

Transparent Silphenylene Elastomers from Highly Branched Monomers

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Electronic Supporting Information

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Synthesis of Linear Polysilphenylene with a Dimethylsiloxane or Phenylmethyl Spacer 4

To an oven-dried 20 mL vial was added 1,4-bis(dimethyl)silyl benzene (7.04 g, 36.2 mmol), dimethyldiethoxysilane (5.37 g, 36.2) and a stir bar. This reagent solution was allowed to stir for 5 min. To an oven-dried 250 mL two necked round-bottomed flask containing a stir bar was added the reagent solution (3 mL) and $B(C_6F_5)_3$ (50 μ L, 10mg/mL solution in toluene). Every 30 min additional reagent solution (3 mL) and $B(C_6F_5)_3$ (20 μ L, 10mg/mL solution in toluene) were added to the two necked round-bottomed flask until all the reagent solution was consumed. 1,4-Bis(dimethyl)silylbenzene (1 mL, 4.50 mmol) was added to reaction mixture. From time to time a small aliquot was removed and analyzed by 1H NMR to confirm the presence of SiH end groups and absence of SiOEt end groups. The reaction mixture was quenched with neutral alumina (\sim 0.5 g), gravity filtered and concentrated under reduced pressure. The linear Me_2SiO -co-silphenylene silicone product **4a** was purified by removal of volatiles using kugelrohr distillation at 200 $^\circ$ C under reduced pressure. The polymer product was a viscous, colorless oil. 1H -NMR (600 MHz, $CDCl_3$) δ 7.55-7.54 (m, 228 H), 4.43 (sept, J = 3.8 Hz, 2 H), 0.34-0.32 (m, 693 H), 0.07-0.06 (m, 247 H). GPC: M_n =19,320, M_w =36,760, D_M =1.90.

The same process could be used to make analogous compounds with a **Phenylmethyl Spacer**: 1,4-bis(dimethyl)silyl benzene (5.45g, 28.0 mmol), diethoxymethylphenylsilane (5.89 g, 28.0 mmol). The linear $PhMeSiO$ -co-silphenylene silicone **4b** was purified using kugelrohr distillation at 200 $^\circ$ C under reduced pressure. Polymer product was a viscous, colorless oil. 1H -NMR (600 MHz, $CDCl_3$) δ 7.54-7.27 (m, 110 H), 7.36-7.27 (m, 20 H), 7.25-7.17 (m, 17 H), 7.22 (sep, 2 H, 3.8 Hz), 0.35-0.19 (m, 237 H). GPC: M_n =8949, M_w =16097, D_M =1.80.

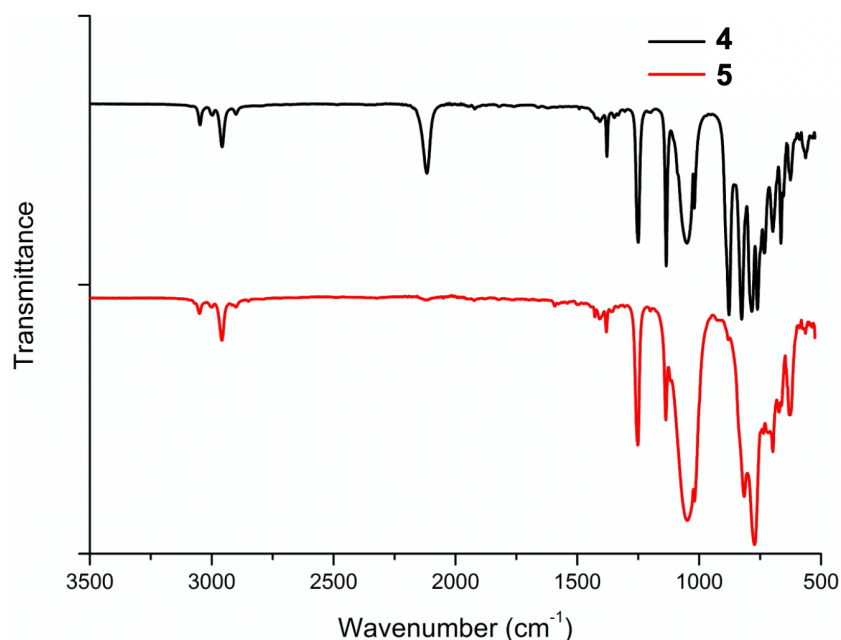
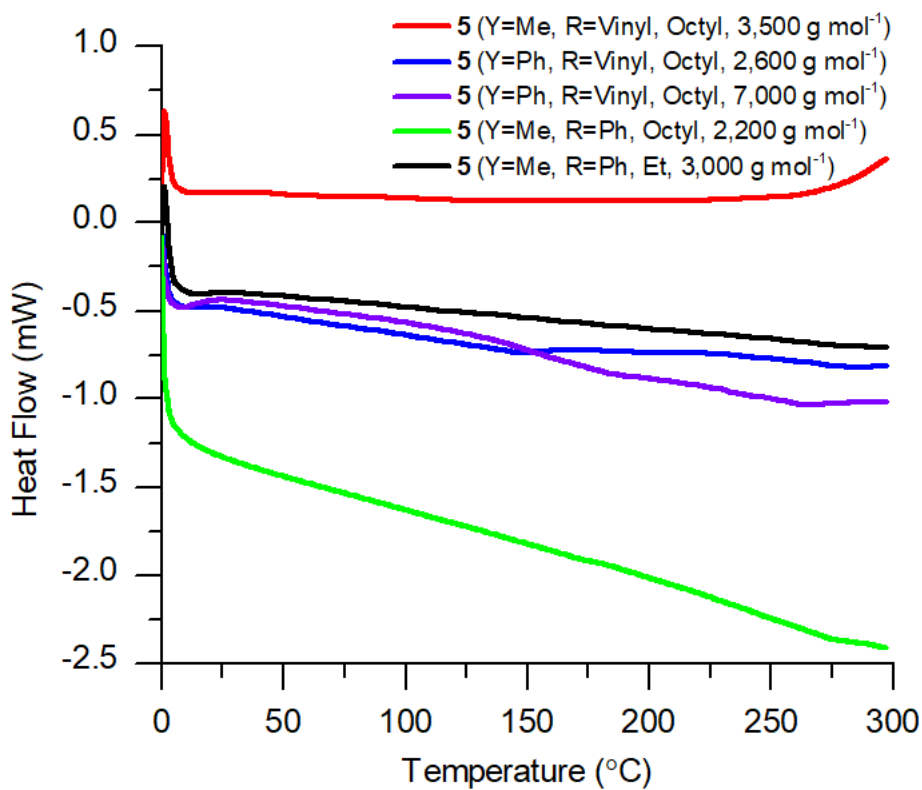
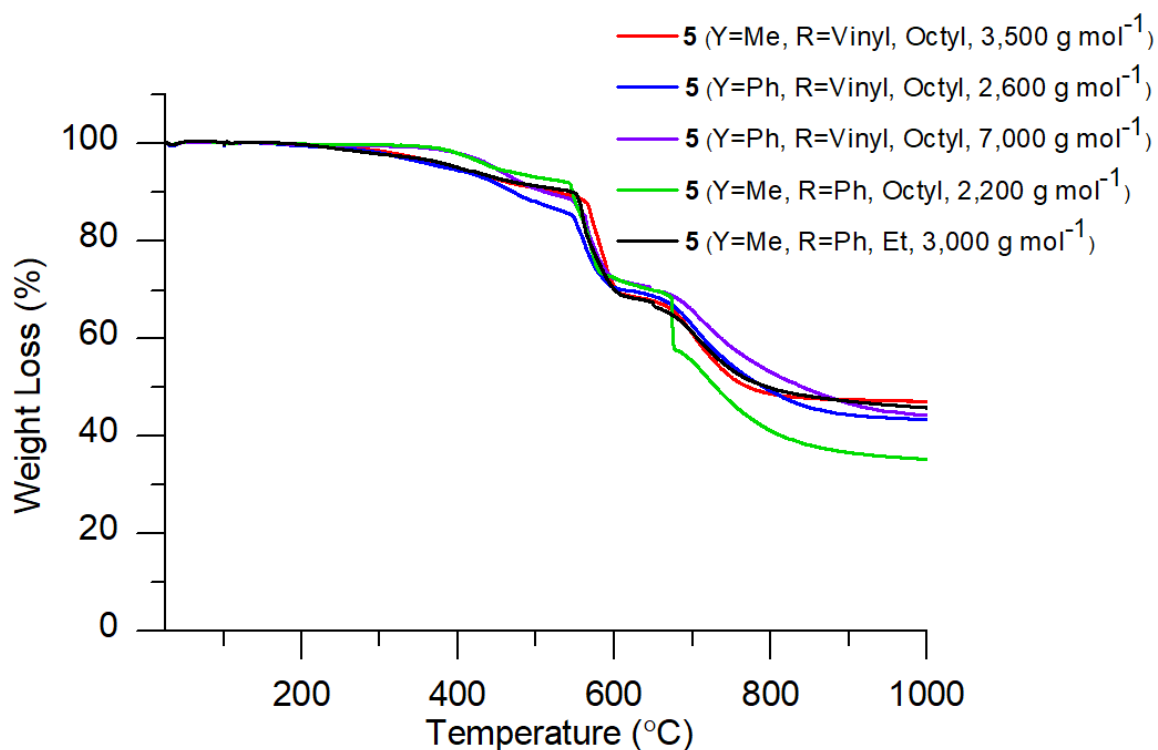


Figure S1. IR spectra for monomer linear alternating polymer **4** and the elastomer **5** prepared by curing **4** with $(OctO)_3SiMe$ as crosslinker, $Y = Me$ (Figure 2).

A



B

Figure S2. Thermal behavior of the elastomers 5. A: TGA in air of the elastomers 5 of various base materials 4. B: DSC showing degradation of the elastomers 5 of various base materials 4 (Figure 2).

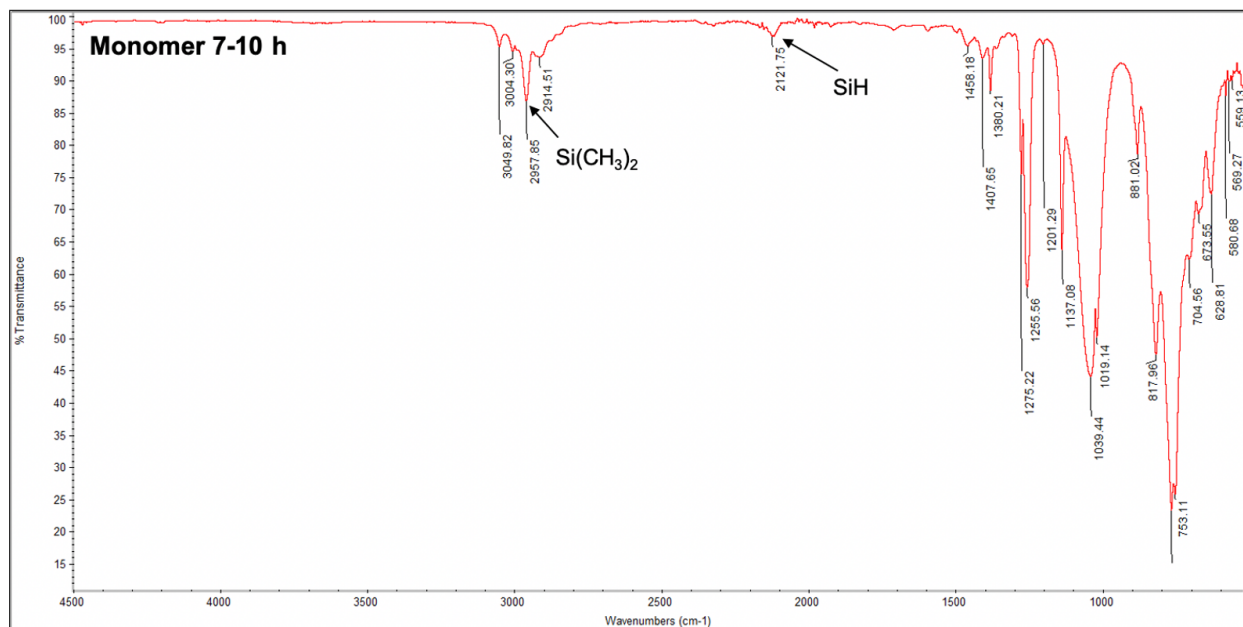


Figure S3. IR spectra of cured product of **7** → **10** after heating at 250 °C for 10 h.

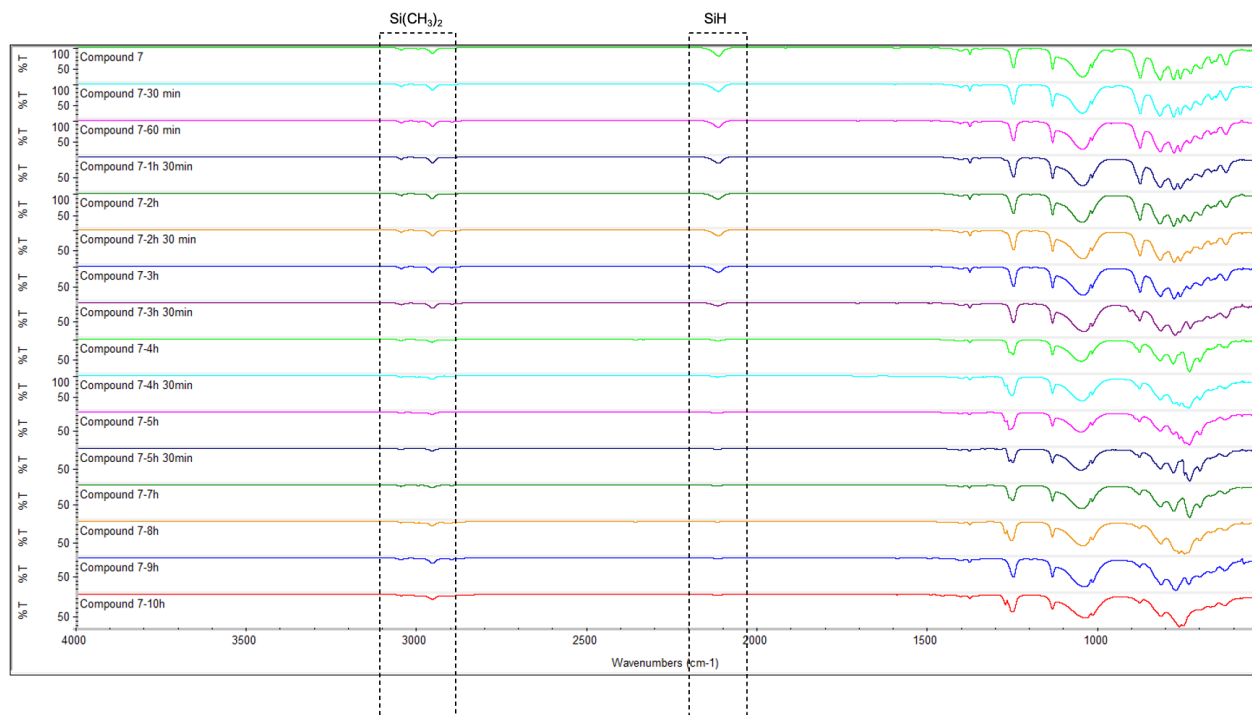


Figure S4. Changes in **7** during crosslinking → **10** with heating at 250 °C via FT-IR.

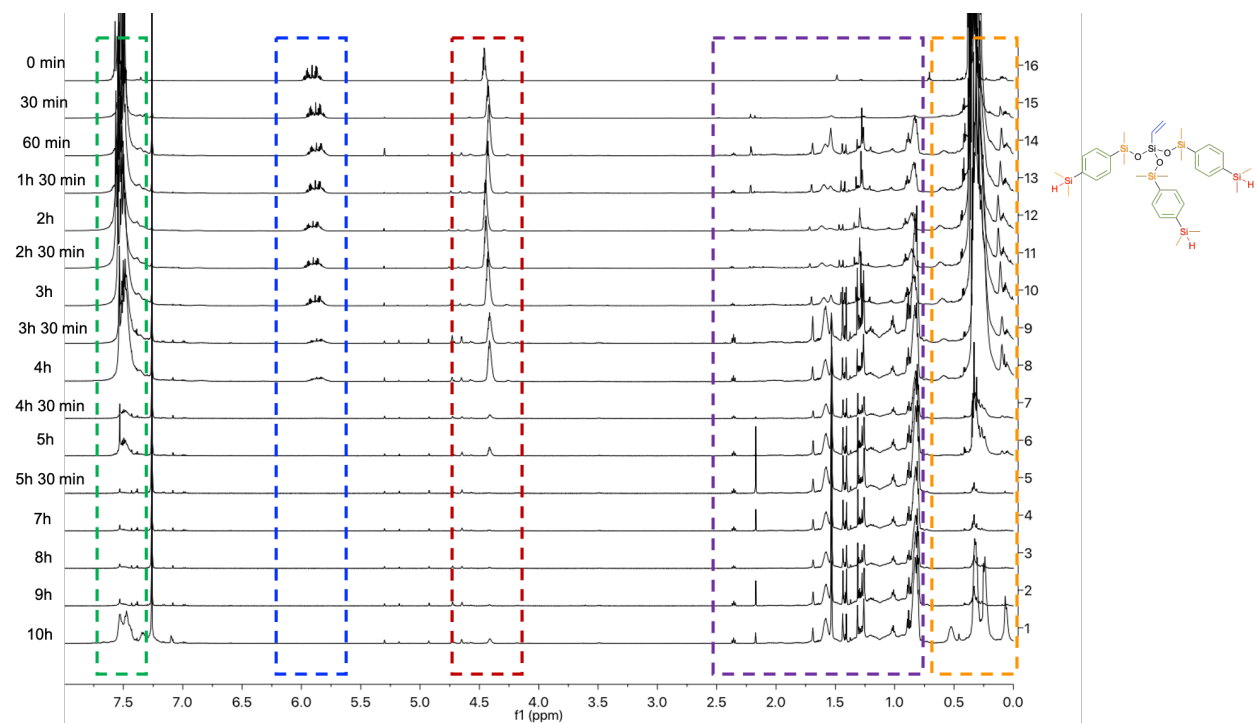


Figure S5. Changes in **7** during crosslinking \rightarrow **10** with heating at 250 °C via ^1H NMR.

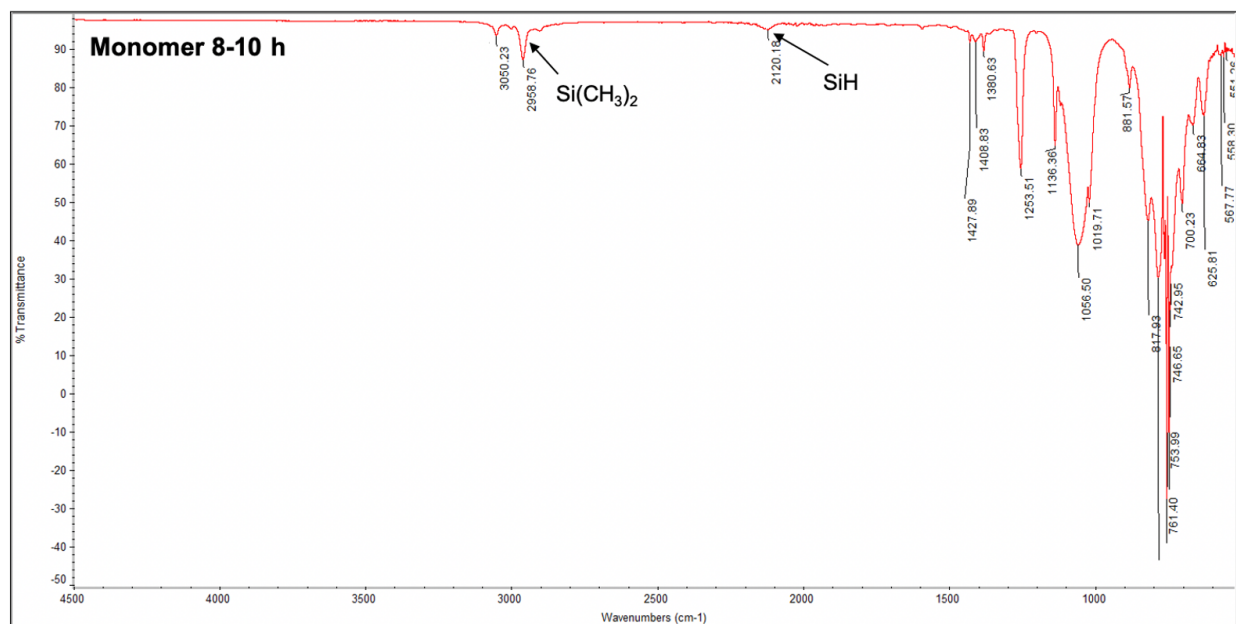


Figure S6. Cured product of **8** \rightarrow **11** after heating at 250 °C for 10 h.

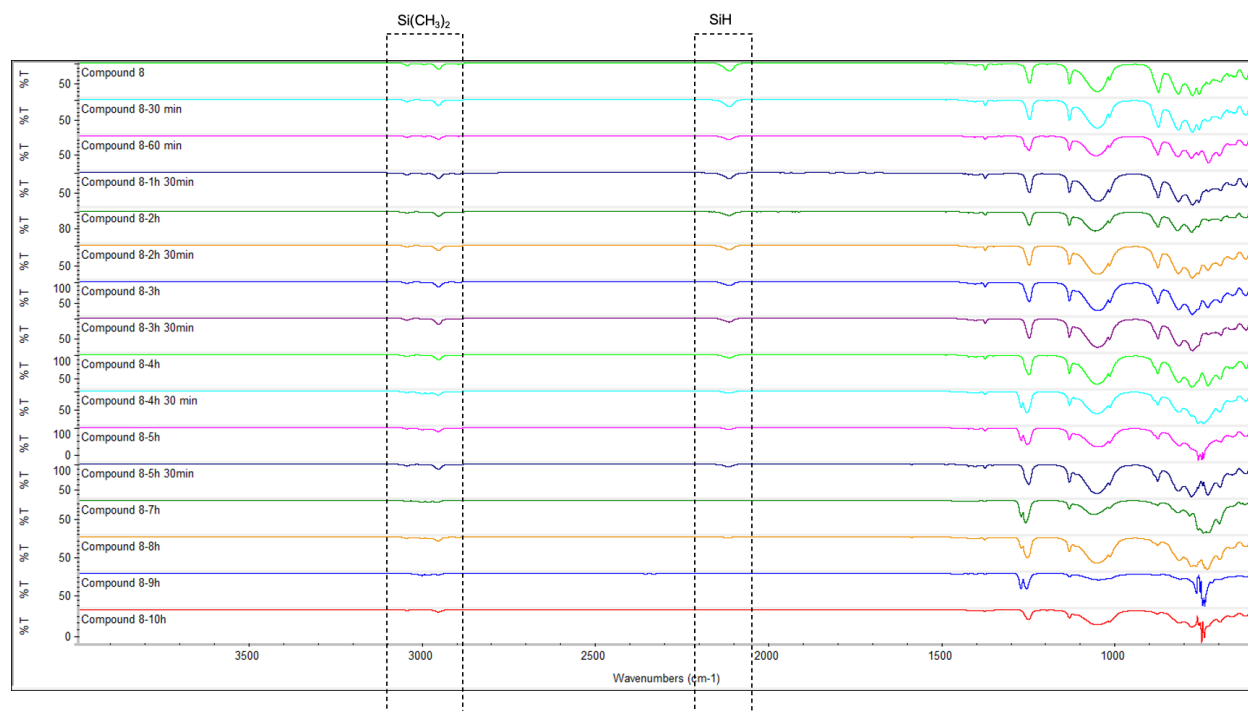


Figure S7. Changes in **8** during crosslinking \rightarrow **11** with heating at 250 °C via FT-IR.

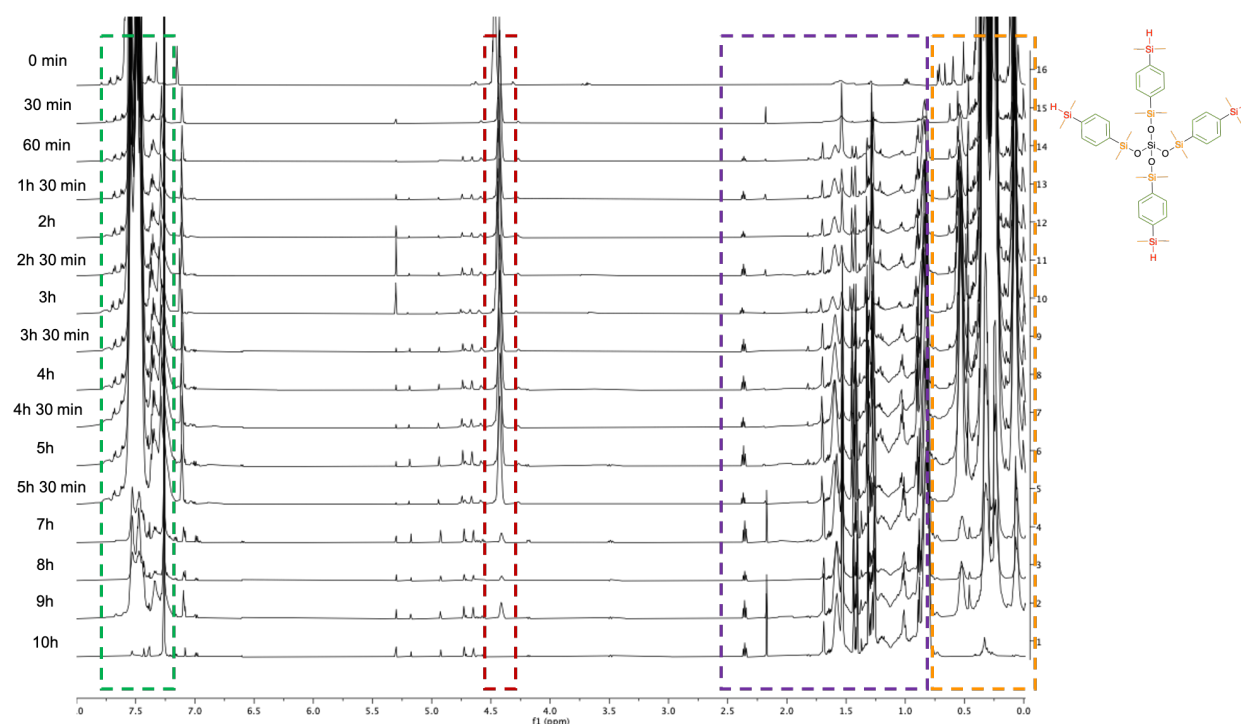


Figure S8. Changes in **8** with during crosslinking \rightarrow **11** with heating at 250 °C via ^1H NMR.

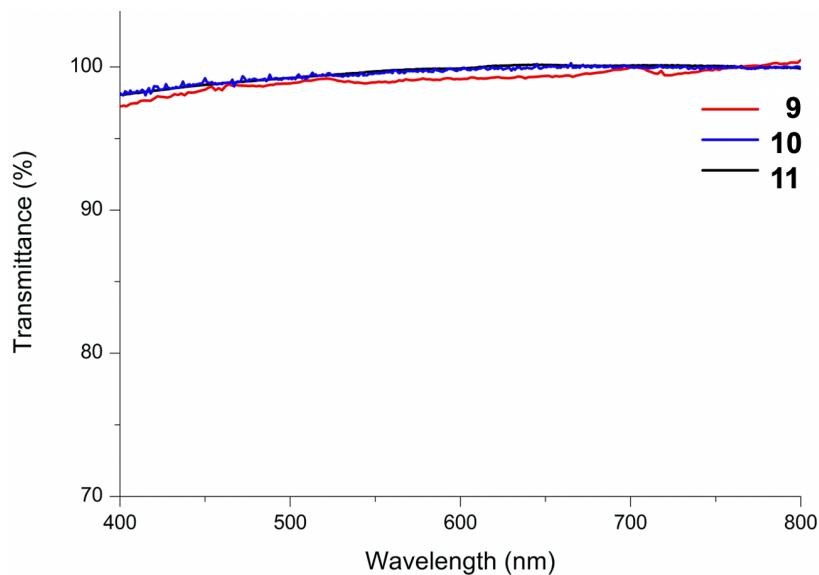


Figure S9. Transmittance data for elastomers **9-11**.

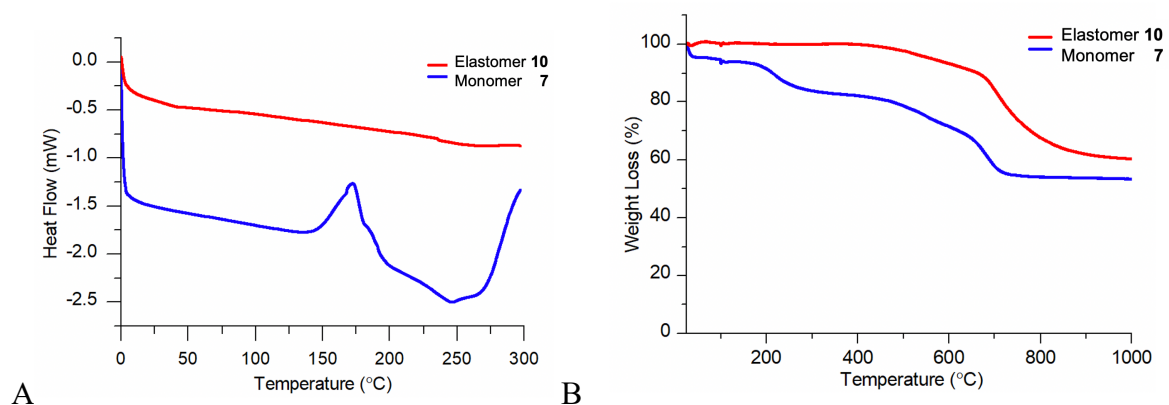


Figure S10. Thermal behavior of the monomer **7** and elastomer **10**. A: DSC under argon of the monomer **7** and elastomer **10**. B: TGA in air showing degradation of the monomer **7** and elastomer **10**.

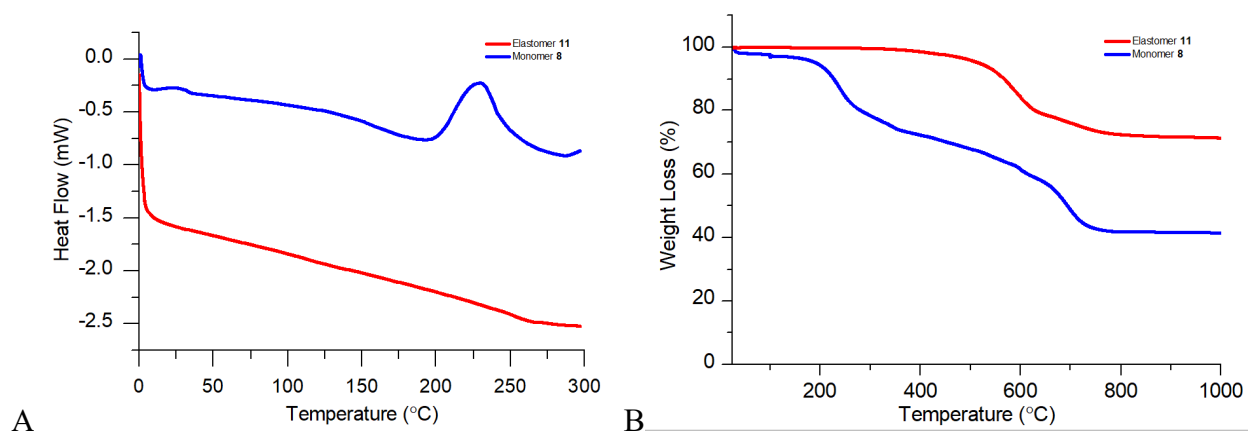


Figure S11. Thermal behavior of the monomer **8** and elastomer **11**. A: DSC under argon of the monomer **8** and elastomer **11**. B: TGA showing degradation in air of the monomer **8** and elastomer **11**.

Compound 2

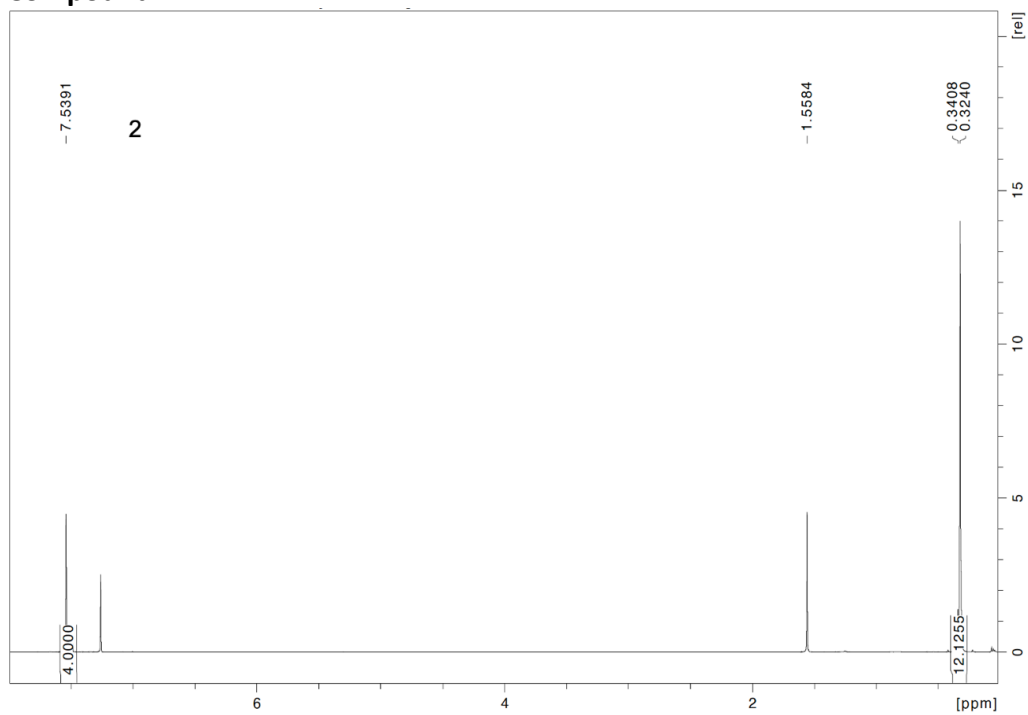


Figure S12. ¹H NMR spectra for compound **2**.

Compound 3

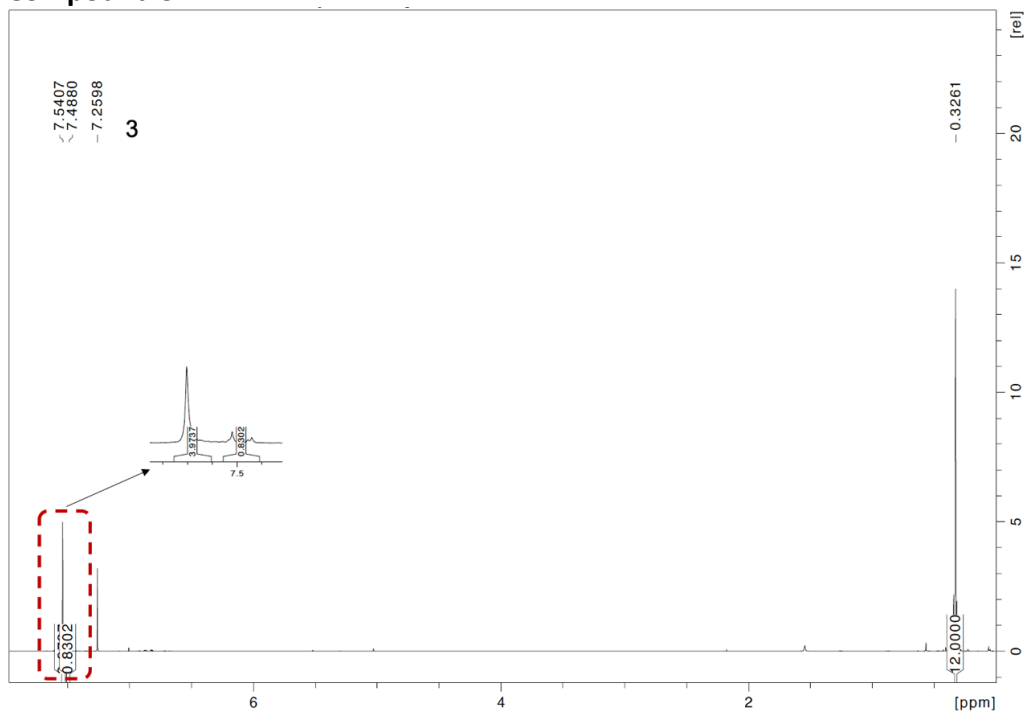


Figure S13. ¹H NMR spectra for compound **3**.

4a

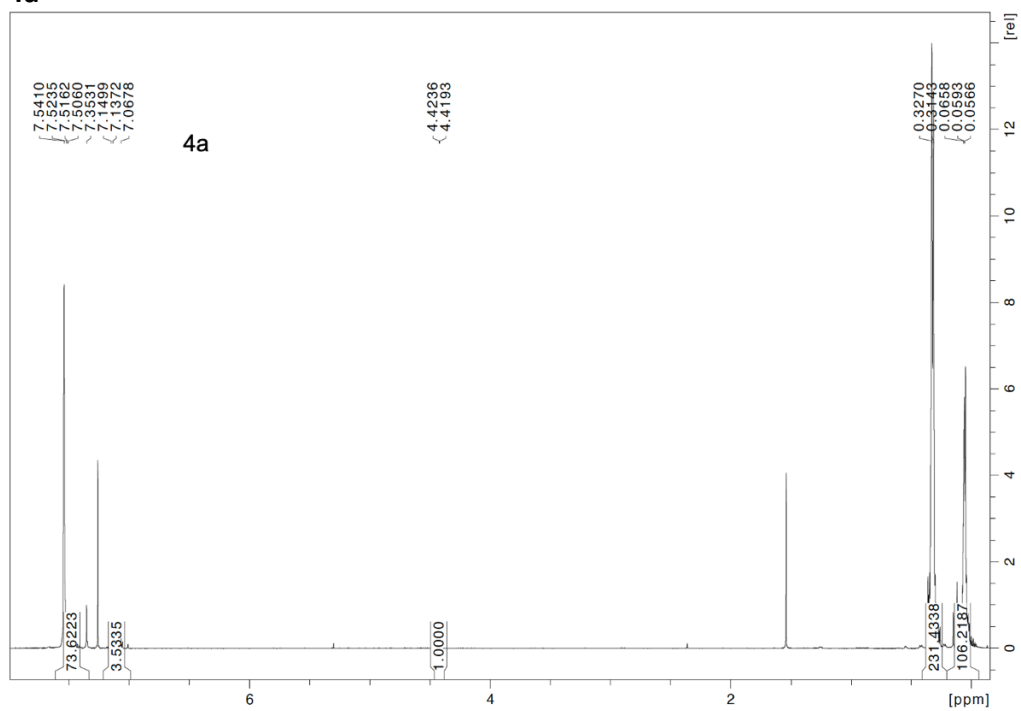


Figure S14. ¹H NMR spectra for compound **4a**.

4b

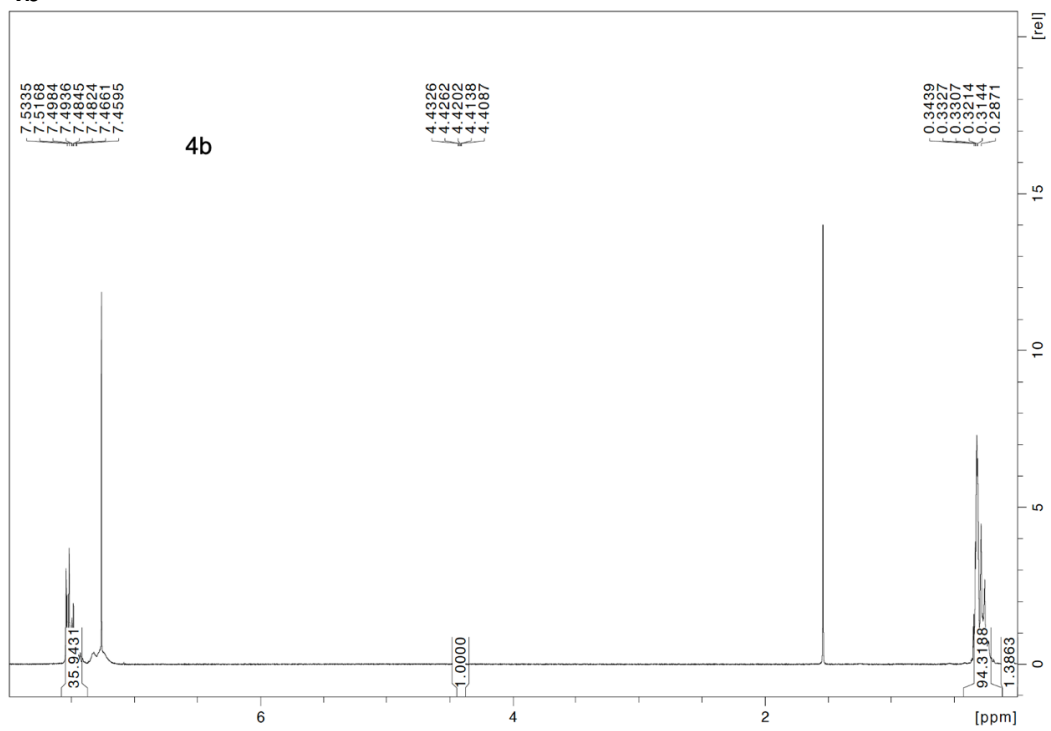


Figure S15. ¹H NMR spectra for compound **4b**.

Compound 6, R = CH₃

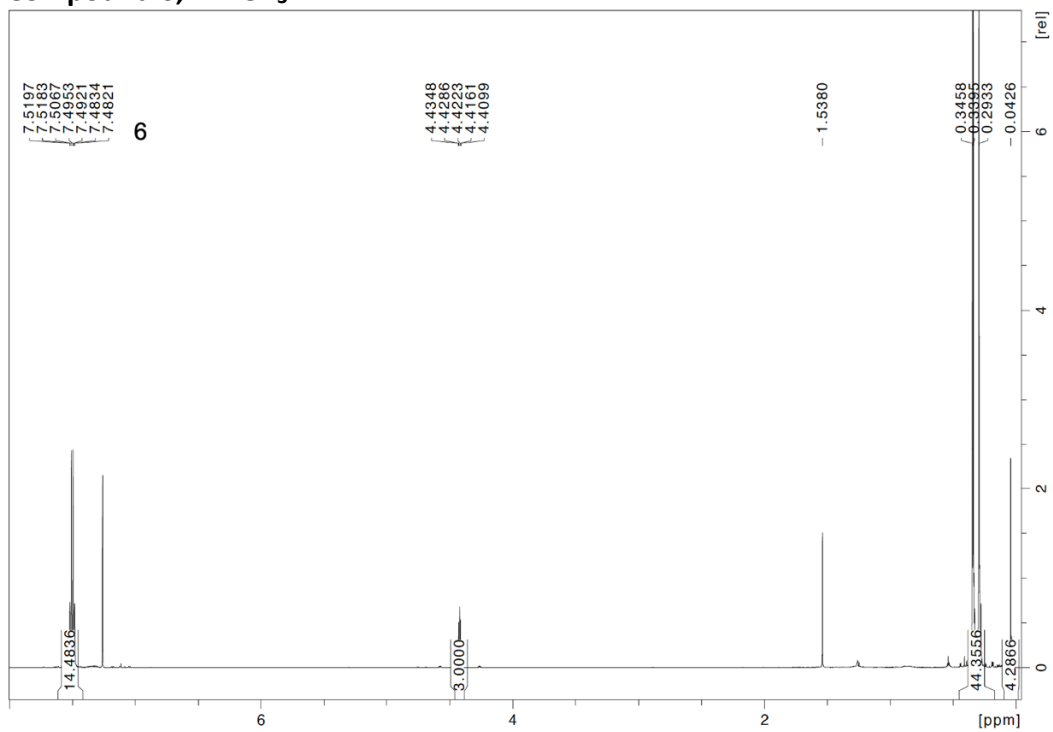


Figure S16. ¹H NMR spectra for compound **6**.

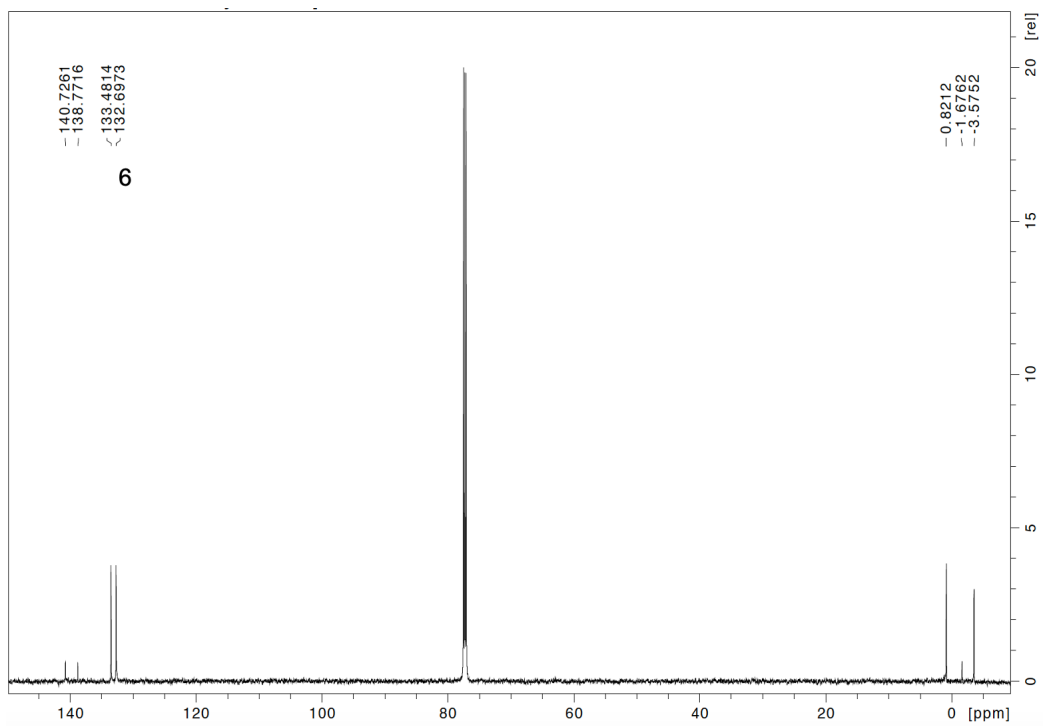


Figure S17. ¹³C NMR spectra for compound **6**.

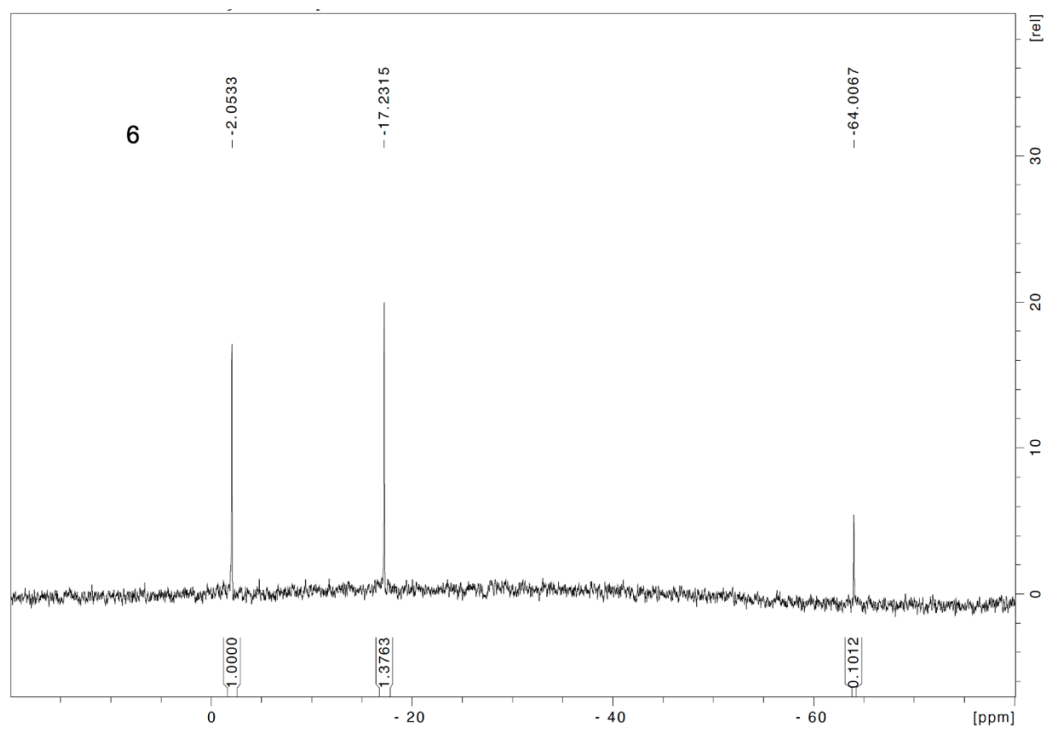


Figure S18. ^{29}Si NMR spectra for compound **6**.

Compound 7, R= Vinyl

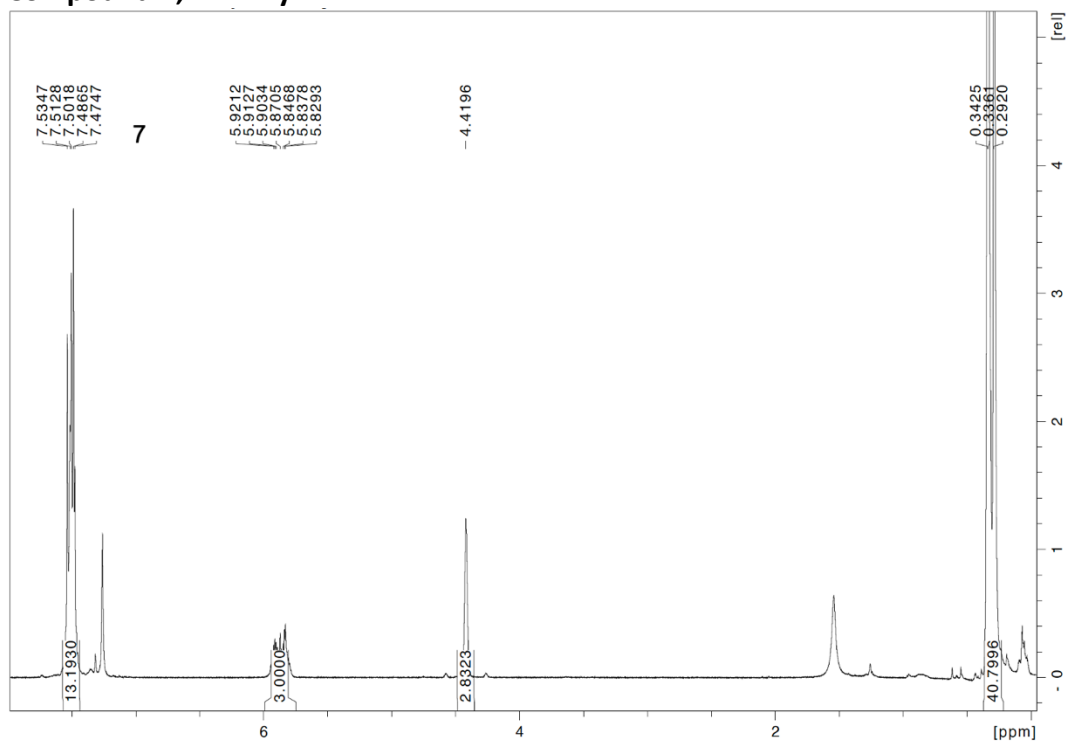


Figure S19. ¹H NMR spectra for compound 7.

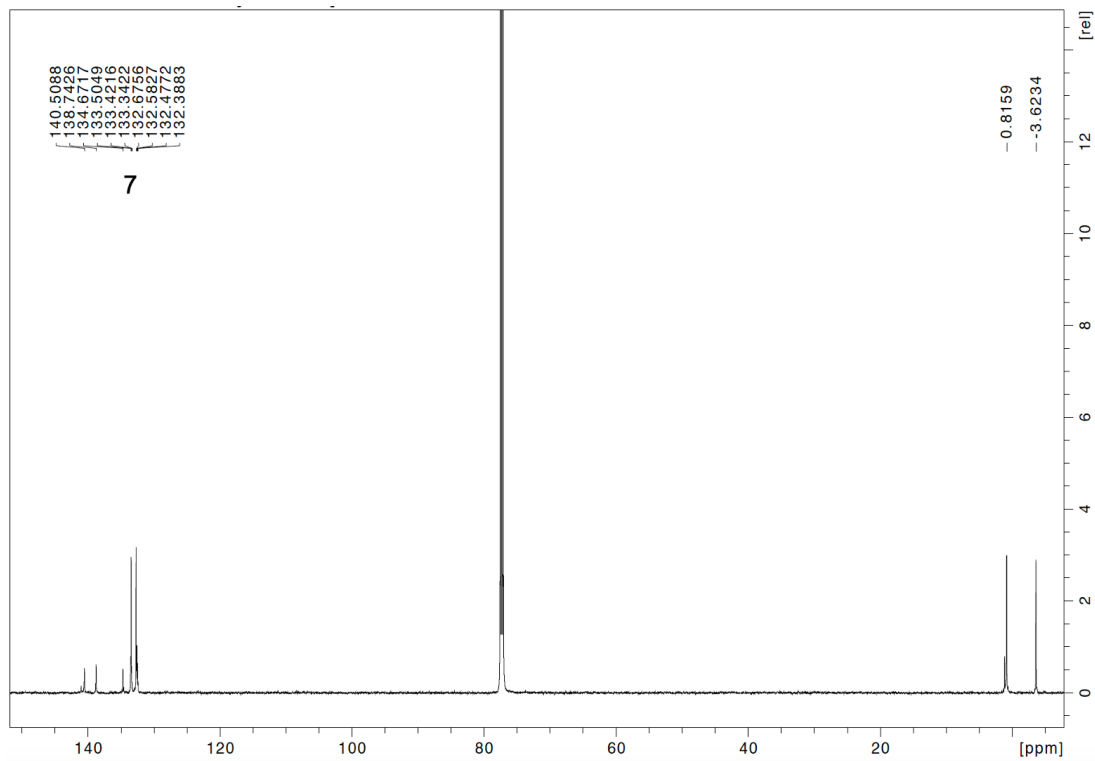


Figure S20. ¹³C NMR spectra for compound 7.

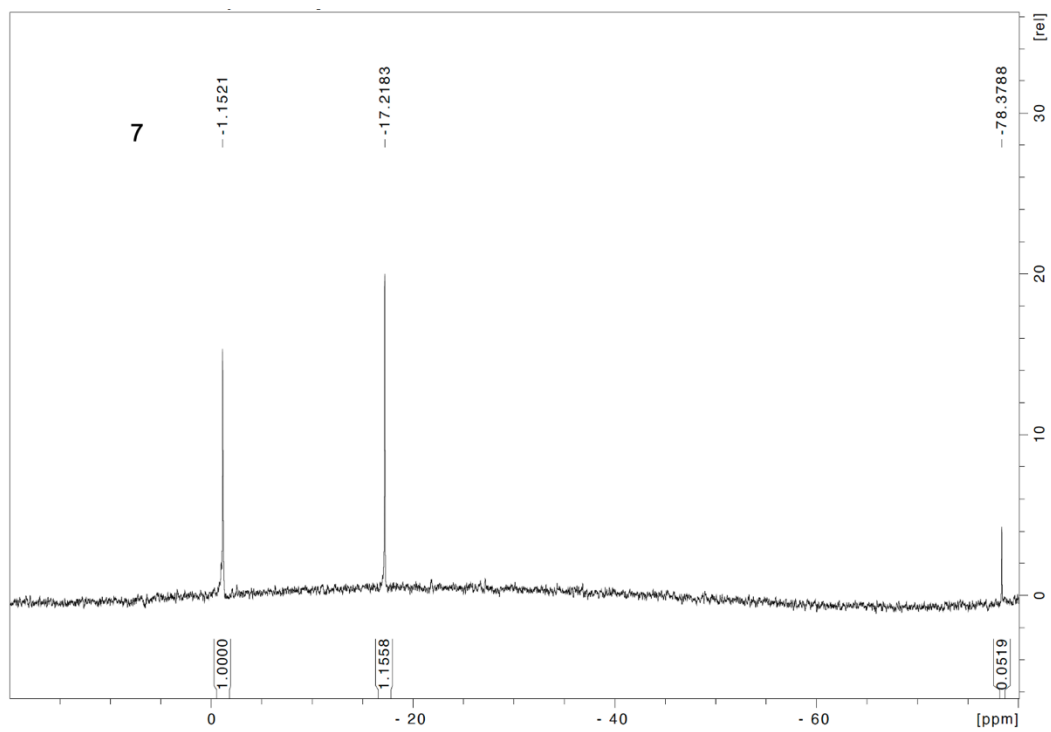


Figure S21. ^{29}Si NMR spectra for compound **7**.

Compound **8**

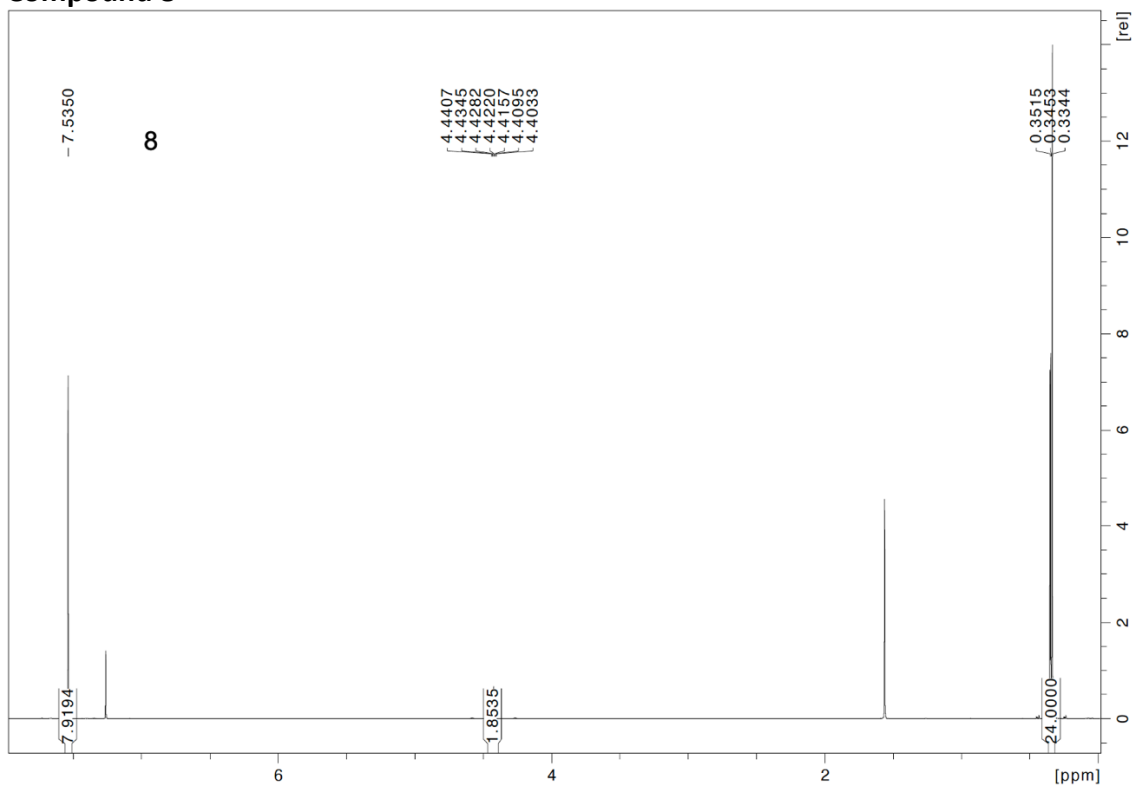


Figure S22. ^1H NMR spectra for compound **8**.

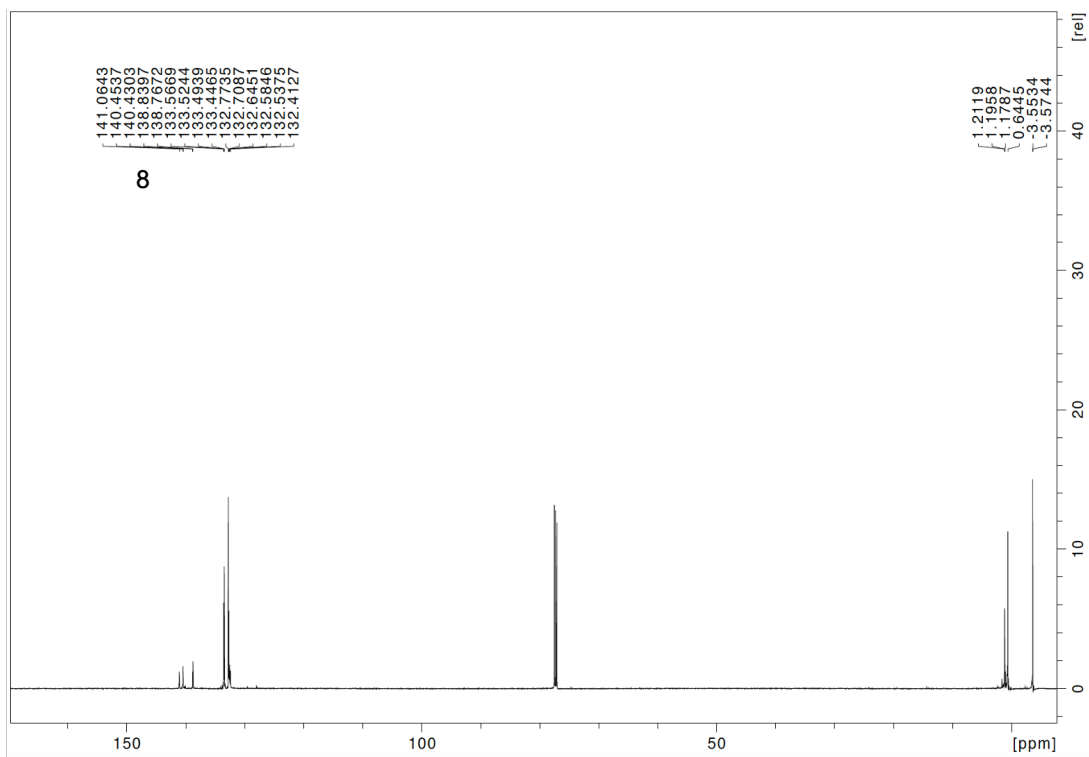


Figure S23. ^{13}C NMR spectra for compound **8**.

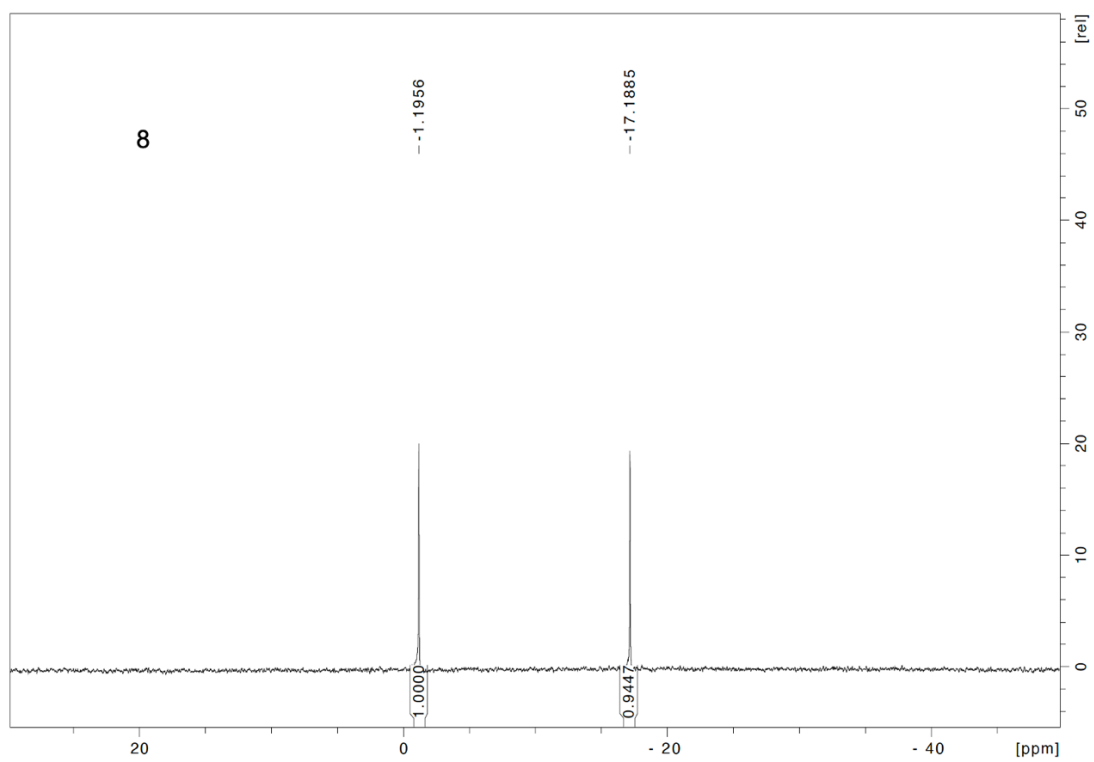


Figure S24. ^{29}Si NMR spectra for compound **8**.

Crosslink density by swelling tests for elastomers 10,11

Fresh elastomers were prepared from the precursors **7,8** (~2.0 g) that were transferred into a 20.0 mL glass vial and placed in a 250 °C oven for 10 h (demonstrating in Figure S25).

Elastomer **10** (0.0076 g, 0.011 mmol) was placed into a 20.0 mL glass vial together with hexanes (10 mL). After soaking for 24 h, the weight of swollen **10** was recorded (0.0095 g, 25.0% swelling), and then dried under vacuum at 635 Torr at 60 °C for 6h and the weight of the dry extracted **10** was recorded (0.0051 g, 67.1% drying).

The procedure was repeated with **11** (0.0056 g, 0.0065 mmol); swollen **11** (0.0082 g, 46.4% swelling); dry extracted (0.0040 g, 71.4% drying, Table S1).

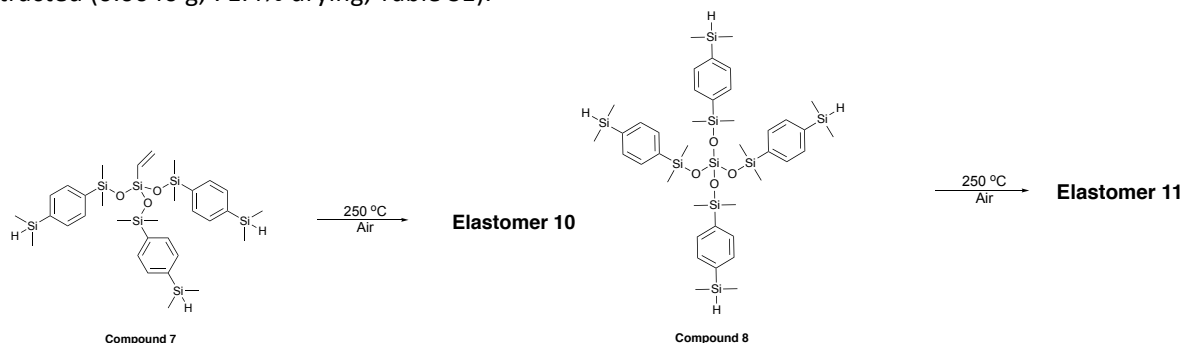


Figure S25. Elastomer synthesis using different silphenylene resin precursors

Swelling (%) and drying (%)

a) The swelling (%) is defined by Equation S1:

$$\text{Swelling (\%)} = (M_w - M_i) / M_i \times 100 \quad \text{Equation S1}$$

Where M_i is the pristine elastomer mass, M_w is the after mass of the swelling elastomer after soaking in hexanes for 24h.

b) The drying (%) is defined by Equation S2:

$$\text{Drying (\%)} = M_w / M_i \times 100 \quad \text{Equation S2}$$

Where M_i is the pristine elastomer mass, M_w is the after mass of the swelling elastomers drying under vacuum at 60 °C for 6h.

Crosslink density calculation

The calculation of the crosslinked density was based on the reported literature.^{1, 2}

a) The volume fraction of silicone in the swollen mass (ϕ) is calculated using Equation S3.

$$\phi = M_w / \rho_2 / [(M_w - M_i) / \rho_1 + M_w / \rho_2] \quad \text{Equation S3}$$

Where:

M_w is the after mass of the swelling elastomer after soaking in hexanes for 24h; M_i is the after mass of the swelling elastomers drying under vacuum at 60 °C for 6h; ρ_1 is the density of hexanes (0.66 g mL⁻¹); ρ_2 is the density of silicone (0.96 g mL⁻¹).

b) The average molecular weight between the crosslinking points (M_c) is determined by Equation S4.

$$M_c = -\rho_2 V (\phi^{1/3} - \phi/2) / [\ln(1-\phi) + \phi + \chi \phi^2] \quad \text{Equation S4}$$

Where:

ρ_2 is the density of silicone (0.96 g mL⁻¹); V is the molar volume of hexanes (130.6 mL mol⁻¹); ϕ is the volume fraction of silicone in the swollen mass; χ is the Flory-Huggins parameter for crosslinked silicone and hexanes (0.40).³

c) The crosslink density (ν) is calculated by Equation S5 as illustrated:

$$\nu = \rho_1 / M_c \quad \text{Equation S5}$$

Where:

ρ_1 is the density of hexanes (0.66 g mL⁻¹); M_c is the average molecular weight between the crosslinking points.

Table S1. Crosslink densities of the elastomers when swollen at equilibrium

Elastomers	$m_{\text{as prepared}}$ (g)	$m_{\text{swelling-24h}}$ (g)	Swelling (%)	$m_{\text{drying-6h}}$ (g)	Drying (%)	Φ	M_c (g mol ⁻¹)	$\nu \times 10^3$ (mol mL)
Elastomer 10	0.0076	0.0095	86.3	0.0051	67.1	0.443	1061.157	0.622
Elastomer 11	0.0056	0.0082	105.0	0.0040	71.4	0.396	1482.765	0.445

1. S. Zheng, M. Zlatin, P. R. Selvaganapathy and M. A. Brook, *Add. Manuf.*, 2018, **24**, 86-92.
2. R. L. Hauser, C. Walker and F. L. Kilbourne, *Ind. Eng. Chem.*, 1956, **48**, 1202-1208.
3. J. Mazan, B. Leclerc, H. Porte, G. Torres and G. Couarraze, *J. Mater. Sci. Mater. Med.*, 1993, **4**, 175-178.