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

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1 **Highly stretchable or extremely soft silicone elastomers? One reaction**
2 **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 1a** 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

25 resulting silicone elastomers is proportional to $M^{0.5}$ based on the Kuhn model, where M is the aver-
26 age molar mass of network strands.⁹ The ultimate extensibility is usually less than 900%, and it is
27 difficult to further increase this value by using longer precursor polymers, since they would bring
28 difficulties to the fabrication process due to their high viscosity.¹⁰ The elastic modulus of the silicone
29 elastomers is determined by the crosslinking density—namely, the molar density of mechanically
30 active strands $\nu = \rho/M$, where ρ is the density. However, the lowest achievable elastic modulus for
31 ideal elastomer networks is around 0.6 MPa due to the fact that entanglements in the cross-linked
32 networks act as topological crosslinks once the molecular weight of network strands (M) exceeds
33 the entanglement molecular weight.¹¹

34 Several strategies have been explored for overcoming limitations on the ultimate extensibility and
35 softness of silicone elastomers. For example, elastomers prepared from long precursor polymers in
36 solution and subjected to solvent evaporation after curing, supramolecular elastomers with mova-
37 ble cross-links, and concatenated ring elastomers have all been developed to improve ultimate ex-
38 tensibility.¹²⁻¹⁷ Approaches such as adding external sol molecules, sparse crosslinking, and cross-
39 linking bottle-brush PDMS have also been used to prepare soft silicone elastomers.¹⁸⁻²³ While the
40 above strategies improve elastomer extensibility or softness to some extent, they either increase
41 process complexity or lead to mechanical instabilities in the resulting elastomers. What is more,
42 none of them are versatile enough to enable the preparation of silicone elastomers that are both
43 highly stretchable *and* very soft. There is thus a lack of available chemistries capable of efficiently
44 preparing silicone elastomers with superior stretchability and softness.

45 Silicone elastomers have been prepared from Si-H functionalized polymers at 250°C in air, where
46 the crosslinking mechanism was found to originate from oxidative crosslinking of Si-H groups in the
47 presence of oxygen.²⁴ In this study, silicone elastomers are prepared from PDMS with
48 telechelic/multiple Si-H groups and a platinum catalyst in air at the much lower temperature of
49 100°C (see **Figure 1b**). In contrast to classical curing chemistries where the network strands are

50 directly related to the length of the precursor polymers, the curing chemistry presented here, when
51 combined with the hydrosilylation reaction, allows network strands to be tailored from normal lin-
52 ear precursors during the curing process. Specifically, we report highly stretchable silicone elasto-
53 mers with ultra-long network strands and extremely soft silicone elastomers with bottle-brush
54 strands, both of which are easily prepared from commercially available linear precursors. Both
55 novel silicone elastomers are based on sequential crosslinking mechanisms in one-pot reactions,
56 where the fast hydrosilylation reaction is followed by a slow crosslinking of residual Si-H functional
57 groups. This allows independent control of network strand size and structure, as well as of cross-
58 linking.

59

Figure 1. (a) Conventional curing reaction to prepare silicone elastomers.⁸ (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

70 further studies in order to elucidate the mechanism of this formation.

71 Hydrosilanes readily undergo hydrolysis and alcoholysis reactions with water and alcohols, respec-

72 tively, under basic or strongly acidic conditions or in the presence of radicals, metals, or transition

73 metal complexes.^{25,26} In the presence of a platinum catalyst and water, telechelic Si-H functional

74 PDMS can thus be hydrolyzed into Si-OH, which may further undergo condensation to form ex-

75 tended chains. However, the hydrolysis and condensation reactions cannot account for the for-

76 mation of elastomers from telechelic Si-H functional PDMS in a conventional manner. Instead, ob-

77 taining elastomers from telechelic Si-H functional PDMS requires either the formation of concate-

78 nated rings through intramolecular condensation reactions or some other unexplored crosslinking

79 reaction.^{15,17} Water and oxygen are the possible reactants in the curing reaction with Si-H-contain-

80 ing precursor PDMS. The reaction was therefore carried out under conditions in which water and

81 oxygen content could be carefully controlled. Specifically, in a series of experiments, a representa-

82 tive telechelic Si-H functional PDMS (DMS-H11, $M_n=1$ kDa) was heated at 100°C for 48 h in a sealed

83 flask under each of the following reaction conditions: dry N₂ (a dried sample under dried nitrogen),

84 wet N₂ (a sample containing water with ~4 molar equivalent of hydrosilanes under dried nitrogen),

85 dry air (a dried sample under dried air), and wet air (a sample containing water with ~4 molar

86 equivalent of hydrosilanes under dried air). DMS-H11 was converted into a solid elastomer only

87 under wet air conditions. As measured by ¹H NMR, the conversion efficiency of Si-H groups for the

88 three liquid products under dry N₂, wet N₂, and dry air conditions were found to be 6.6%, 29.5%,

89 and 52.9%, respectively (**Figure 2a**). These findings indicate that both water *and* oxygen participate

90 in the reaction. A peak at 2.27 ppm in the ¹H nuclear magnetic resonance (NMR) spectrum of the

91 sample from the wet N₂ atmosphere is assigned to a Si-OH structure (**Figure 2a**), suggesting a hy-

92 drolysis process of Si-H during the reaction.²⁷ A further condensation process of Si-OH results in

93 chain extension, as evidenced by the increased molecular weight of the sample (**Figure S1, ESI**). An-

94 other new peak that appears at 3.47 ppm (**Figure 2a**) on the ¹H spectrum of the sample from dry air

atmosphere is contributed to a silyl ether (Si-O-CH₂-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.²⁴ The presence of this silyl ether suggests that branched chains are formed during the oxidation of Si-H. The integration of the ¹H 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 ¹H spectrum. The minimal loss of Si-H (6.6%, Figure 2a) under dry N₂ 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. (a) ¹H 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 N₂, wet N₂, and dry air conditions, respectively. (b) ²⁹Si solid-state NMR spectra

106 of elastomers (Ela_DMS-H11 and Ela_DMS-H21) and a precursor polymer (DMS-H11). (c) Proposed mechanism
 107 of crosslinking Si-H functional groups in the presence of oxygen and a catalyst.

108

109 Direct investigations of the chemical composition of solid elastomers cured under a normal air at-
 110 mosphere and a precursor polymer DMS-H11 were performed using ^{29}Si solid-state NMR. **Figure 2b**
 111 shows that a peak at -7 ppm on the spectrum of the precursor polymer is assigned to Si-H functional
 112 groups.²⁸ This peak vanishes on the spectra of the elastomers, suggesting an efficient conversion of
 113 Si-H after curing. New peaks located at 7 ppm and -64 ppm are observed on spectra of the elasto-
 114 mers and are assigned to $(\text{CH}_3)_3\text{SiO}$ (or $(\text{CH}_3)_2\text{CH}_2\text{SiO}$) and CH_3SiO_3 , respectively.²⁸⁻³⁰ Since the hy-
 115 drolysis of Si-H and further condensation of Si-H with Si-OH would only produce more backbone
 116 chains $(-(\text{CH}_3)_2\text{SiO}-)$, the newly formed structures are the result of oxidation of Si-H functional
 117 groups. Integration of the spectra shows that Si atoms associated with these newly formed struc-
 118 tures account for 1.5-2.5% of Si atoms in the elastomers (**Table S4, ESI**), suggesting that these oxi-
 119 dized structures play a major role in crosslinking.

120 Based on the observations above, it is clear that oxidation of Si-H plays a role in creating branched
 121 chains to form networks, as hydrolysis and subsequent condensation of telechelic chains would only
 122 produce longer, linear chains. The oxidation processes are proposed as follows. Si-H functional
 123 groups are turned into silyl radicals $\text{O}(\text{CH}_3)_2\text{Si}\cdot$ through hydrogen abstraction in the presence of
 124 air (**Figure 2c-A**).^{31,32} After further oxidation processes, the silyl radicals are transformed into
 125 $\text{O}(\text{CH}_3)_2\text{SiO}\cdot$ (**Figure 2c-B and C**).²⁴ Oxidation processes also happen on methyl groups of silicones:
 126 oxygen initially generates a carbon radical $(\text{SiCH}_2\cdot)$ by hydrogen atom abstraction (**Figure 2c-D**).^{33,34}
 127 Branching structures like SiCH_2Si and SiOCH_2Si are formed by combinations of $\text{SiCH}_2\cdot$ with
 128 $\text{O}(\text{CH}_3)_2\text{Si}\cdot$ and $\text{O}(\text{CH}_3)_2\text{SiO}\cdot$, respectively (**Figure 2c-E and F**). A combination of $\text{O}(\text{CH}_3)_2\text{Si}\cdot$ and
 129 $\text{O}(\text{CH}_3)_2\text{SiO}\cdot$ only produces extended chains via the formation of SiOSi (**Figure 2c-G**). Further oxi-
 130 dation of $\text{SiCH}_2\cdot$ leads to the creation of $\text{SiCH}_2\text{OO}\cdot$, which enables the formation of SiO_3CH_3 by a self-

131 reaction (**Figure 2c-H and I**).^{33,34}

132 It should be noted that the same radicals mentioned above were also used to explain crosslinking

133 during the oxidization of Si-H functional PDMS at high temperature (250°C) in the absence of a cat-

134 alyst, in which a silyl ether (Si-O-CH₂-Si) structure was the main oxidized structure produced.²⁴ In

135 our work, however, the oxidation process is faster and occurs at a much lower temperature due to

136 the use of a platinum catalyst; the main oxidized structures produced are (CH₃)₂CH₂SiO and CH₃SiO₃.

137 Si-[Pt]-H complex is known to form by oxidative addition,³⁵⁻³⁷ and [Pt]-oxygen complex has been

138 reported to significantly promote platinum catalyzed hydrosilylation reactions.^{38,39} These com-

139 pounds may allow the reaction with oxygen to occur at moderate temperatures, thereby changing

140 the main oxidized structures produced.

141 This curing chemistry can be extended to the curing of multifunctional Si-H functional PDMS, where

142 both hydrolysis/condensation and oxidation reactions may contribute to crosslinking. The pre-

143 pared elastomers listed in **Table 1** are named according to the precursor polymer used. Overall, the

144 prepared silicone elastomers show tensile strains of 70-360%, Young's moduli of 0.3-0.6 MPa, and

145 tensile strengths of 0.2-0.6 MPa. These mechanical properties are comparable to those of the two

146 conventional silicone elastomers prepared via the classical curing route.¹⁰

147

Table 1. Silicone elastomers prepared from telechelic/multi Si-H functional PDMS in presence of a platinum-divinyl 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 hydrosilylation 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°C. The total concentration of functional groups was the same for both reactions. **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 exclusively 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.^{9,40} 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**):

$$M_{\text{extended}} = \frac{RM_{\text{DMS-H}} + M_{\text{DMS-V}}}{R - 1} \quad (1)$$

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.^{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.^{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:

$$M_{\text{c-SiH}} = \frac{M_{\text{brush}}}{f_{\text{brush}} + 1} \quad (2)$$

203 where M_{brush} (**Equation S3, ESI**) and f_{brush} (**Equation S4, ESI**) are the molecular weight and number
 204 of excess hydrides per chain, respectively, after full side chain grafting.
 205 Representative curing reactions for preparing highly stretchable, extremely soft elastomers were
 206 investigated by tracing the evolution of the storage and loss moduli during the two curing reactions
 207 (**Figure 3b**). Gel points are reached within 5 min at 100°C, suggesting fast curing processes.
 208
 209 Properties of highly stretchable silicone elastomers
 210 A number of stretchable silicone elastomers were prepared using different hydrosilane-to-vinyl-
 211 functional polymer ratios as well as polymers of different molecular weights, as shown in **Table 2**.
 212 **Figure 4a** shows that, when using the same precursor polymers DMS-H21 and DMS-V22, the tensile
 213 strain increases from 1040% to 2400% when R decreases from 1.15 to 1.05. Tensile strain can be
 214 further increased to 2800% by using longer starting polymers DMS-H25 and DMS-V25. Longer ex-
 215 tended chains improve tensile strain by enabling larger slippage lengths upon deformation (**Table**
 216 **2**). The Kuhn model is widely used to estimate the ultimate extensibility of elastomers as $\lambda_{\text{max}} =$
 217 L/h , where L is the strand length in a fully stretched state, and h is the strand length in a random
 218 coil state.⁹ λ_{max} is thus proportional to $M^{0.5}$ based on the relations of $L \propto M$ and $h \propto M^{0.5}$. A linear
 219 relation between λ_{max} and $M_{\text{theo}}^{0.5}$ complies with the Kuhn model (**Figure S3**), suggesting that equa-
 220 tion 1 is a valid description of the molar mass of the network strands, which supports the proposed
 221 curing route. Silicone elastomers with tailored stretchability can thus be realized by designing
 222 strand lengths based on equation 1. Elastomers' linear viscoelastic responses are shown in **Figure**
 223 **4b**. The storage modulus of the conventional elastomer reaches a plateau at low frequencies, while
 224 the storage moduli of the highly stretchable elastomers continue to decrease as the frequency ap-
 225 proaches zero. This unusual behavior is explained by stress relaxation from entanglements of highly
 226 extended strands upon deformation. Stretchable elastomers are often biaxially stretched in practi-
 227 cal use.^{42,43} **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	$M_{\text{DMS-H}}$ (kDa)	$M_{\text{DMS-V}}$ (kDa)	R	M_{extended} (kDa)	λ_{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

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) Biaxial stretching. (c-1) The highly stretchable silicone elastomer is marked with a red 1 cm^2 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 cm^2 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.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 (M_c) (**Equation S6**, **ESI**) are larger than the average molecular weight between Si-H groups on the bottle-brush chains (M_{c_SiH}). Specially, $M_c > 10M_{c_SiH}$ for the elastomers with MCR-V21 side chains. The large differences between M_c and M_{c_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.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.

260 **Table 3.** Specifications for studied soft silicone elastomers.

Samples	R	M_{HMS} (kDa)	$M_{\text{MCR-V}}$ (kDa)	$M_{\text{c-SiH}}$ (kDa)	M_{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

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

269 **CONCLUSION**

270 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.

296 **ASSOCIATED CONTENT**

297 Supporting information is available online

298

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301

302 **Author Contributions**

303 The manuscript was written through contributions of all authors.

304

305 **Notes**

306 The authors declare no competing financial interest.

307

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431 Supporting information

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

434

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439 **EXPERIMENTAL SECTION**

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

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

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

458 **Conventional silicone elastomers** Part A and part B were prepared before the curing reaction. For a
459 reference sample of Ref_DMS-V25, part A was prepared by mixing DMS-V25 (5 g, 3.3×10^{-4} mol)
460 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)
461 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, 1.5×10^{-4} mol) with HMS-301 (0.14 g, 7.3×10^{-5} mol). Part B was prepared by mixing DMS-V41 (4.8 g, 7.7×10^{-5} mol) with catalyst 511 (3 mg, 1.5×10^{-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^a (kDa)	$\bar{D}_M^b$
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 ^1H spectra.

468

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}

469

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

481 **Kinetics study** Two sets of reactions (a) MCR-H21 (2 g) mixed with catalyst SIP6830.3 (2 mg), and (b)
 482 MCR-H21 (1 g) mixed with MCR-V21 (1 g) and SIP6830.3 (2 mg) were run in an oven at 100°C. Samples

483 were taken from the reaction (a) at reaction time of 10 min, 30 min, 60 min, 180 min and 360 min. Samples
484 were taken from reaction (b) at reaction time of 0.5 min, 1 min, 2 min, 5 min and 30 min. All the samples
485 were cooled down immediately by using dry ice, and analyzed by ^1H NMR and SEC.

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

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

494 **Linear viscoelasticity (LVE)** Specimen LVE was measured by a strain-controlled rheometer ARES G2
495 (TA Instruments), using small amplitude oscillatory shear (SAOS). Specimens with a thickness of $\sim 1\text{ mm}$
496 were cut into cylinders with 8 mm-diameter. The shear strain amplitude was fixed to 1%. For highly
497 stretchable elastomers, frequency sweeps from $1.6 \cdot 10^1$ to $1.6 \cdot 10^{-3}\text{ Hz}$ were conducted at 21°C and 200°C ,
498 respectively. Time-temperature superposition was used to create master curves based on a reference tem-
499 perature of 21°C . For extremely soft elastomers, a frequency sweep was performed from $1.0 \cdot 10^2$ to
500 $1.0 \cdot 10^{-2}\text{ Hz}$ at 21°C .

501 **Time sweep in LVE region.** Modulus complex during curing of elastomers was measured by a strain-
502 controlled rheometer AR-2000 (TA Instruments). The mixture of precursor polymers with platinum cat-
503 alysts was sandwiched by two geometries of instruments. The thickness of the mixture layer is around 0.5
504 mm and the diameter of the plates is 20 mm. Oscillatory experiments were performed with a controlled
505 temperature of 100°C , a controlled strain of 1%, and a constant shear frequency of 1 Hz.

506 **Compression test** Two pieces of cylinder elastomers (8 mm in diameter) were stacked with a thickness
507 of around 2 mm. Rheometer ARES G2 was used to compress the elastomers by applying two round plates
508 (8 mm in diameter). Applied forces and gaps between plates were recorded during the compression.

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

513 **NMR measurement** ¹H NMR spectra of samples were performed on a Bruker 300 MHz spectrometer
514 on 50 mg mL⁻¹ solutions in CDCl₃. ²⁹Si solid-state NMR MAS spectra of investigated elastomers were
515 acquired on a Bruker Avance III HD spectrometer operating at a magnetic field of 14.05 T ($\nu_L(^{29}\text{Si}) =$
516 119.2 MHz) and equipped with a 4 mm CP/MAS broadband probe. The spectra were acquired with a
517 spinning frequency of 6 kHz, a $\pi/2$ pulse of 4.75 ms, an acquisition time of 35 ms and 10 seconds of
518 interscan delay. This was determined to be sufficient for full relaxation of the two observed signals for
519 elastomers. High-power ¹H SPINAL64 decoupling ($\nu_{\text{RF}} = 100$ kHz) was employed during acquisition.
520 The prepared elastomers were cut into smaller pieces and packed in 4 mm o.d. zirconia rotors. Chemical
521 shifts are reported relative to TMS (0.0 ppm). High-resolution ²⁹Si NMR spectrum of a precursor PDMS
522 (liquid state) was acquired on a Bruker Avance II spectrometer operating at a magnetic field of 9.4 T (ν_L
523 (²⁹Si) = 79.495 MHz) and equipped with a 5mm BBFO probe. The NMR samples were prepared as-
524 received (i.e. no deuterated solvent was added) and chemical shifts are referenced using the lock-field
525 determined for a secondary CDCl₃ sample. A Pi/6 pulse was used for excitation with an interscan delay
526 of 15 seconds. Inverse-gated ¹H decoupling was applied during acquisition. Data were analyzed using
527 MestReNova-11.

528 **Theoretical average molecular weight of extended chains**

529 For a platinum-catalyzed reaction system of telechelic Si-H functional PDMS with telechelic vinyl func-
 530 tional PDMS using a small excess of Si-H groups, both the hydrosilylation reaction between Si-H and
 531 vinyl groups and the crosslinking of Si-H take place. Assuming the two reactions happen strictly in se-
 532 quence, the hydrosilylation reaction results in extended chains, which are cross-linked into elastomers by
 533 subsequent crosslinking of excess Si-H. According to mass balance equation:

$$(R - 1)M_{\text{extended}} = RM_{\text{DMS-H}} + M_{\text{DMS-V}} \quad (\text{S1})$$

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

$$M_{\text{extended}} = \frac{RM_{\text{DMS-H}} + M_{\text{DMS-V}}}{R - 1} \quad (\text{S2})$$

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

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

$$f_{\text{brush}} = \frac{R - 1}{R} f \quad (\text{S3})$$

$$M_{\text{brush}} = M_{\text{HMS}} + (f - f_{\text{brush}})M_{\text{MCR-V}} \quad (\text{S4})$$

$$M_{\text{c-SiH}} = \frac{M_{\text{brush}}}{f_{\text{brush}} + 1} \quad (\text{S5})$$

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

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

544 M_c are determined based on the measured shear moduli (G) by equation S6.¹

$$M_c = \frac{\rho RT \phi^2}{G} \quad (S6)$$

Where ρ is the density of silicone elastomer. R is the gas constant. T is the absolute temperature. ϕ is the gel fraction of elastomers. G is the shear modulus of elastomers.

SUPPLEMENTARY FIGURES

Table S3 Integration of ^1H 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.

Sample	5.11 ppm to 4.55 ppm	3.52 ppm to 4.34 ppm	2.39 ppm to 2.23 ppm	0.30 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 N ₂	188.02	0	1.17	10000
Wet 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 CH ₂ SiO	Si-H	SiOSi	CH ₃ 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

556

557 **Figure S1.** SEC curves of starting polymer DMS-H11 and its liquid products after heating at 100°C for
 558 48 h under dry N₂, wet N₂ and dry air atmospheres, respectively.

559

560 **Figure S2.** Evolutions of ¹H spectra over time for (a) the reaction of mono-Si-H functional PDMS, and
 561 (b) hydrosilylation reaction between mono-Si-H functional PDMS with mono-vinyl functional PDMS .

562

563 **Figure S3.** Linear fitting of $\lambda_{\max}$ and $M_{\text{extended}}^{0.5}$. For highly stretchable silicone elastomers, M_{extended} is
 564 the theoretical molar mass of precursor polymer calculated by Equation S2. For conventional silicone
 565 elastomers Ref_DMS-V25 and Ref_DMS-V41, M_{extended} approximately equals the molecular weight of
 566 precursor polymers DMS-V25 and DMS-V41, respectively.

567

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

570

571 **Reference**

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