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Supporting Information

Elastomers without Covalent Crosslinking: Concatenated Rings Giving Rise to Elasticity

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EXPERIMENTAL SECTION

The elastomers investigated in this study were compared to two different reference samples: (i) a conventional elastomer, and (ii) an entangled PDMS melt.

Investigated elastomers prepared in bulk: Elastomer-HV15, Elastomer-HV22 and Elastomer-HV31 were prepared from three types of α -monovinyl- ω -monohydride terminated PDMS: DMS-HV15 ($\bar{M}_n \approx 4$ kDa, $\bar{D}_M=1.1$, purity 95-100%, Gelest Inc.), DMS-HV22 ($\bar{M}_n \approx 15$ kDa, $\bar{D}_M=1.2$, purity 95-100%, Gelest Inc) and DMS-HV31 ($\bar{M}_n \approx 27$ kDa, $\bar{D}_M=1.2$, purity 95-100%, Gelest Inc) respectively. These three macromonomers, DMS-HV15, DMS-HV22 and DMS-HV31, are the main constituents of the commercial Exsil® elastomers manufactured by Gelest Inc, which also include silica and a catalyst. In this study, however, we used a non-filled polymer system. A representative preparation procedure for Elastomer-HV15 is as follows:

DMS-HV15 (10 g, $\sim 2.5 \times 10^{-3}$ mol of each reactive group) was mixed with platinum-divinyl tetramethyldisiloxane complex (SIP 6830.3, 10 mg, 1.5×10^{-6} mol, 6.2×10^{-4} equivalent, 3.0% Pt in vinyl terminated polydimethylsiloxane, Gelest Inc.) using a speed mixer (DAC150FVZ, Hauschild Co.) for 1 min at 3500 rpm. The mixture was poured into a mold and placed in an oven at 80°C for 10 h.

Investigated elastomers prepared in diluted states: DMS-HV22 (2 g, $\sim 1.3 \times 10^{-4}$ mol, 2.1 mL) was dissolved in toluene ($\geq 99.9\%$, EMD Millipore Corporation) with dissolution ratios (volume ratio between DMS-HV22 and toluene) of 1:1 and 1:3. A constant amount of catalyst (SIP 6830.3, 2 mg, 3.1×10^{-7} mol, 2.4×10^{-3} equivalent) was added to the solutions. The reaction mixture was kept at 80 °C for 30 h. The same procedure was applied for the reaction of DMS-HV31 with dilution ratio of 1:1 and 1:10.

Both bulk and diluted elastomers were submerged in chloroform ($\geq 99.8\%$, Sigma-Aldrich) at room temperature, after toluene evaporation from the diluted elastomers. The liquid phase was decanted off after 48 h and subjected to rotary evaporation followed by vacuum drying at room

temperature. The remains from the decanting procedure constitute the sol fractions of the original samples. The samples prepared with a large dilution ratio (1:3 and 1:10) were completely soluble in chloroform, while all other samples were only partially soluble.

Reference I: Conventional elastomer: Part A was prepared by mixing vinyl terminated PDMS (DMS-V25, $\bar{M}_n \approx 15$ kDa, 5 g, $\sim 3.3 \times 10^{-4}$ mol, 95-100%, Gelest Inc) with cross-linker (HMS-301, 1.9 kDa, 0.69 g, $\sim 3.6 \times 10^{-4}$ mol, 23 wt% methylhydrosiloxane, purity of 95-100%, Gelest Inc.) using a speed mixer (DAC150FVZ, Hauschild Co.) at 3000 rpm for 2 min. Part B was prepared by mixing DMS-V25 (5 g, $\sim 3.3 \times 10^{-4}$ mol) with platinum cyclovinylmethyl siloxane complex catalyst (catalyst 511, 20 mg, 1.0×10^{-7} mol, 1 wt% Pt, Hanse Chemie) using the same speed mixer. Parts A and B were then mixed together at 3000 rpm for 30 s. The final mixture was poured into a mold and placed in an oven at 120°C for 10 h. The prepared elastomer is denoted as Elastomer-V25.

Reference II: Entangled PDMS melt: A standard PDMS melt, with a known crossover point of storage modulus and loss modulus curves at $(\omega, G') = (5.55 \text{ rad s}^{-1}, 2.6 \times 10^4 \text{ Pa})$ at 30°C, was provided by TA Instruments.

Elastomers prepared in silicone oil: Elastomer-HV15, Elastomer-HV22 and Elastomer-V25 were prepared with the addition of various fractions (10 wt%, 20 wt%, 30 wt%, 40 wt%, 50 wt% and 60 wt%, respectively) of silicon oil (DMS-T15, $\bar{M}_n \approx 4$ kDa, 95-100%, Gelest Inc.). A representative preparation procedure for Elastomer-HV15 and Elastomer-V25 with 20 wt% silicone oil is as follows:

The silicone oil (2 g) was mixed with DMS-HV15 (8 g, $\sim 2.5 \times 10^{-3}$ mol) using a speed mixer, and the resulting mixture was added to catalyst SIP 6830.3 (10 mg, 1.5×10^{-6} mol). The final mixture was poured into a mold and cured at 80°C for 10 h. The conventional elastomer Elastomer-V25 was prepared with addition of silicone oil as in *Reference I* (above), except that Part A was prepared by mixing silicone oil (2.67 g) with vinyl terminated PDMS (DMS-V25,

5 g, $\sim 3.3 \times 10^{-4}$ mol) and cross-linker (HMS-301, 0.69 g, $\sim 3.6 \times 10^{-4}$ mol) using a speed mixer.

The samples listed above are summarized in Table S1.

Table S1. Sample names with corresponding explanations

Classes	Sample names	Explanations
Reactants	DMS-HV15	α -monovinyl- ω -monohydride terminated PDMS with $\bar{M}_n \approx 4$ kDa
	DMS-HV22	α -monovinyl- ω -monohydride terminated PDMS with $\bar{M}_n \approx 15$ kDa
	DMS-HV31	α -monovinyl- ω -monohydride terminated PDMS with $\bar{M}_n \approx 27$ kDa
	DMS-V25	Vinyl terminated PDMS with $\bar{M}_n \approx 15$ kDa
	DMS-T15	Polydimethylsiloxane oil with $\bar{M}_n \approx 4$ kDa
Elastomers	Elastomer-HV15	Concatenated ring elastomer prepared from DMS-HV15
	Elastomer-HV22	Concatenated ring elastomer prepared from DMS-HV22
	Elastomer-HV31	Concatenated ring elastomer prepared from DMS-HV31
Ref. I	Elastomer-V25	Conventional elastomer prepared from DMS-V25 and HMS-301
Ref. II	PDMD melt	Standard PDMS melt with crossover of storage modulus and loss modulus curves at 5.55 rad s^{-1} , $2.6 \times 10^4 \text{ Pa}$ (30°C)
Sol fraction	Sol of Elastomer-HV22-Di1:1	Sol fraction of the elastomer prepared from DMS-HV22 in toluene with volume dilution ratio of 1:1 (partly soluble in chloroform)
	Elastomer-HV22-Di1:3	Product from reaction of DMS-HV22 in toluene with volume dilution ratio of 1:3 (completely soluble in chloroform)
	Elastomer-HV31-Di1:1	Product from reaction of DMS-HV31 in toluene with volume dilution ratio of 1:1 (completely soluble in chloroform)
	Elastomer-HV31-Di1:10	Product from reaction of DMS-HV31 in toluene with volume dilution ratio of 1:10 (completely soluble in chloroform)

Tensile tests: Elastomer stress–strain responses were measured using an Instron 3340 materials testing system (INSTRON, US) at a crosshead speed of 500 mm min⁻¹. Specimens were prepared with a dumbbell shape according to ASTM D-638 Type V (width: 3.18 mm; length: 9.53 mm; thickness: 1 mm). Strain recovery was measured by recording the changes in specimen length after stretching to 80% of strain at break and holding for 10 min, then comparing them to the specimen lengths after removing the applied force for 10 min (strain recovery = (80% of strain at break - permanent strain) / 80% of strain at break) · 100%. In order to better visualize specimen stretch, one specimen was red-dyed by painting a thin layer of red pigment (PGRED01, 50% in silicone oil, Gelest Inc.) on its surface. Elastic moduli were determined by linear fitting of the stress-strain data at a strain range of 0-10%.

Size exclusion chromatography (SEC): SEC was carried out on a chromatographic system consisting of a Viscotek VE 2001 GPC Solvent/Sample Module connected to a Viscotek TriSEC Model 302 Triple Detector Array (RI, Light scattering, Viscometer) and an evaporative light scattering detector (PL-ELS 2100 ELSD). The column set consisted of a PL Guard and two PL gel mixed D columns from Polymer Laboratories connected in series; this column combination provides good resolution up to 300,000 Daltons and was calibrated with narrow molar mass PDMS standards (PSS, Mainz, Germany). The mobile phase was tetrahydrofuran. All samples and calibration standards were analyzed using a flow rate of 1 mL min⁻¹. Samples were analyzed using OmniSEC 5.10 software.

Long term swelling: Extracted sol fraction amounts and elastomer swelling ratios were determined using long-term swelling experiments. A roughly 0.1 g sample (mass = m_i , determined to 4 significant digits) with dimensions of approximately 10 mm × 10 mm × 1 mm was immersed in around 20 mL of chloroform at room temperature. The chloroform was replaced after 1 day and decanted off after 2 days. The swollen sample (mass = m_s) was then washed with fresh chloroform and dried for 24 h at room temperature under ambient pressure (mass = m_d). Following the same procedure, the dried sample (m_d) was immersed in

chloroform for an additional 4 days (6 days in total so far). The swollen sample was then washed with fresh chloroform and dried, and the dried sample was subjected to the same swelling treatment for an additional two 6-day periods. The weight of m_i , m_s and m_d were recorded at each round. The extracted sol fraction (%) was calculated as $\frac{m_i - m_d}{m_i} \times 100\%$, and the swelling ratio was calculated as $\frac{m_s - m_d}{m_d}$. Each sample was triplicated.

Linear viscoelasticity (LVE): Sample LVE was measured using a strain-controlled rheometer ARES G2 (TA Instruments), employing small amplitude oscillatory shear (SAOS). Before measuring, samples with thickness of ~ 1 mm were cut into cylinders 8 mm in diameter. The shear strain amplitude was fixed to 2% (ensured to be within the linear regime), and a frequency sweep was performed from 628 to 0.06 rad s⁻¹. The temperature was controlled using an oven under nitrogen atmosphere. Except for the PDMS melt, all samples were measured at 25°C, 100°C and 200°C. The PDMS melt was measured by an ARES (TA Instruments) equipped with cooling N₂ at -65°C, -50°C and 25°C due to its faster dynamics. Time-temperature superposition was used to create master curves based on a reference temperature of 25°C.

Nuclear magnetic resonance spectroscopy (NMR): ¹H NMR spectra of precursor PDMS and sol fractions of elastomers was performed on a Bruker 300 MHz spectrometer on 50 mg mL⁻¹ solutions in CDCl₃. ²⁹Si solid-state NMR MAS spectra of investigated elastomers were acquired on a Bruker Avance III HD spectrometer operating at a magnetic field of 14.05 T ($\nu_L(^{29}\text{Si}) = 119.2$ MHz) and equipped with a 4 mm CP/MAS broadband probe. The spectra were acquired with a spinning frequency of 6 kHz, a $\pi/2$ pulse of 4.75 ms, an acquisition time of 35 ms and 10 seconds of interscan delay. This was determined to be sufficient for full relaxation of the two observed signals for elastomers. High-power ¹H SPINAL64 decoupling ($\nu_{\text{RF}} = 100$ kHz) was employed during acquisition. The prepared elastomers were cut into smaller pieces and packed in 4 mm o.d. zirconia rotors. Chemical shifts are reported relative to TMS (0.0 ppm). High-resolution ²⁹Si NMR spectrum of a precursor PDMS (DMS-HV15) was acquired on a

Bruker Avance II spectrometer operating at a magnetic field of 9.4 T (ν_L (^{29}Si) = 79.495 MHz) and equipped with a 5mm BBFO probe. The NMR samples were prepared as-received (i.e. no deuterated solvent was added) and chemical shifts are referenced using the lock-field determined for a secondary CDCl_3 sample. A Pi/6 pulse was used for excitation with an interscan delay of 15 seconds. Inverse-gated ^1H decoupling was applied during acquisition. Data were analysed using MestReNova-11.

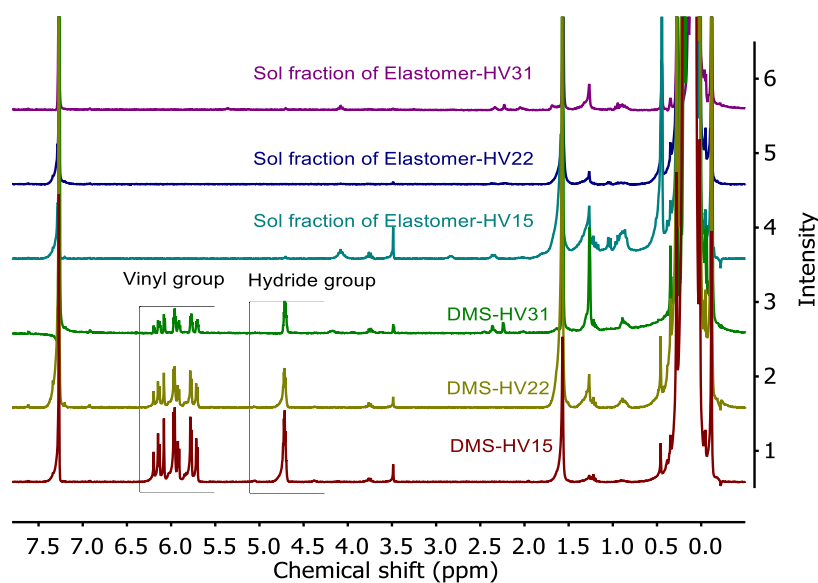


Figure S1. ^1H NMR spectra of precursor PDMS (DMS-HV15, DMS-HV2 and DMS-HV31) and corresponding sol fractions extracted from Elastomer-HV15, Elastomer-HV22 and Elastomer-HV31, respectively. (In CDCl_3 , vinyl group: around 6 ppm; hydride: 4.8 ppm).

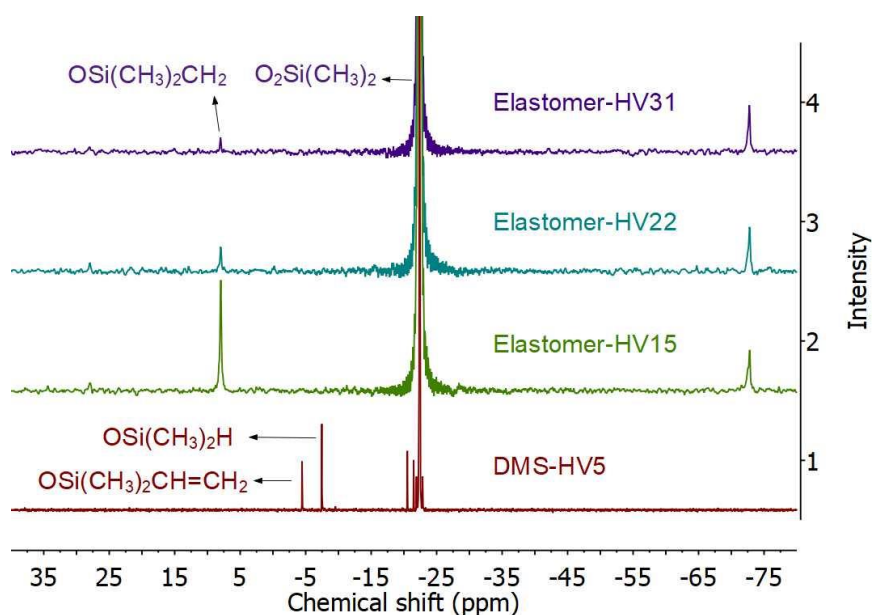


Figure S2. ^{29}Si NMR MAS spectra of precursor PDMS (DMS-HV15) and three types of investigated elastomers (Elastomer-HV15, Elastomer-HV22 and Elastomer-HV31) ($\text{OSi}(\text{CH}_3)_2\text{CH}_2$: 8.0 ppm, $\text{Si}(\text{CH}_3)_2\text{O}_2$: -22.4 ppm, 1st order spinning sideband from signal $\text{Si}(\text{CH}_3)_2\text{O}_2$: 28.0 ppm and -72.8 ppm, $\text{OSi}(\text{CH}_3)_2\text{CH}=\text{CH}_2$: -4.4 ppm, $\text{OSi}(\text{CH}_3)_2\text{H}$: -7.5 ppm).¹⁻

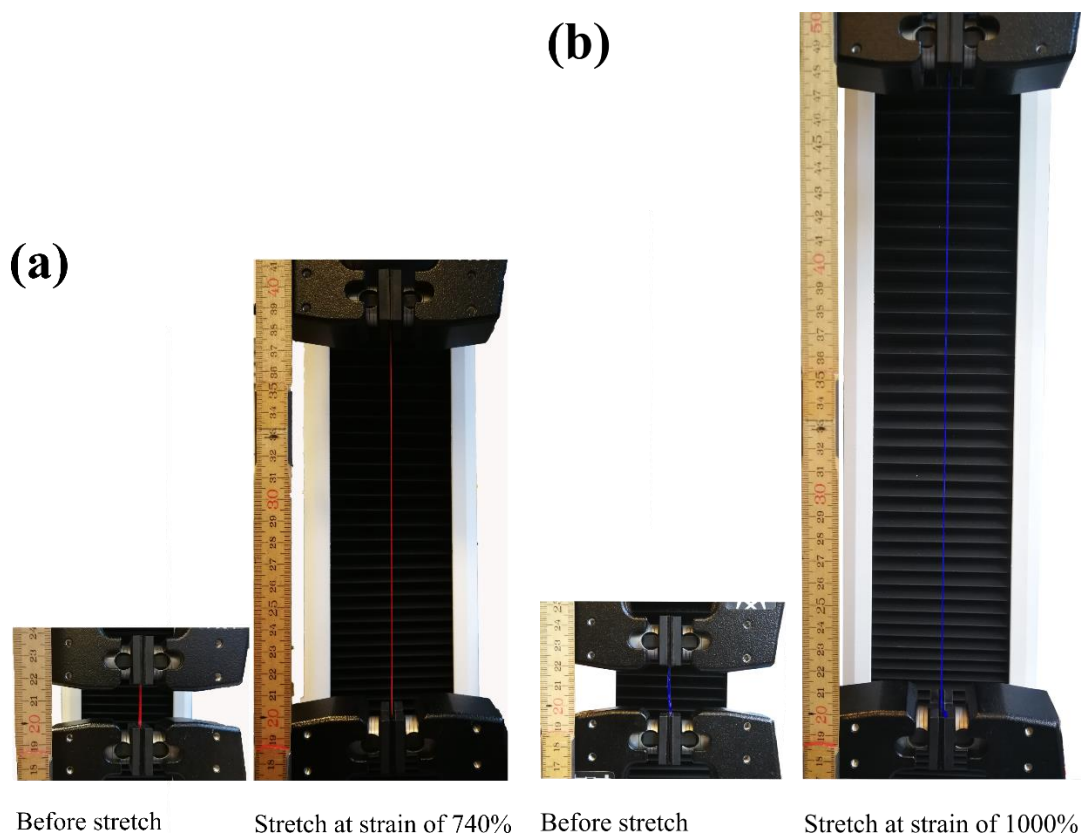


Figure S3. (a) Elastomer-HV22 before stretch and at strain of 740%. (b) Elastomer-HV31 before stretch and at a strain of 1000%.

Table S2. Comparison of tensile tests for reported and prepared elastomers (Elastomer-HV15 , Elastomer-HV22 and Elastomer-HV31).

Macromonomer	Measured results				Reported results ⁴		
	Strain at break (%)	Tensile strength (MPa)	Strain recovery (%)		Strain at break (%)	Tensile strength (MPa)	Strain recovery, 1 cycle (%)
			1 cycle	3 cycles			
DMS-HV15	520	0.42	100	100	700	0.2	100
DMS-HV22	920	0.38	99	99	1050	0.3	100
DMS-HV31	1270	0.07	98	96	2400	0.2	100

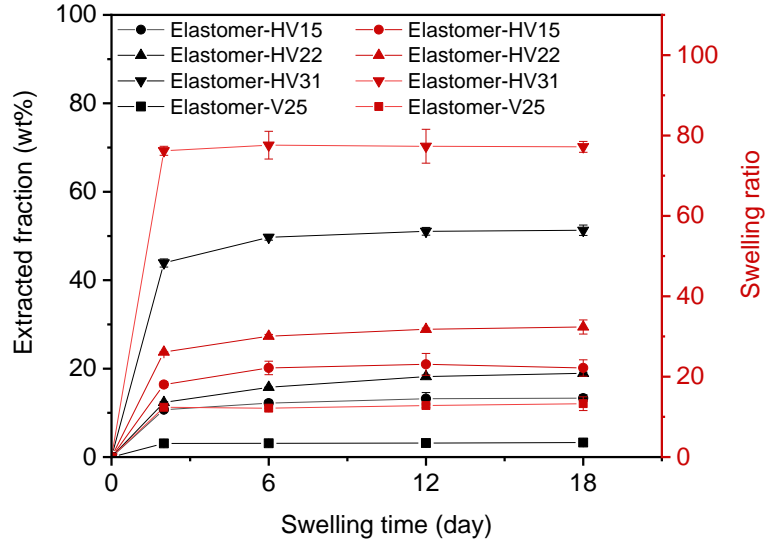


Figure S4. Extracted sol fractions and swelling ratios for Elastomer-HV15, Elastomer-HV22, Elastomer-HV31 and Elastomer-V25 versus swelling time.

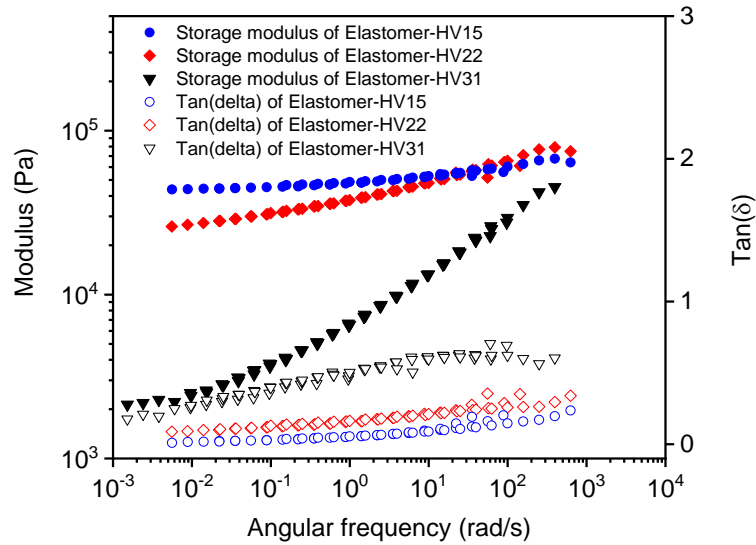


Figure S5. Linear viscoelastic data for Elastomer-HV15, Elastomer-HV22 and Elastomer-HV31.

Elastic modulus versus network concentration: The elastic modulus (E) of a cross-linked network depends on its concentration (ϕ) in solvent. One theoretical study⁵ found that $E \propto \phi$ for strongly cross-linked networks where trapped entanglements are negligible, while $E \propto \phi^{2.3}$ for lightly cross-linked networks where trapped entanglements are not negligible. The

scaling of the tight network corresponds to the linear dilution of the crosslinking density, and scaling of the entanglement-dominated network corresponds to the binary interactions of entanglements (ideally, the exponent should be 2, but the higher exponent indicates that the interaction is slightly higher than 2). An experimental study on conventional silicone elastomers showed that the exponent increases from 1.8 to 1.9 when precursor chain molecular weight increases from 11 kDa to 65 kDa (based on the data in Table 2, reference 4),⁶ suggesting that the exponent does increase when more trapped entanglements are present in the networks. **Figure S6** shows an exponent of 2.3 and 2.7 for Elastomer-HV15 and Elastomer-HV22, respectively, which are much larger than either the exponent of 1.6 for Elastomer-V25 or reported exponents of 1.8-1.9⁶—indicating that the trapped entanglements dominate the dynamics of Elastomer-HV15 and Elastomer-HV22, in contrast to conventional elastomers of similar molecular weight. Because chains of concatenated rings, just like chains of trapped entanglements, can slide to some extent, they are expected to behave similarly to trapped entanglements in the conventional networks. This further confirms the hypothesis that concatenated rings determine the properties of Elastomer-HV15 and Elastomer-HV22.

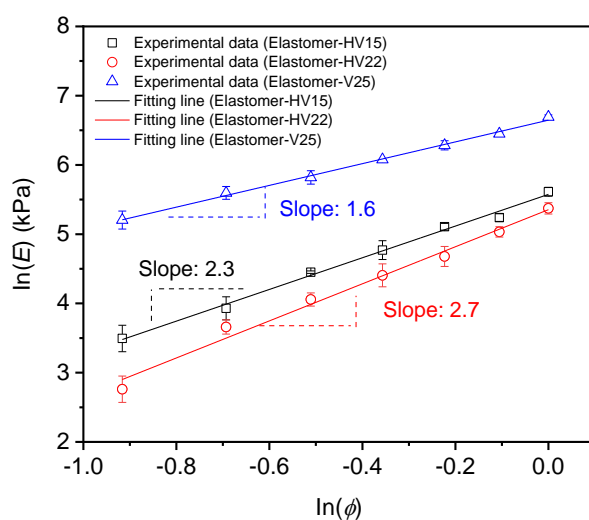


Figure S6. Elastic moduli (E) as function of volume fraction of the gel (ϕ) for Elastomer-HV15 and Elastomer-V25 prepared in different amounts of silicone oil.

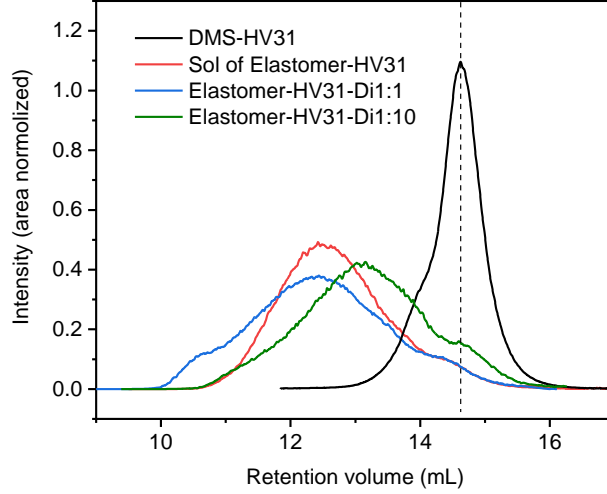


Figure S7 SEC curves of DMS-HV31, sol fraction of Elastomer-HV31, Elastomer-HV31 prepared with dilution ratio of 1:1 (Elastomer-HV31-Di1:1), and Elastomer-HV31 prepared with dilution ratio of 1:10 (Elastomer-HV31-Di1:10)

Network models: The stress-strain relationship of the elastomers as measured by tensile tests was fitted to two classic elasticity models: the affine network model and the slip-link network model. Affine network model^{7,8}:

$$\sigma_{red} = \frac{\sigma_{engr}}{\lambda - \lambda^{-2}} \quad (1)$$

$$\sigma_{red} = G \quad (2)$$

$$\lambda = \frac{L'}{L} \quad (3)$$

Where σ_{red} is the reduced stress, σ_{engr} is the engineering stress, λ is the extension ratio, G is the shear modulus as determined by linear fitting of σ_{engr} with λ in the range of $\lambda = 1.0$ to $\lambda=1.1$, L is the initial length of a specimen, and L' is the length of a stretched specimen.

Slip-link network model^{9,10}:

$$\sigma_{red} = G_c + G_s H(\lambda, \eta) \quad (4)$$

$$H(\lambda, \eta) = \frac{\lambda^2}{\lambda^2 + \lambda + 1} \left[\frac{1}{(\lambda + \eta)^2} + \frac{\lambda + 1}{\lambda(1 + \eta\lambda^2)^2} \right] \quad (5)$$

Where G_c and G_s represent the contribution from chemical cross-links and entanglements, respectively, $H(\lambda, \eta)$ is a strain-dependent term defined by equation 5, η is a measure of a link's freedom to slide compared to a chain's freedom of movement (η is commonly set as 0.2343,⁹ a theoretical value based on the assumption that, on average, each slip link can slide as far as the center of its topologically neighboring links).

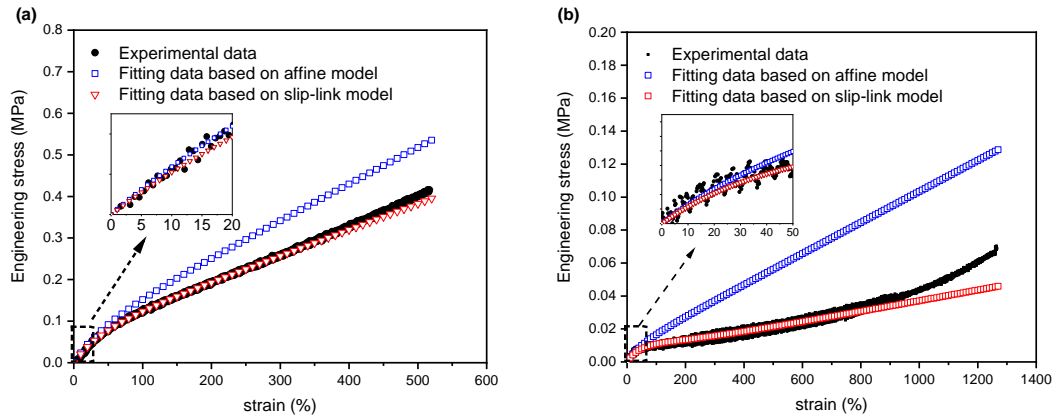


Figure S8 Experimental stress-strain and fitting curves based on the affine and slip-link models, respectively, for (a) Elastomer-HV15 and (b) Elastomer-HV31

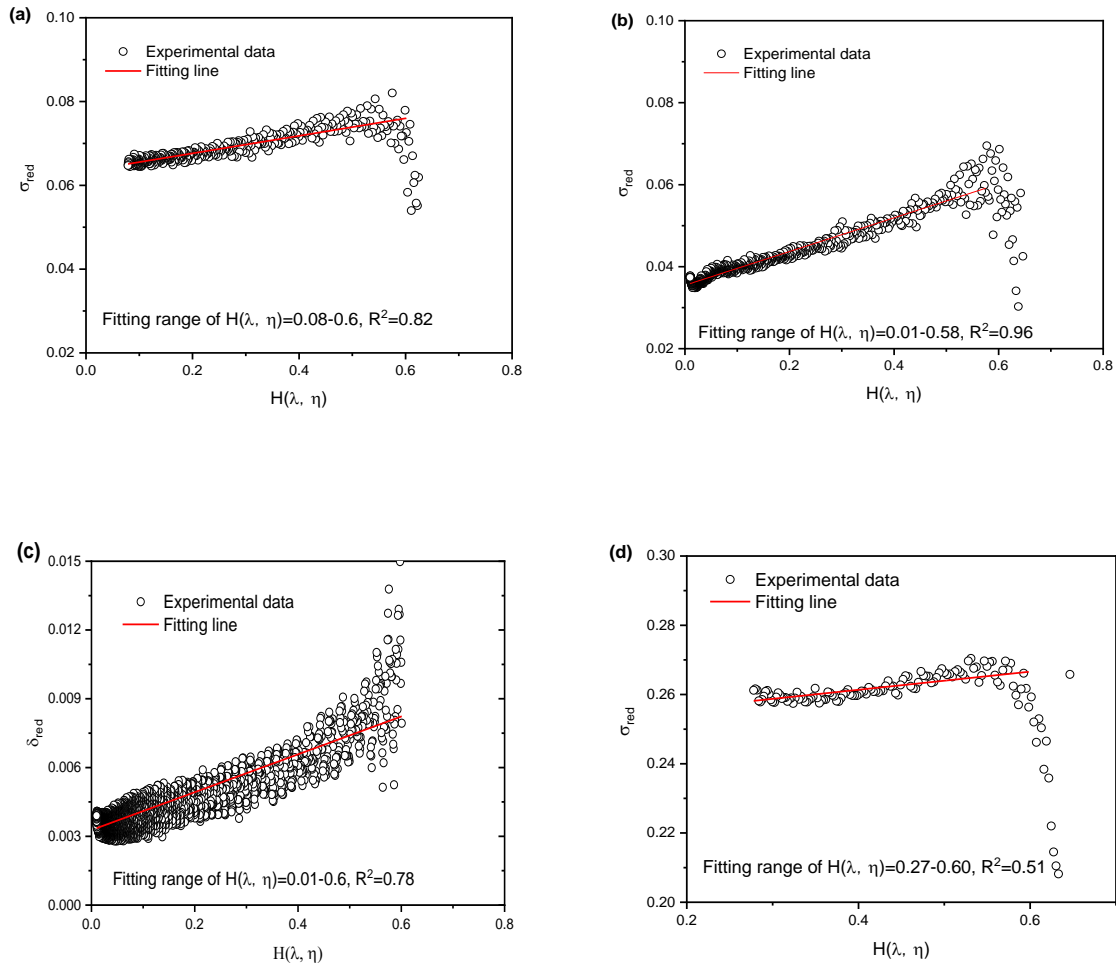


Figure S9. Linear fitting of σ_{red} with $H(\lambda, \eta)$ based on the slip-link model for (a) Elastomer-HV15 (fitting line of $\sigma_{red} = 0.063 + 0.021H(\lambda, \eta)$ at fitting range of $H(\lambda, \eta) = 0.08-0.6$, $R^2=0.82$), (b) Elastomer-HV22 (fitting line of $\sigma_{red} = 0.036 + 0.041H(\lambda, \eta)$ at fitting range of $H(\lambda, \eta) = 0.01-0.58$, $R^2=0.96$), and (c) Elastomer-HV31 (fitting line of $\sigma_{red} = 0.003 + 0.008H(\lambda, \eta)$ at fitting range of $H(\lambda, \eta) = 0.01-0.60$, $R^2=0.78$). (d) Elastomer-V25 (fitting line of $\sigma_{red} = 0.251 + 0.025H(\lambda, \eta)$ at fitting range of $H(\lambda, \eta) = 0.27-0.60$, $R^2=0.51$).

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