

Supplementary Materials for:

Influence of Concentration of Thiol-Substituted Poly(dimethylsiloxane)s on the Properties, Phases, and Swelling Behaviors of Their Crosslinked Disulfides

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Supplementary Materials:

S.I. Purification of T-PDMS materials

SMS-042-[4-6% (3-mercaptopropyl) methylsiloxane]-dimethylsiloxane copolymer (4-6% T-PDMS, Gelest Inc., >97.5%). The 4-6% T-PDMS was heated under vacuum to remove octamethylcyclotetrasiloxane (D4) that was known to be present at <5 wt% [1,2]. See below. The ¹H NMR spectrum of the as-received 4-6% T-PDMS in CDCl₃ is shown in Figure S1. 4-6% T-PDMS (19.44 g) was heated over 1.5 h from 21°C, at an initial pressure of 0.5 mmHg, to 49°C, with a final pressure of 0.15 mmHg. The enthalpy of vaporization of D4 is 57 kJ/mol [3], and the boiling points of D4 at these pressures were calculated to be 31°C and 21°C, at 0.5 mmHg and 0.15 mmHg, respectively [4]. Thus, these conditions are

expected to remove all of the D4. The mass of the 4-6% T-PDMS was decreased by 2.5%. A ^1H NMR spectrum indicated that the distillate was mostly D4. When the process above was repeated, no further change in the mass was found. Based on information from Gelest concerning the initial concentration of D4 and the distillate, the purity of 4-6%T-PDMS after treatment was $\geq 97.5\%$ (Figure S2). ^1H NMR spectroscopy could not be used to demonstrate that all of the D4 was removed, because the 24 protons in D4 resonate at 0.09 ppm [5]. If D4 was present, the peak would overlap with the methylsiloxane proton peaks of T-PDMS (red protons in Figure S3), which are centered at 0.08 ppm, and span from 0.02 to 0.19 ppm. Although the appearance of the peak is similar before (Figure S1) and after (Figure S2) treatment, the proton integration decreased.

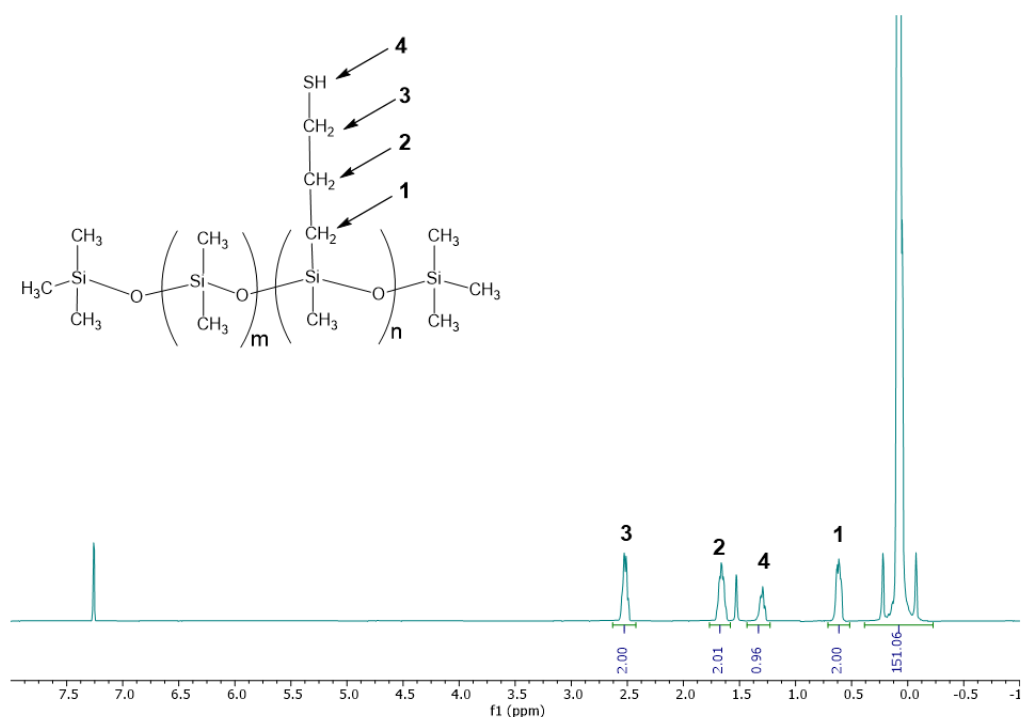


Figure S1. ^1H NMR spectrum with integration ratios of as-received 4-6% T-PDMS.

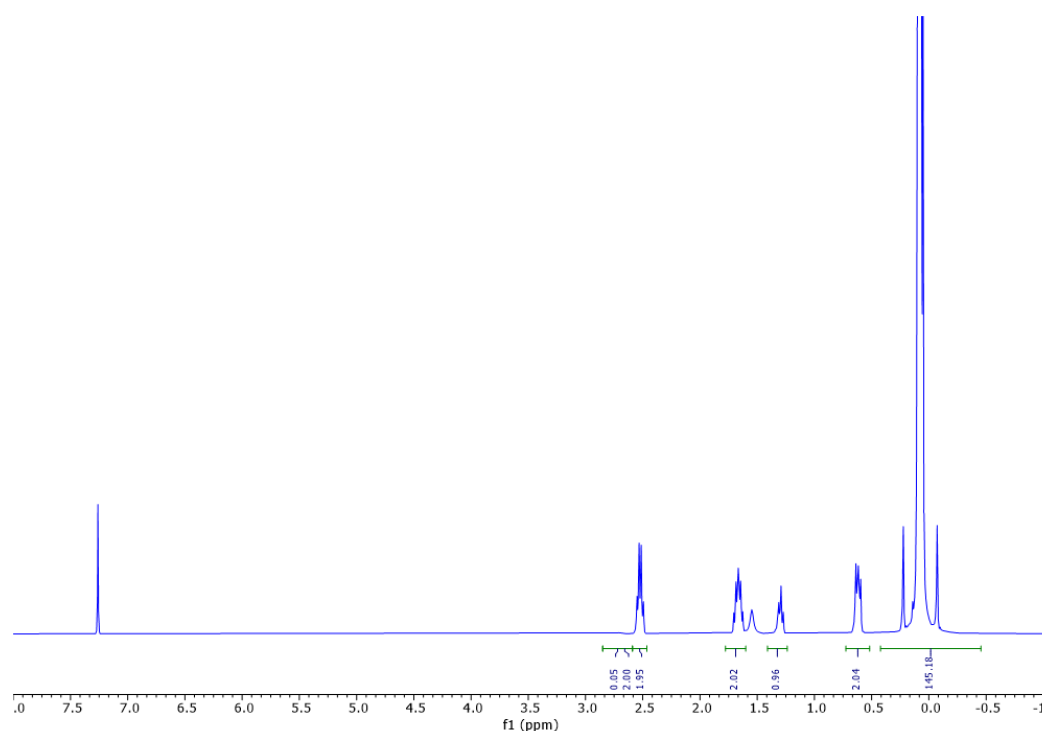


Figure S2. ^1H NMR spectrum with integration ratios of purified 4-6% T-PDMS.

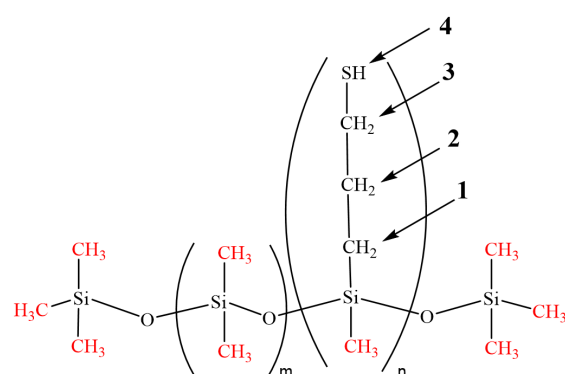


Figure S3. Structure of 4-6%T-PDMS. The methyl groups in red contribute to the large methylsiloxane peak centered at approximately 0.08 ppm in Figures S1 and S2. The numbered groups belong to the thiol-containing co-monomer portion, all of which have unique signals downfield of the methylsiloxane resonance peak.

Purified 4-6% T-PDMS: ^1H NMR δ 0.08 (m, 145H, O-Si-CH₃), 0.61 (m, 2H, OSi-CH₂-CH₂), 1.30 (m, 1H, CH₂-SH), 1.66 (m, 2H, CH₂-CH₂-CH₂SH), 2.52 (q, 2H, $J=7.4$ Hz, CH₂-CH₂SH) (Figure S2). ^{13}C NMR δ -0.33 (OSi-CH₃), 1.02 (OSi-CH₃), 1.19 (OSi-CH₃), 1.94 (OSi-CH₃), 16.07 (OSi-CH₂-CH₂), 28.02 (CH₂-CH₂-CH₂SH or CH₂-CH₂-CH₂SH), 28.13 (CH₂-CH₂-CH₂SH or CH₂-CH₂-CH₂SH) (Figure S4; impurity peaks discussed in Section S.IV).

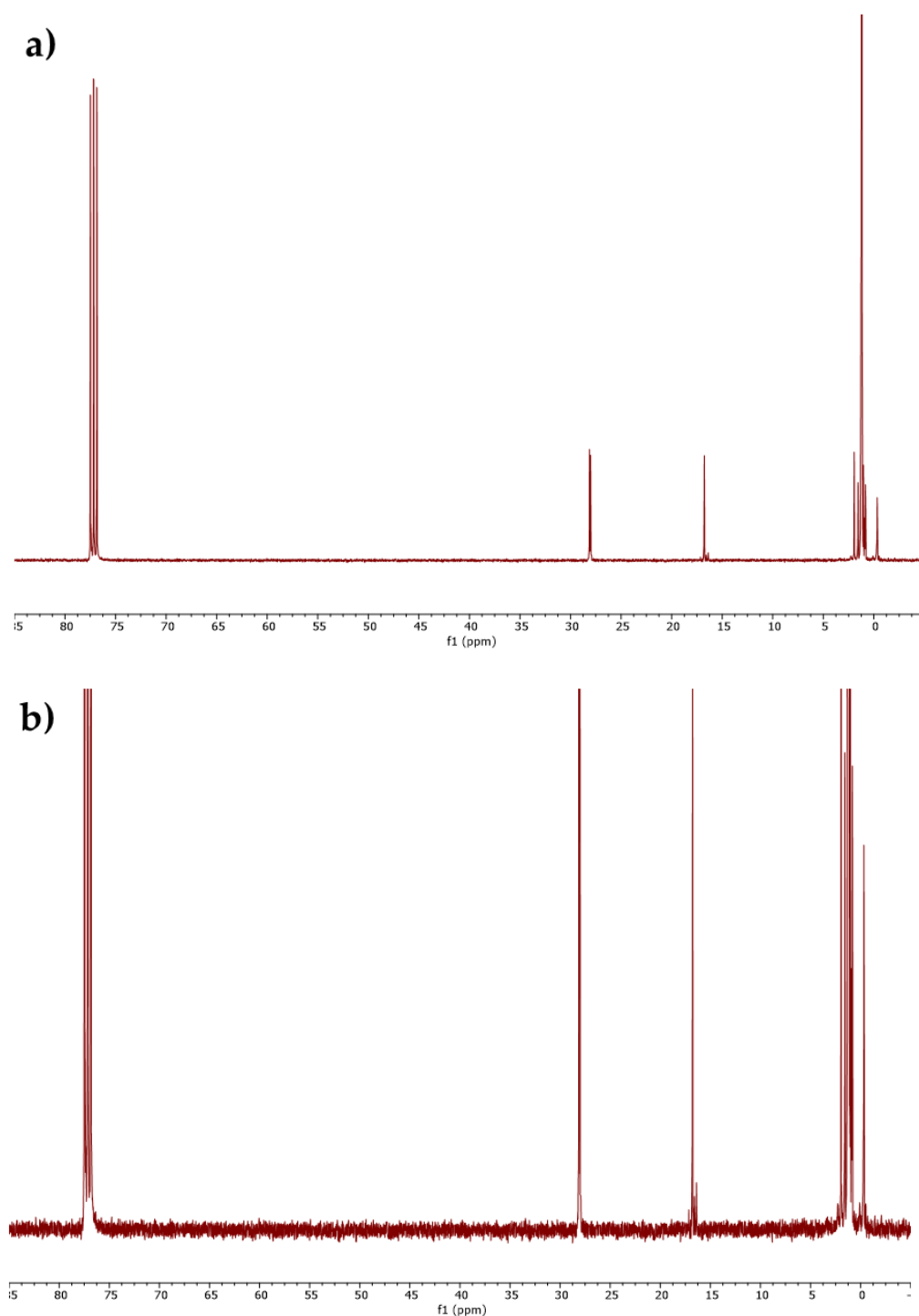


Figure S4. ^{13}C NMR spectrum of purified 4-6% T-PDMS showing: (a) peak height ratios, and (b) amplifying low intensity peaks.

The analogous procedure, used to remove D4 from 13-17% T-PDMS, led to a calculated purity of $\geq 97.5\%$. Both of the T-PDMSs were viscous, straw-colored translucent liquids after treatment.

Purified 13-17% T-PDMS: ^1H NMR δ 0.08 (m, 41H, O-Si-CH₃), 0.61 (m, 2H, OSi-CH₂-CH₂), 1.30 (m, 1H, CH₂-SH), 1.66 (m, 2H, CH₂-CH₂-CH₂SH), 2.52 (q, 2H, J=7.4 Hz, CH₂-CH₂SH) (Figure S5). ^{13}C NMR δ -0.34 (OSi-CH₃), 0.92 (OSi-CH₃), 1.04 (OSi-CH₃), 1.19 (OSi-CH₃), 1.55 (OSi-CH₃), 1.93 (OSi-CH₃), 16.75 (OSi-CH₂-CH₂), 28.01 (CH₂-CH₂-CH₂SH or CH₂-CH₂-CH₂SH), 28.10 (CH₂-CH₂-CH₂SH or CH₂-CH₂-CH₂SH) (Figure S6; impurity

peaks discussed in Section S.IV). A small peak of unknown origin is present at 2.06 ppm in the spectrum of 13-17% T-PDMS, both before and after purification (Figure S5). Its relative intensity and appearance were unchanged after oxidation to 13-17% D-PDMS_{1wt%} (Figure S14) using the procedure described in section S.III.1.

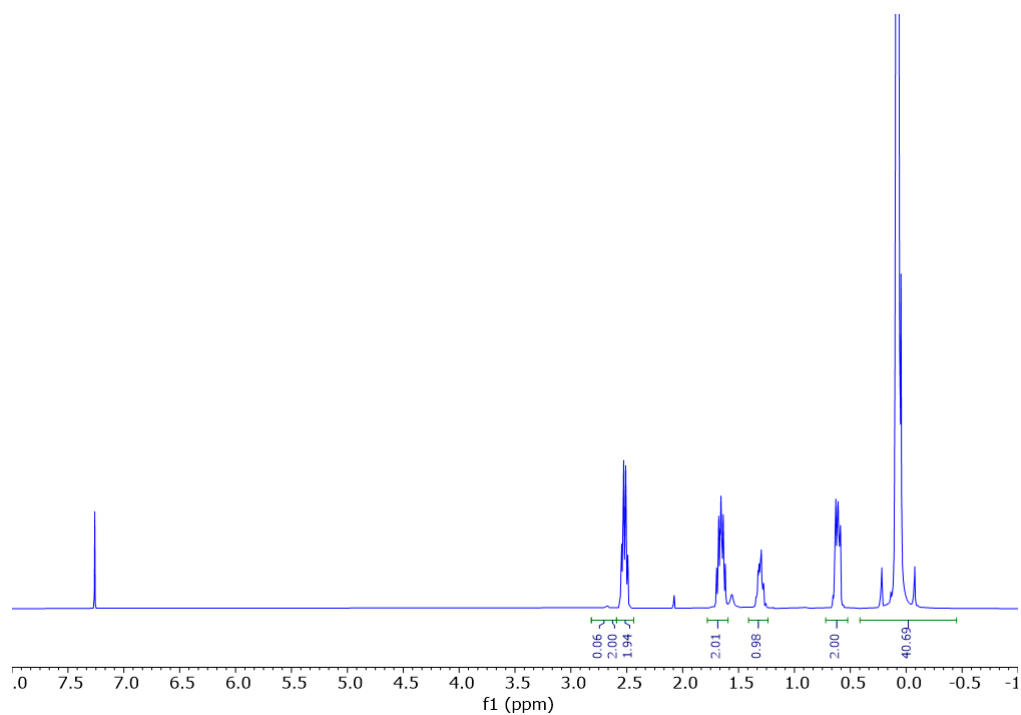


Figure S5. ¹H NMR spectrum with integration ratios of purified 13-17% T-PDMS.

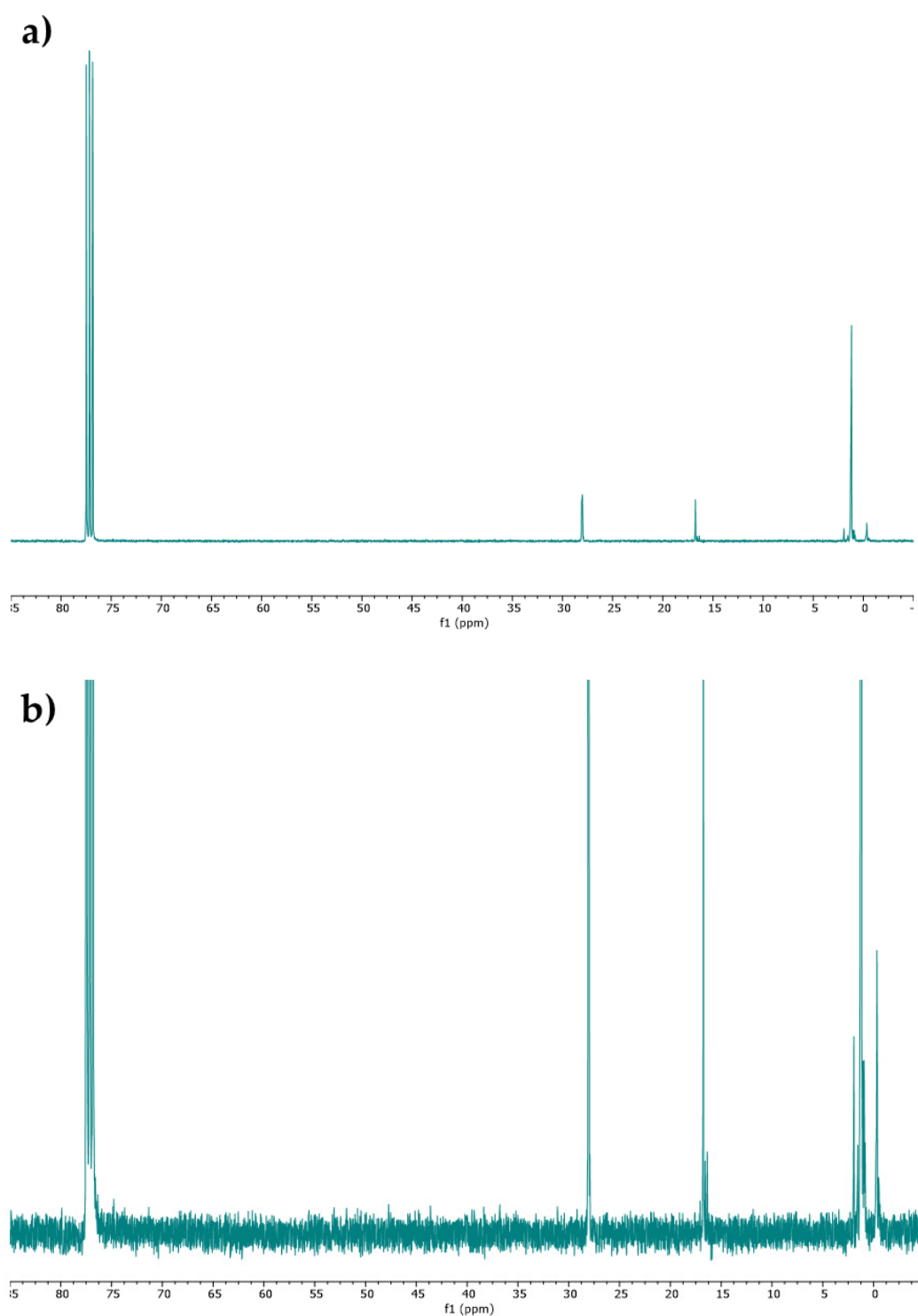


Figure S6. ^{13}C NMR spectrum of purified 13-17% T-PDMS showing: (a) peak height ratios, and (b) amplifying low intensity peaks.

The ^{13}C NMR spectrum of D4 is reported to exhibit one peak at 0.78 ppm [5]. Peaks at 0.78 ppm were not present in the ^{13}C NMR spectra of 4-6% TPDMS (Figure S4) and 13-17% T-PDMS (Figure S6) after the treatments described above.

S.II. Procedure to Determine Lag-Time in TGA-MS Studies

The initial TGA and MS data were recorded simultaneously, allowing the mass spectrum plot to be correlated with the TGA temperature, despite a significant lag between

the mass loss in the thermal gravimetric analyzer furnace and the detection of gasses in the mass spectrometer. To determine the lag time, a molecular sieve was soaked in water and the mass spectrometer was configured to detect ions from 16-19 amu (i.e., including water at 18.08 amu). Background subtraction was used to remove any water signal from residual atmospheric moisture or moisture in the nitrogen purge gas in the furnace. The thermogram from the analysis is depicted in Figure S7.

The maximum rate of water loss occurred at 124°C, which was 27 min into the experiment, based on the maximum in the derivative plot (blue line; Figure S7). In the absence of a lag time between the loss of water in the TGA furnace and its detection in the MS, the time at which maximum water loss occurred in the TGA corresponds to the highest ion current in the 3D MS plot. However, the ion current peaked at 32 min in the mass spectrum (not depicted), indicating a lag time of 5 min.

An example of how the lag time calculations were used to correlate MS results (Figure S7) with TGA thermograms is shown in Figure S8 for 13-17% D-PDMS_{55wt%}. The mass spectrometer scanned for ions between 33.8-35.0 amu as soon as the TGA experiment started ($t = 0$ min.), allowing the MS and thermogram (Figure S8, where the x-axis is time) to be correlated. Due to the 5 min lag time between loss of material in TGA and its detection by MS, the ions detected between 60.0 – 80.5 min were generated during TGA decomposition between 55.0 – 75.5 min. The two red boxes in the thermogram (Figure S9) indicate the mass percentage and temperature during which H₂S ions were detected, after correcting for the detection lag. The green boxes show the same information for the uncorrected times. The corrected thermogram indicates that H₂S generation and 13-17% D-PDMS_{55wt%} decomposition occur simultaneously. Without correcting for lag time, these data suggest that H₂S loss occurs shortly after the onset of decomposition.

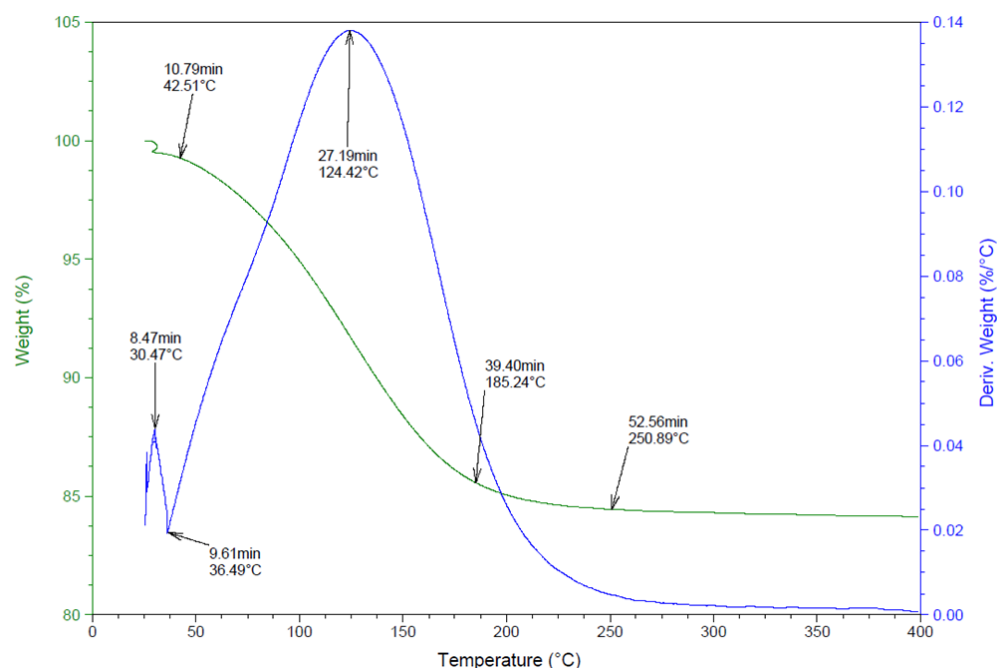


Figure S7. TGA thermogram (black line), showing water lost from a wet molecular sieve, as a function of time from the paired TGA-MS experiment. The annotations on the spectra give the time, temperature, and weight percent remaining. The blue line plots the derivative of weight percent as a function of time.

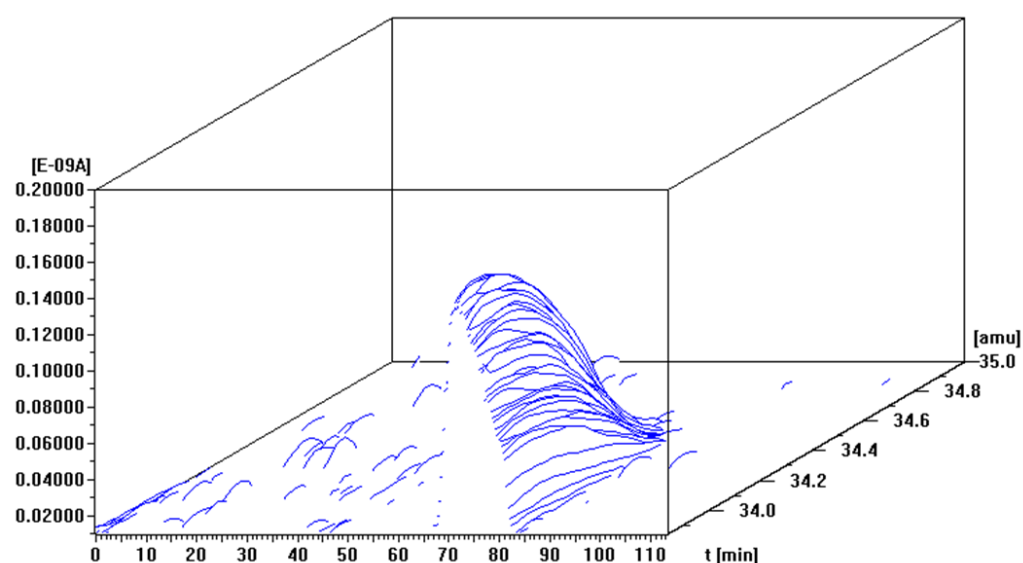


Figure S8. Mass spectrum of 13-17% T-PDMS_{55wt%} from the paired TGA-MS experiment.

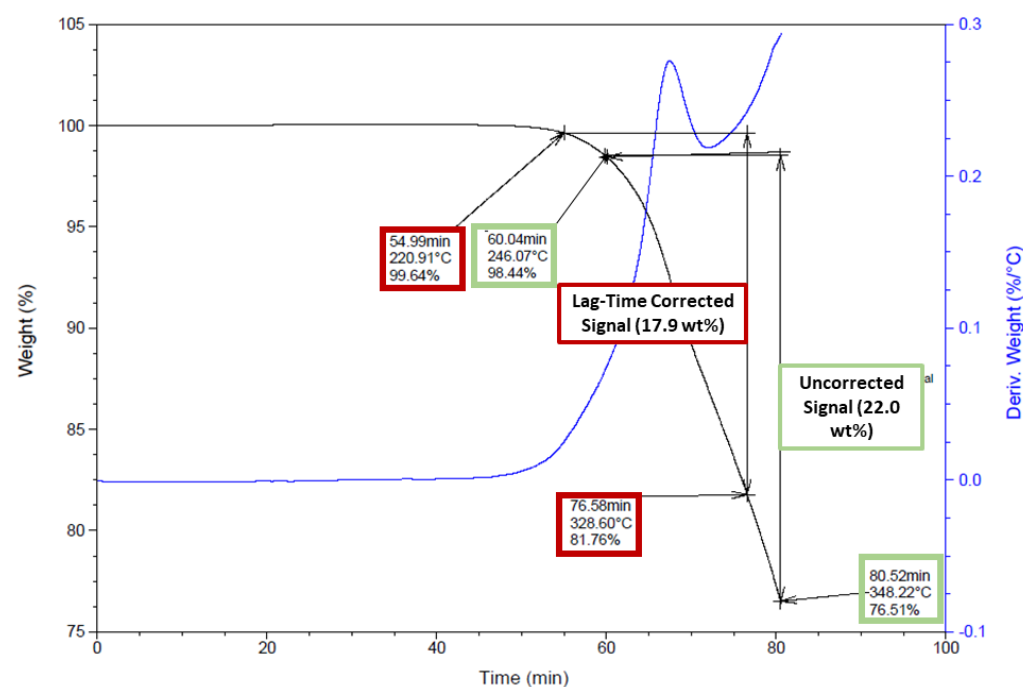


Figure S9. TGA thermogram of (black line) of 13-17% D-PDMS_{55wt%} correlating MS ion detection start and end times with the TGA thermogram times, temperatures, and mass percentages. The uncorrected times are shown in green. Due to the 5.0 min. lag between loss of mass during TGA and detection of the corresponding ions by the mass spectrometer, the times associated with the loss of ions detected by the mass spectrometer have been corrected, and are highlighted in red. The blue line plots the derivative of weight percent as a function of time.

S.III. Syntheses of D-PDMS materials

Table S1 expresses the initial concentration of T-PDMS prior to the addition of the I₂ solution, and the final concentration of T-PDMS after the addition of the I₂ solution.

Table S1. D-PDMS materials from reactions of 4-6% T-PDMS and 13-17% T-PDMS at different initial and final concentrations

D-PDMS material	Thiol monomer substitution in T-PDMS	M _w range (Da) of T-PDMS	Initial concentration of T-PDMS	Final concentration of T-PDMS	Initial concentration in thiol (M)	Product phase
4-6% D-PDMS _{2wt%}	4-6%	6,000- 8,000	2 wt%	0.6 wt%	0.02	Liquid
4-6% D-PDMS _{6wt%}	4-6%	6,000- 8,000	6 wt%	3 wt%	0.06	Liquid
4-6% D-PDMS _{15wt%}	4-6%	6,000- 8,000	15 wt%	6 wt%	0.18	Liquid
4-6% D-PDMS _{55wt%}	4-6%	6,000- 8,000	55 wt%	12 wt%	0.47	Solid
13-17% D-PDMS _{1wt%}	13-17%	3,000- 4,000	1 wt%	0.4 wt%	0.02	Liquid
13-17% D-PDMS _{6wt%}	13-17%	3,000- 4,000	6 wt%	1.5 wt%	0.16	Solid
13-17% D-PDMS _{15wt%}	13-17%	3,000- 4,000	15 wt%	6 wt%	0.32	Solid
13-17% D-PDMS _{55wt%}	13-17%	3,000- 4,000	55 wt%	9 wt%	1.14	Solid

Two assumptions were made when calculating the moles of thiol (listed in Table 1 and Table S1). First, that each T-PDMS had the highest M_w value, relative to the manufacturer-provided range (8 and 4 kDa for 4-6% T-PDMS and 13-17% T-PDMS, respectively). Second, that each T-PDMS had the maximum percentage of thiol substitution, relative to the manufacturer-provided range (6% and 17% for 4-6% T-PDMS and 13-17% T-PDMS, respectively). The dark blue and dark orange boxes in Table S2 provide the moles of thiol per mole of 4-6% T-PDMS and 13-17% T-PDMS, respectively, based on these assumptions.

Table S2. Moles of thiol and dimethylsiloxane monomers per mole of T-PDMS copolymer shown for different combinations of thiol substitution percentages and molecular weights (based on the ranges provided by the manufacturer)

4-6%	M _w (Da)	Moles of thiol monomer per mole of polymer for:			Moles of dimethylsiloxane monomers per mole of polymer for:		
		4% thiol	5% thiol	6% thiol	4% thiol	5% thiol	6% thiol
T-PDMS	6,000	3.05	3.78	4.50	73.19	71.86	70.55
	7,000	3.57	4.43	5.28	79.77	84.17	82.64
	8,000	4.09	5.08	6.05	98.26	96.48	94.72
13-17%	M _w (Da)	Moles of thiol monomer per mole of polymer for:			Moles of dimethylsiloxane monomers per mole of polymer for:		
		13% thiol	15% thiol	17% thiol	13% thiol	15% thiol	17% thiol
T-PDMS	3,000	4.50	5.11	5.72	30.12	29.02	27.91
	3,500	5.29	6.02	6.75	35.42	34.18	32.93
	4,000	6.09	6.93	7.77	40.73	39.34	37.95

For example, 4-6% D-PDMS_{6wt%}, was synthesized from 5.00 g of 4-6% T-PDMS. Based on the assumptions mentioned above, the mmols of 4-6% T-PDMS (mmol_{4-6% T-PDMS}) was calculated using equation S1 as follows:

$$\frac{5.00 \text{ g}}{8,000 \text{ g/mol}} \times 1000 \text{ mmol/mol} = 0.625 \text{ mmol}_{4-6\% \text{ T-PDMS}}, \quad (\text{S1})$$

Based on Table S2, there are 6.06 mmols of thiol (mmol_{SH}) per mmol_{4-6% T-PDMS}, so the mmol_{SH} was calculated using equation S2 as follows:

$$0.625 \text{ mmol}_{4-6\% \text{ T-PDMS}} \times 6.06 \frac{\text{mmol}_{4-6\% \text{ T-PDMS}}}{\text{mmol}_{\text{SH}}} = 3.79 \text{ mmol}_{\text{SH}}, \quad (\text{S2})$$

The total (initial) volume (V_T) of the solution is expressed by equation S3 as follows:

$$\left(0.98 \frac{\text{g}}{\text{mL}} \times \text{mass}_{4-6\% \text{ T-PDMS}}\right) + \left(0.726 \frac{\text{g}}{\text{mL}} \times \text{mass}_{\text{Et}_3\text{N}}\right) + V_{\text{CHCl}_3} = V_T, \quad (\text{S3})$$

For the synthesis of 4-6% T-PDMS_{6wt%} (see section S.III.1) V_T was calculated as 59 mL. The initial molar concentration of thiol (M_{SH}) for this reaction was calculated using equation S4 as follows:

$$\frac{\text{mmol}_{\text{SH}}}{V_T} = \frac{3.79 \text{ mmol}_{\text{SH}}}{59 \text{ mL}} = 0.06 M_{\text{SH}} \quad (\text{S4})$$

S.III.1. Procedures for Syntheses of Non-Solid D-PDMS Materials

The syntheses of the non-solid D-PDMS materials in Table 1 and Table S1 were conducted using the representative methodology described for 4-6% D-PDMS_{6wt%}. 4-6% T-PDMS (5.00 g, 3.8 mmol *thiol*) and triethylamine (Et_3N ; 0.38 g, 3.8 mmol) in CHCl_3 (54 mL) were placed in a round-bottom flask with a compensated addition funnel charged with I_2 (0.620 g, 2.4 mmol) dissolved in CHCl_3 (66.5 mL). The solution was sparged with N_2 for ca. 5 minutes with stirring and closed. The I_2 solution was slowly added to the flask while stirring (1 drop every 2-3 s). The initially colorless solution turned brownish-red, ultimately becoming orange-yellow after all of the I_2 solution had been added. After stirring for 3 additional days, the solution was washed with saturated aqueous sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$; 95 mL), 0.1 M hydrochloric acid (HCl ; 95 mL), and deionized (DI) water (95 mL). The three-step wash was repeated, and the CHCl_3 layer was dried over anhyd. MgSO_4 . Most of the solvent was removed on a rotary evaporator. The remaining oil was placed in a vacuum oven (23-200 mmHg) at room temperature (RT), and the mass was tracked daily until the no changes were detected. The isolated material, 4-6% D-PDMS_{6wt%}, was a yellow, viscous liquid (4.18 g, 84% yield).

4-6% D-PDMS_{6wt%}: ^1H NMR δ : 0.07 (m, 152H, , O-Si-CH₃), 0.61 (m) and 0.74 (m) overlap (2H total, OSi-CH₂-CH₂), 1.26 (s, 0.1H), 1.72 (m) and 1.80 (m) overlap (2H total, CH₂-CH₂SH), and 2.67 (m, 2H, CH₂-CH₂SH) (Figure S10).

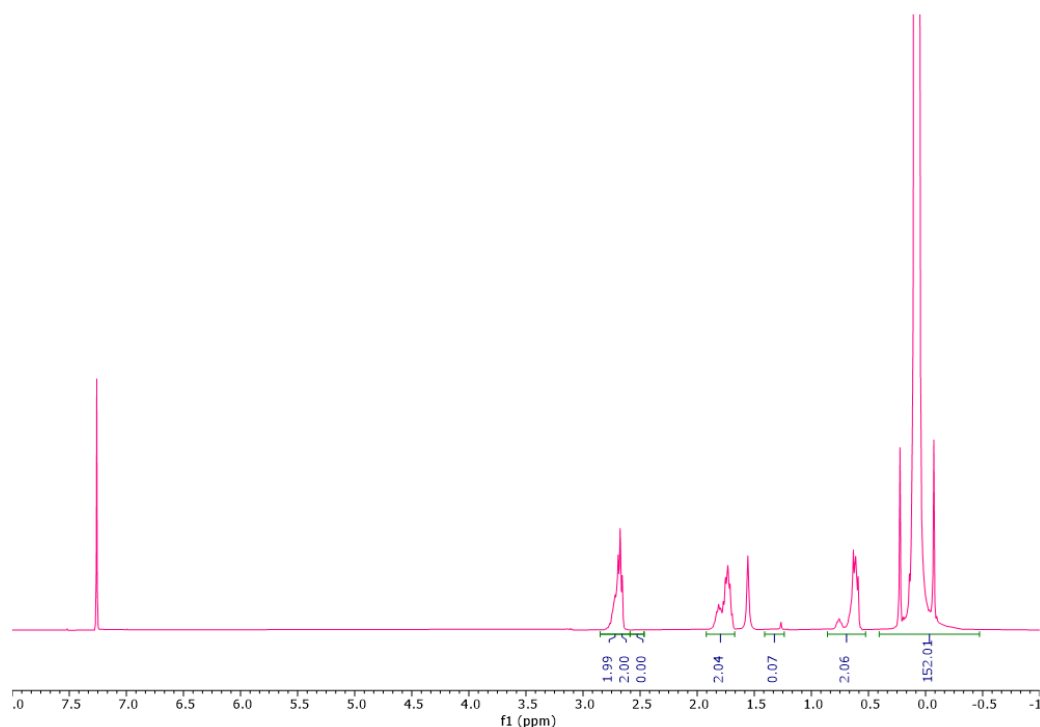


Figure S10. ^1H NMR spectrum with integration ratios of 4-6% D-PDMS_{6wt%}.

^1H NMR spectra of other non-solid D-PDMS materials in Table 1 and Table S1 and their ^1H NMR spectra are shown in Figures S11 – S14.

4-6% D-PDMS_{2wt%}: 4-6% T-PDMS yielded 4-6% D-PDMS_{2wt%} (94% yield), as a slightly yellow oil. ^{13}C NMR δ : -0.33 (OSi- $\underline{\text{C}}$ H₃), 0.81 (OSi- $\underline{\text{C}}$ H₃), 1.19 (OSi- $\underline{\text{C}}$ H₃), 1.56 (OSi- $\underline{\text{C}}$ H₃), 1.94 (OSi- $\underline{\text{C}}$ H₃), 16.80 (OSi- $\underline{\text{C}}$ H₂-CH₂), 23.12 (CH₂-CH₂- $\underline{\text{C}}$ H₂SS-), and 42.40 (CH₂-CH₂- $\underline{\text{C}}$ H₂SS-) (Figure S12; impurity peaks discussed in Section S.IV).

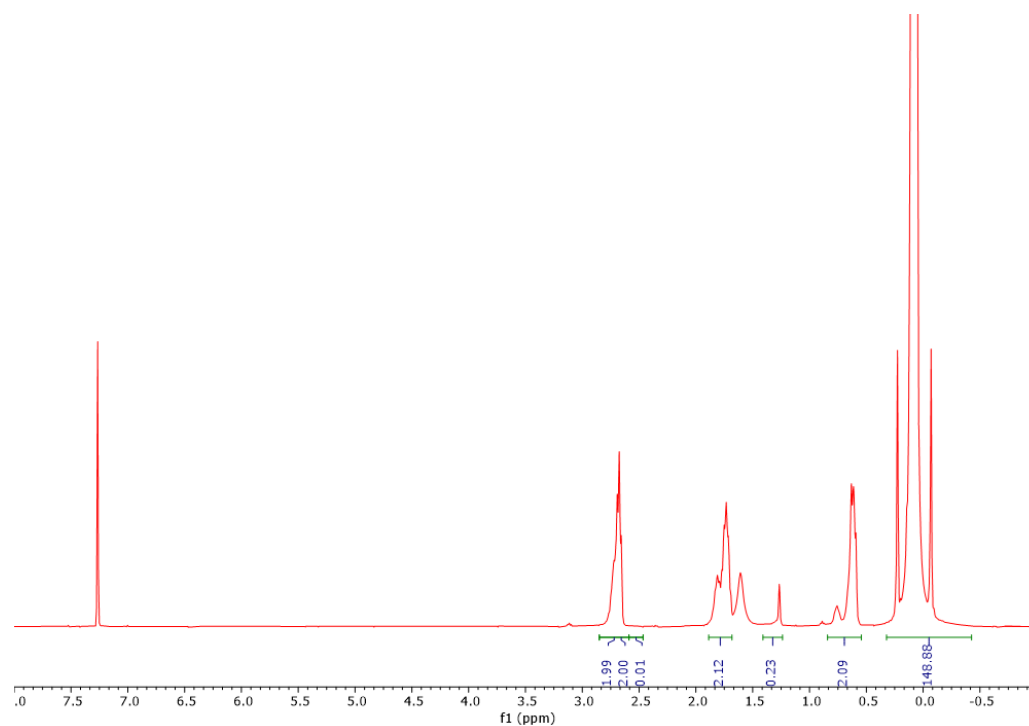


Figure S11. ^1H NMR spectrum with integration ratios of 4-6% D-PDMS_{2wt%}.

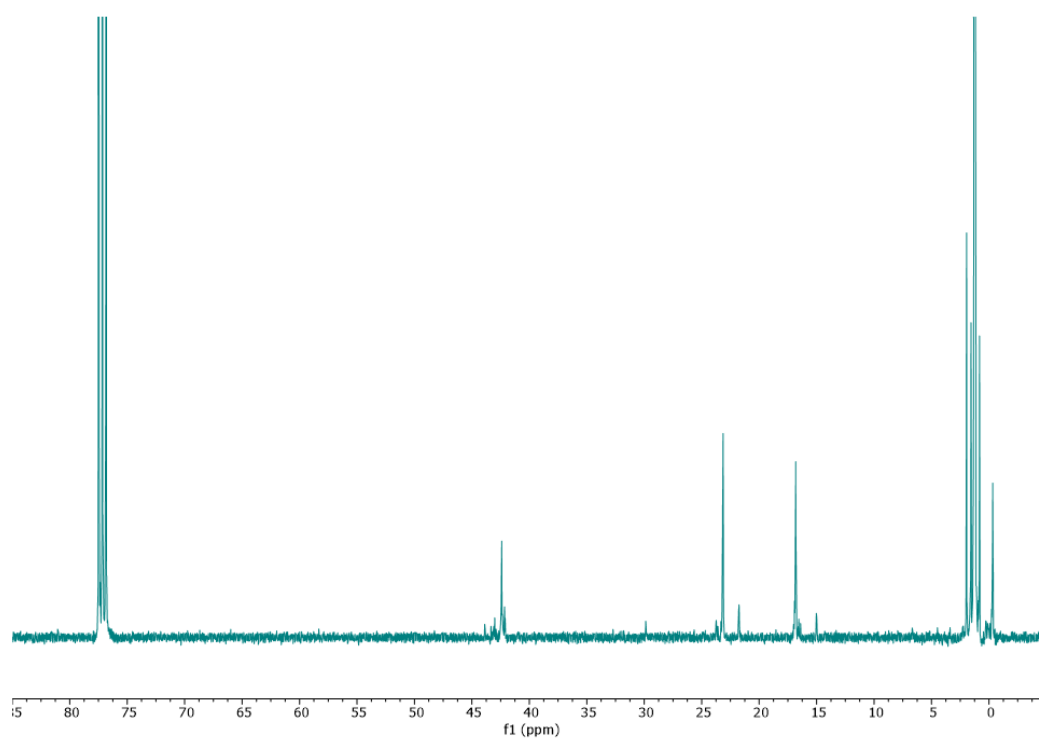


Figure S12. ^{13}C NMR spectrum of 4-6% D-PDMS_{2wt%}.

4-6% D-PDMS_{15wt%}: 4-6% T-PDMS yielded 4-6% D-PDMS_{15wt%} (78% yield) as a viscous, amber oil.

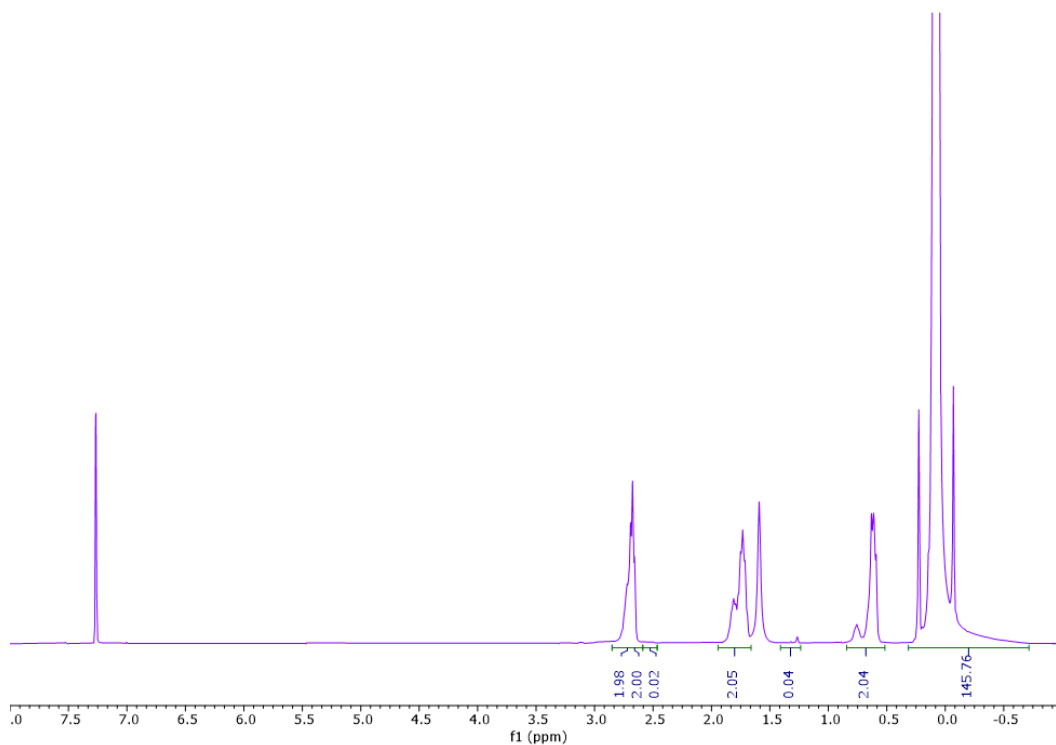


Figure S13. ¹H NMR spectrum with integration ratios of 4-6% D-PDMS_{15wt%}.

13-17% D-PDMS_{15wt%}: 13-17% T-PDMS yielded 13-17% D-PDMS_{1wt%} (91% yield) as a viscous, dark amber oil.

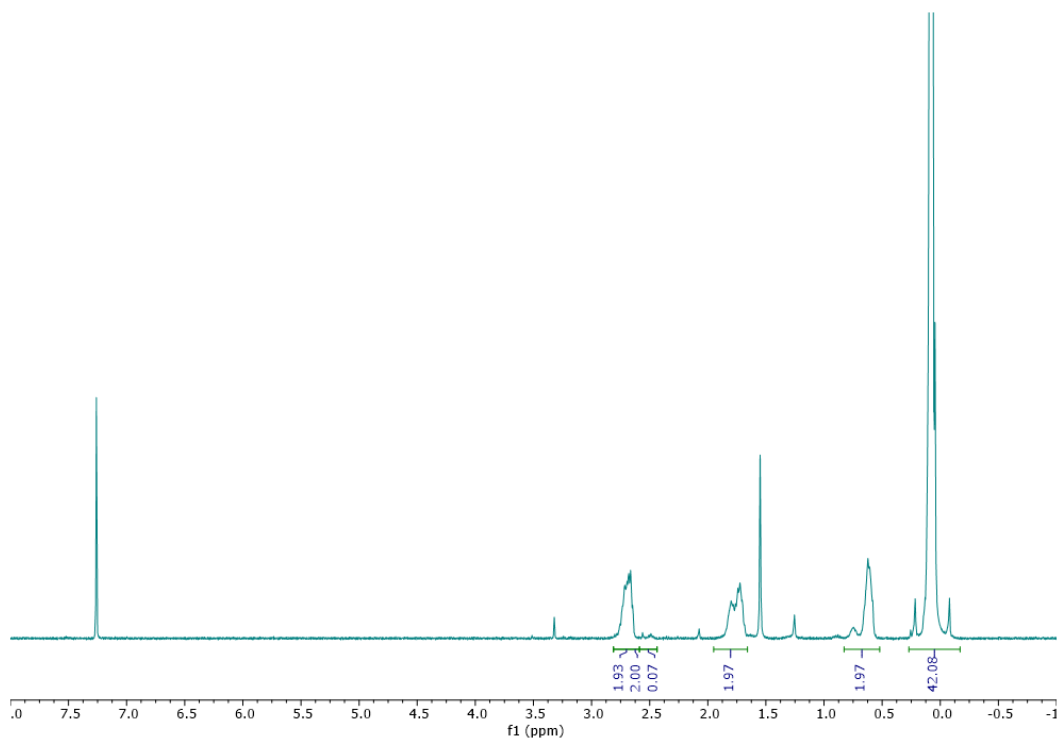


Figure S14. ¹H NMR spectrum with integration ratios of 13-17% D-PDMS_{1wt%}.

S.III.2. Procedures for syntheses of solid D-PDMS materials

The syntheses of the solid D-PDMS materials in Table 1 and Table S1, *except for 13-17% D-PDMS_{6wt%}*, were conducted using the methodology described for 4-6% D-PDMS_{55wt%}. 4-6% T-PDMS (1.8 g, 1.4 mmol *in thiol*) and Et₃N (0.15 g, 1.5 mmol) in CHCl₃ (2.9 mL) were placed in a round-bottom flask with a compensated addition funnel charged with I₂ (0.22 g, 0.9 mmol) dissolved in CHCl₃ (7.5 mL). The solution was sparged with N₂ for ca. 5 minutes with stirring and closed. The I₂ solution was slowly added to the flask while stirring (1 drop every 2-3 s). After stirring for an additional 7 days, the reaction mixture was condensed under a stream of N₂, resulting in a red, gelatinous solid. The crude product was combined with acetone (120 mL). The acetone became yellow, consistent with the solubilization of excess I₂ [6]. Concomitantly, the solid product turned from red to amber yellow. The acetone was removed by gravity filtration. The solid was collected and the process was repeated until the acetone appeared clear after filtration (correspondingly, to when the polymer became straw colored and remained so). After filtration, the polymer was sonicated in a mixture of acetone (60 mL) and CHCl₃ (10 mL) for one hour, after which it was filtered. The solid was then swelled in CHCl₃ (60 mL) and filtered. Finally, the solid was rinsed with DI water, soaked in acetone, filtered, and finally immersed in CHCl₃ and filtered. Residual solvent was removed in vacuo (23-200 mmHg) at RT. The isolated material, 4-6% D-PDMS_{55wt%}, was a gummy, straw-colored solid (0.91 g, 51% yield).

S.III.3. Synthesis of 13-17% D-PDMS_{6wt%}

An amount of 13-17% T-PDMS was oxidized at a concentration of 6wt%, and the product, 13-17% D-PDMS_{6wt%}, was isolated using the reaction methodology described for the non-solid products in section S.III.1. After the aqueous washes, the CHCl₃ solution containing 13-17% D-PDMS_{6wt%} was dried over anhyd MgSO₄. Prior to the removal of solvent, the solution formed a solid gel. After all solvent was removed from the gel, the clear, light-yellow solid was insoluble in all tested solvents. The list of solvents is included in the main text. The 13-17% D-PDMS_{6wt%} was later swelled and filtered using the same methodology used for the other solid products.

S.III.4. Attempted synthesis of 13-17% D-PDMS in solvent free conditions

The ¹H NMR spectra of 13-17% T-PDMS and its oxidation product formed using solvent-free conditions are shown in Figure S15.

The peak at 2.69 ppm (1.49H, -CH₂SS-) indicates that ca. 75% of the thiols were converted to disulfides. The peaks at 2.52 ppm (0.32H, -CH₂SH) and 1.32 ppm (0.13H, -CH₂SH) indicate that ca. 13-16% of the thiol groups remain. The peaks at 3.21 (t, 0.17H), 2.96 (m, 0.05H), and 1.38 (t, 0.27H) are due to unknown impurities that formed during the reaction.

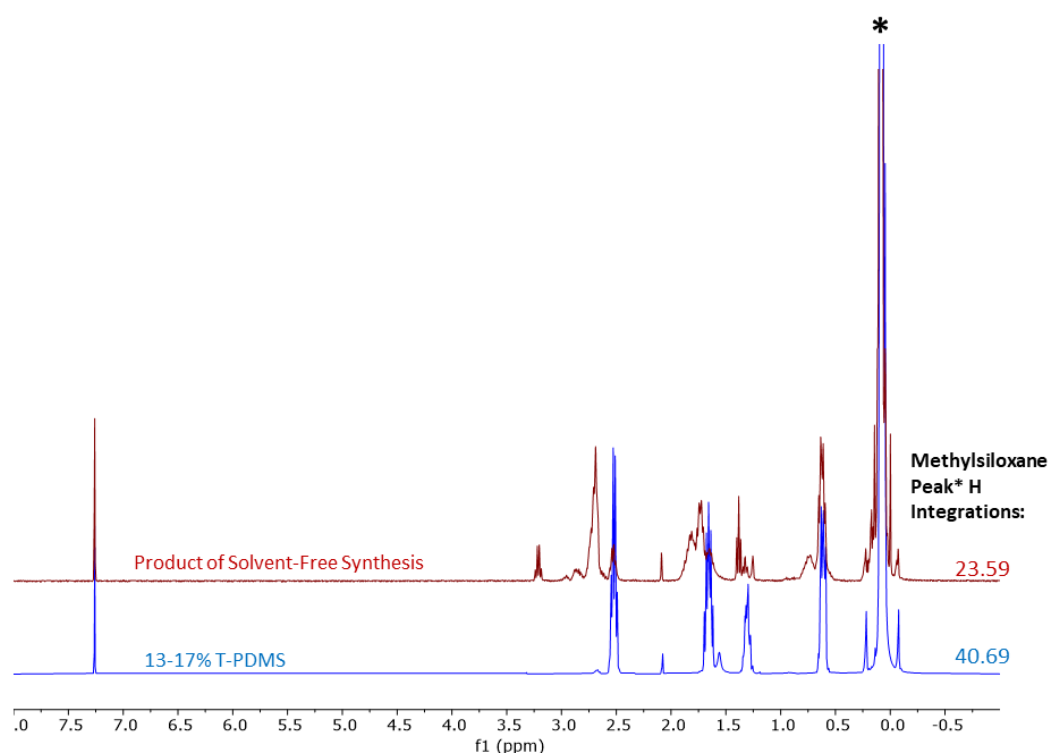


Figure S15. ^1H NMR spectra of 13-17% T-PDMS (blue) and the oxidation product formed under solvent-free conditions (red). Methylsiloxane peak integrations are relative to the $-\text{SiCH}_2\text{CH}_2-$ peak, which was set to 2H.

S.IV. Solution-State COSY and ^{13}C NMR spectroscopy of liquid 4-6% T-PDMS and 4-6% D-PDMS_{2wt%}

The peaks from -1 to 2.2 ppm in the solution-state ^{13}C NMR spectra of 4-6% T-PDMS (Figure S4) and 4-6% D-PDMS_{2wt%} (Figure S12) can be attributed to the methylsiloxane carbon atoms (Figure S3). Some small peaks, due to impurities of an unknown origin, are visible in these spectra, which are shown staggered in Figure S16. 4-6% T-PDMS and 13-17% T-PDMS each exhibit a small impurity peak at 16.39 and 16.35 ppm, respectively. The solution-state NMR spectrum of 4-6% D-PDMS_{2wt%} has several small impurity peaks at 15.0, 21.77, 23.99, 23.75, 29.86, 43.16, and 43.88 ppm.

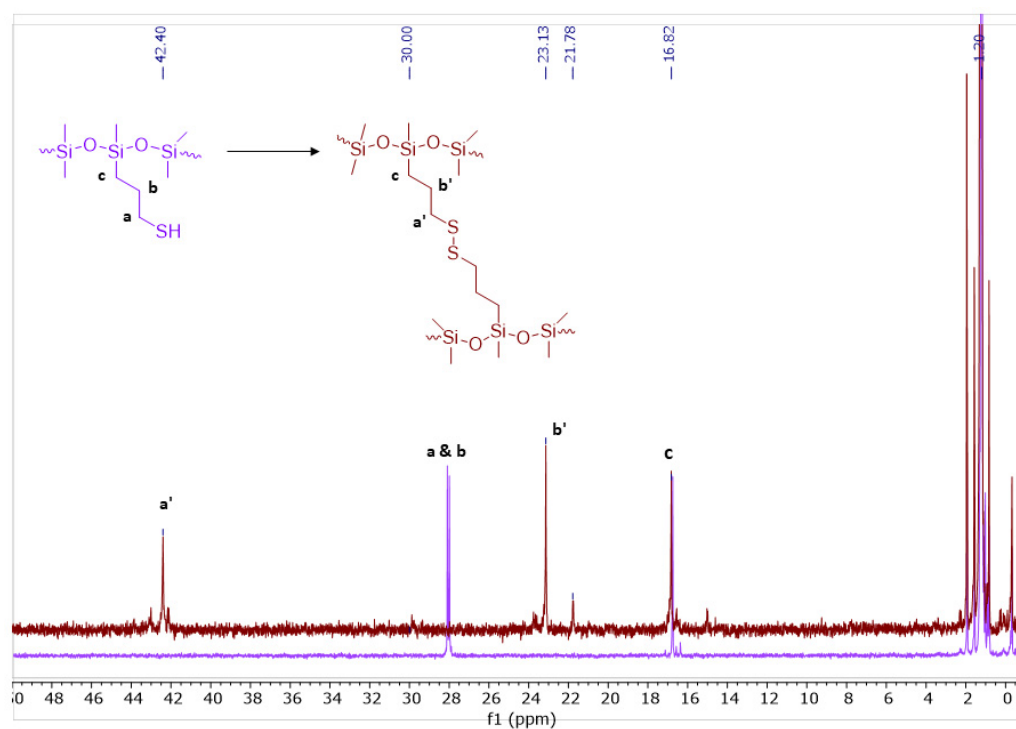


Figure S16. Solution-Phase ^{13}C NMR spectra of 4-6% T-PDMS (purple) and its oxidation product 4-6% D-PDMS_{2wt%} (red).

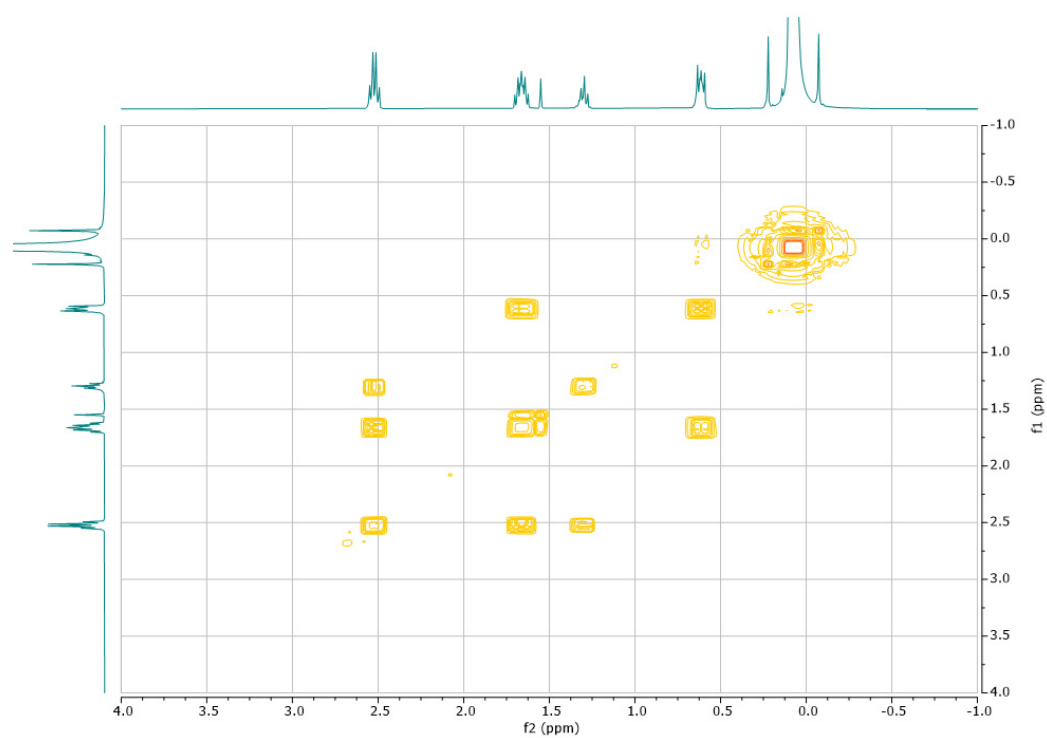


Figure S17. Solution-Phase homonuclear ^1H - ^1H correlation (COSY) spectrum of 4-6% T-PDMS.

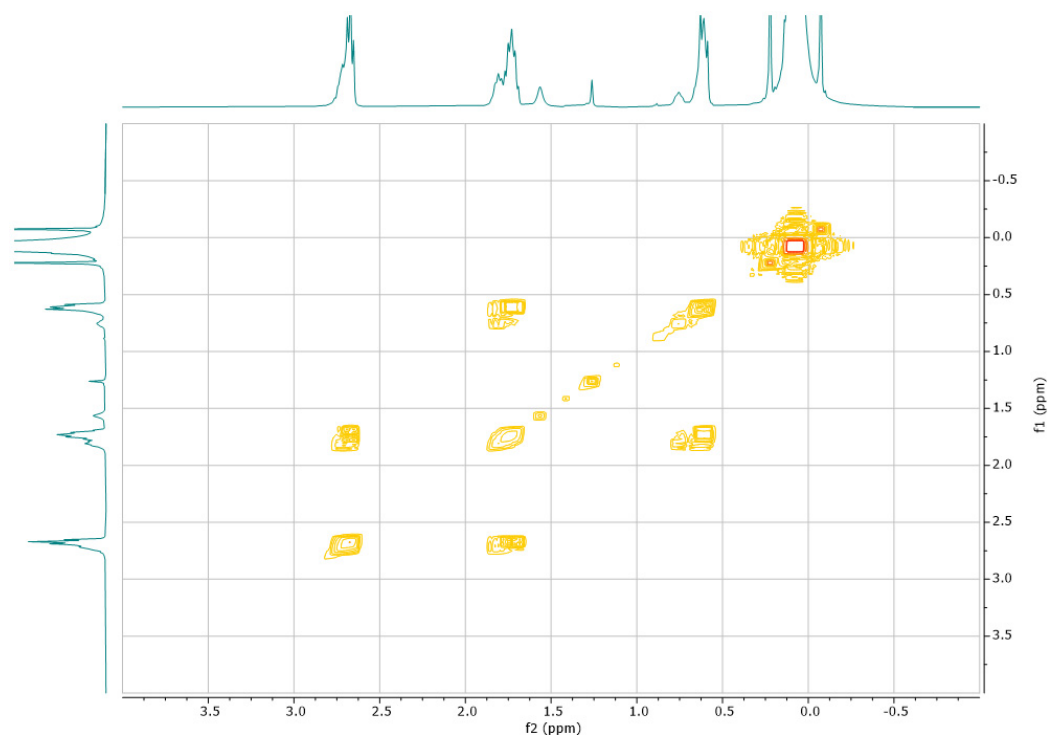


Figure S18. Solution-phase COSY spectrum of 4-6% T-PDMS_{2wt%}.

S.V. Alternative methodologies for the quantification of thiol content in D-PDMS materials

An assay of the liquid T-PDMSs and D-PDMSs was attempted using 4,4'-dithiodipyridine (DTDP; 4,4'-dithiodipyridine from Sigma-Aldrich, 96%, used as received), which reacts similarly to, but is more hydrophobic than, Ellman's reagent [7]. Thiols and DTDP are reported to react quantitatively, producing a cyclic thiopyridone that strongly absorbs in the ultraviolet-visible range [8]. However, it was not possible to generate a linear calibration curve (absorbance vs. concentration) using procedures from the literature [9,10].

S.VI. Rheological measurements of liquid D-PDMS materials

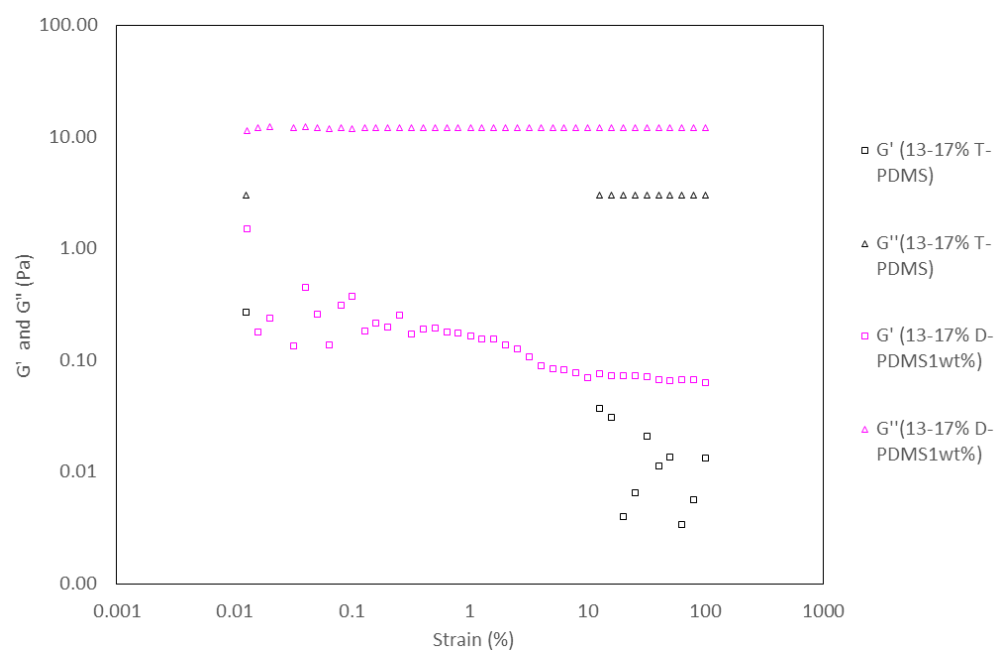


Figure S19. Amplitude sweeps of 13-17% T-PDMS and 13-17% D-PDMS_{1wt%}.

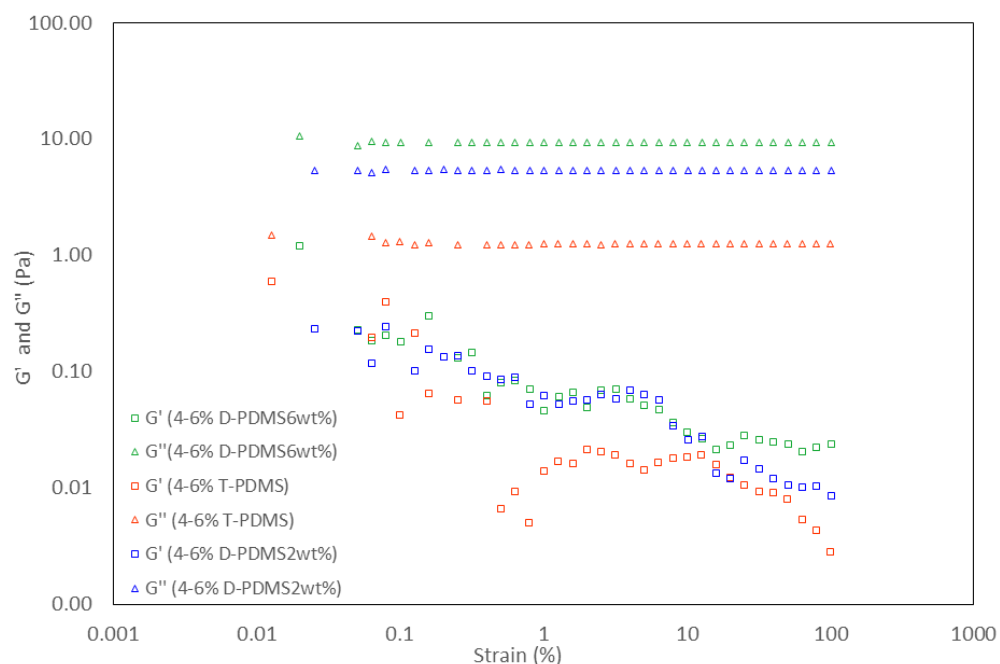


Figure S20. Amplitude sweeps of 4-6% T-PDMS, 4-6% D-PDMS_{2wt%}, and 4-6% D-PDMS_{6wt%}.

S.VII. Swelling studies of solid D-PDMS materials

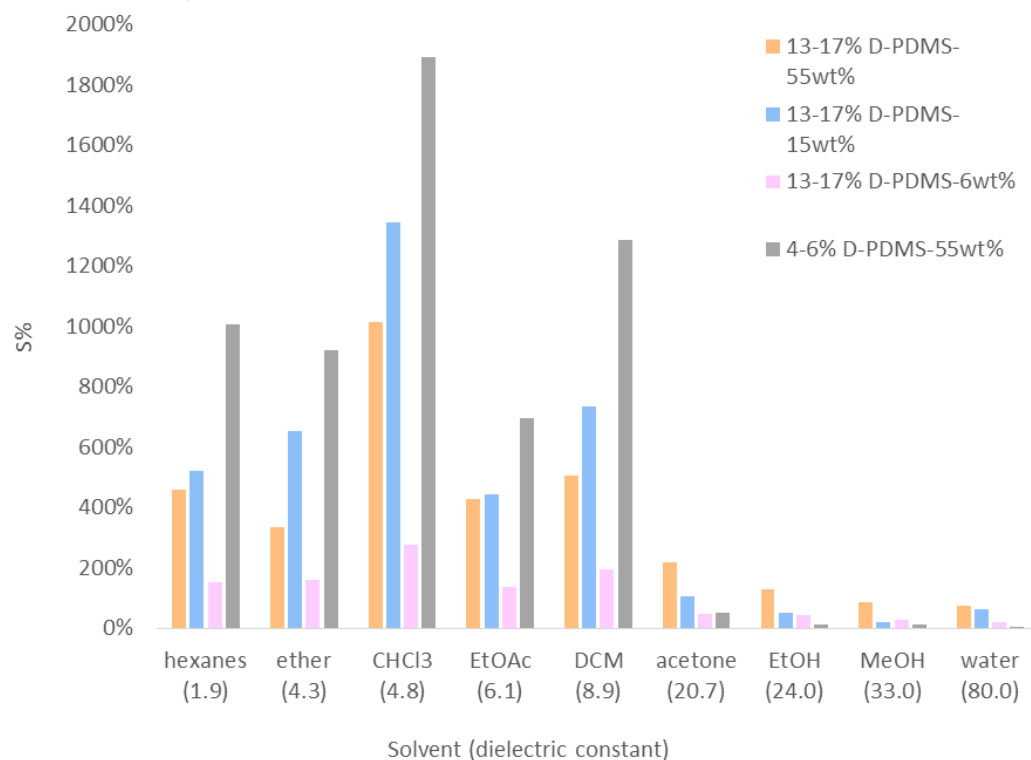


Figure S21. Percent increase in polymer mass (S%; see main text for specific explanation) of solid D-PDMS materials due to swelling in various solvents. Note: the dielectric constant (ϵ) of the solvent increases from left to right; values are provided in parentheses under each solvent name.

Table S3. Solvent Hildebrand solubility parameter (δ) and dielectric constant (ϵ), and swelling rankings based on mass (where 1 is best) for 4-6% D-PDMS_{55wt%} and other crosslinked PDMS materials.

Solvent	δ [11]	ϵ [12,13]	Relative swelling rank from ref. [11] ¹	4-6% D-PDMS _{55wt%}		PDMS-based materials in the literature (S%)		
				Swelling rank (based on S%)	S%	ref. [14] ²	ref. [15] ¹	ref. [16] ³
hexanes	7.3	1.9 ⁴	3	3	1010%	390%	130%	
ether	7.5	4.3	2	4	920%	360%	145%	
CHCl ₃	9.2	4.8	1	1	1890%	1050%		
EtOAc	9.0	6.1	5	5	700%	495%		75%
DCM	9.9	8.9	4	2	1290%	705%	180%	
acetone	9.9	20.7	6	6	50%	100%		30%
EtOH	12.7	24.0	7	7	10%	25%	10%	6%
MeOH	14.5	33.0	8	8	10%			
water	23.5	80.0	9	9	>10%	0%	0%	

¹ Reference [11] and [15] data for Sylgard 184 silicone, a two-part PDMS elastomer prepared with 10:1 (wt:wt) ratio of PDMS base; ² Reference [14] data for 3-aminopropylmethylsiloxane-dimethylsiloxane copolymer with 6-7% amino content, after crosslinking with CS₂; ³ Reference [16] data for dense silicone rubber samples prepared from a two-part system comprised of 10:1 (wt:wt) vinyl terminated silicone oil: silane tetrafunctional compounds; ⁴ ϵ of n-hexane.

S.VIII. TGA and TGA-MS of T-PDMS and D-PDMS materials

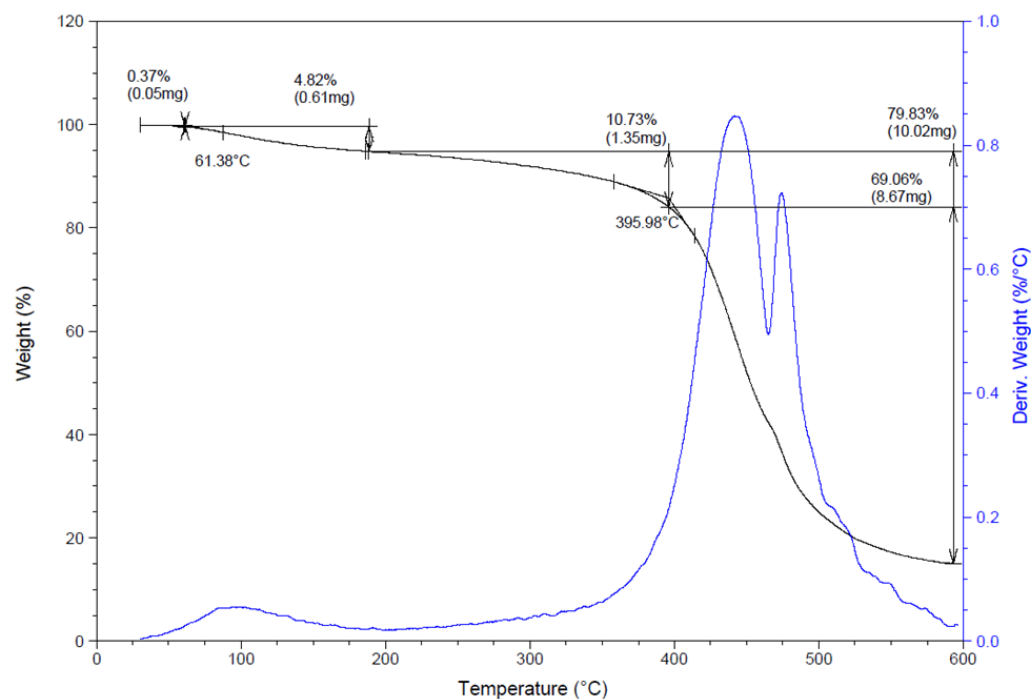


Figure S22. TGA thermogram (green) of 4-6% T-PDMS and its first derivative (blue).

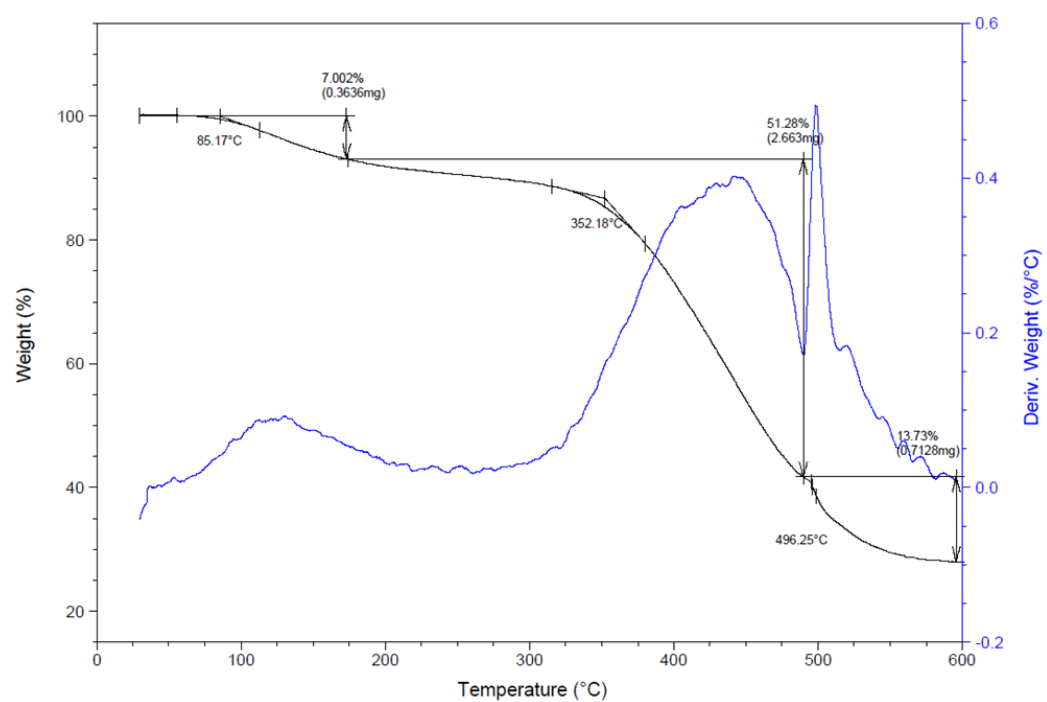


Figure S23. TGA thermogram (black) of 13-17% T-PDMS and its first derivative (blue).

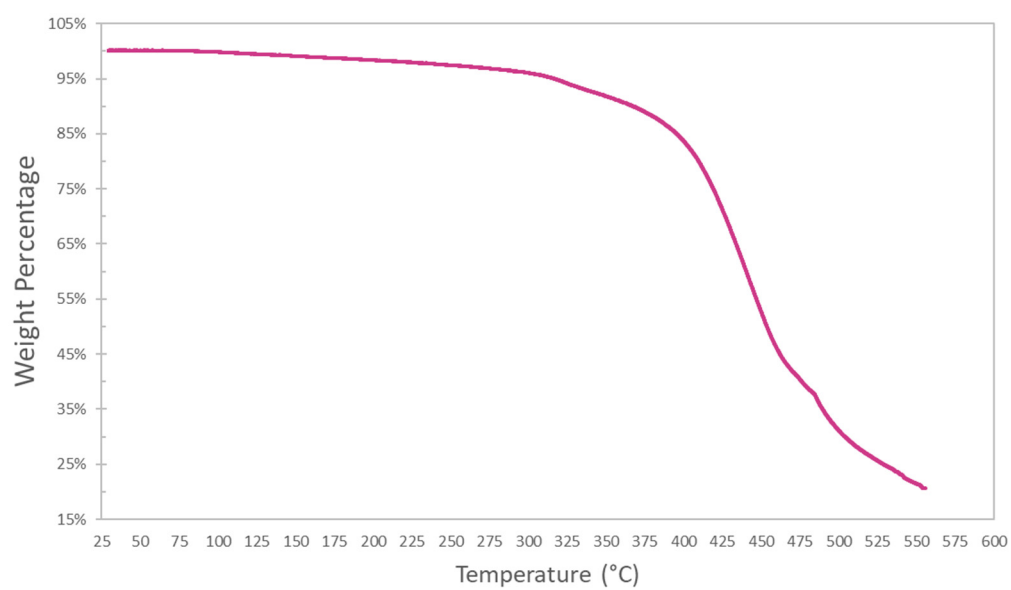


Figure S24. TGA thermogram of 4-6% D-PDMS_{2wt%}.

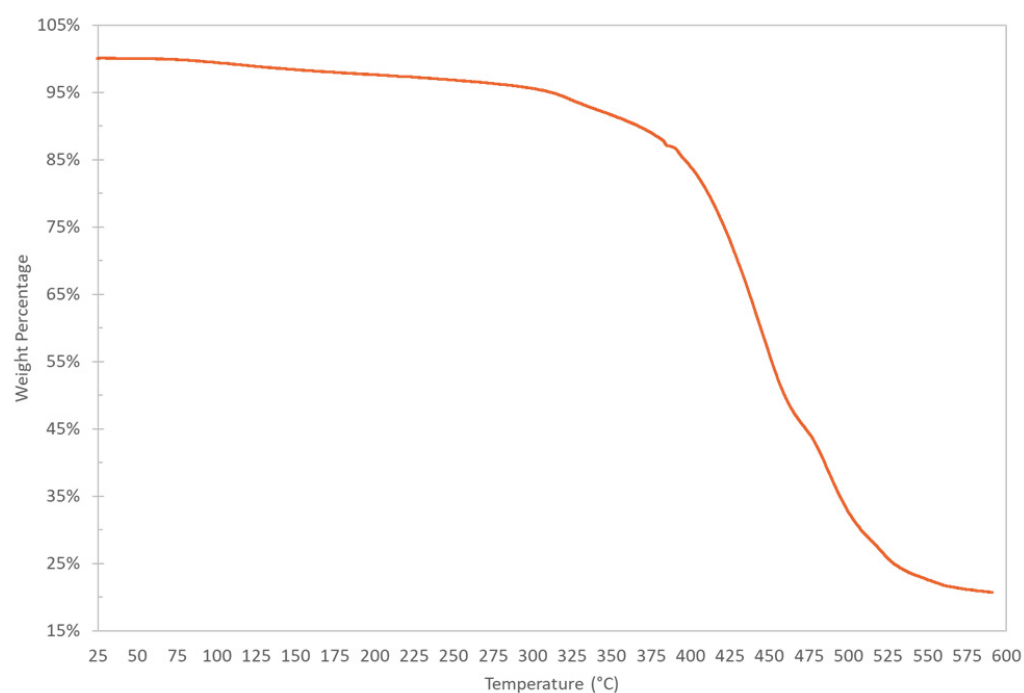


Figure S25. TGA thermogram of 4-6% D-PDMS_{6wt%}.

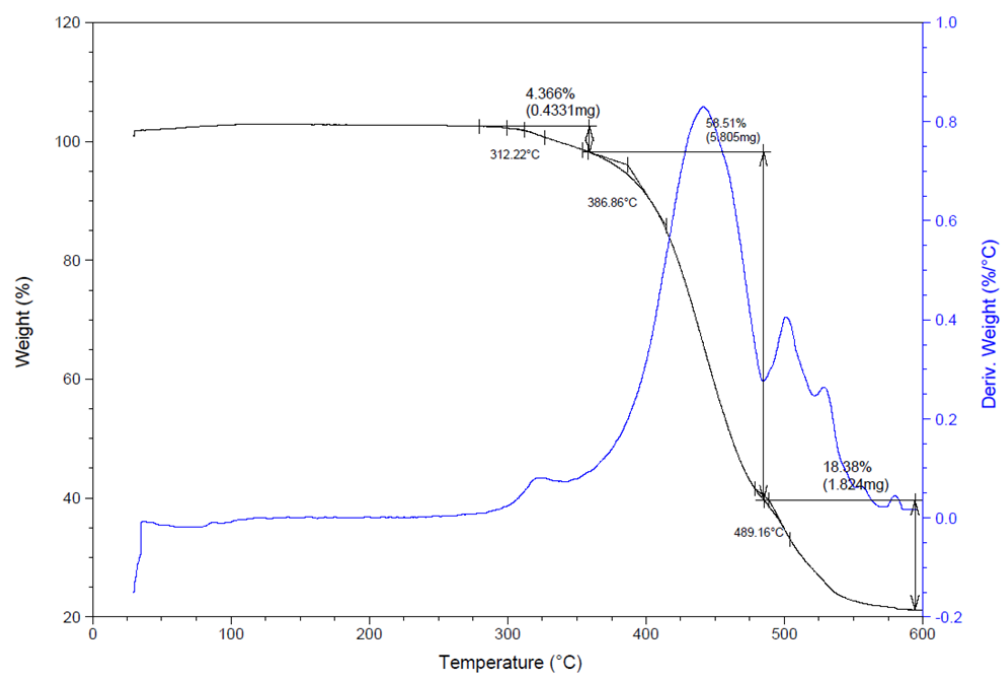


Figure S26. TGA thermogram (black) of 4-6% D-PDMS_{55wt%} and its first derivative (blue).

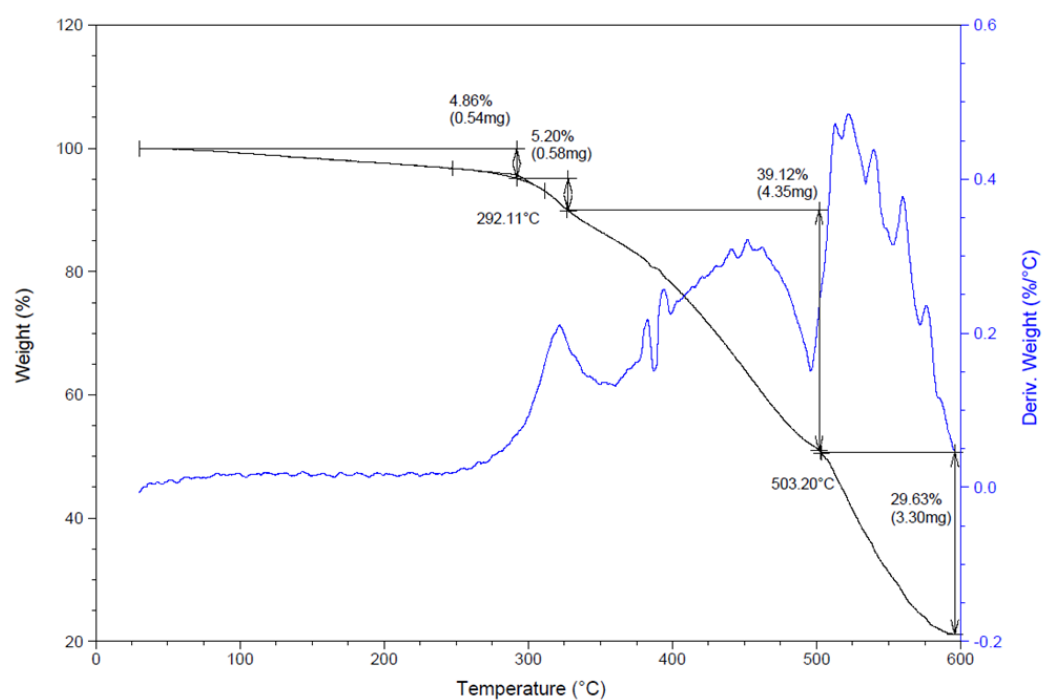


Figure S27. TGA thermogram (black) of 13-17% D-PDMS_{6wt%} and its first derivative (blue).

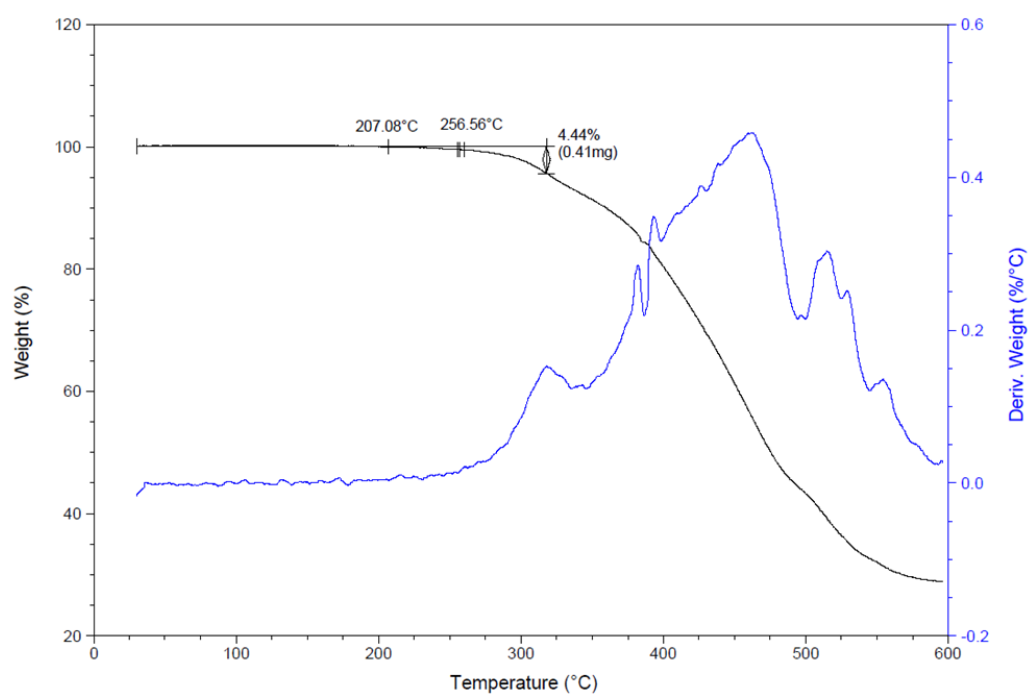


Figure S28. TGA thermogram (black) of 13-17% D-PDMS_{15wt%} and its first derivative (blue).

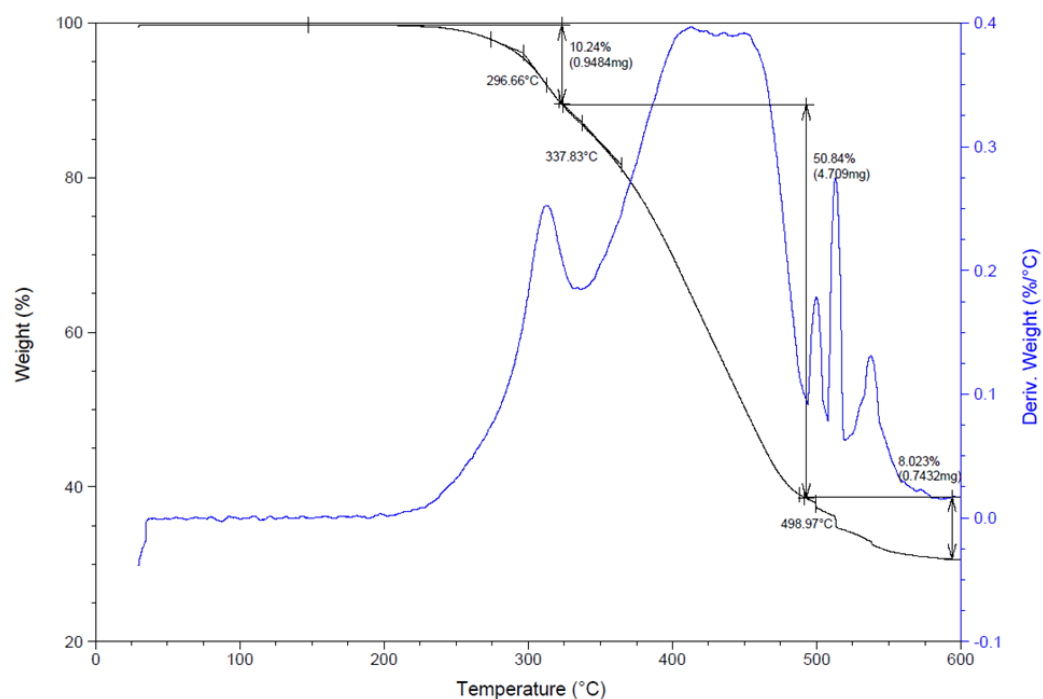


Figure S29. TGA thermogram (black) of 13-17% D-PDMS_{55wt%} and its first derivative (blue).

The TGA thermogram and corresponding MS from the paired TGA-MS experiments on 13-17% T-PDMS are shown in Figure S29 and Figure S30, respectively. Ions close to 34 amu were first detected in the MS (Figure 30S) at ca. 78 minutes. Correcting for the 5-minute lag time between the production of ions during TGA, and their detection by the mass spectrometer, the ions were produced 73 minutes into the TGA experiment, at about 309°C, which is far above the initial thermal decomposition onset (82.6°C) in the thermogram.

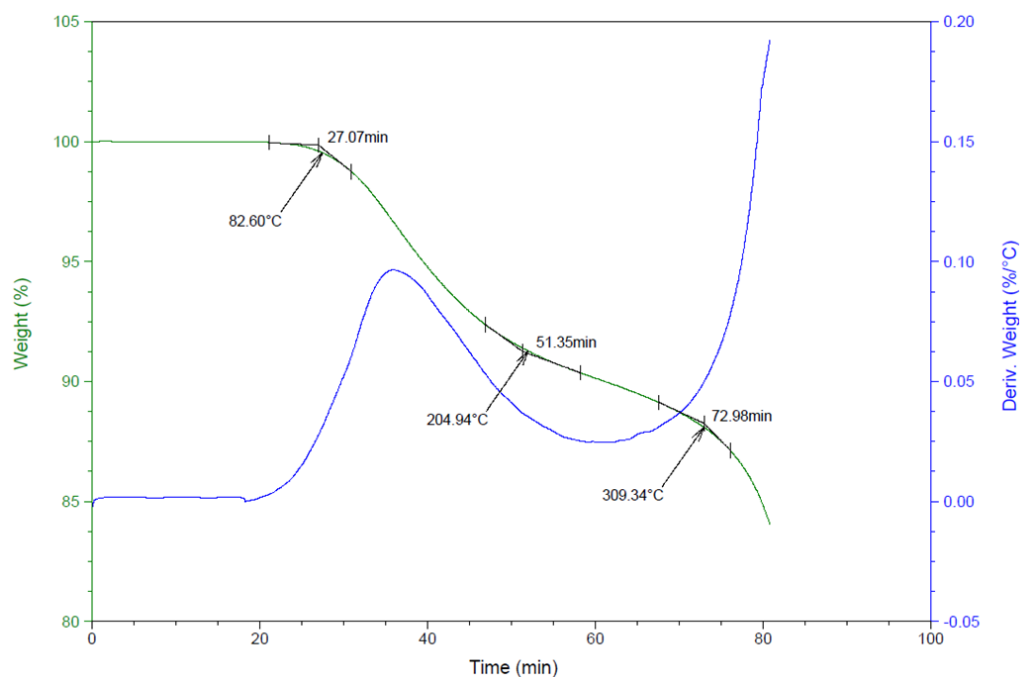


Figure S30. TGA thermogram of 13-17% T-PDMS from the paired TGA-MS experiment.

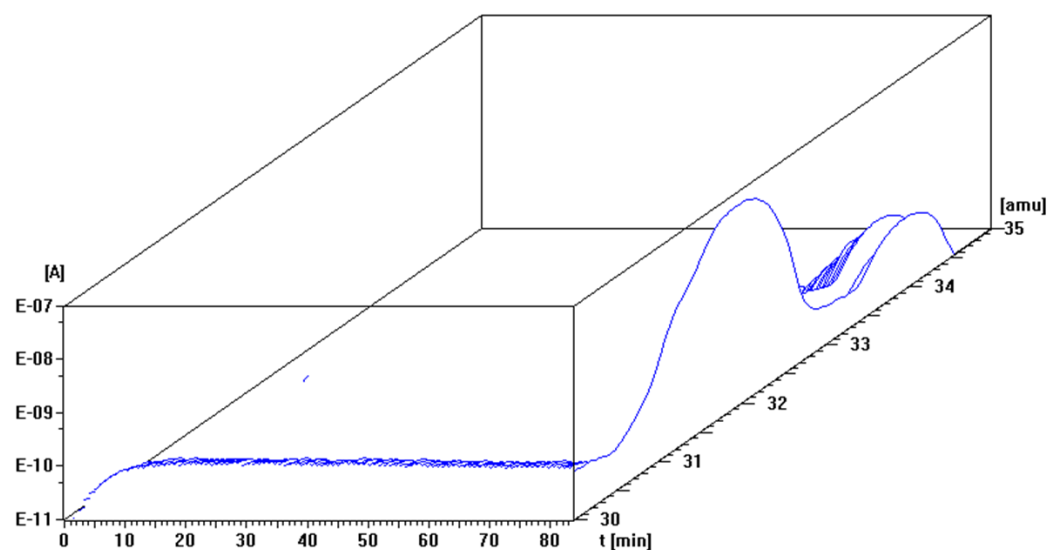


Figure S31. Mass spectrum of 13-17% T-PDMS from the paired TGA-MS experiment.

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