Divanillin Crosslinkers Give Dynamic Silicone Elastomers in a Catalyst-Free Process

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Supporting Information
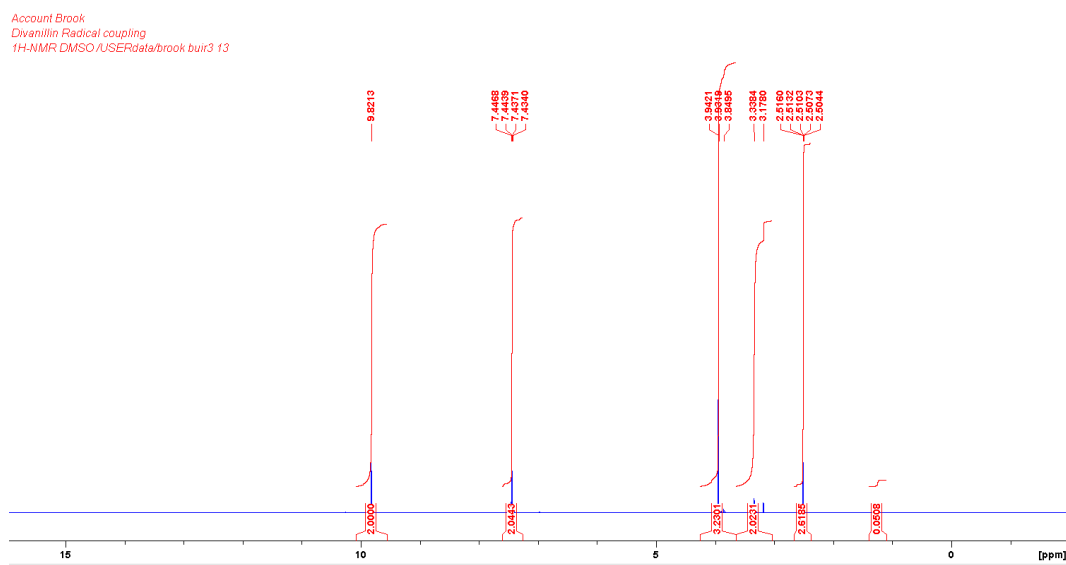

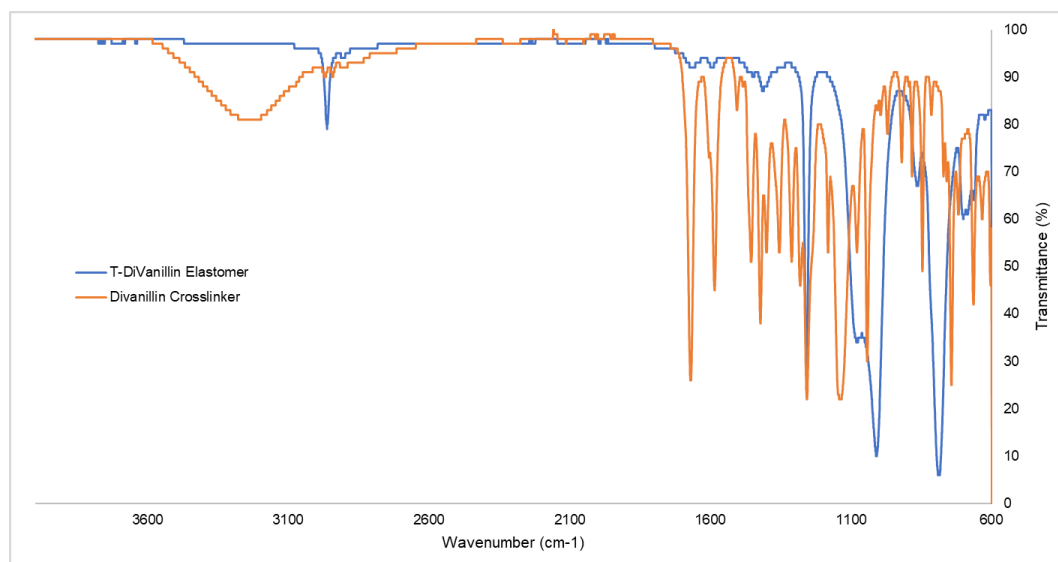Figure S1. NMR spectrum of the **DiVan** crosslinker dissolved in DMSO-d_6.

Figure S2. Infrared spectra from the reaction between divanillin and α,ω-(3-aminopropyl)polydimethylsiloxanes, showing the conversion of aldehydes to imines.

Preparation of Terephthaldehyde Crosslinked Elastomers and DiPhen-P Controls

Terephthaldehyde and 4,4'-diphenyldialdehyde crosslinked elastomers with various functional group concentrations were fabricated as a comparison of viscoelastic properties with divanillin crosslinked elastomers. Elastomer were only formed using (3-aminopropyl)methylsiloxane-dimethylsiloxane copolymers, while α,ω-(3-aminopropyl)-polydimethylsiloxanes resulting in viscous fluids instead of elastomers.

In a typical preparation, terephthaldehyde (41.77 mg, 0.311 mmol) was first dissolved in chloroform (1 mL); there were no significant differences in the outcomes as a function of solvent), then added to a vial containing AMS-152 (5% mol aminopropylmethylsiloxane, 8500 g mol^{-1}, 0.923 g, 0.115 mmol), and rapidly stirred until homogenous. The mixture was then poured into the desired mold, or cast as a thin film. Similarly, 4,4'-diphenyldialdehyde (67.27 mg ,0.320 mmol) was dissolved in chloroform (0.8 mL), then added to a vial containing AMS-152 (5% mol aminopropylmethylsiloxane, 8500 g mol^{-1}, 0.923 g, 0.115 mmol), and stirred. The mixture was cast as a thin film or into the desired mold for tensile testing.

Table S1. Formulations of **DiVan-T** elastomers using different molecular weights of α,ω-(3-aminopropyl)polydimethylsiloxanes and **DiVan-P** elastomers using pendent (3-aminopropyl)methylsiloxane-dimethylsiloxane copolymers in which the mol% aminopropyl mole groups varied in a 1:1, or 1:1.1 ratio; the latter being used exclusively for determining physical properties.

Telechelic Divanillin Elastomers (**DiVan-T**)	Molar mass (Da)	% Amine Functionality	[Amine] (M)	Mass of Aminosilicone (g)	[Amine] (mmol)	Mass DiVanillin	Silicone to Divanillin Mass Ratio
T-19	0.9k	Telechelic	2.17	5.102	11.3	1.714	25.1%
T-5	3k	Telechelic	0.653	5.052	3.36	0.509	9.2%
T-3	5k	Telechelic	0.392	5.082	2.03	0.307	5.7%
T-0.6	25k	Telechelic	0.0784	5.009	0.401	0.061	1.2%
T-0.3	50k	Telechelic	0.0392	5.074	0.203	0.031	0.6%
Pendent Divanillin Elastomers (**DiVan-P**)							
P-3	5.5k	3	0.387	5.066	2.01	0.302	5.6%
P-5	8k	5	0.675	5.017	3.45	0.522	9.4%
P-7	4k	7	0.946	5.101	4.92	0.744	12.7%
P-11	2.5k	11	1.35	5.038	6.94	1.049	17.2%

Table S2.Physical properties of **DiPhen-P** elastomers made using 4'4-diphenyldialdehye and pendent (3-aminopropyl)methylsiloxane-dimethylsiloxane copolymers in which the mol% aminopropyl differ

DiPhen-P Starting Material[a] P-B	Molar mass (kDa)	YM[b] MPa	Shore A[c]	Tensile Stress (Mpa)	Tensile Strain at Break (%)
P-3	5.5k	0.36	30 (OO)	0.764	165
P-5	8k	0.881	55 (OO)	1.11	132
P-7	4k	2.1	13	2.54	118
P-11	2.5k	4.47	20	3.93	112

[a] The number refers to the % amine-containing monomers in the starting aminosilicone polymer. [b] YM Young's modulus. [c] Where indicated, Shore OO Hardness measurements were made on softer samples.
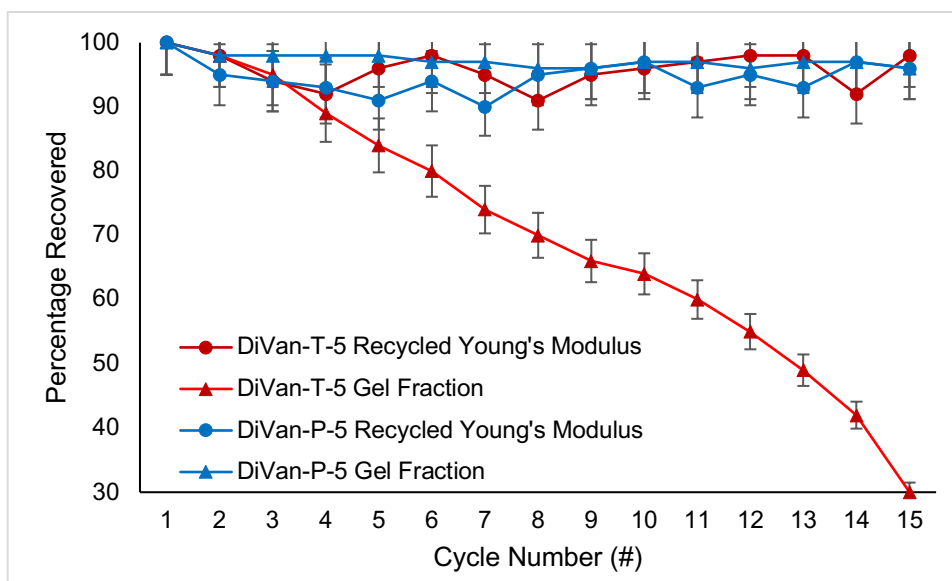
Figure S3: Swelling and Young's Modulus of **DiVan-T-5** and **DiVan-P-5** after multiple cycles of swelling crumbled elastomer and heat pressing to obtain new monolithic samples.
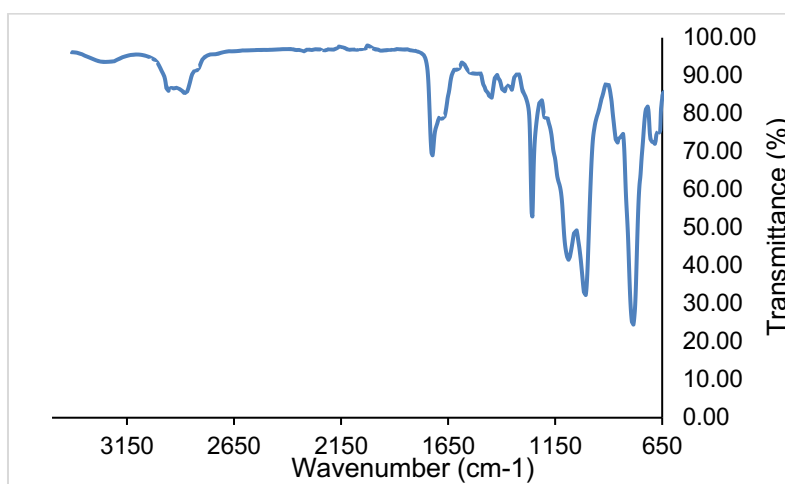

Figure S4: Infrared spectrum of the products from degrading **DiVan-P** elastomers with excess phenylhydrazine for 48 h.

Table S3. Formulations of elastomers **DiVan-P-B-3CL** with the same crosslink density made from pendent (3-aminopropyl)methylsiloxane-dimethylsiloxane copolymers in which the mol% aminopropyl differ, but with the same amount of divanillin (leading to different excesses

| Pendent Divanillin Elastomers for Self-Healing	Molar Mass (kDa)	% Amine Functionality	[Amine] (M)	Mass of Amino-silicone	mmols Amine	Amine to Aldehyde Ratio	Mass DiVanillin	mmol DiVanillin	Amine Excess (mmol)	[Amine] Excess (M)
P-3-3CL	5.5k	3	0.387	5.062	1.92	1:1	0.291	0.959	0.00	0.00
P-5-3CL	8k	5	0.675	5.088	3.37	5:3	0.293	0.966	1.43	0.287
P-7-3CL	4k	7	0.946	5.011	4.65	7:3	0.297	0.979	2.69	0.537
P-11-3CL	2.5k	11	1.35	4.992	6.60	11:3	0.290	0.956	4.70	0.938
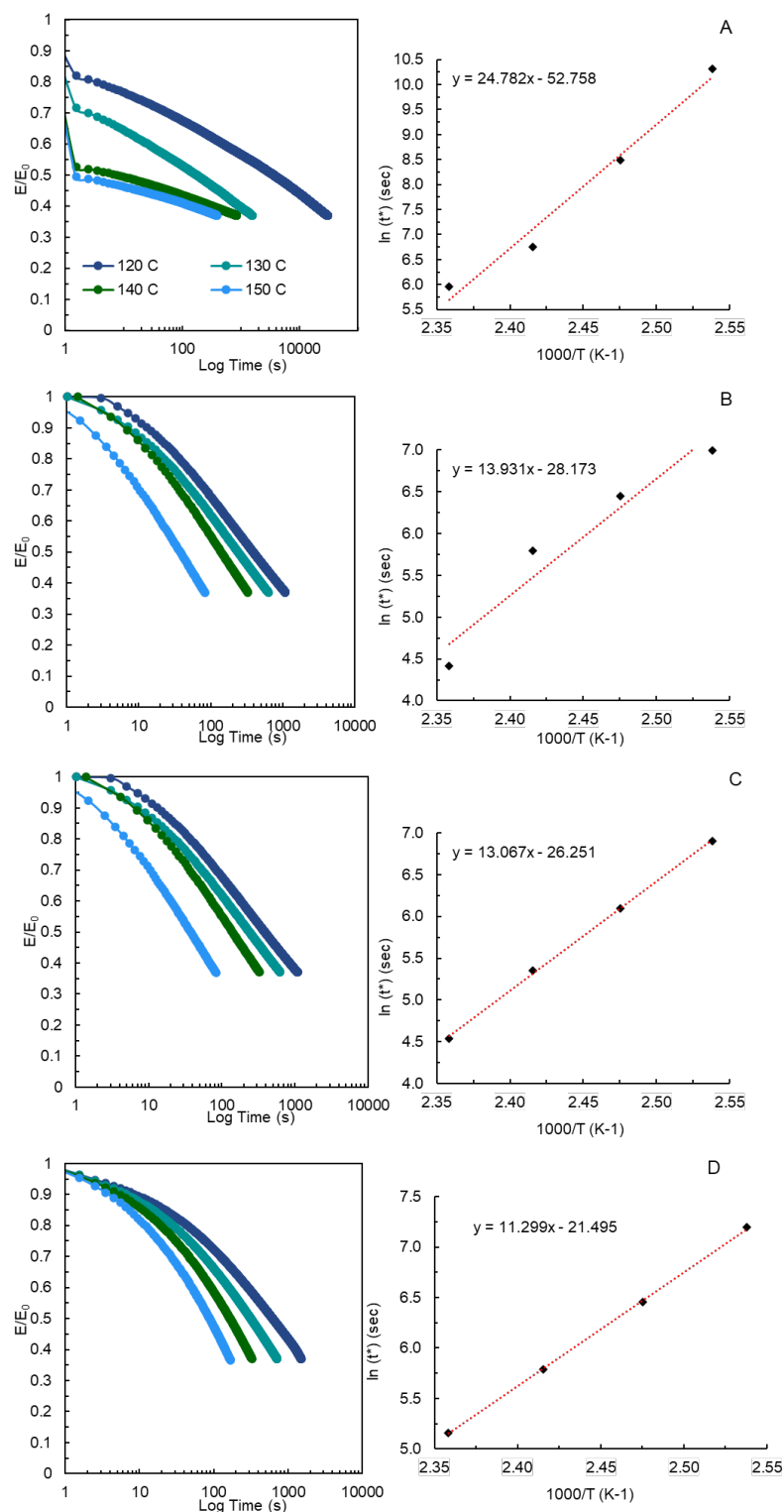
Figure S5. Arrhenius thermal stress-relaxation of A) **DiVan-T-19**, B) **DiVan-T-5**, C) **DiVan-T-3** and D) **DiVan-T-0.6** elastomers under constant strain (10%) from 120-150 °C and at 25 °C as a control. Showing the relaxion of the material from initial stress, to $E/E_0 = 1/e$ (~0.37), and Arrhenius plot modeling the Maxwell viscoelastic relaxation.

Table S4. Calculated material relaxation activation energies of **DiVan-T** elastomers using different molecular weights of telechelic 3-(aminopropyl)-terminated polydimethylsiloxanes determined using DMTA

Sample Name	[Amine] (M)	Slope	Averaged Calculated Activation Energy of Relaxation (kJ mol^{-1})
DiVan-T-19	900	24.782	206.03
DiVan-T-5	3000	13.931	115.82
DiVan-T-0.6	5000	13.067	108.64
DiVan-T-0.3	25000	11.299	93.94

Equation S1. Arrhenius model of elastomer relaxation where t_R is the relaxation time, E_a is activation energy, R is the Boltzmann's constant, and T is temperature

$$t_R = Ae^{\frac{-E_a}{RT}}$$

$$\ln(t_R) = \ln(A) + \frac{-E_a}{RT} \quad (1)$$