

Supplementary Materials for:

Dual stimuli triggerable degradation of graft copolymers

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General considerations

Unless stated all reagents were purchased from commercial suppliers and used as received. Butyl acrylate (BA) and anhydrous dioxane were passed through activated basic aluminum oxide and discarded after several uses. All NMR spectrums were recorded on a Bruker 400 MHz spectrometer in CDCl₃. All NMR spectrums were processed using Mestrenova. Volumes of solvents (including initiator stock solution) were measured by weight based on densities reported by manufacturers. Initiator (AIBN) stock solution was prepared as 20 mg/ml in the solvent used for polymerization. For simplicity, molar concentration of the reacting species here is defined by moles of the reactants divided by the total volume of the solvent, without consideration for the volume taken up by non-solvent components. Experiments were carried out in either 3.7 ml scintillation vials with a diameter of 15 mm, or in 20 ml scintillation vials with a diameter of 28 mm. Reaction containers were sealed with a 14/20 rubber septum. Thermo Scientific digital baths (Digital Dry Baths/Block Heaters – PROMO, catalog number: 88870001) equipped with heat block (holds 15 x 16 mm diameter, catalog number: 88870106) were used to maintain constant temperature.

For kinetic analysis A 22-gauge, 4 inch hypodermic needle (air-tite product) was used to sample the reaction mixture under argon flow. Typically, a single needle and syringe was used to take sample for both THF-SEC and ¹H-NMR spectroscopy, by drawing out approximately 50 to 100 μL and dropping a few drops into a vial for ¹H-NMR and the remaining mixture left in the needle was flushed out with THF (or vice versa) in a separate vial for SEC analysis.

Molecular weight characterization

Conventional SEC analysis of the crude polymerization mixture was carried out using polystyrene calibration in THF. SEC chromatograms were measured on a Waters 2695 separations module liquid chromatograph equipped with two Agilent ResiPore columns (linear SEC separation range up to 500k) maintained at 35°C, and a Waters 2412 refractive index detector. THF (with BHT as the inhibitor) was used as the mobile phase and the flow rate was set to 1 ml/min. Some experiments used THF without BHT, and separate calibration curves were created and used for this de-inhibited THF to ensure accuracy of the results. All samples were run with 100 μL injection volume.

Theoretical average molecular weight

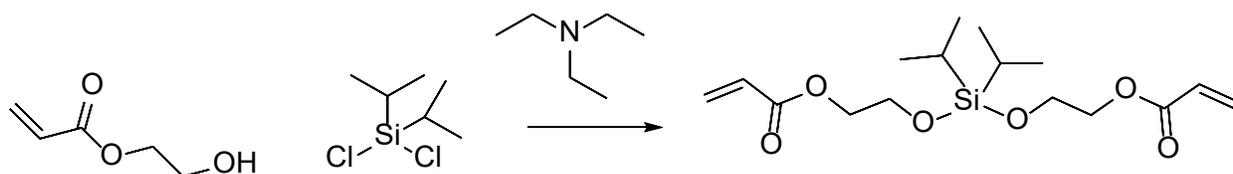
The evolution of number-average (M_n), weight-average (M_w) and Z-average (M_z) molecular weight of the crude reaction mixture were determined by SEC analysis. These were plotted together with conversion determined by ¹H-NMR with expected molecular averages for linear step-growth polymerization according to Flory's equation which assumes no cyclization:¹

$$M_{n,th} = M_0 \frac{1}{1-p}$$

$$M_{w,th} = M_0 \frac{1+p}{1-p}$$

$$M_{z,th} = M_0 \frac{1+4p+p^2}{1-p^2}$$

Procedure for Synthesis of DPSA (M₂):



Triethylamine (8.7 g, 86 mmol) and 2-hydroxyethyl acrylate (10 g, 86 mmol) were added into a sealed round bottom flask (RBF) with dichloromethane (DCM). The reaction was cooled to 0 °C. Dichlorodiisopropylsilane (4.0 g, 22 mmol) was added slowly. After 16 hours, the reaction mixture was washed three times with water. Then, dried with sodium sulfate and concentrated. The crude mixture was passed through Silica gel eluting with DCM to isolate 2 g of colourless oil (yield = 26 %).

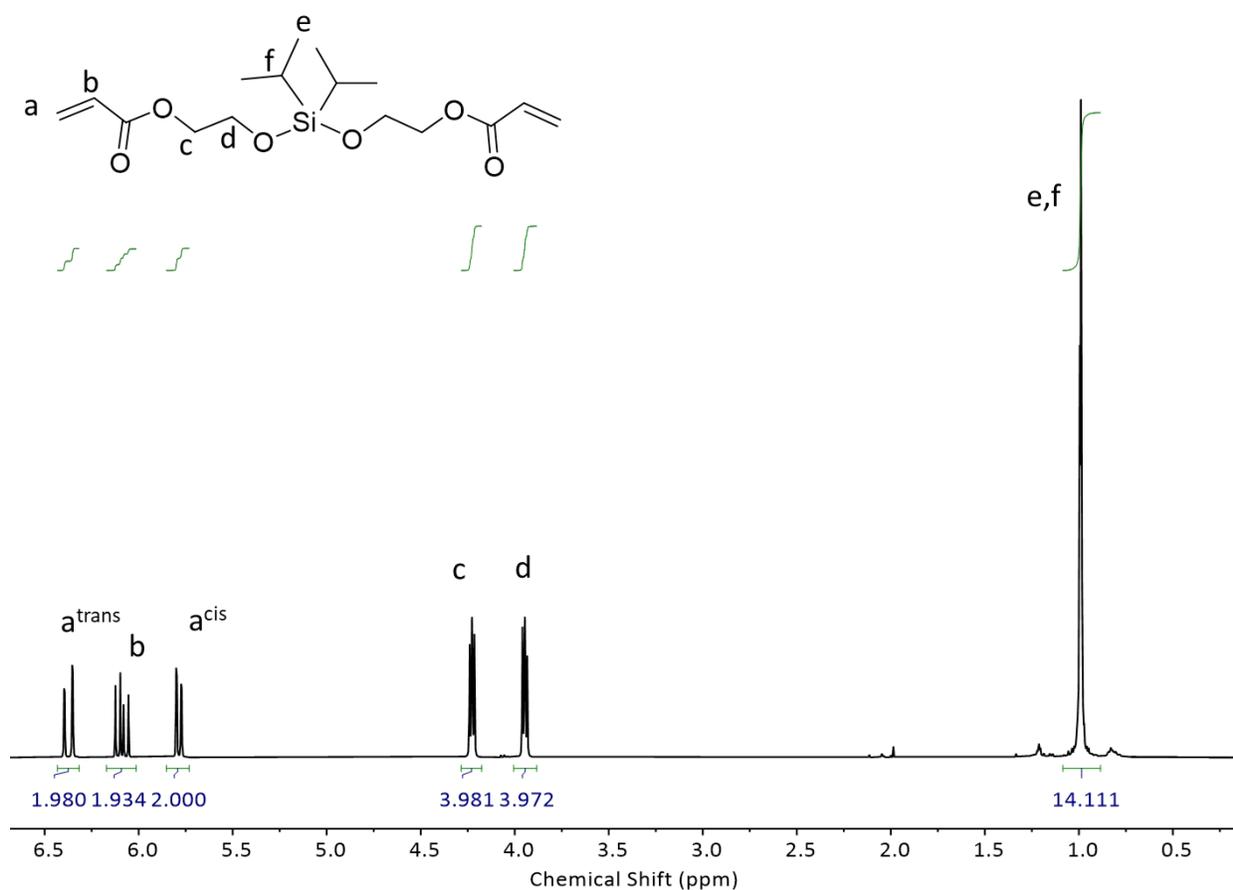
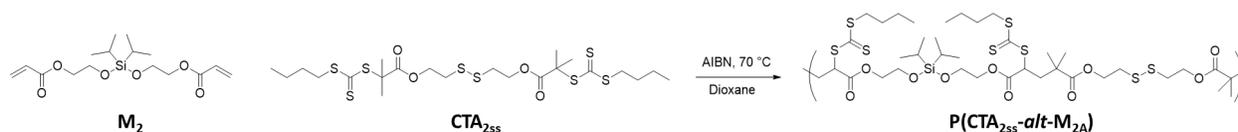


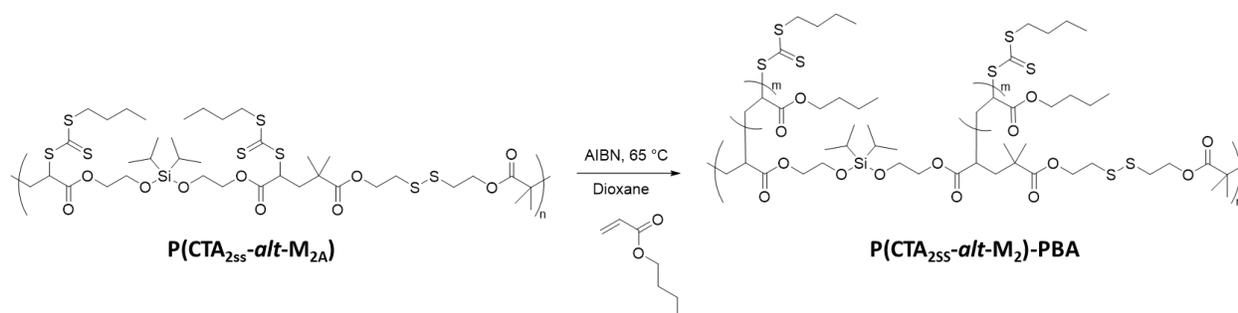
Figure S1: ¹H-NMR (CDCl₃, 400 MHz) spectrum of M₂.

Procedure for backbone polymerization:



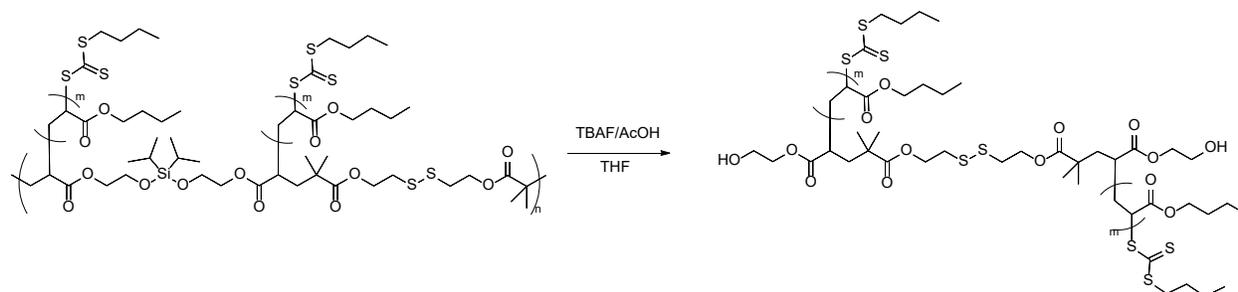
Bifunctional monomer, M_2 (1500 mg, 4.35 mmol) was first charged into a 20.0 ml vial, followed by bifunctional CTA, CTA_{2SS} (2712.87 mg, 4.35 mmol). Next, 35.75 mg AIBN and 4.354 ml 1,4-Dioxane was added to target molar concentration of $[M_2]_0:[CTA_{2SS}]_0:[AIBN]_0 = 1.0 : 1.0 : 0.05$ M (without consideration for the volume taken up by non-solvent components). The vial was then equipped with a stir bar and rubber septum. The reaction vials were then purged with argon for 10 minutes and then placed inside the heat block set to 70°C for 4 hours to react. The polymer was then purified by precipitation from hexanes.

Procedure for brush polymerization:



Polymer backbone, $P(CTA_{2SS}\text{-alt-}M_2)$ (96 mg, 0.20 mmol of CTA repeat units) was first charged into a 3.7 ml vial, followed by Butyl acrylate (1000 mg, 7.80 mmol). Next, 40.14 μl of AIBN stock solution (20 mg/ml of AIBN in 1,4-dioxane) and 1.437 ml 1,4-dioxane were added to target molar concentration of $[BA]_0:[P(CTA_{2SS}\text{-alt-}M_2)]_0:[AIBN]_0 = 3.0 : 0.075 : 0.001875$ M (without consideration for the volume taken up by non-solvent components). The vial was then equipped with a stir bar and rubber septum. The reaction vial was then purged with argon for 10 minutes and then placed inside the heat block set to 65°C for 4 hours to react. The graft copolymer was then purified by precipitation from methanol with a couple drops of water.

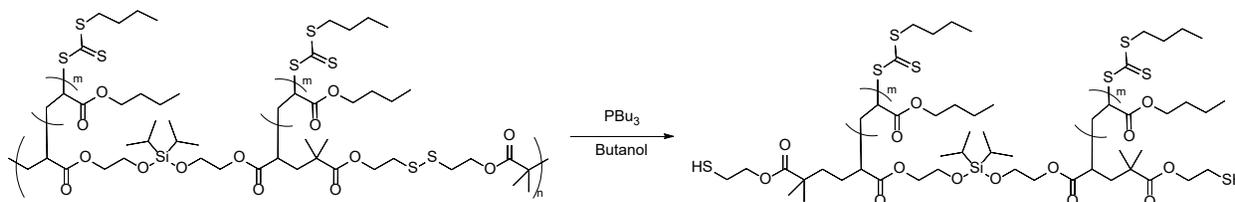
Procedure for brush degradation by cleavage of silyl ether group:



Polymer brush, $P(CTA_{2SS}\text{-alt-}M_2)\text{-g-PBA}$ (10 mg, 0.00115 mmol of silyl ether groups), was dissolved in 1 ml of THF in a 3.7 ml scintillation vial. To this solution, acetic acid (1.20 μl , 20 equivalents w.r.t silyl ether groups) was added, followed by 1 M tetra-*n*-butylammonium fluoride (20.8 μl , 20 equivalents w.r.t silyl ether groups). After 2 hours, an aliquot of the reaction mixture

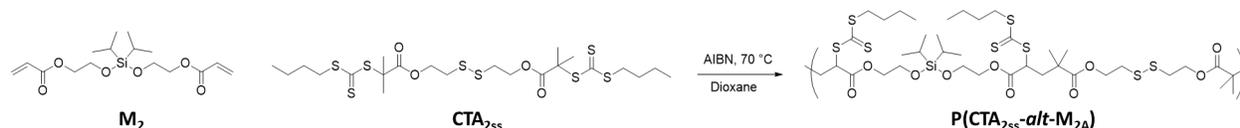
was removed and analyzed by THF-SEC chromatography. Aliquots were diluted 1:10 in THF, although this was not expected to completely quench the reaction. For sequential brush degradation, THF was removed by rotary evaporator.

Procedure for brush degradation by cleavage of disulfide group:



Polymer brush, P(CTA_{2SS}-*alt*-M₂)-*g*-PBA (10 mg, 0.00115 mmol of disulfide bonds), was dissolved in 1 ml of butanol in a 3.7 ml scintillation vial. To this solution, tributyl phosphine (5.14 μ l, 20 equivalents w.r.t disulfide bonds) was added. After 2 hours, an aliquot of the reaction mixture was removed and analyzed by THF-SEC chromatography. Aliquots were diluted 1:10 in THF, although this was not expected to completely quench the reaction. For sequential brush degradation, butanol was removed by gently blowing air into the reaction vial overnight.

Table S1: Kinetic analysis of A₂+B₂ RAFT step-growth polymerization of M₂ with CTA_{2SS}



Time (hr) ^a	<i>p</i> ^b	<i>r</i> _{th}	<i>M</i> _{W,th} ^c	<i>M</i> _{W,th} (<i>r</i> _{th})	<i>M</i> _W ^d	<i>M</i> _W / <i>M</i> _n ^d	<i>M</i> _Z / <i>M</i> _W ^d
0.0	0.00	1.000	484	484	590	1.01	1.01
0.5	0.323	0.996	945	944	1.1k	1.31	1.38
1.0	0.544	0.992	1.6k	1.6k	1.9k	1.57	1.58
2.0	0.800	0.985	4.3k	4.2k	4.9k	2.06	1.71
4.0	0.926	0.974	12.7k	10.8k	12.2k	2.67	1.77

^a Duration of the polymerization. ^b Monomer conversion determined by ¹H-NMR. ^c Theoretical value according to Flory's equation.¹ ^d Determined by THF-SEC analysis using polystyrene calibration.

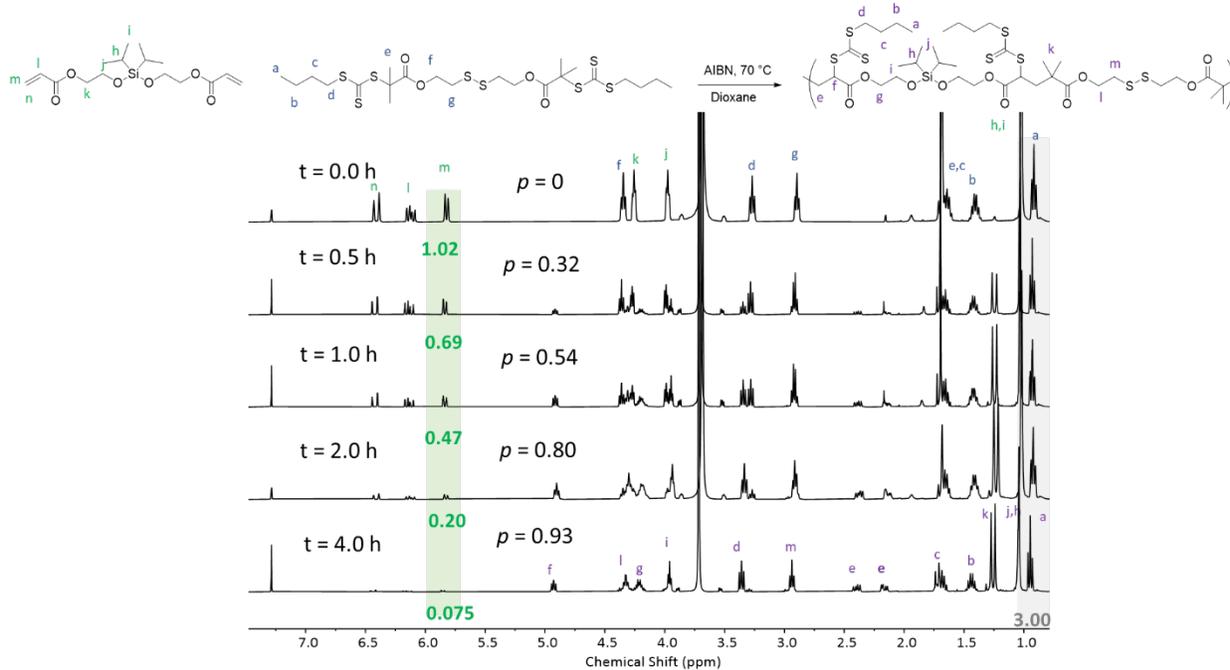


Figure S2: $^1\text{H-NMR}$ (CDCl₃, 400 MHz) analysis of $\text{A}_2 + \text{B}_2$ RAFT step-growth polymerization with M_2 and $\text{CTA}_{2\text{SS}}$. The numbers correspond to relative integral of the monomer peak (green region) with respect to the Z-group CH_3 (grey region) as 3 for reference.

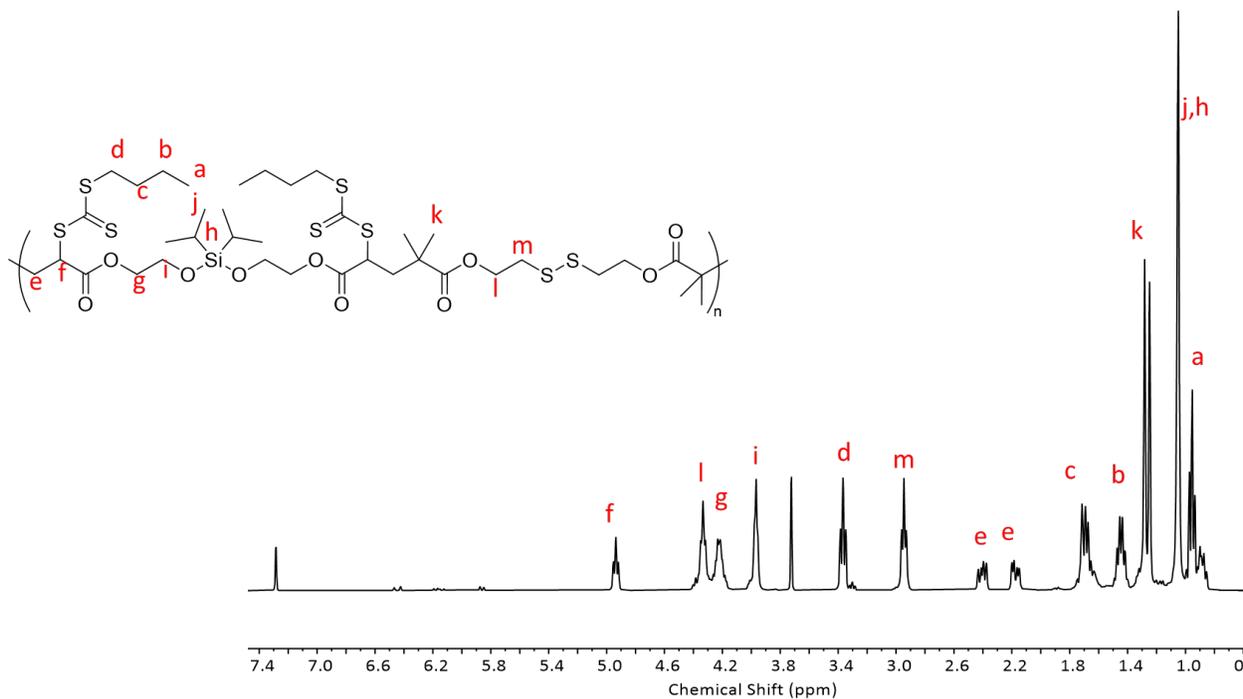


Figure S3: $^1\text{H-NMR}$ (CDCl₃, 400 MHz) spectrum of $\text{P}(\text{CTA}_{2\text{SS}}\text{-alt-}\text{M}_2)$.

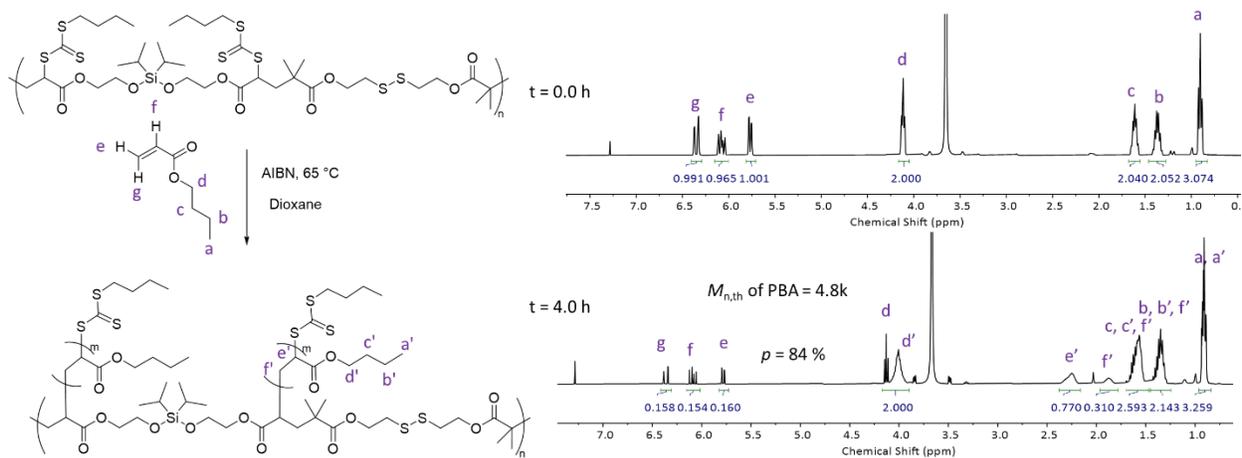


Figure S4: $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) analysis of RAFT polymerization of Butyl Acrylate to graft from $\text{P}(\text{CTA}_{2\text{SS-}alt\text{-M}_2})$. The integrals of vinyl proton (H_e) with respect to monomeric and polymeric- OCH_2 signal (H_d and $\text{H}_{d'}$) was used to determine monomer conversion.

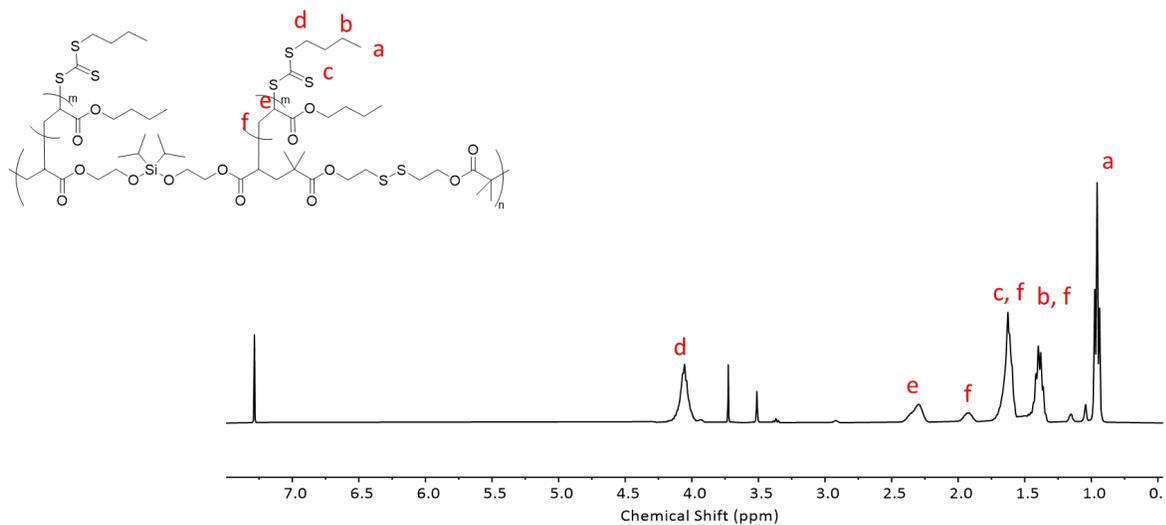


Figure S5: $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) spectrum of $\text{P}(\text{CTA}_{2\text{SS-}alt\text{-M}_2})\text{-g-PBA}$.

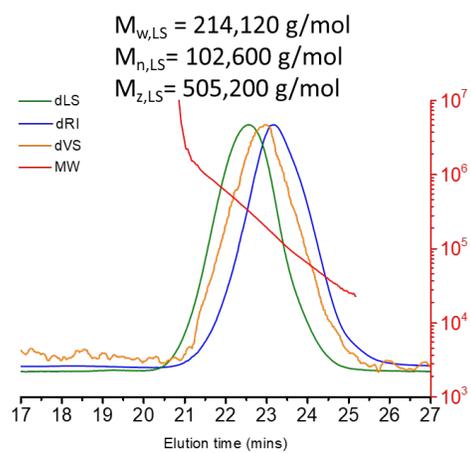
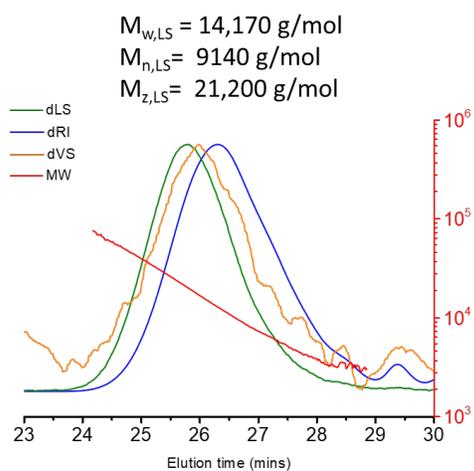
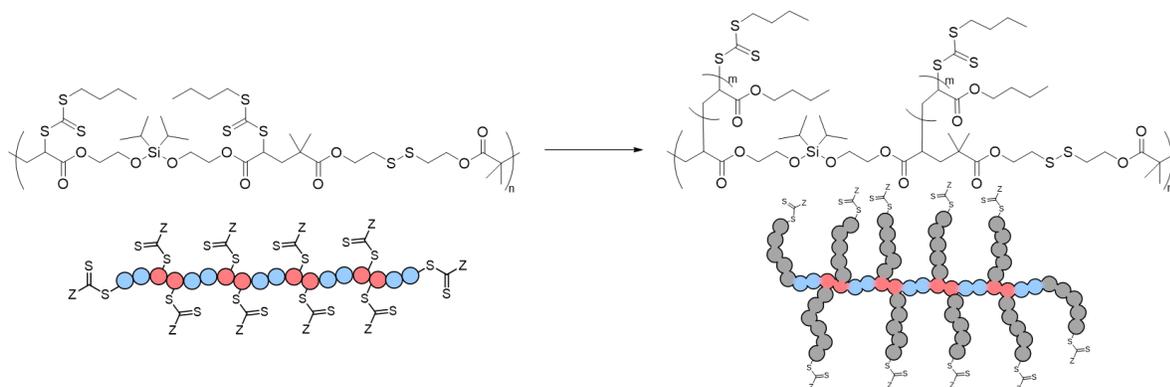


Figure S6: Molecular weight distribution obtained via triple-detection analysis. **Left,** P(CTA₂SS-*alt*-M₂) backbone. **Right,** P(CTA₂SS-*alt*-M₂)-g-PBA.

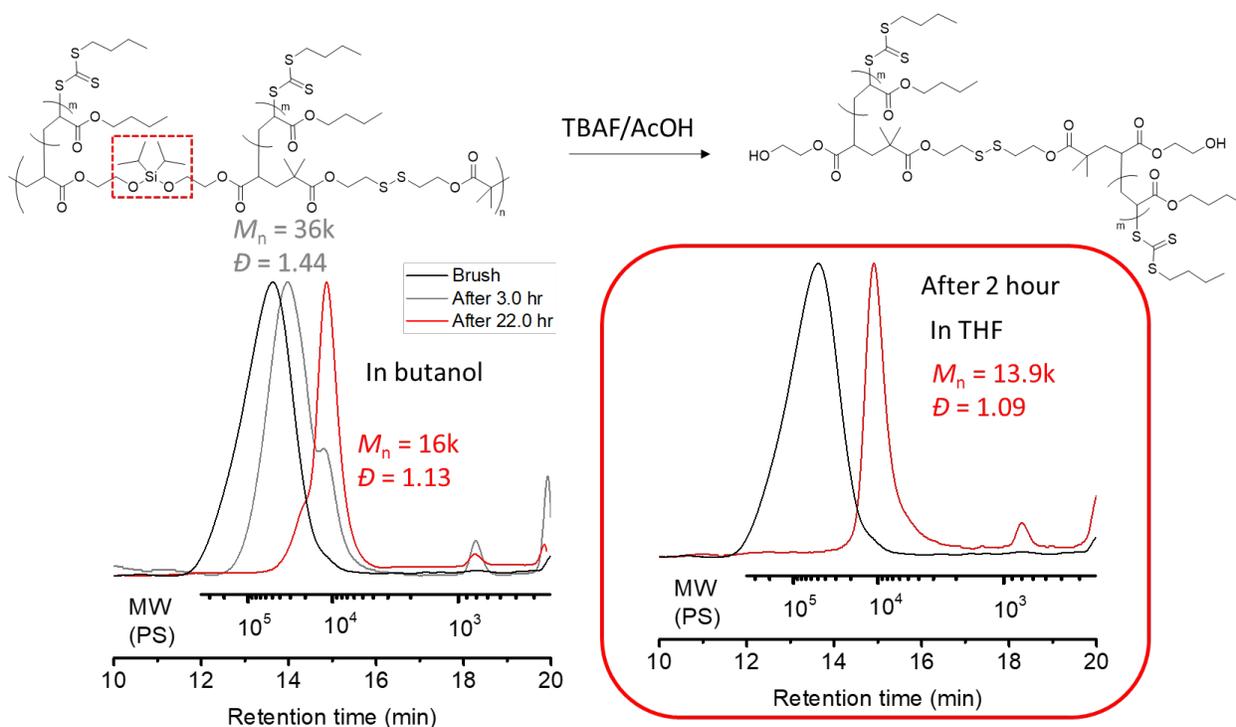


Figure S7: THF-SEC (normalized dRI) chromatograms of P(CTA_{2SS-*alt*}-M₂)-*g*-PBA (black curve, $M_n = 69k$, $\bar{D} = 1.65$) degradation of the silyl ether group. **Left**, in butanol after 3.0 hours (grey) and 22.0 hours (red). **Right**, in THF after 2.0 hours.

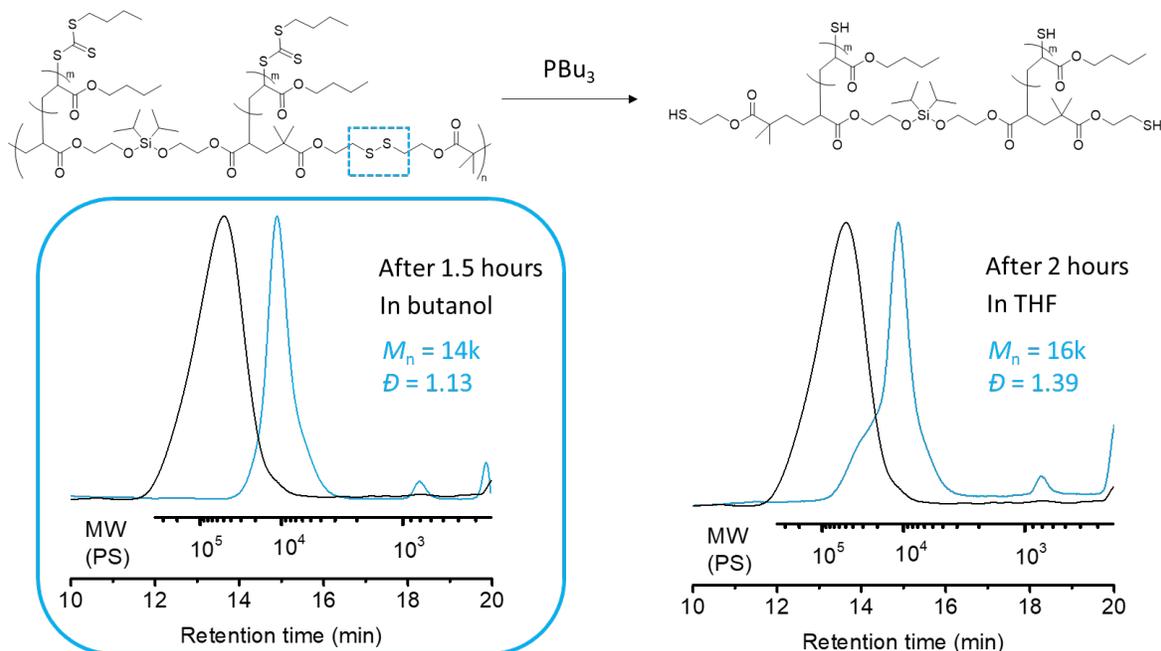


Figure S8: THF-SEC (normalized dRI) chromatograms of P(CTA_{2SS-*alt*}-M₂)-*g*-PBA (black curve, $M_n = 69k$, $\bar{D} = 1.65$) degradation of the disulfide bond. **Left**, in butanol after 1.5 hours (blue). **Right**, in THF after 2.0 hours.

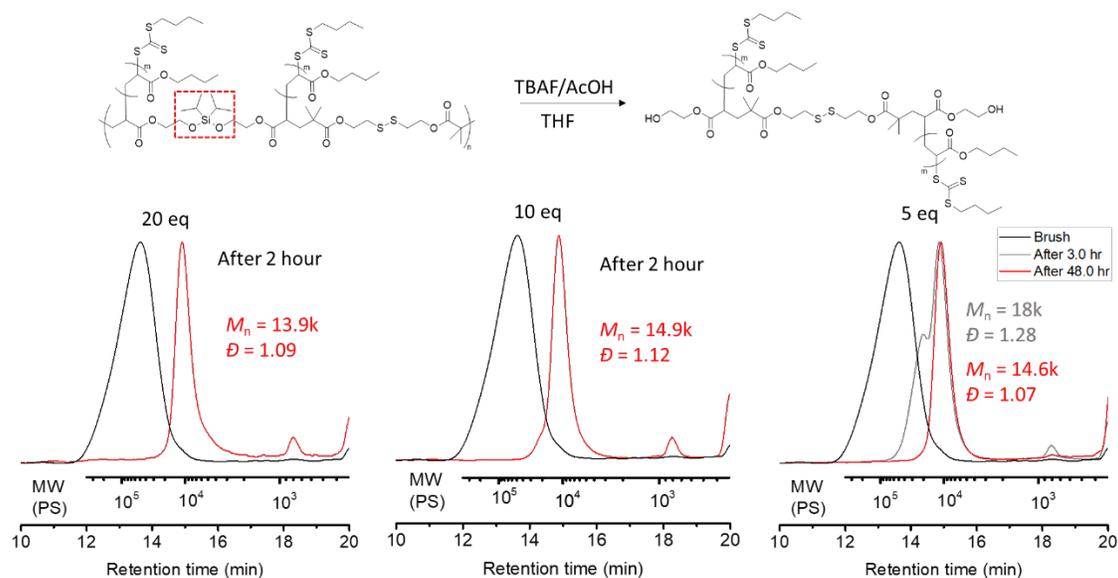


Figure S9: THF-SEC (normalized dRI) chromatograms of P(CTA_{2SS}-*alt*-M₂)-*g*-PBA (black curve, $M_n = 69k$, $\mathcal{D} = 1.65$) degradation of the silyl ether group. **Left**, 20 equivalence after 2.0 hours (red). **Middle**, 10 equivalence after 2.0 hours. **Right**, 5 equivalence after 3.0 hours (grey) and 48.0 hours (red).

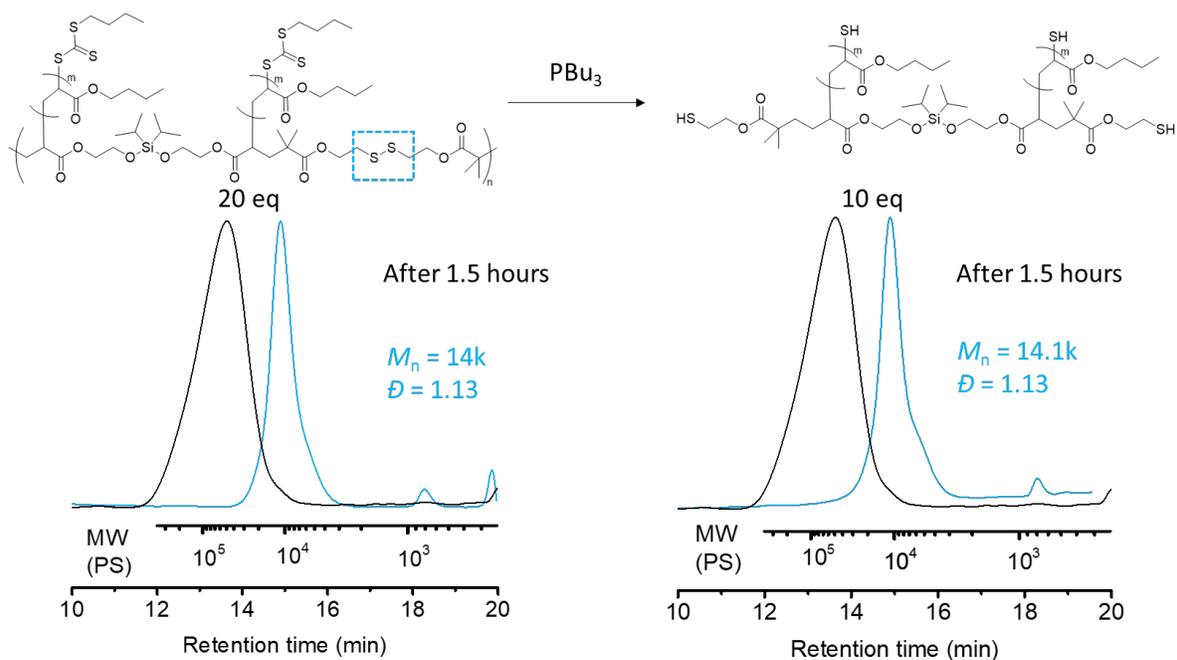


Figure S10: THF-SEC (normalized dRI) chromatograms of P(CTA_{2SS}-*alt*-M₂)-*g*-PBA (black curve, $M_n = 69k$, $\mathcal{D} = 1.65$) degradation of the disulfide bond. **Left**, 20 equivalence after 1.5 hours (blue). **Right**, 10 equivalence after 1.5 hours (blue).

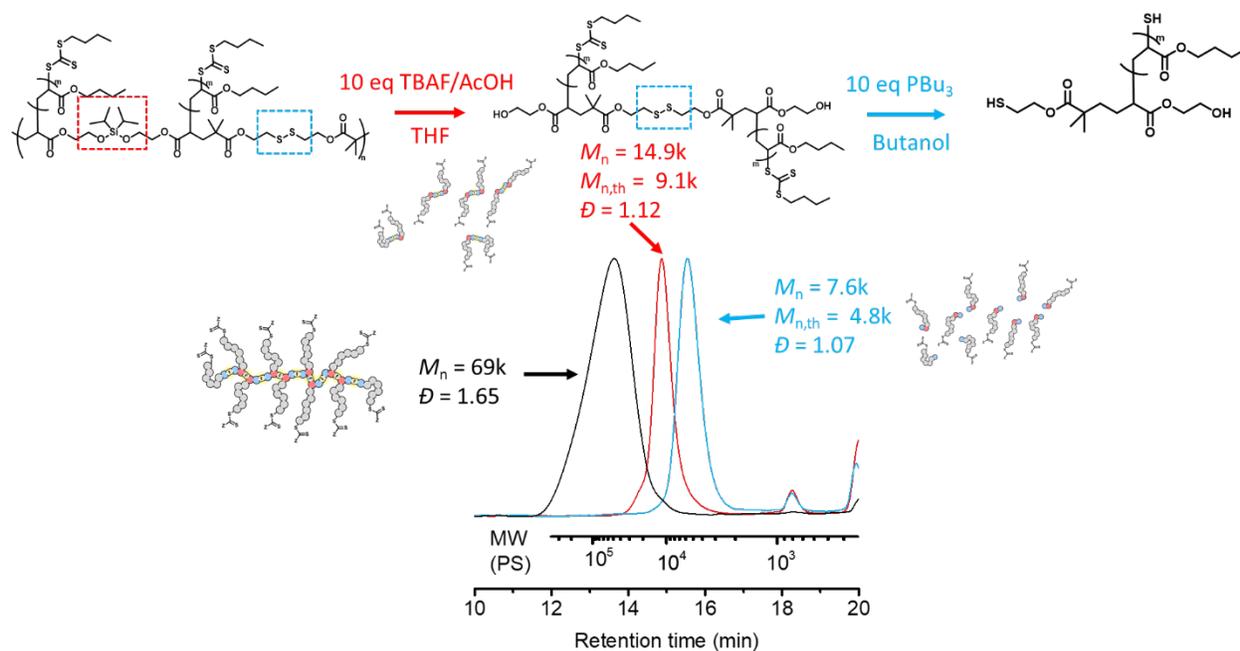


Figure S11: THF-SEC (normalized dRI) chromatograms of P(CTA_{2SS}-*alt*-M₂)-*g*-PBA (black curve, $M_n = 69k$, $\mathcal{D} = 1.65$) dual stimuli degradation of silyl ether group (red), then the disulfide bond (blue). Both degradation conditions were done with 10 equivalences of the appropriate reagent.

1. P. J. Flory, *J. Am. Chem. Soc.*, 1936, **58**, 1877–1885.