

Supporting Information  
for  
**Vitrimeric Silicone Elastomers Enabled by Dynamic Meldrum's Acid-Derived Crosslinks**

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### ***General Considerations and Instrumentation***

Solvents were purchased from Fisher Scientific and used as received. Siloxane polymers were purchased from Gelest (SMS-142, Molecular weight 3000–4000 13–17% thiol content and SMS-042, Molecular weight 6000–8000 4-6% thiol content) and used as received. Meldrum's acid alkylidene **1** was synthesized according to the method of Wentrup.<sup>1</sup>

NMR spectroscopy was performed using a Varian Inova 500 spectrometer. Thermal analyses (thermogravimetric analysis, differential scanning calorimetry) were performed using a Netzsch STA 449 F1 “Jupiter” simultaneous thermal analyzer. Infrared spectroscopy was performed on a Thermo Nicolet iS10 with a ZnSe crystal ATR attachment. Shear rheology experiments were carried out using an Anton Paar MCR 302 Modular Compact Rheometer. Tensile tests and dynamic mechanical thermal analysis (DMTA) were performed using a TA Instruments RSA G2 DMA. Gel permeation chromatography (GPC) measurements were performed in stabilized, HPLC-grade tetrahydrofuran using an Agilent 1260 Infinity II system with variable-wavelength diode array (254, 450, and 530 nm) and refractive index detectors, guard column (Agilint PLgel; 5 $\mu$ m; 50 x 7.5 mm), and three analytical columns (Agilent PLgel; 5 $\mu$ m; 300 x 7.5 mm; 10<sup>5</sup>, 10<sup>4</sup>, and 10<sup>3</sup> Å pore sizes). The instrument was calibrated with narrow-dispersity polystyrene standards between 640 Da and 2300 kDa (Polymer Standards Service GmbH). All runs were performed at 1.0 mL/min flow rate and 40 °C. Molecular weight values and dispersities were calculated based on the refractive index signal. High-performance liquid chromatography-mass spectrometry (LCMS) data for kinetic measurements were obtained using an Agilent 6120 Quadrupole LC/MS equipped with a Poroshell 120 EC-C18 2.7  $\mu$ m column (2.1 x 50 mm) and a variable-wavelength diode array detecting at 254 nm. Acetonitrile/water mixtures were used as the mobile phase.

## **Network preparation**

### **Vitrimers (E1)**

Thiol-functionalized PDMS (4 g of 4–6% or 13–17% SH content) was combined with crosslinker **1** (264 mg, 0.991 mmol, 2 mol% relative to siloxane repeat units) and xylenes (2 mL, equal to half the volume of PDMS). The mixture was mixed thoroughly using a vortexer and placed into a heating block at 120 °C. Though the crosslinker is not entirely solubilized in the mixture, heating produces a homogeneous mixture and promotes crosslinking. The mixture was manually mixed every 5 minutes by swirling the vial. Just before the gel point (about 30 minutes at 120 °C), the still-liquid mixture was poured into a mold. Curing was finished over 14 hours in an oven at 120 °C. Vacuum (~50 torr) was applied at 120 °C for 2 hours to ensure complete evaporation of the solvent. Notably, heating thiol-functionalized PDMS without crosslinker under air returns a clear, colorless liquid, demonstrating that dithiol linkages are unlikely to be responsible for the observed dynamic crosslinking.

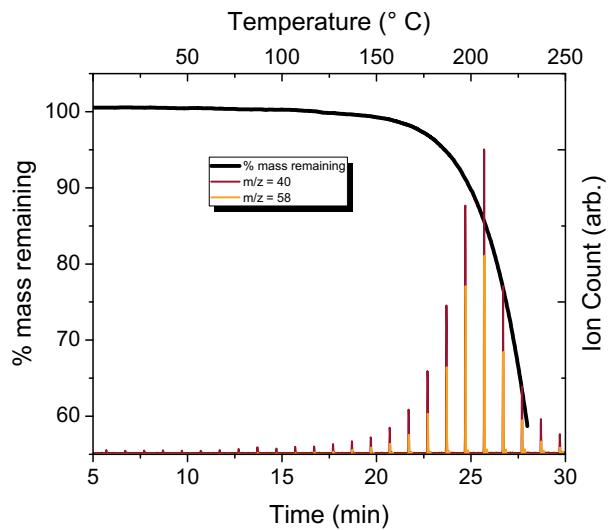
*Note: This reaction evolves methanethiol gas, which is a malodorous nuisance. All manipulations were carried out in the fume hood, and any spills can be deodorized using a bleach solution.*

### **Control Network (E2)**

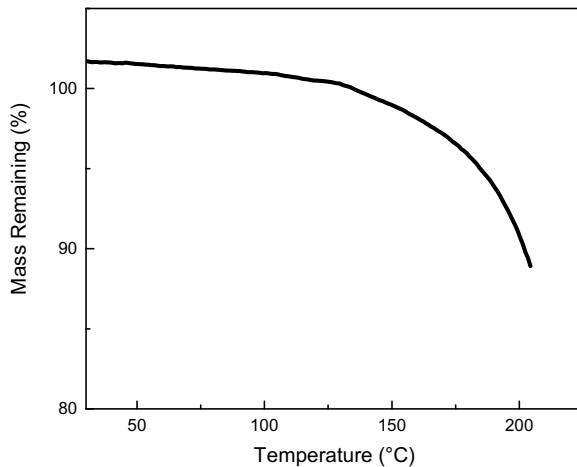
This procedure was adapted from Hawker and coworkers.<sup>2</sup> 1,4-diallyloxybenzene (51 mg, 0.27 mmol, 2 mol% of all the siloxane repeats) was combined with the 13–17% SH functional PDMS (1 g) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (2 mg, 6.6 μmol) were combined and mixed thoroughly using a vortexer. This mixture was poured into a circular mold and irradiated for 2 hours at 365 nm using a handheld UV lamp.

### *Thermal Gravimetric Analysis-Mass Spectrometry*

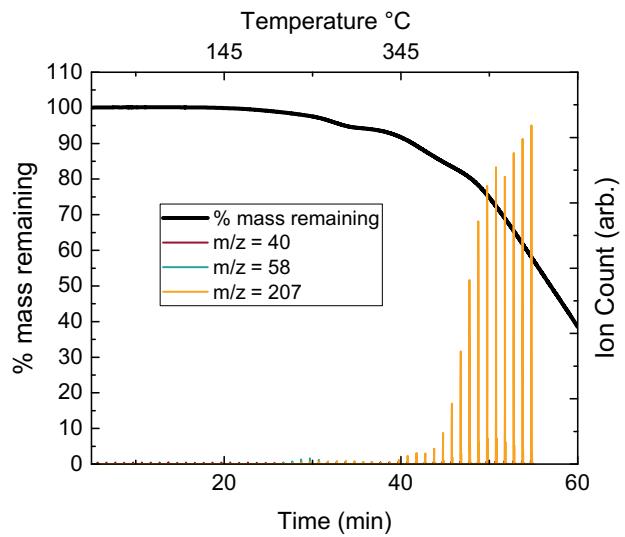
Thermograms were obtained using a 10 K/min heating rate.



**Figure S-1:** Thermogram of **1** under helium (50 mL/min)



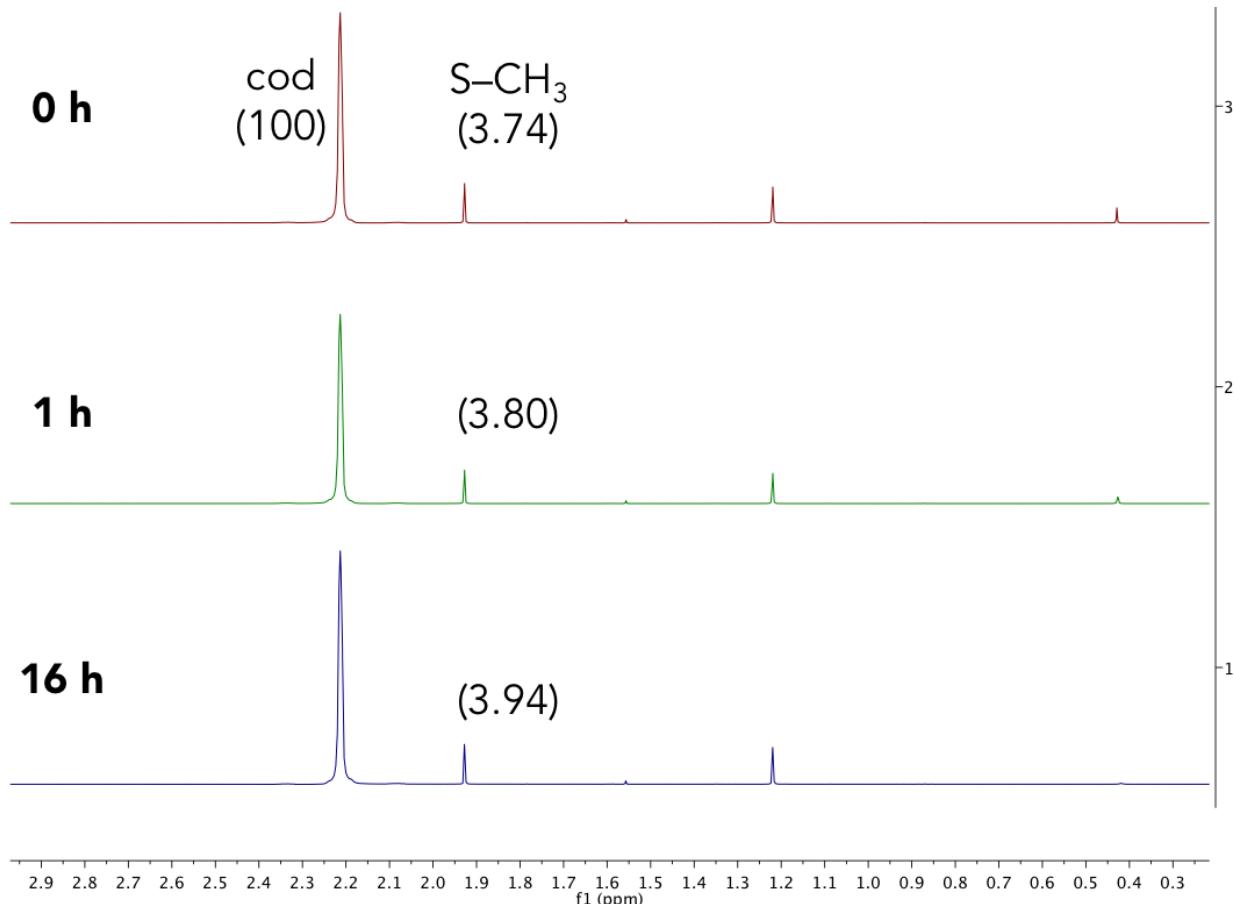
**Figure S-2:** Thermogram of **1** under air (50 mL/min)



**Figure S-3:** Thermogram of vitrimeric elastomer **E-1** under helium (50 mL/min) The  $m/z = 207$  signal corresponds to a siloxane oligomer.

### NMR Stability Study

Compound **1** and 1,4-cyclooctadiene (cod) were sealed in a J-Young tube in C<sub>6</sub>D<sub>6</sub> under ambient conditions, and the mixture was heated to 100 °C for 16 hours. NMR spectra were periodically collected to evaluate the thermal stability of **1**.



**Figure S-4:** NMR study of **1** at 100 °C in C<sub>6</sub>D<sub>6</sub> shows 5% change in the integration of S-CH<sub>3</sub> protons versus a cyclooctadiene internal standard.

### *Vitrimer Reprocessing*

The cut samples of crosslinked siloxane polymer were sandwiched between two metal plates with 2 mm or 1 mm spacers to regulate the thickness of the resulting re-molded polymer. Nonstick polyimide sheets were placed between the polymer and the metal plates to facilitate the removal of the re-molded polymer. The sandwich was placed in a hot press at 150 °C for 15 minutes using 9 ram tons of force. Samples were cut out of the resulting re-molded mass and subjected to shear rheological testing, tensile testing, or DMTA.



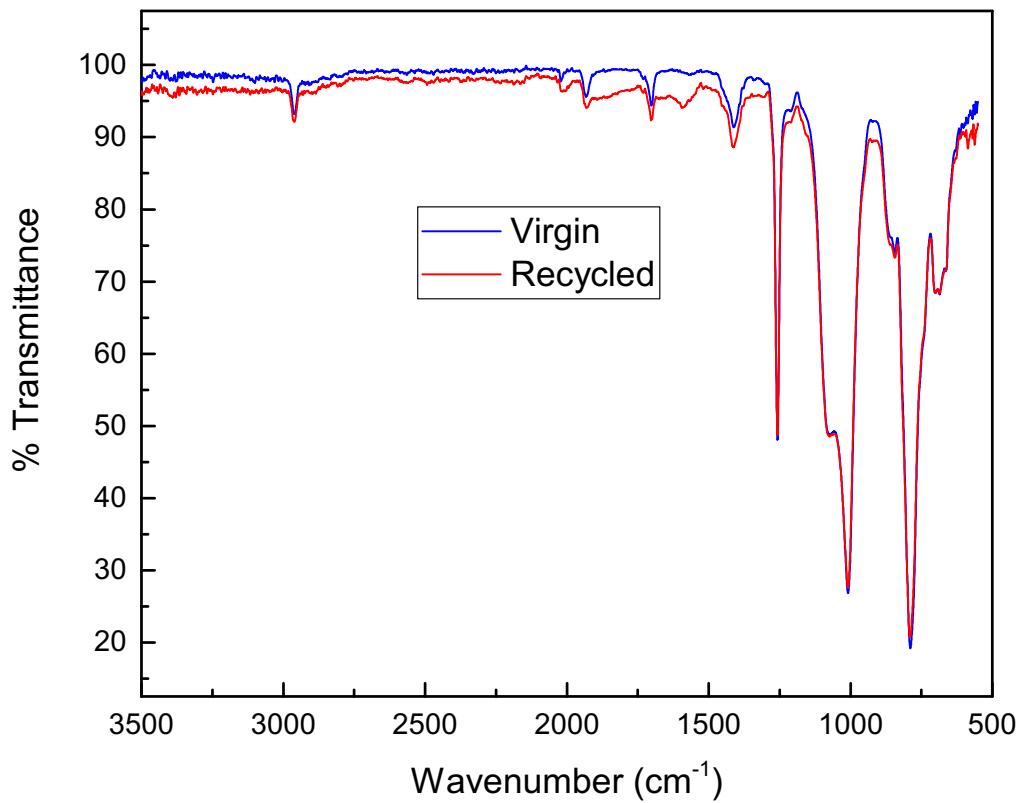
**Figure S-5:** The hot press.

As recycling progressed, gel fraction experiments were carried out in the following manner. A sample (~80–100 mg) was allowed to equilibrate in toluene at 70 °C for 24 hours. The solvent was removed from the swollen samples which were then placed in a vacuum oven connected to the house vacuum (250 torr) at 70 °C for 18 hours. The gel fraction was taken to be the ratio of the starting mass to the mass after the sample was removed from the vacuum oven.

**Table S-1: Gel fraction as a function of number of reprocessing cycles**

# times recycled	virgin	1	2	3	10
gel fraction	0.69	0.64	0.61	0.65	0.56

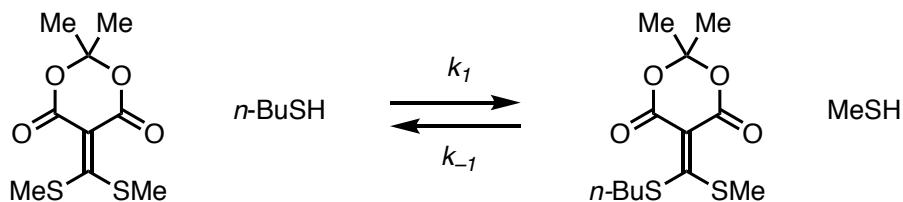
*Infrared Spectra of Virgin and Reprocessed Samples*



**Figure S-6:** IR Spectra of virgin and reprocessed samples.

## Small Molecule Kinetics

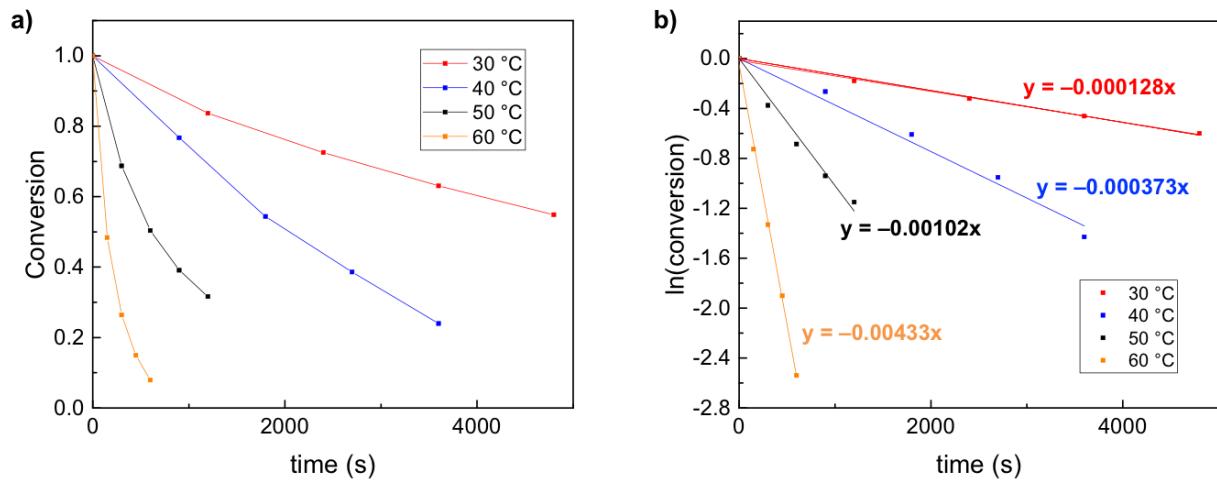
A stock solution of Meldrum's acid alkylidene **1** (15 mg/mL) and mesitylene (internal standard, 27 mg/mL) was made using dry acetonitrile. Each separate run was carried out using 1 mL of the stock solution. Conversion was monitored by HPLC. Reactions were run under pseudo-first order conditions (15 equiv. *n*-butanethiol) and under a slow dynamic flow of nitrogen. Without dynamic nitrogen flow, negligible conversion of the starting material was observed. This observation implies that the reverse reaction's rate constant is comparable to that of the forward reaction.



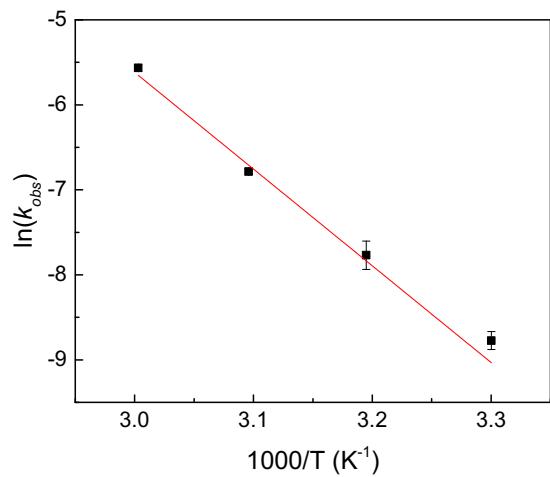
The dynamic flow of nitrogen ensures removal of methanethiol from the reaction mixture, allowing the decay of the signal of the starting material to correspond directly to the rate of thiol exchange. Each reported data point is the average of three trials:

**Table S-2: Individual observed rate constants for the disappearance of 1**

Temperature (°C)	$k_{obs} 1$ (x 10 <sup>4</sup> s <sup>-1</sup> )	$k_{obs} 2$ (x 10 <sup>4</sup> s <sup>-1</sup> )	$k_{obs} 3$ (x 10 <sup>4</sup> s <sup>-1</sup> )	$k_{obs} \text{ average}$ (x 10 <sup>4</sup> s <sup>-1</sup> )
30	2.08	1.28	1.28	1.55 ± 0.04
40	2.53	6.42	3.73	4.23 ± 0.16
50	11.7	10.2	12.1	11.3 ± 0.1
60	36.5	43.3	35.1	38.3 ± 0.4



**Figure S-7:** Representative plots of (a) conversion vs. time (lines are to guide the eye only) and (b)  $\ln(\text{conversion})$  vs. time with linear fit for pseudo-first order rate constants  $k_{\text{obs}}$ .



**Figure S-8:** Arrhenius plot tracking the disappearance of **1** with 15 equiv *n*-butanethiol at 30, 40, 50, and 60 °C.  $E_A = 88.9 \pm 4.8 \text{ kJ/mol}$  ( $21.2 \pm 1.2 \text{ kcal/mol}$ ),  $A = 3.0 \times 10^{11} \text{ s}^{-1}$ .

## Rheology

All shear rheology tests were carried out using an Anton Paar MCR-302 Rheometer in parallel-plate configuration. For stress relaxation experiments, 1 N normal force was applied to begin each run. High-temperature experiments were carried out using the flat Peltier plate accessory. The sample was allowed to equilibrate at the given temperature for 10 minutes before data were collected. Stress relaxation experiments were executed at 10% strain.

Stress relaxation can be understood to follow the Maxwell equation for viscoelasticity:

$$\frac{G(t)}{G_0} = e^{\frac{-t}{\tau^*}}$$

where  $G(t)$  is the relaxation modulus at time  $t$ ,  $G_0$  is the initial relaxation modulus, and  $\tau^*$  is the characteristic relaxation time constant. Where  $t = \tau^*$ ,  $G(t)/G_0 = 1/e$  or about 0.37. In our measurements,  $G_0$  was taken to be the relaxation modulus at  $t = 2$  s. By this time, fast relaxation processes associated with small reorganizations have already taken place, and stress relaxation occurring subsequent to these initial processes at short time-scale should correspond in large part to the exchanging crosslinks or the long-range reorganization of polymer chains. These  $\tau^*$  values determined at 120, 130, 140, and 150 °C were plotted against the inverse of those temperatures using an Arrhenius-like model:

$$\ln(\tau^*) = \ln(A) + \frac{E_A}{RT}$$

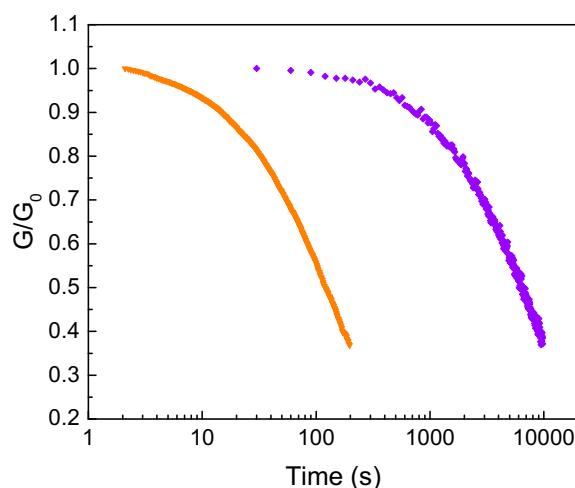
The activation energies reported in the main text are the average of three independent trials:

**Table S-3: Measured relaxation times for E1**

<b>1x Recycled</b>			<b>2x Recycled</b>			<b>τ* (s)</b>		
Temperature (°C)	Sample 1	Sample 2	Sample 3	Temperature (°C)	Sample 1	Sample 2	Sample 3	
120	843	773	672	120	716	716	741	
130	733	430	538	130	426	459	361	
140	326	319	326	140	300	297	257	
150	198	198	204	150	191	182	165	
<b>E<sub>A</sub> (kJ/mol)</b>	71.0	60.7	56.2	<b>E<sub>A</sub> (kJ/mol)</b>	59.7	62.7	67.1	

<b>3x Recycled</b>			<b>10x Recycled</b>			<b>τ* (s)</b>		
Temperature (°C)	Sample 1	Sample 2	Sample 3	Temperature (°C)	Sample 1	Sample 2	Sample 3	
120	863	787	791	120	858	760	838	
130	652	507	516	130	467	484	529	
140	315	306	363	140	288	307	323	
150	205	195	213	150	193	198	217	
<b>E<sub>A</sub> (kJ/mol)</b>	69.5	64.8	59.2	<b>E<sub>A</sub> (kJ/mol)</b>	68.7	62.0	62.6	



**Figure S-9:** Comparison of stress relaxation for lower thiol-content networks (4-6% thiol, purple trace) as compared to network E1 (orange trace) both at 150 °C.

### ***Tensile Testing***

The Young's moduli and strain-at-break data reported in the main text (Figure 3) are the average of three independent trials:

**Table S-4: Measured Young's moduli and strain at break values for E1**

times reprocessed	<i>Young's Modulus (kPa)</i>			<i>Strain at Break (%)</i>		
	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>
1	442	448	440	18	18	13
2	547	568	471	11	14	8
3	495	490	522	11	18	22
10	519	532	530	10	23	12

**Table S-6: Measured Young's moduli and strain at break values for different elastomers**

	<i>Young's Modulus (kPa)</i>			
	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Average</i>
2.5 mol% crosslinker <b>1</b> 13–17% SH	779	786	791	785 ± 5
3 mol% crosslinker <b>1</b> 13–17% SH	1451	1475	1377	1434 ± 41
2 mol% crosslinker <b>1</b> 4–6% SH	434	401	402	412 ± 15
Control elastomer <b>E2</b>	903	825	857	862 ± 32

	<i>Strain at Break</i>			
	<i>Sample 1</i>	<i>Sample 2</i>	<i>Sample 3</i>	<i>Average</i>
2.5 mol% crosslinker <b>1</b> 13–17% SH	6	12	21	13 ± 6
3 mol% crosslinker <b>1</b> 13–17% SH	17	22	9	16 ± 6
2 mol% crosslinker <b>1</b> 4–6% SH	29	35	25	30 ± 4
Control elastomer <b>E2</b>	16	18	36	23 ± 9

### **Dynamic Mechanical Thermal Analysis**

The rubbery plateau storage moduli ( $E'$ ) and  $T_g$  (taken to be the peak of  $\tan(\delta)$ ) for elastomer **E1** reported in the main text are the average of three independent trials:

**Table S-7: Measured storage moduli and  $T_g$  for E1**

times reprocessed	$E'$ (kPa)			$T_g$ (°C)		
	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>
1	333	349	368	-105.7	-105.7	-105.5
2	350	337	313	-105.5	-105.6	-106.1
3	426	412	410	-106.2	-105.4	-105.9
10	421	401	416	-106.6	-106.4	-106.3

As the loading of crosslinker **1** increases, the storage and Young's moduli increase, suggesting an increased crosslink density. A loading of 1 mol% crosslinker **1** yields a sticky material that is difficult to work with and could not be mounted on the DMA instrument.

**Table S-8: Measured storage moduli for different elastomers**

**$E'$  (kPa) Varying the Crosslinker Loading and SH Content**

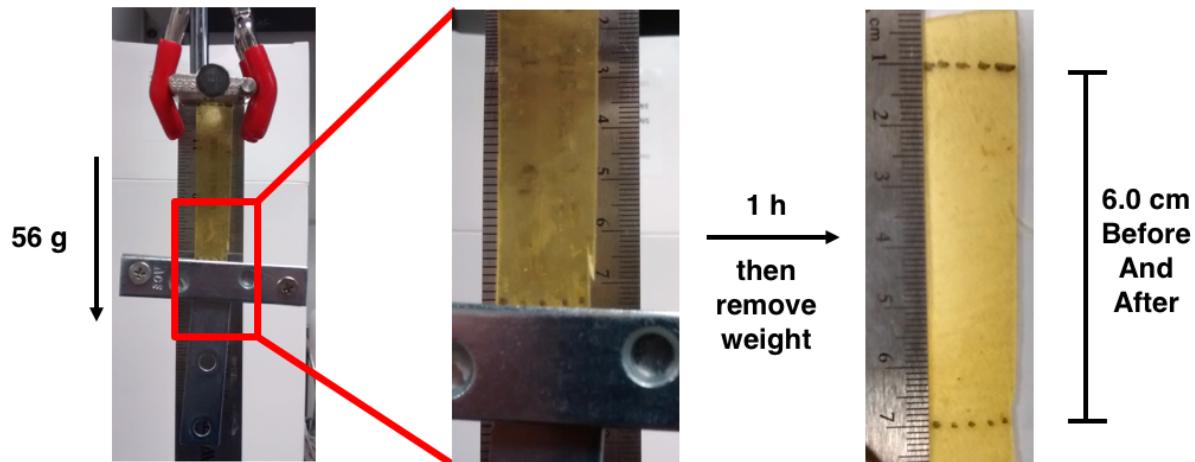
	<b>Sample 1</b>	<b>Sample 2</b>	<b>Sample 3</b>	<b>Average</b>
2.5 mol% crosslinker <b>1</b> 13–17% SH	796	884	947	875 ± 62
3 mol% crosslinker <b>1</b> 13–17% SH	1433	1419	1339	1397 ± 42
2 mol% crosslinker <b>1</b> 4–6% SH	517	576	498	531 ± 33
Control elastomer <b>E2</b>	720	725	884	776 ± 76

### Photos of Silicone Networks Unsuitable for Analysis



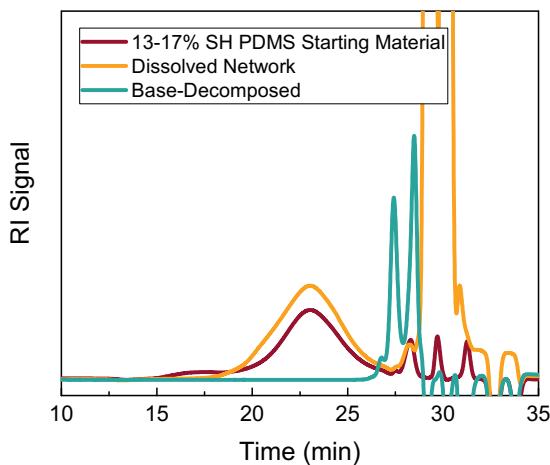
**Figure S-10:** Left: Elastomer made with 1 mol% crosslinker 1 is sticky enough to adhere to a gloved hand and suspend vertically. Sample appears hazy because it partially adhered to the polyamide sheet. Right: 5 mol% crosslinker is easily broken into small pieces.

### Creep Recovery Experiment



**Figure S-11:** Creep recovery experimental setup.

### Gel Permeation Chromatography



**Figure S-12:** GPC Chromatogram for the PDMS starting material and the dissolved network after treating recycled **E1** with mercaptoethanol **2** and after treating the PDMS starting material with tetramethylammonium hydroxide pentahydrate.

Starting PDMS (maroon trace):  $M_n = 9228$ , PDI = 3.86

Dissolved network (goldenrod trace):  $M_n = 8520$ , PDI = 2.37

Starting PDMS with  $\text{Me}_4\text{NOH}$  (30 mol%) (teal trace):  $M_n = 998$ , PDI = 1.04 (First Peak).

### Procedure for Network Dissolution

A thrice-recycled sample of **E1** (90 mg) was swollen in 5 mL THF at 55 °C for 24 hours with the addition of an excess of 1-mercaptopropanol **2** (200 mg). The sample was allowed to cool to room temperature over 24 hours. A 1:1 (v:v) mixture of this solution and fresh THF was subjected to GPC analysis. The calibrated region of the chromatogram ends at 27.5 minutes (corresponds to polystyrene of molecular weight 640). Because no new peaks corresponding to oligomers appear in the calibrated region, we argue that most of the observed stress relaxation corresponds to the dynamic crosslinking action of **1** rather than the free thiols acting as basic catalysts for siloxane exchange.

### **Procedure for Base-Induced PDMS Decomposition**

The 13-17% propylthiol PDMS (100 mg) and tetramethylammonium hydroxide pentahydrate were combined with 2 mL THF. The mixture was briefly sonicated then heated to 60 °C for 2 hours. A 1:1 (v:v) mixture of this solution and fresh THF was subjected to GPC analysis. The loss of the polymer peak and the appearance of a peak corresponding to lower molecular weight species indicates that base does act as a depolymerization agent.

### ***References***

- (1) Ben Cheikh, A.; Chuche, J.; Manisse, N.; Pommelet, J. C.; Netsch, K. P.; Lorencak, P.; Wentrup, C. *J. Org. Chem.* **1991**, *56*, 970–975.
- (2) Campos, L. M.; Truong, T. T.; Shim, D. E.; Dimitriou, M. D.; Shir, D.; Meinel, I.; Gerbec, J. A.; Hahn, H. T.; Rogers, J. A.; Hawker, C. *J. Chem. Mater.* **2009**, *21*, 5319–5326.