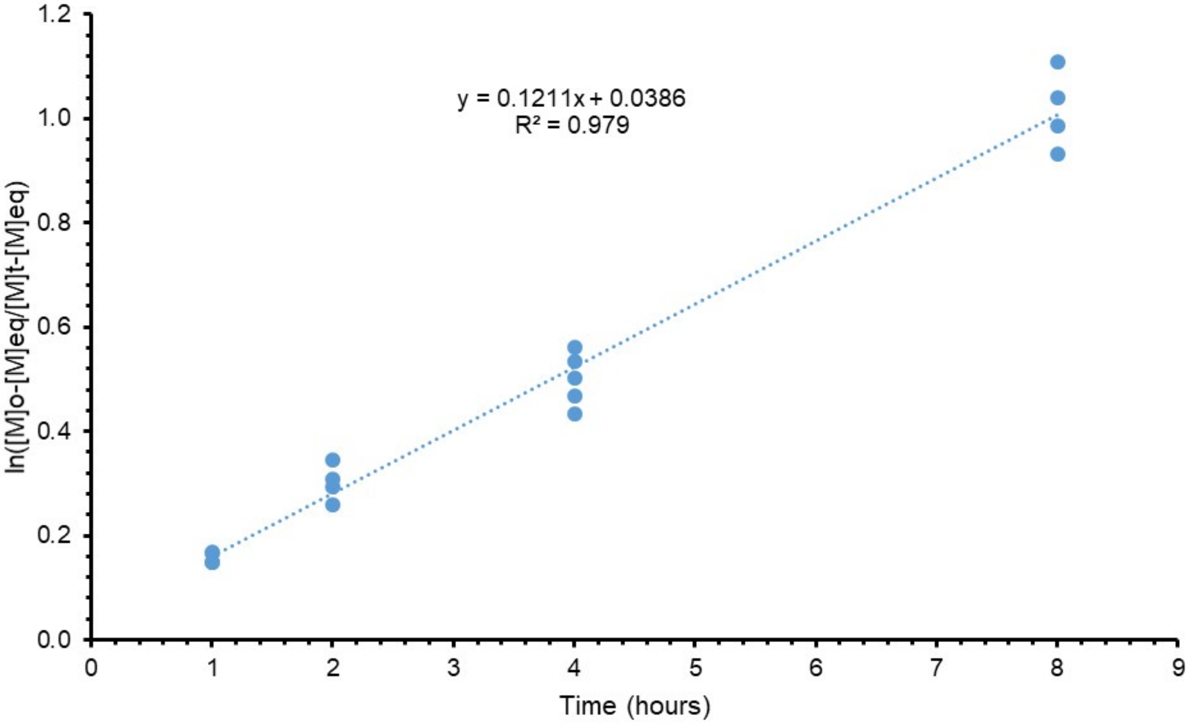


Figure S13: Linearized average kinetic data for the first 8 h of depolymerization of 22 RU PODMSMA7 assuming equilibrium kinetics and a $[M]_{eq} = 2.84 \times 10^{-2}$ M from the average of four depolymerizations.

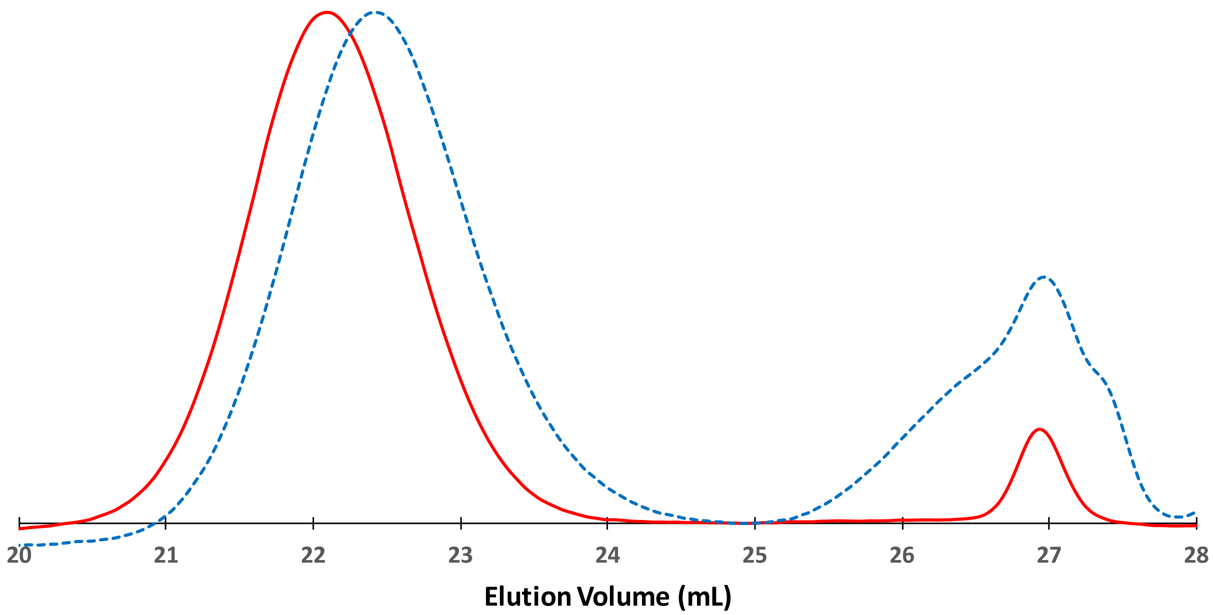


Figure S14. SEC elution curves for the depolymerization of a 48 RU PODMSMA7 in 1,4-dioxane at 70 °C for 60 h with an initial polymerized monomer concentration of 0.05 M (red line, $M_n = 30.5$ kg/mol, Đ = 1.25) at 60 h (blue line, $M_n = 20.4$ kg/mol, Đ = 1.40). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 15 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

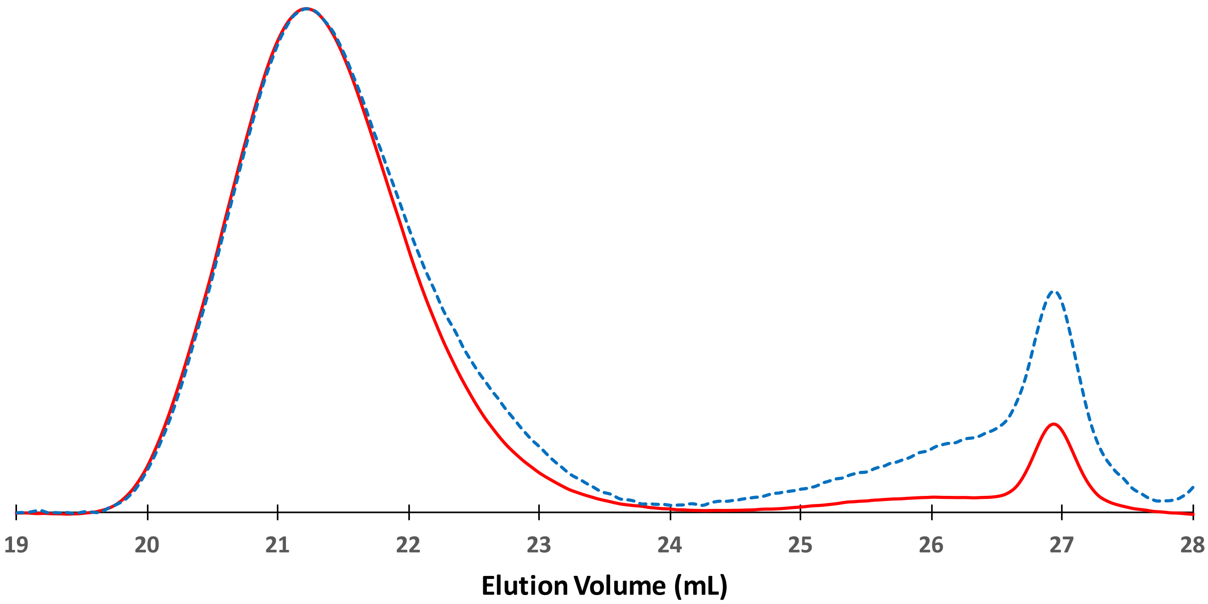


Figure S15. SEC elution curves for the depolymerization of an 89 RU PODMSMA7 in 1,4-dioxane at 70 °C for 60 h with an initial polymerized monomer concentration of 0.05 M (red line, M_n = 55.7 kg/mol, Đ = 1.32) at 60 h (blue line, M_n = 47.9 kg/mol, Đ = 1.61). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 8 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

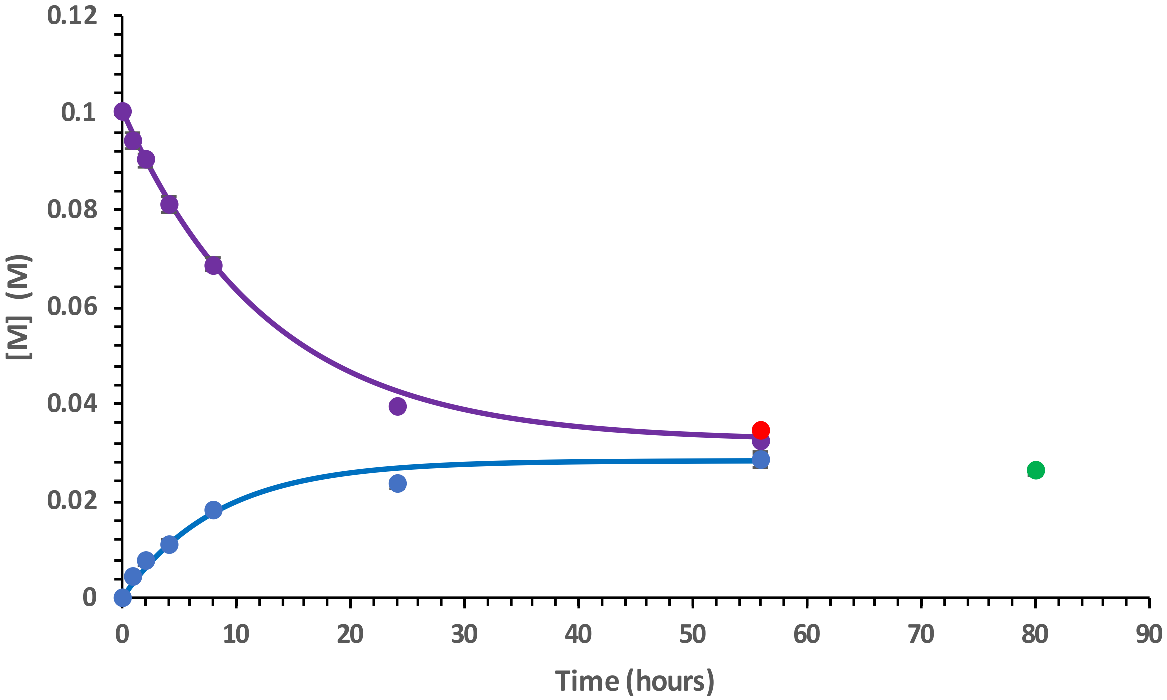


Figure S16: Average macromonomer concentration for the polymerization of ODMSMA7 (purple line) at 70 °C, at 0.1 M initial macromonomer concentration, in 1,4-dioxane, and at a molar ratio of 25:1:0.2 (macromonomer:CDTP:AIBN), and, average kinetic data for the depolymerization at 70 °C of a 22 RU PODMSMA7 (blue line) at a 0.1 M initial RUs in 1,4-dioxane. Also plotted are theoretical monomer profiles for the polymerization of ODMSMA7 and depolymerization of PODMSMA7 using the respective measured values for $[M]_{eq}$ and k_{app}. Also included on the plot are the monomer concentrations for the polymerization re-addition of AIBN experiment with the macromonomer concentration before re-addition of AIBN (red point) and after (green point) the re-initiated polymerization of PODMSMA7 crude solution following the addition of AIBN at a 1:0.2 molar ratio of CDTP:AIBN and additional reaction period of 24 hours. Error bars are one standard deviation with n ≥ 3 replications.

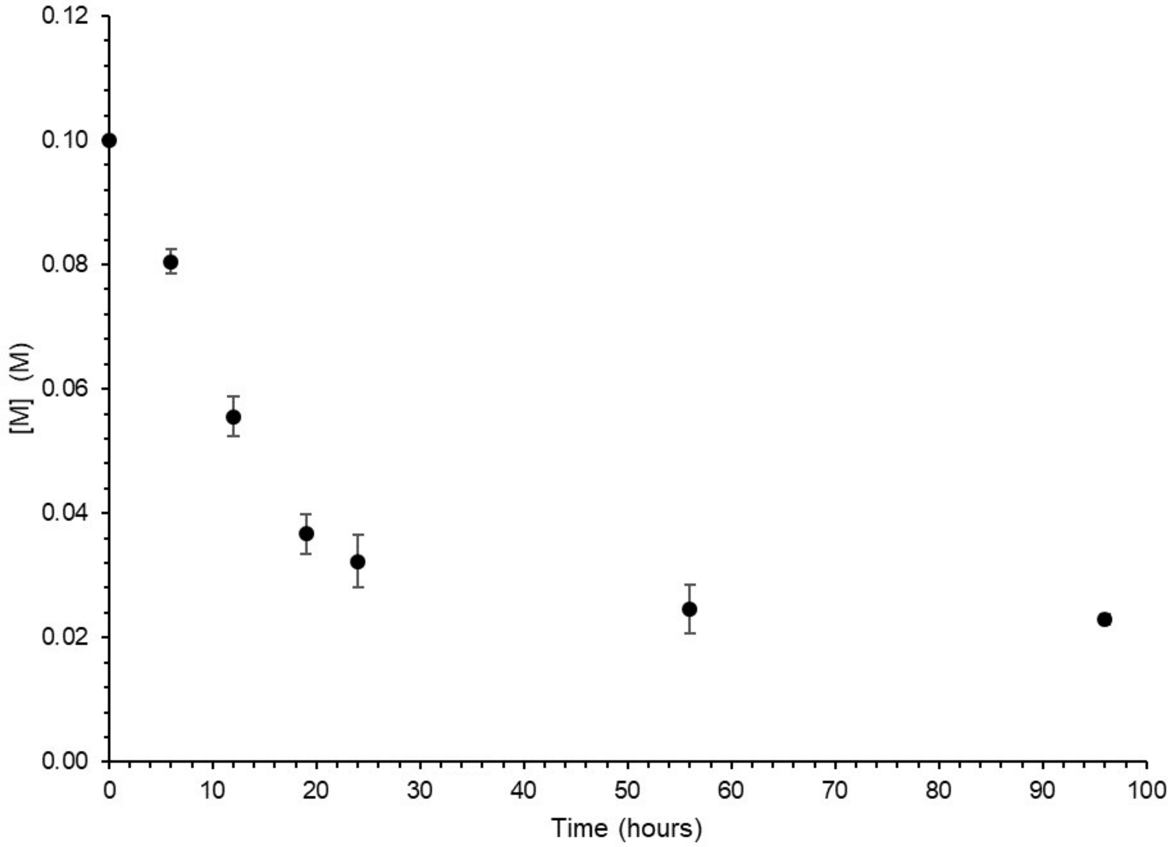


Figure S17. Monomer concentration as a function of polymerization time for ODMSMA70 monomer at 70 °C in 1,4-dioxane. Error bars are one standard deviation with n ≥ 3 replications.

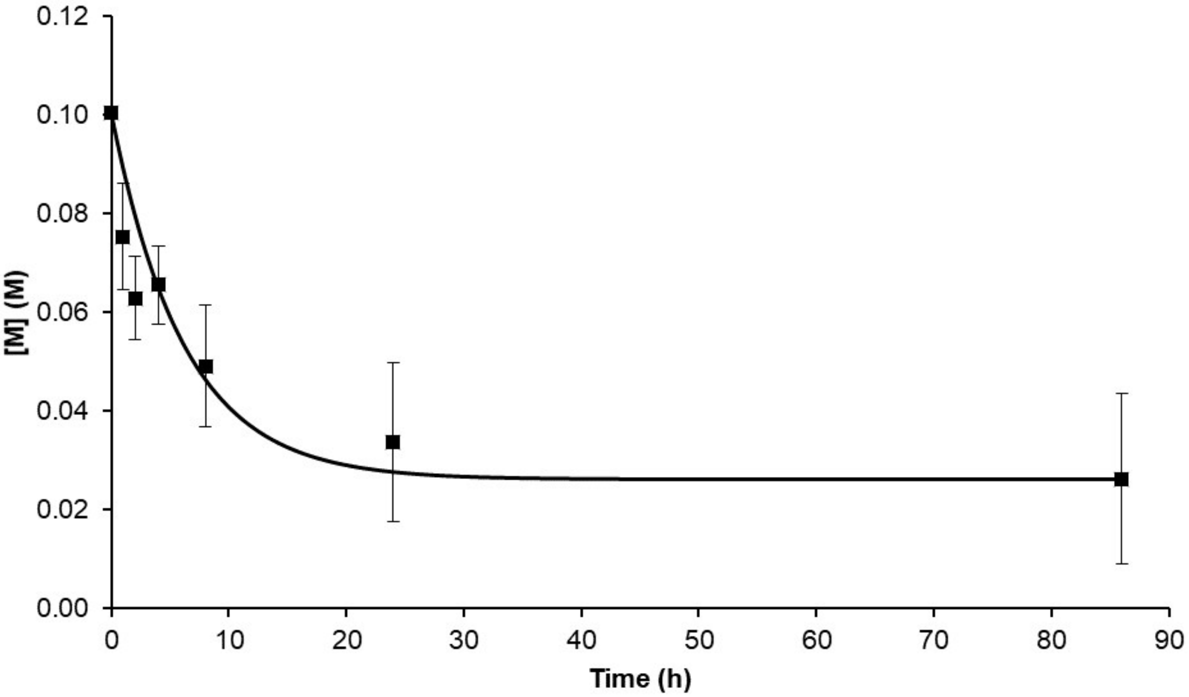


Figure S18. Monomer concentration as a function of time for the RAFT polymerization of MMA in 1,4-dioxane at 70 °C with initial monomer concentration of 0.1 M (25:1:0.2 monomer:CTA:initiator). Also plotted are theoretical monomer profiles for the polymerization of MMA using the measured values for $[M]_{eq,p}$ and $k_{app,p}$. Error bars are one standard deviation (n≥3).

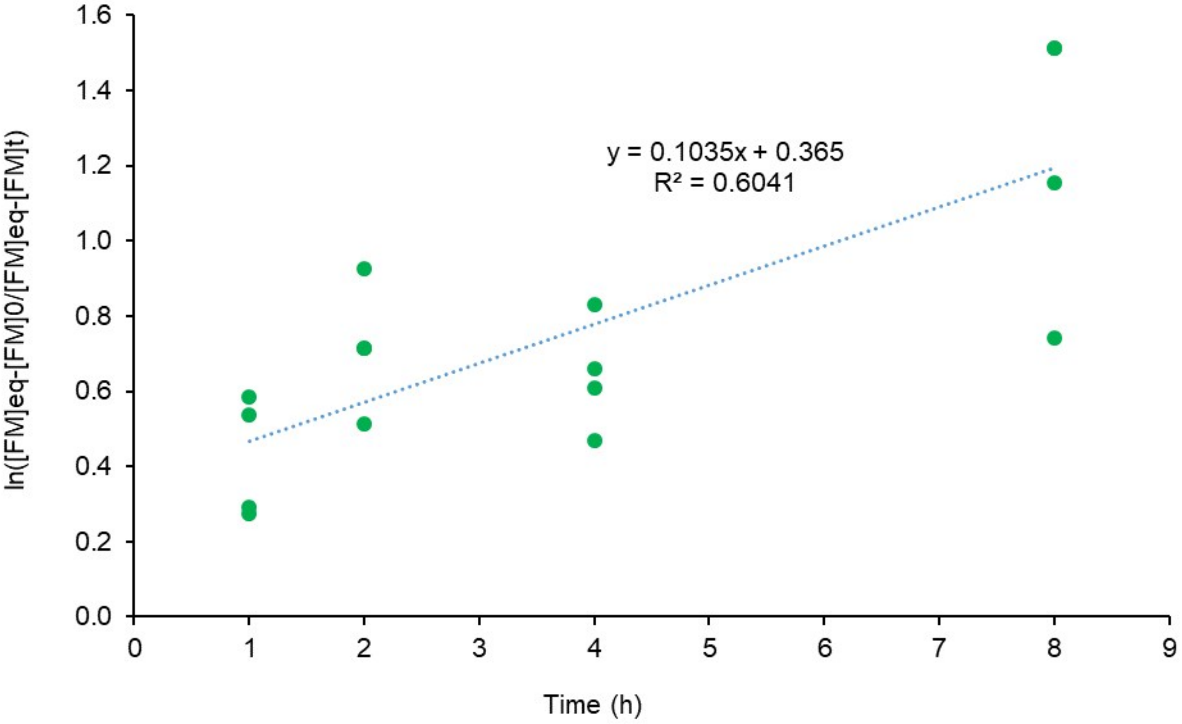


Figure S19. Linearized kinetic data for the first 8 h of polymerization of MMA assuming equilibrium kinetics and a $[M]_{eq} = 2.7 \times 10^{-2}$ M from the average of four polymerizations. The low R^2 value and deviation of the intercept of the linear fit from the origin is likely due to the inherent uncertainty of the gravimetric method used to measure the monomer concentration as a function of time.

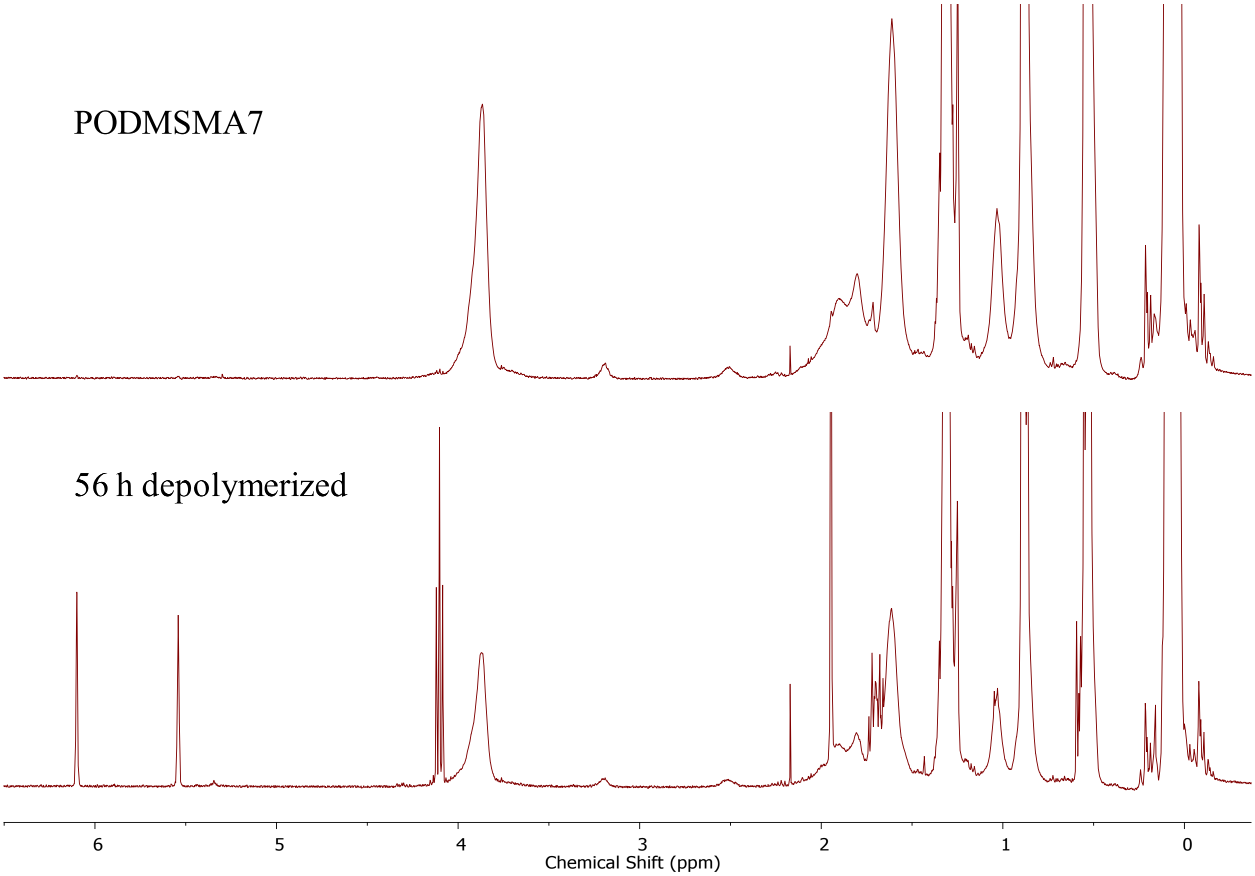


Figure S20. ^{1}H NMR spectra of 22 RU PODMSMA7 and crude product of the polymer heated for 56 h at 70 °C.

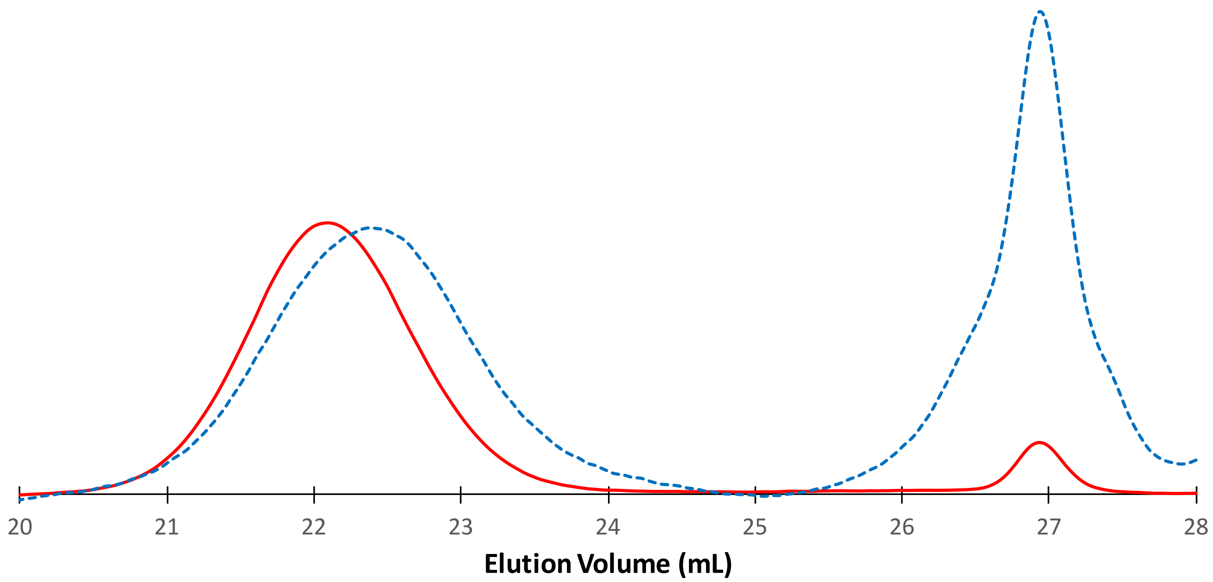


Figure S21. SEC elution curves for the depolymerization of a 48 RU PODMSMA7 (red line, M_n = 30.5 kg/mol, Đ = 1.25) with an initial polymerized monomer concentration of 28 mM in 1,4-dioxane at 70 °C and at 56 h (blue line, M_n = 22.8 kg/mol, Đ = 1.43). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 17 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

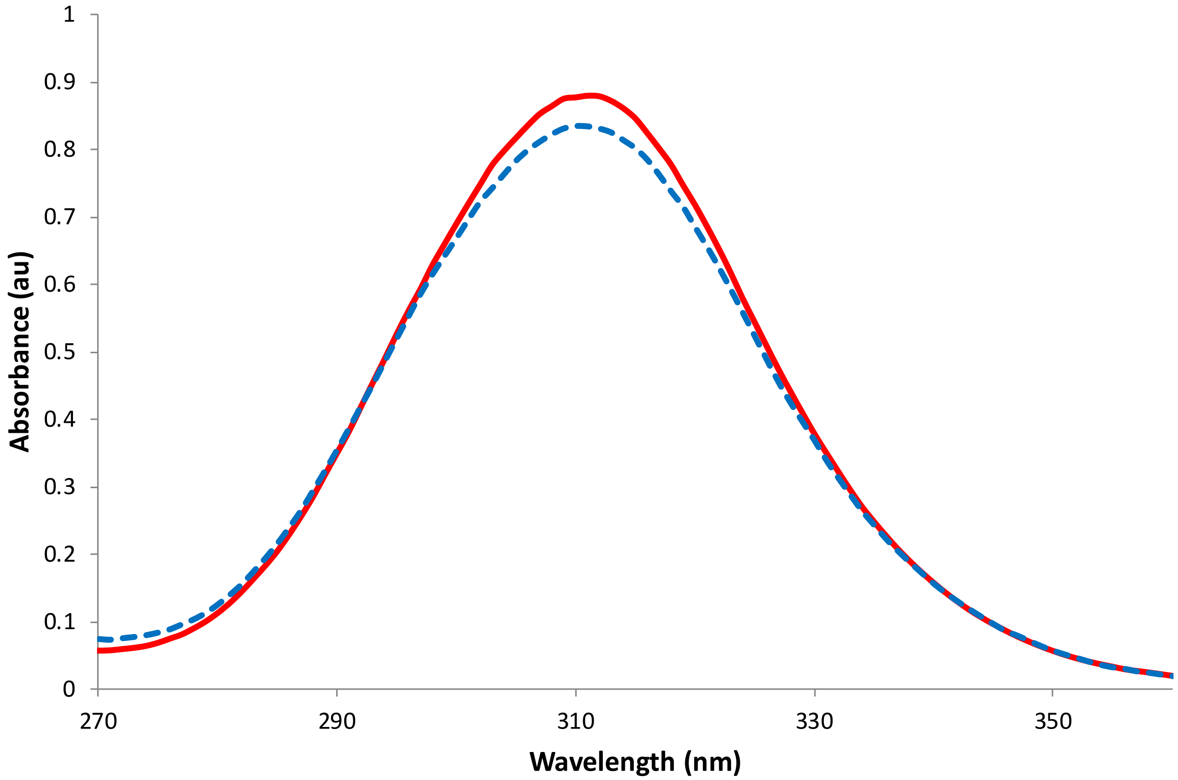


Figure S22. UV-Vis absorbance spectra of 22 RU PODMSMA7 homopolymer (red), and a crude sample after heating in dioxane for 56 h at 70 °C (blue). Both samples were measured at a 1 mg/mL concentration in THF.

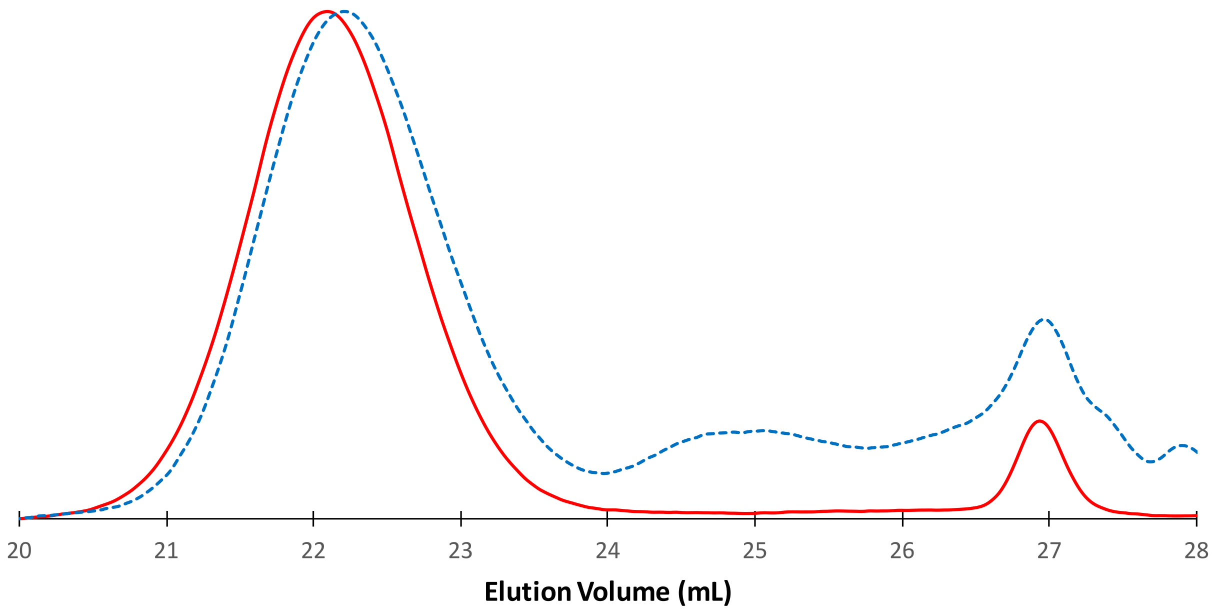


Figure S23. SEC elution curves for the depolymerization of a 48 RU PODMSMA7 (red line, M_n = 30.5 kg/mol, Đ = 1.25) with an initial polymerized monomer concentration of 0.05 M in tetrahydrofuran at 70 °C and at 60 h (blue line, M_n = 26.2 kg/mol, Đ = 1.28). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 8 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

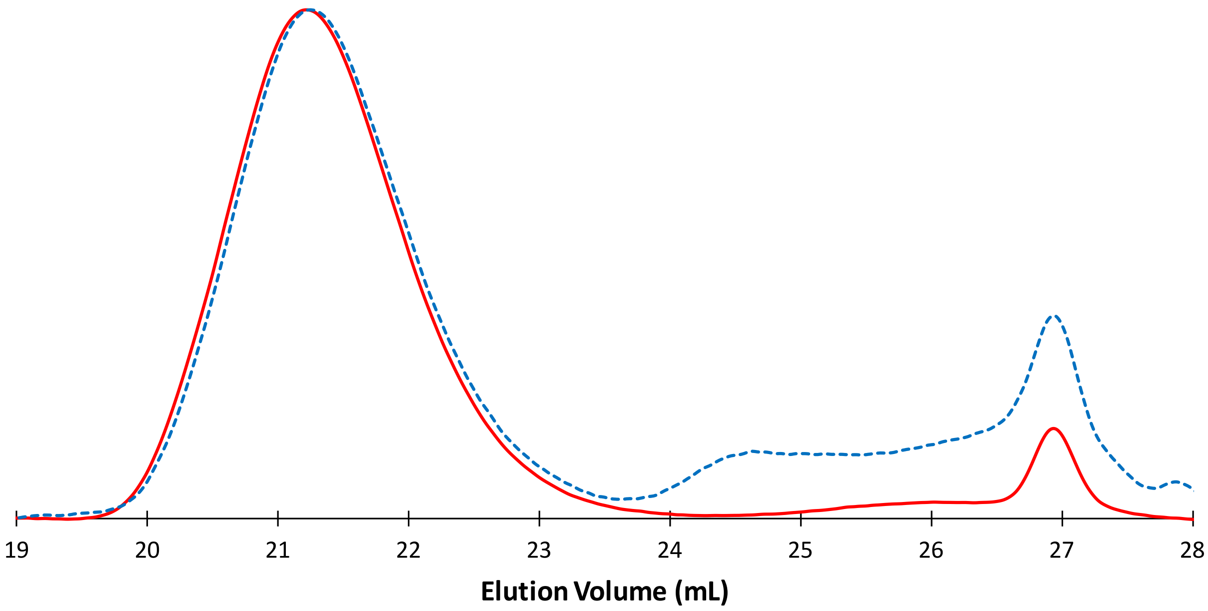


Figure S24. SEC elution curves for the depolymerization of an 89 RU PODMSMA7 (red line, M_n = 55.7 kg/mol, Đ = 1.32) with an initial polymerized monomer concentration of 0.05 M in tetrahydrofuran at 70 °C and at 60 h (blue line, M_n = 50.2 kg/mol, Đ = 1.48). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 10 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

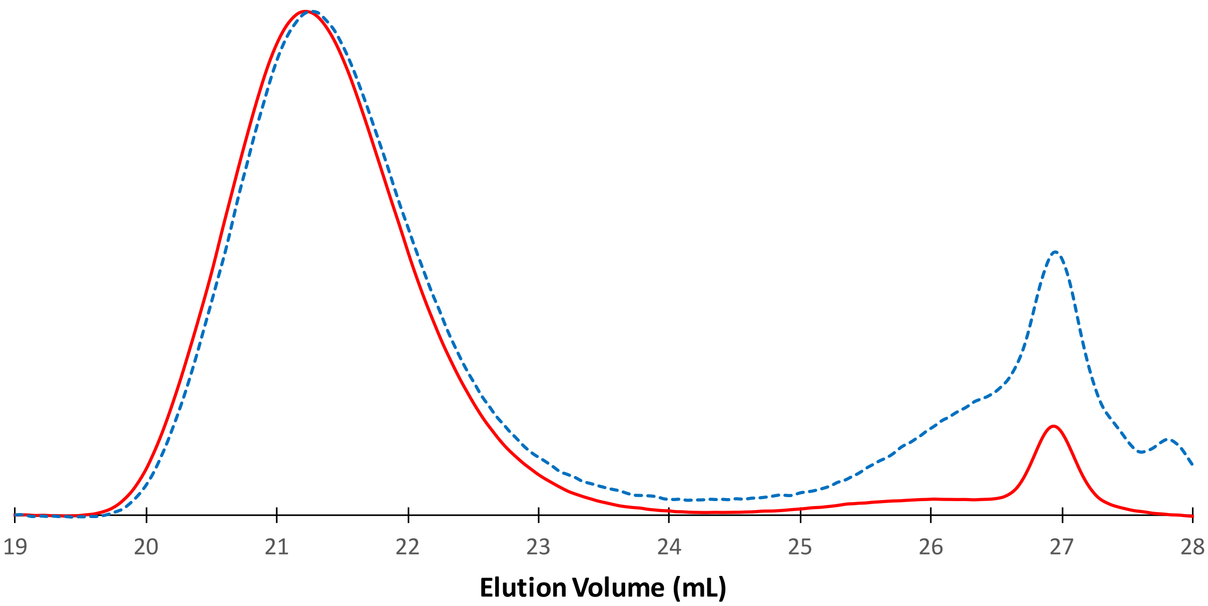


Figure S25. SEC elution curves for the depolymerization of an 89 RU PODMSMA7 (red line, M_n = 55.7 kg/mol, Đ = 1.32) with an initial polymerized monomer concentration of 0.05 M in xylenes at 70 °C and at 60 h (blue line, M_n = 50.9 kg/mol, Đ = 1.37). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 17 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

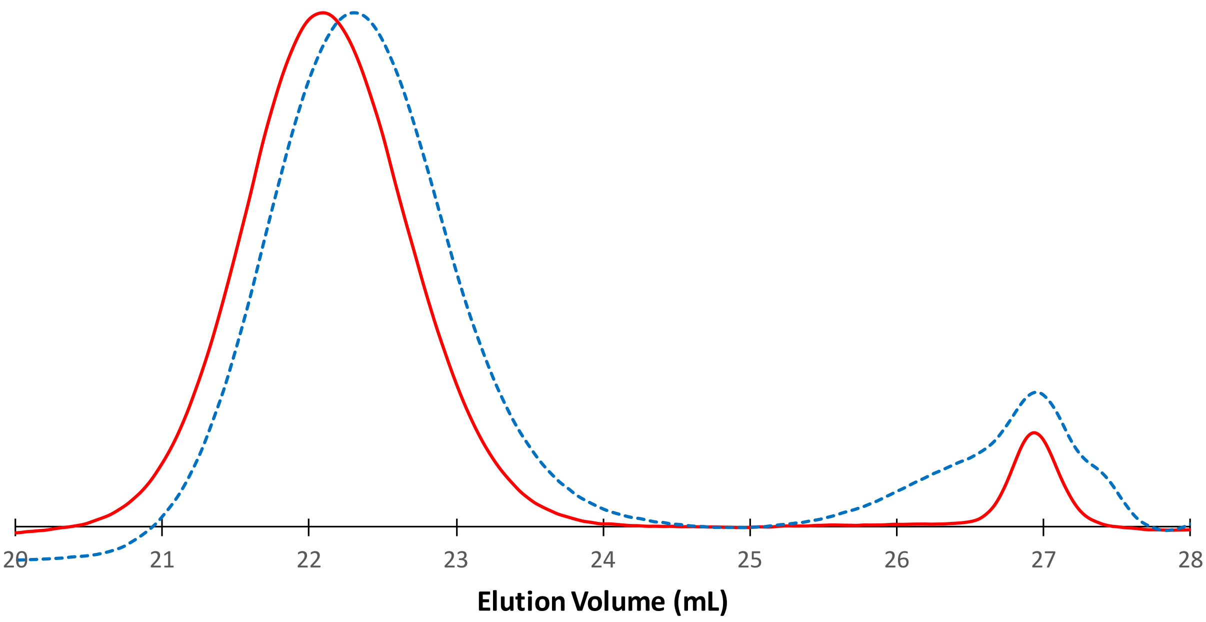


Figure S26. SEC elution curves for the covered (i.e. protected from ambient light) depolymerization of a 48 RU PODMSMA7 (red line, M_n = 30.5 kg/mol, Đ = 1.25) with an initial polymerized monomer concentration of 0.05 M in 1,4-dioxane at 70 °C and at 60 h (blue line, M_n = 22.4 kg/mol, Đ = 1.37). ^{1}H-NMR analysis demonstrates that this polymer depolymerized on average, 7 RU of ODMSMA7 per polymer chain. Residual monomer curve is visible at an elution volume of ca. 27 mL and increases with depolymerization.

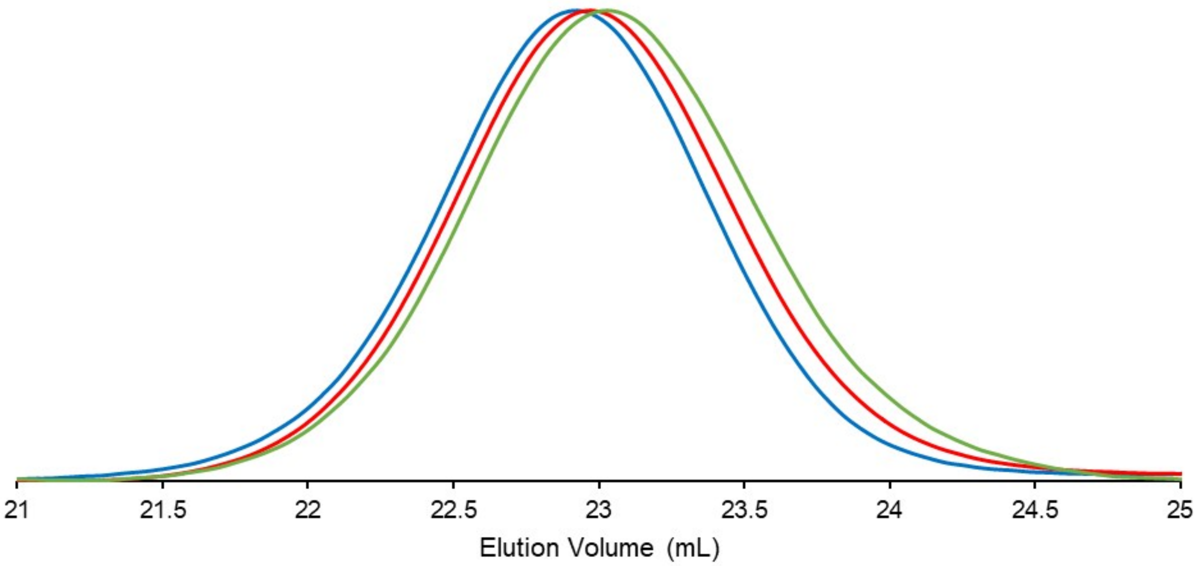


Figure S27. SEC elution curves for the BHT inhibited depolymerization of 22 RU PODMSMA7 (blue line, M_n = 17.5 kg/mol, Đ = 1.16) at 56 h (red line, M_n = 16.2 kg/mol, Đ = 1.17) and 120 h (green line, M_n = 15.2 kg/mol, Đ = 1.19).

Calculations for ceiling macromonomer molecular weight (M_{cmm})

The M_{cmm} can be calculated from the equation below.

$$M_{cmm} = \frac{\rho_{bulk}}{[M]_{eq}}$$

ODMSMA

$\rho_{bulk} = 960\,\frac{g}{L}$ and $[M]_{eq} = 33 \times 10^{-3}\frac{mol}{L}$, gives $M_{cmm} = 29{,}090\frac{g}{mol}$ or 393 RU.

OEGMA

$\rho_{bulk} = 1080\,\frac{g}{L}$ and $[M]_{eq} = 27 \times 10^{-3}\frac{mol}{L}$, gives $M_{cmm} = 40{,}000\frac{g}{mol}$ or 909 RU.

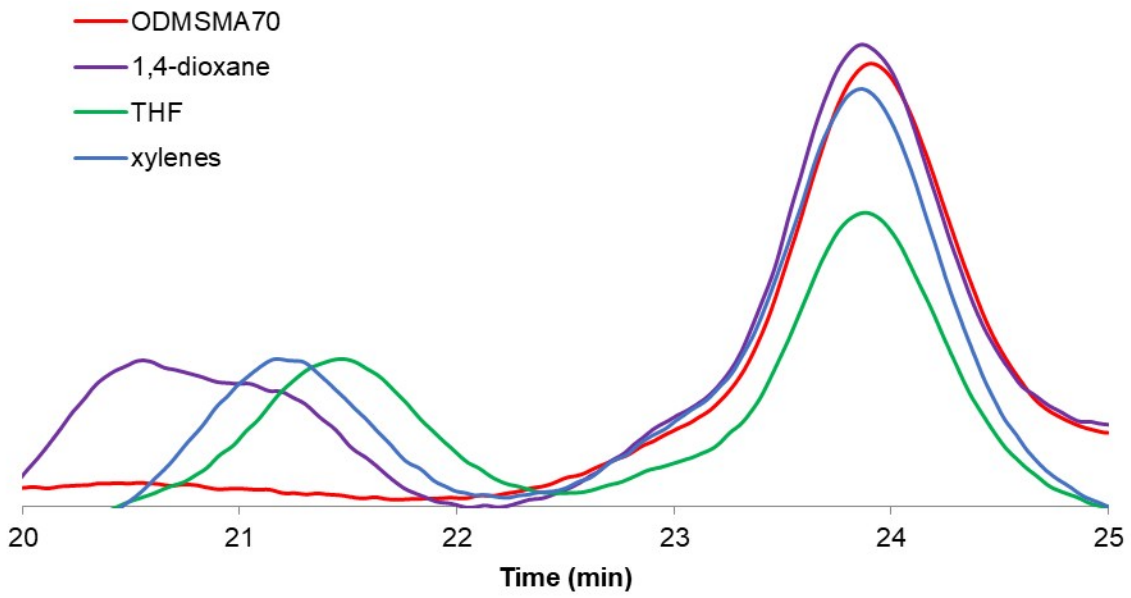


Figure S28. SEC elution curves of ODMSMA70 (M_n = 8.8 kg/mol, Đ = 1.14) and crude reaction mixtures of polymerizations of ODMSMA70 conducted in 1,4-dioxane (M_n = 102 kg/mol, Đ = 1.22), THF (M_n = 73 kg/mol, Đ = 1.15), and xylenes (M_n = 60 kg/mol, Đ = 1.24).

References

[1] G. Moad, Y. K. Chong, A. Postma, E. Rizzardo, S. H. Thang. Advances in RAFT polymerization: the synthesis of polymers with defined end-groups. *Polymer* 2005, **46**, 8458 – 8468.

[2] Y. Kwak, A. Goto, Y. Tsujii, Y. Murata, K. Komatsu, T. Fukuda. A kinetic study on the rate retardation in radical polymerization of styrene with addition-fragmentation chain transfer. *Macromolecules* 2002, **35**, 3026 – 3029.

[3] Blazejowski, J.; Szychlinski, J. 1,4-dioxane as a solvent in spectroscopy and photochemistry. *Analytica Chimica Acta* 1984, **159**, 369 – 373.

[4] Sharma, A. S.; Kaur, H. Au NPs polystyrene resin for mild and selective aerobic oxidation of 1,4-dioxane to 1,4-dioxan-2-ol. *Catalysis Communications* 2017, **90**, 56 -59.