Highly stretchable or extremely soft silicone elastomers? One reaction to make them all - from easily available materials!

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Article

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Highly stretchable or extremely soft silicone elastomers? One reaction to make them all - from easily available materials!

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ABSTRACT: An easy curing reaction to prepare silicone elastomers is reported, in which a platinum-catalyzed reaction of telechelic/multi-hydrosilane (Si-H) functional polydimethylsiloxane (PDMS) in the presence of oxygen and water leads to slow crosslinking. This curing chemistry allows versatile tailoring of elastomer properties, which exceed their intrinsic limitations. Both highly stretchable silicone elastomers and extremely soft silicone elastomers are prepared by creating highly entangled elastomers and bottle-brush elastomers from commercial precursor polymers, respectively. The highly stretchable elastomers can be uniaxially stretched to a maximum strain of 2800% and their areas can be biaxially extended 180-fold. The extremely soft silicone elastomers exhibit shear moduli of 1.2-7.4 kPa, depending on composition, values that are comparable to hydrogels and human soft tissues. The reported curing chemistry can be used to prepare a range of silicone elastomers with carefully tailored mechanical properties.

INTRODUCTION

Highly stretchable, soft silicone elastomers are of great interest for the fabrication of stretchable electronics, soft actuators, medical devices, and microfluidics.1–5 High stretchability provides long-term device stability in various distortion scenarios and permits exceptional deformations. Significant effort has been devoted to preparing silicone elastomers with a combined softness and elasticity resembling that of human soft tissue for use in soft robotics.6,7 Silicone elastomers are typically prepared by crosslinking linear polymers with cross-linkers. Figure 1 presents one of the most commonly used crosslinking reactions—i.e., the hydrosilylation reaction of telechelic vinyl functional polydimethylsiloxane (PDMS) with a multi-hydrosilane (Si–H) functional cross-linker in the presence of a platinum catalyst.8 Based on classical curing chemistry, network strands possess the same size and structure as the precursor polymers which ultimately determine the mechanical properties of the silicone elastomers. The ultimate extensibility of the
The resulting silicone elastomers are proportional to $M^{0.5}$ based on the Kuhn model, where $M$ is the average molar mass of network strands. The ultimate extensibility is usually less than 900%, and it is difficult to further increase this value by using longer precursor polymers, since they would bring difficulties to the fabrication process due to their high viscosity. The elastic modulus of the silicone elastomers is determined by the crosslinking density—namely, the molar density of mechanically active strands $\nu = \rho / M$, where $\rho$ is the density. However, the lowest achievable elastic modulus for ideal elastomer networks is around 0.6 MPa due to the fact that entanglements in the cross-linked networks act as topological crosslinks once the molecular weight of network strands ($M$) exceeds the entanglement molecular weight.

Several strategies have been explored for overcoming limitations on the ultimate extensibility and softness of silicone elastomers. For example, elastomers prepared from long precursor polymers in solution and subjected to solvent evaporation after curing, supramolecular elastomers with movable cross-links, and concatenated ring elastomers have all been developed to improve ultimate extensibility. Approaches such as adding external solvent molecules, sparse crosslinking, and crosslinking bottle-brush PDMS have also been used to prepare soft silicone elastomers. While the above strategies improve elastomer extensibility or softness to some extent, they either increase process complexity or lead to mechanical instabilities in the resulting elastomers. What is more, none of them are versatile enough to enable the preparation of silicone elastomers that are both highly stretchable and very soft. There is thus a lack of available chemistries capable of efficiently preparing silicone elastomers with superior stretchability and softness.

Silicone elastomers have been prepared from Si–H functionalized polymers at 250°C in air, where the crosslinking mechanism was found to originate from oxidative crosslinking of Si–H groups in the presence of oxygen. In this study, silicone elastomers are prepared from PDMS with telechelic/multiple Si–H groups and a platinum catalyst in air at the much lower temperature of 100°C (see Figure 1b). In contrast to classical curing chemistries where the network strands are
directly related to the length of the precursor polymers, the curing chemistry presented here, when combined with the hydrosilylation reaction, allows network strands to be tailored from normal linear precursors during the curing process. Specifically, we report highly stretchable silicone elastomers with ultra-long network strands and extremely soft silicone elastomers with bottle-brush strands, both of which are easily prepared from commercially available linear precursors. Both novel silicone elastomers are based on sequential crosslinking mechanisms in one-pot reactions, where the fast hydrosilylation reaction is followed by a slow crosslinking of residual Si-H functional groups. This allows independent control of network strand size and structure, as well as of crosslinking.
Figure 1. (a) Conventional curing reaction to prepare silicone elastomers. (b) Novel curing reaction to prepare silicone elastomers. (c) Highly stretchable silicone elastomers and (d) extremely soft silicone elastomers prepared from a one-pot curing reaction by combining hydrosilylation and subsequent Si-H crosslinking reactions.

RESULTS AND DISCUSSION

Elucidation of curing reaction.

In our previous work with platinum-catalyzed hydrosilylation reactions, we observed that elastomers were formed when only telechelic Si-H-functional PDMS and a platinum catalyst were present. This discovery of a potentially simple method for preparing elastomers prompted us to perform...
further studies in order to elucidate the mechanism of this formation.

Hydrosilanes readily undergo hydrolysis and alcoholysis reactions with water and alcohols, respectively, under basic or strongly acidic conditions or in the presence of radicals, metals, or transition metal complexes.\textsuperscript{25,26} In the presence of a platinum catalyst and water, telechelic Si-H functional PDMS can thus be hydrolyzed into Si-OH, which may further undergo condensation to form extended chains. However, the hydrolysis and condensation reactions cannot account for the formation of elastomers from telechelic Si-H functional PDMS in a conventional manner. Instead, obtaining elastomers from telechelic Si-H functional PDMS requires either the formation of concatenated rings through intramolecular condensation reactions or some other unexplored crosslinking reaction.\textsuperscript{15,17} Water and oxygen are the possible reactants in the curing reaction with Si-H-containing precursor PDMS. The reaction was therefore carried out under conditions in which water and oxygen content could be carefully controlled. Specifically, in a series of experiments, a representative telechelic Si-H functional PDMS (DMS-H11, $M_n=1$ kDa) was heated at 100°C for 48 h in a sealed flask under each of the following reaction conditions: dry $\text{N}_2$ (a dried sample under dried nitrogen), wet $\text{N}_2$ (a sample containing water with ~4 molar equivalent of hydrosilanes under dried nitrogen), dry air (a dried sample under dried air), and wet air (a sample containing water with ~4 molar equivalent of hydrosilanes under dried air). DMS-H11 was converted into a solid elastomer only under wet air conditions. As measured by $^1\text{H}$ NMR, the conversion efficiency of Si-H groups for the three liquid products under dry $\text{N}_2$, wet $\text{N}_2$, and dry air conditions were found to be 6.6%, 29.5%, and 52.9%, respectively (\textbf{Figure 2a}). These findings indicate that both water and oxygen participate in the reaction. A peak at 2.27 ppm in the $^1\text{H}$ nuclear magnetic resonance (NMR) spectrum of the sample from the wet $\text{N}_2$ atmosphere is assigned to a Si-OH structure (\textbf{Figure 2a}), suggesting a hydrolysis process of Si-H during the reaction.\textsuperscript{27} A further condensation process of Si-OH results in chain extension, as evidenced by the increased molecular weight of the sample (\textbf{Figure S1, ESI}). Another new peak that appears at 3.47 ppm (\textbf{Figure 2a}) on the $^1\text{H}$ spectrum of the sample from dry air
The atmosphere is contributed to a silyl ether (Si-O-CH$_2$-Si) structure which has been reported to originate from oxidation reactions of Si-H with oxygen and methyl groups at much higher temperatures in the absence of a platinum catalyst.\textsuperscript{24} The presence of this silyl ether suggests that branched chains are formed during the oxidation of Si-H. The integration of the $^1$H spectrum shows that the amount of hydrogen on silyl ether only accounts for 1.4\% of the Si-H loss (Table S3, ESI), suggesting that most Si-H are oxidized into other structures which are not identified in the $^1$H spectrum. The minimal loss of Si-H (6.6\%, Figure 2a) under dry N$_2$ conditions is most likely due to trace amounts of air and water in the starting polymer, as well as a small amount of vinyl groups associated with the platinum catalyst.

![Figure 2](image-url)

**Figure 2.** (a) $^1$H NMR spectra of a telechelic Si-H functional PDMS (DMS-H11) and its reaction products after heating at 100°C for 48 h under dry N$_2$, wet N$_2$, and dry air conditions, respectively. (b) $^{29}$Si solid-state NMR spectra...
of elastomers (Ela_DMS-H11 and Ela_DMS-H21) and a precursor polymer (DMS-H11). (c) Proposed mechanism of crosslinking Si-H functional groups in the presence of oxygen and a catalyst.

Direct investigations of the chemical composition of solid elastomers cured under a normal air atmosphere and a precursor polymer DMS-H11 were performed using $^{29}$Si solid-state NMR. Figure 2b shows that a peak at -7 ppm on the spectrum of the precursor polymer is assigned to Si-H functional groups. This peak vanishes on the spectra of the elastomers, suggesting an efficient conversion of Si-H after curing. New peaks located at 7 ppm and -64 ppm are observed on spectra of the elastomers and are assigned to (CH$_3$)$_2$SiO (or (CH$_3$)$_2$CH$_2$SiO) and CH$_3$SiO$_3$, respectively. Since the hydrolysis of Si-H and further condensation of Si-H with Si-OH would only produce more backbone chains (-$(CH_3)_2SiO$-), the newly formed structures are the result of oxidation of Si-H functional groups. Integration of the spectra shows that Si atoms associated with these newly formed structures account for 1.5-2.5% of Si atoms in the elastomers (Table S4, ESI), suggesting that these oxidized structures play a major role in crosslinking.

Based on the observations above, it is clear that oxidation of Si-H plays a role in creating branched chains to form networks, as hydrolysis and subsequent condensation of telechelic chains would only produce longer, linear chains. The oxidation processes are proposed as follows. Si-H functional groups are turned into silyl radicals (O(CH$_3$)$_2$Si·) through hydrogen abstraction in the presence of air (Figure 2c-A). After further oxidation processes, the silyl radicals are transformed into O(CH$_3$)$_2$SiO· (Figure 2c-B and C). Oxidation processes also happen on methyl groups of silicones: oxygen initially generates a carbon radical (SiCH$_2$·) by hydrogen atom abstraction (Figure 2c-D). Branching structures like SiCH$_2$Si and SiOCH$_2$Si are formed by combinations of SiCH$_2$· with O(CH$_3$)$_2$Si· and O(CH$_3$)$_2$SiO·, respectively (Figure 2c-E and F). A combination of O(CH$_3$)$_2$Si· and O(CH$_3$)$_2$Si-O· only produces extended chains via the formation of SiOSi (Figure 2c-G). Further oxidation of SiCH$_2$· leads to the creation of SiCH$_2$OO·, which enables the formation of SiO$_3$CH$_3$ by a self-
reaction (Figure 2c-H and I).\textsuperscript{33,34}

It should be noted that the same radicals mentioned above were also used to explain crosslinking during the oxidization of Si-H functional PDMS at high temperature (250°C) in the absence of a catalyst, in which a silyl ether (Si-O-CH\textsubscript{2}-Si) structure was the main oxidized structure produced.\textsuperscript{24} In our work, however, the oxidation process is faster and occurs at a much lower temperature due to the use of a platinum catalyst; the main oxidized structures produced are (CH\textsubscript{3})\textsubscript{2}CH\textsubscript{2}SiO and CH\textsubscript{3}SiO\textsubscript{3}. Si-[Pt]-H complex is known to form by oxidative addition,\textsuperscript{35–37} and [Pt]-oxygen complex has been reported to significantly promote platinum catalyzed hydrosilylation reactions.\textsuperscript{38,39} These compounds may allow the reaction with oxygen to occur at moderate temperatures, thereby changing the main oxidized structures produced.

This curing chemistry can be extended to the curing of multifunctional Si-H functional PDMS, where both hydrolysis/condensation and oxidation reactions may contribute to crosslinking. The prepared elastomers listed in Table 1 are named according to the precursor polymer used. Overall, the prepared silicone elastomers show tensile strains of 70-360%, Young’s moduli of 0.3-0.6 MPa, and tensile strengths of 0.2-0.6 MPa. These mechanical properties are comparable to those of the two conventional silicone elastomers prepared via the classical curing route.\textsuperscript{10}
Table 1. Silicone elastomers prepared from telechelic/multi Si-H functional PDMS in presence of a platinum-divi-
yl tetramethyldisiloxane complex. Conventional elastomers (Ref_DMS-V25 and Ref_DMS-V41) were prepared
as references from telechelic vinyl functional PDMS, a multi-Si-H functional PDMS, and a platinum catalyst.

| Sample       | Precursor length (kDa) | Tensile strain (%) | Tensile strength (MPa) | Young’s modulus (MPa) |
|--------------|------------------------|--------------------|------------------------|-----------------------|
| Ela_DMS-H11  | 1                      | 71                 | 0.24                   | 0.37                  |
| Ela_DMS-H21  | 6                      | 70                 | 0.35                   | 0.60                  |
| Ela_DMS-H25  | 14                     | 235                | 0.49                   | 0.40                  |
| Ela_DMS-H31  | 24                     | 363                | 0.46                   | 0.29                  |
| Ela_HMS-064  | 60                     | 118                | 0.52                   | 0.52                  |
| Ref_DMS-V25  | 14                     | 127                | 0.54                   | 0.84                  |
| Ref_DMS-V41  | 35                     | 482                | 0.44                   | 0.19                  |

In order to compare the reaction kinetics of the Si-H functional PDMS system with those of the hy-
drosilylation reaction between Si-H and vinyl groups, platinum-catalyzed reactions of mono-Si-H
functional PDMS and mono-Si-H functional PDMS with mono-vinyl functional PDMS, respectively,
were conducted at 100℃. The total concentration of functional groups was the same for both reac-
tions. Figure 3a shows that the reaction of mono-Si-H functional PDMS takes 6 h to complete 100%,
compared to 2 min for the hydrosilylation reaction. In addition, the reaction of mono-Si-H functional
PDMS products a fraction of products that are more than 10-time molecular weight of precursor
polymers (Figure 3a). This is consistent with the branching nature of Si-H oxidation. In comparison,
the hydrosilylation reaction of mono-Si-H functional PDMS with mono-vinyl functional PDMS exclu-
sively produces chains with double initial molecular weight (Figure 3a).
Figure 3 (a) Reaction progression over time for the platinum-catalyzed reactions at 100°C of mono-hydrosilane functional PDMS, and mono-hydrosilane functional PDMS with mono-vinyl functional PDMS (stoichiometric amounts of hydride and vinyl). The inserts show molecular weight distributions over time during the two reactions. (b) Dependence of storage and loss moduli of representative highly stretchable and extremely soft silicone elastomers on curing time measured at 100°C, 1 Hz, and with a fixed strain of 1.0%.

Curing chemistries for highly stretchable/extremely soft silicone elastomers.

Preparing silicone elastomers with long strands is one way to efficiently obtain high stretchability. However, doing so using conventional curing chemistry requires exceptionally long precursor polymers whose high viscosity brings difficulties to fabrication process. Here, highly stretchable silicone elastomers are prepared from a platinum-catalyzed reaction between telechelic Si-H functional PDMS and telechelic vinyl functional PDMS using a small excess of Si-H groups (Figure 1c). In a one-pot reaction, both the hydrosilylation reaction between Si-H and vinyl groups and the water and oxygen-mediated crosslinking of Si-H (see above) take place. Due to the significant kinetic advantage of the hydrosilylation reaction over Si-H crosslinking (Figure 3a), the hydrosilylation reaction is expected to proceed to high conversion before any significant crosslinking occurs. Assuming the two reactions happen strictly in sequence, the hydrosilylation reaction results in extended chains which are subsequently cross-linked into elastomers through the reaction of excess Si-H with...
oxygen and water. In this case, the average molar mass of the network strands can be expressed using equation 1 (derived from Equation S1, ESI):

\[
M_{\text{extended}} = \frac{RM_{\text{DMS-H}} + M_{\text{DMS-V}}}{R - 1}
\]  

where \( M_{\text{DMS-H}} \) is the molecular weight of telechelic Si-H functional PDMS, \( M_{\text{DMS-V}} \) is the molecular weight of telechelic vinyl functional PDMS, and \( R \) is the molar ratio of the Si-H-to-vinyl functional groups. According to equation 1, even when the values of \( M_{\text{DMS-H}} \) and \( M_{\text{DMS-V}} \) are relatively low, ultra-long network strands can be achieved by setting \( R \) close to unity.

Expanding the diameter of the polymer by attaching polymer brushes is a known method for diluting entanglements without markedly increasing chain stiffness. The resulting bottle-brush elastomers are intrinsically soft, with shear moduli of 1-100 kPa.\textsuperscript{21,22,41} However, preparing bottle-brush elastomers generally involves relatively complex multistep syntheses, including preparation of bottle-brush polymers followed by subsequent crosslinking reactions.\textsuperscript{23,41} Here, soft silicone elastomers are obtained by preparing bottle-brush elastomers through a platinum-catalyzed, one-pot curing reaction of multi-Si-H functional PDMS with mono-vinyl functional PDMS in the presence of excess of Si-H functional groups (Figure 1d). During the reaction, bottle-brush polymers are preferentially formed by grafting mono-vinyl functional PDMS onto the multi-Si-H functional PDMS through hydrosilylation. The resulting bottle-brush polymers are subsequently cross-linked into bottle-brush elastomers through the relatively slow crosslinking of Si-H in the presence of oxygen and water. Side chain lengths, and thus polymer diameter, are governed by the length of the mono-vinyl functional PDMS. Assuming crosslinking of Si-H takes place strictly after full side chain grafting, the molecular weight between Si-H groups on the bottle-brush chains can be determined as:

\[
M_{c,\text{SiH}} = \frac{M_{\text{brush}}}{f_{\text{brush}} + 1}
\]  

where \( M_{\text{brush}} \) is the molar mass of the bottle-brush polymers.
where $M_{\text{brush}}$ (Equation S3, ESI) and $f_{\text{brush}}$ (Equation S4, ESI) are the molecular weight and number of excess hydrides per chain, respectively, after full side chain grafting.

Representative curing reactions for preparing highly stretchable, extremely soft elastomers were investigated by tracing the evolution of the storage and loss moduli during the two curing reactions (Figure 3b). Gel points are reached within 5 min at 100°C, suggesting fast curing processes.

Properties of highly stretchable silicone elastomers

A number of stretchable silicone elastomers were prepared using different hydrosilane-to-vinyl-functional polymer ratios as well as polymers of different molecular weights, as shown in Table 2. Figure 4a shows that, when using the same precursor polymers DMS-H21 and DMS-V22, the tensile strain increases from 1040% to 2400% when $R$ decreases from 1.15 to 1.05. Tensile strain can be further increased to 2800% by using longer starting polymers DMS-H25 and DMS-V25. Longer extended chains improve tensile strain by enabling larger slippage lengths upon deformation (Table 2). The Kuhn model is widely used to estimate the ultimate extensibility of elastomers as $\lambda_{\text{max}} = L/h$, where $L$ is the strand length in a fully stretched state, and $h$ is the strand length in a random coil state. $\lambda_{\text{max}}$ is thus proportional to $M^{0.5}$ based on the relations of $L \propto M$ and $h \propto M^{0.5}$. A linear relation between $\lambda_{\text{max}}$ and $M_{\text{theo}}^{0.5}$ complies with the Kuhn model (Figure S3), suggesting that equation 1 is a valid description of the molar mass of the network strands, which supports the proposed curing route. Silicone elastomers with tailored stretchability can thus be realized by designing strand lengths based on equation 1. Elastomers’ linear viscoelastic responses are shown in Figure 4b. The storage modulus of the conventional elastomer reaches a plateau at low frequencies, while the storage moduli of the highly stretchable elastomers continue to decrease as the frequency approaches zero. This unusual behavior is explained by stress relaxation from entanglements of highly extended strands upon deformation. Stretchable elastomers are often biaxially stretched in practical use. Figure 4c shows the area of stretchable silicone elastomer, Ela_DMS-H21_DMS-
V22_R1.05, is biaxially extended 180-fold from an initial state—20 times greater extension than that of the conventional silicone elastomer Ref_DMS-V41. This significantly enhanced stretchability demonstrates the very high mechanical integrity of the elastomers studied here.

Table 2. Specifications for studied highly stretchable silicone elastomers.

| Samples                        | $M_{DMS-H}$ (kDa) | $M_{DMS-V}$ (kDa) | $R$   | $M_{extended}$ (kDa) | $\lambda_{max}$ |
|--------------------------------|-------------------|-------------------|-------|---------------------|------------------|
| Ela_DMS-H21_DMS-V22_R1.05     | 6                 | 8                 | 1.05  | 286                 | 2493             |
| Ela_DMS-H21_DMS-V22_R1.10     | 6                 | 8                 | 1.10  | 146                 | 1602             |
| Ela_DMS-H21_DMS-V22_R1.15     | 6                 | 8                 | 1.15  | 99                  | 1142             |
| Ela_DMS-H25_DMS-V25_R1.05     | 14                | 14                | 1.05  | 574                 | 2864             |

(a) Engineering stress (MPa) vs. Strain (%)
(b) Storage modulus (Pa) vs. Frequency (Hz)

(c-1) Ela_DMS-H21_DMS-V22_R1.05
(c-2) Cover the football surface
(c-3) Biaxial stretch
(c-4) 180-time extended in area
(c-5) 9-time extended in area
Figure 4. Properties of highly stretchable silicone elastomers and a conventional silicone elastomer. (a) Uniaxial stress-strain curves. (b) Frequency dependence of storage and loss moduli measured at room temperature. (c) Bi-axial stretching. (c-1) The highly stretchable silicone elastomer is marked with a red 1 cm² square; (c-2) the area of the same film is manually extended 180-fold. (c-3) The extended film subsequently covers the surface of a football with a diameter of 21 cm. (c-4) The conventional silicone elastomer marked with a 1 cm² red square is extended to a maximum of 9 times its original area.

Properties of extremely soft silicone elastomers

A range of bottle-brush elastomers were fabricated according to the formulations in Table 3. Shear moduli of the prepared elastomers (G) are taken to be equivalent to the plateau values of storage moduli at low oscillatory frequency (Figure 5a), and decrease from 7.4 kPa to 1.2 kPa when using either smaller R or 4-fold longer side chains. Such low shear moduli are comparable to those of hydrogels and human soft tissue.\textsuperscript{44} Linear viscoelastic responses (Figure 5a) show that the prepared elastomers have near frequency-independent storage moduli, making them resemble a perfect rubber. Table 3 shows that the molecular weights of bottle-brush network strands (Mₐ) (Equation S6, ESI) are larger than the average molecular weight between Si-H groups on the bottle-brush chains (Mₐ,SIH). Specially, Mₐ>10Mₐ,SIH for the elastomers with MCR-V21 side chains. The large differences between Mₐ and Mₐ,SIH can be explained by the preferentially intramolecular reactions of the multifunctional bottle-brush chains, which result in a large fraction of elastically inactive loops and dangling.\textsuperscript{45} Figure 5b shows the compressibility of the bottle-brush elastomer Ela_HMS-064_MCR-V21_R1.05 compared to that of the conventional elastomer Ref_DMS-V41. The bottle-brush elastomer is compressed to a strain of 88% under a pressure of 0.16 MPa, while the conventional elastomer only shows a compression strain of 19% under the same pressure. Importantly, despite the large compression strain imposed on the bottle-brush elastomer, it recovers to its initial state almost instantaneously upon pressure being released, displaying superior elasticity compared to normal soft elastomers, which often recover only partially.
Table 3. Specifications for studied soft silicone elastomers.

| Samples                        | $R$ | $M_{\text{HMS}}$ (kDa) | $M_{\text{MCR-V}}$ (kDa) | $M_{\text{c, SiH}}$ (kDa) | $M_{\text{c}}$ (kDa) |
|-------------------------------|-----|------------------------|--------------------------|----------------------------|---------------------|
| Ela_HMS-064_MCR-V21_R1.05    | 1.05| 60                     | 6                        | 130                        | 631                 |
| Ela_HMS-064_MCR-V21_R1.20    | 1.20| 60                     | 6                        | 42                         | 525                 |
| Ela_HMS-064_MCR-V21_R1.50    | 1.50| 60                     | 6                        | 18                         | 224                 |
| Ela_HMS-064_MCR-V25_R1.05    | 1.05| 60                     | 23                       | 342                        | 543                 |

Figure 5. (a) Frequency dependence of storage and loss moduli of extremely soft silicone elastomers and a conventional silicone elastomer measured at room temperature. (b) Two stacked extremely soft specimens (8 mm in diameter) are compressed to a strain of 88% by a pressure of 0.16 MPa (the excess polymer is displaced up and down the sides of the geometries). After the pressure is released, the films are recovered from the compressed state. In comparison, two stacked conventional specimens (8 mm in diameter) were compressed to a strain of only 19% under the same pressure.

CONCLUSION

Silicone elastomers with bespoke properties can be prepared via classical hydrosilylation chemistry
combined with a platinum-catalyzed reaction of telechelic/multi-hydride functional PDMS, without using any additional cross-linker. The mechanism of the curing reaction is consistent with platinum-mediated crosslinking of hydrosilanes in the presence of trace water and oxygen, and thus may be considered a side-reaction in conventional formulations. Compared with classical curing chemistry—i.e., hydrosilylation reaction—Si-H crosslinking in the presence of moisture and oxygen proceeds much more slowly, thereby providing formulations with an inherent delayed crosslinking opportunity and allowing the preparation of highly diverse networks using simple one-pot reactions.

Highly stretchable silicone elastomers and extremely soft silicone elastomers were developed by combining this curing chemistry with hydrosilylation reactions: the fast hydrosilylation reactions controlled the size and structures of network strands, after which elastomers were created through the much slower crosslinking of Si-H functional groups. Specifically, highly stretchable silicone elastomers were prepared by creating highly entangled (long-chain) silicone elastomers from the reaction between telechelic Si-H functional PDMS and telechelic vinyl functional PDMS. Tensile strains could be tailored from 1500% to 2800% by varying precursor length and the molar ratio of Si-H-to-vinyl groups. We demonstrated a 180-fold extension in area by biaxial stretch for one such highly stretchable silicone elastomer. Extremely soft silicone elastomers were made by creating bottle-brush silicone elastomers from the reaction between multi-Si-H functional PDMS and mono-vinyl functional PDMS. The shear moduli of the prepared bottle-brush elastomers could be adjusted from 1.2 kPa to 7.4 kPa by changing the molar ratio of reactive groups and the side chain lengths.

Both highly stretchable silicone elastomers and extremely soft silicone elastomers can be easily prepared via one-pot reactions using commercial precursors. In addition to enabling the preparation of highly stretchable or extremely soft elastomers, the general methodology based on slow crosslinking presented here enables the easy development of silicone elastomers with a wide range of functionalities.
ASSOCIATED CONTENT

Supporting information is available online

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Son, D.; Kang, J.; Vardoulis, O.; Kim, Y.; Matsuhisa, N.; Oh, J. Y.; To, J. W.; Mun, J.; Katsumata, T.; Liu, Y.; McGuire, A. F.; Krason, M.; Molina-Lopez, F.; Ham, J.; Kraft, U.; Lee, Y.; Yun, Y.; Tok, J. B.; Bao, Z. An Integrated Self-Healable Electronic Skin System Fabricated via Dynamic Reconstruction of a Nanostructured Conducting Network. Nat. Nanotechnol. 2018, 13 (11), 1057–1065.

(2) Kim, D. H.; Ahn, J. H.; Won, M. C.; Kim, H. S.; Kim, T. H.; Song, J.; Huang, Y. Y.; Liu, Z.; Lu,
(3) Pelrine, R.; Kornbluh, R.; Pei, Q.; Joseph, J. High-Speed Electrically Actuated Elastomers with Strain Greater than 100%. *Science* **2000**, 287 (5454), 836–839.

(4) Tybrandt, K.; Khodagholy, D.; Dielacher, B.; Stauffer, F.; Renz, A. F.; Buzsáki, G.; Vörös, J. High-Density Stretchable Electrode Grids for Chronic Neural Recording. *Adv. Mater.* **2018**, 30 (15), 1706520.

(5) van Erp, R.; Soleimanzadeh, R.; Nela, L.; Kampitsis, G.; Matioli, E. Co-Designing Electronics with Microfluidics for More Sustainable Cooling. *Nature* **2020**, 585 (7824), 211–216.

(6) Ilami, M.; Bagheri, H.; Ahmed, R.; Skowronek, E. O.; Marvi, H. Materials, Actuators, and Sensors for Soft Bioinspired Robots. *Adv. Mater.* **2020**, 33(19), 2003139.

(7) Miriyev, A.; Stack, K.; Lipson, H. Soft Material for Soft Actuators. *Nat. Commun.* **2017**, 8 (1), 1–8.

(8) Marciniec, B.; Maciejewski, H.; Pietraszuk, P. P. Hydrosilylation: A Comprehensive Review on Recent Advances; Springer: Poland, **2013**; Vol. 1.

(9) Kuhn, W. Dependence of the Average Transversal on the Longitudinal Dimensions of Statistical Coils Formed by Chain Molecules. *J. Polym. Sci.* **1946**, 1 (5), 380–388.

(10) Vaicekauskaite, J.; Mazurek, P.; Vudayagiri, S.; Skov, A. L. Mapping the Mechanical and Electrical Properties of Commercial Silicone Elastomer Formulations for Stretchable Transducers. *J. Mater. Chem. C* **2020**, 8, 1273.

(11) De Gennes, P. G.; Leger, L. Dymanics of Entangled Polymer Chains. *Ann. Rev. Phys. Chem* **1982**, 33, 49–61.

(12) Kohjiya, S.; Urayama, K.; Ikeda, Y. Poly(Siloxane) Network of Ultra-High Elongation. *Kautschuk Gummi Kunststoffe* **1997**, 50 (12), 868–870.
(13) Li, C. H.; Wang, C.; Keplinger, C.; Zuo, J. L.; Jin, L.; Sun, Y.; Zheng, P.; Cao, Y.; Lissel, F.;
Linder, C.; You, X.; Bao, Z. A Highly Stretchable Autonomous Self-Healing Elastomer. Nat.
Chem. 2016, 8 (6), 618–624.

(14) Hayashi, M.; Noro, A.; Matsushita, Y. Highly Extensible Supramolecular Elastomers with Large
Stress Generation Capability Originating from Multiple Hydrogen Bonds on the Long Soft
Network Strands. Macromol. Rapid Commun. 2016, 37 (8), 678–684.

(15) Goff, J.; Sulaiman, S.; Arkles, B.; Lewicki, J. P. Soft Materials with Recoverable Shape Factors
from Extreme Distortion States. Adv. Mater. 2016, 28 (12), 2393–2398.

(16) Hu, P.; Huang, Q.; Madsen, J.; Skov, A. L. Soft Silicone Elastomers with No Chemical Cross-
Linking and Unprecedented Softness and Stability. Electroactive Polymer Actuators and Devices
(EAPAD) XXII, SPIE 2020, 11375

(17) Hu, P.; Madsen, J.; Huang, Q.; Skov, A. L. Elastomers without Covalent Cross-Linking:
Concatenated Rings Giving Rise to Elasticity. ACS Macro Lett. 2020, 9 (10), 1458–1463.

(18) Heinrichs, V.; Dieluweit, S.; Stellbrink, J.; Pyckhout-Hintzen, W.; Hersch, N.; Richter, D.; Merkel,
R. Chemically Defined, Ultrasoft PDMS Elastomers with Selectable Elasticity for
Mechanobiology. PLoS One 2018, 13 (4), 1–22.

(19) Lenhart, J. L.; Cole, P. J. Adhesion Properties of Lightly Crosslinked Solvent-Swollen Polymer
Gels. J. Adhes. 2006, 82 (10), 945–971.

(20) Larsen, A. L.; Sommer-Larsen, P.; Hassager, O. How to Tune Rubber Elasticity. Electroactive
Polymer Actuators and Devices (EAPAD), SPIE 2004, 5385

(21) Daniel, W. F. M.; Burdyńska, J.; Vatankhah-Varnoosfaderani, M.; Matyjaszewski, K.; Paturej, J.;
Rubinstein, M.; Dobrynin, A. V.; Sheiko, S. S. Solvent-Free, Supersoft and Superelastic
Bottlebrush Melts and Networks. Nat. Mater. 2016, 15 (2), 183–189.

(22) Cai, L. H.; Kodger, T. E.; Guerra, R. E.; Pegoraro, A. F.; Rubinstein, M.; Weitz, D. A. Soft
Poly(Dimethylsiloxane) Elastomers from Architecture-Driven Entanglement Free Design. Adv.
(23) Reynolds, V. G.; Mukherjee, S.; Xie, R.; Levi, A. E.; Atassi, A.; Uchiyama, T.; Wang, H.; Chabinyc, M. L.; Bates, C. M. Super-Soft Solvent-Free Bottlebrush Elastomers for Touch Sensing. *Mater. Horizons* **2020**, *7* (1), 181–187.

(24) Wong, M. Y.; Schneider, A. F.; Lu, G.; Chen, Y.; Brook, M. A. Autoxidation: Catalyst-Free Route to Silicone Rubbers by Crosslinking Si-H Functional Groups. *Green Chem.* **2019**, *21* (23), 6483–6490.

(25) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: Canada, 1999; pp 176.

(26) Lukevics E.; Dzintara M. The alcoholysis of Hydrosilanes. *Journal of Organometallic Chemistry* **1985**, *295*(3), 265-315.

(27) Chauhan, B. P. S.; Sarkar, A.; Chauhan, M.; Roka, A. Water as Green Oxidant: A Highly Selective Conversion of Organosilanes to Silanols with Water. *Appl. Organomet. Chem.* **2009**, *23* (10), 385–390.

(28) Hill, D. J. T.; Preston, C. M. L.; Whittaker, A. K. NMR Study of the Gamma Radiolysis of Poly(Dimethyl Siloxane) under Vacuum at 303 K. *Polymer* **2002**, *43* (4), 1051–1059.

(29) Patai, S.; Rappoport, Z. The Chemistry of Organic Silicon Compounds. John Wiley &Sons: Singapore, 1989, pp 517, 523.

(30) Israël, Y.; Lacoste, J.; Cavezzan, J.; Lemaire, J. Photo-Oxidation of Polydimethylsiloxane Oils Part III-Effect of Dimethylene Groups. *Polym. Degrad. Stab.* **1993**, *42* (3), 267–279.

(31) Helbich, T.; Lyuleeva, A.; Höhlein, I. M. D.; Marx, P.; Scherf, L. M.; Kehrle, J.; Fässler, T. F.; Lugli, P.; Rieger, B. Radical-Induced Hydrosilylation Reactions for the Functionalization of Two-Dimensional Hydride Terminated Silicon Nanosheets. *Chem. - A Eur. J.* **2016**, *22* (18), 6194–6198.

(32) Yang, Z.; Iqbal, M.; Dobbie, A. R.; Veinot, J. G. C. Surface-Induced Alkene Oligomerization: Does Thermal Hydrosilylation Really Lead to Monolayer Protected Silicon Nanocrystals? *J. Am. Chem.
(33) Xiao, R.; Zammit, I.; Wei, Z.; Hu, W.-P.; MacLeod, M.; Spinney, R. Kinetics and Mechanism of the Oxidation of Cyclic Methylsiloxanes by Hydroxyl Radical in the Gas Phase: An Experimental and Theoretical Study. *Environmental Science & Technology* **2015**, *49*(22), 13322-13330.

(34) Sommerlada, R.; Parlar, H.; Wrobel, D.; Kochs, P. Product Analysis and Kinetics of the Gas-Phase Reactions of Selected Organosilicon Compounds with OH Radicals Using a Smog Chamber-Mass Spectrometer System. *Environmental Science & Technology* **1993**, *27*(12), 2435-2440.

(35) Tsukada, N.; Hartwig, J. F. Intermolecular and Intramolecular, Platinum-Catalyzed, Acceptorless Dehydrogenative Coupling of Hydrosilanes with Aryl and Aliphatic Methyl C-H Bonds. *J. Am. Chem. Soc.* **2005**, *127*(14), 5022-5023.

(36) Corey, J. Y. Reactions of Hydrosilanes with Transition Metal Complexes. *Chemical Reviews* **2016**, *116*(19), 11291-11435.

(37) Nagai, Y. Hydrosilanes as Reducing Agents. A Review. *Org. Prep. Proced. Int.* **1980**, *12* (1–2), 13–48.

(38) Lewis, L. N. On the Mechanism of Metal Colloid Catalyzed Hydrosilylation: Proposed Explanations for Electronic Effects and Oxygen Cocatalysis. *J. Am. Chem. Soc.* **1990**, *112* (16), 5998–6004.

(39) Onopchenko, A.; Sabourin, E. T. Activation of Platinum Catalysts with Oxygen To Enhance Hydrosilylation of Unactivated Alkyl-, Dialkyl-, and Trialkylsilanes with 1-Alkenes: Synthesis of Tetraalkylsilanes. *J. Org. Chem.* **1987**, *52* (18), 4118–4121.

(40) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. Connection between Polymer Molecular Weight, Density, Chain Dimensions, and Melt Viscoelastic Properties. *Macromolecules* **1994**, *27* (17), 4639–4647.

(41) Abbasi, M.; Faust, L.; Wilhelm Abbasi, M. M.; Faust, L.; Wilhelm, M. Comb and Bottlebrush Polymers with Superior Rheological and Mechanical Properties. *Adv. Mater.* **2019**, *31*(26), 1806484.
(42) Geliebter, A.; Melton, P. M.; McCray, R. S.; Gage, D.; Heymsfield, S. B.; Abiri, M.; Hashim, S. A. Clinical Trial of Silicone-Rubber Gastric Balloon to Treat Obesity. *Int. J. Obes.* **1991**, 15 (4), 259–266.

(43) Wang, S.; Xu, J.; Wang, W.; Wang, G. J. N.; Rastak, R.; Molina-Lopez, F.; Chung, J. W.; Niu, S.; Feig, V. R.; Lopez, J.; Lei, T.; Kwon, S.; Kim, Y.; Foudeh, A. M.; Ehrlich, A.; Gasperini, A.; Yun, Y.; Murmann, B.; Tok, J. B.; Bao, Z. Skin Electronics from Scalable Fabrication of an Intrinsically Stretchable Transistor Array. *Nature* **2018**, 555 (7694), 83–88.

(44) Shim, H. J.; Sunwoo, S. H.; Kim, Y.; Koo, J. H.; Kim, D. H. Functionalized Elastomers for Intrinsically Soft and Biointegrated Electronics. *Adv. Healthc. Mater.* **2021**, 2002105, 1–33.

(45) Aharoni, S. M. Intramolecular Crosslinking. *Die Angew. Makromol. Chemie* **1977**, 62 (1), 115–133.
Supporting information

Highly stretchable or extremely soft silicone elastomers? One reaction
to make them all - from easily available materials!

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EXPERIMENTAL SECTION

**Materials** Information of chemicals used in this studies is shown in Table S1, in which all the chemicals were purchased from Gelest, except that Catalyst 511 was purchased from Hanse Chemie. As a precursor polymer for condition controlling experiments, DMS-H11 (10 mL) was diluted in hexane (20 mL, ≥95%, Sigma-Aldrich) and dried with silica gel (5 g, particle size of 63-200 μm, high-purity grade, Sigma-Aldrich) in a sealed flask at a room temperature for 2 days. The upper layer was transferred into a dried flask through a syringe mounted with a filter. Subsequently, the hexane was thoroughly distilled under a vacuum pressure condition at room temperature for 6 h. Red pigment (PGRED01, 50% in silicone oil) was purchased from Gelest.

**Silicone elastomers prepared from hydrosilane (Si-H) containing PDMS.** All the telechelic Si-H functional PDMS and multi-Si-H functional PDMS in Table S1 were used to prepare silicone elastomers, respectively. A representative procedure is as follows: DMS-H11 (10 g, 1.00 × 10⁻² mol) was mixed with catalyst SIP 6830.3 (2 mg, 3.08 × 10⁻⁷ mol) using a speed mixer (DAC150FVZ, Hauschild Co.) at 3000 rpm for 2 min. The mixture was poured into a mold and placed in an oven at 100°C for 24 h.

**Highly stretchable silicone elastomers and extremely soft silicone elastomers** Vinyl functional PDMS and catalyst SIP 6830.3 (2 mg, 3.08 × 10⁻⁷ mol) were well mixed using a speed mixer. Subsequently, Si-H functional PDMS was added into the mixture and well-mixed. The final mixture was poured on a mold and placed in an oven at 100°C for 24 h. The prepared elastomers listed in Table S2 are named according to the precursor polymer used.

**Conventional silicone elastomers** Part A and part B were prepared before the curing reaction. For a reference sample of Ref_DMS-V25, part A was prepared by mixing DMS-V25 (5 g, 3.3 × 10⁻⁴ mol) with HMS-301 (0.69 g, 3.6 × 10⁻⁴ mol). Part B was prepared by mixing DMS-V25 (5 g, 3.3 × 10⁻⁴ mol) with catalyst 511 (2 mg, 1.0 × 10⁻⁷ mol). For a reference sample of Ref_DMS-V41, part A was prepared...
by mixing DMS-V41 (10 g, $1.5 \times 10^{-4}$ mol) with HMS-301 (0.14 g, $7.3 \times 10^{-5}$ mol). Part B was prepared by mixing DMS-V41 (4.8 g, $7.7 \times 10^{-5}$ mol) with catalyst 511 (3 mg, $1.5 \times 10^{-7}$ mol). Parts A and B were then mixed together using a speed mixer at 3000 rpm for 30 s. The final mixture was poured on the surface of a polyethylene terephthalate (PET) substrate and evenly distributed by applying an automatic applicator. The PET substrate together with the mixture was placed in an oven at 100°C for 5 h.

**Table S1.** Information of chemicals used in this study

| Type of chemical                        | Chemical structure | Abbreviation | $M_n$ (kDa) | $D_n$ |
|-----------------------------------------|--------------------|--------------|-------------|-------|
| **Telechelic Si-H functional PDMS**     |                    | DMS-H11      | 1           | 1.3   |
|                                         |                    | DMS-H21      | 6           | 1.6   |
|                                         |                    | DMS-H25      | 14          | 1.5   |
|                                         |                    | DMS-H31      | 24          | 1.5   |
| **Mono-Si-H functional PDMS**           |                    | MCR-H21      | 7           | 1.1   |
| **Multi-Si-H functional PDMS**          |                    | HMS-301c     | 2           | -     |
|                                         |                    | HMS-064c     | 60          | -     |
| **Telechelic vinyl functional PDMS**    |                    | DMS-V22      | 8           | 2.1   |
|                                         |                    | DMS-V25      | 14          | 1.5   |
|                                         |                    | DMS-V41      | 35          | 2.0   |
| **Mono-vinyl functional PDMS**          |                    | MCR-V21      | 6           | 1.1   |
|                                         |                    | MCR-V25      | 23          | 1.3   |
| **Platinum-divinyl tetramethyl-disiloxane complex, 3.0 wt% Pt** | | SIP 6830.3 | - | - |
| **Platinum cyclo-vinylmethyl siloxane complex, 1.0 wt% Pt** | | Catalyst 511 | - | - |

a: Number average molecular weight. b: Poly-dispersity index. c: Concentrations of Si-H groups on HMS-301 and HMS-064 were determined to be 3.74 mol/kg and 0.830 mol/kg, respectively, based on integrations of $^1$H spectra.
Table S2. Formulations of preparing highly stretchable and extremely soft silicone elastomers

| Sample                        | Si-H functional PDMS | Vinyl functional PDMS |
|-------------------------------|----------------------|-----------------------|
|                               | Mass (g)             | Molar amount of Si-H  |
|                               |                      | group (mol)           |
|                               |                      | Mass (g)              |
|                               |                      | Molar amount of vinyl |
|                               |                      | group (mol)           |
| Ela_DMS-H21_DMS-V22_R1.05    | 4.46                 | 1.55×10^{-3}          |
|                               |                      | 5.54                  |
|                               |                      | 1.47×10^{-3}          |
| Ela_DMS-H21_DMS-V22_R1.10    | 4.57                 | 1.59×10^{-3}          |
|                               |                      | 5.43                  |
|                               |                      | 1.44×10^{-3}          |
| Ela_DMS-H21_DMS-V22_R1.15    | 4.68                 | 1.63×10^{-3}          |
|                               |                      | 5.32                  |
|                               |                      | 1.41×10^{-3}          |
| Ela_DMS-H25_DMS-V25_R1.05    | 5.16                 | 7.27×10^{-4}          |
|                               |                      | 4.84                  |
|                               |                      | 6.92×10^{-4}          |
| Ela_HMS_064-MCR-V21_R1.05    | 1.39                 | 1.16×10^{-3}          |
|                               |                      | 8.61                  |
|                               |                      | 1.10×10^{-3}          |
| Ela_HMS_064-MCR-V21_R1.20    | 1.56                 | 1.30×10^{-3}          |
|                               |                      | 8.44                  |
|                               |                      | 1.08×10^{-3}          |
| Ela_HMS_064-MCR-V21_R1.50    | 1.88                 | 1.56×10^{-3}          |
|                               |                      | 8.12                  |
|                               |                      | 1.04×10^{-3}          |
| Ela_HMS_064-MCR-V25_R1.05    | 0.52                 | 4.36×10^{-4}          |
|                               |                      | 9.48                  |
|                               |                      | 4.15×10^{-4}          |

Condition controlling experiments Before reactions, glassware was dried at 120°C overnight. Platinum catalyst SIP 6830.3 (1 mg) and dried DMS-H11 (1 g) were added in 50 mL-round-bottom flasks sealed with a rubber septum and a stopcock adapter. The mixture was well mixed by vigorous shaking. Four reactions under four different atmospheres were created as follows: (a) Dry N₂ atmosphere was created by evacuating air from the flask and then backfilling with dry N₂ for 4 cycles before the addition of the precursor polymer and the catalyst. (b) Wet N₂ atmosphere was created as same as (a) but adding 3 drops of water in the flask and dispersing into the precursor polymer by vigorous shaking. (c) Dry air was created as same as protocol (a) but replacing the dry N₂ with dry air. (d) Wet air was created as same as protocol (b) but replacing the dry N₂ with dry air. Subsequently, the four flasks were heated at 100 °C for 48 h. The resulting liquid products were analyzed by ¹H nuclear magnetic resonance (NMR) and size-exclusion chromatography (SEC).

Kinetics study Two sets of reactions (a) MCR-H21 (2 g) mixed with catalyst SIP6830.3 (2 mg), and (b) MCR-H21 (1 g) mixed with MCR-V21 (1 g) and SIP6830.3 (2 mg) were run in an oven at 100°C. Samples
were taken from the reaction (a) at reaction time of 10 min, 30 min, 60 min, 180 min and 360 min. Samples were taken from reaction (b) at reaction time of 0.5 min, 1 min, 2 min, 5 min and 30 min. All the samples were cooled down immediately by using dry ice, and analyzed by $^1$H NMR and SEC.

**Uniaxial tensile test** Stress–strain responses of elastomers were measured using an Instron 3340 materials testing system (INSTRON, US) at a crosshead speed of 500 mm min$^{-1}$. Specimens were cut with a dumbbell shape according to ASTM D-638 Type V (width: 3.18 mm; length: 9.53 mm; thickness: 1 mm). Elastic moduli were determined by linear fitting of the stress-strain data at a strain range of 0-10%.

**Biaxial tension test** An elastomer film (1 mm × 50 mm × 50 mm) was marked with a 1 cm-square in the center by using red pigment (PGRED01, 50% in silicone oil, Gelest Inc.). The film was biaxially stretched until it was close to break. The stretched film was placed above a grid pad on a table in order to estimate the size changes of the red square, then it covered the surface of a standard football with a 21 cm-diameter.

**Linear viscoelasticity (LVE)** Specimen LVE was measured by a strain-controlled rheometer ARES G2 (TA Instruments), using small amplitude oscillatory shear (SAOS). Specimens with a thickness of ∼1 mm were cut into cylinders with 8 mm-diameter. The shear strain amplitude was fixed to 1%. For highly stretchable elastomers, frequency sweeps from $1.6 \cdot 10^1$ to $1.6 \cdot 10^{-3}$ Hz were conducted at 21°C and 200°C, respectively. Time–temperature superposition was used to create master curves based on a reference temperature of 21°C. For extremely soft elastomers, a frequency sweep was performed from $1.0 \cdot 10^2$ to $1.0 \cdot 10^{-2}$ Hz at 21°C.

**Time sweep in LVE region.** Modulus complex during curing of elastomers was measured by a strain-controlled rheometer AR-2000 (TA Instruments). The mixture of precursor polymers with platinum catalysts was sandwiched by two geometries of instruments. The thickness of the mixture layer is around 0.5 mm and the diameter is the plates is 20 mm. Oscillatory experiments were performed with a controlled temperature of 100°C, a controlled strain of 1%, and a constant shear frequency of 1 Hz.
Compression test Two pieces of cylinder elastomers (8 mm in diameter) were stacked with a thickness of around 2 mm. Rheometer ARES G2 was used to compress the elastomers by applying two round plates (8 mm in diameter). Applied forces and gaps between plates were recorded during the compression.

SEC measurement SEC was performed on a Tosoh EcoSEC HLC8320GPC instrument equipped with RI and UV detectors and SDV Linear S columns from Polymer Standards Service (PSS). Samples were run in toluene at 35°C at a rate of 1 mL min\(^{-1}\). Molecular weights and \(D_M\) were calculated using WinGPC Unity 7.4.0 software and standard linear PDMS were acquired from PSS.

NMR measurement \(^1\)H NMR spectra of samples were performed on a Bruker 300 MHz spectrometer on 50 mg mL\(^{-1}\) solutions in CDCl\(_3\). \(^{29}\)Si solid-state NMR MAS spectra of investigated elastomers were acquired on a Bruker Avance III HD spectrometer operating at a magnetic field of 14.05 T \((\nu_L(^{29}\text{Si}) = 119.2 \text{ MHz})\) and equipped with a 4 mm CP/MAS broadband probe. The spectra were acquired with a spinning frequency of 6 kHz, a \(\pi/2\) pulse of 4.75 ms, an acquisition time of 35 ms and 10 seconds of interscan delay. This was determined to be sufficient for full relaxation of the two observed signals for elastomers. High-power \(^1\)H SPINAL64 decoupling \((\nu_{RF} = 100 \text{ kHz})\) was employed during acquisition.

The prepared elastomers were cut into smaller pieces and packed in 4 mm o.d. zirconia rotors. Chemical shifts are reported relative to TMS (0.0 ppm). High-resolution \(^{29}\)Si NMR spectrum of a precursor PDMS (liquid state) was acquired on a Bruker Avance II spectrometer operating at a magnetic field of 9.4 T \((\nu_L(^{29}\text{Si}) = 79.495 \text{ MHz})\) and equipped with a 5mm BBFO probe. The NMR samples were prepared as-received (i.e. no deuterated solvent was added) and chemical shifts are referenced using the lock-field determined for a secondary CDCl\(_3\) sample. A Pi/6 pulse was used for excitation with an interscan delay of 15 seconds. Inverse-gated 1H decoupling was applied during acquisition. Data were analyzed using MestReNova-11.

Theoretical average molecular weight of extended chains
For a platinum-catalyzed reaction system of telechelic Si-H functional PDMS with telechelic vinyl functional PDMS using a small excess of Si-H groups, both the hydrosilylation reaction between Si-H and vinyl groups and the crosslinking of Si-H take place. Assuming the two reactions happen strictly in sequence, the hydrosilylation reaction results in extended chains, which are cross-linked into elastomers by subsequent crosslinking of excess Si-H. According to mass balance equation:

\[(R - 1)M_{\text{extended}} = RM_{\text{DMS-H}} + M_{\text{DMS-V}} \]  

(S1)

Where \(M_{\text{DMS-H}}\) is the molecular weight of telechelic Si-H functional PDMS, \(M_{\text{DMS-V}}\) is the molecular weight of telechelic vinyl functional PDMS, \(M_{\text{extended}}\) is the average molar mass of the extended network strands and \(R\) is the molar ratio of the Si-H to vinyl functional groups. \(M_{\text{extended}}\) is expressed as:

\[M_{\text{extended}} = \frac{RM_{\text{DMS-H}} + M_{\text{DMS-V}}}{R - 1} \]  

(S2)

**Theoretical molecular weight between Si-H groups on intermediate bottlebrush polymers**

Assuming crosslinking of Si-H takes place strictly after the full grafting of side chains, molecular weight between Si-H groups on intermediate bottlebrush polymers (\(M_{\text{c, SiH}}\)) is expressed as equation S5.

\[f_{\text{brush}} = \frac{R - 1}{R}f \]  

(S3)

\[M_{\text{brush}} = M_{\text{HMS}} + (f - f_{\text{brush}})M_{\text{MCR-V}} \]  

(S4)

\[M_{\text{c, SiH}} = \frac{M_{\text{brush}}}{f_{\text{brush}} + 1} \]  

(S5)

Where \(M_{\text{brush}}\) and \(f_{\text{brush}}\) are the molecular weight and number of Si-H groups of the intermediate bottle-brush polymer. \(f\) and \(M_{\text{HMS}}\) is the functionality and molecular weight of multi-Si-H functional PDMS. \(M_{\text{HMS-V}}\) is the molecular weight of mono-vinyl functional PDMS.

**Calculation of molecular weights of bottle-brush network strands (\(M_c\))**

\(M_c\) are determined based on the measured shear moduli (\(G\)) by equation S6.¹
\[ M_c = \frac{\rho RT \phi^2}{G} \]

Where \( \rho \) is the density of silicone elastomer, \( R \) is the gas constant, \( T \) is the absolute temperature, \( \phi \) is the gel fraction of elastomers, \( G \) is the shear modulus of elastomers.

**SUPPLEMENTARY FIGURES**

**Table S3** Integration of \(^1\)H NMR spectra of a telechelic Si-H functional PDMS (DMS-H11) and its reaction products after heating at 100°C for 48 h under dry \( \text{N}_2 \), wet \( \text{N}_2 \) and dry air conditions, respectively.

| Sample     | 5.11 ppm to 4.55 ppm | 3.52 ppm to 4.34 ppm | 2.39 ppm to 2.23 ppm | 0.50 ppm to 0.18 ppm |
|------------|----------------------|----------------------|----------------------|----------------------|
|            | Si-H                 | SiOCH\(_2\)Si        | Si-OH                | CH\(_3\) except at the two ends |
| DMS-H11    | 201.28               | 0                     | 0                    | 10000                |
| Dry \( \text{N}_2 \) | 188.02               | 0                     | 1.17                 | 10000                |
| Wet \( \text{N}_2 \) | 141.91               | 0                     | 2.77                 | 10000                |
| Dry air    | 94.84                | 1.36                  | 0.51                 | 10000                |

**Table S4** Integration of \(^{29}\)Si solid state NMR spectra of a telechelic Si-H functional PDMS (DMS-H11) and solid elastomers prepared under normal air conditions.

| Sample     | 9.08 ppm to 6.20 ppm | -6.67 ppm to -8.08 ppm | -21.64 ppm to -23.44 ppm | -62.92 ppm to -65.33 ppm |
|------------|----------------------|------------------------|--------------------------|--------------------------|
|            | (CH\(_3\))\(_2\)SiO \( \text{Si-H} \) \( \text{SiOSi} \) \( \text{CH}_3\text{SiO}_3 \) | \( \text{Si-H} \) \( \text{SiOSi} \) \( \text{CH}_3\text{SiO}_3 \) |
| DMS-H11    | 0                    | 19.56                  | 100                      | 0                        |
| Ela_DMS-H11 | 1.44                 | 0                      | 100                      | 0.97                     |
| Ela_DMS-H21 | 0.43                 | 0                      | 100                      | 1.19                     |

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Figure S1. SEC curves of starting polymer DMS-H11 and its liquid products after heating at 100°C for 48 h under dry N₂, wet N₂ and dry air atmospheres, respectively.

Figure S2. Evolutions of ¹H spectra over time for (a) the reaction of mono-Si-H functional PDMS, and (b) hydrosilylation reaction between mono-Si-H functional PDMS with mono-vinyl functional PDMS.
**Figure S3.** Linear fitting of $\lambda_{\text{max}}$ and $M_{\text{extended}}^{0.5}$. For highly stretchable silicone elastomers, $M_{\text{extended}}$ is the theoretical molar mass of precursor polymer calculated by Equation S2. For conventional silicone elastomers Ref_DMS-V25 and Ref_DMS-V41, $M_{\text{extended}}$ approximately equals the molecular weight of precursor polymers DMS-V25 and DMS-V41, respectively.

**Figure S4.** Uniaxial stress-strain curves of extremely soft silicone elastomers and a conventional silicone elastomer.
Reference

(1) Vasiliev, V. G.; Rogovina, L. Z.; Slonimsky, G. L. Dependence of Properties of Swollen and Dry Polymer Networks on the Conditions of Their Formation in Solution. Polymer 1985, 26 (11), 1667–1676.