Orthogonally Deconstructable and Depolymerizable Polysilylethers via Entropy-Driven Ring-Opening Metathesis Polymerization

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Contents

1. Materials and experimental methods

Materials: All reagents were purchased from commercial suppliers and were used without further purification unless otherwise noted. Polymerizations were conducted in anhydrous Sure/Seal DCM or dioxane (Sigma-Aldrich). Reagents were acquired from commercial vendors, including Sigma-Aldrich, Thermo Fisher Scientific, Acros Organics, and Cambridge Isotope Laboratories.

Nuclear Magnetic Resonance (NMR) Spectroscopy: ^{1}H nuclear magnetic resonance (^{1}H NMR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were acquired at the MIT Department of Chemistry Instrumentation Facility on a Bruker AVANCE III DRX 400 or Neo 500. Chemical shifts are reported in ppm relative to signals from the NMR solvent: for $CDCl_3$, this corresponds to 7.26 for ^{1}H and 77.0 for ^{13}C spectra.

High Resolution Mass Spectrometry (HRMS): High-resolution mass spectrometry (HRMS) measurements were obtained on JEOL AccuTOF 4G LC-plus equipped with an ionSense DART at the MIT Department of Chemistry Instrumentation Facility.

Size Exclusion Chromatography (SEC): Analytical gel permeation chromatography was performed on a Tosoh EcoSEC HLC-8320 with dual TSKgel SuperH3000 columns and an ethanol-stabilized chloroform mobile phase, with sample concentrations of ~1 mg/mL. Samples were filtered through 0.2 μm PTFE syringe filters before injection into the instrument. Molar mass values were calculated according to linear polystyrene calibration standards.

Thermal Gravimetric Analysis (TGA): TGA studies were performed on ~2-3 mg samples. Analyses were performed on a TGA/DSC 2 STAR System (Mettler-Toledo) equipped with a Gas Controller GC 200 Star System. Studies were performed under a constant stream of nitrogen gas at a temperature ramp of 20 °C/min.

Differential Scanning Calorimetry (DSC): Initial DSC analyses were performed on a TGA/DSC 2 STAR System (Mettler-Toledo) equipped with a RCS1-3277 DSC cell and a DSC1-0107 cooling system. Each sample (~6-8 mg) was sealed in an aluminum pan and subjected to three heating/cooling cycles from -50 °C to 125 °C at a rate of 10 °C/min. Low temperature DSC analyses were performed on a NETZSCH 360° system equipped with 214 Corona Sensor and cooled with liquid nitrogen. Each sample (~6-8 mg) was sealed in an aluminum pan and subjected to three heating/cooling cycles from -160 °C to 220 °C at a rate of 10 °C/min. In both cases, the T_g values were recorded from the second heating ramp using the maximum absolute value of the derivative of heat flow with respect to temperature. DSC traces on the second and third heating cycles were identical for all samples reported.

Gas Chromatography-Mass Spectrometry (GC-MS): GC-MS experiments were performed on Agilent 5977B mass spectrometer detector attached to a 7890B gas chromatograph at the MIT Department of Chemistry Instrumentation Facility.

2. Monomer and polymer synthesis

a. ^{i}PrSi7 synthesis

^{i}PrSi7 was prepared following previously reported procedures.[1]

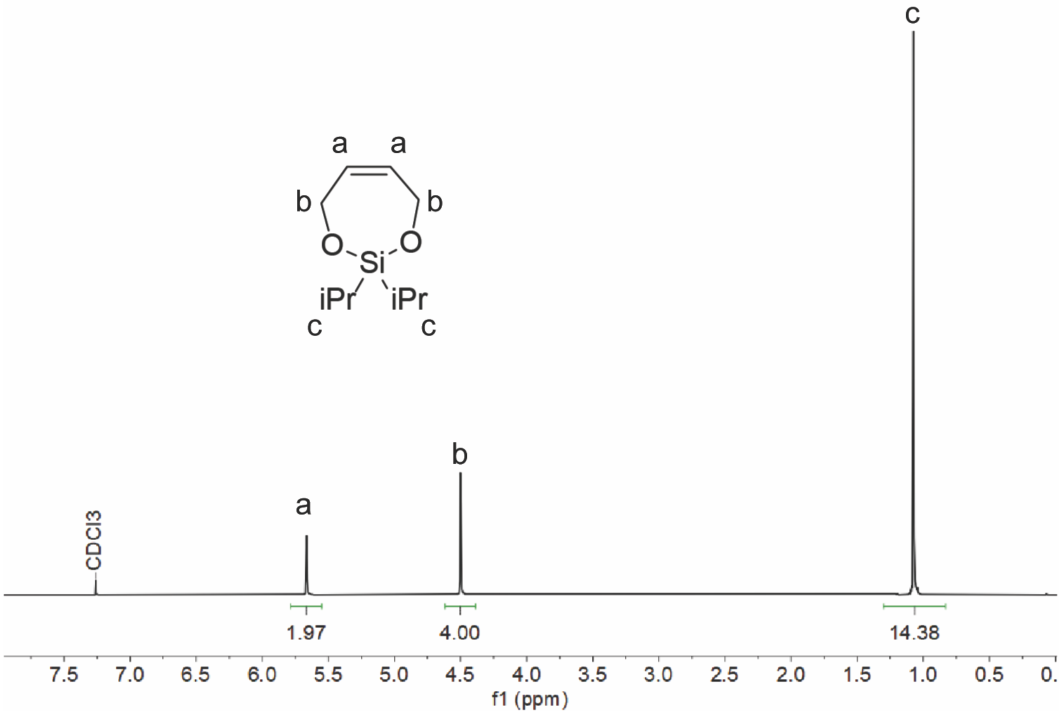


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ^{i}PrSi7.

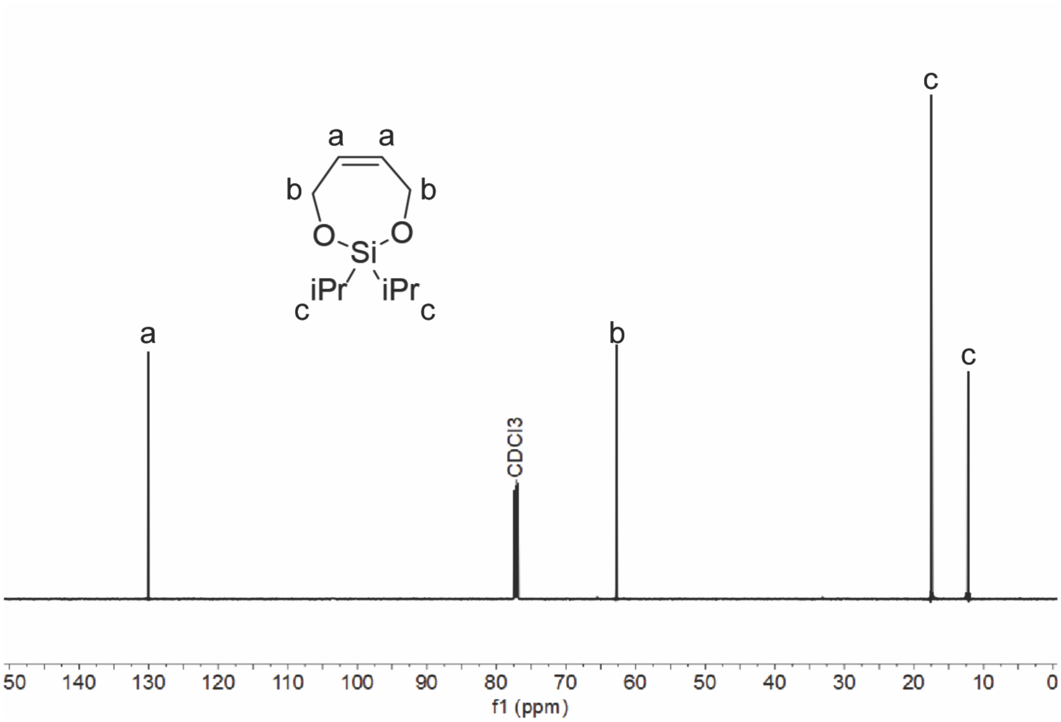


Figure S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of ^{i}PrSi7.

b. Homopolymerization of *ⁱ*PrSi7

Freshly distilled ^{i}PrSi7 (121 mg, 0.61 mmol) and anhydrous dioxane (978 µL) were added to a 4 mL scintillation vial equipped with a magnetic stir bar in a nitrogen-filled glovebox. A solution of G3 in dioxane (0.87 mg in 87 µL anhydrous dioxane, 1.20 µmol) was added and the mixture was stirred for two hours. An excess of ethyl vinyl ether was added to quench the reaction and was stirred for 15 min. The reaction was concentrated under a flow of nitrogen and the crude product was analyzed by ^{1}H NMR and SEC.

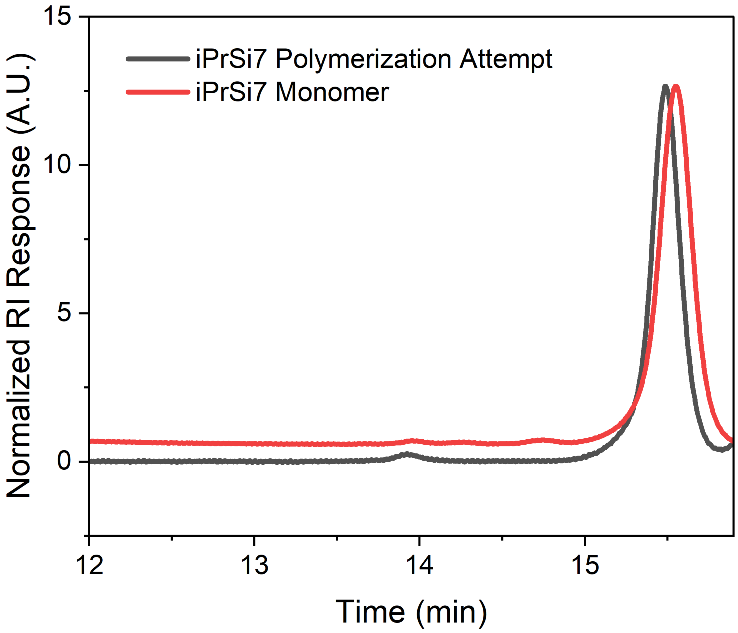


Figure S3. SEC traces of ^{i}PrSi7 monomer (red) and its attempted homopolymerization (gray).

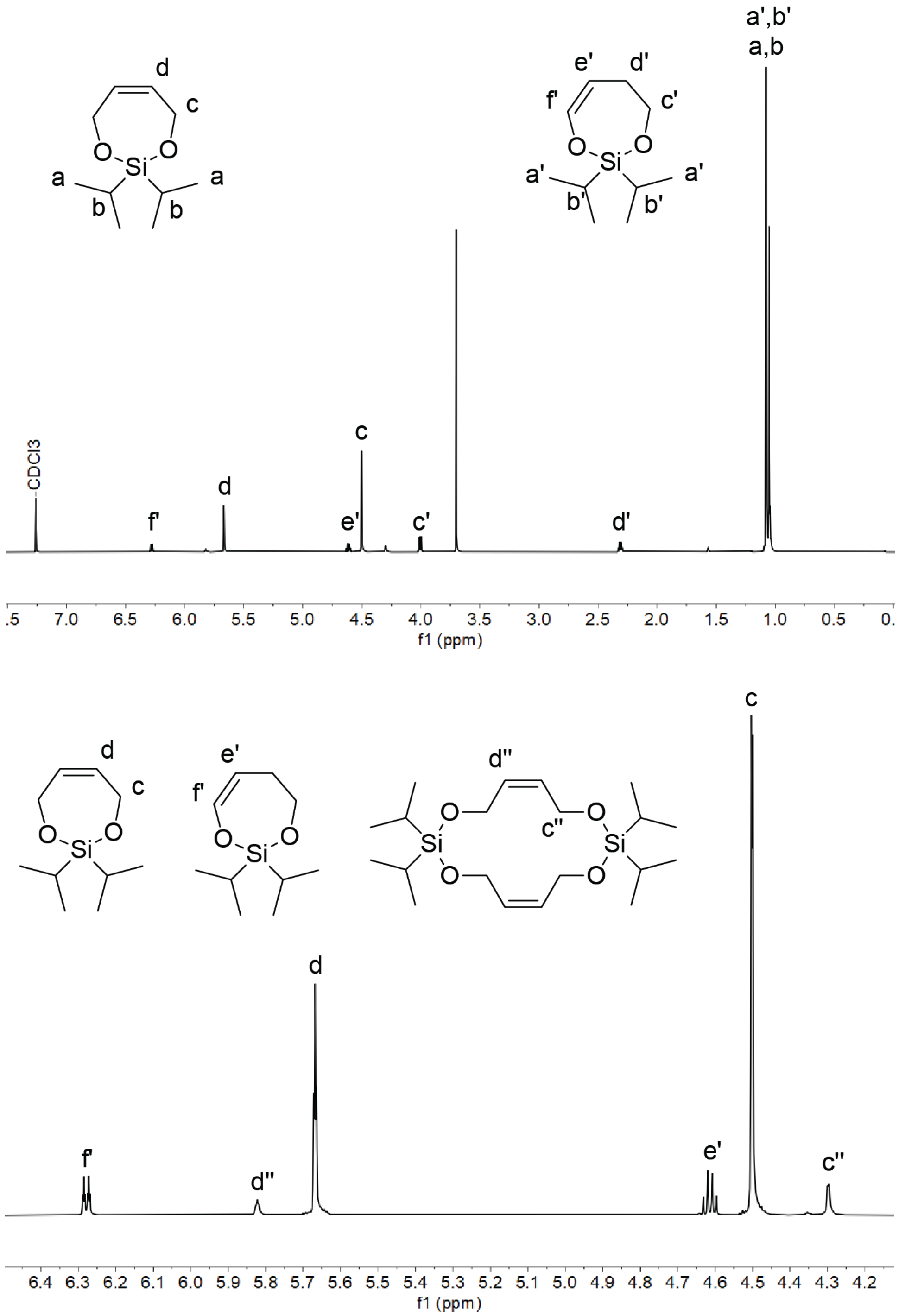
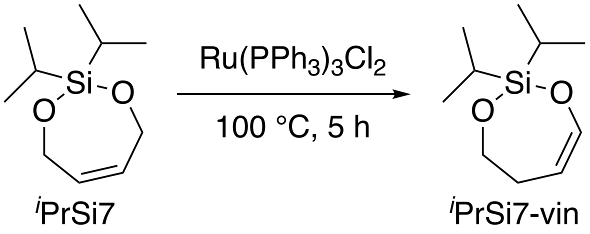


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude polymerization attempt of ^{i}PrSi7. Full spectrum (top) and close-up of olefin region (bottom).

c. ^{i}PrSi7 isomerization product synthesis



^{i}PrSi7 (1.06 g, 5.3 mmol) and Ru(PPh$_3$)$_3$Cl$_2$ (50 mg, 0.05 mmol) were added to a 10 mL oven-dried flask. The flask was then evacuated and backfilled with dry nitrogen three times before heating the mixture to 100 °C with magnetic stirring. After 5 hours, the reaction was complete as measured by crude NMR spectroscopy. The flask was cooled to room temperature and fitted with a Hickmann distillation head. The crude reaction was distilled under high vacuum to afford 2,2-diisopropyl-4,5-dihydro-1,3,2-dioxasilepine (^{i}PrSi7-vin, 732 mg, 69% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.28 (dt, J = 6.5, 1.5 Hz, 1H), 4.61 (dt, J = 6.5, 5.6 Hz, 1H), 4.05 – 3.96 (m, 2H), 2.31 (tdd, J = 5.6, 4.3, 1.6 Hz, 2H), 1.05 (s, 14H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.16, 106.93, 63.84, 30.83, 17.11, 12.43. HMRS Calculated for $C_{10}H_{21}O_2Si$: m/z = 201.13053 $[M + H]^+$; Found: 201.13053 $[M + H]^+$.

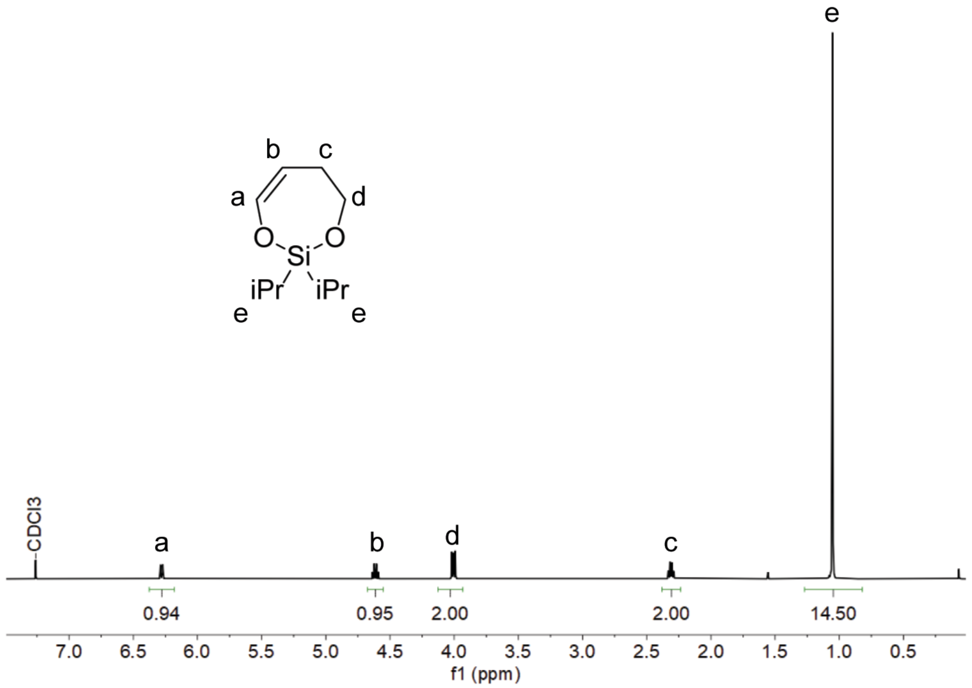


Figure S5. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of ^{i}PrSi7-vin.

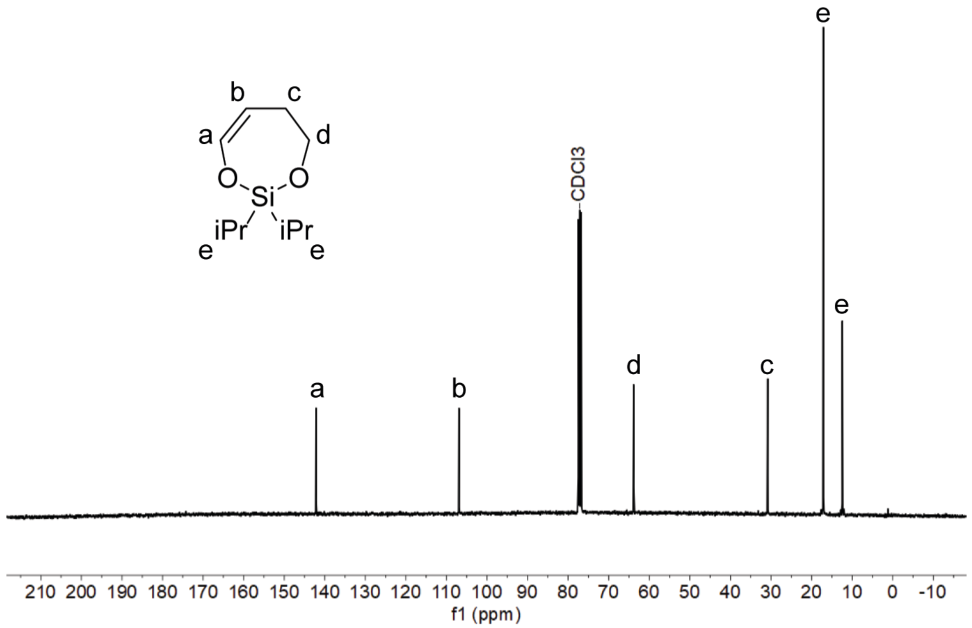


Figure S6. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of ^{i}PrSi7-vin.

d. *ⁱ*PrSi8 synthesis

^{i}PrSi8 was prepared following previously reported procedures.[1] A prepared 1L bottle of the monomer was stored in a 3°C refrigerator for approximately six months and exhibited no signs of decomposition.

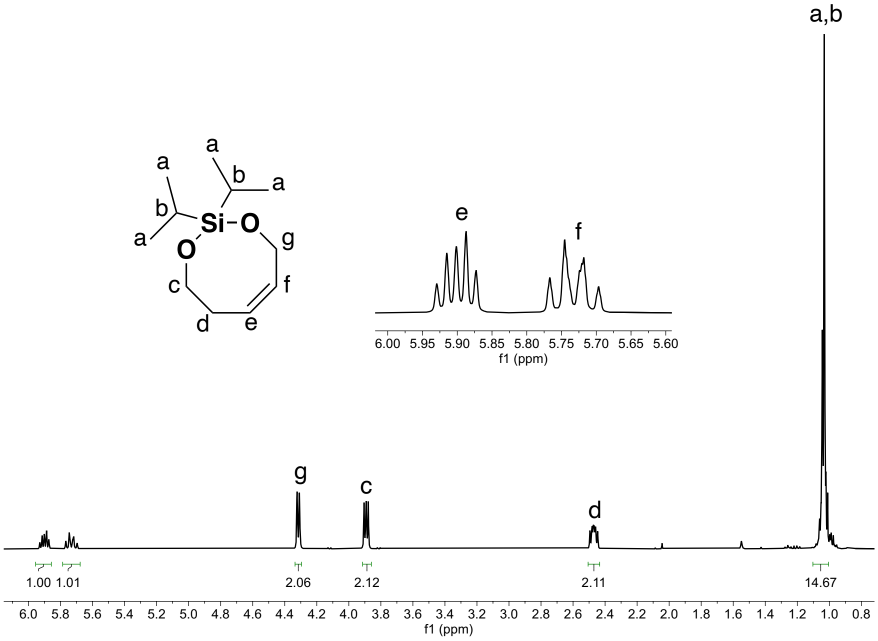


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of ^{i}PrSi8.

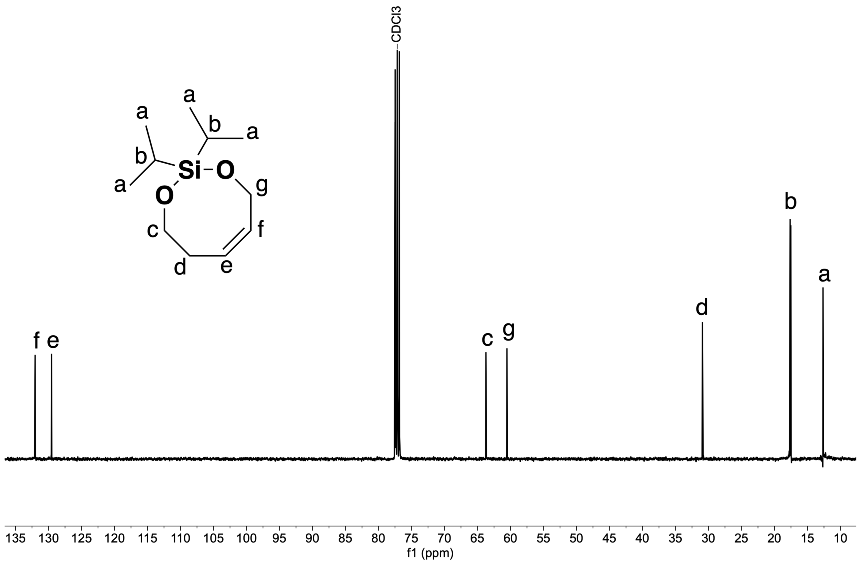


Figure S8. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of ^{i}PrSi8.

e. Homopolymerization of ^{i}PrSi8

The following is a specific example of the general procedure we used to prepare poly(^{i}PrSi8) [Table 1, entry 12, $[\mathrm{M}]_0$:[G3] = 500]. ^{i}PrSi8 (107 mg, 0.50 mmol) and anhydrous dioxane (815 µL) were added to a 40 mL scintillation vial equipped with a magnetic stir bar under nitrogen. A solution of G3 in dioxane (0.742 mg in 74.2 µL anhydrous dioxane, 0.001 mmol) was added and the mixture was stirred for two hours. An excess of ethyl vinyl ether was added to quench the reaction and was stirred for 15 min.

The polymerization solution was concentrated under vacuum to remove residual ethyl vinyl ether. The crude polymer was dissolved in ~10 mL toluene and added dropwise to a 10-fold excess of rapidly stirring MeOH, which was submerged in an ice bath. The precipitate was a gummy oil, which was collected and then this procedure was repeated twice more. To avoid excessive mechanical losses, especially on a small scale, pentane was used to quantitatively recombine the precipitated solid before each subsequent precipitation. After the final precipitation, residual solvents were removed from the sample under high vacuum until the mass remained constant.

Monomer conversions were calculated with ^{1}H NMR spectra by integrating the methine regions of the polymers and monomers against a 1,3,5-trimethoxybenzene internal standard. Conversion by ^{1}H NMR spectroscopy of the crude mixture was 96.1%, and gravimetric yield after precipitation was 89%. M_n of the precipitated polymer was found to be 159 kDa by SEC with a dispersity of 1.76. Cyclic oligomer content was calculated by following adaptations of previously reported procedures.^{2}

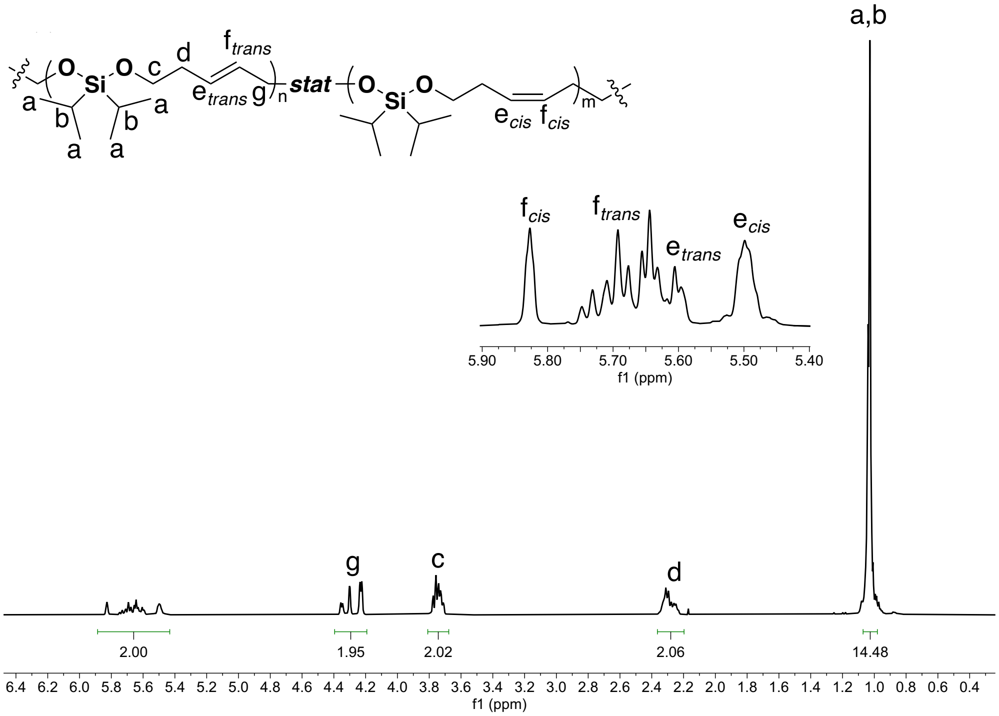


Figure S9. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of poly(^{i}PrSi8).

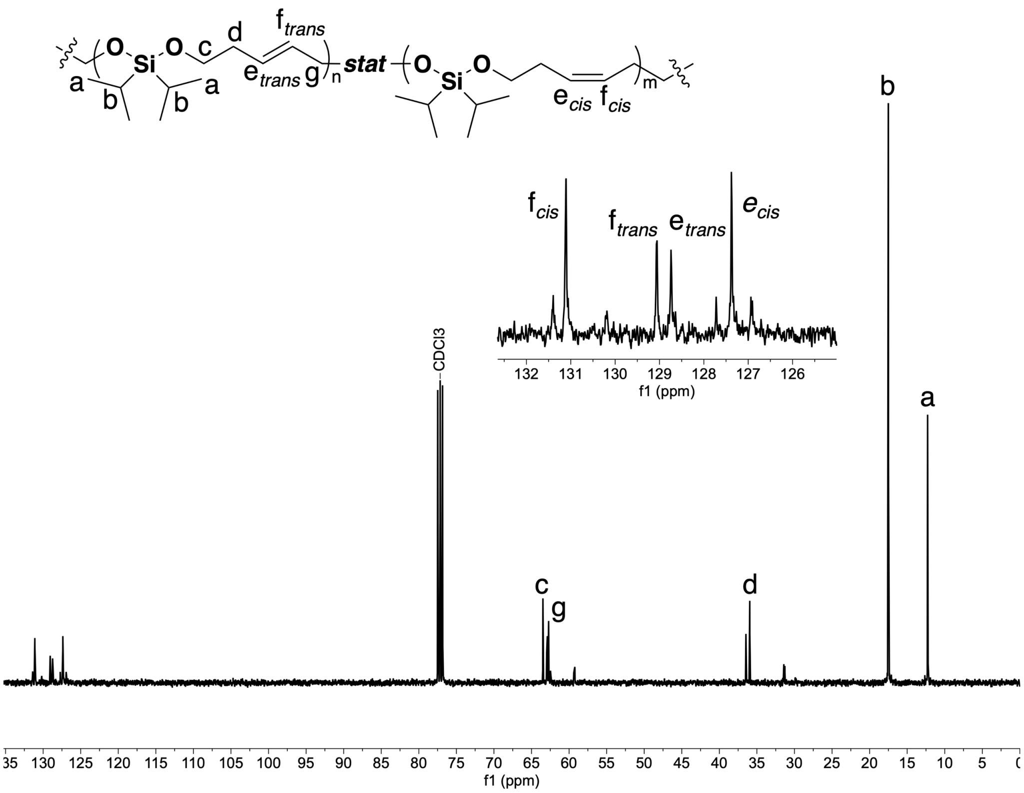


Figure S10. ^{13}C NMR spectra (101 MHz, CDCl$_3$) of poly(^{i}PrSi8).

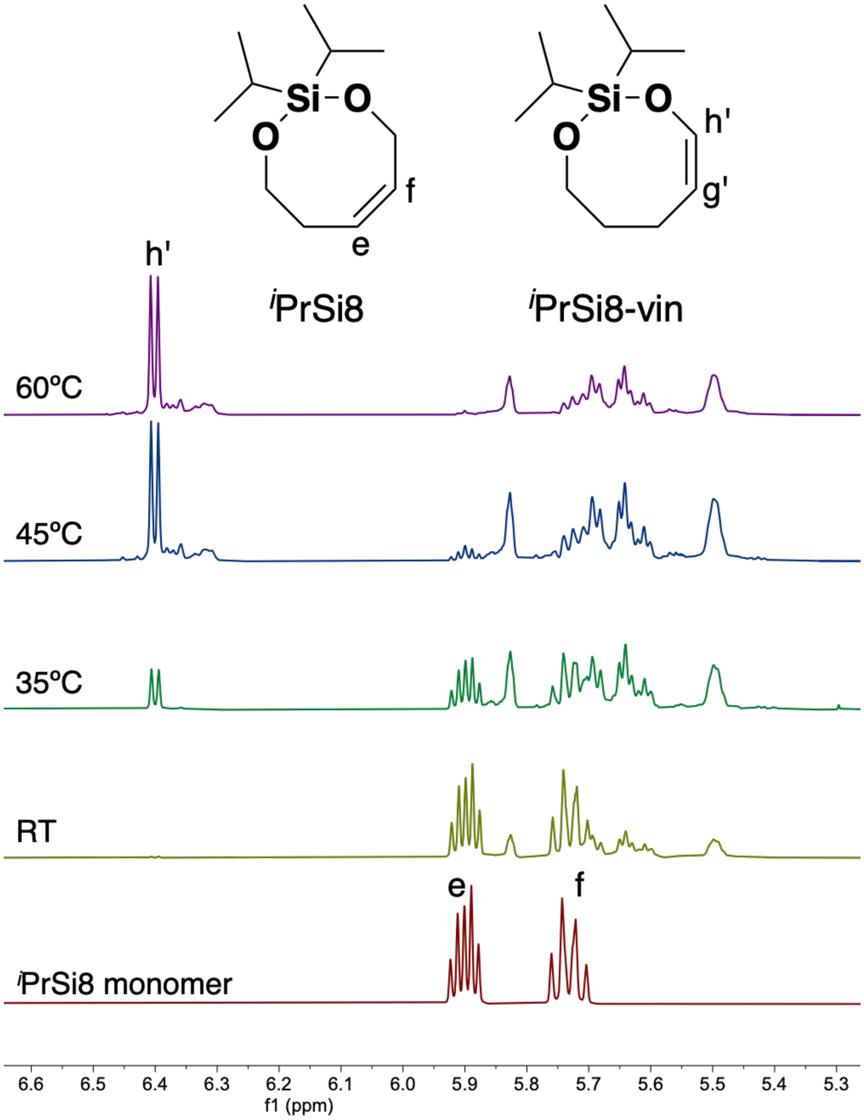


Figure S11. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of olefin region during ROMP of ^{i}PrSi8 at increasing temperature.

3. Eyring analysis for the determination of thermodynamic parameters

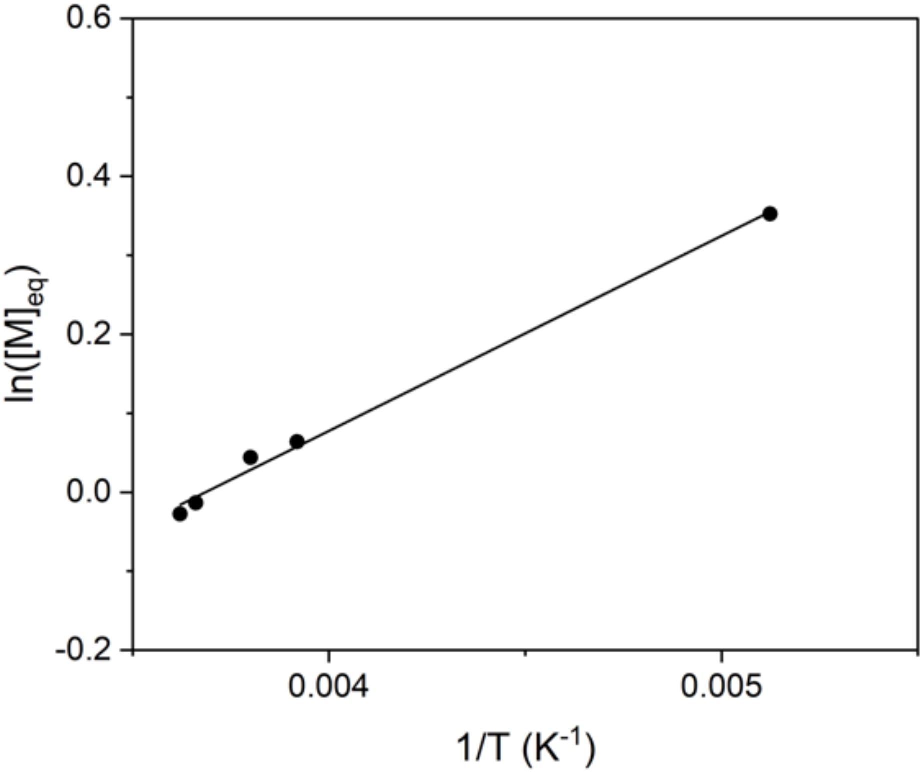


Figure S12. Plot of ln($[M]_{eq}$) as a function of the inverse of temperature. Line of best fit $\ln([M]_{eq}) = \frac{247}{T} - 0.91$ with a corresponding $R^2 = 0.995$.

4. Determination of homopolymerization rate

Homopolymerization kinetics were determined following adaptations of previously reported procedures.[3,4]

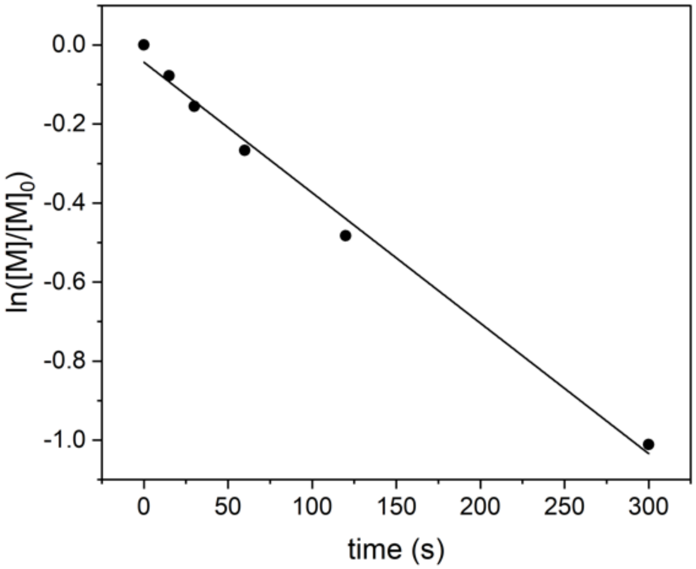


Figure S13. Plot of $\ln([M]/[M]_0)$ as a function of time with $R^2 = 0.992$.

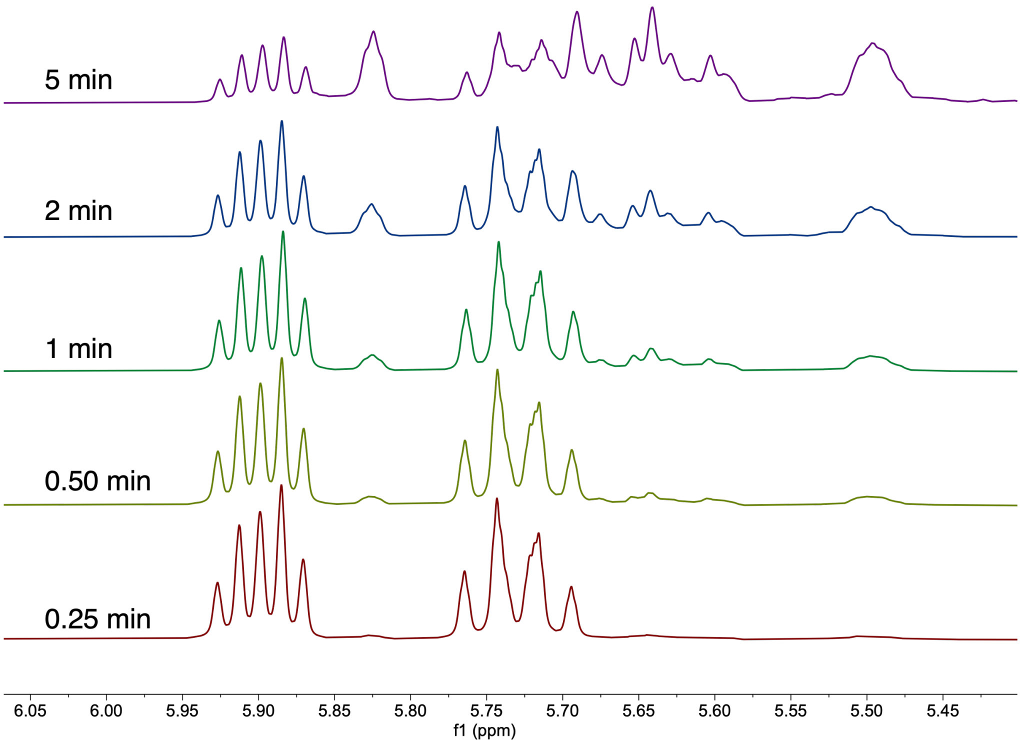


Figure S14. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of olefin region during ROMP of ***i*PrSi8** using 0.002 equivalents of G3.

5. Polymer deconstruction and depolymerization

a. G3-mediated depolymerization of poly(^{i}PrSi8)

^{i}PrSi8 (107 mg, 0.50 mmol) and anhydrous dioxane (815 µL) were added to a 40 mL scintillation vial equipped with a magnetic stir bar under nitrogen. A solution of G3 in dioxane (0.742 mg in 74.2 µL anhydrous dioxane, 0.001 mmol) was added and the mixture was stirred for two hours. 50 µL of the reaction was immediately quenched with excess ethyl vinyl ether. 50 µL each were transferred to vials prepared with 0.036 mg (5 x 10^{-6} mmol), 0.36 mg (5 x 10^{-4} mmol), and 3.6 mg (0.005 mmol) additional G3 under nitrogen. After an additional 2 h stirring, each was quenched with excess ethyl vinyl ether, concentrated under vacuum to remove residual ethyl vinyl ether, and analyzed by GPC and ^{1}H NMR without further purification.

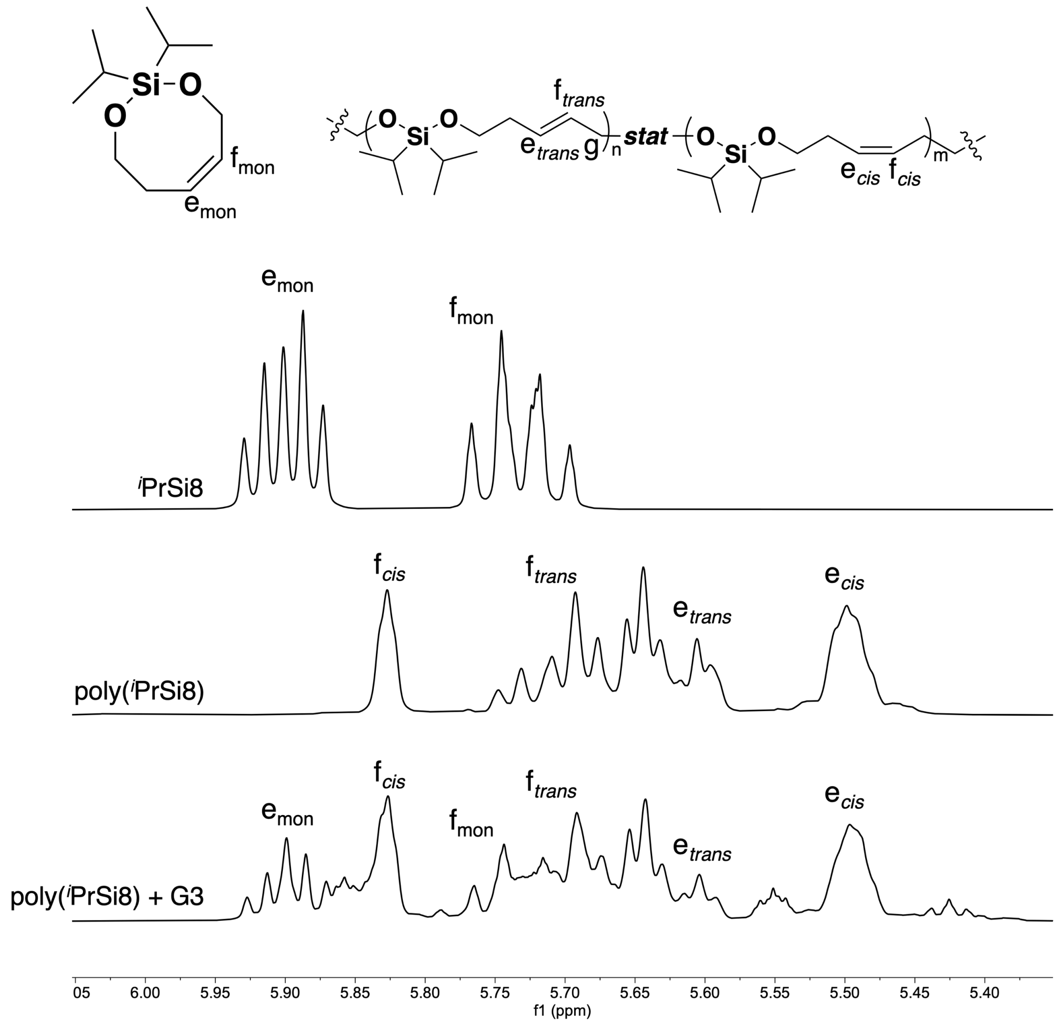


Figure S15. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of olefin region of ^{i}PrSi8, poly(^{i}PrSi8), and poly(^{i}PrSi8) treated with 5 x 10^{-4} mmol additional G3 initiator. The yield of reformed monomer was estimated by integrating the e_{mon} features in the depolymerized spectrum.

^{i}PrSi8 (150 mg, 0.70 mmol) and anhydrous dioxane (155 µL) were added to a 10 mL scintillation vial equipped with a magnetic stir bar under nitrogen. A solution of G3 in dioxane (0.52 mg mg in 14.0 µL anhydrous dioxane, 0.0007 mmol) was added and the mixture was stirred for two hours. Half of the reaction was immediately quenched with excess ethyl vinyl ether. The remaining half was transferred to a vial prepared with 2.6 mg (0.0035 mmol) additional G3 under nitrogen. After an additional 2 h stirring, the reaction was quenched with excess ethyl vinyl ether. Both solutions were concentrated under vacuum to remove residual ethyl vinyl ether and analyzed by GPC.

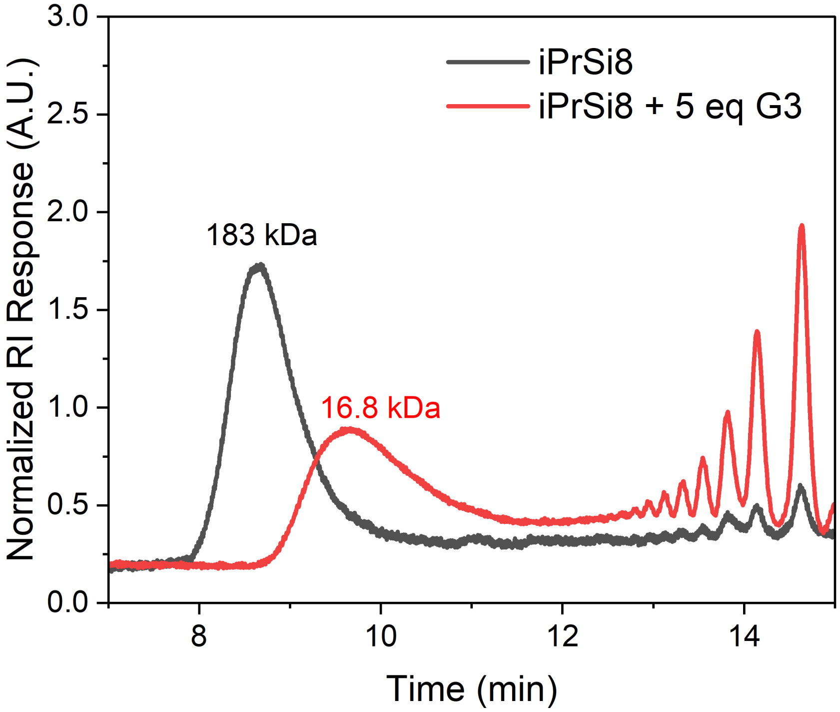


Figure S16. SEC traces of crude DP 1000 poly(^{i}PrSi8) (gray) and DP 1000 poly(^{i}PrSi8) treated with 0.0035 mmol additional G3. A molar mass decrease from 183 kDa to 16.8 kDa is observed upon depolymerization.

b. Fluoride-mediated deconstruction of poly(^{i}PrSi8)

The polymerization solution was concentrated under vacuum to remove residual ethyl vinyl ether. The solutions were treated with an excess of 0.2 TBAF in THF and the mixture was stirred for 30 minutes. Excess AmberChrom® 50WX2 was added and the mixture was allowed to sit for 5 min. Finally, the mixture was extracted with DCM, filtered with a 0.2 μm nylon filter, concentrated to remove volatile difluorodiisopropylsilane, and analyzed by GPC.

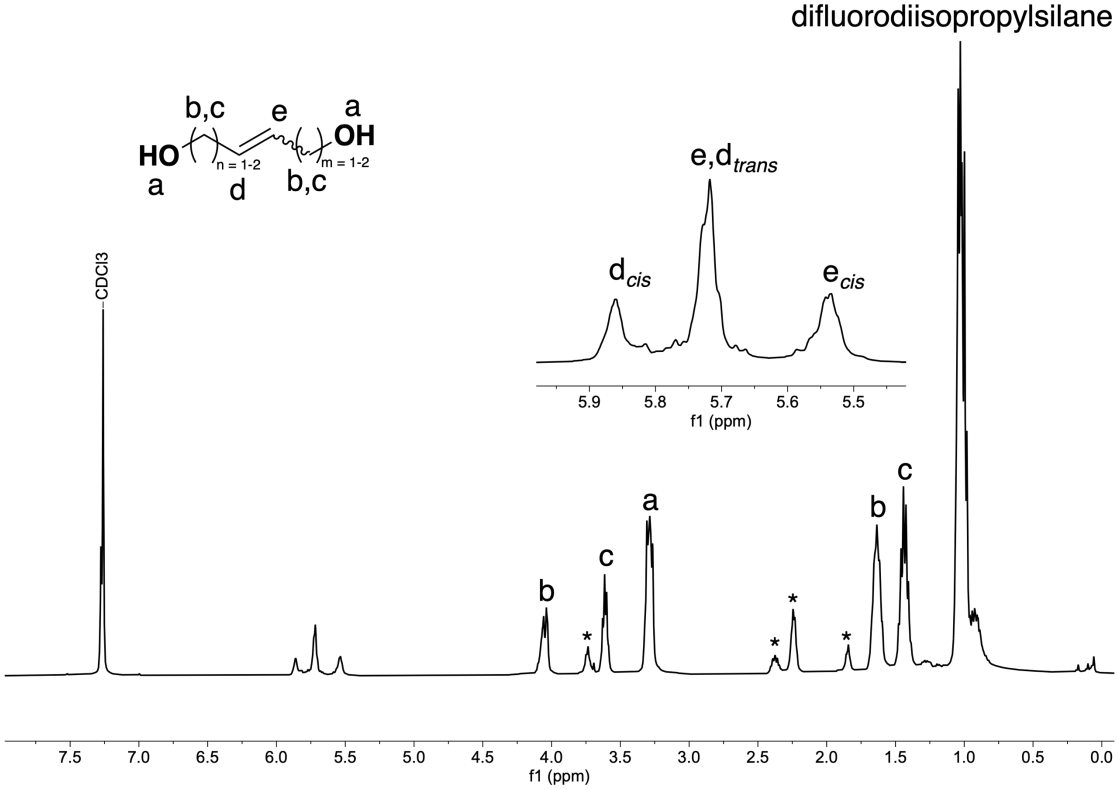


Figure S17. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of fluoride-treated poly(^{i}PrSi8).

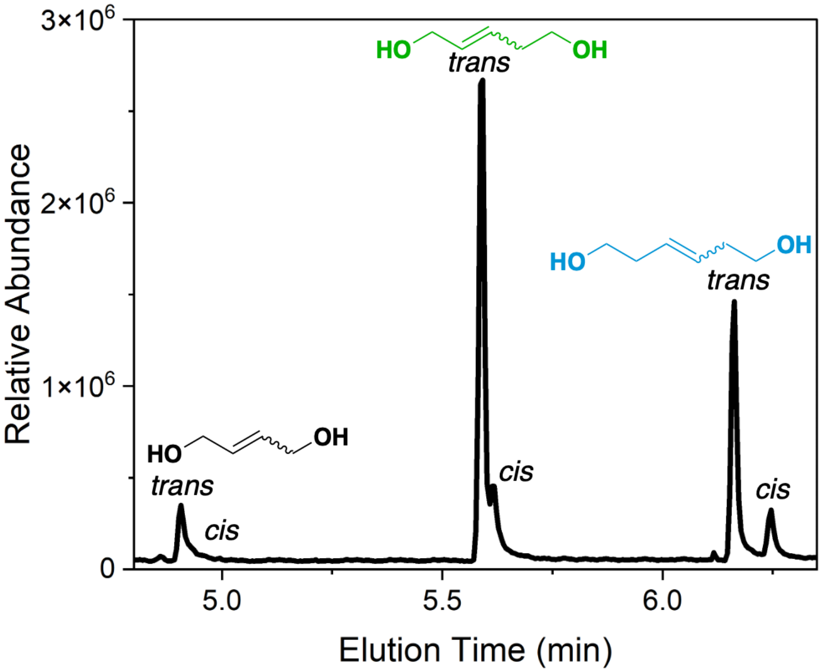


Figure S18. GCMS output of fluoride-treated poly(^{i}PrSi8). C4, C5, and C6 regions are easily separable from each other, but *cis*/*trans* isomers are not separable, preventing quantitative analysis.

c. Acid-mediated deconstruction of poly(^{i}PrSi8)

The polymerization solution was concentrated under vacuum to remove residual ethyl vinyl ether. The solutions were treated with an excess of 0.5 M HCl in dioxane and the mixture was stirred for 30 minutes. Excess sodium sulfate was added and the mixture was allowed to sit for 5 min. Finally, the mixture was extracted with DCM, filtered with a 0.2 μm nylon filter, concentrated to remove volatile diisopropylsilanediol, and analyzed by GPC.

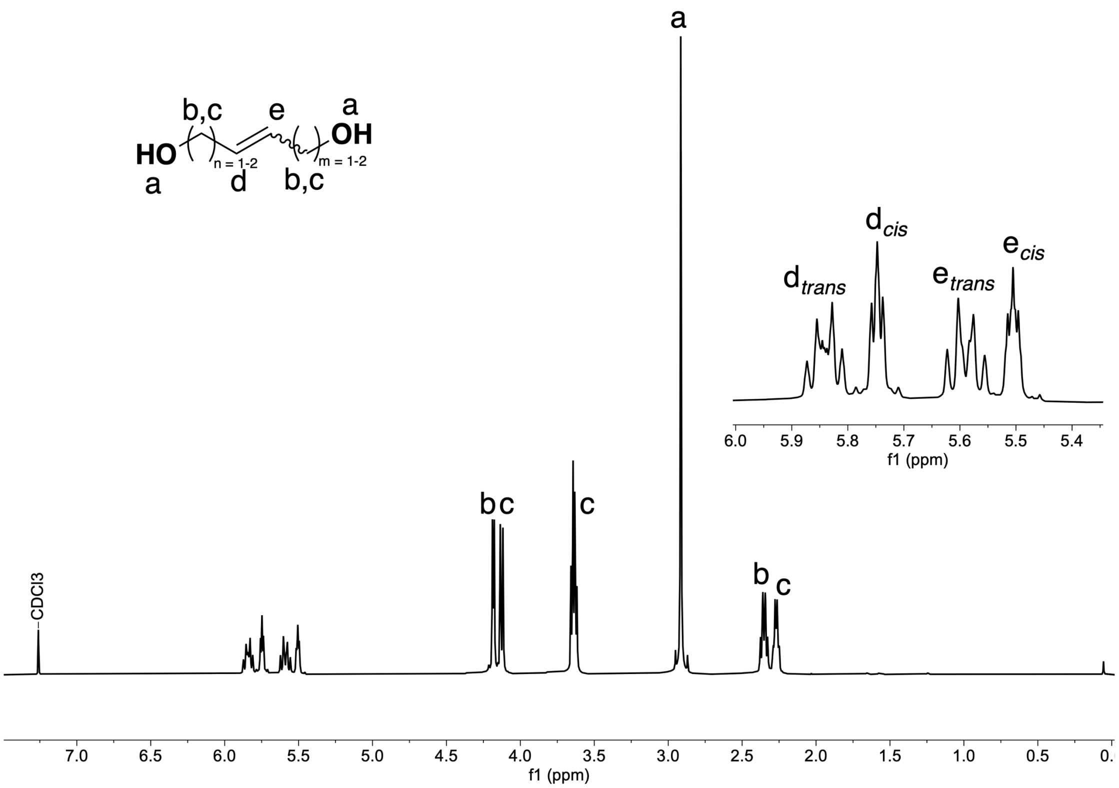


Figure S19. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of acid-treated poly(^{i}PrSi8).

6. Regioselectivity experiments

a. Acetylation of ene-diols

A 40 mL scintillation vial equipped with a stir bar was charged with the fluoride-deconstructed ene diol mixture (0.35 g, 3.62 mmol), 4-dimethylaminopyridine (22 mg, 0.181 mmol), and triethylamine (1.47 g, 14.5 mmol). The reaction was cooled in an ice bath under N_2 and acetic anhydride (1.11 g, 10.9 mmol) was added dropwise over 15 min. The reaction was allowed to warm to room temperature overnight. The brown mixture was washed with HCl (pH 3, 2 x 20 mL x 2), $NaHCO_3$ (2 x 20 mL), and brine (20 mL). The organic layer was collected, dried over $NaSO_4$, and concentrated to yield a brown oil (>98% crude).

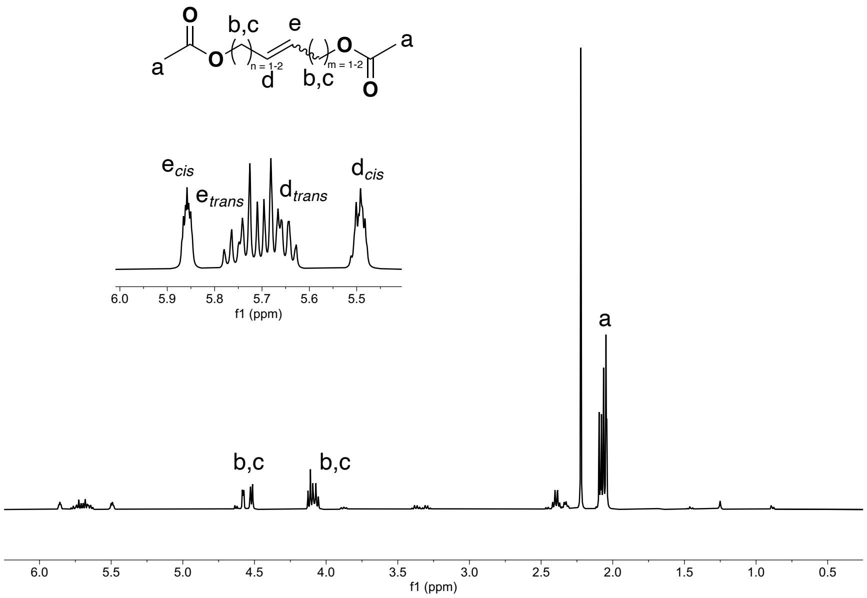


Figure S20. ${}^1H$ NMR spectrum (400 MHz, $CDCl_3$) of crude mixture of acteylated ene-diols.

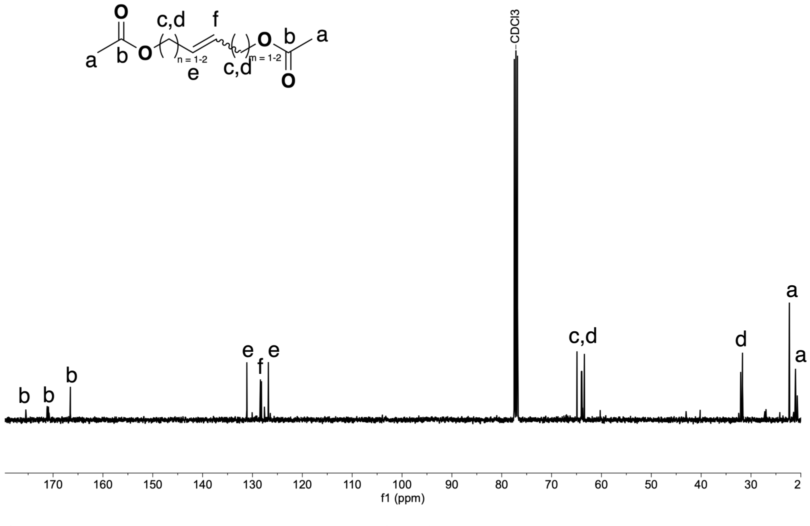


Figure S21. ${}^{13}C$ NMR spectrum (101 MHz, $CDCl_3$) of crude mixture of acetylated ene-diols.

b. Hydrogenation of acetylated ene-diols

Pd/C (5 mg, 0.05 mmol) was weighed into a 50 mL RBF equipped with a stir bar under N_2 and suspended in anhydrous THF (~5 mL). The acetylated ene-diol mixture (100 mg, 0.5 mmol) was added via microsyringe. The reaction was allowed to stir overnight under a balloon of H_2. The reaction was poured over a pad of celite, washed with ~30 mL DCM, concentrated to yield a brown oil (>98% crude).

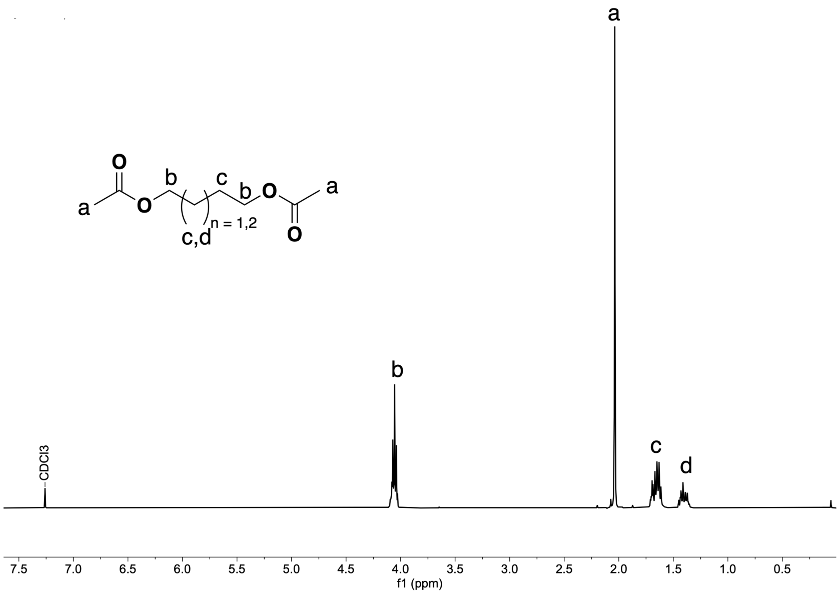


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of hydrogenated ene-diols.

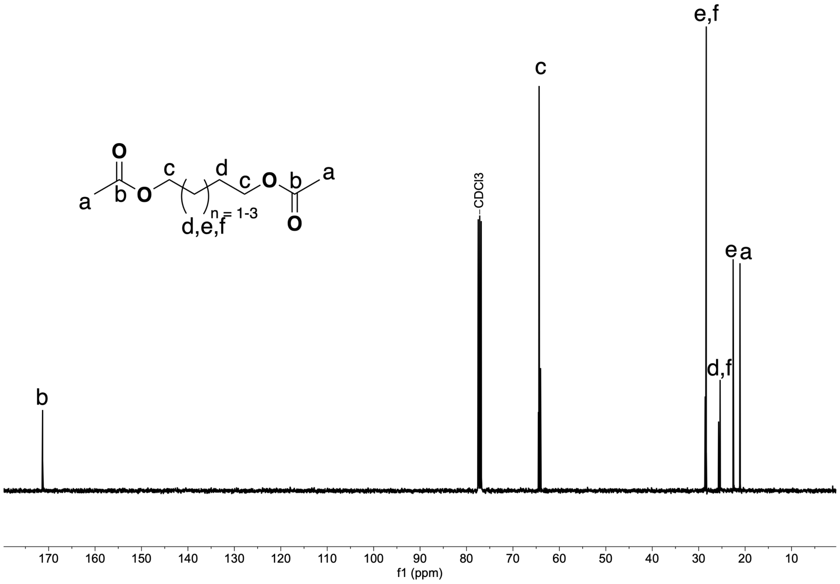


Figure S23. ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of hydrogenated ene-diols.

c. GC-MS calibration and regiochemical analysis

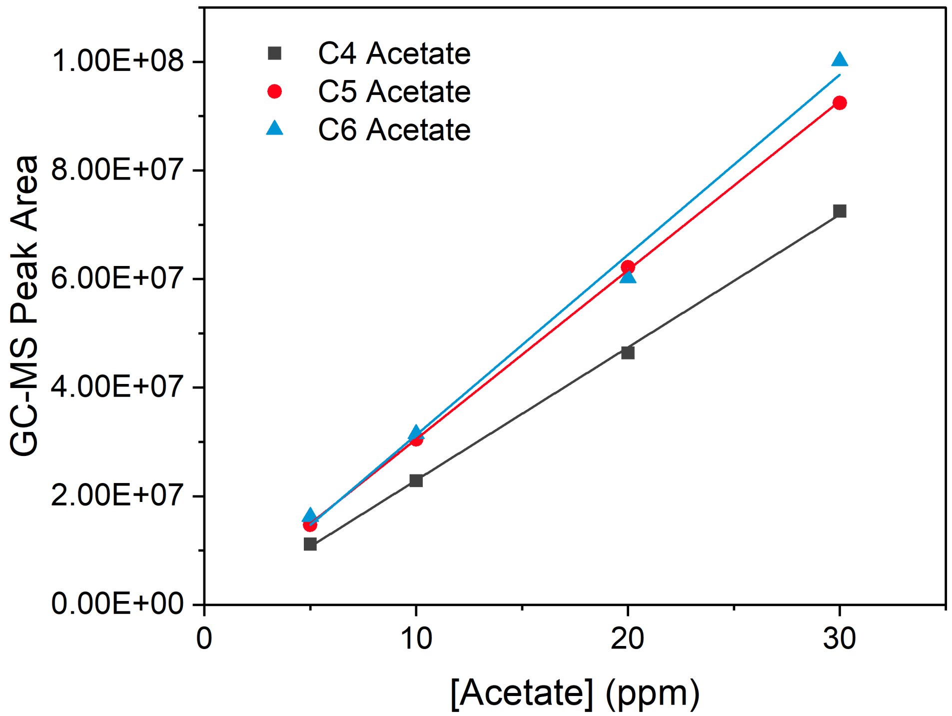


Figure S24. GC-MS calibration curves. C4 R^2=0.999, C5 R^2=0.999, C6 R^2=0.993.

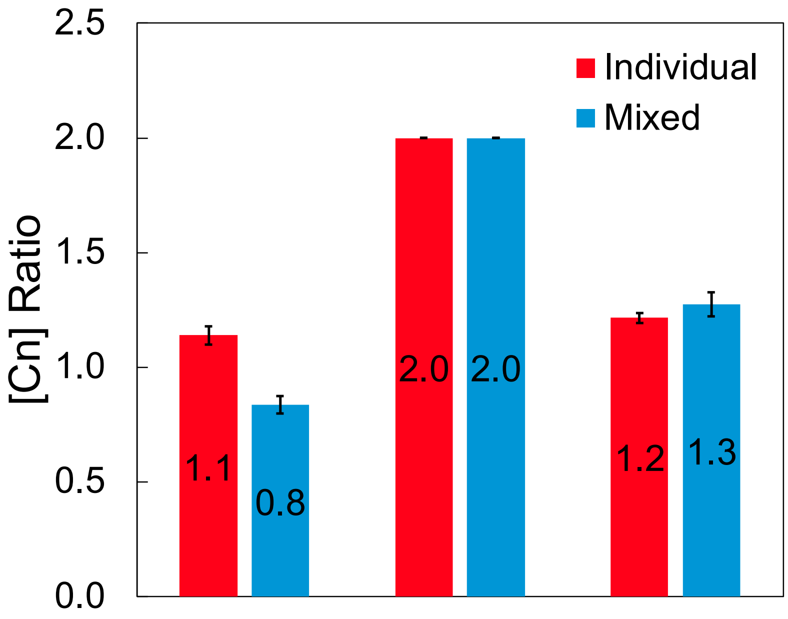


Figure S25. GC-MS signal suppression of C4 acetates in the presence of C5 and C6 acetates probed by measuring the response of known concentrations of acetate individually and mixed.

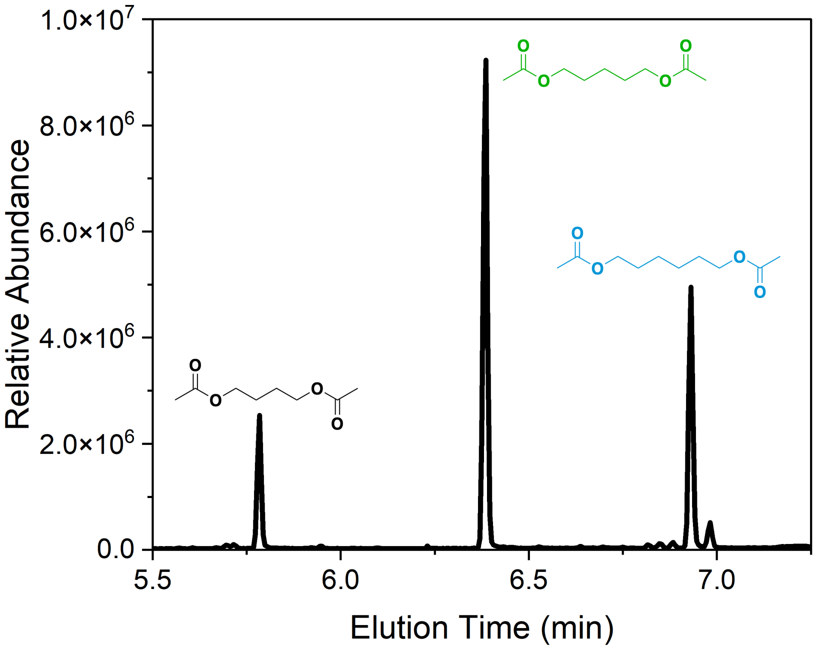


Figure S26. GCMS output of the mixture obtained in **Figure 2A**, which reflects the regiochemical makeup of the original polymer. Comparison to a series of calibration standards reveals a 1:2:1 ratio of the C4, C5, and C6 products, which is consistent with a regiorandom polymer.

Table S1. GC-MS data. The relative concentration of each sized acetate was found by normalizing the concentration of [C5] to 2.0.

entry	C4 Peak Area	[C4] (ppm)	[C4] relative	C5 Peak Area	[C5] relative	[C5] (ppm)	C6 Peak Area	[C6] (ppm)	[C6] (ppm)
1	10151965	4.8	0.9	32796863	2.0	10.7	21824231	1.3	7.2
2	17841951	7.9	0.9	57038321	2.0	18.5	36813535	1.3	11.2
3	26897400	11.6	0.8	90172306	2.0	29.2	60982700	1.3	19.0
4	22410887	9.8	0.8	75401222	2.0	24.4	46462559	1.2	14.6
5	28478833	12.3	0.8	90437707	2.0	29.3	60534800	1.3	18.8
Average			0.8		2.0			1.3	
Std Dev.			0.0386		–			0.0520	

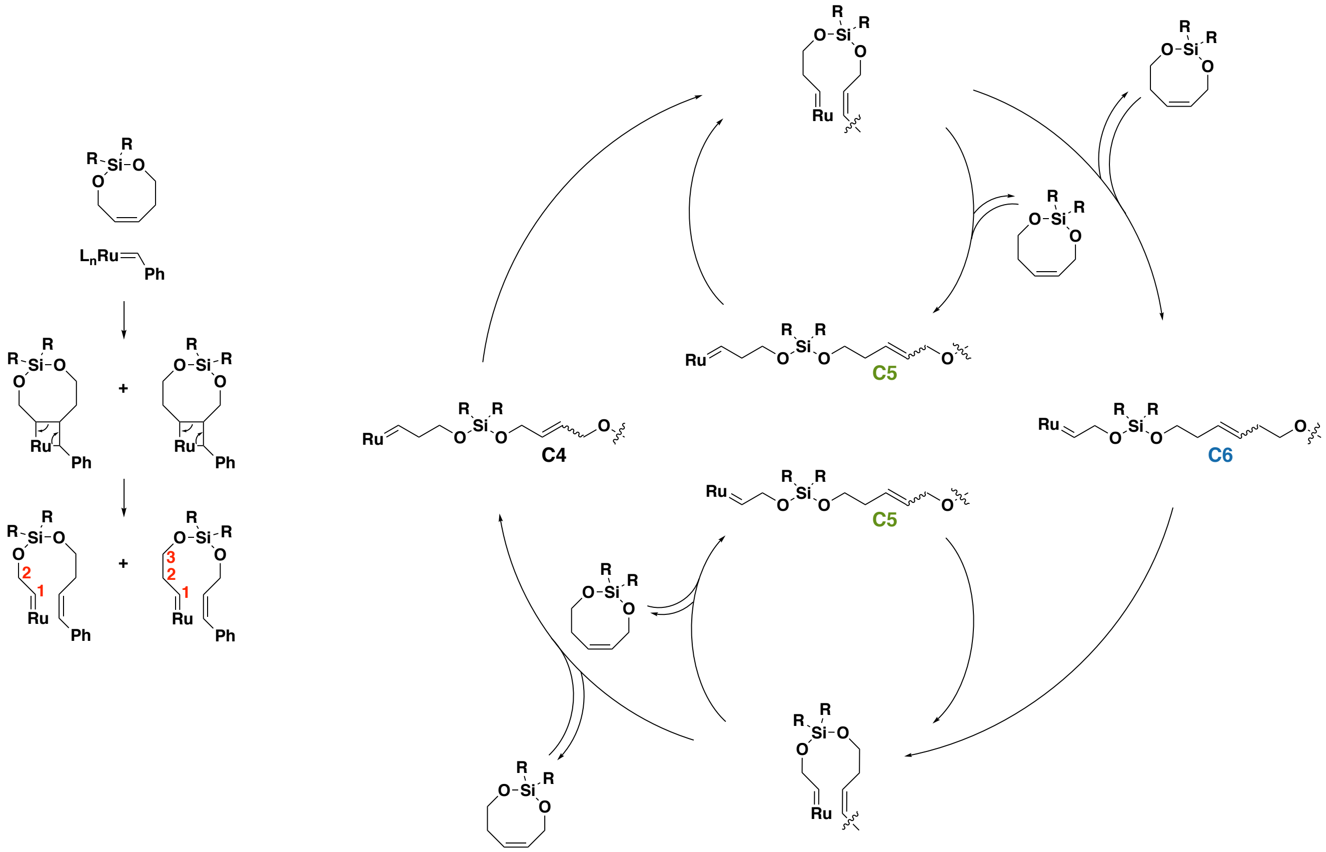


Figure S27. Proposed mechanism for the formation of 4-, 5-, and 6- carbon segments along the polymer chain

7. Thermal characterization

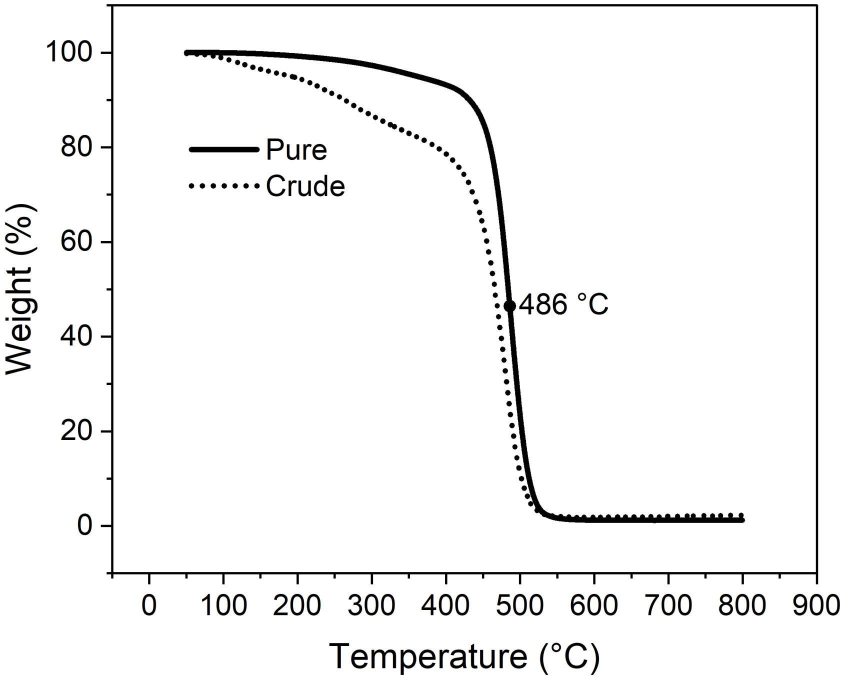


Figure S28. Thermal characterization of poly(^{i}PrSi8) (DP = 1000). Thermogravimetric analysis of crude homopolymer (dotted line) and purified polymer (solid line) under nitrogen atmosphere with a heating rate of 20 °C/min. The first derivative of the weight % reaches a minimum at 486 ºC.

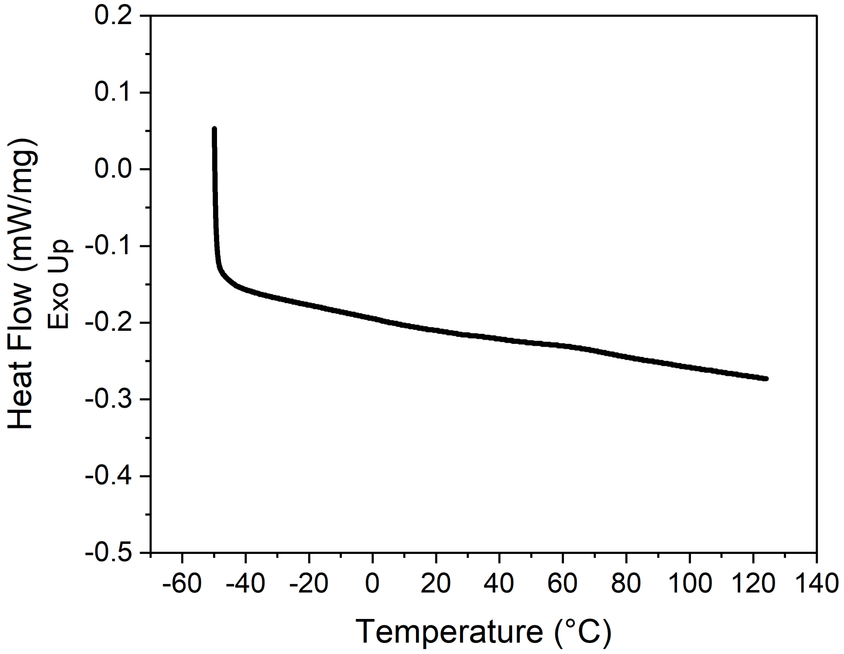


Figure S29. Differential scanning calorimetry traces of poly(^{i}PrSi8) showing no T_g above -78 ºC.

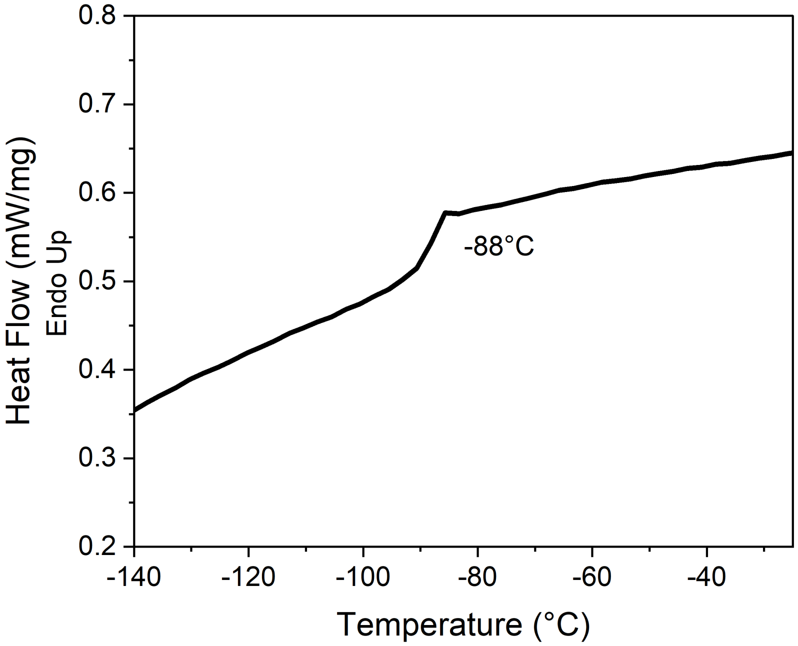


Figure S30. Thermal characterization of poly(^{i}PrSi8) (DP = 1000). Differential scanning calorimetry thermogram. The third heating scan under nitrogen at a heating rate of 10 °C/min reveals a glass transition temperature of -88 °C.

References

(1) Shieh, P.; Nguyen, H. V. T.; Johnson, J. A. Tailored Silyl Ether Monomers Enable Backbone-Degradable Polynorbornene-Based Linear, Bottlebrush and Star Copolymers through ROMP. *Nat. Chem.* **2019**, *11*, 1124–1132.

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