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Supporting Information

Converting commercial-grade silicone into a vitrimer using elemental sulfur

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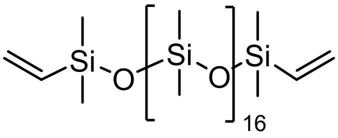
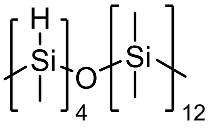
S1. Quantitative analysis of commercial silicone

For Part A, the integration for the terminal vinyl groups was normalised to 6 (6H). The methyl hydrogens integrated to 110.76, so once divided by the normalised value of 6 (2Me/Si), indicated the presence of a total 18 methyl groups. This led to the identification of a DP_n of 16 when considering the terminal ends both likely contain a vinyl substituent and 2 methyl substituents.

For Part B, the vinyl group integration was similarly normalised to 6 for consistency. From this, it was concluded that there were four hydrogens corresponding to four units of -O-SiHMe. The integration corresponding to the methyl substituents from Part A was subtracted from Part B's total, isolating the methyl substituents corresponding to the PHMS-co-PDMS in Part B. Once this value was divided by 3, it revealed there were 30 methyl groups. Taking into account 4 of these methyl groups associated with the -O-SiHMe groups and the 2 terminal methyl groups, it was determined that Part B contains 12 repeating PDMS units as show in the structures below.



Vinyl PDMS



PHMS-co-PDMS

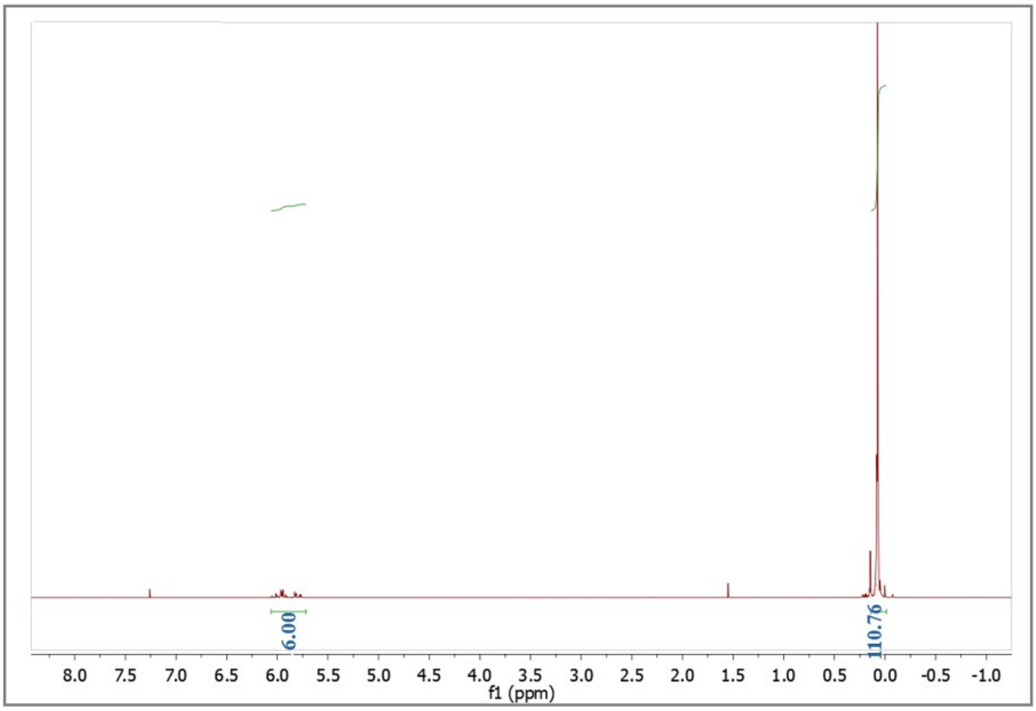


Figure S1. ^{1}H NMR spectrum of Gelest elastomer Part A, in $CDCl_3$

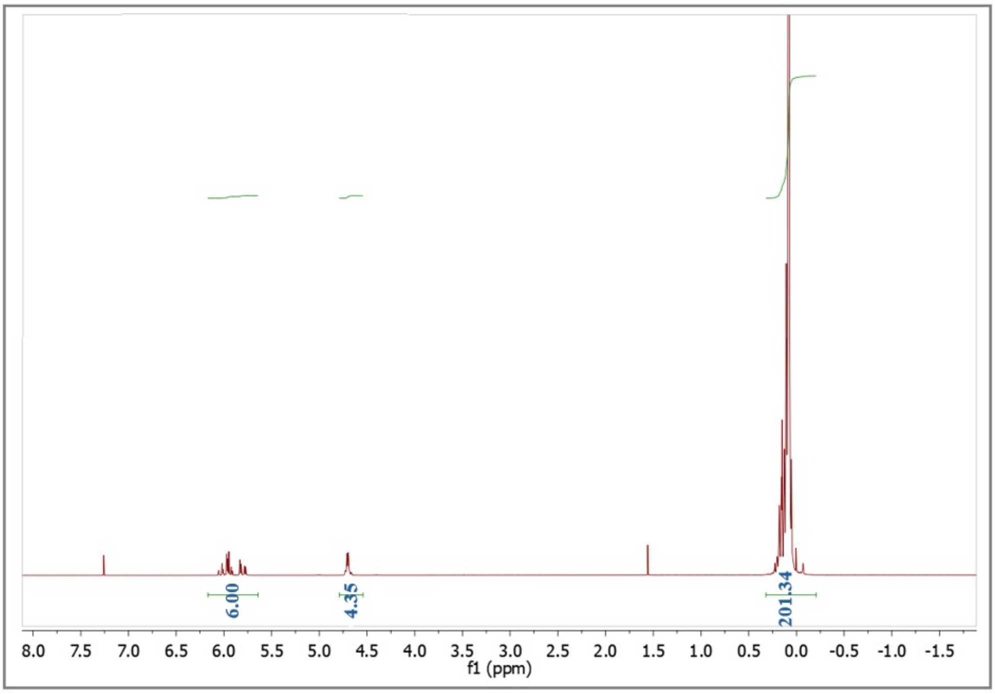


Figure S2. ^{1}H NMR spectrum of Gelest elastomer Part B, in $CDCl_3$

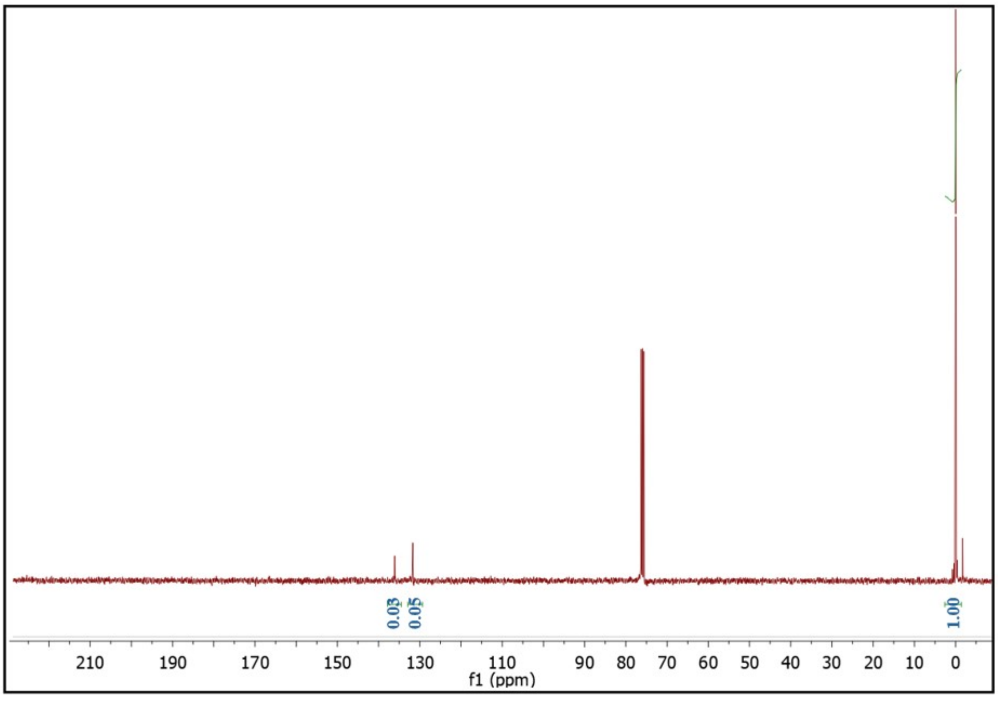


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of Gelest elastomer Part A, in $CDCl_3$

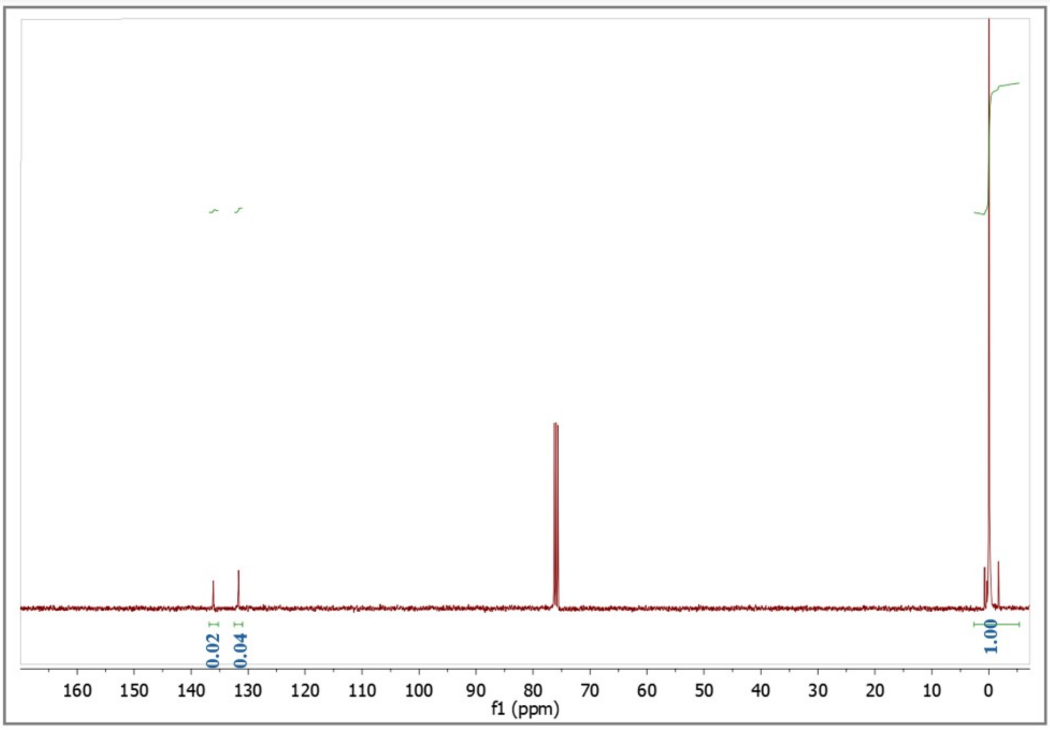


Figure S4. $^{13}C\{^1H\}$ NMR spectrum of Gelest elastomer Part B, in $CDCl_3$.

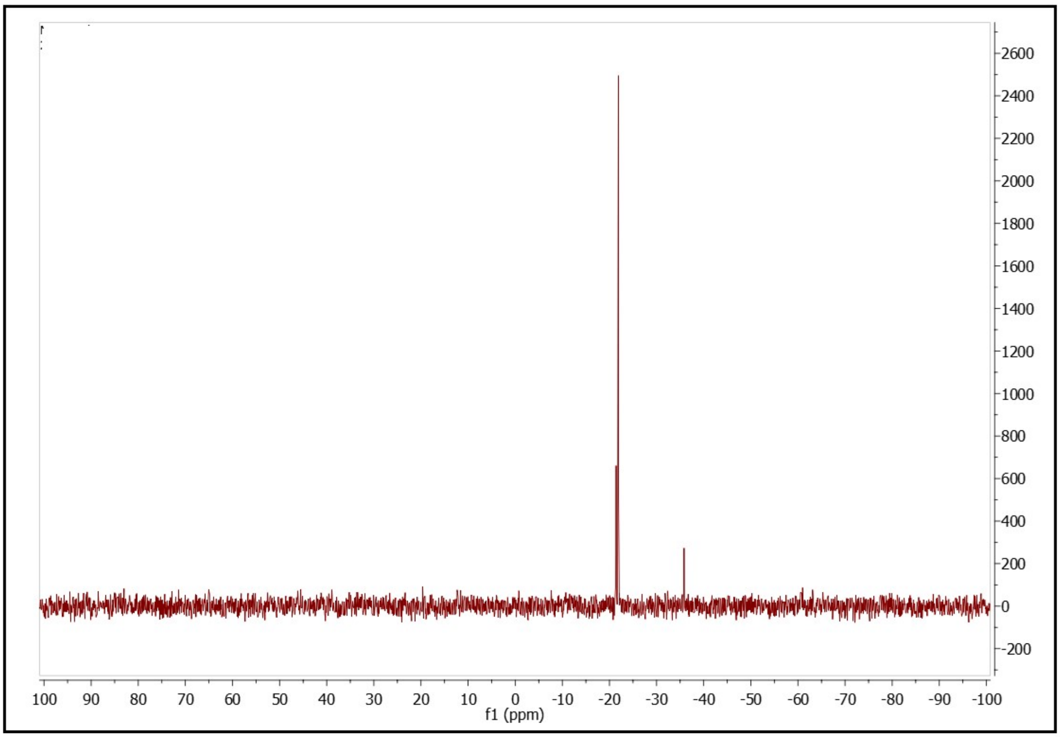


Figure S5. ^{29}Si NMR spectrum of Gelest elastomer Part A, in $CDCl_3$.

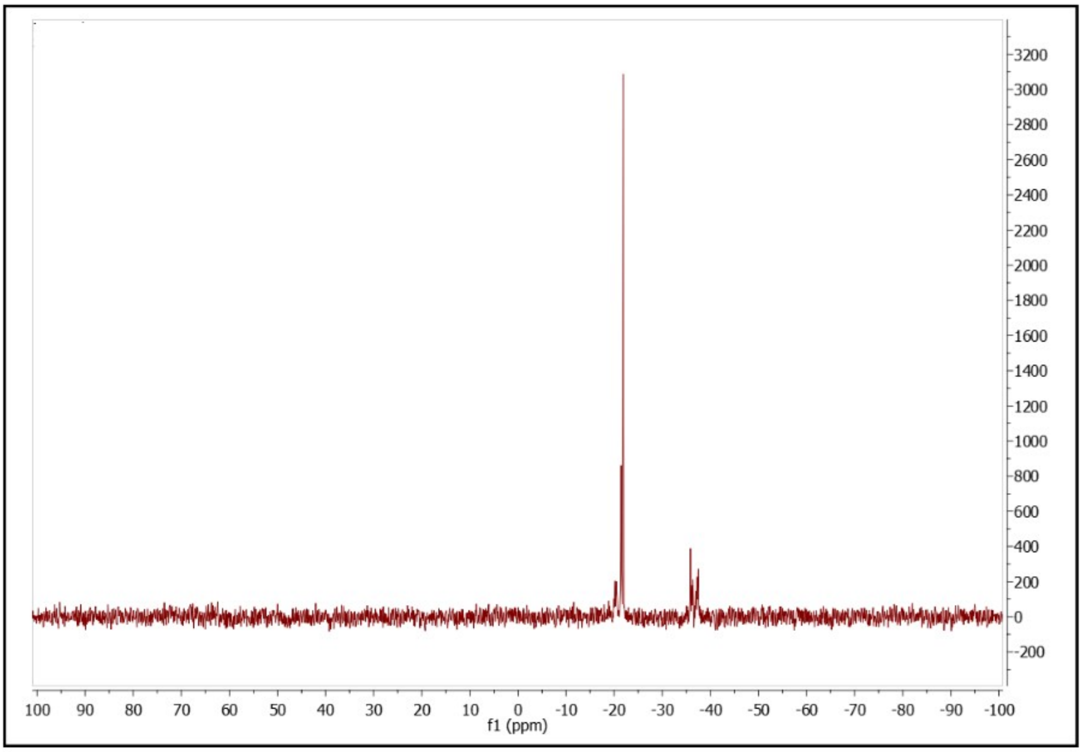
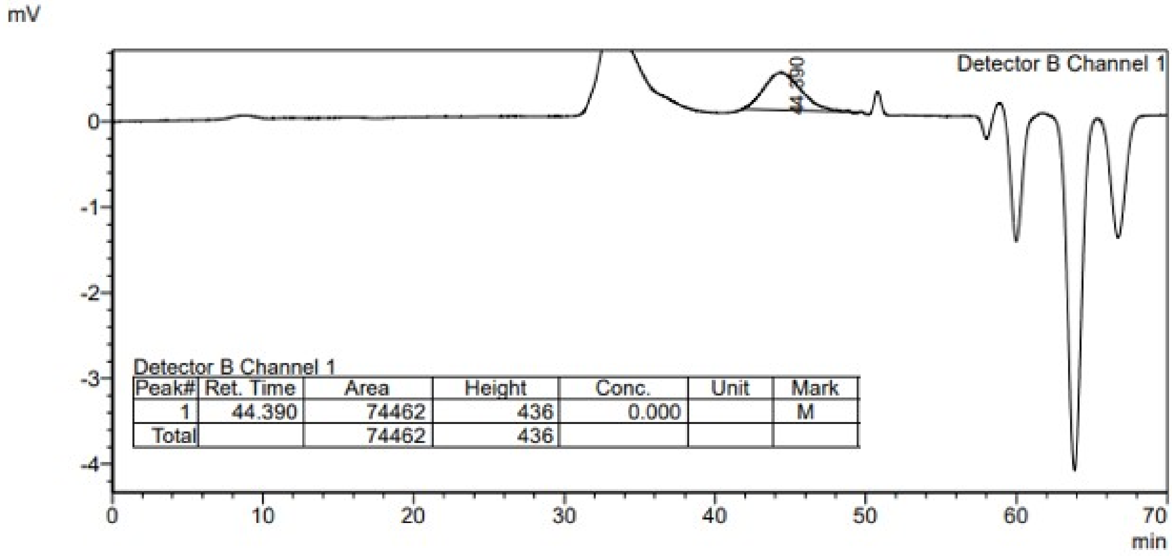
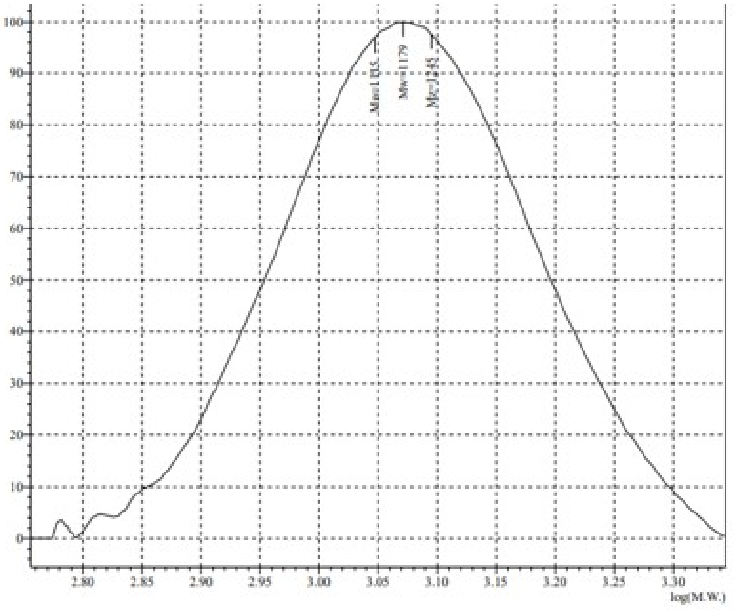


Figure S6. ^{29}Si NMR spectrum of Gelest elastomer Part B, in $CDCl_3$.



Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark
1	44.390	74462	436	0.000		M
Total		74462	436			



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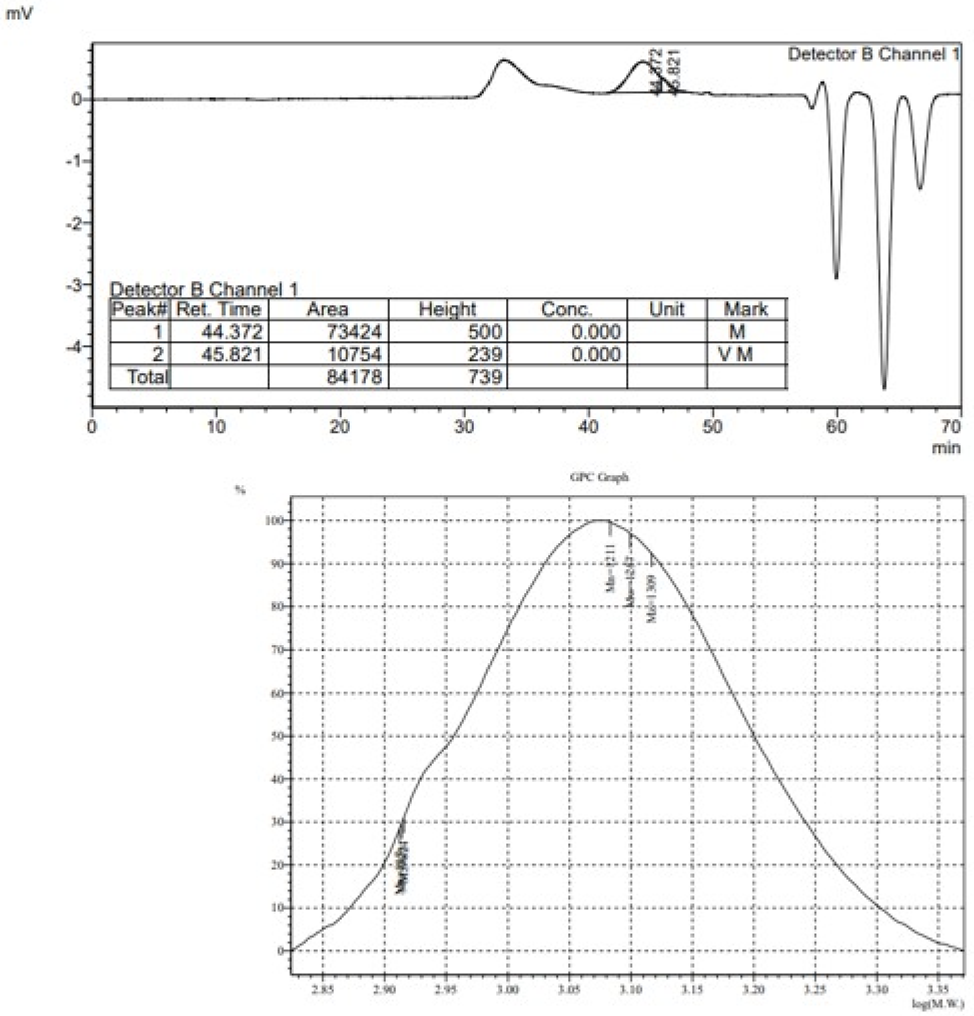
Peak#:1 (Detector B Channel 1)
[Average Molecular Weight]
 Number Average Molecular Weight(Mn)            1115
 Weight Average Molecular Weight(Mw)            1179
 Z Average Molecular Weight(Mz)                 1245
 Z+1 Average Molecular Weight(Mz1)              1313
 Viscosity Average Molecular Weight(Mv)         0
 Mw/Mn                                          1.05729
 Mv/Mn                                          0.00000
```

Figure S7. An example of a GPC chromatogram and associated data of Gelest elastomer Part A using the refractive index signal as a function of retention time



Detector B Channel 1

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark
1	44.372	73424	500	0.000		M
2	45.821	10754	239	0.000		V M
Total		84178	739			

```
[Average Molecular Weight]
 Number Average Molecular Weight(Mn)           817
 Weight Average Molecular Weight(Mw)           820
 Z Average Molecular Weight(Mz)                824
 Z+1 Average Molecular Weight(Mz1)             827
 Viscosity Average Molecular Weight(Mv)        0
 Mw/Mn                                         1.00431
 Mv/Mn                                         0.00000

Detector B Channel 1
[Average Molecular Weight(Total)]
 Number Average Molecular Weight(Mn)           1141
 Weight Average Molecular Weight(Mw)           1201
 Z Average Molecular Weight(Mz)                1266
 Z+1 Average Molecular Weight(Mz1)             1335
 Viscosity Average Molecular Weight(Mv)        0
 Mw/Mn                                         1.05296
 Mv/Mn                                         0.00000
```

Figure S8. An example of a GPC chromatogram and associated data of Gelest elastomer Part B using the refractive index signal as a function of retention time.

Table S1. DP_n determined using NMR spectroscopy as compared to GPC

	NMR	**GPC**			
Polymer	DP_n	DP_n	M_w [Da]	M_n [Da]	$Đ$
Vinyl PDMS	16	14	1199.4 ± 12.36	1137.4 ± 12.70	1.054 ± 0.0037
PHMS-co-PDMS	4:12	4:8 or 3:9	816.6 ± 3.05	812.6 ± 4.04	1.005 ± 0.0006

S2. Characterisation of X-poly(siloxane-*r*-S)

Table S2. Elemental analysis of X-poly(siloxane-*r*-S)

Name	Method	N [%]	C [%]	H [%]	S [%]	Predicted [S%]
0-poly(siloxane-*r*-S)	5mg 90s	0	29.38	7.737	0	0
5-poly(siloxane-*r*-S)	5mg 90s	0	30.86	8.046	1.985	4.99
10-poly(siloxane-*r*-S)	5mg 90s	0	31.81	8.13	2.117	9.91
15-poly(siloxane-*r*-S)	5mg 90s	0	28.02	7.216	11.985	14.16

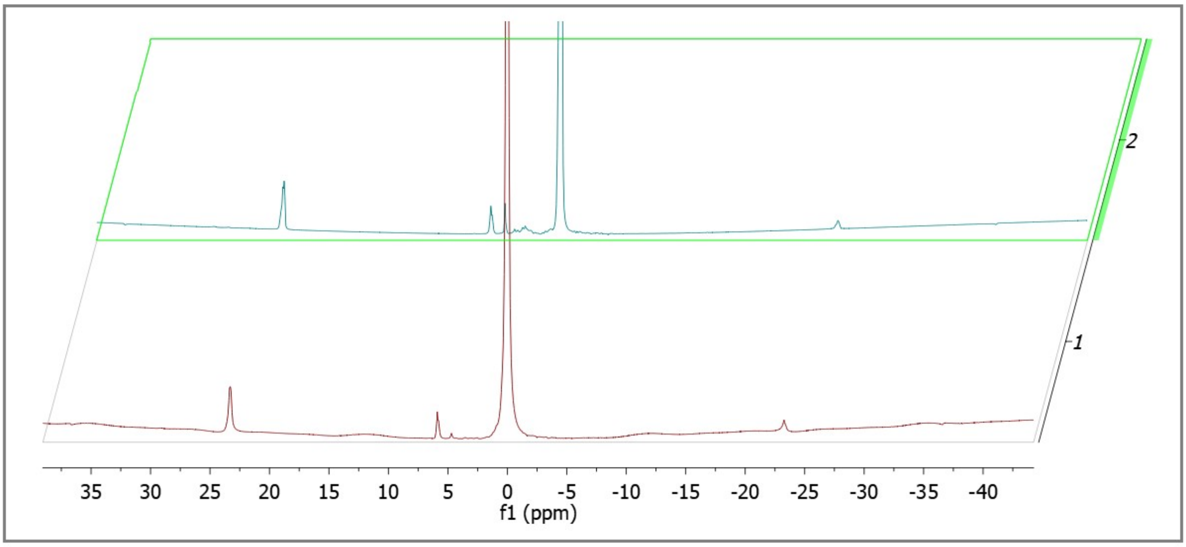


Figure S9. SS^{1}H NMR spectra of 0-poly(siloxane-*r*-S) (red) and 10-poly(siloxane-*r*-S) (blue)

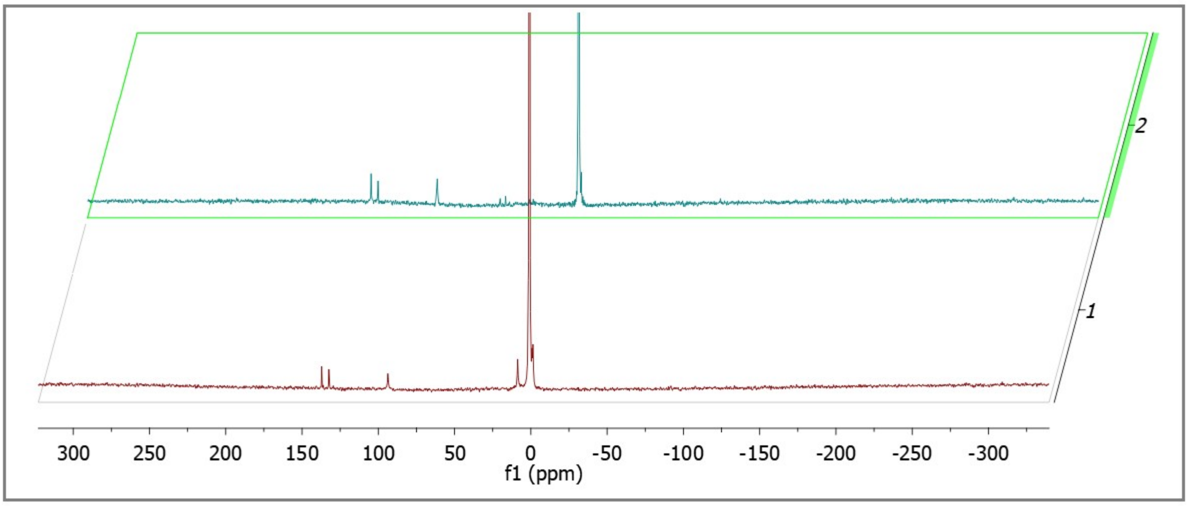


Figure S10. SS^{13}C NMR spectra of 0-poly(siloxane-*r*-S) (red) and 10-poly(siloxane-*r*-S) (blue)

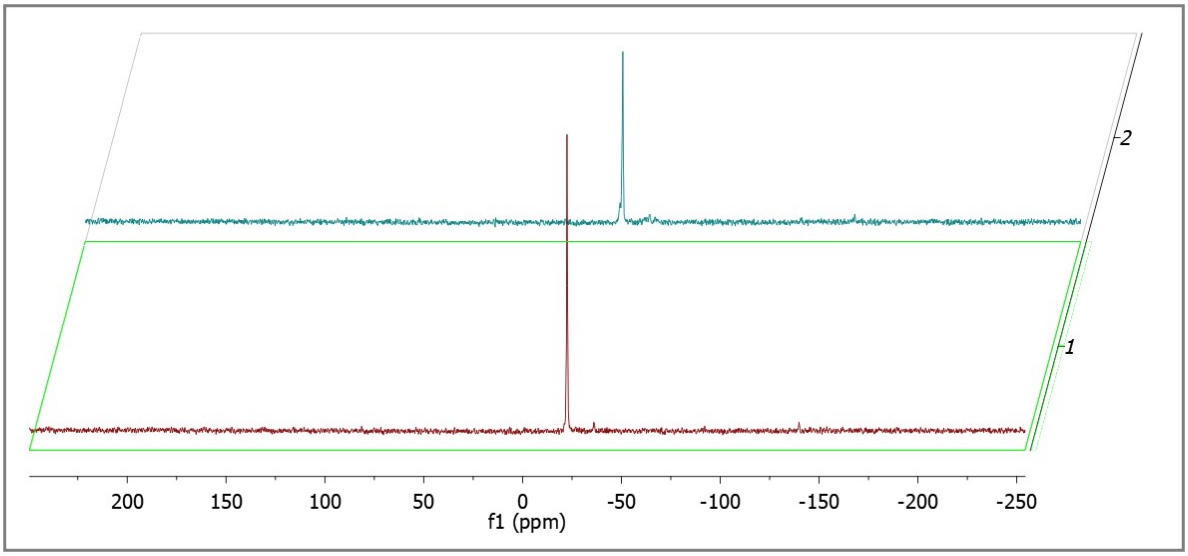


Figure S11. SS^{29}Si NMR spectra of 0-poly(siloxane-*r*-S) (red) and 10-poly(siloxane-*r*-S) (blue)

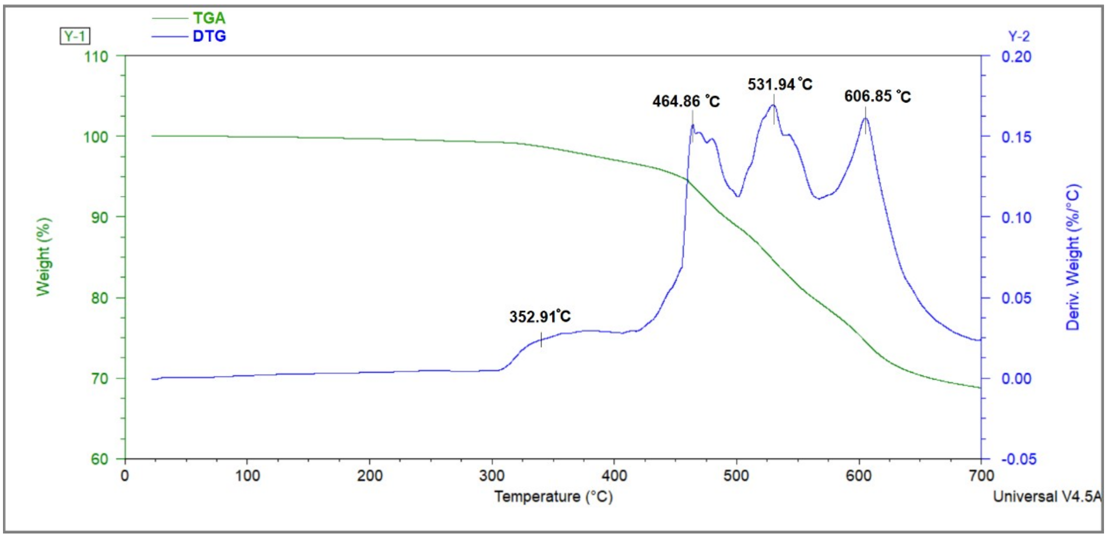


Figure S12. TGA (green, left) and DTG (blue, right) thermogram of 0-poly(siloxane-*r*-S)

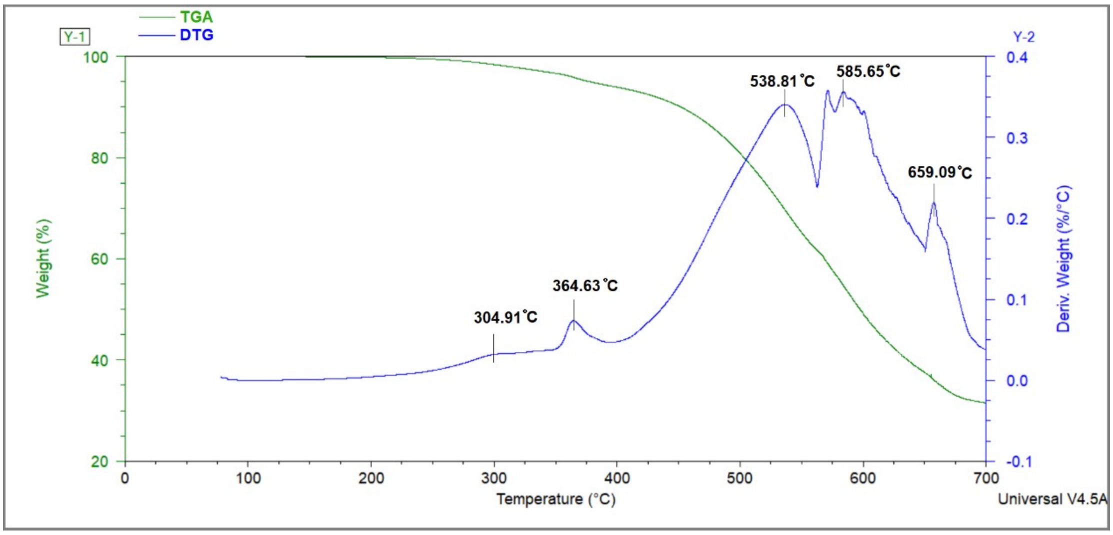


Figure S13. TGA (green, left) and DTG (blue, right) thermograms of 5-poly(siloxane-*r*-S)

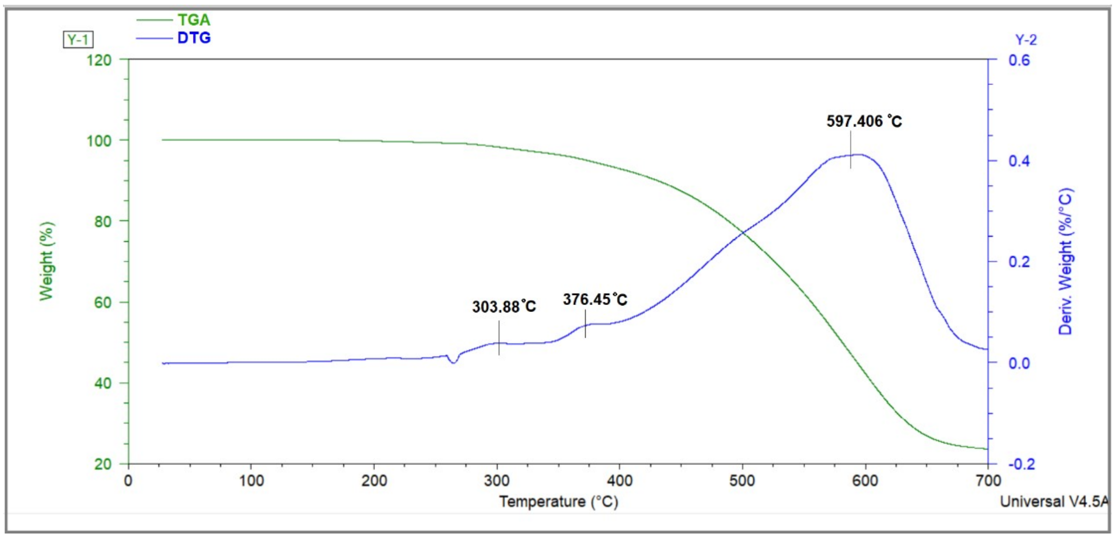


Figure S14. TGA (green, left) and DTG (blue, right) thermogram of 10-poly(siloxane-*r*-S)

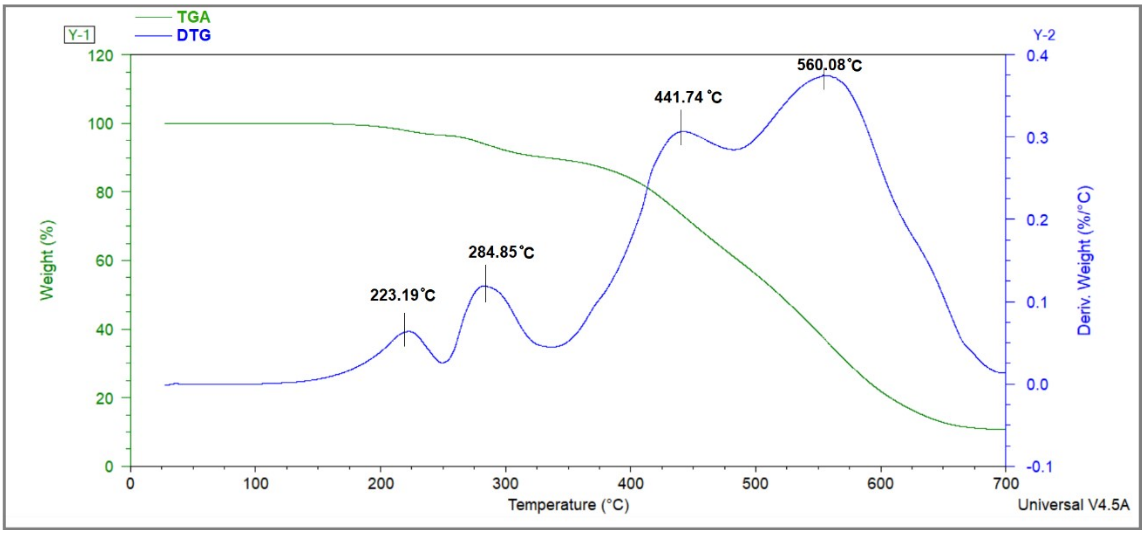


Figure S15. TGA (green, left) and DTG (blue, right) thermogram of 15-poly(siloxane-*r*-S)

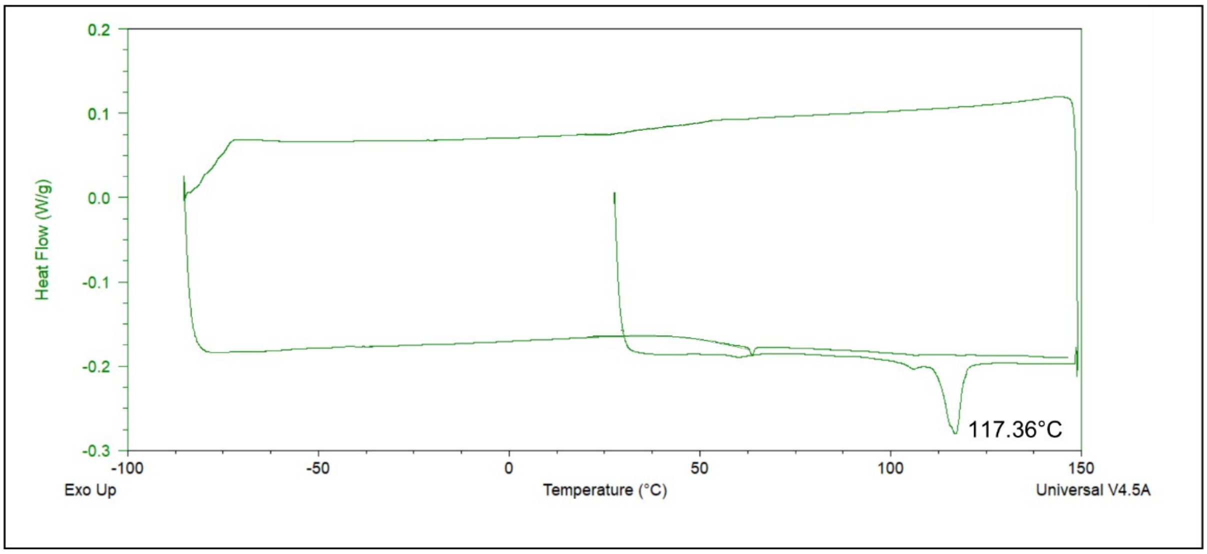


Figure S16. DSC thermogram of 15-poly(siloxane-*r*-S) sample showing no T_g and an endothermic peak corresponding to elemental sulfur

S4. Characterisation and property comparison of X-poly(siloxane-*r*-S) (X = 0, 5, 10) before and after healing

S5. Solubility assessment of X-poly(siloxane-*r*-S)

We conducted solubility tests on both the control sample 0-poly(siloxane-*r*-S) and the sulfur-containing samples X-poly(siloxane-*r*-S) (X = 5, 10, 15). Due to the clear and transparent nature of the control sample, it was necessary to use quantitative tests to assess its solubility. For the samples containing sulfur, visual observations were mainly employed to evaluate the solubility.

Control sample 0-poly(siloxane-*r*-S) solubility:
The control sample showed signs of swelling in DCM, THF, and Hexane. This indicates some interaction with these solvents.
The solubility rates in the tested solvents were: THF (0.20%), DMF (0.10%), Hexane (0.21%), DCM (0.23%), and Acetone (0.12%). These findings suggest limited solubility, likely due to the silicone's cross-linked structure.

X-poly(siloxane-*r*-S) solubility:
Samples with sulfur were partially soluble in DMF, indicating some breakdown of the sulfide bonds within the material using this solvent.[1]
Like the control sample, sulfur-containing samples also swelled in DCM, THF, and Hexane, showing a similar interaction pattern across all samples.

These samples did not show any solubility in the solvents, except for DMF, showing a unique behavior compared to the control sample (Table S3, Figure S18).

Table S3. Solubility of X-poly(siloxane-*r*-S) compared with 0-poly(siloxane-*r*-S)

	THF	DMF	Hexane	DCM	Acetone
0-poly(siloxane-*r*-S)	Sw	Sw	Sw	Sw	Sw
5-poly(siloxane-*r*-S)	Sw	P	Sw	Sw	Sw
10-poly(siloxane-*r*-S)	Sw	P	Sw	Sw	Sw
15-poly(siloxane-*r*-S)	Sw	P	Sw	Sw	Sw

S = soluble; I = insoluble; P = partially soluble; Sw = swells

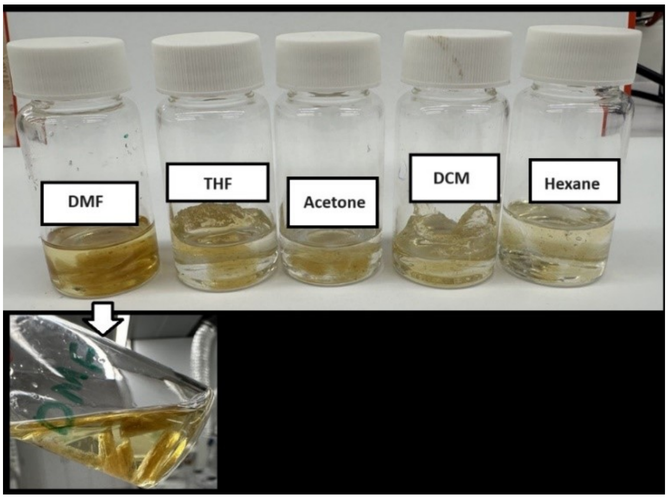


Figure S17. Solubility of X-poly(siloxane-*r*-S) in various solvents

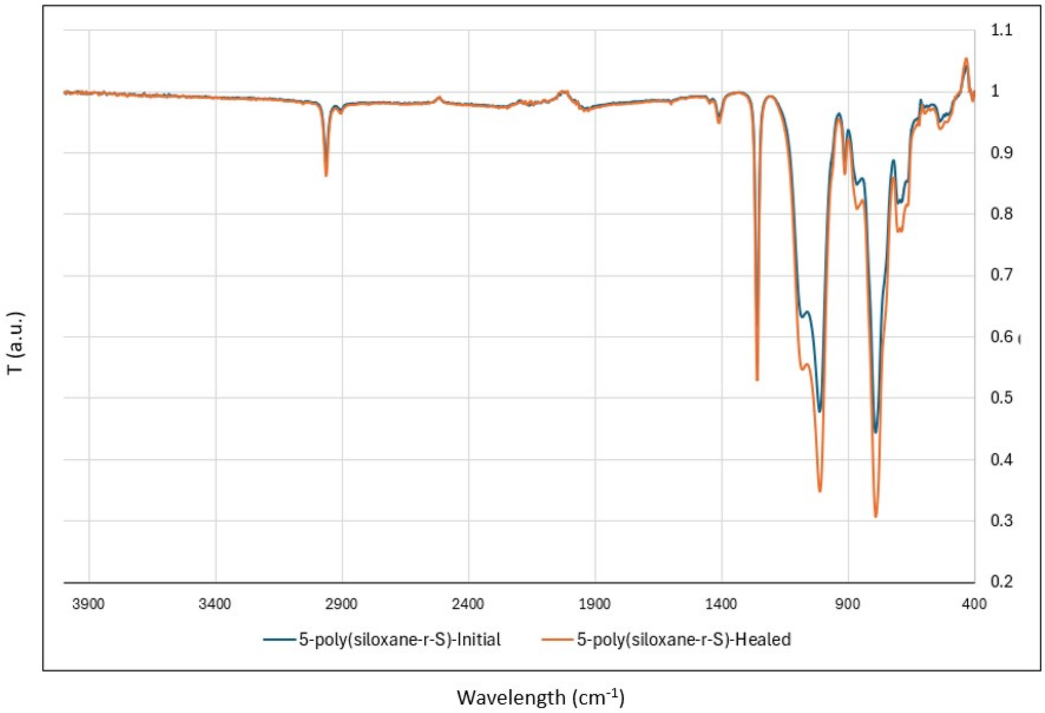


Figure S18. FTIR spectra for initial (blue) and healed (orange) samples of 5-poly(siloxane-*r*-S)

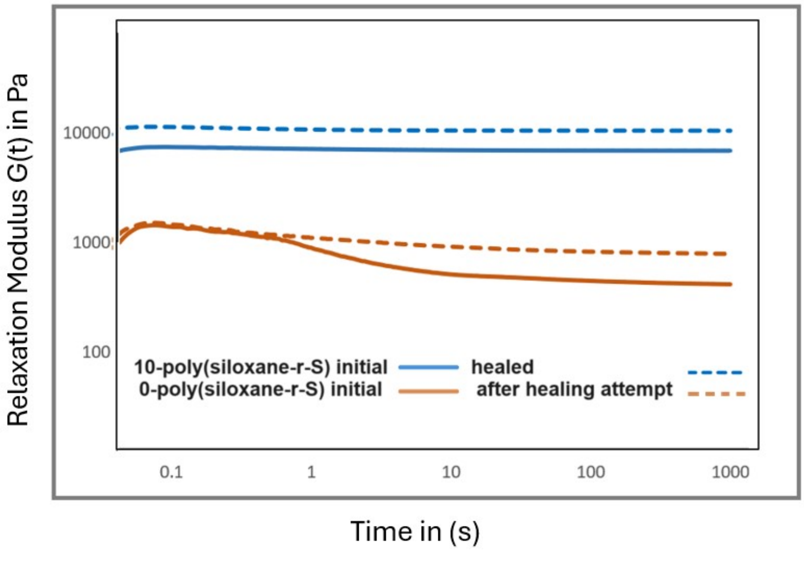


Figure S19. Relaxation modulus of 10-poly(siloxane-*r*-S) before (solid blue line) and after (dotted blue line) healing as compared to 0-poly(siloxane-*r*-S) before (solid brown line) and after healing attempt (dotted brown line).

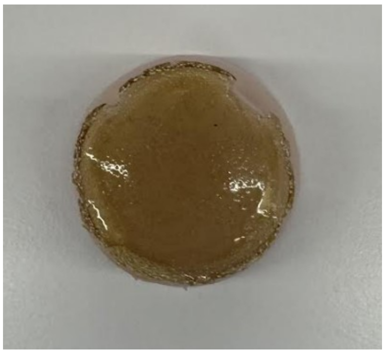


Figure S20. Image of Part A (vinyl-terminated PDMS) after inverse vulcanisation with 10 wt% sulfur at 180°C.

References:

(1) Yan, P.; Zhao, W.; Tonkin, S. J.; Chalker, J. M.; Schiller, T. L.; Hasell, T. Stretchable and Durable Inverse Vulcanized Polymers with Chemical and Thermal Recycling. *Chem. Mater.* **2022**, *34* (3), 1167–1178. https://doi.org/10.1021/acs.chemmater.1c03662.