Electronic Supplementary Material (ESI) for Polymer Chemistry.

Controlling silicone networks using dithioacetal crosslinks

Ayodele Fatona,[a] Jose Moran-Mirabal,[a] and Michael A. Brook*[a]

SUPPORTING INFORMATION

Effect of different acids on the thioacetalization process

Table S1. Efficacy of acidic catalyst and optimization of the thioacetalization reaction

Entry	Catalyst (ppm)	Observation
1	$BF_3{\cdot}OEt_2$ (50 ppm)	reaction too fast, irreproducible (does not disperse efficiently in PDMS), transparent elastomer,
2	$AlCl_3$ (200 ppm)	reaction too fast, irreproducible (long induction time then extremely rapid reaction), transparent elastomer
3	MsOH (150 ppm)	reaction controllable, reproducible (dispensing less convenient), transparent elastomer
4	p-TsOH (150 ppm) (~0.25mol% vs HS-PDMS)	reaction controllable, reproducible, flexible, transparent elastomer

Changes in UV-Visible Absorption during cure of silicones using Fluorene-CHO

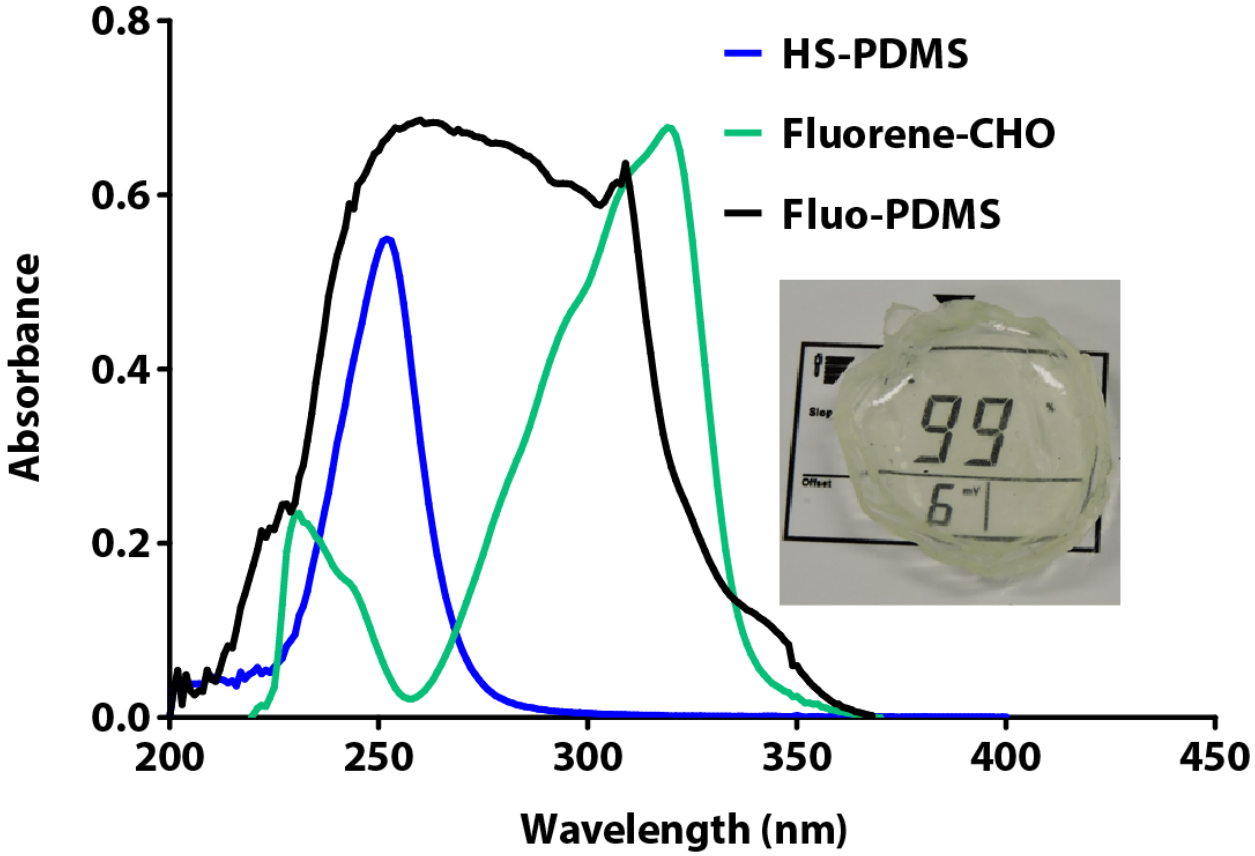


Figure S1. UV-vis absorption spectra of (a) **SMS 022**; (b) Fluorene-2-carboxaldehyde and (c) **Fluo-PDMS**, where **Fluo-PDMS** shows a blue shift upon the consumption of the aldehyde functionality during dithioacetal formation. Photo (inset) of **Fluo-PDMS**.

Differences between glutaraldehyde and aromatic aldehydes as crosslinkers.

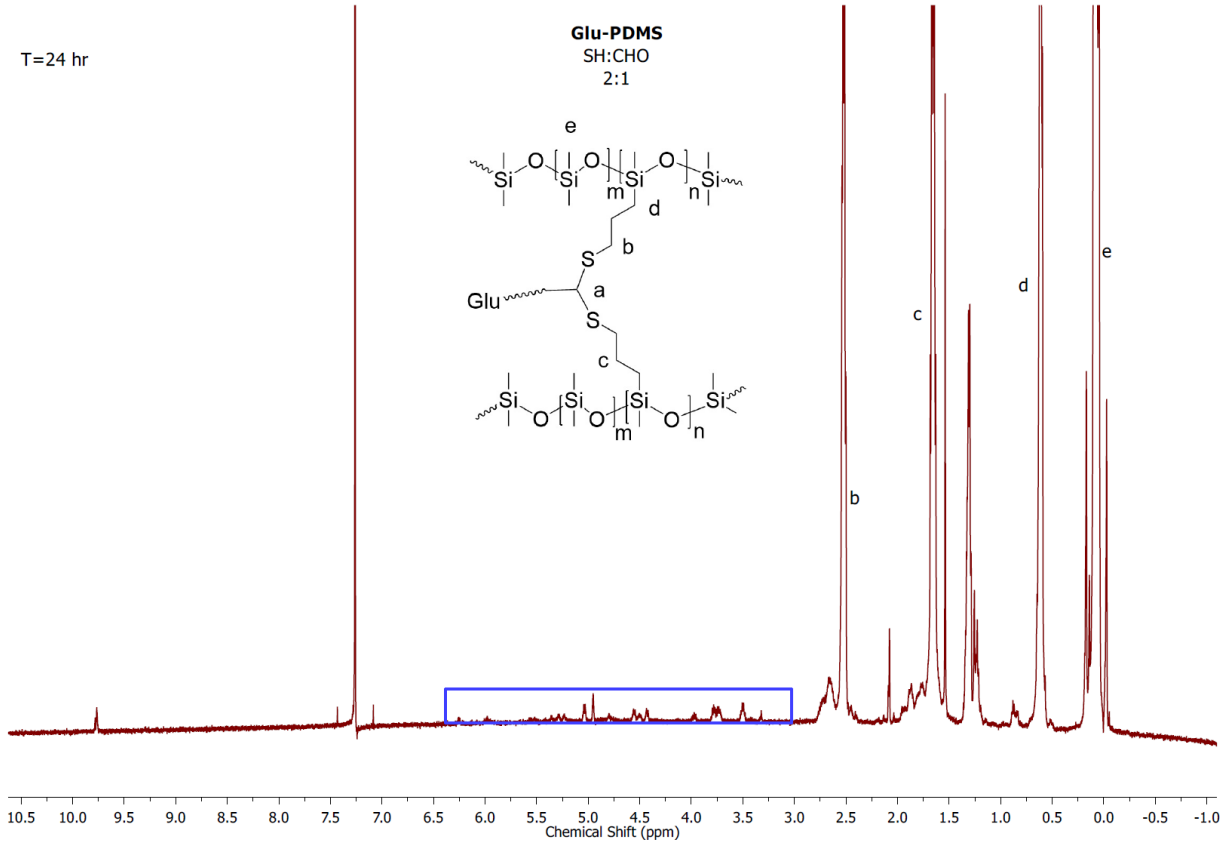


Figure S2. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **Glu-PDMS** elastomer at 60 ^{o}C after 24 h reaction (above) showing the inefficiency of aliphatic aldehydes for the formation of silicone dithioacetals. The blue box shows characteristic dithioacetal protons (δ=4.81 ppm) accompanied by aldol products.

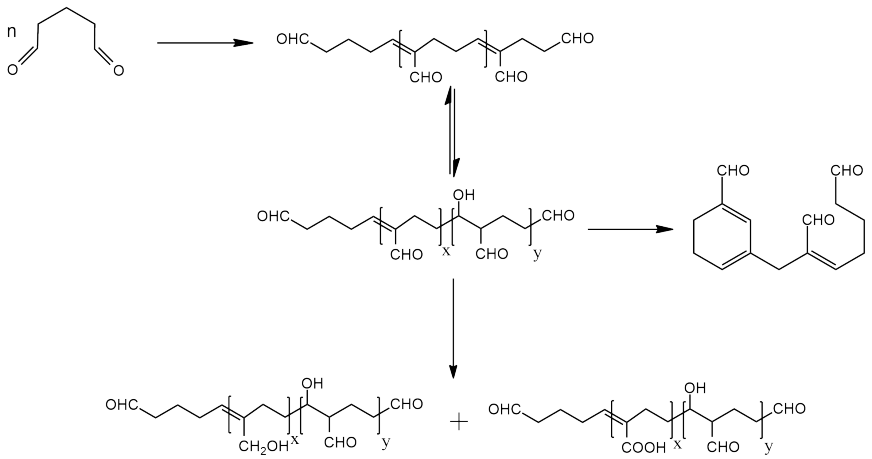


Figure S3. Possible structures of poly(glutaraldehyde)-derived components found in the mercaptopropylsilicones cured using glutaraldehyde.[1, 2]

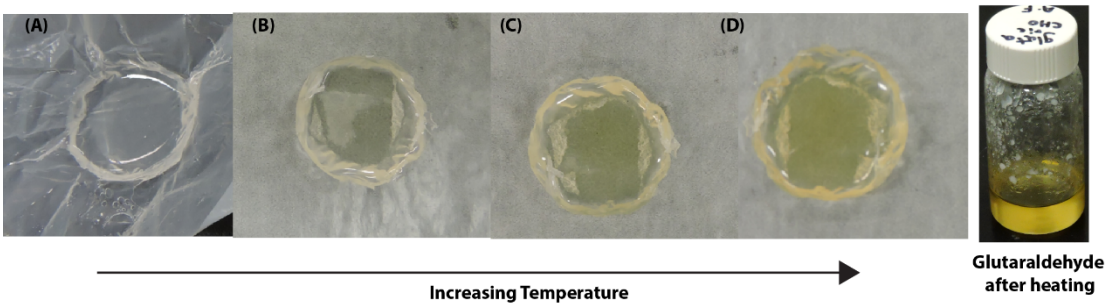


Figure S4. Thermal stability of **Glu-PDMS** (A) room temperature (B) 80 °C (C) 100 °C and (D) 130 °C. To the right, glutaraldehyde after heating at 80 °C.

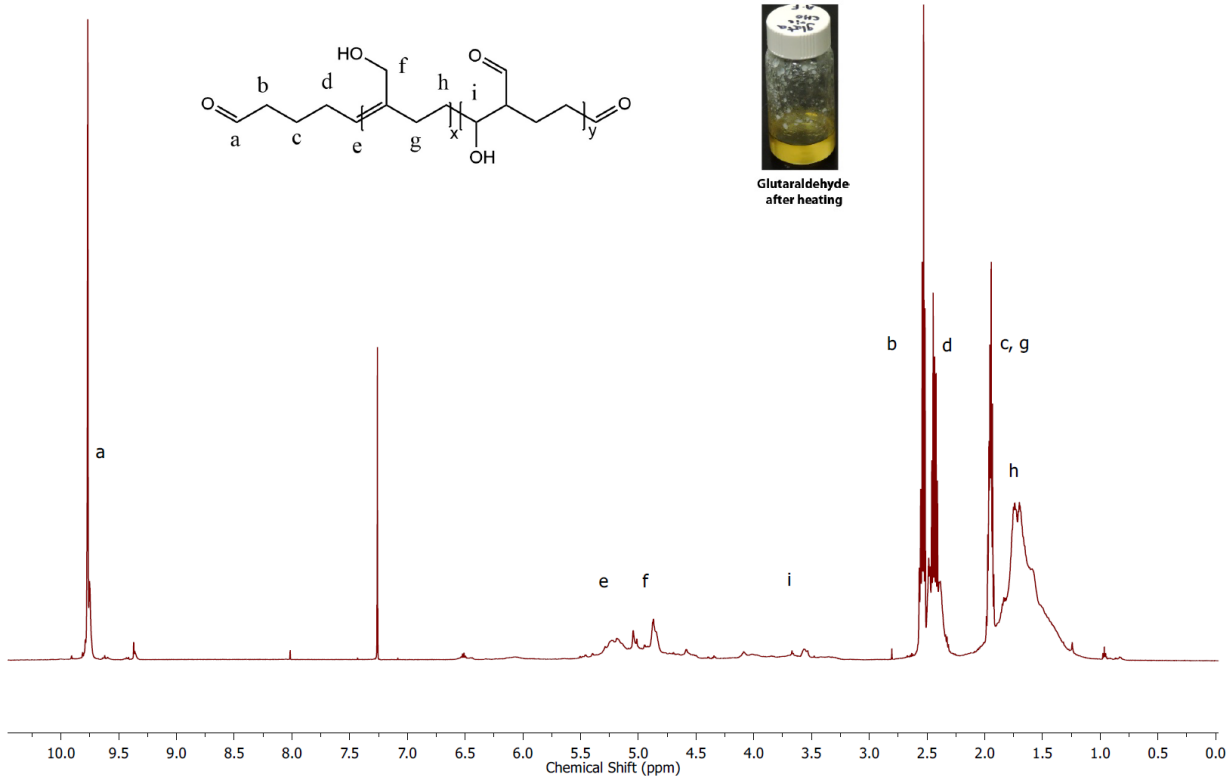


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of glutaraldehyde after heating overnight at 80 ^{o}C.

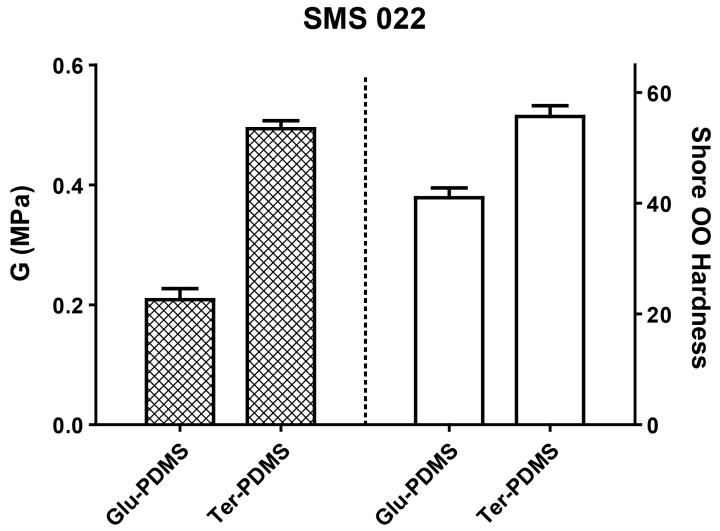
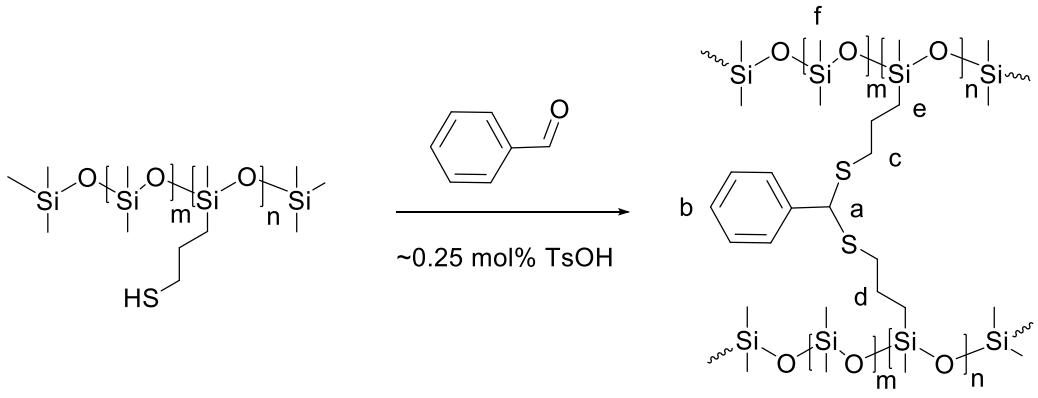


Figure S6. Comparison of stoichiometric amounts of aliphatic and aromatic aldehydes in the formation of silicone dithioacetals (products with glutaraldehyde were accompanied by aldol reactions, see above).

Curing of silicone dithioacetals using benzaldehyde



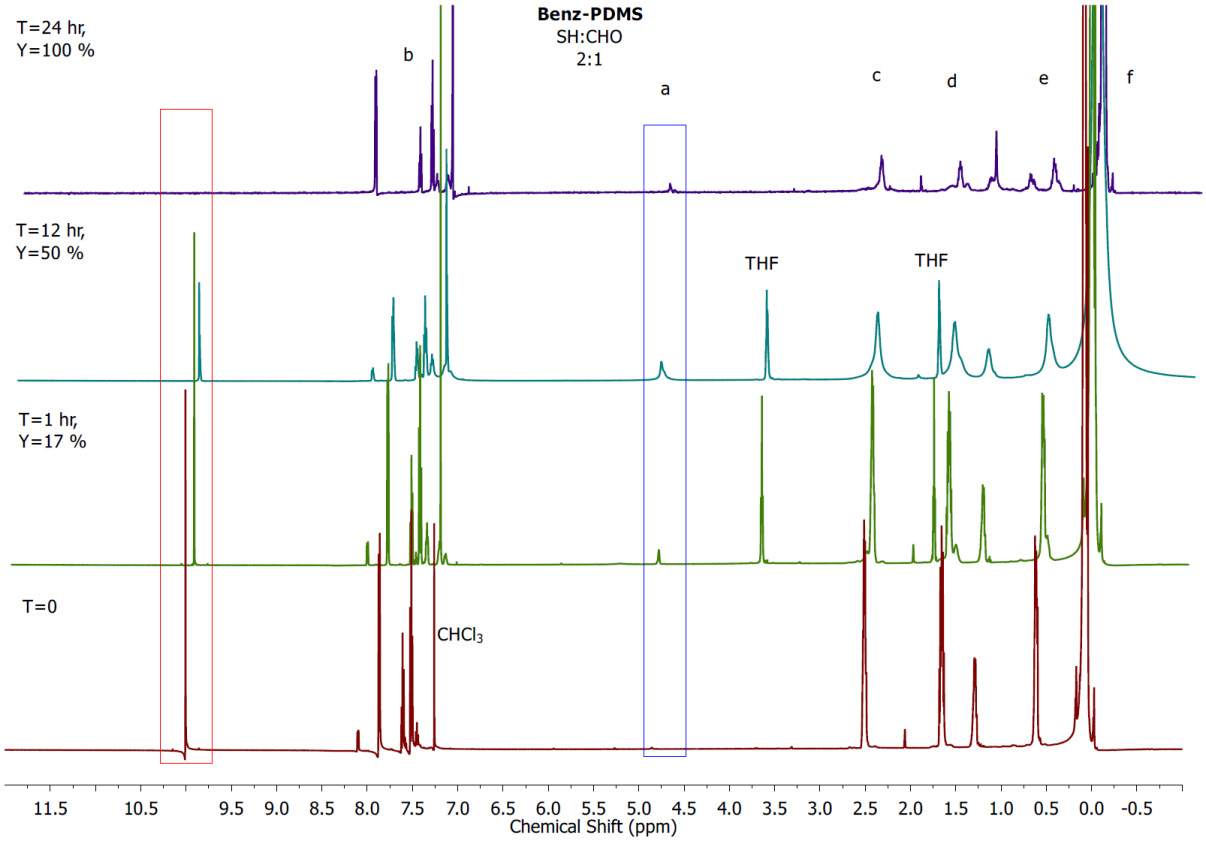


Figure S7. Stacked ^{1}H NMR spectra (600 MHz, $CDCl_3$) of benzaldehyde/HS-PDMS mixture in stoichiometric amounts and corresponding elastomers at room temperature over the course of 24 h. The blue box shows characteristic dithioacetal protons (δ=4.81 ppm) while the red box shows disappearance of aldehydic protons (δ=10.00 ppm).

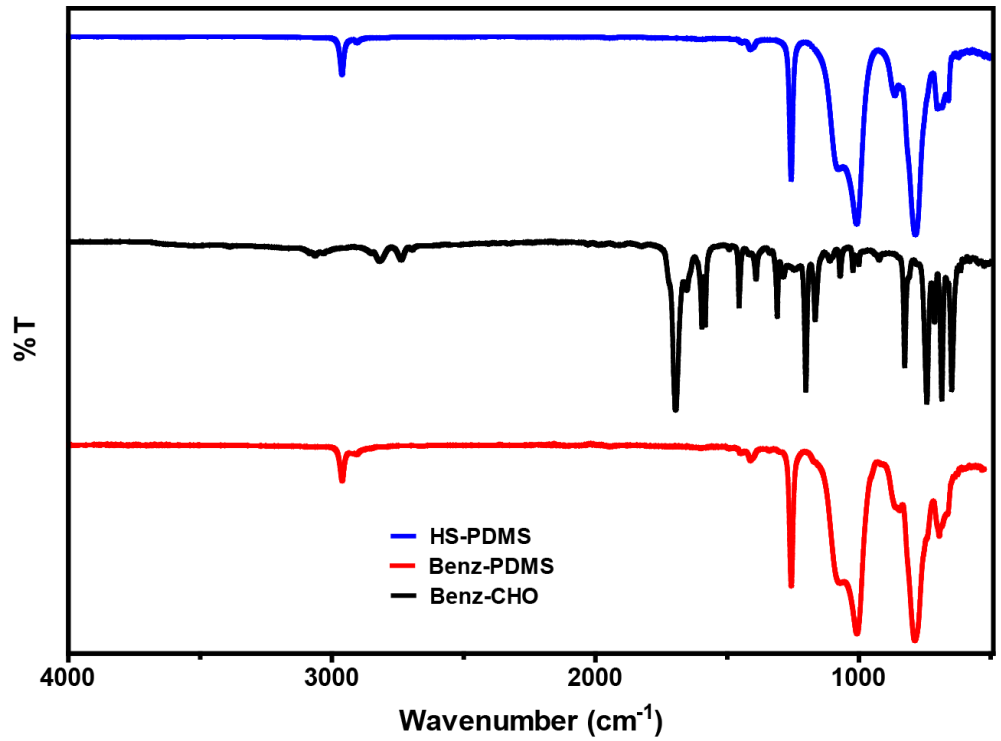


Figure S8. FTIR-ATR spectra of HS-PDMS, Benzaldehyde and **Benz-PDMS**.

Pre-adsorption of p-TsOH on silica

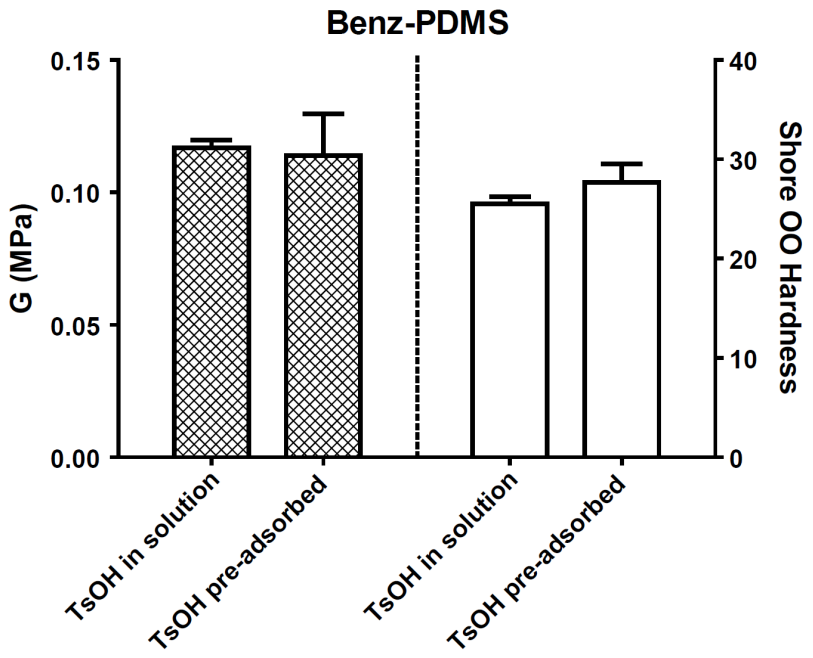


Figure S9. Comparison of elastomer outcomes of *p*-TsOH addition with and without pre-adsorption onto silica (1 wt%). Reactions occurred smoothly. Young's moduli tracked well with silica incorporation.

Physical property similarities between thioacetal cured and traditional hydrosilylation cured silicones.

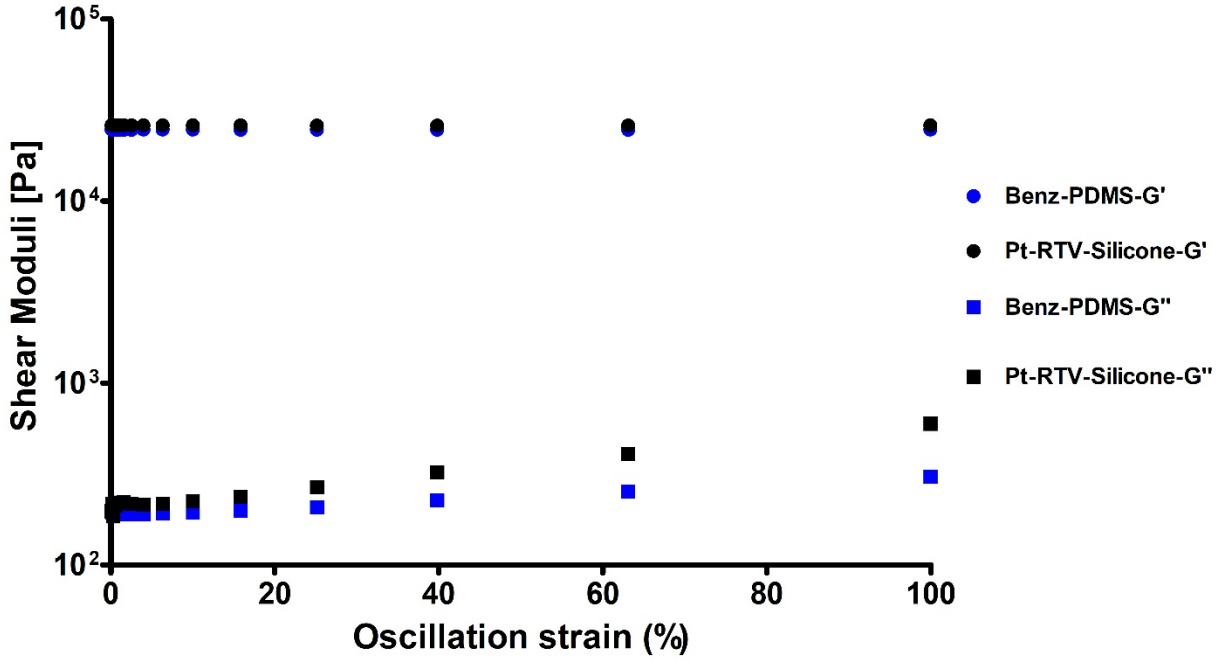


Figure S10. Shear modulus of **Benz-PDMS** and platinum-cured silicone rubber (logarithmic scale) with increasing shear strain, showing the different cure chemistries result in elastomers with similar properties. Neither silicone contained silica fillers.

Critical gel point determination

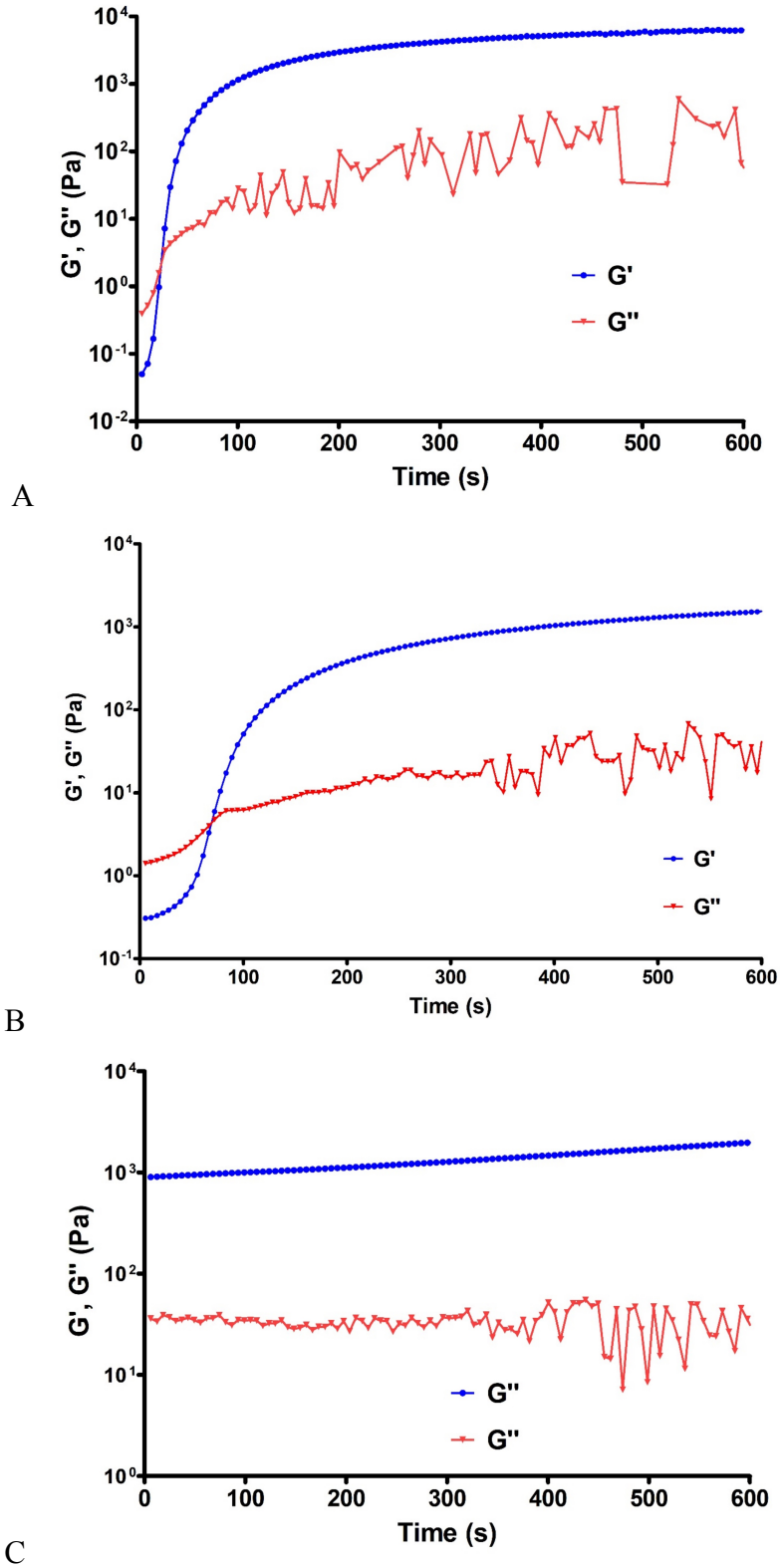


Figure S11. Shear moduli as a function of time during crosslinking reaction of Benz-PDMS under 6.28 rad · s^{-1} for 600s at 60 °C. A: (unfilled); B: (1% silica); and C: (5% silica).

Model Reaction of dodecanethiol with benzaldehyde: Preparation of (phenylmethylene)bis(dodecylsulfane)

To 1-dodecanethiol (1g, 4.94 mmol, 1.183 mL) weighed into a glass scintillation vial containing benzaldehyde (0.262g, 2.47 mmol, 0.251 mL) was added *p*-TsOH (1.262 mL of a 0.0105M solution dissolved in 50 % THF/chloroform, 0.0132 mmol). The reaction mixture was stirred (1000 rpm) at room temperature over the course of 8 h with 100 µL aliquots taken at various time intervals and analyzed by ^{1}H NMR spectroscopy to permit on to track the changes in functional group concentrations during dithioacetal formation.

To track pH changes during the reaction, the reaction mixture (200 µL) at t = 0 (pipetted immediately after adding the catalyst) was added to 10 mL of milliQ H_2O and the pH measured to be 4.04; at t= 8 h (at the end of the reaction) 200 µL of reaction mixture was added to 10 mL of milliQ H_2O and the pH measured to be 4.01. Thus, there was no change in the acid concentration during thioacetalization.

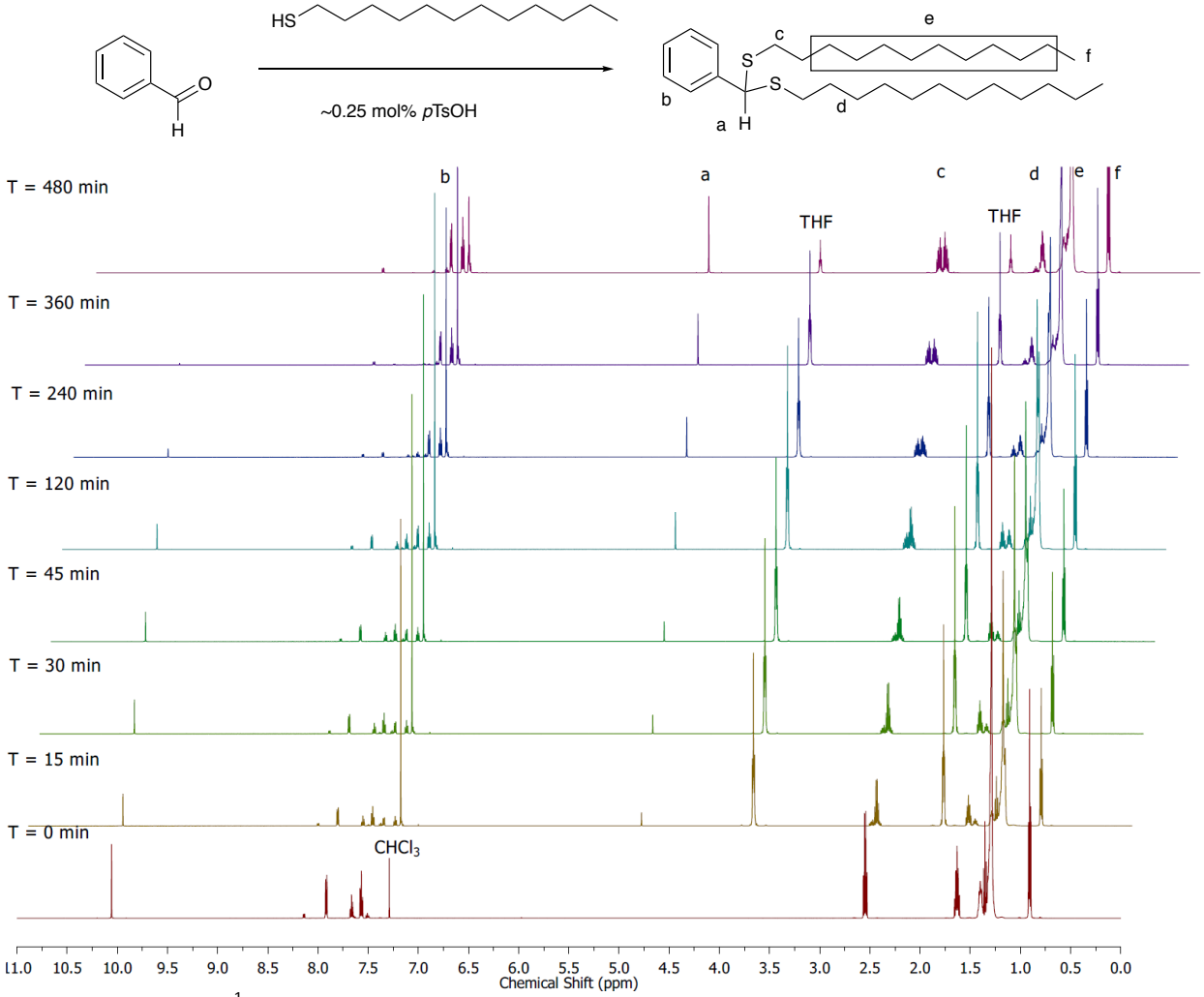


Figure S12. Stacked ^{1}H NMR spectra (600 MHz, $CDCl_3$) of model benzaldehyde/dodecane-thiol mixture in stoichiometric amounts. Showing characteristic dithioacetal protons (δ=4.81 ppm) with the disappearance of aldehydic protons (δ=10.00 ppm) at room temperature over the course of 8h.

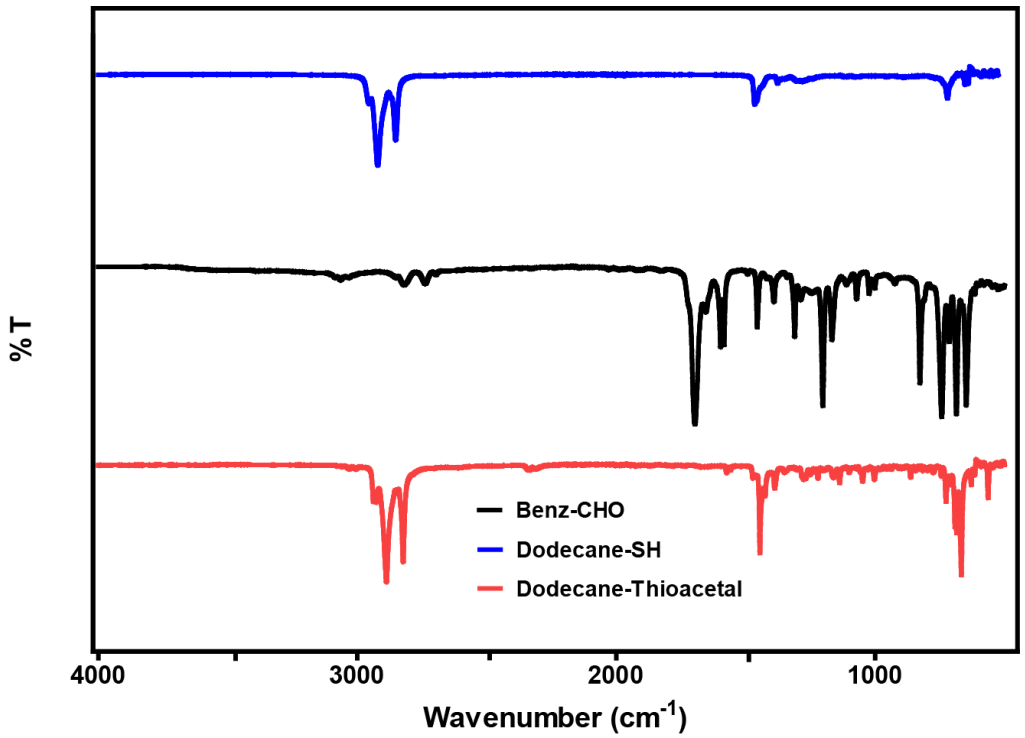


Figure S13. FTIR-ATR spectra of dodecanethiol, benzaldehyde and dodecanethioacetal.

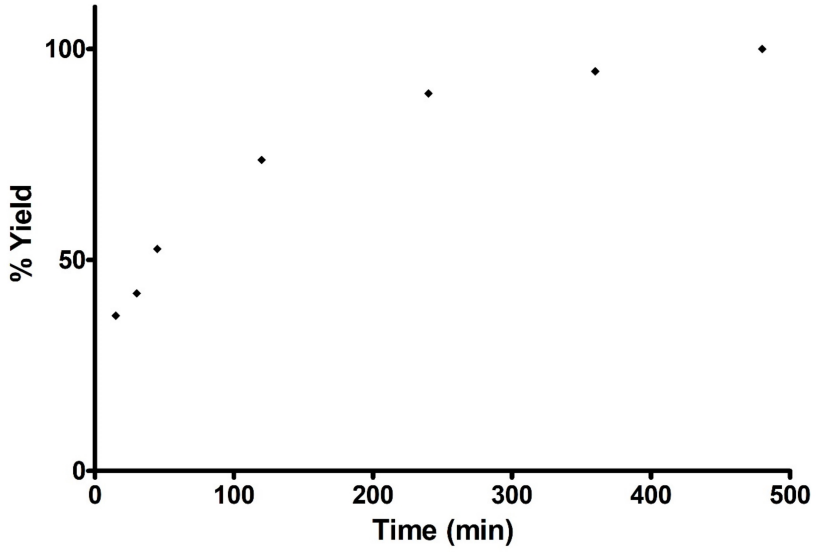
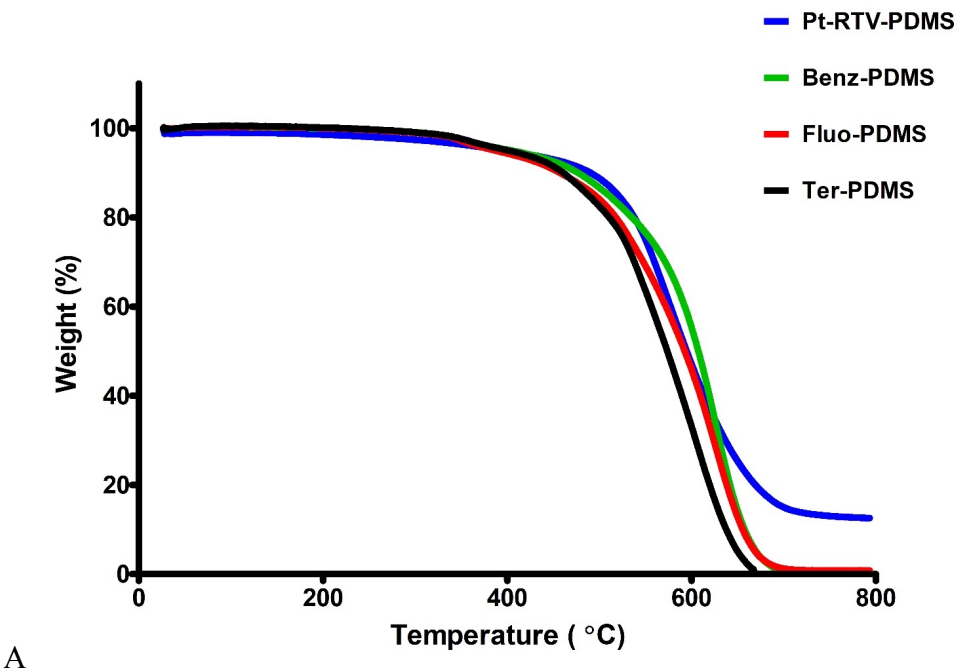
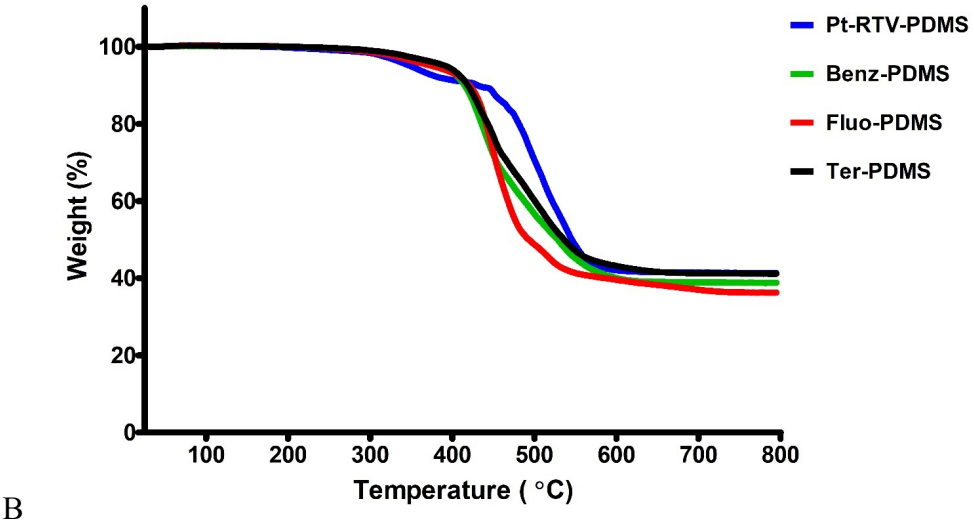


Figure S14. Formation of dithioacetal as a function of reaction time for the dodecanethiol-benzaldehyde model study based on the overall conversion of benzaldehyde and dodecanethiol.

TGA data in argon demonstrating thermal stability of thioacetal linkages



A



B

Figure S15. TGA thermograms of **Fluo-PDMS**, **Benz-PDMS**, **Ter-PDMS** and Pt-RTV-PDMS. A: under argon, B: in air (the samples did not contain silica fillers).

Heat flow data of dithioacetal crosslinked silicones

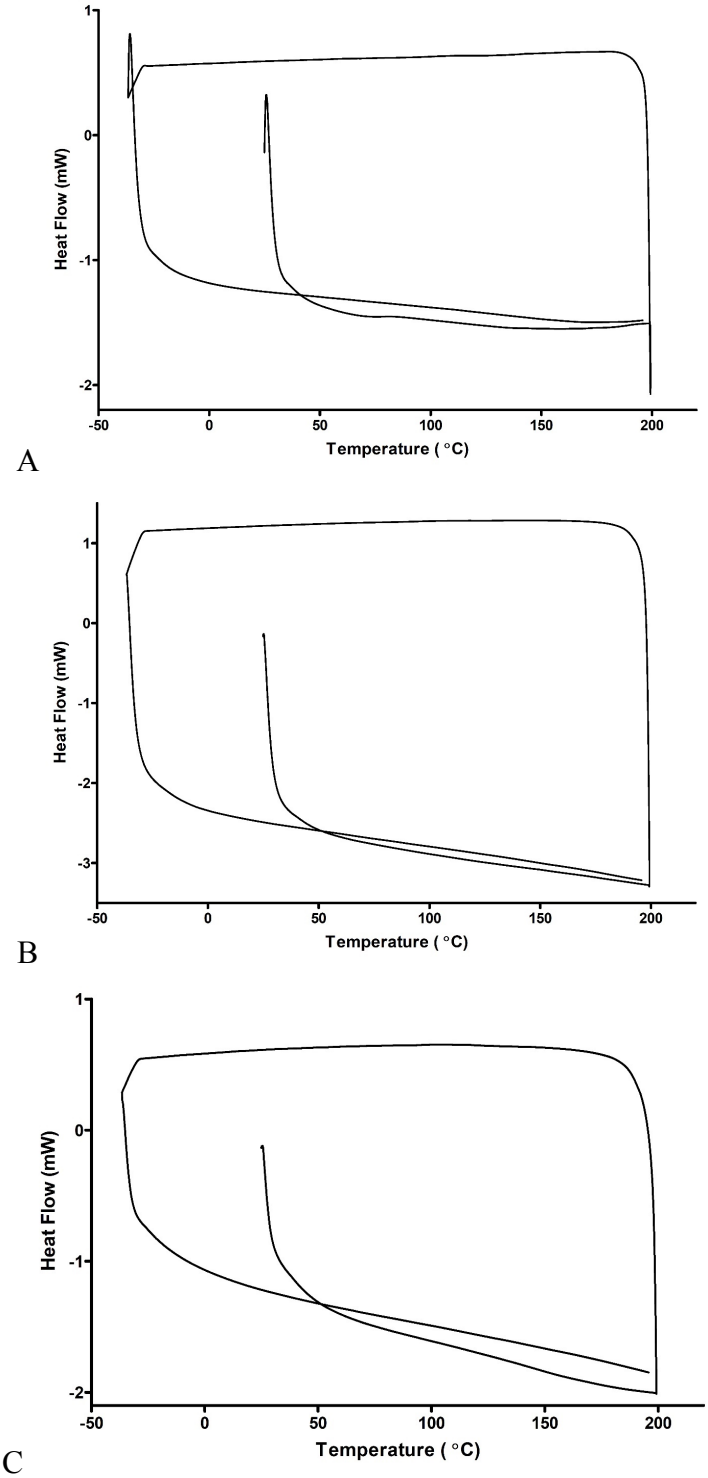


Figure S16. DSC thermograms of A: **Benz-PDMS** (unfilled); B: **Fluo-PDMS** (unfilled); and C: **Ter-PDMS** (unfilled).

References

1. S. Margel and A. Rembaum, *Macromolecules*, 1980, **13**, 19-24.
2. C. Isabelle Migneault, *BioTechniques*, 2004, 37.