Autoxidation: Catalyst-Free Route to Silicone

Rubbers by Crosslinking Si-H Functional Groups

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SUPPORTING INFORMATION

Table S1 Changes in the ¹H NMR integration of signals for Si-H and silvl ether groups during DMS-H11 curing in air ($SiOCH_2Si \leftarrow SiH \rightarrow SiOH \rightarrow SiOSi (+ H_2O)$, total of Si = 100%).

| Time (h) | Remaining Si-H ^a | %SiH remaining | %Si-H consumed for silyl ether | %Si-H consumed for silanol | SiOH/SiOSi | MW data (M_n, D_M) |
|-------------|--------------------------------|-------------------|--------------------------------------|----------------------------------|------------|----------------------|
| 0 | 2.00 | 100 | 0.00 | 0.00 | 0 | bdl ^b |
| 1 | 0.88 | 43.84 | 2.71 | 53.50 | 1.99 | bdl |
| 2 | 0.40 | 20.20 | 3.69 | 76.16 | 1.69 | bdl |
| 4 | 0.03 | 1.48 | 6.16 | 92.41 | 1.46 | bdl |
| 8 | 0.00 | 0 | 5.42 | 94.58 | 1.28 | 6894, 4.88 |
| 13.5 | 0.00 | 0 | 6.16 | 92.41 | 1.21 | 49112, 6.44 |

^a Based on ¹H NMR integration normalized to 2 SiH/telechelic silicone chain.^b Below detection limit of the GPC, which is 2000 g mol⁻¹.

| Time (h) | Remaining Si- Ha | %SiH remaining | %Si-H consumed for silyl ether | %Si-H consumed for silanol | SiOH/SiOSi | |
|-------------|---------------------|-------------------|-----------------------------------|-------------------------------|------------|--|
| 0 | 1.00 | 100.00 | 0.00 | 0.00 | 0.00 | |
| 1 | 0.90 | 90.13 | 1.92 | 0.02 | 7.96 | |
| 2 | 0.79 | 79.30 | 4.18 | 0.04 | 16.52 | |
| 4 | 0.68 | 68.37 | 6.65 | 0.07 | 24.99 | |
| 8 | 0.57 | 57.10 | 9.46 | 0.09 | 33.46 | |
| 13.5 | 0.45 | 44.76 | 12.74 | 0.13 | 42.51 | |

Table S2 Changes in the ¹H NMR integration of signals for Si-H and silvl ether groups during HMS-071 curing in air ($SiOCH_2Si \leftarrow SiH \rightarrow SiOH \rightarrow SiOSi (+ H_2O)$, total of Si = 100%).^a

^a MW of the products was below 2000 g mol⁻¹.^b Based on ¹H NMR integration normalized to 1 SiH on the pendently-modified silicone chain.

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Figure S1 Photograph of A: MCR-H21 (before cure), and B: MCR-H21-X elastomer after heating

for 7 days at 300 °C under air.



Figure S2. Infrared (IR) spectra of DMS-H11 macromer (top red) and DMS-H11-X elastomer (bottom blue). The disappearance of Si-H group with characteristic vibrational frequency at 2130 cm⁻¹ was observed after curing (highlighted in black dash box). Another Si-H frequency at 910 cm⁻¹ also vanished after curing (not highlighted).



functionality gradually diminished upon curing, which was consistent to ¹H NMR results (Table S1).



Figure S4. Infrared spectrum of HMS-082 at cured at 200 °C for 3 days showing incomplete cure via the presence of an SiH group at 2160 cm⁻¹.



Figure S5. ¹H NMR spectrum of DMS-H31 cured at 300 °C for 1 hour (bottom in red). Corresponding spectrum cured at 250 °C for 13.5 hours is also shown (top in blue). Integration of Si-CH₃ are normalized to 100 in both cases.



Figure S6. ¹H NMR spectrum of DMS-H11 A: after curing in air at 250 °C for 6 hours, and B: after heating the cured sample in water at 100 °C for 1 h. The silyl ether resonance at 3.47 ppm did not change at all, with integration of Si-CH₃ being normalized to 100 in both cases.



Figure S7. Showing, in separate experiments on separate days, increased in molecular weight of of DMS-H11 after exposure at 250 °C to Dry Air (left) or wet N_2 (right).

| Table S3 Shore Hardnesses o | of Silicone Elastomers Pre | epared by RTV or Platinum Cure. ^a |
|-----------------------------|----------------------------|--|
|-----------------------------|----------------------------|--|

| RTV (Moisture Cure) | 1 | | | | | |
|--|-----------|----------------|-------------------------|---------------|----------|---------|
| OMe/SiOH=1:1 | | | | | Shore OO | Shore A |
| | MW | Weight, g | mmol | OMe/SiOH | 91 | 68 |
| Silanol terminated polydimethylsiloxane, DMS-S14 | 1100 | 2.0 | 1.82 | 1 | | |
| Tetramethoxysilane | 152.22 | 0.5535 | 3.64 | 1 | | |
| Water | | 0.0277 | | 5w/w% to TMOS | | |
| DBTL Tin Catalyst | | 0.0255 | 1 w/w% | total wt% | | |
| OMe/SiOH=1:1 | | | | | | |
| | MW | Weight, g | mmol | OMe/SiOH | 81 | 22 |
| Silanol terminated polydimethylsiloxane, DMS-S31 | 26000 | 2.0 | 0.08 | 1 | | |
| Tetramethoxysilane | 152.22 | 0.0234 | 0.15 | 1 | | |
| Water | | 0.0012 | | 5w/w% to TMOS | | |
| DBTL Tin Catalyst | | 0.0202 | 1 w/w% | total wt% | | |
| OMe/SiOH=1:1 | | | | | | |
| | MW | Weight, g | mmol | OMe/SiOH | 71 | 15 |
| Silanol terminated polydimethylsiloxane, DMS-S32 | 36000 | 2.0 | 0.06 | 1 | | |
| Tetramethoxysilane | 152.22 | 0.0169 | 0.11 | 1 | | |
| Water | | 0.0008 | | 5w/w% to TMOS | | |
| DBTL Tin Catalyst | | 0.0202 | 1 w/w% | total wt% | | |
| Platinum Cure (Hydrosilylation) | | | | | | |
| | Viscosity | MW(or | g | Vi/SiH | 62 | |
| | (cSt) | Equivalent MW) | | | | |
| Vinyl | | | | 1:1 | | |
| DMS-V21 | 100.0000 | 6000 | 4 | | | |
| SiH | | | | | | |
| HMS-501 | 10-15 | 135 | 0.18 | | | |
| Karstedt's catalyst | | | 4 ppm | | | |
| Cure temperature | | | $r.t. \rightarrow 80 C$ | | | |

^a The telechelic polymer lengths were chosen to be comparable to the HSi polymers that were oxidized. The elastomers were produced using the ingredients provided above and allowed to cure for 24 hours at room temperature (RTV) or 4h at 80 °C platinum cure. DBTL is dibutyltin dilaurate.