

Electronic Supplementary Material (ESI) for Chemical Communications.
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ELECTRONIC SUPPLEMENTARY INFORMATION

A robust depolymerization route for polysiloxanes

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1. General Information

All reagents and chemicals were of high-purity grade and were used as purchased without further purification. DMS T56 (polydimethylsiloxane, trimethylsiloxy terminated, 600,000 cSt) was purchased from Gelest Inc.; Tetrabutylammonium Difluorotriphenylsilicate (TBAT), tetrabutyl ammonium fluoride (TBAF, obtained as a 1 M THF solution in a sure-seal container), cyclomethicone, tetrahydrofuran (THF), acetone, toluene, cyclohexanone, ethyl acetate were purchased from Sigma-Aldrich; Sylgard-184 elastomeric kit was purchased from Fisher-Scientific.

Reaction condition: DMS T56 polymer (100 mg) was dissolved in 1 mL of the organic solvent over couple of hours in room temperature. Solids of Tetrabutylammonium Difluorotriphenylsilicate (TBAT), (0.5-1 mol %) were added in the polymer solution and placed in a closed vial in a stirring condition at room temperature for 12 h, and the reaction mixture is used subsequently for analytical studies. For additional rheology studies and comparison with control monomers like cyclomethicone, the reaction mixture is quenched with 1 g of CaCl_2 and filtered, and the solvent was removed under reduced pressure. Similar depolymerization procedure was adopted using two different temperatures, four different solvents, and two different TBAT catalyst loadings all at a 12-hour reaction time and using a 1 mL to 0.1 gram solvent to DMS T56 ratio.

Curing of Sylgard 184

Sylgard 184 was cured at room temperature ($23 \pm 2^\circ\text{C}$) for 72 hours. Parts A and B were thoroughly mixed in a 10:1 (w/w) ratio using a Thinky® mixture to minimize air entrapment. The mixture was then poured into glass-vial and allowed to cure undisturbed for the specified time. The cured Sylgard 184 was then subjected for further depolymerization experiments.

Thermo-gravimetric analysis: Thermo-gravimetric analysis (TGA) was carried out with TA Instruments TGA5500 Thermogravimetric Analyzer System at a heating rate of $2^\circ\text{C}/\text{min}$ under nitrogen. Isothermal test was conducted by holding at 100°C for 2880 minutes (48 hours, 2 days).

Mass Spectrometry: Samples of either DMS T56 or Sylgard were diluted in Acetone, Ethyl Acetate, THF, IPA, or CHN, and were analyzed using an Agilent 6890N (Agilent Labs, Santa Clara, CA) gas chromatograph with a mass selective detector (5973MSD) mass spectrometer. The individual components were separated using a J&W DB5-MS capillary column (60 m \times 0.32 mm \times 0.25 μm film thickness). The initial column temperature was set at 100°C (for 3 min) and programmed to 300°C (for 10 min) at 10°C per min. Method parameters: 1 μL injection, 300°C inlet, 10:1 split ratio, 1.6 mL/min helium flow. Compounds were identified by matching mass spectra to the NIST 2015 mass spectral library. Match factors provided are out of 1,000 and are a measure of the confidence in the identification. Match factors over 800 are generally considered good.

Rheology: Rheological experiments were performed on a Discovery Hybrid Rheometer (TA instruments DHR-3) using a 40mm aluminum 1.998° cone-plate geometry. A Peltier plate with a solvent trap was utilized to limit the evaporation of volatile solvents. Samples with varying concentrations of DMS T56 were hand-mixed with cyclohexanone or acetone at 1:1 solvent:PDMS by wt and placed on the Peltier plate before lowering the cone to 1 mm. Excess cyclohexanone/acetone solvent was placed onto the cone solvent trap to minimize solvent evaporation (Figure S8). The experimental procedure consisted of a combination of viscosity flow sweeps and isothermal holds to probe degradation kinetics. The Peltier plate was preheated to the experimental temperature. The samples were placed on the Peltier plate where they were subjected to a 10s conditioning step at 25

°C. A sequential flow sweep at 25 °C from 0.1 to 10 s⁻¹ utilized steady-state sensing with a 3% tolerance and 90 s maximum equilibration time. The sample was then held at 25 °C for 20 mins to examine the effects of time at 25 °C on depolymerization, as evidenced by the decrease in viscosity over time.

Gel Permeation Chromatography (GPC): GPC was performed using a Malvern Panalytical (Malvern, UK) OMNISEC system equipped with refractive index and right-angle/low-angle light scattering detectors and two T6000M mixed bed columns. The column temperature was maintained at 30 °C and the flow rate was maintained at 1 mL/min. Samples for analysis were dissolved in toluene at a concentration of approximately 10 mg/mL and an injection volume of 100 µL was used. The refractive index increment (dn/dc) of PDMS in toluene is negative, therefore the typical presentation of GPC traces via the refractive index detector response consists of inverted peaks. Consequently, all GPC traces presented in this work were inverted for the sake of clarity.

Nuclear Magnetic Resonance (NMR): ¹H NMR spectroscopy of depolymerized siloxane species, TBAT, TBAF, DMS-T56, and cyclomethicone were performed on a Bruker Avance III 500 MHz instrument in room temperature with THF-*d*8 as solvent.

2. Thermogravimetric Analysis

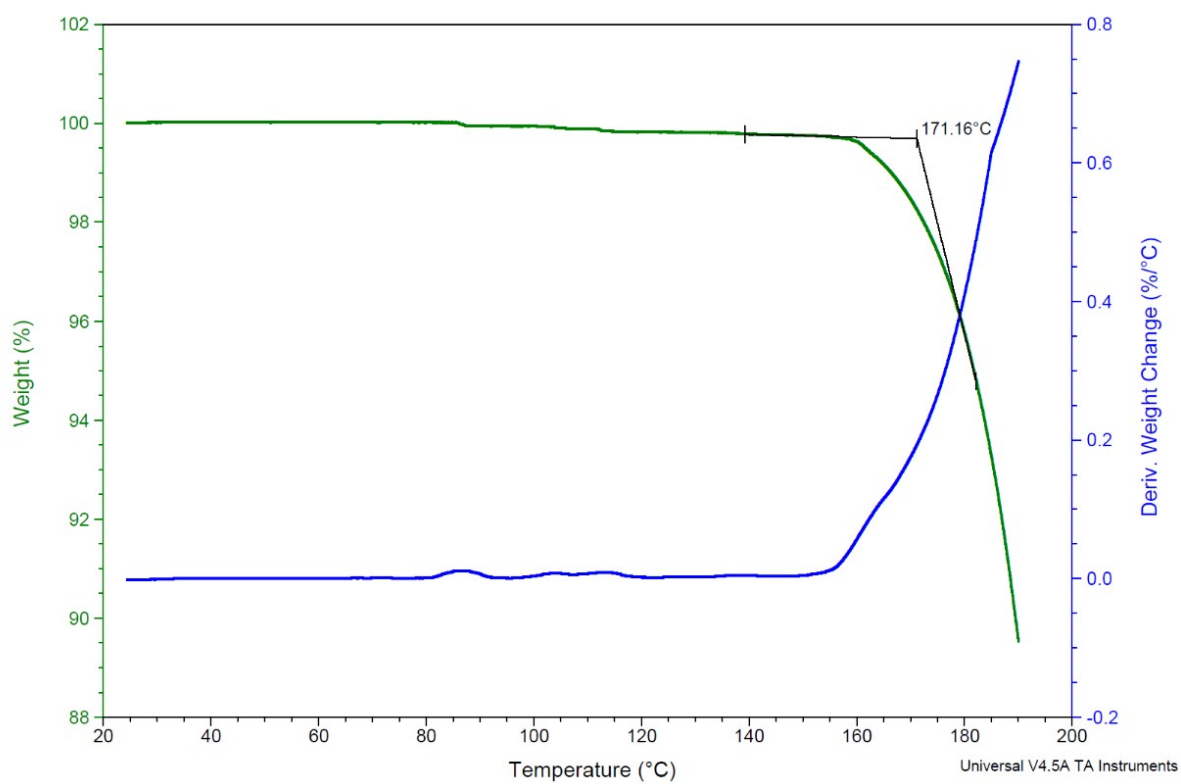


Figure S1. TGA data of the TBAT catalyst

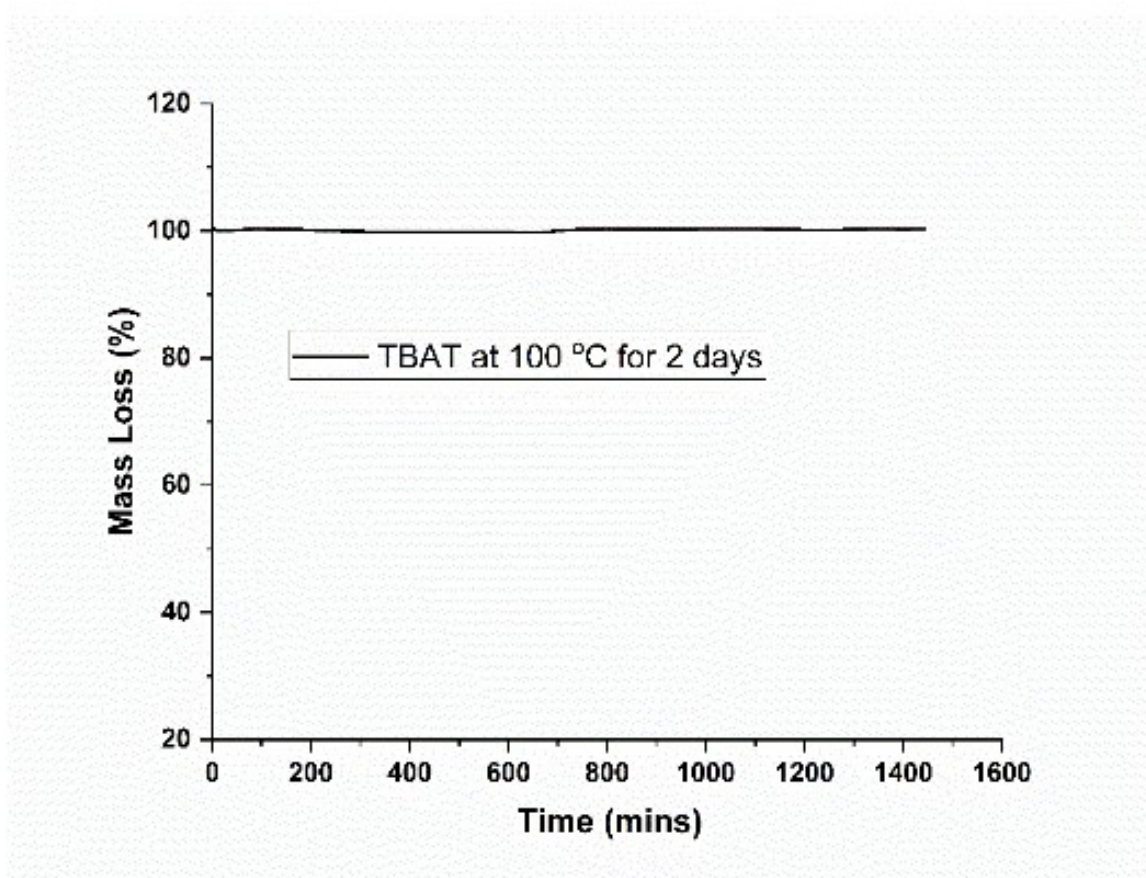


Figure S2. Isothermal TGA of TBAT kept at 100 °C for 2 days

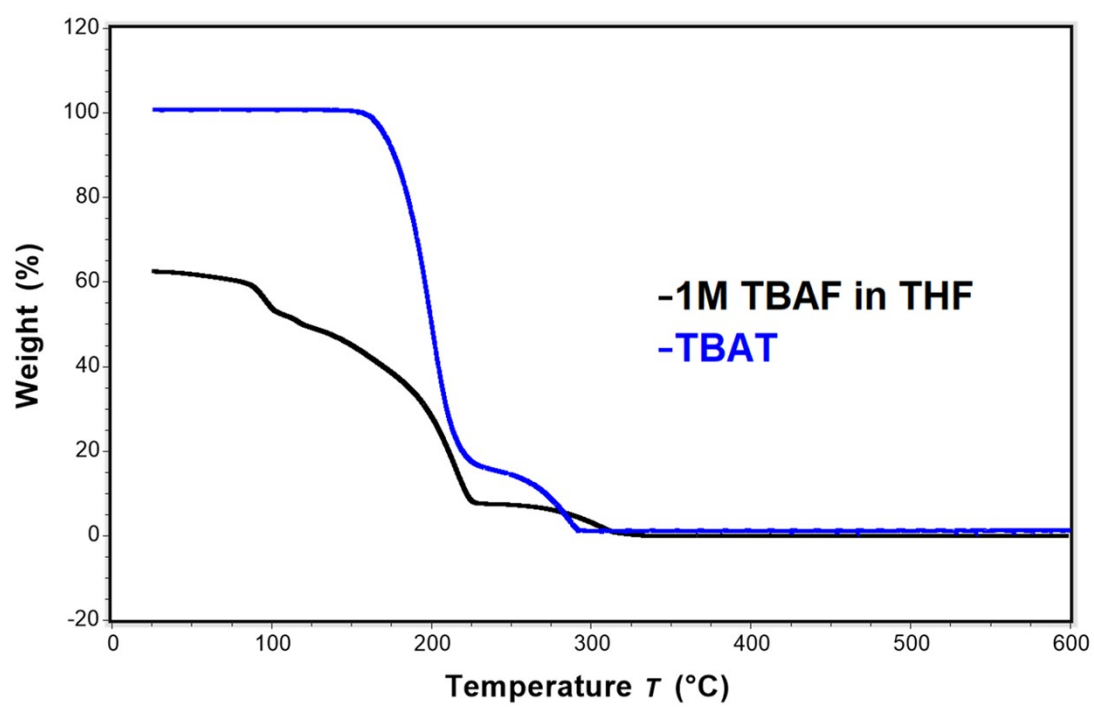


Figure S3. TGA data of 1M TBAF in THF comparing with the TBAT.

3. Mass Spectrometry data

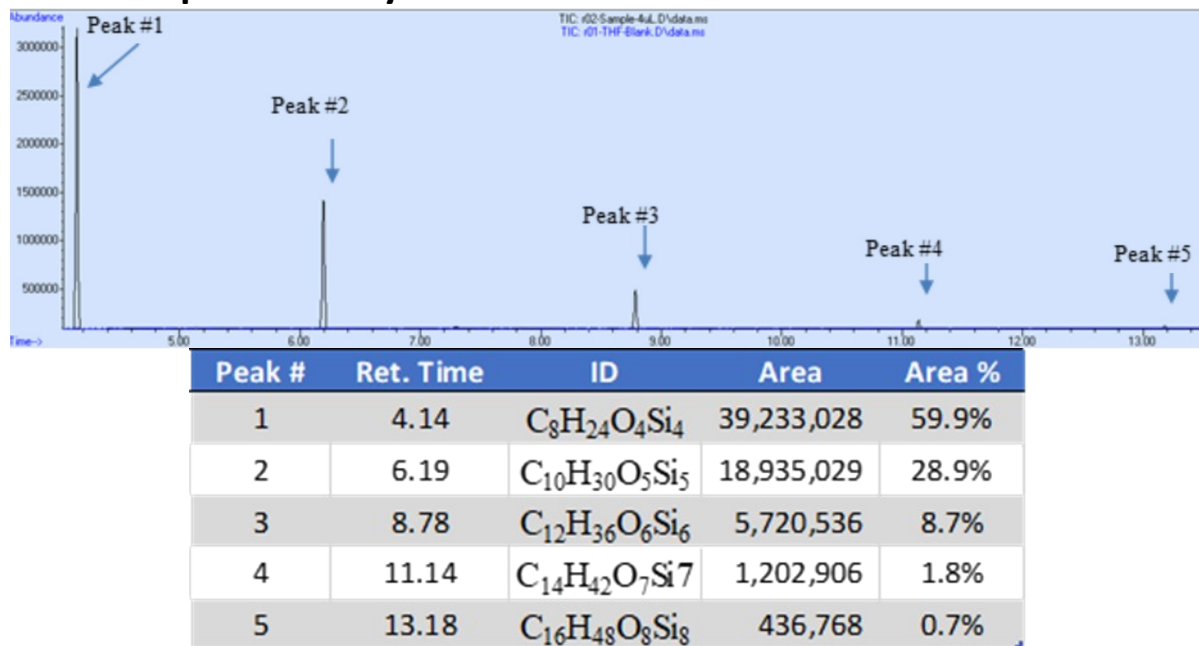


Figure S4. Depolymerization products with THF as the solvent

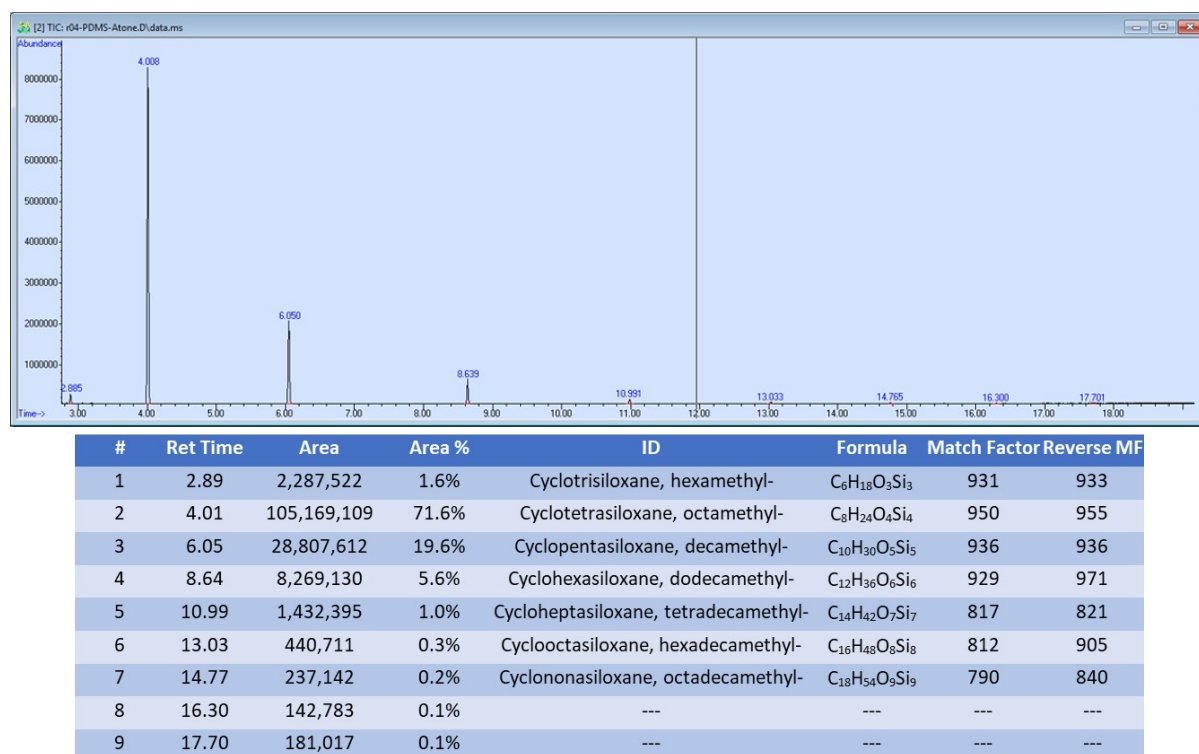


Figure S5. Depolymerization products with acetone as solvent

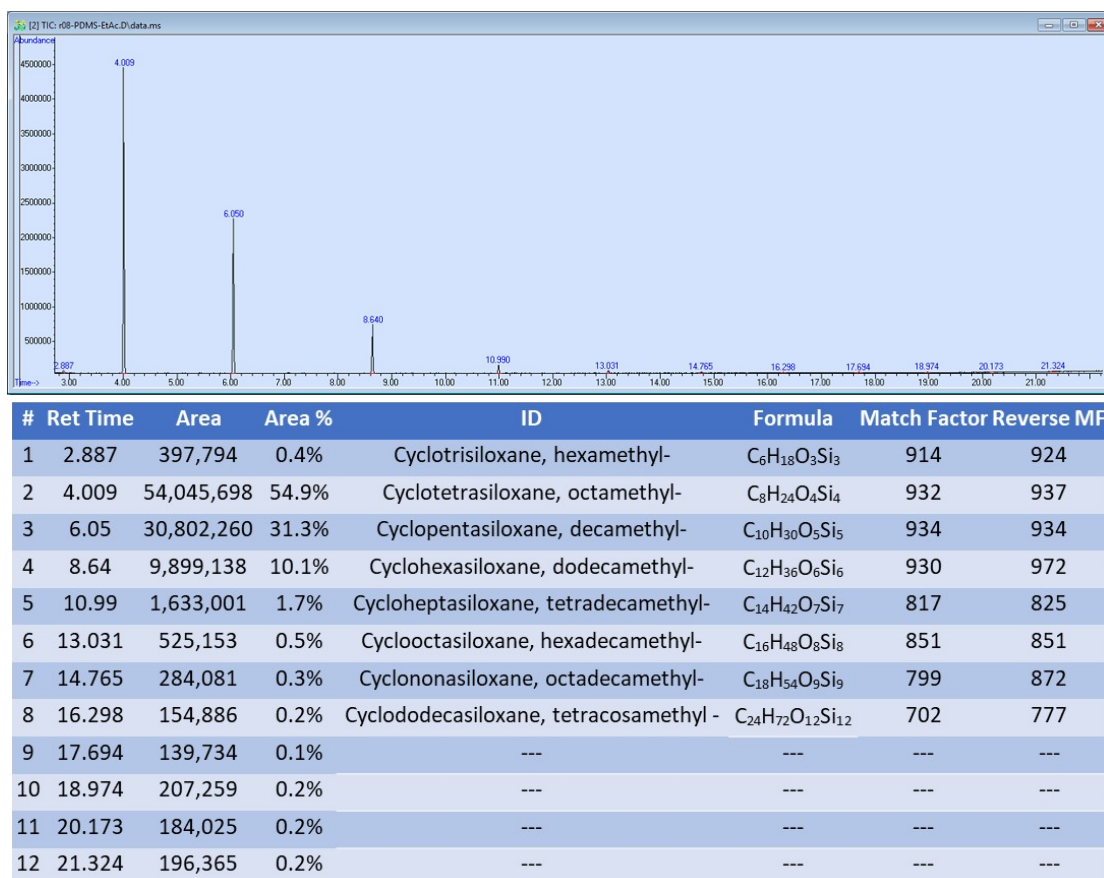


Figure S65. Depolymerization products with ethyl acetate as solvent

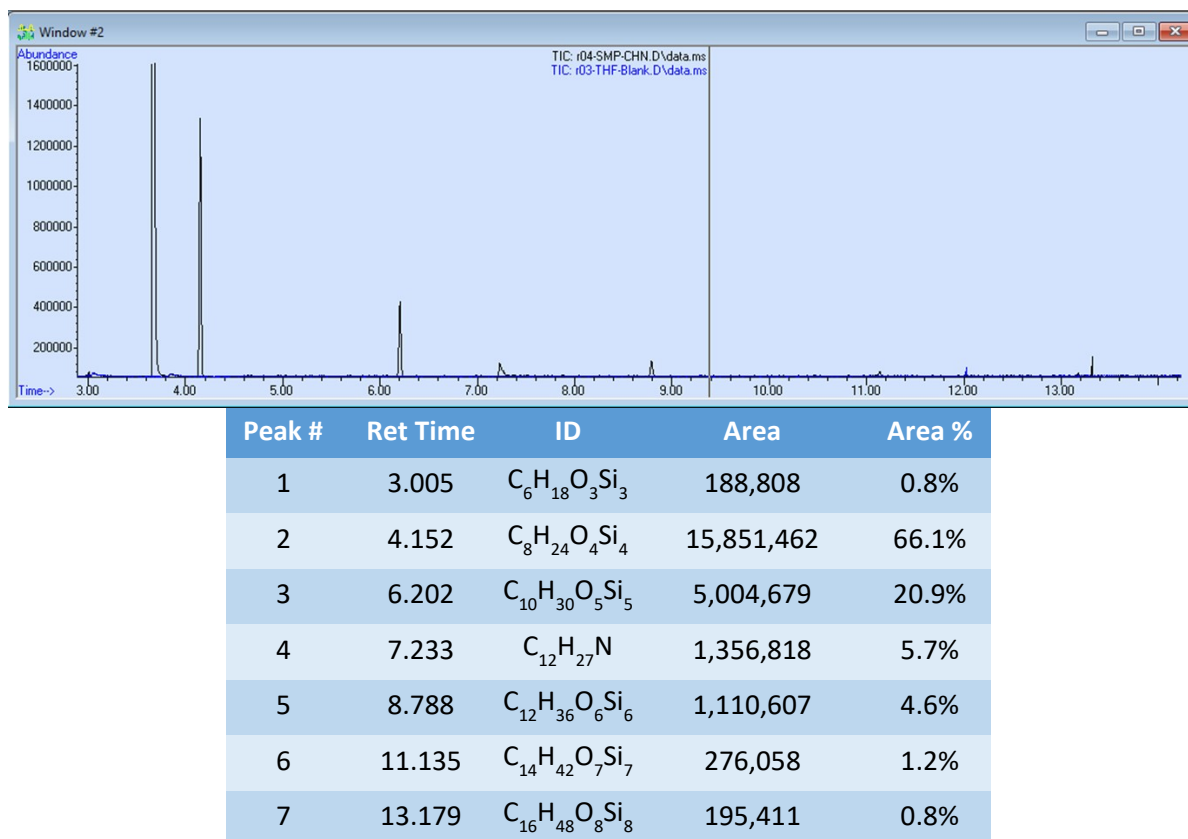


Figure S7 Depolymerization products with cyclohexanone as solvent

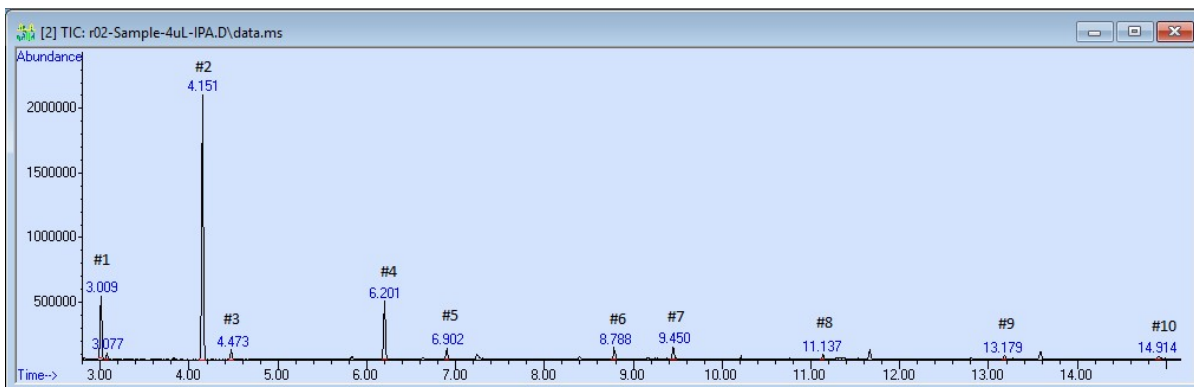


Figure S8. Depolymerization products with Isopropanol as solvent. In contrast to other non-nucleophilic solvents, the products from IPA as the reaction medium generates a complex mixture of small molecules

4. Rheology Data

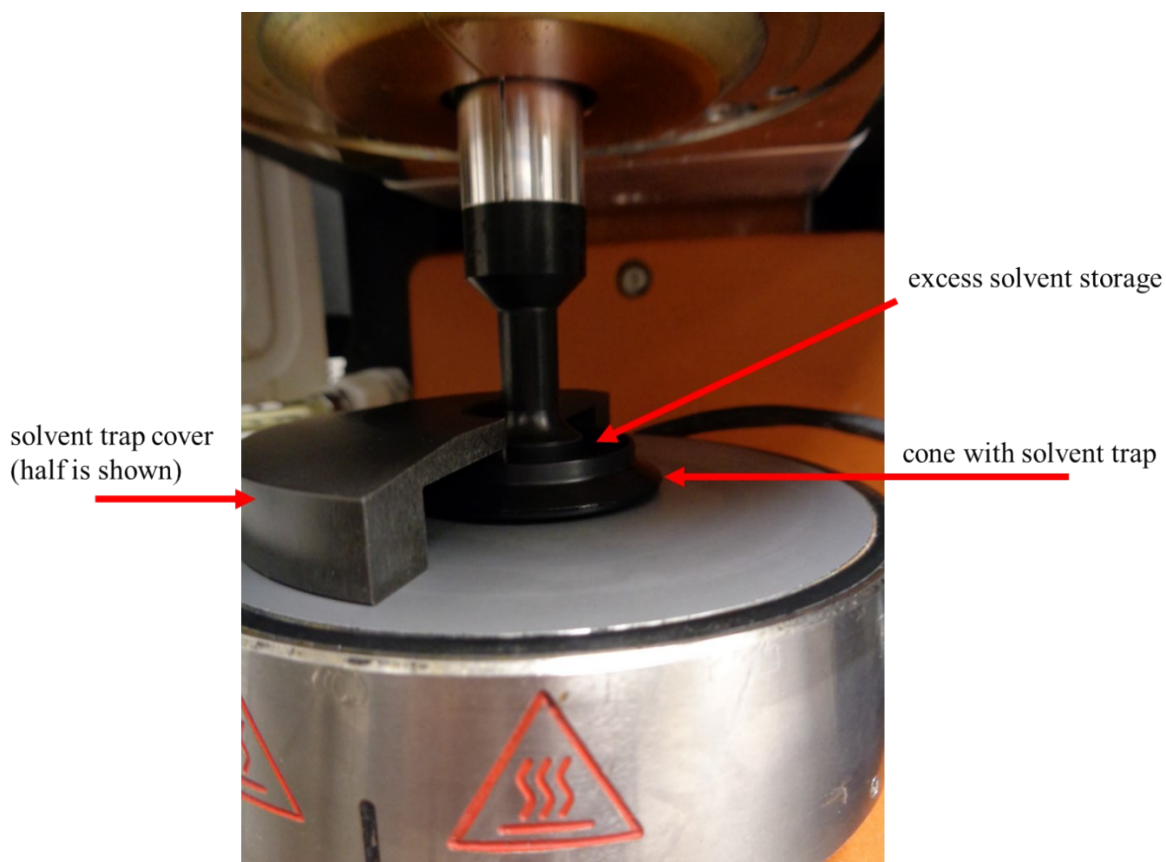
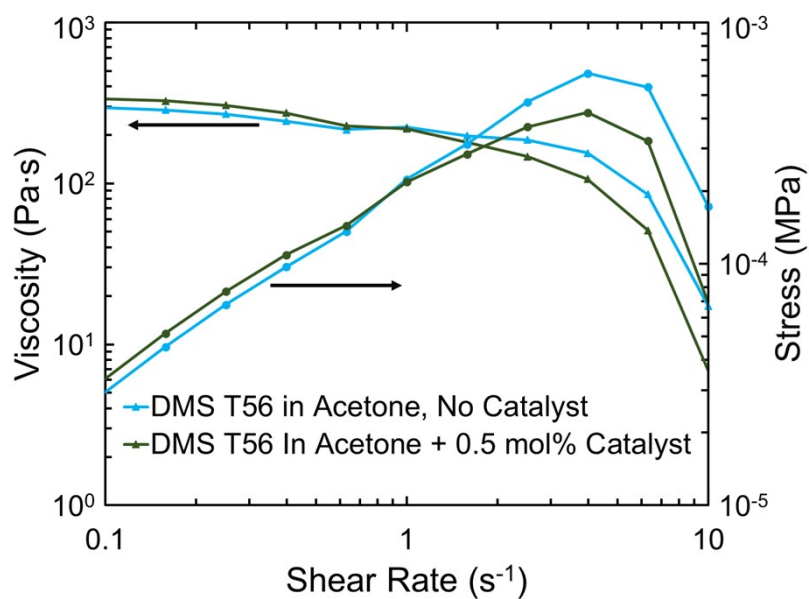


Figure S9. Cone with solvent trap and Peltier plate set-up on the DHR

A.



B.

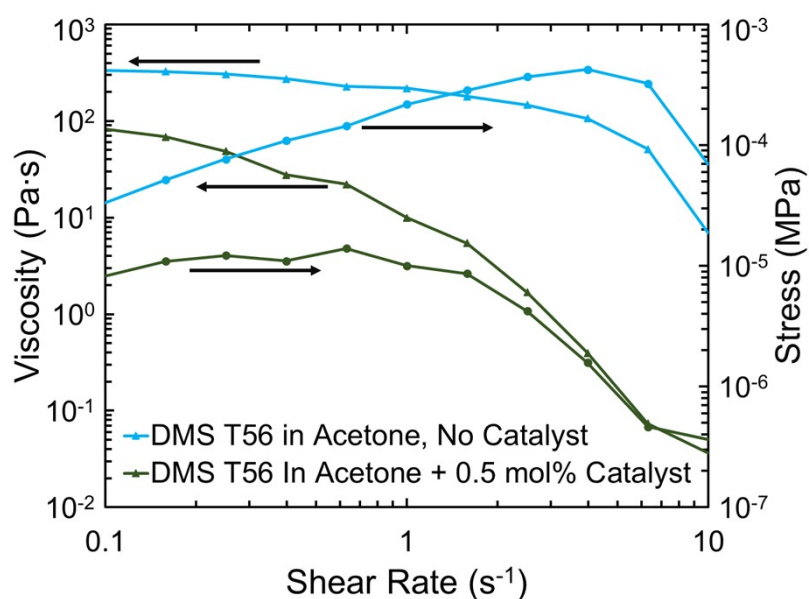


Figure S10. Depolymerization of DMS T56 in acetone is monitored by cone-plate rheology A. Flow-sweep data with shear rate from 0.1/s to 10/s with no catalyst and 0.5 mol% catalyst loading. B. Flow-sweep data with shear rate from 0.1/s to 10/s with no catalyst and 0.5 mol% catalyst loading. The difference in starting viscosity is attributed to the different treatment of DMS T56. Before loading with catalyst, in second case, DMS T56 is premixed with acetone in a Thinky® mixture.

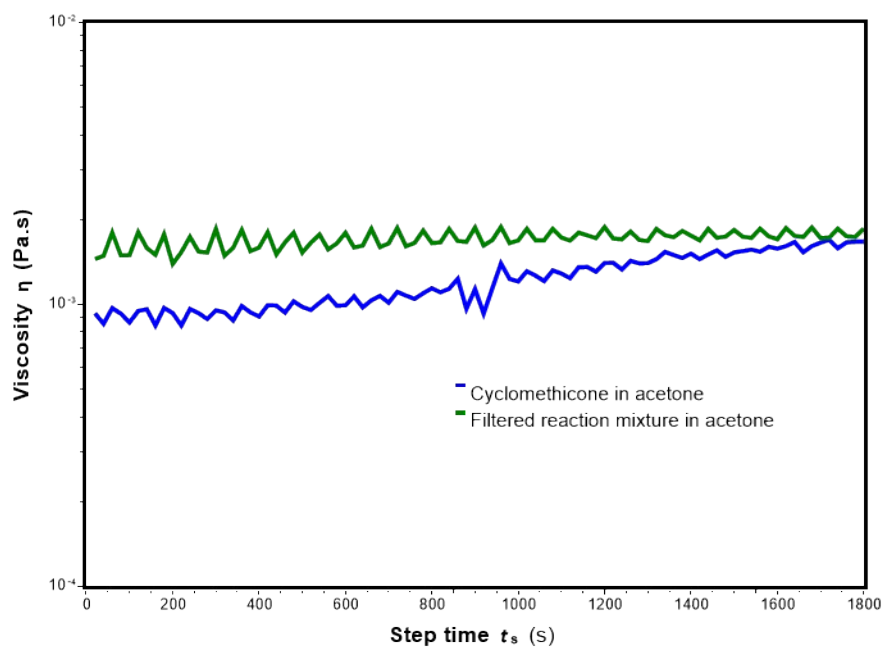


Figure S11. Comparison of depolymerized siloxane reaction mixture (filtered over CaCl_2) and cyclomethicone in acetone at room temperature monitored by measuring viscosity over time using cone-plate rheology.

5. GPC data

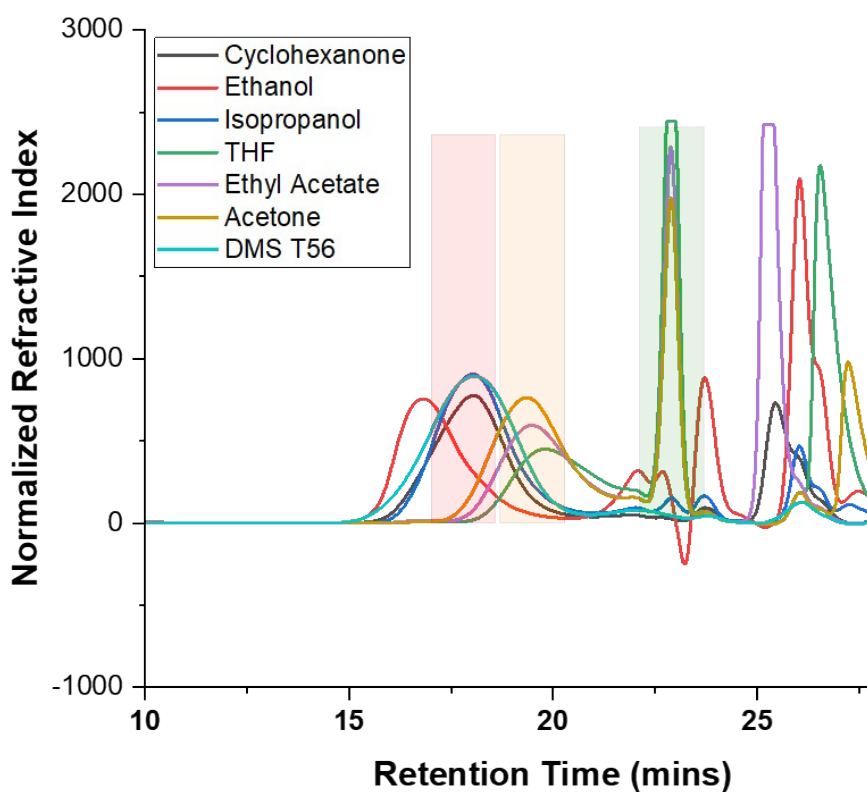


Figure S12. Depolymerization products of linear PDMS conducted in different solvents and measured using GPC. In all the cases, 0.1 mol% TBAT catalyst is used at room temperature with a 12 hour reaction time. Two distinct depolymerization results can be observed for homogeneous (ethyl acetate, THF, acetone) and heterogeneous (cyclohexanone, ethanol, isopropanol) reaction conditions where under homogeneous conditions, nearly complete depolymerization takes place.

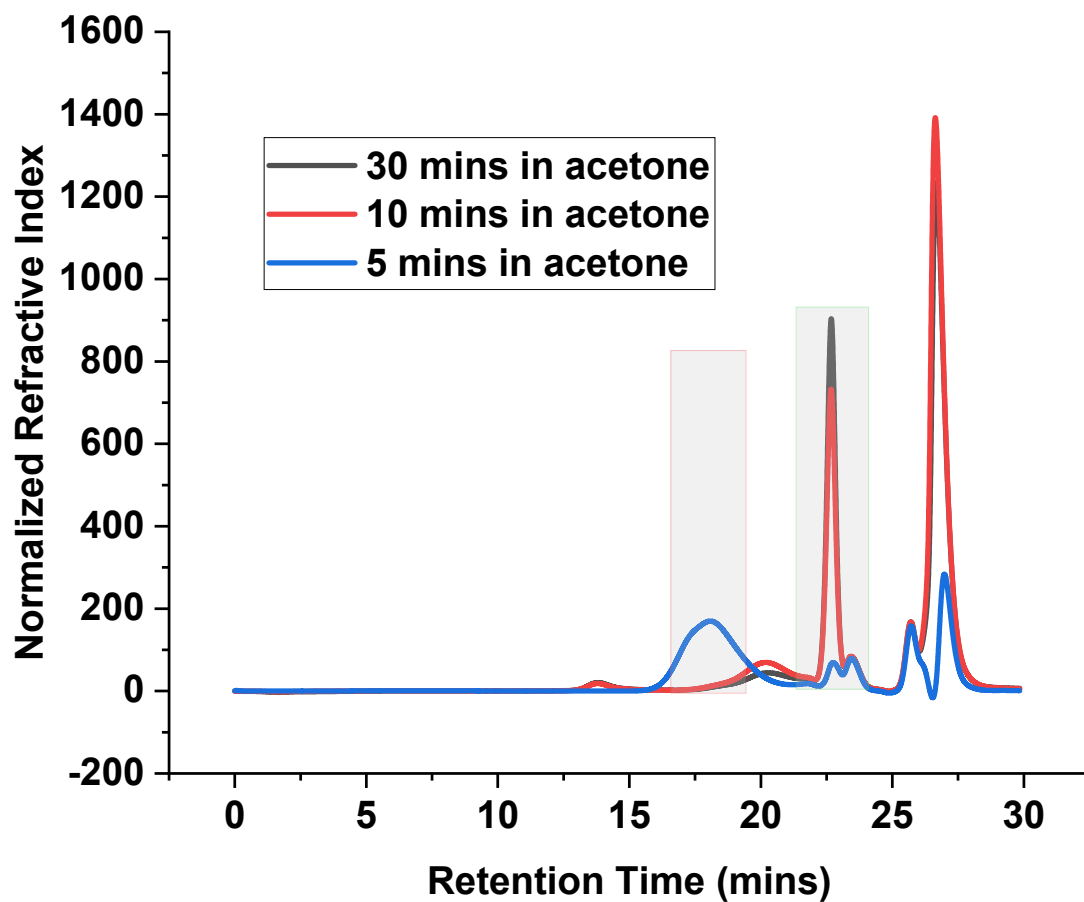


Figure S13. Depolymerization reaction was monitored by GPC with reaction time as the key variable. Solvent, catalyst concentration, and temperature were kept constant. With acetone as the reaction medium, complete depolymerization was observed as fast as 30 mins at room temperature with 0.5 mol% of TBAT catalyst loading.

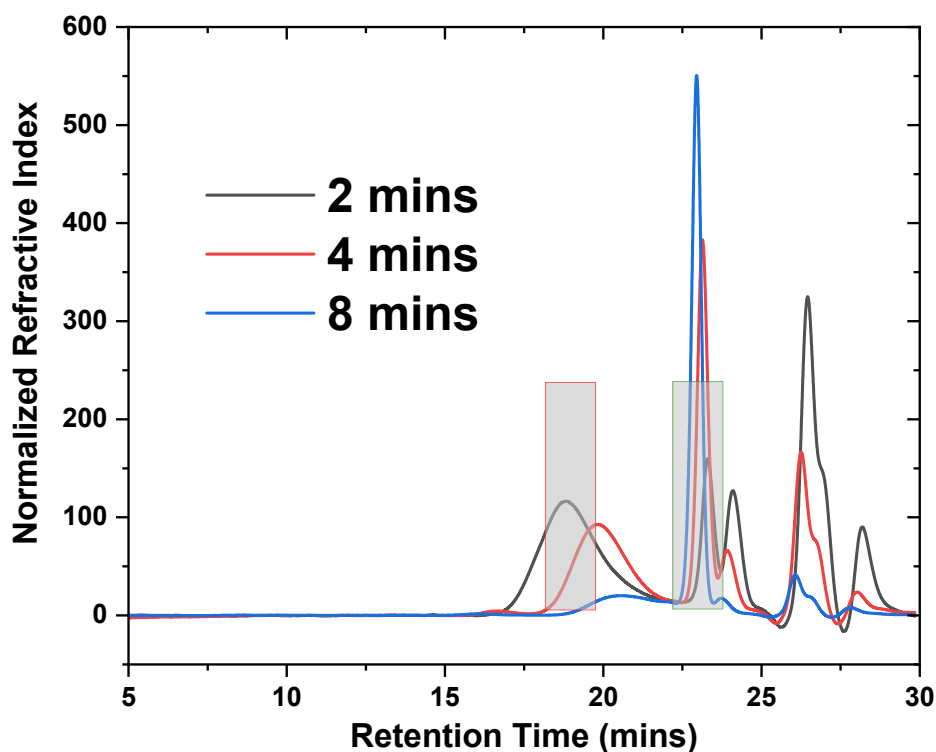


Figure S14. Depolymerization reaction in the Thinky Mixer was monitored by GPC with reaction time as the key variable and solvent, catalyst concentration, and temperature were kept constant. With acetone as the reaction medium, complete depolymerization was observed as fast as 8 mins at room temperature with 0.5 mol% of TBAT catalyst loading. This observation supports the observation made at Figure S9 where we observed fast depolymerization kinetics in homogeneous reaction conditions. The Thinky[®] is a planetary centrifugal mixer which generates significant centrifugal force with the cup of material 's rotation about its own axis and the mixer's revolution about the mixer's central axis.

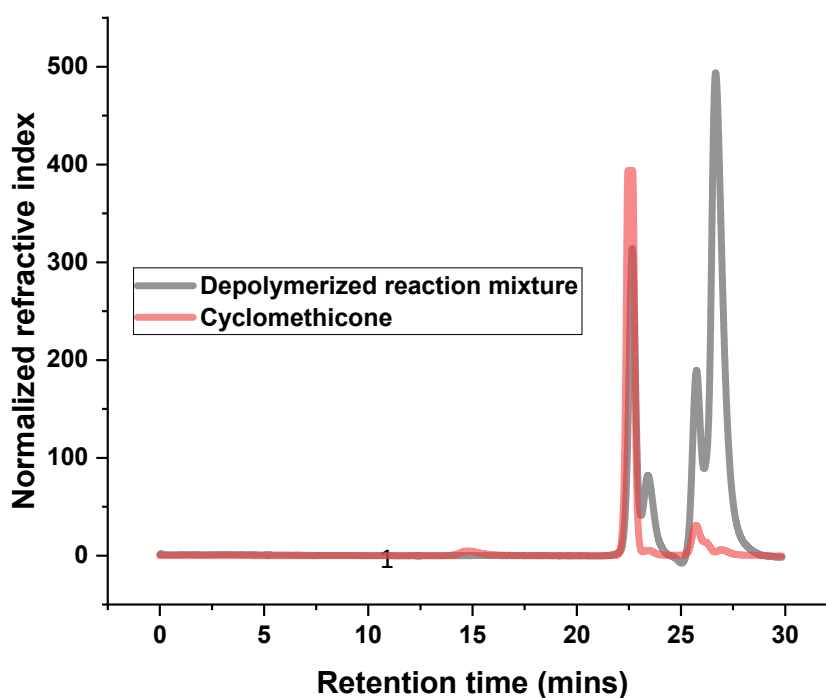


Figure S15. GPC data of depolymerized reaction mixture along with cyclomethicone as the model reference substrate for depolymerized species

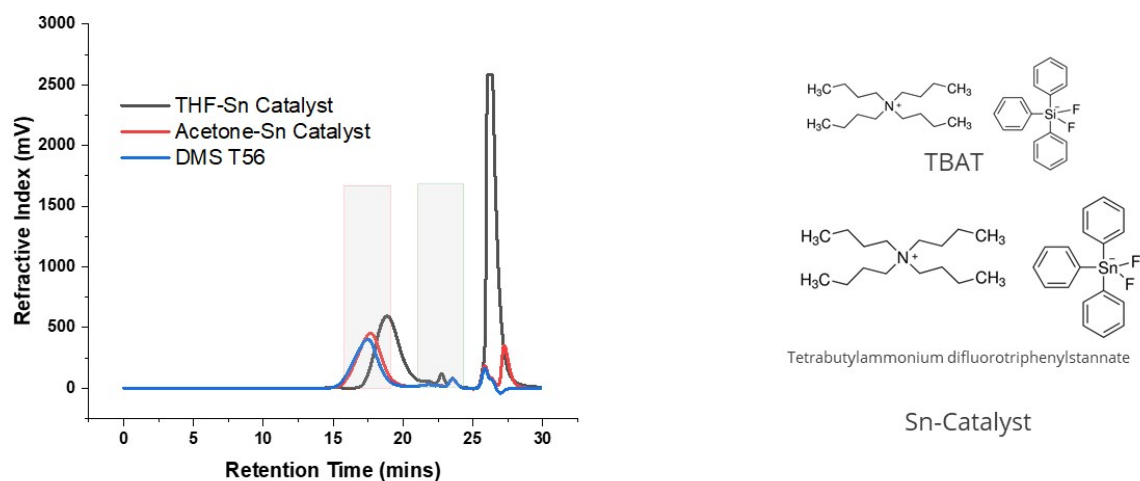


Figure S16. Depolymerization reaction with Sn analogue of TBAT with acetone and THF as the reaction medium. Compared to TBAT, Sn analogue did not show significant depolymerization with 0.5 mol% catalyst loading and 12 hours as the reaction time in room temperature

6. NMR data

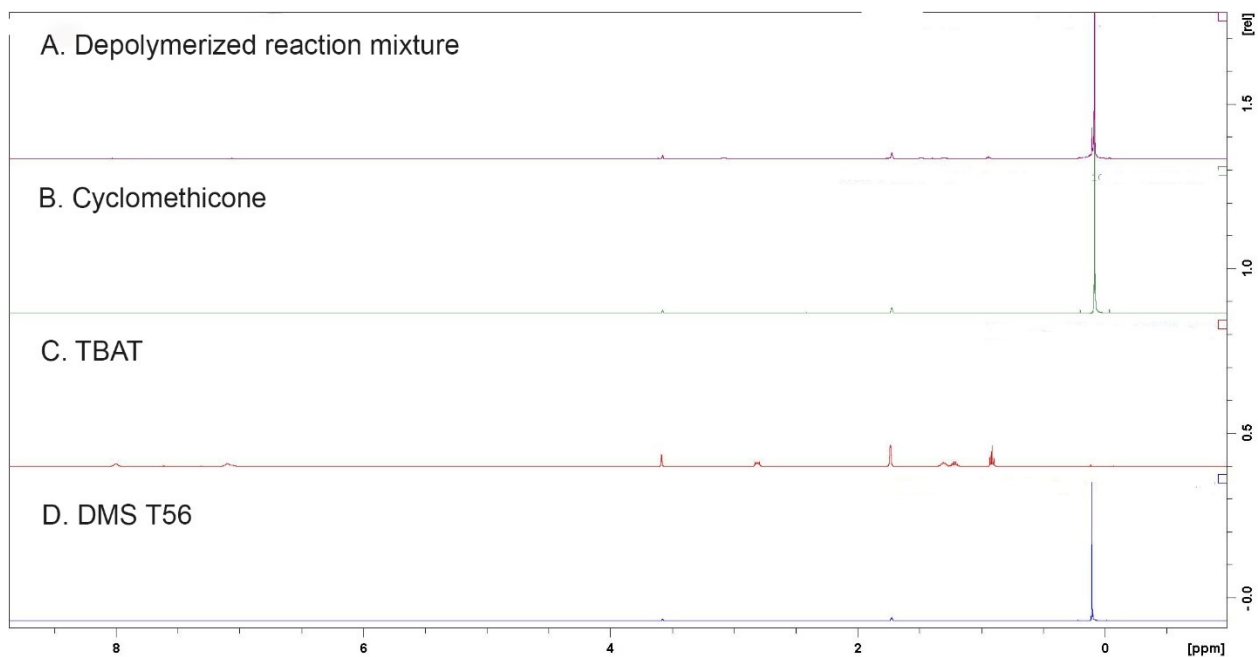


Figure S17. ¹H NMR in THF-*d*₈ as solvent for A. Depolymerized reaction mixture from the reaction of DMS T56 and TBAT, B. Cyclomethicone (a model representative of depolymerized siloxane species), C. TBAT, and D. DMS T56

7. Reaction mechanism:

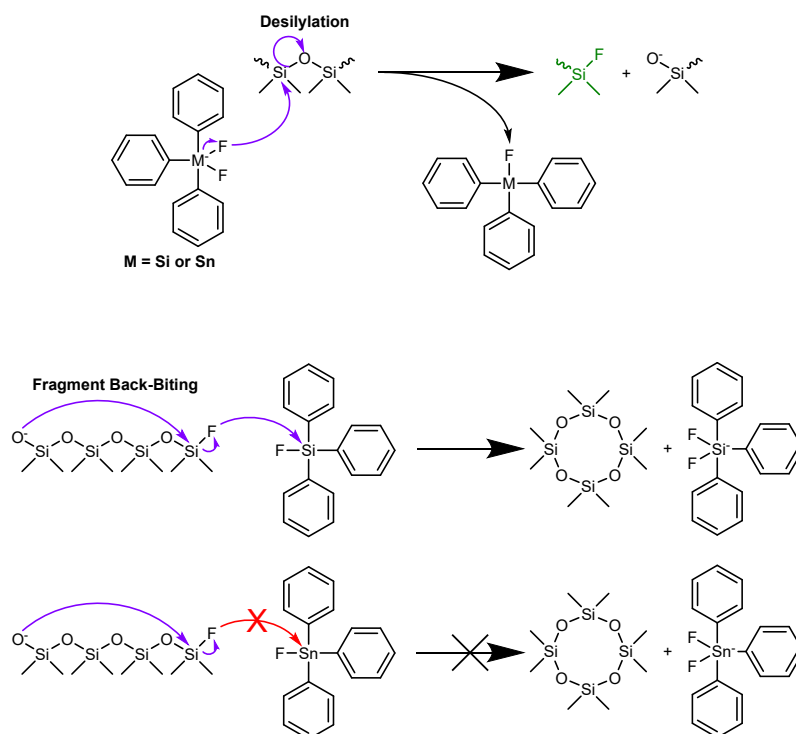


Figure S18. Proposed silicone depolymerization mechanism utilizing TBAT as the catalyst. Depolymerization first involves desilylation of a silicone chain, then subsequent cyclic rearrangement of the fragments with accompanying catalyst regeneration. Compared to TBAT, there is a lower bond dissociation energy between fluorine and the Sn analogue (565 and 414 kJ/mol for the Si-F and Sn-F bonds respectively). Therefore, it is less likely that catalyst regeneration occurs during the fragment backbiting step.

8. Comparison of TBAT and TBAF

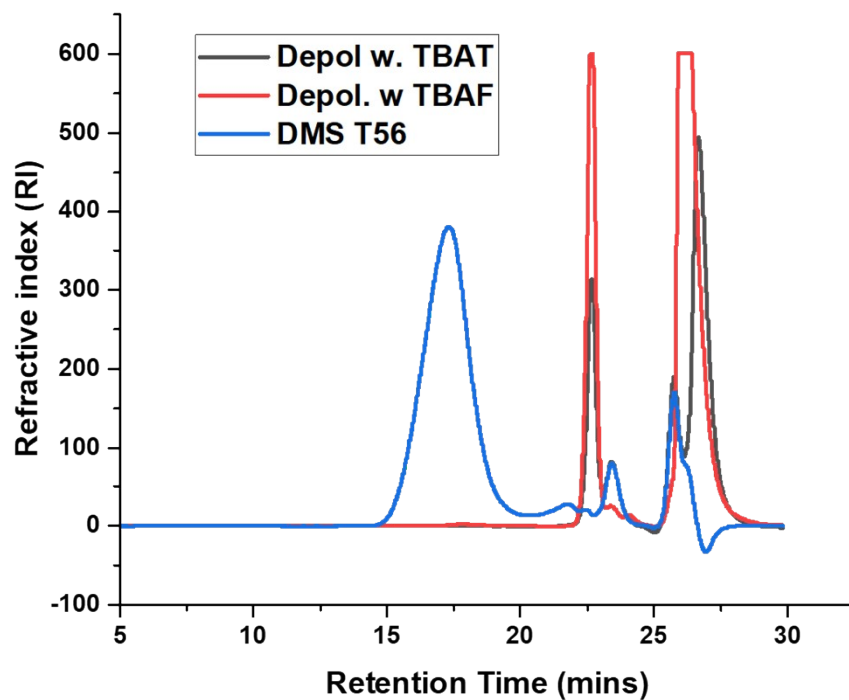


Figure S19. GPC plots comparing the depolymerized reaction mixture with TBAT and TBAF as the catalysts with 1 mol% catalysts. In both the cases the reactions were conducted in THF in room temperature for 12 hours and toluene was used as eluent

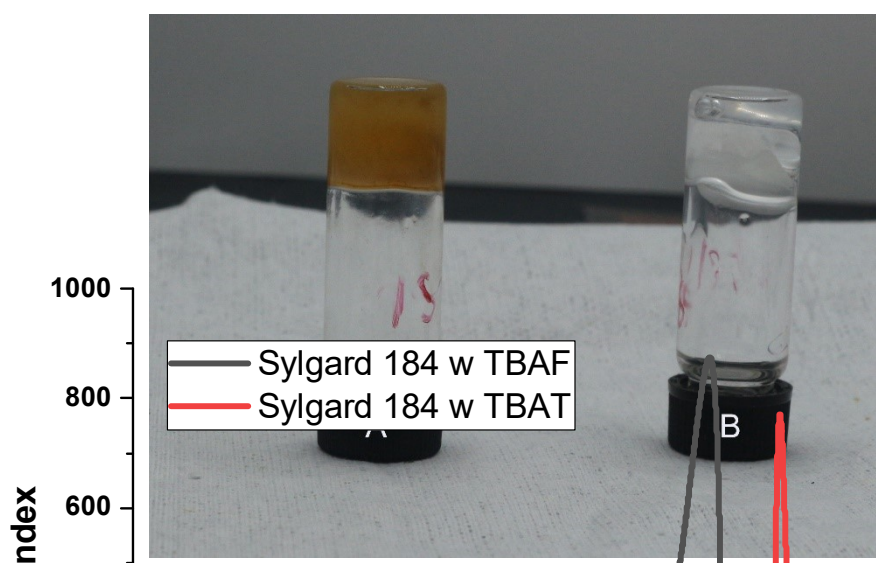


Figure S20: Inverted vial experiments with the attempted depolymerization reactions in A. at 100 °C in cyclohexanone over 16 hours, and B. in room temperature over THF for 3 days

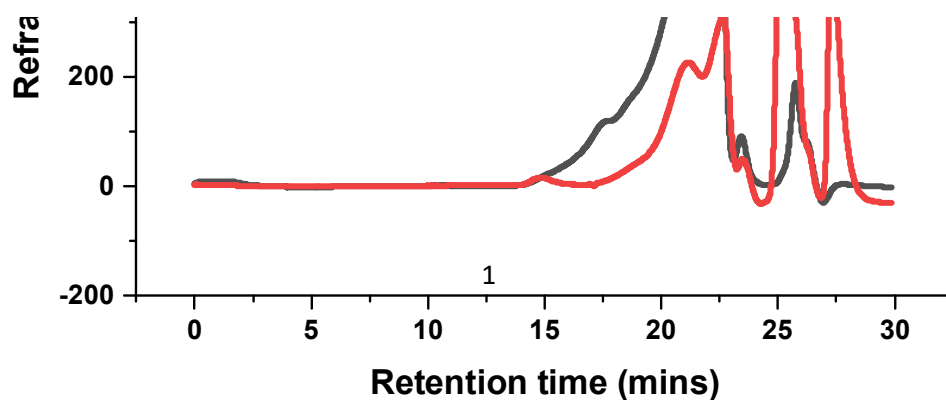


Figure S21: GPC of extracted molecules from the reaction mixtures of depolymerized sylgard 184 with TBAT and TBAF. Depolymerization reactions were conducted at 100 °C with cyclohexanone as the solvent

9. Preliminary experiments toward programmable material

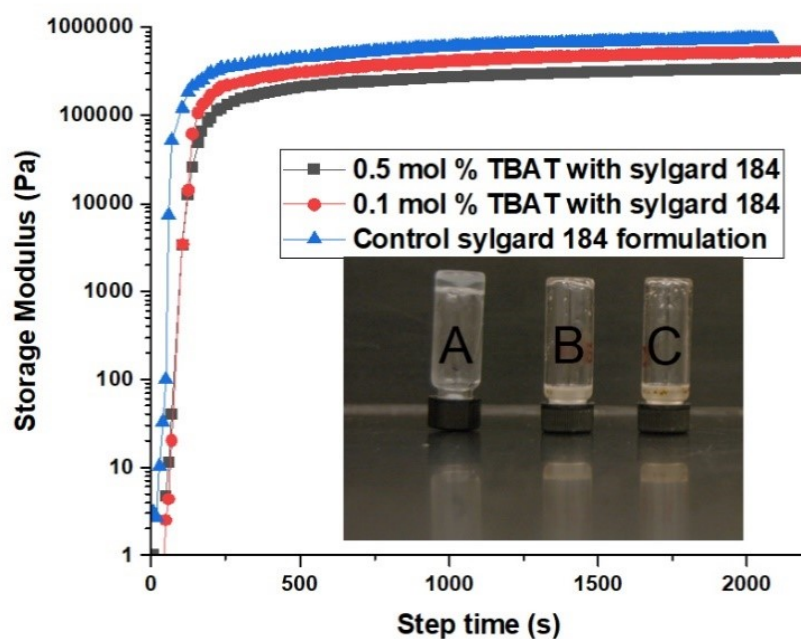


Figure S22. Storage modulus of Sylgard 184 co-cured with different levels of TBAT (0.1% and 0.5 mol%). Inset diagram showing the depolymerization of Sylgard containing TBAT in presence of cyclohexanone vapor at 100 °C (A. Control: sylgard 184, B: sylgard with 0.1 mol% TBAT, C: sylgard with 0.5 mol% TBAT)