Electronic Supplementary Material (ESI) for Polymer Chemistry.

Influence of the Tetraalkoxysilane Crosslinker on the Properties of Polysiloxane-based Elastomers Prepared by the Lewis Acid-Catalysed Piers-Rubinsztajn Reaction

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Supporting Information

Table S1 Experimental setup of polymer **1a** compositions with varied catalyst amounts, at fixed polymer & crosslinker molar ratio and general outcome of reaction.

Entry	Polymer[a]	Moles of Polymer / mmol (Volume)	Crosslinker[b]	Moles of Crosslinker / mmol (Volume)	Concentration of Catalyst	Moles of Catalyst (Volume)	Outcome
1	1a	1.7 (0.85 mL)	**2**	0.08 (0.179 mL)	0.1M	2×10^{-7} (20 µL)	Foam
2	1a	1.7 (0.85 mL)	**2**	0.08 (0.179 mL)	0.01M	5×10^{-8} (50 µL)	Gel with defect
3	1a	1.7 (0.85 mL)	**2**	0.08 (0.179 mL)	0.01M	2×10^{-8} (20 µL)	Gel / gel with defect[c]
4	1a	1.7 (0.85 mL)	**3**	0.08 (0.231 mL)	0.1M	2×10^{-7} (20 µL)	Foam
5	1a	1.7 (0.85 mL)	**3**	0.08 (0.231 mL)	0.01M	5×10^{-8} (50 µL)	Gel with defect
6	1a	1.7 (0.85 mL)	**3**	0.08 (0.231 mL)	0.01M	2×10^{-8} (20 µL)	Gel / gel with defect[c]
7	1a	1.7 (0.85 mL)	**4**	0.08 (0.286 mL)	0.1M	2×10^{-7} (20 µL)	Foam
8	1a	1.7 (0.85 mL)	**4**	0.08 (0.286 mL)	0.01M	5×10^{-8} (50 µL)	Gel with defect
9	1a	1.7 (0.85 mL)	**4**	0.08 (0.286 mL)	0.01M	2×10^{-8} (20 µL)	Gel / gel with defect[c]
10	1a	1.7 (0.85 mL)	**5**	0.08 (0.388 mL)	0.1M	2×10^{-7} (20 µL)	Partial cure
11	1a	1.7 (0.85 mL)	**5**	0.08 (0.388 mL)	0.01M	5×10^{-8} (50 µL)	Partial / no cure
12	1a	1.7 (0.85 mL)	**5**	0.08 (0.388 mL)	0.01M	2×10^{-8} (20 µL)	Partial / no cure
13	1a	1.7 (0.85 mL)	**6**	0.08 (0.291 mL)	0.1M	2×10^{-7} (20 µL)	Foam
14	1a	1.7 (0.85 mL)	**6**	0.08 (0.291 mL)	0.01M	5×10^{-8} (50 µL)	Foam / gel with defect
15	1a	1.7 (0.85 mL)	**6**	0.08 (0.291 mL)	0.01M	2×10^{-8} (20 µL)	Gel with defect / gel

[a]polymer **1a**= hydride terminated PDMS 400-500 g mol^{-1} (DMS-H03) [b]**2**=ethyl **3**=propyl **4**=*n*-butyl **5**=2-ethylbutyl **6**=s-butyl [c]Secondary outcome (undesired) is sporadic, occuring infrequently - possibly due to difficult to control factors (including room temperatue, heat conduction handling vial). Primary outcome listed first. Outcome determined by visual observation and gentle probing of the sample.

Table S2 Experimental setup of polymer **1b** compositions with varied catalyst amounts, at fixed polymer & crosslinker molar ratio and general outcome of reaction.

Entry	Polymer[a]	Moles of Polymer / mmol (Volume)	Crosslinker[b]	Moles of Crosslinker / mmol (Volume)	Concentration of Catalyst	Moles of Catalyst (Volume)	Outcome
1	1b	0.85 (0.960 mL)	**2**	0.04 (0.089 mL)	0.1M	1×10^{-7} (20 µL)	Foam
2	1b	0.85 (0.960 mL)	**2**	0.04 (0.089 mL)	0.01M	2.5×10^{-8} (50 µL)	Gel with defect / foam
3	1b	0.85 (0.960 mL)	**2**	0.04 (0.089 mL)	0.01M	1×10^{-8} (20 µL)	Gel / gel with defect[c]
4	1b	0.85 (0.960 mL)	**3**	0.04 (0.115 mL)	0.1M	1×10^{-7} (20 µL)	Foam
5	1b	0.85 (0.960 mL)	**3**	0.04 (0.115 mL)	0.01M	2.5×10^{-8} (50 µL)	Gel with defect
6	1b	0.85 (0.960 mL)	**3**	0.04 (0.115 mL)	0.01M	1×10^{-8} (20 µL)	Gel / gel with defect[c]
7	1b	0.85 (0.960 mL)	**4**	0.04 (0.143 mL)	0.1M	1×10^{-7} (20 µL)	Foam
8	1b	0.85 (0.960 mL)	**4**	0.04 (0.143 mL)	0.01M	2.5×10^{-8} (50 µL)	Gel with defect
9	1b	0.85 (0.960 mL)	**4**	0.04 (0.143 mL)	0.01M	1×10^{-8} (20 µL)	Gel
10	1b	0.85 (0.960 mL)	**5**	0.04 (0.194 mL)	0.1M	1×10^{-7} (20 µL)	Partial cure
11	1b	0.85 (0.960 mL)	**5**	0.04 (0.194 mL)	0.01M	2.5×10^{-8} (50 µL)	Partial / no cure
12	1b	0.85 (0.960 mL)	**5**	0.04 (0.194 mL)	0.01M	1×10^{-8} (20 µL)	Partial / no cure
13	1b	0.85 (0.960 mL)	**6**	0.04 (0.146 mL)	0.1M	1×10^{-7} (20 µL)	Foam
14	1b	0.85 (0.960 mL)	**6**	0.04 (0.146 mL)	0.01M	2.5×10^{-8} (50 µL)	Foam / gel with defects
15	1b	0.85 (0.960 mL)	**6**	0.04 (0.146 mL)	0.01M	1×10^{-8} (20 µL)	Gel with defects / gel

[a]polymer **1b**= hydride terminated PDMS 1000-1100 g mol^{-1} (DMS-H11) [b]**2**=ethyl **3**=propyl **4**=*n*-butyl **5**=2-ethylbutyl **6**=*s*-butyl [c]Secondary outcome (undesired) is sporadic, occuring infrequently - possibly due to difficult to control factors (including room temperatue, heat conduction handling vial). Primary outcome listed first. Outcome determined by visual observation and gentle probing of the sample.

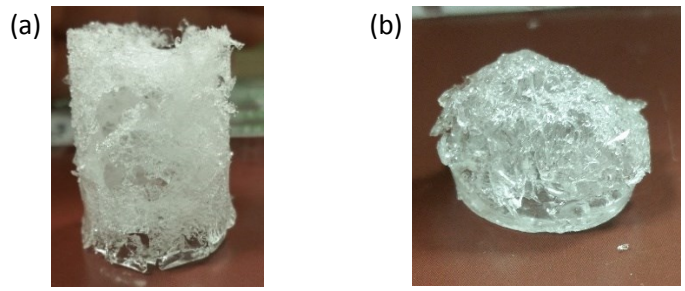


Figure S1: Photographs of bulk samples of PDMS-based polymer networks illustrating the reduction of foaming (left to right) with by tailoring the reaction conditions. Samples were prepared by reacting hydride-terminated PDMS **1a** with: (a) tetraethoxysilane **2** and 2 × 10^{-3} mmol $B(C_6F_5)_3$; and (b) tetra-*n*-butoxysilane **4** and 2 × 10^{-3} mmol $B(C_6F_5)_3$

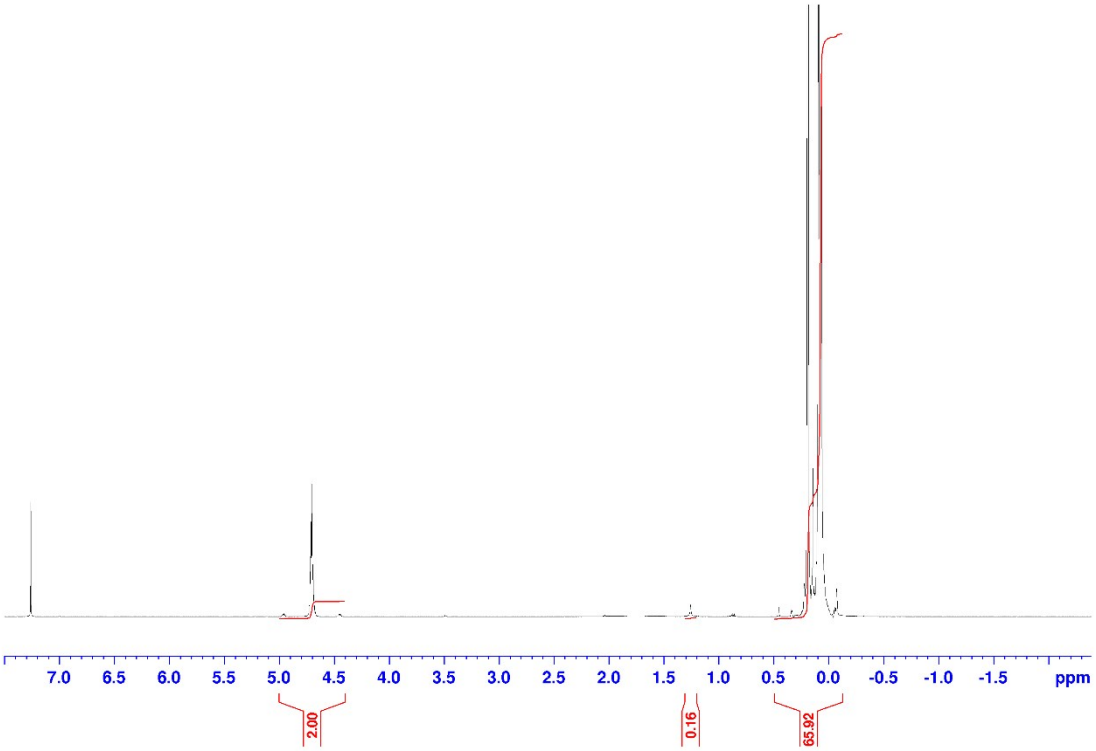


Figure S2: ^{1}H NMR spectrum of DMS-H03 (400-500g mol^{-1} hydride terminated poly(dimethylsiloxane))

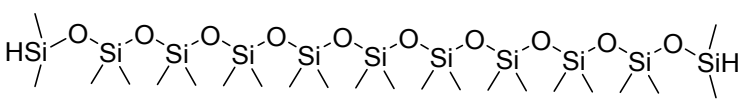
Si-*H* peaks, accounting for the ^{29}Si satellites peaks, were assigned an integration of 2.

C*H*$_3$ peaks, accounting for the ^{29}Si satellites peaks, were integrated giving a value of 65.92 (66H).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.4 – 5.0 (m, 2H, 2 × Si-*H*), δ -0.10 – 0.50 (m, 66H, 22 × Si-C*H*$_3$)

Number average molecular mass (M_n) was calculated by dividing total CH_3 hydrogens (66H) by the amount of hydrogens found per Silicon i.e. 6

$$No.\ of\ Si = 66 \div 6\ (H\ per\ Si) = 11\ \text{Silicons per chain}$$



$C_{22}H_{68}O_{10}Si_{11}$ M_n= 801.71

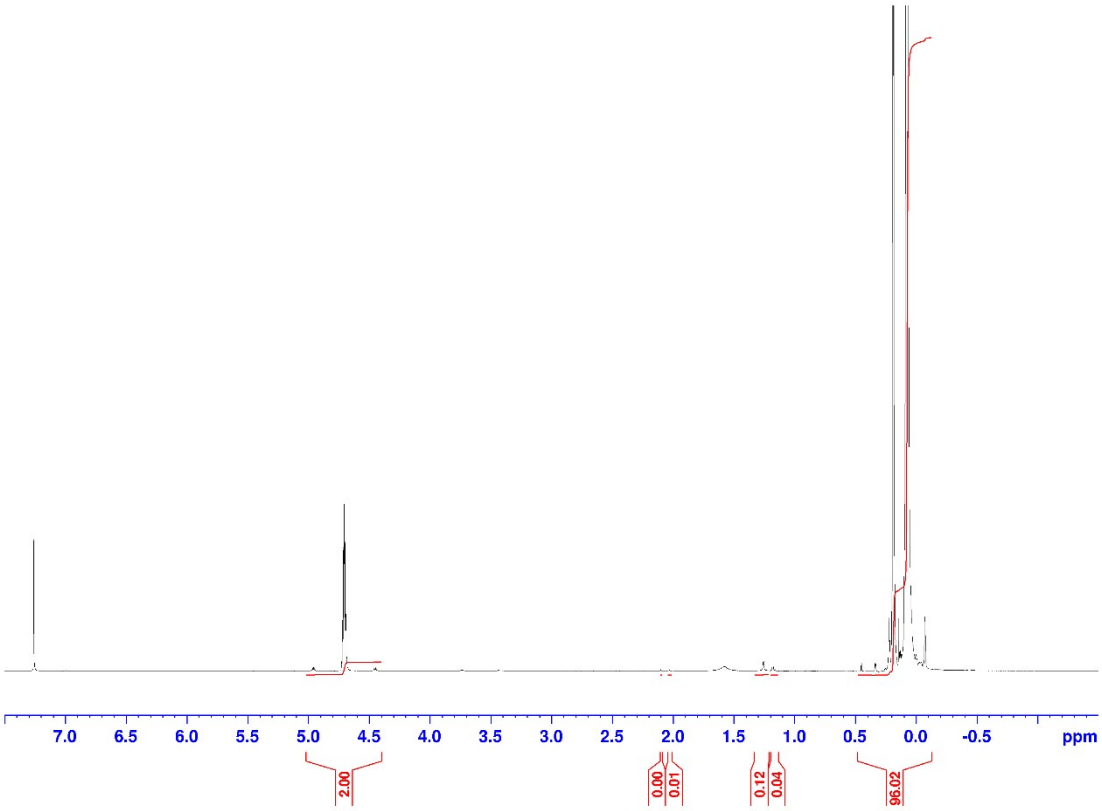


Figure S3: ^{1}H NMR spectrum of DMS-H11 (1000-1100 g mol^{-1} hydride terminated poly(dimethylsiloxane))

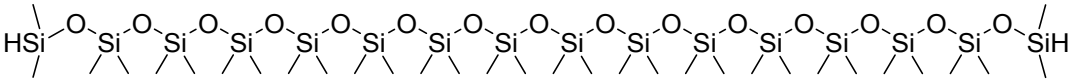
Si-*H* peaks, accounting for the ^{29}Si satellites peaks, were assigned an integration of 2.

C*H*$_3$ peaks, accounting for the ^{29}Si satellites peaks, were integrated giving a value of 96.02 (96H)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.7068 ppm (m, 2H, 2 × Si-*H*), δ -0.14 – 0.50 (m, 96H, 32 × Si-C*H*$_3$)

Number average molecular mass (M_n) was calculated by dividing total CH_3 hydrogens (96H) by the amount of hydrogens found per Silicon i.e. 6

$$No.\ of\ Si = 96 \div 6\ (H\ per\ Si) = 16$$



$C_{32}H_{98}O_{15}Si_{16}$ M_n= 1172.48

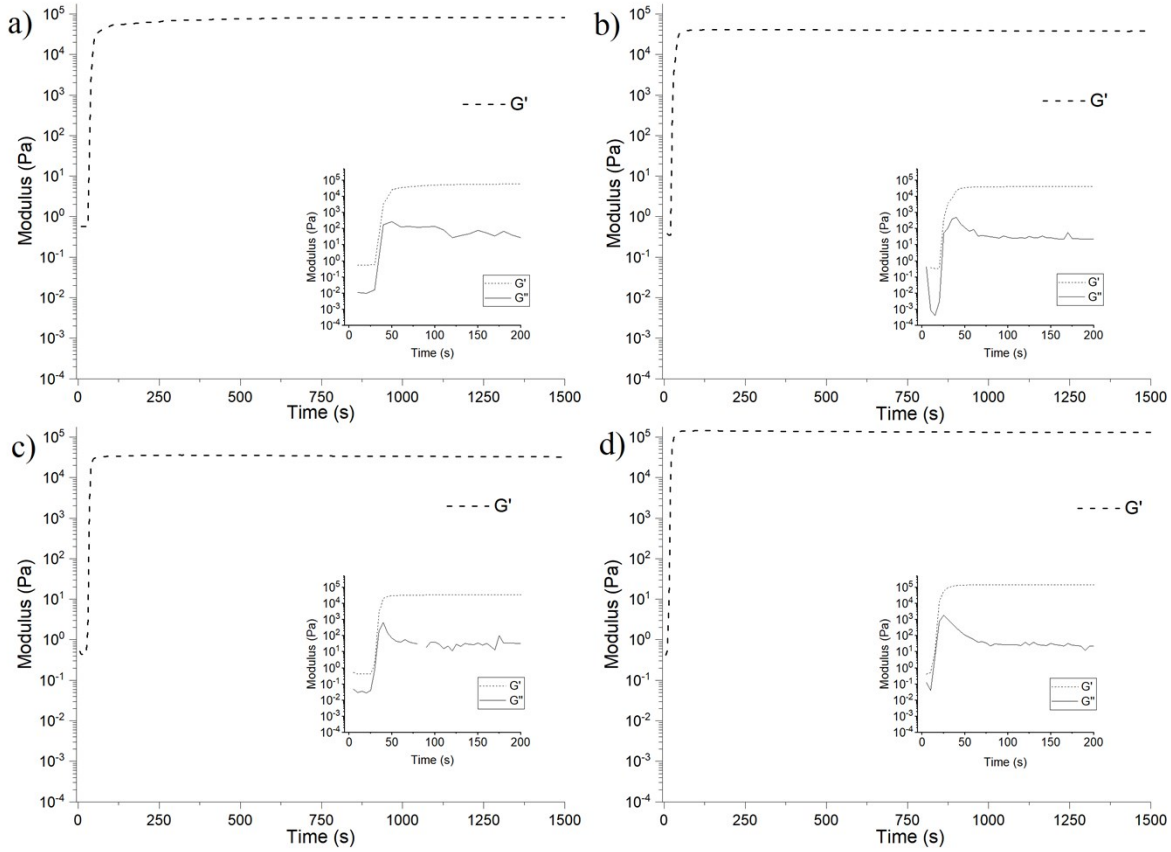


Figure S4: Time-resolved rheology, full scale gelation curves shown by G' for elastomers derived from PDMS **1a** and the (a) ethyl **2**, (b) propyl **3**, (c) *n*-butyl **4**, and (d) *s*-butyl **6** alkoxysilane (also see Entries 1-5, Table 1). Note the omitted data as per Table 1. Insets show G' & G'' during earlier stages of curing.

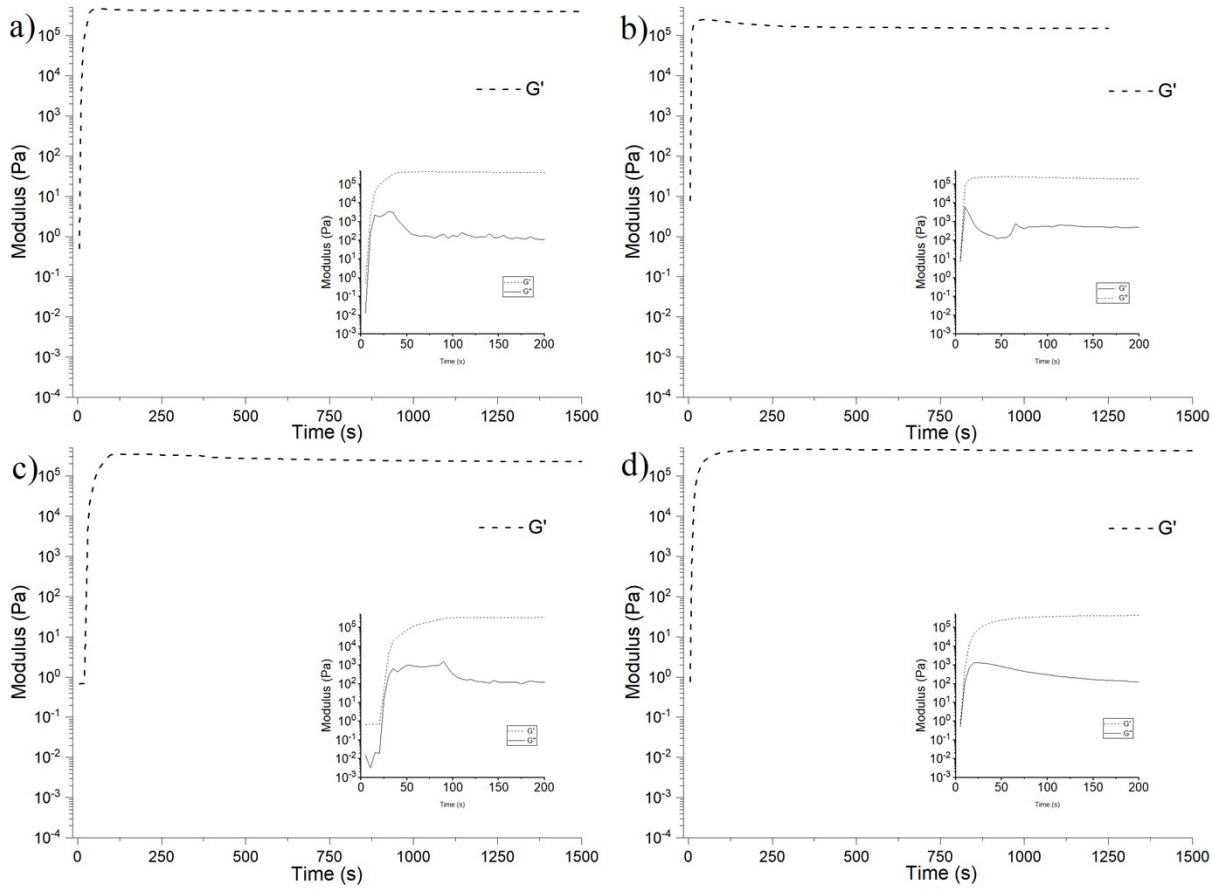


Figure S5: Time-resolved rheology, full scale gelation curves shown by G' for elastomers derived from PDMS **1b** and the (a) ethyl **2**, (b) propyl **3**, (c) *n*-butyl **4**, and (d) *s*-butyl **6** alkoxysilane (also see Entries 6-10, Table 1). Note the omitted data as per Table 1. Insets show G' & G'' during earlier stages of curing.