THE ROLE OF HYDROSILANES IN THE PREPARATION OF SILICONES

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A Thesis
Submitted to the School of Graduate Studies
In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

Doctor of Philosophy (2021)

McMaster University (Chemistry), Hamilton, Ontario

TITLE:

The Role of Hydrosilanes in the Preparation of Silicones

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NUMBER OF PAGES:	xvi, 262

Abstract

Silicone polymers (PDMS) are widely used for a large range of applications from automotive to cosmetic industries owing to their unique properties, such as electrical resistance, biocompatibility, and gas permeability. Conventionally, linear silicone polymers are produced by acid or base-catalyzed equilibration, leading to broad molecular weight dispersities, and high concentrations of a controversial monomer that requires removal. Therefore, in the first part of the research, we developed a new hydrolytic route to linear silicone polymers that is both simple and inexpensive. The small hydrosilane tetramethyldisiloxane ($HSi(CH_3)_2OSi(CH_3)_2H$) was polymerized to hydride-terminated PDMS (HSi-PDMS-SiH) using only water as a reagent, a process that has industrial potential. The product can further be converted into silicone block copolymers, elastomers, foams and resins.

We broadened the studies to consider the incorporation of different functional groups (vinyl and alkoxy groups) into silicones, including developing methods to control their precise locations in polymers and to synthesize dendritic hyperbranched silicone polymers in a controllable manner.

The ability of silanes to behave as functional reducing agents was examined. A series of model compound studies, including reduction with benzyl disulfide and tetrasulfide, were conducted to illustrate the mechanism of S-S bond cleavage using a catalytic amount of $B(C_6F_5)_3$. The effect of sterics on the rates of hydrolysis of the product S-Si compounds allowed consideration of the use of this strategy to protect for thiol groups. In addition, the relative reactivities of hydrosilane with different functional groups including mercaptan (SH), disulfide (SS) and ethoxy

(SiOEt) were also mapped out as follows: S-H>S-S>SiOEt. These investigations allowed us to exploit hydrosiloxanes for the reduction of the sulfur crosslinks in used rubber tires; current reuse methodologies either utilize harsh conditions or occur in low yields.

父母之恩,云何可报?慈如河海,孝若涓尘。

——致父母亲

Acknowledgements

This dissertation has been a labor of love, but it would never have been possible without the support and encouragement from my supervisor, Dr. Michael Brook who offered me tremendous and insightful commentaries and guidance that helped the project take shape. It is both an honor and a privilege to be your student. I would like to thank him and also everyone in my committee, Dr. Jose Moran-Mirabal and Dr. Ryan Wylie, for guiding this dissertation generously and shaping my intellectual life over the past five years. As with any research activity there were many, many challenges. I am very grateful that the committee stuck with me. Here, I would also like to thank Dr. Kirk Green, Dr. Bob Berno and Dr. Hilary Jenkins who offered me valuable suggestions for characterizations.

To all the labmates in Brook's lab, thank you for providing me a friendly and supportive working environment, Dr. Miguel Melendez, Scott Laengert, Dr. Alyssa Schneider, and the list go on. Especially, I would like to thank Dr. Yang Chen for offering me substantial advice and assistance along the way. I would also like to thank Dr. Sijia Zheng and Dr. Shuai Liang for being great friends to me and I have gained comfort and consolations from our endless conversations that propelled this project to completion. I would also like to take the chance to thank the friends that I met at McMaster, Dr. Fei Xu and Mr. Chenlong Xie, Dr. Jing Zhao and Dr. Wenwen Xu, Sheilan Sinjari (and more) for all the jokes and complaints!

I would like to thank my friends Wenzhen Cao, Qing He, Weiwei Zhao and Jingshu Yin for all the delicious food and happy gatherings together. I would also like to thank Sheila for her support and encouragement throughout the process.

Moreover, I would like to express my sincere thanks to ‘ready-to-be’ Dr.-Ing. Fengze Jiang for his encouragement and suggestions that consoled me during the last stage of my Ph.D. life.

Last but certainly not least, I would like to thank my parents for their immense trust and supports throughout my life. Thank you for your hard work and sacrifice, thank you for being proud of me. And also, my grandparents, thank you for the encouragement and caring.

感谢祖父母，外祖父母在求学路上给予的鼓励与支持。

Even though there’s an end to the words, there is never an end to their meaning.

Table of content

List of Figures and Tables

Figures

Tables

List of Abbreviations and Symbols

Acetone-d_6	Deuterated acetone
$B(C_6F_5)_3$	Tris(pentafluorophenyl)borane
$CDCl_3$	Deuterated chloroform
$Cr(acac)_3$	Chromium (III) acetylacetonate
D_3	Hexamethylcyclotrisiloxane
D_4	Octamethylcyclotetrasiloxane
D_5	Decamethylcyclopentasiloxane
D_4^H	Tetramethylcyclotetrasiloxane
DBTL	Di-*n*-butyltin dilaurate
DCM	Dichloromethane
$Đ_M$	Dispersity
FTIR	Fourier-transform infrared spectroscopy
GC-MS	Gas chromatography/mass spectrometry
GPC	Gel permeation chromatography
HTV	High temperature vulcanization
IPA	Isopropanol
LED	Light emitting diode
MM	Hexamethyldisiloxane
MM^H or PentaH	Pentamethyldisiloxane
MD^HM or BisH	Bis(trimethylsiloxy)methylsilane
M_3T^H or TrisH	Tris(trimethylsiloxy)silane
M^HM^H	Tetramethyldisiloxane
MHz	Megahertz
MW	Molecular weight
NMR	Nuclear magnetic resonance
PDMS	Polydimethylsiloxane
$PhMe_2SiH$ or Phenyl-H	Dimethylphenylsilane
ppm	Parts per million
PR	Piers-Rubinsztajn
RTV	Room temperature vulcanization
TBAF	Tetra-n-butylammonium fluoride
TESPD	Bis[3-(triethoxysilyl)propyl] disulfide
TESPT	Bis[3-(triethoxysilyl)propyl] tetrasulfide
T_g	Glass transition temperature
THF	Tetrahydrofuran

Declaration of Academic Achievement

Published Manuscripts

(1) **Liao, M**.; Chen, Y.; Brook, M. A. Spatially Controlled Highly Branched Vinylsilicones. *Polymers.* **2021**, *13*(6), 859.
(2) **Liao, M**.; Chen, Y.; Brook, M. A. When Attempting Chain Extension, Even Without Solvent, It Is Not Possible to Avoid Chojnowski Metathesis Giving D_3. *Molecules*. **2021**, *26*(1), 231.
(3) **Liao, M**.; Schneider, A. F.; Laengert, S. E.; Gale, C. B.; Chen, Y.; Brook, M. A. Living Synthesis of Silicone Polymers Controlled by Humidity. *Eur. Polym. J.* **2018**, *107*(7), 287–293.
(4) Zheng, S.; **Liao, M**.; Chen, Y.; Brook, M. A. Dissolving Used Rubber Tires. *Green Chem.* **2020**, *22*(1), 94–102.
(5) Liang, S.; Wong, M. Y.; Schneider, A.; **Liao, M**.; Kräuter, G.; Tchoul, M. N.; Chen, Y.; Brook, M. A. Transparent Silphenylene Elastomers from Highly Branched Monomers. *Polym. Chem.* **2021**, *12*(2), 209–215.

Accepted Manuscript

(6) **Liao, M**.; Zheng, S.; Brook, M. A. Silylating disulfides and thiols with hydrosilicones catalyzed by $B(C_6F_5)_3$. *European Journal of Organic Chemistry*.

Patents:

(1) Brook, M.; **Liao, M**.; Chen, Y.; Near Cyclic Siloxane-free Silicones,Patent, Patent number: CA3006651.
(2) Brook, M.; Zheng, S.; **Liao, M**.; Chen, Y.; Process for Cleaving Sulfur-Sulfur and Sulfur -hydrogen Bonds in Organic Compound, *Patent*, Patent number: CA2020050455.

Chapter 1: Introduction

1.1. Polysiloxanes: From a historical perspective

The origin of organosilicon compounds can be traced back to 1863. Friedel and Crafts discovered the first compound containing C-Si bonds (**Figure 1.1**). A few years beyond this, the first observation of Si-O-C bonds, synthesized by Ebelmen, was reported.[1,2] Ladenburg continued this work and recognized, upon the exposure of aqueous HI to $(C_2H_5)_2Si(OC_2H_5)_2$, a syrup-like, "silicon diethyloxide", was formed (**Figure 1.2**). Although the same product, now generally acknowledged as polysiloxane, was actually first obtained by Friedel and Crafts through the oxidation process of the tetraethylsilane product evolved from **Figure 1.1**, Ladenburg provided a more practical method for synthesis.[3,4]

$$2Zn(C_2H_5)_2 + SiCl_4 \rightarrow (C_2H_5)_4Si + 2ZnCl_2$$

Figure 1.1. The synthesis of organosilicon compound using diethyl zinc.

$$n\,(C_2H_5)_2Si(OC_2H_5)_2 + 2nHI \rightarrow [(C_2H_5)_2SiO]_n + 2n\,C_2H_5I + nH_2O$$

Figure 1.2. The synthesis of polysiloxane using HI.

Standing on the shoulders of giants, F.S. Kipping laid the foundations for the industrialization of polysiloxanes by creating alkylchlorosilanes using Grignard reagents (**Figure 1.3**).[5,6] The nomenclature "silicone" was coined by him to describe the oligosiloxanes $(R_2SiO)_n$ resulting from the controlled hydrolysis of a variety of chlorosilanes.[7]

$$2C_2H_5MgCl + SiCl_4 \rightarrow (C_2H_5)_2SiCl_2 + 2MgCl_2$$

Figure 1.3. Synthesis of organosiloxanes using Grignard reagents.

The majority of silicone research was initially carried out in industry laboratories, primarily General Electric (GE) and Dow Corning.[8] The first practical silicone product, electrically insulating "resinous polymers", was developed by J.F. Hyde in Dow Corning using phenyl-containing siloxanes heated with aqueous HCl.[9,10] Later on, inspired by Hyde, E.G. Rochow at GE and R. Müller independently discovered a so-called "direct synthesis" method for the precursors to polysiloxanes – chloromethylsilanes – at the industrial scale by reacting hydrocarbon halides with powdered elemental silicon/copper mixtures at elevated temperatures (**Figure 1.4**).[4,11,12]

The direct synthesis technology was developed during WWII and, due to the outstanding properties of organosilicones, it was widely used in military-related applications ranging from damping fluids to lubricating oils for aircrafts.[13,14] The development of the silicone chemistry was largely hampered until the end of the war because of national security. However, only few decades later, the global silicone market size had grown dramatically because of the ever-increasing demands for different types of silicone products.[15]

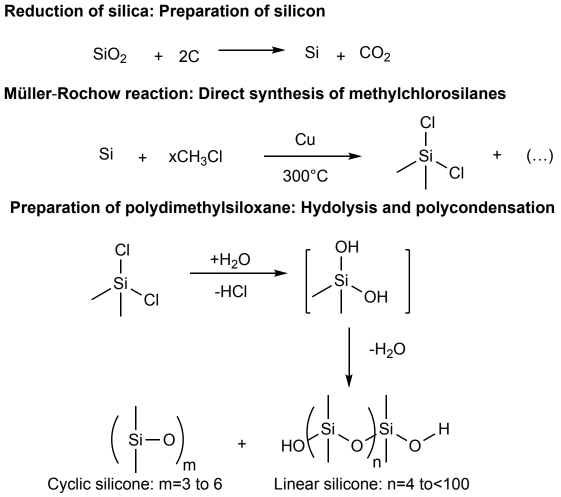


Figure 1.4. Preparation of linear silicone polymers using hydrolysis and condensation reactions of chlorosilanes.[12]

1.2. Silicones: From structures to properties

Polysiloxanes (silicones) describe a class of polymers composed of repeating siloxane bonds ($-R_2SiO-$, where R= alkyl, aryl and other functional groups) on the backbone as presented in **Figure 1.5**; most silicones are based on Me_2SiO monomers. The unique physiochemical properties of siloxane bonds account for the unusual properties of silicones when compared to their carbon-based counterparts.[16–18] For a better understanding of the tremendous differences between silicones *versus* organic polymers, it is important to differentiate the characters of (-Si-O-) and (-C-O-) bonds.

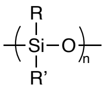


Figure 1.5. Chemical structure of the siloxane bond in silicones.

Two features profoundly affect the properties of siloxanes: electronegativity and covalent radius. The large discrepancy of electronegativity, defined as the tendency of an element to attract or hold on to electrons toward itself, between Si

(1.9) and O (3.5) atoms, in contrast to C (2.5), results in the highly ionic character (51%) of the -Si-O- bond.[19–21] The large electronegativity differences are not limited to oxygen; Si-X (X=Cl, N or even H) also facilitate the nucleophilic substitution reactions at silicon, making it vulnerable towards acid and base-catalyzed reactions.[22,23]

In comparison with carbon, silicon has a covalent radius of 1.17 Å which is 0.4 Å larger, while oxygen has a diameter of 0.66 Å. Therefore, theoretically, the bond lengths of -C-O- and -Si-O- are expected to be 1.43 and 1.83 Å, respectively. However, from the experimental studies, surprisingly, the value of -Si-O- bond length is 1.62 Å, much shorter than expected, while -C-O- bond corresponds to the theoretical value (1.43 Å).[15,16,24] The fundamental origin of the shortening of -Si-O- bond is still under debate; one on hand it is attributed to its ionic character, on the other hand, to the hyperconjugation of -Si-O- that leads to a partial double bond.[15,25]

Either hyperconjugation or ionic character could be the origin of the observed large bond angle of -Si-O- with the value of 140°, much wider than -C-O- (109.5°).[25–27] The large angle leads to very low rotational barriers on silicone polymer chains that leads to the outstanding mobility of silicones.[25,28] The torsional backbone flexibility further shields the -Si-O- bond with Me groups that provide a water repellency feature to silicones.[29] Also, due to the free volume of siloxane chains, silicones exhibit ubiquitous gas permeability, which has been extensively investigated in contact lens and membrane technologies.[30–32]

The other feature that greatly affects the behaviors of silicone polymers compared to organic polymers is the high value of bond dissociation energy, which are recorded as 460 and 345 kJ mol^{-1} for -Si-O- and -C-O-, respectively.[16,33] The high bond dissociation energy of -Si-O- contributes to the pronounced thermal stability of silicones that has permitted their application in the aerospace industry as thermal insulators.[34]

The unique chemical structure of siloxane bonds is associated with other properties that outcompete many natural or synthetic carbon-based polymers. These properties include low T_g (-120 °C, glass transition), low surface tension (21-24 mN m^{-1}), UV resistance, optical transparency (240-1100 nm), low flammability and also biocompatibility.[29,35–39] The combinations of these exceptional properties of silicones has elicited extensive interest from both academia and industry in their use in areas ranging from microfluidic sensors, coatings, sealants, antifoaming agents to implantable materials and personal care products. That is, silicones are involved in most aspects of our daily life.[39–44] In consideration of the importance of silicones, the question arises: How can we make them in a more controlled fashion?

1.3. Silicones: Traditional chemistry for preparation

The range of traditional synthetic approaches for silicones is rather limited regardless of the desired forms, e.g., linear fluids or crosslinked materials. We will detail the chemistry for making both types of materials in the following section.

1.3.1. Synthesis of polydimethylsiloxanes fluids

1.3.1.1. Polysiloxanes synthesis: Ring-chain equilibration using acid / base as catalyst

Conventionally, the preparation of valuable high molecular weight polydimethylsiloxanes involves the scission and reformation of siloxane bonds using linear low molecular weight hexamethyldisiloxane (MM) (end groups) and octamethylcyclotetrasiloxane (D_4) (the backbone) catalyzed by acid or base (**Figure 1.6**).[23] The process is completely reversible regardless of the catalyst used and the molecular weights of the obtained polymers are manipulated by the amounts of D_4 and the end-capping M units present (General Electric silicone nomenclature: M = Me_3Si, D = $Me_2SiO_{2/2}$, T = $MeSiO_{3/2}$ and Q = $SiO_{4/2}$).[35,45,46] Moreover, simply replacing one or more of the methyl groups on silicon atom in MM or D_4 with versatile functional groups including SiH, vinyl, etc., leads to functional terminal or pendent polysiloxanes.[24,47]

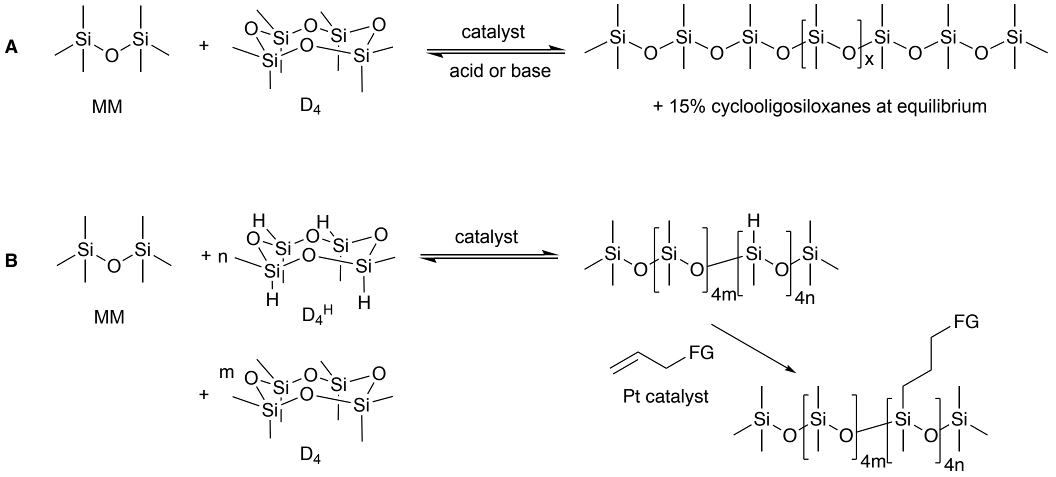


Figure 1.6. (A). Preparation of linear silicone polymers using ring-chain equilibration; (B). Preparation of functionalized linear silicone polymers using ring-chain equilibration.[24]

One of the consequences associated with the equilibration process is the difficulty to control and maintaining the molecular weight (MW) of silicones. As shown in **Figure 1.7**, under acidic conditions it is hard to build the molecular weight while under basic conditions the molecular weight increases dramatically at the beginning of the reaction but, once a certain MW is reached, rapidly decreases to form the same equilibrium MW polymer as the acid reactions.[23] Also problematic, the dispersity ($Đ_M$) of the polymer products is high and the product typically contains, at equilibrium, around 15% cyclooligosiloxanes.[48]

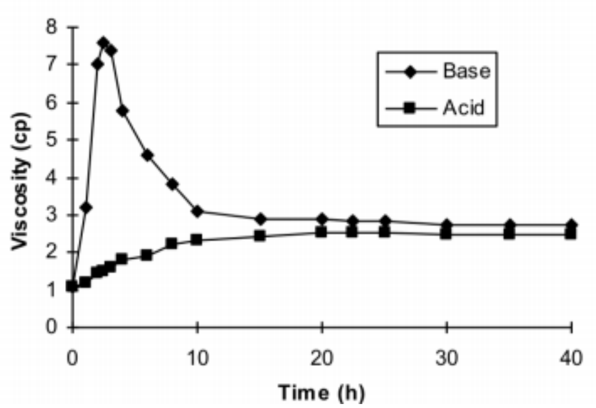


Figure 1.7. Plot of viscosity against time for the polymerization of linear silicone fluids using acid- or base- catalyzed D_4 + MM.[23]

1.3.1.2. Polysiloxanes synthesis: Anionic/cationic ring-opening polymerization

Another widely used method for preparing polysiloxanes is anionic polymerization using hexamethylcyclotrisiloxane (D_3), which provides polysiloxanes with narrow dispersity.[49,50] Due to the larger ring strain of D_3 (50-63 kJ mol^{-1}), compared with essentially zero ring strain for D_4, anionic ring-opening polymerization is efficient, typically with butyl lithium as initiator **Figure 1.8**.[24] Cyclotrisiloxanes bearing functionality (e.g., vinyl ~$CH=CH_2$, D_3^{Vi} = $(OSiMeVi)_3$) may be utilized in order to yield functionalized polysiloxanes with defined branching.[51] Moreover, the introduction of different lithium initiators (for instance, trimethylsilylmethyl lithium and R_2NLi) allows one to tune the functionality of the end-groups.[52,53] Although the obtained polysiloxanes exhibit narrow molecular weight distributions, undesired side reactions including termination, chain transfer, and backbiting can take place if the starting materials are not rigorously dried and purified.[54,55]

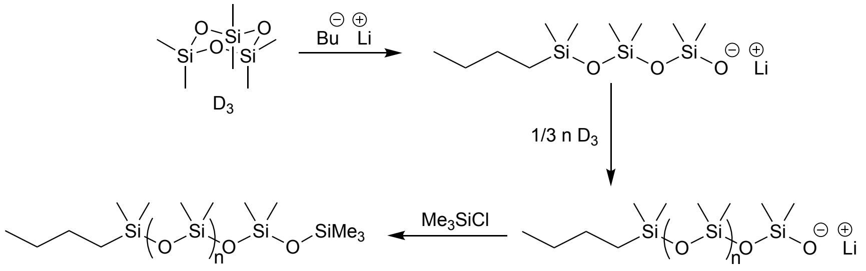


Figure 1.8. Preparation of linear silicone polymers using anionic ring-opening polymerization.

It should be noted that polysiloxanes bearing functional groups that are sensitive towards nucleophiles, such as SiH, can be compromised during anionic polymerization (either kinetic or equilibration), and accompanied by the formation of undesired crosslinks and/or rapid dehydrogenation.[56] Cationic polymerization is regarded as an alternative synthetic route for these functional groups, for example, methylhydrosiloxanes that serve as common starting materials for commercial, functionalized silicones (for example, amines and epoxides, that are made by hydrosilylation of SiH polymers).[57–59]

1.3.2. Syntheses of crosslinked silicone materials

While silicone oils have many uses, silicone polymers are often desired in solid formats, including as elastomers and resins. To achieve these, versatile cross-linking chemistries were developed that can be roughly classified in three categories: high temperature vulcanization (HTV), room temperature vulcanization (RTV) and hydrosilylation, typically using platinum catalysts.

1.3.2.1. High temperature vulcanization (HTV)

The stoichiometric reaction of benzoyl peroxide with polydimethylsiloxane under high temperature was discovered to form crosslinked silicones as early as the 1940s (**Figure 1.9**).[60] Under high temperature, benzoyl peroxide undergoes thermal decomposition to form peroxide radicals that further abstract hydrogen atoms from the methyl silicones to give $SiCH_2$• radicals. Subsequently, bimolecular coupling reactions occur between two $SiCH_2$• radicals to build up the carbon-carbon bridge ($SiCH_2$-CH_2Si), leading to crosslink sites.[61] However, since all methyl groups can potentially be crosslink sites under these vigorous reaction conditions, both network structure and total crosslink density are difficult to control. Better control over the location of crosslinks and less vigorous reaction conditions are required when some of the methyl groups along the silicone backbone are replaced by vinyl groups, preferentially 0.03-2wt%, to provide crosslinked silicones with tunable crosslinking density and therefore mechanical properties (for example, elongation).[62,63] Yet, drawbacks of the method are remain: 1) the acidic byproducts generated from the peroxide initiators can facilitate the degradation of silicones;[64] and 2) the formed crosslinked silicone network is a random structure with plenty of dangling chains present.[65]

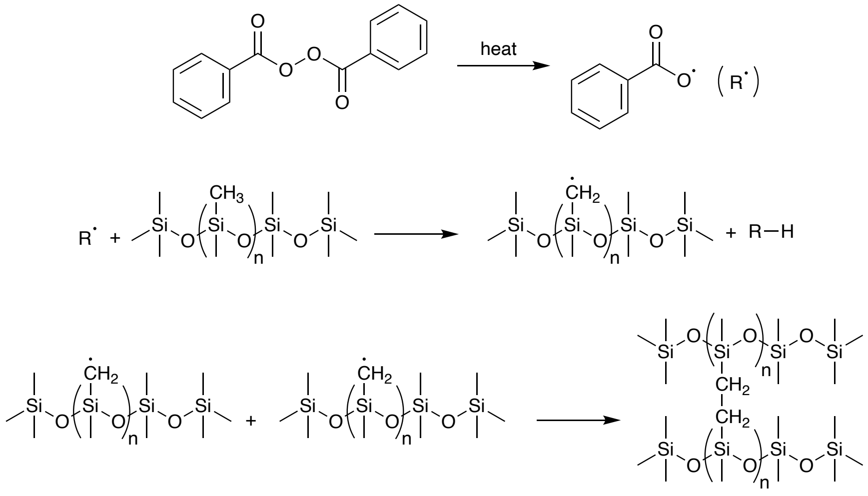


Figure 1.9. Mechanism of high temperature vulcanization using benzoyl peroxide with polydimethylsiloxanes.

1.3.2.2. Room temperature vulcanization (RTV)

Room temperature vulcanization (RTV), also referred as condensation or moisture cure, usually involves reactions between hydroxyl end-blocked polydimethylsiloxanes and small tri- or tetrafunctionalsilanes as crosslinkers, catalyzed by tin- or titanium-derived catalysts, for instance, octoate and di-*n*-butyltin dilaurate (DBTL) as illustrated in **Figure 1.10**.[66] Tin-catalyzed RTV has been widely applied to adhesives and sealant manufacturing because of its economic viability and user friendliness, however, the repugnant odor from of the tin, including byproducts, together with the toxicity of organotin catalyst limits its use in food and biomaterial industries.[42,67] Titanium catalysts avoid some of these issues, but they suffer from incompatibility with the silane-based adhesive promoters (aminosilanes) and, by comparison with their relatively unsatisfactory catalytic activity.

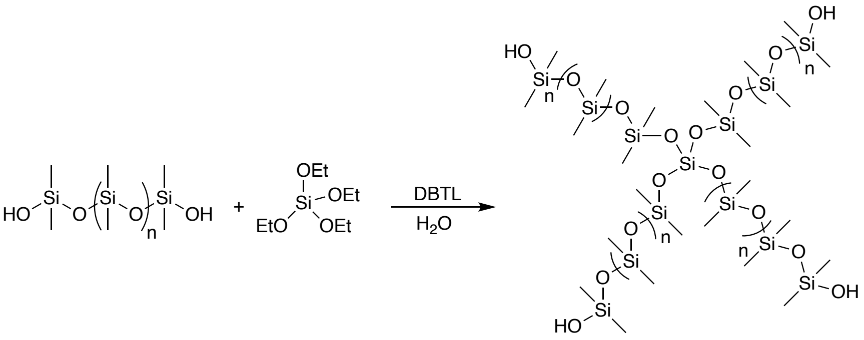


Figure 1.10. Typical RTV using hydroxy-terminated PDMS and tetraethoxysilane with DBTL as catalyst.

1.3.2.3. Hydrosilylation

Hydrosilylation has become the 'go to' method for silicone elastomer synthesis. It involves the addition reaction of hydrosilanes to unsaturated multiple bonds (usually C=C double bond) to give a silicon carbon bond (Si-C), as illustrated in **Figure 1.11**.

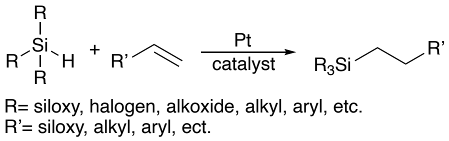


Figure 1.11. Hydrosilylation between hydrosilane and C=C double bonds using a platinum catalyst.[68]

The utility of first widely used platinum catalyst in the silicone industry, Speier's catalyst, was demonstrated in the late 1950s and became renowned for its effectiveness as a homogenous platinum-based catalyst.[69] It is comprised of chloroplatinic acid hexahydrate in isopropanol (**Figure 1.12A**), however, even with acceptable catalytic activity, it suffers from a long induction period.[70] Thus, in 1973, the platinum complex (platinum divinyltetramethyl-disiloxane complex, **Figure 1.12 (B)**) with high solubility in silicones together with pronounced catalytic activity and selectivity towards the addition reaction, was developed for silicone cure; it is referred to as "Karstedt's" catalyst.[71,72] The above-mentioned catalysts are extensively used for the preparation of silicone elastomers, resins, silsesquioxane cage and silicones bearing different functionalities.[73–75] The drawback of the platinum-catalyzed hydrosilylation process is the residual platinum complex is trapped in silicone elastomers after curing, leading to the yellowing of the silicone materials which limits their usage in LED applications.[76,77] The platinum catalyst is also expensive.

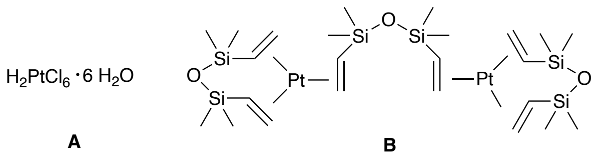


Figure 1.12. Platinum-based catalyst for hydrosilylation; A: Speier's catalyst; B: Karstedt's catalyst.[70,71]

1.4. Research frontiers for organosilicon – Develop methods to permit structural control and introduction of functional groups

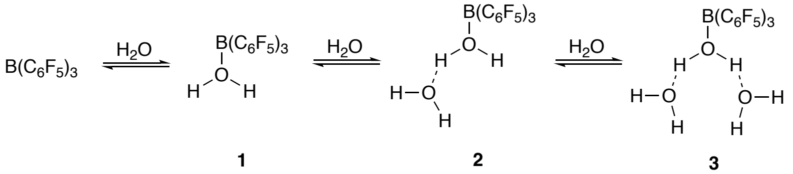
The susceptibility of siloxane bonds to acids and bases, allowing equilibration to form small cyclic molecules from silicone polymers (the reverse of polymerization, **Figure 1.6**) can be problematic. The presence of any such catalysts can restart equilibration, leading to side reactions including metathesis/redistribution of the siloxane bonds compromising the integrity of the evolving silicone materials. In an effort to seize more control over silicone structures, and to avoid degradation, attention has turned to other methods for silicone synthesis. An important new strategy to create silicones is the Piers-Rubinsztajn reaction. The key features of the Piers-Rubinsztajn reaction involve the combination of a weak SiH bond (330-380 kJ mol^{-1}) together with a powerful metal-free, Lewis acidic catalyst $B(C_6F_5)_3$.[78] These compounds, in combination with a selection of readily reduced functional groups, permit the introduction of organofunctionalities into silicones. Of particular relevance, even though $B(C_6F_5)_3$ is a strong Lewis acid catalyst, it is relatively ineffective at catalyzing silicone equilibration.

1.4.1. Hydrosilane (SiH)- A synthetic handle

Due to the relatively large difference of the electronegativity between Si (1.9) *versus* H (2.2), hydrosilanes are polarized and therefore, reactive towards nucleophilic substitutions at silicon atom that subsequently lead to hydride transfer,[78] unlike hydrocarbons that more typically undergo proton transfer. Exploiting the nature of the Si-H bond, hydrosilanes have been well-utilized as reducing agents for many different organic functional groups and, in comparison with the commonly used reductants such as lithium aluminum hydride, can be more selective reducing agents and also ones that operate under milder conditions.[79,80] Additionally, the activation of SiH bonds by transition-metal catalysts including Ru, Pd, and Ni expands the role of silicon hydrides in the modern synthetic chemistry.[81,82] Silanes are also susceptible to radical reactions. In terms of the bond energy difference, Si-H exhibits a lower bond energy than C-H (414 kJ mol^{-1}), which favors the abstraction of hydrogen atom from silicon in the presence of carbon-centered radicals. This provides another strategy for materials preparation, organic synthesis and silicon chemistry.[83] In summary, compounds containing SiH groups are important precursors from a synthetic point of view, as they are activated by base, transition metals and radicals.

1.4.2. $B(C_6F_5)_3$- A strong Lewis acid catalyst

Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) is a metal-free, hydrophobic and thermally stable (up to 270 °C) compound that is renowned for its effectiveness as a co-initiator for industrial olefin polymerization; it was first synthesized by *Massey et al.* in 1966.[84–86] Traditional Lewis acid catalysts, for instance BF_3 and $AlCl_3$, readily undergo decomposition upon contact with water leading to protic acid byproducts that are harmful to the integrity of silicone materials. By contrast, $B(C_6F_5)_3$ is relatively water stable.[78,87] However, $B(C_6F_5)_3$ is highly hygroscopic and forms a variety of adducts with water in a stepwise manner up to $B(C_6F_5)_3 \cdot 3H_2O$ as shown in **Figure 1.13** (**1**→**3**).[88] Interestingly, adduct **2** is viewed as a very strong Brønsted acid with a pK_a of 8.4 in acetonitrile, similar to the acidity of HCl.[78]



1 **2** **3**

Figure 1.13. Adducts formation using titration of $B(C_6F_5)_3$ with water.[88]

1.4.3. The Piers-Rubinsztajn reaction

$B(C_6F_5)_3$ has been combined with hydrosilanes in many contexts. Piers initially demonstrated that reactions involving the combination of hydrosilane and $B(C_6F_5)_3$ can be classified into two major categories: hydrosilylations; and condensation reactions.[89] The hydrosilylation refers to the reduction of multiple bonds (C=Y, Y=C, O and S etc.) by hydrosilane in the presence of $B(C_6F_5)_3$ as shown in **Figure 1.14.**[90–92]

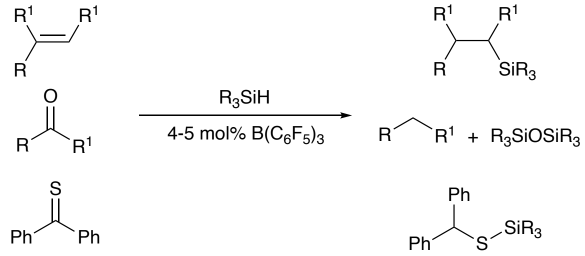


Figure 1.14. Hydrosilylation reactions using hydrosilane and $B(C_6F_5)_3$

Piers also examined the catalytic mechanism of hydrosilylation under these conditions.[93] Typical Lewis acid/base chemistry would suggest nucleophilic addition to the C=O is facilitated by complexation of the carbonyl complex **4**

(**Figure 1.15**). However, a series of experiments established that the increase of carbonyl concentration leads to the decrease of hydrosilylation rate suggesting that the evolving adduct **4** inhibits the hydrosilylation reaction. Based on the observations, the mechanism is proposed to involve the activation of Si-H bond by $B(C_6F_5)_3$ to give boron-hydrosilane complex (**Figure 1.15**, **5**), followed by nucleophilic attack at silicon by C=Y (Y=O in **Figure 1.15**) leading to adducts **6** and **7** (**Figure 1.15**). Hydride-transfer then occurs from silicon to boron atom to afford zwitterionic oxonium ion **8** (**Figure 1.15**) that eventually undergoes displacement of hydride from borohydride to yield silyl ether *via* inversion (favored) or retention.[94,95]

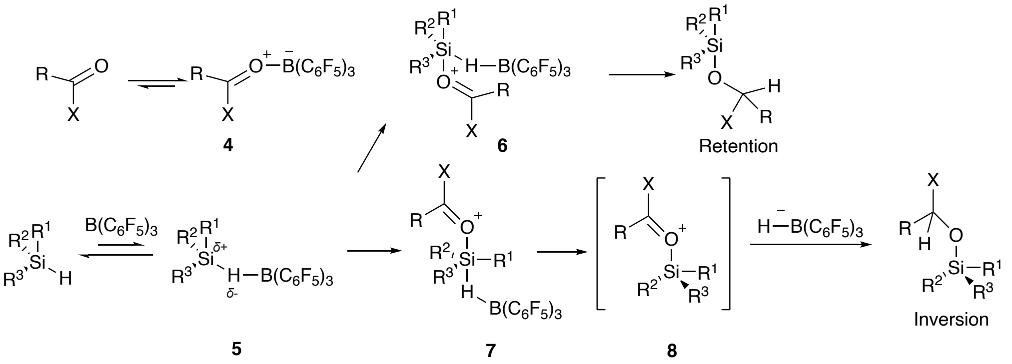


Figure 1.15. Proposed catalytic mechanism of hydrosilylation for C=O using $B(C_6F_5)_3$[94]

In addition to hydrosilylation, a plethora of studies have focused on condensation reactions of hydrosilanes with various functional groups (**Figure 1.16**) including heteroatom-containing S-H and C-S bonds. These provide a way to introduce more functionalities into silicone.[78,96–98]

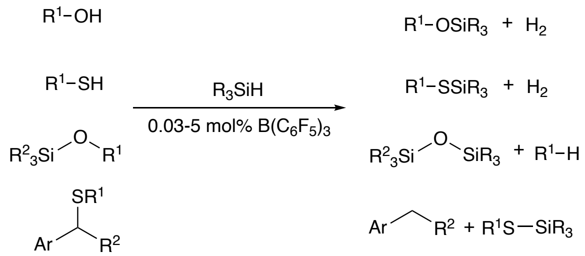


Figure 1.16. Condensation reactions using hydrosilane and $B(C_6F_5)_3$

An important condensation reaction catalyzed by $B(C_6F_5)_3$ occurs between alkoxysilanes and hydrosilanes, namely, the Piers-Rubinsztajn (PR) reaction. The PR mechanism is similarly thought to involve the complexion of hydrosilane with $B(C_6F_5)_3$. Such a complex facilitates the nucleophilic attack on silicon by an oxygen atom in the alkoxysilane to form oxonium ions that further undergo hydride-transfer to complete the catalytic cycle with concomitant formation of siloxane bond and production of an alkane gas and release of free $B(C_6F_5)_3$.[78]

The PR reaction proceeds under mild conditions – room temperature – with low levels of $B(C_6F_5)_3$ catalyst. Surprisingly, hygroscopic $B(C_6F_5)_3$ catalyst remains active for PR not only in organic solvents such as hexanes and toluene, but also in aqueous emulsions.[99] Thus, PR reaction provides new opportunities to control the structure of silicones, including the introduction of more functionalities.

1.4.4. Other nucleophiles and relative reactivities

Our group has previously examined the relative reactivities of various functional groups under PR conditions. For example, in lignin in the presence of hydrosilane and $B(C_6F_5)_3$ the reactivity order of functional groups follows: phenol > primary alcohol > methoxy > silyl ether.[100] In addition, Kazuhiro and co-workers initially described a simple and versatile synthesis of sequence-controlled oligosiloxanes using a series of reagents bearing two functional groups including carbonyl and alkoxy with hydrosilane and $B(C_6F_5)_3$ in a one-pot manner providing new platform for the preparation of controlled functionalized silicones.[101]

Most of the reactions using hydrosilane and $B(C_6F_5)_3$ mentioned above are carried under inert blankets (for example, under nitrogen) to prevent the interference of water. Surprisingly, we found that with the introduction of water, the unexpected formation of high molecular weight linear polysiloxanes in the presence of hydrosilanes and $B(C_6F_5)_3$ catalyst was observed, and that demands a thorough probe to unearth the underlying mechanism of how water is involved. As discussed above, water can participate in reactions, as $B(C_6F_5)_3$ scavengers through a series of complexations (**Figure 1.13**). If these complexation processes are favored, the free $B(C_6F_5)_3$ will be deactivated upon exposure to water, immediately terminating the reaction. However, as is discussed in Chapter **2** and Chapter **3**, we observed instant and vigorous bubble formation from hydrosilanes and $B(C_6F_5)_3$ catalyst when exposed to water, implying that the water serves as the nucleophile instead of the quenching agent in this reaction. Thus, for Chapter **2** and Chapter **3** of this thesis, we will focus on elucidating the mechanism of this reaction together with exploring its synthetic applications.

1.4.5. The metathesis of hydrosilanes with itself

It must be noted that there can be issues associated with hydrosilanes in the presence of $B(C_6F_5)_3$. The hydrosilane, and HSi-containing silicones, can undergo metathesis in the presence of $B(C_6F_5)_3$. Chojnowski and Rubinsztajn first described the mechanism of $B(C_6F_5)_3$-catalyzed hydrosilane metathesis using small silicone moieties such as tetramethyldisiloxane (M^HM^H) under Schlenk line conditions. The dismutation of hydrosilane takes place when treated with $B(C_6F_5)_3$ (**Figure 1.17**,

9→10) to afford a series of linear oligomers, in addition of cyclics (D_3 and D_4) and the distinct product H_2SiMe_2.[102]

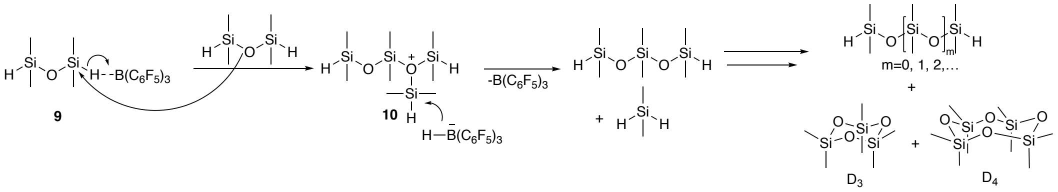


Figure 1.17. Mechanism of metathesis using hydrosilane and $B(C_6F_5)_3$

Even though the cleavage of siloxane bonds does not often occur in the presence of free $B(C_6F_5)_3$ catalyst, Chojnowski and Rubinsztajn further reported that various hydrosilanes with $B(C_6F_5)_3$ could initiate ring-opening metathesis with the strained cyclic monomer D_3. The generated oxonium-borohydride ion pair (**Figure 1.18**, **11**) was proposed to decompose in two ways: ring-opening reaction of D_3 (**Figure 1.18**, **a**) followed by hydride transfer back to the starting material M^HM^H (**Figure 1.18**, **b**). They also mapped out the relative reactivity of different hydrosilanes as followed: $PhMeSiH_2 > M^HM^H > PhMe_2SiH > M^HM^H$.[103]

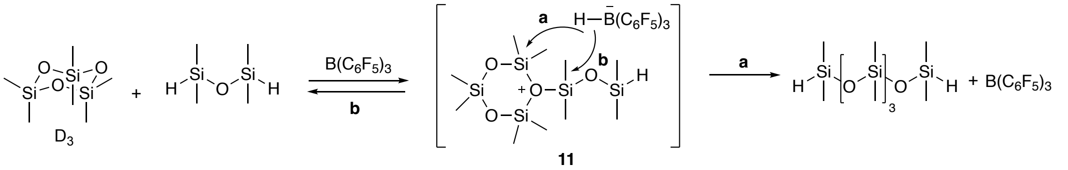


Figure 1.18. Mechanism of ring-opening metathesis of M^HM^H and D_4

Nishiura and co-workers investigated the cross-metathesis of Si-C and Si-H catalyzed by $B(C_6F_5)_3$ with electron-rich aryl groups, for example, $Me_2NC_6H_4$, at 100 °C (**Figure 1.19**).[104]

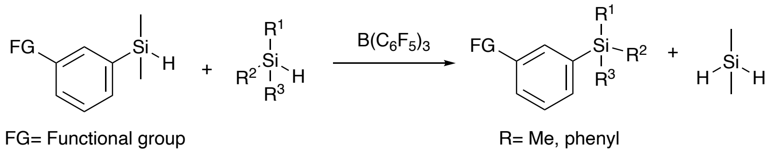


Figure 1.19. Cross-metathesis of Si-C and Si-H bond.[104]

1.4.6. Preparation of structured silicone copolymers *via* PR reaction

The PR reaction has been shown to be a rapid, efficient and powerful route to controlled silicone products with functionalities under mild conditions. In 2014, Skov and co-workers were able to first synthesize a variety of functionalized silicone copolymers (for example, vinyl- and chloro-) with spatial control of the functional groups using the PR reaction, a new facile and tunable strategy for the preparation of functionalized silicone copolymers (**Figure 1.20**).[105] In addition, Xu and co-workers discovered structured silicone copolymer containing novel Si-O-Si-N bonds could be accessed using the PR reaction, providing an alternative method to siloxazanes (**Figure 1.21**).[106]

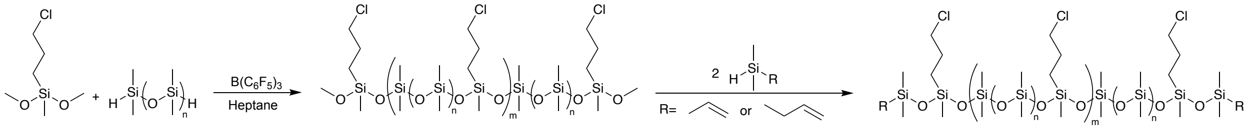


Figure 1.20. Chloride pendent and telechelic vinyl/allyl siloxane copolymers *via* a PR reaction.[105]

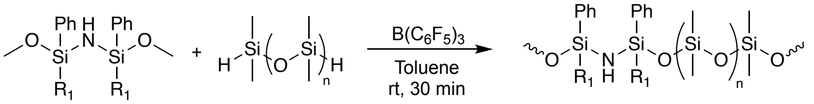


Figure 1.21. Polymerization of methoxydisilazane and oligosiloxane *via* PR reaction.[106]

1.4.7. Preparation of branched silicones *via* PR reaction and then platinum-catalyzed hydrosilylation

Our group established a facile route to precise, defect-free dendrons with molecular weights up to 5,000 g mol^{-1} using an iterative approach involving the PR reaction and platinum-catalyzed hydrosilylation.[107] We further advanced this methodology to allow the preparation of highly branched silicones with tunable molecular weight and branching frequency. However, full conversion of the SiH groups was unattainable due, we infer, to the steric hinderance originating from random branched clusters; only a maximum of ~60% of SiH conversion was obtained from an HSi-homo polymer.[108] If we altered the pendant functional group units in a spatially controlled manner, can we resolve this challenge? Examining this question is the objective of Chapter **4** in this thesis.

1.5. Research frontiers for organosilicon- Exploration into sulfur

1.5.1. Thiol-functionalized silicones

Compared to vinyl or SiH functional silicone polymers, there is far less work done with other organofunctional polymers. Organosulfur compounds have a long and storied history, but not in silicones. The availability of thiol functional groups into silicone materials has encouraged researchers to exploit new applications of sulfur chemistry. One of the most widely used reactions by organic chemists in sulfur chemistry is the thiol-ene reaction, which refers to the radical reaction between S-H with unsaturated C=C bond initiated by photo- or thermally-generated radicals as demonstrated in **Figure 1.22**.[109] The thiol-ene reaction exhibits high efficiency, less sensitivity towards oxygen and tolerance for a wide range of functional groups under mild condition.[110]

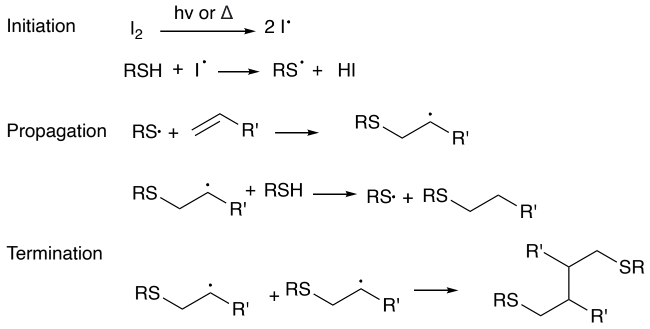


Figure 1.22. The mechanism for photo- or thermally- initiated thiol-ene reaction.[109]

Given the versatilities of thiol-ene reaction, Bowman and co-workers extended this reaction into silicone polymers by using thiol- and vinyl-containing polysiloxanes for the synthesis of dental materials, taking advantage of the biocompatibility, elasticity, reliability and hydrophobicity natures of silicones.[111] We further tested the potential of thiol-ene reaction in the application of 3D printing and showed that it was straightforward to tune the tunable mechanical properties of the elastomers by adjusting either thiol and vinyl concentrations in the linear silicone starting materials.[112] However, little is known about sulfur based silicones, with the exception of sulfonate-modified silicones that are sold as surfactants (Siltech Corp.).

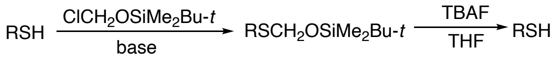
1.5.2. Organosilicon in organic synthesis

Silyl ethers are widely used as protecting groups in organic synthesis particularly for alcohols (shown in **Figure 1.23**) due to their stability to many reaction conditions, the ease with which Si-O bonds can be formed, and the selective manner in which they can be selectively cleaved to release the parent alcohol.[113]

$$\mathrm{ROH} \xrightarrow[\mathrm{NEt_3}]{\mathrm{ClSiMe_3}} \mathrm{ROSiMe_3} \xrightarrow[\mathrm{THF}]{\mathrm{TBAF}} \mathrm{ROH}$$

Figure 1.23. Silyl ether as protection group for alcohol with TBAF as deprotecting group.[113]

Clive and co-workers extended the scope of organosilicon protecting groups for thiols under mild conditions, as demonstrated in **Figure 1.24**. These SiS compounds successfully survive exposure to hydride reducing agents (for example, $NaBH_4$ and $LiAlH_4$) H_2, Pd/C and piperidine.[114]



$$\mathrm{RSH} \xrightarrow[\mathrm{base}]{\mathrm{ClCH_2OSiMe_2Bu}\text{-}t} \mathrm{RSCH_2OSiMe_2Bu}\text{-}t \xrightarrow[\mathrm{THF}]{\mathrm{TBAF}} \mathrm{RSH}$$

Figure 1.24. [[(*tert*-Butyl)dimethylsilyl]oxy]-methyl for thiol protection.[114]

The above-mentioned routes to the protection of functional groups are impractical for silicone materials, since bases are often required in the protection process. These bases can also potentially threaten the integrity of siloxane bonds. Therefore, considering the importance and versatility of the thiol-containing silicones as we discussed, a mild, efficient, and reliable strategy needed to be developed to protect thiol without the loss of silicone structural integrity. This serves as one of the objectives in Chapter **5**.

1.5.3. Organosilicon in vulcanized rubber synthesis

As noted above, hydrosilanes are potent reducing agents in the presence of $B(C_6F_5)_3$. Surprisingly, my colleague Dr. Sijia Zheng and I discovered that the disulfide bond can be easily reduced by hydrosilanes in the presence of $B(C_6F_5)_3$ catalyst to give S-Si and S-H compounds; if sufficient hydrosilanes are present, S-H groups will also further react with SiH to eventually form S-Si compounds as the only sulfur-containing product.[97] We implemented this new chemistry to recycle used automobile rubber tires under mild conditions with good yield, and then oxidized the recovered polymeric oil to reform new elastomers (**Figure 1.25**).[115]

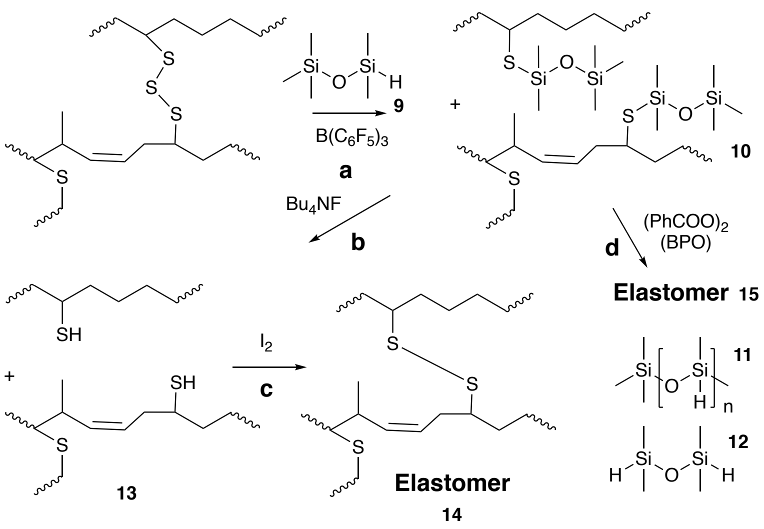


Figure 1.25. The full cycle of rubber to recovered polymeric oil and again rubber; (a) Reductive silylation; (b) Cleavage of SiS bonds; (c) Oxidative coupling produces elastomers crosslinked by disulfides; (d) Radicals form elastomers from alkene-containing oils. Steps e and f can optionally use recovered inorganic constituents as reinforcing agents in the elastomers.[115]

Rubber tires are produced *via* vulcanization with elemental sulfur of alkene-containing hydrocarbon polymers to give strong S-S bonds as crosslinks.[116] The process greatly improves the mechanical properties of natural rubbers including greater tensile strength and lower hysteresis;[117] yet further improvements in modulus arise from the use of reinforcing fillers such as carbon black.[118] Greener tires arise additionally from the use of silica an alternative or complementary filler that improves tear strength, resistance towards aging, and abrasion while delivering lower rolling resistance.[119,120] Silica on its own is not a very effective reinforcing filler. Therefore, the hydrophilic silanol groups on the silica particles are modified, typically with sulfur-containing coupling agents such as bis[3-

(triethoxysilyl)propyl] tetrasulfide (TESPT) and bis[3-(triethoxysilyl)propyl] disulfide (TESPD) (**Figure 1.26**). These dual-functional silanes use ethoxysilyl groups to modify the silica surface through condensation reactions, and oligosulfides to facilitate interaction with sulfur moieties.[121,122]

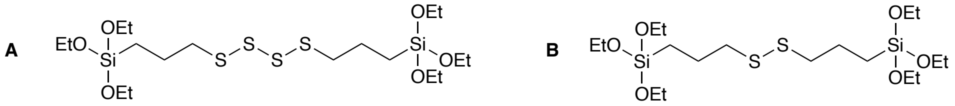


Figure 1.26. Structure of bis[3-(triethoxysilyl)propyl] tetrasulfide (**A**); Structure of bis[3-(triethoxysilyl)propyl] disulfide (**B**).

The commercial coupling agents shown in **Figure 1.26** bear two functional groups, disulfides and ethoxy groups, both of which undergo reactions with hydrosilanes catalyzed by $B(C_6F_5)_3$. Considering the exploration of PR reactions into the precise synthesis of silicones containing hetero-atoms, the relative reactivities of different nucleophilic functional groups in the exposure of hydrosilanes needed to be mapped out.[78] Such a study is the focus of Chapter **5**.

1.6. Thesis objectives

The overall objective of this research is focused on the exploitation of the scope of hydrosilane and $B(C_6F_5)_3$ catalyst to introduce novel routes to a series of silicone materials and rationalize the mechanism for those reactions.

1.6.1. New route to silicone materials using hydrosilane and water in the presence of $B(C_6F_5)_3$ catalyst

As mentioned above, polysiloxanes are greatly desired because of their interesting and unusual properties. However, there are still many limits to their controlled synthesis. Traditional routes are compromised by: 1) products with high concentrations of residual monomer are found in linear silicone polymers produced by acid or base-catalyzed equilibration; 2) residual acids or bases as catalysts may deteriorate the integrity of silicone structure; 3) anionic polymerization using lithium initiators suffers from side reactions such as backbiting if the materials are not scrupulously dried.[48,54,55] There are analogous drawbacks in synthesis of crosslinked silicone materials, including: 1) any generated acidic byproducts facilitating the degradation of silicones; 2) the random structure of the obtained silicone elastomers has plentiful dangling chains; 3) possible toxicity of cure catalysts; 4) moderate catalytic activity; and, 5) in the case of platinum cure, a yellowing effect.[64,65,76,77] Thus, there remains a need for alternative routes to silicone materials. This first focus of this thesis is about our attempts to address some of these needs.

In Chapter **2**, we present a facile, novel, efficient and promising alternative for the preparation of high molecular weight linear polysiloxanes with using relatively inexpensive tetramethyldisiloxane (M^HM^H) and water in the presence of $B(C_6F_5)_3$. This process overcomes the difficulties of building up the molecular weight we encountered using base-catalyzed equilibrium. Moreover, in consideration of the large quantities of undesired D_4 formed *via* acid catalyzed equilibrium, we performed careful studies to examine ways to mitigate the efficiency of cyclic monomer production (D_3, D_4 and D_5) as followed using ^{29}Si NMR. Surprisingly, with the assistance of solvent, equally expensive ring-strained D_3 was preferentially formed when compared to D_4 (<3%) together with the formation of desirable high molecular weight PDMS.[123] In addition, the exposure of moisture does not contaminate the starting materials which, as mentioned, is problematic in anionic polymerization. Instead, water is used as a reagent for chain extension here.

In Chapter **3**, we further extended this new, efficient chemistry using hydrosilanes and water with catalytic amounts of water to the preparation of a broad range of appropriately functional (telechelic SiOH, SiH) silicones including dimethyl- or methylphenylsilicones to give silicone block (co)polymers with different functionalities and the ability to tune molecular weight (~2000 - 183,000 g mol^{-1}). Mismatched stoichiometries leading to low MW materials were readily overcome simply by adding additional HSi polymer (or more rarely, more water). Water could be provided as bulk water, in toluene, or from humidity in the air. Model compound studies of pentamethyldisiloxane (MM^H) or bistrimethylsiloxymethylsilane (MD^HM) were conducted to prove that water is a reagent in the process, rather than an undesired contaminant that can quench the $B(C_6F_5)_3$ catalyst, as has been observed in some related reactions. Alternating block copolymers could be analogously produced using the same catalyst by combining HO-terminated silicones with HSi-terminated silicones in the absence of water. Silicone materials including elastomers, foams and resins could also be prepared using this process. The PR reaction provides a mild and flexible route to simple or alternating block silicone polymers using readily available commercial starting materials without the formation of acidic by-products that potentially destroy the integrity of silicone structure; no yellowing effect was observed.

1.6.2. Spatially controlled silicones

The second focus of this thesis is to develop a suite of linear silicones with vinyl functional groups spatially distributed along the backbones to serve as starting materials for hyperbranched polysiloxane synthesis. Here, we have resolved the steric problem often encountered by hyperbranched polymers as a result of random distribution of the pendant functional units which prevents further dendritic modification.

In Chapter **4**, we prepared a wide range of structurally controlled vinyl-pendant linear silicones with different chain spacing using the PR reaction that successfully achieved full conversion of the pendant vinyl functional groups with the introduction of triethoxysilyl branching. Based on the obtained spatially controlled branched polymers, it was possible to increase the branching degree.

1.6.3. Silylation and desilylation of sulfur compounds

The third focus of this thesis is to incorporate sulfur chemistry into silicones. We discovered that hydrosilanes combined with $B(C_6F_5)_3$ can be used to reduce the disulfide bonds that are the crosslinking sites for rubber tires in automobile industry. We started by implementing this reaction in recycling used rubber tires as a primary application and surprisingly, observed tunable stability of the resulting S-Si (conventionally, S-TMS bond is regarded as incredibly unstable group to hydrolysis) with various silicone substrates. This provides a new route to protect thiols without the use of base catalysts that could be expected to cleave siloxane bonds. Moreover, it was possible to map out the relative reactivities of different functional groups to permit the precise synthesis of silicones containing sulfur atom.

In Chapter **5**, we report a new method to cleave disulfide bonds using hydrosilane with $B(C_6F_5)_3$ catalyst that enlarge the scope of using hydrosilane as reducing agent.[115] A series of model compound studies, including with benzyl disulfide and tetrasulfide, were conducted to illustrate the mechanism of disulfide bond cleavage leading to silyl thioethers in up to 90% yield with <1 mol% $B(C_6F_5)_3$ catalyst. When exposed to catalytic amount of $B(C_6F_5)_3$ (0.8 mol%), relative reactivities of hydrosilane with different functional groups including thiols (SH), disulfides (SS) and ethoxysilanes (SiOEt) were also mapped out. The relative reactivity of commercially available disulfide coupling agents with bis(trimethylsiloxy)methylsilane (MD^HM) was shown to be S-H>S-S>SiOEt. We further advanced this methodology into thiol protection and examined a series of organic thiols and disulfide compounds as well as different hydrosilane compounds. With various silyl thioethers prepared, we then investigated several methods for deprotection including alcohol, H_2O and TBAF. Unexpectedly, the usage TBAF leads to the formation of disulfide compound, and the stability of silyl thioethers under those deprotecting conditions is determined by the substituent adjacent to sulfur together with the bulkiness of the silane source. This mild process constitutes a facile route to reutilize the organic polymers found in automobile and other sulfur-crosslinked rubbers and also to generate silicone precursors that contain the synthetically useful SH group.[115,124] Although not a chapter in the thesis, expansion of this technology to the decrosslinking of rubber tires was published in *Green Chemistry* (DOI: 10.1039/C9GC03545A).

1.7. References

(1) Müller, R.; Rochow, E. G. One Hundred Years of Organosilicon Chemistry. *J. Chem. Educ.* **1965**, *42* (1), 41–47.

(2) Friedel, C.; Crafts, J. M. Ueber Einige Neue Organische Verbindungen Des Siliciums Und Über Das Atomgewicht Dieses Elements. *J. für Prakt. Chemie* **1864**, *91* (1), 371–374.

(3) Ladenburg, A. Ueber Die Reductionsproducte Des Kieselsäureäthers Und Deren Derivate. *Justus Liebigs Ann. Chem.* **1872**, *164* (2), 300–332.

(4) Seyferth, D. Dimethyldichlorosilane and the Direct Synthesis of Methylchlorosilanes. The Key to the Silicones Industry †. *Organometallics* **2001**, *20* (24), 4978–4992.

(5) Thomas, N. R. Frederic Stanley Kipping—Pioneer in Silicon Chemistry: His Life & Legacy. *Silicon* **2010**, *2* (4), 187–193.

(6) Kipping, F. S. Organic Derivative of Silicon. Preparation of Alkylsilicon Chlorides. In *Proc. Chem. Soc*; 1904; Vol. 20, p 15.

(7) Martin, G.; Kipping, F. S. XXXVIII.—Benzyl and Ethyl Derivatives of Silicon Tetrachloride. *J. Chem. Soc. Trans.* **1909**, *95*, 302–314.

(8) Warrick, E. L. *Forty Years of Firsts: The Recollections of a Dow Corning Pioneer*; McGraw-Hill Companies, 1990.

(9) Hyde, J. F.; DeLong, R. C. Condensation Products of the Organo-Silane Diols. *J. Am. Chem. Soc.* **1941**, *63* (5), 1194–1196.

(10) Mar, P.; Hyde, J. F. Organo-Silicon Polymers and Method of Making Them. Google Patents March 6, 1945.

(11) Rochow, E. G. The Direct Synthesis of Organosilicon Compounds. *J. Am. Chem. Soc.* **1945**, *67* (6), 963–965.

(12) Wang, D.; Klein, J.; Mejía, E. Catalytic Systems for the Cross-Linking of Organosilicon Polymers. *Chem. - An Asian J.* **2017**, *12* (11), 1180–1197.

(13) Currie, C. C. Silicone Fluids. *Wear* **1972**, *19* (3), 357–358.

(14) Huber, P.; Kaiser, W. Silicone Fluids: Synthesis, Properties and Applications. *J. Synth. Lubr.* **1986**, *3* (2), 105–120.

(15) Pouget, E.; Tonnar, J.; Lucas, P.; Lacroix-desmazes, P.; Boutevin, B. Well-Architectured Poly (Dimethylsiloxane) -Containing Copolymers Obtained by Radical Chemistry. *Chem. Rev.* **2010**, *110*, 1233–1277.

(16) Yilgör, E.; Yilgör, I. Silicone Containing Copolymers: Synthesis, Properties and Applications. *Prog. Polym. Sci.* **2014**, *39* (6), 1165–1195.

(17) Han, Z.; Fina, A.; Camino, G. Organosilicon Compounds as Polymer Fire Retardants. In *Polymer Green Flame Retardants*; Elsevier, 2014; pp 389–418.

(18) Shit, S. C.; Shah, P. A Review on Silicone Rubber. *Natl. Acad. Sci. Lett.* **2013**, *36* (4), 355–365.

(19) Comparisons, O. S. Calculated Influence of Steric Effects on Polymerization-Depolyrtlerization EquiIibria in The. **1967**, *5*, 355–363.

(20) Pauling, L. The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms. *J. Am. Chem. Soc.* **1932**, *54* (9), 3570–3582.

(21) Fugel, M.; Hesse, M. F.; Pal, R.; Beckmann, J.; Jayatilaka, D.; Turner, M. J.; Karton, A.; Bultinck, P.; Chandler, G. S.; Grabowsky, S. Covalency and Ionicity Do Not Oppose Each Other—Relationship Between Si−O Bond Character and Basicity of Siloxanes. *Chem. - A Eur. J.* **2018**, *24* (57), 15275–15286.

(22) Kuciński, K.; Hreczycho, G. Catalytic Formation of Silicon–Heteroatom (N, P, O, S) Bonds. *ChemCatChem* **2017**, *9* (11), 1868–1885.

(23) Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. The Mechanism of the Acid- and Base-Catalyzed Equilibration of Siloxanes. *J. Am. Chem. Soc.* **1954**, *76* (20), 5190–5197.

(24) Brook, M. A. *Scholar*; Jhon Wiley & Sons,INC, 1999.

(25) Weinhold, F.; West, R. The Nature of the Silicon-Oxygen Bond. *Organometallics* **2011**, *30* (21), 5815–5824.

(26) Weinhold, F.; West, R. Hyperconjugative Interactions in Permethylated Siloxanes and Ethers: The Nature of the SiO Bond. *J. Am. Chem. Soc.* **2013**, *135* (15), 5762–5767.

(27) West, R.; Whatley, L. S.; Lake, K. J. Hydrogen Bonding Studies. V. The Relative Basicities of Ethers, Alkoxysilanes and Siloxanes and the Nature of the Silicon-Oxygen Bond. *J. Am. Chem. Soc.* **1961**, *83* (4), 761–764.

(28) Mark, J. E. Overview of Siloxane Polymers. *Am. Chem. Soc. Polym. Prepr. Div. Polym. Chem.* **1998**, *39* (1), 437–438.

(29) Owen, M. J. The Surface Activity of Silicones: A Short Review. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19* (1), 97–103.

(30) Merkel, T. C.; Bondar, V. I.; Nagai, K.; Freeman, B. D.; Pinnau, I. Gas Sorption, Diffusion, and Permeation in Poly (Dimethylsiloxane). *J. Polym. Sci. Part B Polym. Phys.* **2000**, *38* (3), 415–434.

(31) Zwerling, C. S. Forensic Analysis of a Contact Lens in a Murder Case. *J. Forensic Sci.* **2016**, *61* (2), 534–539.

(32) Zhang, H.; Ph, D.; Cloud, A. The Permeability Characteristics of Silicone Rubber. **2006**.

(33) Du, B. X.; Li, Z. L.; Li, J. Surface Charge Accumulation and Decay of Direct-Fluorinated RTV Silicone Rubber. *IEEE Trans. Dielectr. Electr. Insul.* **2014**, *21* (5), 2338–2342.

(34) Kim, E. S.; Kim, E. J.; Shim, J. H.; Yoon, J. Thermal Stability and Ablation Properties of Silicone Rubber Composites. *J. Appl. Polym. Sci.* **2008**, *110* (2), 1263–1270.

(35) Noll, W. *Chemistry and Technology of Silicones*; Elsevier, 2012.

(36) Huang, W.; Zhang, Y.; Yu, Y.; Yuan, Y. Studies on UV-stable Silicone–Epoxy Resins. *J. Appl. Polym. Sci.* **2007**, *104* (6), 3954–3959.

(37) Hamdani, S.; Longuet, C.; Perrin, D.; Lopez-cuesta, J. M.; Ganachaud, F. Flame Retardancy of Silicone-Based Materials. *Polym. Degrad. Stab.* **2009**, *94* (4), 465–495.

(38) Cai, D. K.; Neyer, A.; Kuckuk, R.; Heise, H. M. Optical Absorption in Transparent PDMS Materials Applied for Multimode Waveguides Fabrication. *Opt. Mater. (Amst).* **2008**, *30* (7), 1157–1161.

(39) Brook, M. A. Platinum in Silicone Breast Implants. *Biomaterials* **2006**, *27* (17), 3274–3286.

(40) Han, C.; Zhang, Q.; Ma, R.; Xie, L.; Qiu, T.; Wang, L.; Mitchelson, K.; Wang, J.; Huang, G.; Qiao, J.; et al. Integration of Single Oocyte Trapping, in Vitro Fertilization and Embryo Culture in a Microwell-Structured Microfluidic Device. *Lab Chip* **2010**, *10* (21), 2848–2854.

(41) Eduok, U.; Faye, O.; Szpunar, J. Recent Developments and Applications of Protective Silicone Coatings: A Review of PDMS Functional Materials. *Prog. Org. Coatings* **2017**, *111* (August 2016), 124–163.

(42) De Buyl, F. Silicone Sealants and Structural Adhesives. *Int. J. Adhes. Adhes.* **2001**, *21* (5), 411–422.

(43) Jha, B. K.; Christiano, S. P.; Shah, D. O. Silicone Antifoam Performance: Correlation with Spreading and Surfactant Monolayer Packing. *Langmuir* **2000**, *16* (26), 9947–9954.

(44) Nazir, H.; Zhang, W.; Liu, Y.; Chen, X.; Wang, L.; Naseer, M. M.; Ma, G. Silicone Oil Emulsions: Strategies to Improve Their Stability and Applications in Hair Care Products. *Int. J. Cosmet. Sci.* **2014**, *36* (2), 124–133.

(45) Scott, D. W. Equilibria between Linear and Cyclic Polymers in Methylpolysiloxanes. *J. Am. Chem. Soc.* **1946**, *68* (11), 2294–2298.

(46) Carmichael, J. B.; Winger, R. Cyclic Distribution in Dimethylsiloxanes. *J. Polym. Sci. Part A Gen. Pap.* **1965**, *3* (9), 3360–3360.

(47) White, J. W. *Recent Achievements in Industrial Silicon Polymer Science*; Gordon and Breach, Basel, 1995.

(48) Wright, P. V; Semlyen, J. A. Equilibrium Ring Concentrations and the Statistical Conformations of Polymer Chains: Part 3. Substituent Effects in Polysiloxane Systems. *Polymer (Guildf).* **1970**, *11* (9), 462–471.

(49) Lee, C. L.; Frye, C. L.; OK, J. Selective Polymerization of Reactive Cyclosiloxanes to Give Non-Equilibrium Molecular Weight Distributions. Monodisperse Siloxane Polymers. In Abstracts of Papers of the American Chemical Society; Amer Chemical Soc 1155 16th ST, NW, WASHINGTON, DC 20036, 1969; p P133.

(50) Frye, C. L.; Salinger, R. M.; Fearon, F. W. G.; Klosowski, J. M.; Deyoung, T. Reactions of Organolithium Reagents with Siloxane Substrates. *J. Org. Chem.* **1970**, *35* (5), 1308–1314.

(51) Chojnowski, J.; Cypryk, M.; Fortuniak, W.; Ścibiorek, M.; Rózga-Wijas, K. Synthesis of Branched Polysiloxanes with Controlled Branching and Functionalization by Anionic Ring-Opening Polymerization. *Macromolecules* **2003**, *36* (11), 3890–3897.

(52) Zundel, T.; Yu, J. M.; De France, C. Trimethylsilylmethyllithium: A Novel Initiator for the Anionic Polymerization of Cyclosiloxanes and Vinyl Monomers. In *Macromolecular Symposia*; Wiley Online Library, 1994; Vol. 88, pp 177–189.

(53) Suzuki, T.; Yamada, S.; Okawa, T. Synthesis of Polydimethylsiloxanes Containing Aminosilyl or Amidosilyl Groups at One Chain End. *Polym. J.* **1993**, *25* (4), 411–416.

(54) McGrath, J. E. Synthetic Importance and Industrial Applications of Ring-opening Polymerization. In *Makromolekulare Chemie. Macromolecular Symposia*; Wiley Online Library, 1991; Vol. 42, pp 69–91.

(55) Fuchise, K.; Igarashi, M.; Sato, K.; Shimada, S. Organocatalytic Controlled/Living Ring-Opening Polymerization of Cyclotrisiloxanes Initiated by Water with Strong Organic Base Catalysts. *Chem. Sci.* **2018**, *9* (11), 2879–2891.
(56) Gupta, S. P.; Moreau, M.; Masure, M.; Sigwalt, P. Cationic Polymerization of 1,3,5,7 Tetramethylcyclotetrasiloxane Initiated by Trifluoromethanesulphonic Acid. *Eur. Polym. J.* **1993**, *29* (1), 15–22.
(57) Maisonnier, S.; Favier, J. C.; Masure, M.; Hémery, P. Cationic Polymerization of 1,3,5,7-Tetramethylcyclotetrasiloxane in Aqueous Emulsion. Part I. Preliminary Results. *Polym. Int.* **1999**, *48* (3), 159–164.
(58) Schäfer, O.; Frey, V.; Pachaly, B.; Bauer, A. Preparation of Amino-Functional Siloxanes. Google Patents March 18, 2003.
(59) Crivello, J. V; Lee, J. L. The Synthesis, Characterization, and Photoinitiated Cationic Polymerization of Silicon-containing Epoxy Resins. *J. Polym. Sci. Part A Polym. Chem.* **1990**, *28* (3), 479–503.
(60) Wright, J. G. E.; Oliver, C. S. Dimethyl Silicone Elastomers and Method of Preparing the Same. Google Patents September 7, 1948.
(61) Dunham, M. L.; Bailey, D. L.; Mixer, R. Y. New Curing System for Silicone Rubber. *Ind. Eng. Chem.* **1957**, *49* (9), 1373–1376.
(62) Moretto, H.; Schulze, M.; Wagner, G. Silicones. *Ullmann's Encycl. Ind. Chem.* **2000**.
(63) Marsden, J. U. S. Patent 2,445,794. July 1948.
(64) Dluzneski, P. R. Peroxide Vulcanization of Elastomers. *Rubber Chem. Technol.* **2001**, *74* (3), 451–492.
(65) Stricher, a. M.; Rinaldi, R. G.; Barrès, C.; Ganachaud, F.; Chazeau, L. How I Met Your Elastomers: From Network Topology to Mechanical Behaviours of Conventional Silicone Materials. *RSC Adv.* **2015**, *5*, 53713–53725.
(66) Cervantes, J.; Zárraga, R.; Salazar-Hernández, C. Organotin Catalysts in Organosilicon Chemistry. *Appl. Organomet. Chem.* **2012**, *26* (4), 157–163.
(67) Kimbrough, R. D. Toxicity and Health Effects of Selected Organotin Compounds: A Review. *Environ. Health Perspect.* **1976**, *vol.14* (April), 51–56.
(68) Stein, J.; Lewis, L. N.; Smith, K. A.; Lettko, K. X. Mechanistic Studies of Platinum-Catalyzed Hydrosilylation T. **1991**, *1* (3).
(69) Nakajima, Y.; Shimada, S. Hydrosilylation Reaction of Olefins: Recent Advances and Perspectives. *RSC Adv.* **2015**, *5* (26), 20603–20616.
(70) Speier, J. L.; Webster, J. A.; Barnes, G. H. The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts. *J. Am. Chem. Soc.* **1957**, *79* (4), 974–979.
(71) Meister, T. K.; Riener, K.; Gigler, P.; Stohrer, J.; Herrmann, W. A.; Kühn, F. E. Platinum Catalysis Revisited-Unraveling Principles of Catalytic Olefin Hydrosilylation. *ACS Catal.* **2016**, *6* (2), 1274–1284.
(72) Pan, Z.; Liu, M.; Zheng, C.; Gao, D.; Huang, W. Study of Karstedt's Catalyst for Hydrosilylation of a Wide Variety of Functionalized Alkenes with Triethoxysilane and Trimethoxysilane. *Chinese J. Chem.* **2017**, *35* (8), 1227–1230.
(73) Wang, Y.; Zhang, B.; Zhou, S.; Chen, Y.; Liang, M.; Zou, H. Preparation of

High-Performance Epoxy-Containing Silicone Rubber via Hydrosilylation Reaction. *J. Appl. Polym. Sci.* **2020**, *137* (8), 1–10.

(74) Ji, J.; Ge, X.; Liang, W.; Liang, R.; Pang, X.; Liu, R.; Wen, S.; Sun, J.; Chen, X.; Ge, J. A Simple Preparation Route for Bio-Phenol MQ Silicone Resin via the Hydrosilylation Method and Its Autonomic Antibacterial Property. *Polymers (Basel).* **2019**, *11* (9).

(75) Seino, M.; Hayakawa, T.; Ishida, Y.; Kakimoto, M. A.; Watanabe, K.; Oikawa, H. Hydrosilylation Polymerization of Double-Decker-Shaped Silsesquioxane Having Hydrosilane with Diynes. *Macromolecules* **2006**, *39* (10), 3773–3775.

(76) Ren, Z.; Yan, S. Polysiloxanes for Optoelectronic Applications. *Prog. Mater. Sci.* **2016**, *83*, 383–416.

(77) Chung, D. W.; Kim, T. G. Study on the Effect of Platinum Catalyst for the Synthesis of Polydimethylsiloxane Grafted with Polyoxyethylene. *J. Ind. Eng. Chem.* **2007**, *13* (4), 571–577.

(78) Brook, M. A. New Control Over Silicone Synthesis Using SiH Chemistry: The Piers Rubinsztajn Reaction. *Chem. - A Eur. J.* **2018**.

(79) Pesti, J.; Larson, G. L. Tetramethyldisiloxane: A Practical Organosilane Reducing Agent. *Org. Process Res. Dev.* **2016**, *20* (7), 1164–1181.

(80) L. Larson, G.; L. Fry, J. Ionic and Organometallic-Catalyzed Organosilane Reductions. *Org. React.* **2008**, *71*, 1–737.

(81) Marciniec, B. Catalysis by Transition Metal Complexes of Alkene Silylation - Recent Progress and Mechanistic Implications. *Coord. Chem. Rev.* **2005**, *249* (21–22), 2374–2390.

(82) Corey, J. Y.; Braddock-Wilking, J. Reactions of Hydrosilanes with Transition-Metal Complexes: Formation of Stable Transition-Metal Silyl Compounds. *Chem. Rev.* **1999**, *99* (1), 175–292.

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

(84) Piers, W. E. The Chemistry of Perfluoroaryl Boranes. *Adv. Organomet. Chem.* **2004**, *52* (04), 1–76.

(85) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. Lewis Acid Properties of Tris (Pentafluorophenyl) Borane. Structure and Bonding in L− B (C6F5) 3 Complexes. *Organometallics* **1999**, *18* (9), 1724–1735.

(86) Fenton, D. E.; Massey, A. G.; Urch, D. S. Perfluorophenyl Derivatives of the Elements IX. (Pentafluorophenyl)Germanes. *J. Organomet. Chem.* **1966**, *6* (4), 352–358.

(87) Piers, W. E.; Chivers, T. Pentafluorophenylboranes: From Obscurity to Applications. *Chem. Soc. Rev.* **1997**, *26* (5), 345–354.

(88) Amato, M. E.; Caponetti, E.; Martino, D. C.; Pedone, L. ^{1}H and ^{19}F NMR Investigation on Mixed Hydrocarbon−Fluorocarbon Micelles. *J. Phys. Chem. B.* **2003**, *107* (37), 10048–10056.

(89) Oestreich, M.; Hermeke, J.; Mohr, J. A Unified Survey of Si-H and H-H Bond Activation Catalysed by Electron-Deficient Boranes. *Chem. Soc. Rev.* **2015**, *44* (8), 2202–2220.

(90) Rubin, M.; Schwier, T.; Gevorgyan, V. Highly Efficient $B(C_6F_5)_3$-Catalyzed

Hydrosilylation of Olefins. *J. Org. Chem.* **2002**, *67* (6), 1936–1940.
(91) Chandrasekhar, S.; Raji Reddy, C.; Nagendra Babu, B. Rapid Defunctionalization of Carbonyl Group to Methylene with Polymethylhydrosiloxane- $B(C_6F_5)_3$. *J. Org. Chem.* **2002**, *67* (25), 9080–9082.
(92) Harrison, D. J.; McDonald, R.; Rosenberg, L. Borane-Catalyzed Hydrosilylation of Thiobenzophenone: A New Route to Silicon-Sulfur Bond Formation. *Organometallics* **2005**, *24* (7), 1398–1400.
(93) Parks, D. J.; Blackwell, J. M.; Piers, W. E. Studies on the Mechanism of $B(C_6F_5)_3$-Catalyzed Hydrosilation of Carbonyl Functions. *J. Org. Chem.* **2000**, *65* (10), 3090–3098.
(94) Brook, M. A.; Grande, J. B.; Ganachaud, F. New Synthetic Strategies for Structured Silicones Using B (C 6 F 5) 3. In *Silicon Polymers*; Springer, 2010; pp 161–183.
(95) Rendler, S.; Oestreich, M. Conclusive Evidence for an SN_2-Si Mechanism in the $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Carbonyl Compounds: Implications for the Related Hydrogenation. *Angew. Chemie - Int. Ed.* **2008**, *47* (32), 5997–6000.
(96) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J. X.; Yamamoto, Y. A Novel $B(C_6F_5)_3$-Catalyzed Reduction of Alcohols and Cleavage of Aryl and Alkyl Ethers with Hydrosilanes. *J. Org. Chem.* **2000**, *65* (19), 6179–6186.
(97) Grande, J. B.; Thompson, D. B.; Gonzaga, F.; Brook, M. A. Testing the Functional Tolerance of the Piers-Rubinsztajn Reaction: A New Strategy for Functional Silicones. *Chem. Commun.* **2010**, *46* (27), 4988–4990.
(98) Saito, K.; Kondo, K.; Akiyama, T. $B(C_6F_5)_3$-Catalyzed Hydrodesulfurization Using Hydrosilanes - Metal-Free Reduction of Sulfides. *Org. Lett.* **2015**, *17* (13), 3366–3369.
(99) Longuet, C.; Joly-Duhamel, C.; Ganachaud, F. Copolycondensation of Regular Functional Silane and Siloxane in Aqueous Emulsion Using $B(C_6F_5)_3$ as a Catalyst A. *Macromol. Chem. Phys.* **2007**, *208* (17), 1883–1892.
(100) Zhang, J.; Chen, Y.; Brook, M. A. Reductive Degradation of Lignin and Model Compounds by Hydrosilanes. *ACS Sustain. Chem. Eng.* **2014**, *2* (8), 1983–1991.
(101) Matsumoto, K.; Shimada, S.; Sato, K. Sequence-Controlled Catalytic One-Pot Synthesis of Siloxane Oligomers. *Chem. - A Eur. J.* **2019**, *25* (4), 920–928.
(102) Chojnowski, J.; Fortuniak, W.; Kurjata, J.; Rubinsztajn, S.; Cella, J. A. Oligomerization of Hydrosiloxanes in the Presence of Tris(Pentafluorophenyl)Borane. *Macromolecules* **2006**, *39* (11), 3802–3807.
(103) Chojnowski, J.; Rubinsztajn, S.; Fortuniak, W.; Kurjata, J. Oligomer and Polymer Formation in Hexamethylcyclotrisiloxane (D_3) - Hydrosilane Systems under Catalysis by Tris(Pentafluorophenyl) Borane. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17* (1), 173–187.
(104) Ma, Y.; Zhang, L.; Luo, Y.; Nishiura, M.; Hou, Z. $B(C_6F_5)_3$-Catalyzed C-Si/Si-H Cross-Metathesis of Hydrosilanes. *J. Am. Chem. Soc.* **2017**, *139* (36), 12434–12437.

(105) Madsen, F. B.; Javakhishvili, I.; Jensen, R. E.; Daugaard, A. E.; Hvilsted, S.; Skov, A. L. Synthesis of Telechelic Vinyl/Allyl Functional Siloxane Copolymers with Structural Control. *Polym. Chem.* **2014**, *5* (24), 7054–7061.

(106) Ai, L.; Chen, Y.; He, L.; Luo, Y.; Li, S.; Xu, C. Synthesis of Structured Polysiloxazanes: Via a Piers-Rubinsztajn Reaction. *Chem. Commun.* **2019**, *55* (93), 14019–14022.

(107) Grande, J. B.; Urlich, T.; Dickie, T.; Brook, M. A. Silicone Dendrons and Dendrimers from Orthogonal SiH Coupling Reactions. *Polym. Chem.* **2014**, *5* (23), 6728–6739.

(108) Morgan, J.; Chen, T.; Hayes, R.; Dickie, T.; Urlich, T.; Brook, M. A. Facile Synthesis of Dendron-Branched Silicone Polymers. *Polym. Chem.* **2017**, *8* (18), 2743–2746.

(109) Nguyen, K. D. Q.; Megone, W. V.; Kong, D.; Gautrot, J. E. Ultrafast Diffusion-Controlled Thiol–Ene Based Crosslinking of Silicone Elastomers with Tailored Mechanical Properties for Biomedical Applications. *Polym. Chem.* **2016**, *7* (33), 5281–5293.

(110) Lowe, A. B. Thiol-Ene "Click" Reactions and Recent Applications in Polymer and Materials Synthesis: A First Update. *Polym. Chem.* **2014**, *5* (17), 4820–4870.

(111) Cole, M. A.; Jankousky, K. C.; Bowman, C. N. Thiol-Ene Functionalized Siloxanes for Use as Elastomeric Dental Impression Materials. *Dent. Mater.* **2014**, *30* (4), 449–455.

(112) Zheng, S.; Zlatin, M.; Selvaganapathy, P. R.; Brook, M. A. Multiple Modulus Silicone Elastomers Using 3D Extrusion Printing of Low Viscosity Inks. *Addit. Manuf.* **2018**, *24* (August), 86–92.

(113) Lalonde, M.; Chan, T. H. Use of Organosilicon Reagents as Protective Groups in Organic Synthesis. *Synthesis (Stuttg).* **1985**, *1985* (09), 817–845.

(114) Wang, L.; Clive, D. L. J. [[(Tert-Butyl)Dimethylsilyl]Oxy]-MethylGroup for Sulfur Protection. *Org. Lett.* **2011**, *13* (7), 1734–1737.

(115) Zheng, S.; Liao, M.; Chen, Y.; Brook, M. A. Dissolving Used Rubber Tires. *Green Chem.* **2020**, *22* (1), 94–102.

(116) Guise-Richardson, C. Redefining Vulcanization: Charles Goodyear, Patents, and Industrial Control, 1834-1865. *Technol. Cult.* **2010**, *51* (2), 357–387.

(117) Fisher, H. L. Vulcanization of Rubber. *Ind. Eng. Chem.* **1939**, *31* (11), 1381–1389.

(118) Rattanasom, N.; Prasertsri, S.; Ruangritnumchai, T. Comparison of the Mechanical Properties at Similar Hardness Level of Natural Rubber Filled with Various Reinforcing-Fillers. *Polym. Test.* **2009**, *28* (1), 8–12.

(119) Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohjiya, S. The Effect of Bis (3-Triethoxysilylpropyl) Tetrasulfide on Silica Reinforcement of Styrene-Butadiene Rubber. *Rubber Chem. Technol.* **1998**, *71* (2), 289–299.

(120) Zhang, P.; Morris, M.; Doshi, D. Materials Development for Lowering Rolling Resistance of Tires. *Rubber Chem. Technol.* **2016**, *89* (1), 79–116.

(121) Vilmin, F.; Bottero, I.; Travert, A.; Malicki, N.; Gaboriaud, F.; Trivella, A.; Thibault-Starzyk, F. Reactivity of Bis[3-(Triethoxysilyl)Propyl] Tetrasulfide (TESPT) Silane Coupling Agent over Hydrated Silica: Operando IR Spectroscopy and Chemometrics Study. *J. Phys. Chem. C* **2014**,

118 (8), 4056–4071.

(122) Reuvekamp, L. A. E. M.; Ten Brinke, J. W.; Van Swaaij, P. J.; Noordermeer, J. W. M. Effects of Time and Temperature on the Reaction of Tespt Silane Coupling Agent during Mixing with Silica Filler and Tire Rubber. *Rubber Chem. Technol.* **2002**, *75* (2), 187–198.

(123) Larsen, A. L.; Sommer-Larsen, P.; Hassager, O. Some Experimental Results for the End-Linked Polydimethylsiloxane Network System. *E-Polymers* **2004**, No. 050, 1–18.

(124) Zheng, S.; Brook, M. A. Reversible Redox Crosslinking of Thiopropylsilicones. *Macromol. Rapid Commun.* **2020**, *2000375*, 1–5.

Chapter 2: When Attempting Chain Extension, Even Without Solvent, It Is Not Possible to Avoid Chojnowski Metathesis Giving D_3&

2.1. Abstract

A simple, mild and efficient method to prepare HSi- or HOSi-telechelic, high molecular weight polydimethylsiloxane polymers (to 41,600 g mol^{-1}) using the one-shot hydrolysis of M^HM^H is reported; titration of the water allowed for higher molecular weights (to 153,900 g mol^{-1}). The 'living' character of the chain extension processes was demonstrated by adding a small portion of M^HM^H and $B(C_6F_5)_3$ (BCF) to a first formed polymer, which led to an ~2 fold, second growth in molecular weight. The heterogeneous reaction reached completion in less than 30 minutes, much less in some cases, regardless of whether it was performed neat or 50wt% in dry toluene; homogeneous reactions in toluene were much slower. The process does not involve traditional redistribution, as judged by the with low quantities (<3%) of D_4 produced. However, it is not possible to avoid Chojnowski metathesis from M^HDDM^H giving D_3, which occurs competitively with chain extension.

2.2. Introduction

Polydimethylsiloxane (PDMS) oil is the parent commercial silicone polymers from which almost all other silicones are derived. PDMS possesses unique

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Mengchen Liao performed all the experiments and Chen provided guidance for experimental design.

properties including, low T_g, good thermal-stability, high optical transparency, excellent dielectric properties and excellent biocompatibility, etc. Conventionally, two methods dominate the commercial preparation of high molecular weight PDMS oil, dehydration of silanol-terminated oligomers,[1] and, acid- and particularly base-catalyzed equilibration of cyclic monomers[2] (**Figure 2.1**A,B). However, each of these approaches suffers from inherent shortcomings. The former process, as with all condensation processes, slows down with increasing conversion, which makes challenging the synthesis of high molecular weight polymers; both processes typically lead to polymers with high dispersities $Đ_M$. In the latter case, with base-catalyzed equilibration that has an equilibrium constant near 1, the desired polymer is accompanied by the formation of large quantities of cyclic monomers, e.g., <15% for D_4 (D = ~Me_2SiO~)[3,4] (**Figure 2.1**B). Cyclooligosiloxanes, particularly D_4, have attracted different levels of concerns by regulatory agencies because of their purported environmental behaviors[5,6]; D_4 concentrations are regulated in Canada and the UK[7,8]. Hence, there is an increasing consensus that the value of silicone polymers would be increased if they contained lower cyclooligosiloxane concentrations. Note that the removal of cyclic monomers from silicone oils becomes more difficult as the MW and viscosities of both cyclics and oils increase.

The competing commercial process for synthesis of high MW silicones oils is ring opening polymerization[9], typically initiated by anions[10-12] (**Figure 2.1**C). Polymers with high MW can result, but the process is challenged by the need to be scrupulously dry to avoid premature termination; higher MW PDMS polymers with narrow dispersity $Đ_M$ are more easily achieved when the more expensive, ring strained monomer D_3 is utilized as a starting material instead of D_4.

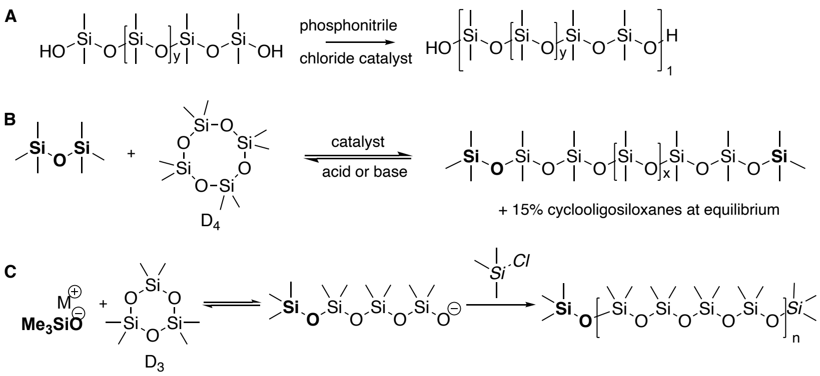


Figure 2.1. Traditional routes to silicone polymers: A: silanol condensation; B: Redistribution; C: Ring-opening polymerization.

Hydrosilane monomers, particularly $HMeSiCl_2$ and HMe_2SiCl are produced in the Direct Process[13] in concentrations that typically exceed commercial needs. As a consequence, oligomers $HMe_2SiOSiMe_2H$) (M^HM^H) and polymers $Me_3Si(OSiMeH)_nOSiMe_3$ (PHMS) based on these monomers are readily available. The compounds are potent reducing agents and, as Larson has noted, both efficacious and inexpensive[14,15]. In organic synthesis, benefit is made of the ease with which silicone products, after reduction, are readily separated from the desired organic product(s).

Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ (BCF), a metal-free, water-tolerant[16] and thermally stable (up to 270 °C) compound[17], is renowned for its effectiveness as a co-initiator for industrial olefin polymerization[18]. In his extensive and elegant studies of reduction of carbonyl groups Piers showed that it was also a potent catalyst for hydrosilane reductions[17]. We used M^HM^H in the presence of BCF to reduce the sulfur crosslinks in automobile rubber tire, permitting reuse of the organic constituents[19]. When using $HSiEt_3$ in the presence of BCF, Piers et al. originally reported that overreduction of carbonyl groups led first to silyl ethers and then to alkanes plus disiloxanes.

Rubinsztajn and Cella recognized the Piers reduction was a new route to silicones that was first patented, and then published in the open literature[20]. Chojnowski et al. have made several seminal contributions to our understanding of the mechanism of this process[21,22]. It is worth noting that growing optically active siloxanes from silanols, rather than alkoxysilanes, using $B(C_6F_5)_3$ was pioneered by Kawakami[23]. In retrospect, perhaps we should have named the reaction the Piers-Chojnowski-Rubinsztajn- Kawakami (PCRK) reaction, rather than the PR reaction[24] and will do so for this paper.

The PCRK reaction is a particularly convenient route to synthesize silicone polymers. One simply chooses the number of alkoxysilane, or silanol substituents, or water, required for the synthesis of a given linear or branched monomer, and adds the appropriate mono-, di- or oligofunctional HSi-containing molecules in the presence of BCF[25]. It is thus possible to create linear polymers, including block-copolymers, simply by combining telechelic HSi + HOSi silicones or HSi silicones + water[26-28]. We have previously exploited this method to reliably introduce branches along linear silicone backbones[29] including, in the limit, highly branched dendron-like structures[30], including MDTQ resins ($D = Me_2SiO_{2/2}$)[31] (**Figure 2.2**).

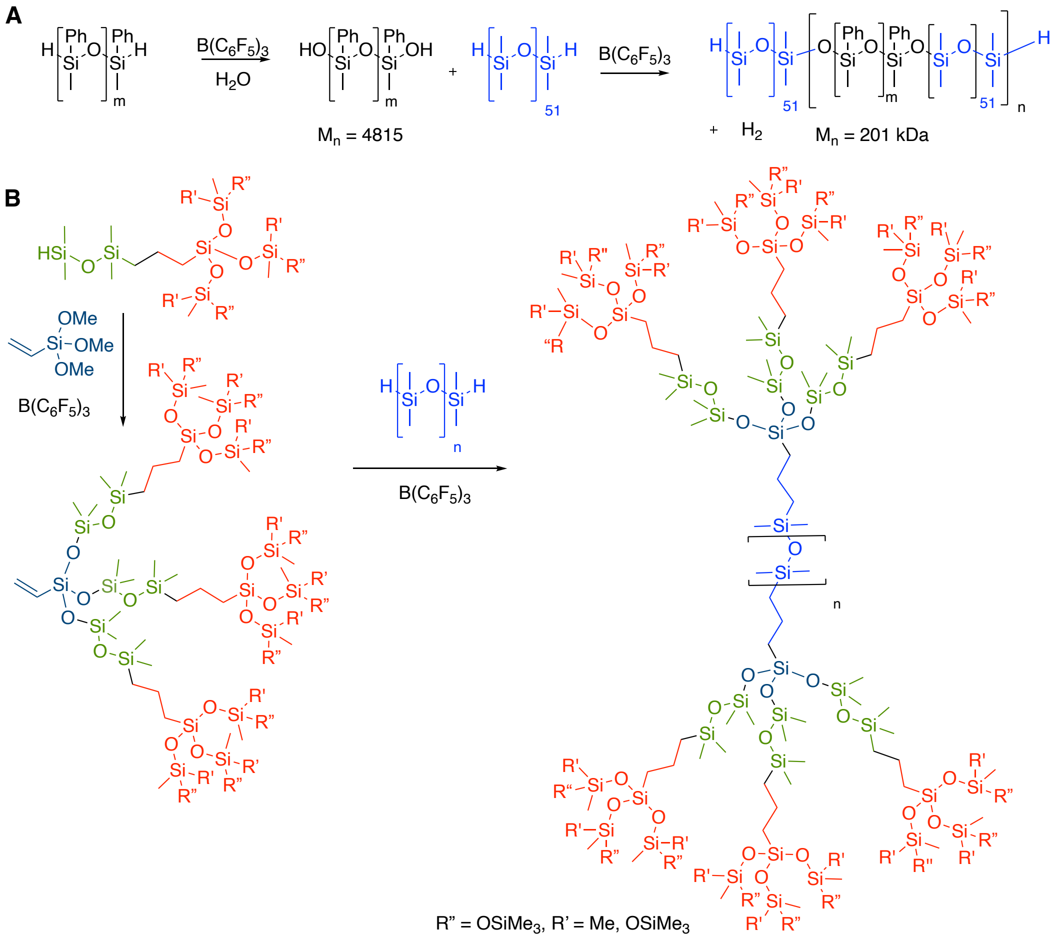


Figure 2.2. A: Polymerization of telechelic HSi-silicones and water to give block copolymers; B: Formation of highly branched silicones using the PCRK reaction.

Tetramethyldisiloxane (M^HM^H) is an inexpensive, atom-efficient hydrosilane that has been selected as a silane source for a number of reactions[14,32,33]. Attempts to produce high molecular weight PDMS oil from M^HM^H and H_2O in aqueous media, a traditional PCRK reaction (mole ratio, [OH]/[SiH]=56) was made by the group of Ganachaud who reported formation of an elastomer; it was concluded that the reaction was not readily controllable[34]. Chojnowski et al. showed under anhydrous Schlenk line conditions that the oligomerization of M^HM^H (**Figure 2.3**H-J) in the presence of BCF catalyst led to HSi-terminated oligomers and D_3 – Chojnowski metathesis[22]; however, with large quantities of D_3 that were produced

M^HDDM^H; secondary copolymerization of D_3 and M^HM^H with activation with $B(C_6F_5)_3$ could be used to lead to higher molecular weight polymers[35].

Neither the Ganachaud nor Chojnowski outcomes with M^HM^H matched our experience of HSi-terminated silicones in the presence of water and $B(C_6F_5)_3$, which led smoothly to high molecular weight PDMS oils[26] (**Figure 2.2**). We hypothesized that differences arose because of the quantity of available water and BCF and, perhaps, other experimental conditions. Herein, we report a simple and mild process for the formation of HOSi- or HSi-terminated high molecular weight PDMS oil by the hydrolysis of M^HM^H in a kinetic process that generates relatively low quantities of D_4 (<3%). However, dilution with good solvents for silicone enhances the fraction of D_3 produced alongside the polymer.

2.3. Experimental

2.3.1. Materials

Tetramethyldisiloxane (M^HM^H) was purchased from Gelest and dried over molecular sieves (obtained from Sigma Aldrich, Molecular sieves, 4 Å beads, 8-12 mesh) before use. Ultrapure water (18 MΩ-cm) was obtained from Easy pure RF (Barnstead). The $B(C_6F_5)_3$ catalyst was provided by Alfa Aesar. Toluene (Caledon) was dried over an activated alumina column (2.3 ppm water present). 'Wet' DCM (72.5 ppm water present) and 'wet' toluene (466.6 ppm water present) were purchased from Caledon.

2.3.2. Methods

^1H and ^{29}Si NMR spectra were recorded on a Bruker Advance 600 MHz nuclear magnetic resonance spectrometer using deuterated solvent chloroform-*d*.

Chromium(III) acetylacetonate ($3 \cdot 10^{-3}$ mol L^{-1}) was added as relaxation reagent for some of these measurements.

Gel permeation chromatography was carried out using a Viscotek GPC Max (VE 2001 GPC Solvent/Sample Module) was used. The system was equipped with a Viscotek VE 3580 RI Detector, a Viscotek 270 Dual Detector, and a PolyAnalytik SupeRes PAS-101 (8 mm Å~ 30 cm) column with a single pore, styrene-divinylbenzene gel, 6 µm particle size. It was additionally calibrated using a single narrow polydispersity polystyrene standard (93 kDa) from Polymer Laboratories. Toluene was used as the eluent at a flow rate of 1.0 mL min^{-1}. FTIR data was collected on a Nicolet 6700 FTIR using Thermo Electron's OMNIC software. GC-MS analyses were performed using an Agilent 6890N gas chromatograph (Santa Clara, CA, USA) equipped with a DB-17ht column (30 m × 0.25 mm i.d. x 0.15 µm film, J & W Scientific), and coupled to an Agilent 5973 MSD single quadruple mass spectrometer. One microliter of sample was injected using Agilent 7683 autosampler using an injector temperature was 250 °C and a carrier gas (helium) flow of 0.8 mL/min. The transfer line was set to 280 °C and the MS source temperature was 230 °C. The column temperature started at 40 °C, raised to 70 °C at 5 °C/min, raised to 95 °C at 10 °C/min, raised to 300 °C at 40 °C/min, and then held at 300 °C for 8 min for a total run time of 21.73 min. Full scan mass spectra between m/z 50 and 800 were acquired, with the MS detector turned off between 2.0-2.8 min for solvent. Please note that the sample is dissolved in propyl formate. Water concentrations were determined using Karl Fischer titrations (Mettler Toledo DL39 Coulometer) with a one-component system containing a Hydranal Composite solution.

2.3.2.1. Experimental procedures for Table 2.1

One shot addition, entries 1-3: $B(C_6F_5)_3$ stock solution in dry toluene

To a pre-dred 25.0 mL vial added $B(C_6F_5)_3$ (0.052 g, 0.01 mmol) catalyst together with dry toluene (1.0156 mL, 0.881 g) to prepare a $B(C_6F_5)_3$ stock solution in dry toluene (0.01M).

entry 1 ([BCF]/[SiH]=0.02 mol%; [OH]/[SiH]=1; one-shot):

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 3.13 g, 0.02 mol) and distilled water (18 g mol^{-1}, 0.402 mL, 0.02 mol) and then capped with a septum with a needle with a bubbler open to atmosphere to balance the pressure. The mixture was stirred for 5-10 minutes prior to the addition of $B(C_6F_5)_3$ stock solution in dry toluene (0.01 M, 0.094 mL, 0.0094 mmol). The $B(C_6F_5)_3$ stock solution was added by Eppendorf Pipette into the flask through opening the septa. Once the $B(C_6F_5)_3$ stock solution was added, immediately, vigorous bubbling inside of the round bottle flask was observed. The mixture was stirred at room temperature for 3h and the reaction was quenched by alumina for 5h and the residual water droplet was removed by adding sodium sulfate.

entry 2 ([BCF]/[SiH]=0.02 mol%; [OH]/[SiH]=3.2; one-shot):

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 5.01 g, 0.037 mol) and distilled water (18 g mol^{-1}, 2.144 mL, 0.119 mol) and then capped with a septum with a needle with a bubbler open to atmosphere to balance the pressure. The mixture was stirred for 5-10 minutes prior to the addition of $B(C_6F_5)_3$ stock solution in dry toluene (0.01 M, 0.149 mL, 0.0149 mmol). The $B(C_6F_5)_3$ stock solution was added by Eppendorf Pipette into the flask through opening the septa. Once the $B(C_6F_5)_3$ stock solution was added, immediately, vigorous bubbling inside of the round bottle flask was observed. The mixture was stirred at room temperature for 3h and the reaction was quenched by alumina for 5h and the residual water droplet was removed by adding sodium sulfate.

entry 3 ([BCF]/[SiH]=0.1 mol%; [OH]/[SiH]=1; one-shot):

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 1.00 g, 0.0074 mol) and distilled water (18 g mol^{-1}, 0.134 mL, 0.0074 mol) and then capped with a septum with a needle with a bubbler open to atmosphere to balance the pressure. The mixture was stirred for 5-10 minutes prior to the addition of $B(C_6F_5)_3$ stock solution in dry toluene (0.01 M, 0.150 mL, 0.015 mmol). The $B(C_6F_5)_3$ stock solution was added by Eppendorf Pipette into the flask through opening the septa. Once the $B(C_6F_5)_3$ stock solution was added, immediately, vigorous bubbling inside of the round bottle flask was observed. The mixture was stirred at room temperature for 3h and the reaction was quenched by alumina for 5h and the residual water droplet was removed by adding sodium sulfate. The mixture was stirred at room temperature for 3 h and the reaction was quenched by alumina. The product was collected by filtration through Celite under reduced pressure.

Portion by portion addition, entries 4,5

entry 4 (overall [BCF]/[SiH]=0.008 mol%; [OH]/[SiH]=1; portion by portion adding of $B(C_6F_5)_3$ catalyst, neat):

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 5.01 g, 0.037 mol) and the distilled water (18 g mol^{-1}, 0.67 mL, 0.037 mol) and then capped with a septum with a needle with a bubbler open to atmosphere to balance the pressure. The mixture was stirred for 5-10 minutes prior to the addition of $B(C_6F_5)_3$ stock solution in dry toluene (0.001 M, 0.149 mL, 0.00149 mmol, [BCF]/[SiH]=0.002 mol%, first portion of catalyst). The $B(C_6F_5)_3$ stock solution was added by Eppendorf Pipette into the flask through opening the septa. Bubbles immediately formed once the catalyst was added. After no bubble formation was observed (throughout the reaction, water droplet always existed indicating sufficient amount of water), once again, $B(C_6F_5)_3$ stock solution in dry toluene (0.001 M, 0.149 mL, 0.00149 mmol, [BCF]/[SiH]=0.002 mol%, second portion of catalyst) was added and vigorous bubbling occurred again. The procedure of adding $B(C_6F_5)_3$ stock solution in dry toluene (0.001 M, 0.149 mL, 0.00149 mmol, [BCF]/[SiH]=0.002 mol%) repeated until no bubbles were observed even after the addition of a fresh portion of catalyst was added, overall, four portions of catalyst were added (0.008 mol%). The mixture was stirred at room temperature for 22h and the reaction was quenched by alumina for 5h and the residual water droplet was removed by adding sodium sulfate.

entry 5 (overall [BCF]/[SiH]=0.006 mol%; [OH]/[SiH]=0.73; portion by portion, 1.3 g mL^{-1}, mass of M^{H}M^{H} *versus* volume of DCM)

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^{H}M^{H}) (134 g mol^{-1}, 4.12 g, 0.031 mol) and 'wet' DCM (3 mL, 72.5 ppm water, 0.016 mmol of water present) and then capped with a septum with a needle with a bubbler open to atmosphere to balance the pressure. The mixture was stirred for 5-10 minutes prior to the addition of $B(C_6F_5)_3$ stock solution in dry toluene (0.001 M, 0.119 mL, 0.0012 mmol, [BCF]/[SiH]=0.002 mol%, first portion of catalyst) follow by a quick addition of the distilled water (18 g mol^{-1}, 0.074 mL, 0.0041 mol, [OH]/[SiH]=0.13, first portion). The $B(C_6F_5)_3$ stock solution and water were added by Eppendorf Pipette into the flask through opening the septa and the vigorous bubble formation was observe immediately after the addition of water. Here is how we decide to whether add catalyst or water: First add the distilled water (18 g mol^{-1}, 0.055 mL, 0.0031 mol, [OH]/[SiH]=0.1, second portion); 1) if bubble formation was observed, indicates the cease of bubbles was originated from insufficient amount of water. 2) if no bubble formation was observed after the addition of the water indicating the catalyst was insufficient, then $B(C_6F_5)_3$ stock solution in dry toluene (0.001 M, 0.119 mL, 0.0012 mmol, [BCF]/[SiH]=0.002 mol%) was added. The above-mentioned procedure repeated until no bubbles formed regardless of the addition of catalyst or water, overall, [BCF]/[SiH]=0.006 mol%; [OH]/[SiH]=0.73. The mixture was stirred at room temperature for 5.6h and the reaction was quenched by alumina for 5h and the residual water droplet was removed by adding sodium sulfate.

Capturing the volatiles, entries 7,8

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 10.38 g, 77.5 mmol) with distilled water (18 g mol^{-1}, 1.34 mL, 74.4 mmol). To the mixture was added $B(C_6F_5)_3$ stock solution in dry toluene (0.1 M, 0.298 ml, 0.0298 mmol). The cold trap condenser was submerged in dry ice/acetone with the addition of acetone and was directly connected to the round-bottomed flask through 6 mm O.D. Pyrex tubing. The mixture in the round bottle flask was stirred at room temperature for 3h and the reaction was quenched by alumina and the residual water droplet was removed by adding sodium sulfate with 5h quenching time. Before the work up procedures, the mixtures in the round bottle flask were weighted and characterized by ^{1}H, ^{29}Si NMR (SR) followed by filtration through Celite under reduced pressure.

2.3.2.2. Experimental procedure for Table 2.2

In neat water, or in water/toluene mixtures (entries 1-9)

To a series of pre-dried 25.0 ml vials was added M^HM^H (134 g mol^{-1}, 1.04 g, 7.8 mmol) with distilled water (18 g mol^{-1}, 0.134 mL, 7.4 mmol). To the mixtures were added $B(C_6F_5)_3$ stock solution in dry toluene (0.1 M, 0.03 ml, 0.003 mmol, respectively) and stirred at room temperature. At time points from 2-180 min alumina was added to quench the reaction at different time intervals together with ~0.5g of sodium sulfate to remove the residual water. Before the work up procedures, the products were characterized by ^{1}H, ^{29}Si NMR (SR) followed by filtration through Celite under reduced pressure. The same process was repeated for the experiments that also included toluene: M^HM^H (134 g mol^{-1}, 1.04 g, 7.8 mmol) with distilled water (18 g mol^{-1}, 0.134 mL, 7.4 mmol), dry toluene (0.677 mL, 0.585 g) and $B(C_6F_5)_3$ stock solution in dry toluene (0.1 M, 0.03 ml, 0.003 mmol), respectively, the mixture was then stirred at room temperature.

Chain extension (entry 10, Table 2.2)

To a 10.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 0.015 mL, 0.011 g, 0.085 mmol) with pre-prepared PDMS oil terminated with silanol (21,300 g mol^{-1}, 0.90 g, 0.042 mmol, entry 4, **Table 2.1**). To be noted here, the pre-prepared silanol PDMS was performed kugelrohr distillation at 100°C under vacuum (635 mmHg) for 60 min before running the GPC to remove the residual water and volatile small molecules. The mixture was added $B(C_6F_5)_3$ stock solution in dry toluene (0.01 M, 0.0086 mL, 0.086 µmol) and stirred at room temperature. After 3 h, alumina was added to the mixture to quench the reaction. The product was collected by filtration through Celite under reduced pressure.

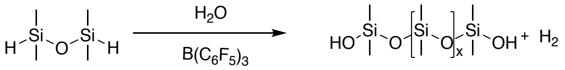
2.4. Results

The reaction between M^HM^H and water leads first to disiloxanol **1** and then to the tetrasiloxane formation **2** (**Figure 2.3**A,B); both reactions are rapid and lead to the concomitant formation of hydrogen at the water droplet interface (*Note: caution must be taken, as this can lead to a pressure spike of this flammable gas*); repetition of these processes lead to PDMS polymer initially terminated with SiH and then SiOH groups **Figure 2.3**C-E). The processes were followed using ^{1}H NMR (particularly the relationship between integrated peak areas of Si-*H* (~ 4.7 ppm vs Si-CH_3 ~0.1-0.2 ppm[36,37])) and ^{29}Si NMR spectra, as well as gel permeation chromatography (GPC) and Fourier-transform infrared spectroscopy (FTIR, Supplementary Material, SM).

The objective of the research was to identify simple, efficient processes that would lead to linear PDMS, optionally terminated with SiH groups. Preliminary experiments examined the impact of reaction parameters, including catalyst concentration, solvent and, in particular, the effect of homogeneity between water and silicone phases during the course of hydrolysis. In addition, the impact of ‘one shot’ addition of reagents was compared to a titration in which water and/or additional BCF were added when reaction ceased.

Simply mixing M^HM^H, $B(C_6F_5)_3$ stock solution in dry toluene, with bulk water led to linear silicones (entries 1-3, **Table 2.1**). Unsurprisingly, reactions were faster with more catalyst, but satisfactory rates were already achieved with only 0.02mol% of this not inexpensive catalyst (< 30 min, see below). Adding water in excess to the stoichiometric requirement did not lead to an improved outcome – cyclics were formed as a by-product (see below, SM). Dilution with solvent, initially dichloromethane (containing 72.5 ppm water), demonstrated that much higher molecular weight polymers were accessible, with even lower levels of catalyst; however, D_4 was also a by-product of these reactions (SM). Thus, if high molecular weight is most desired, using small amounts of organic solvents is beneficial (entries 5,6, **Table 2.1**; if suppression of cyclics is key, use slightly more BCF (entry 1, **Table 2.1**). Note that the use of a completely homogeneous reaction was disadvantageous for practical or kinetic reasons. For example, the reaction of 1g of M^HM^H would require 14.3 mL of ‘wet’ toluene (saturated with sufficient water to complete SiH hydrolysis), so scale up would not be practicable. When we did attempt the reaction at small scale under these conditions, it proceeded to only a small extent over 5 hours and then remained unchanged even after 24 hours (see SM).

Table 2.1. High molecular weight PDMS preparation using hydrolysis



optional - dry toluene, wet DCM, addition in portions

Entry[a]	[BCF]/ [SiH] mol%	[OH]/ [SiH][a]	Addition[b]	M^HM^H/DCM[c] (g mL^{-1})	Cyclics %[d]	PDMS %[d]	M_n (g mol^{-1})	M_w (g mol^{-1})	Đ$_M$	Mass bal[e]
1	0.1	1	O	-	2	98	43,700	129,200	2.97	70.1
2	0.02	1	O	-	26	74	52,700	105,400	2.00	71.3
3	0.02	3.2	O	-	5.9	94	41,600	101,500	2.44	70.6
4	0.008	1	P	-	5.9	92	20,700	32,500	1.57	79.3
5	0.006	0.73	P	1.3	12.9	87	111,400	221,500	1.99	95.6
6	0.004	0.75	P	1	5.7	94	152,500	314,000	2.06	82.9
				M^HM^H/$PhCH_3$[c] (g mL^{-1})						
7	0.02	1	O	-	18.9	81.2	20,500	37,400	1.82	73.8[f]
8	0.02	1	O	1.53	47.9	52.1	40,000	63,100	1.58	89.1[g]

[a] Stoichiometric addition of bulk water except for entries 5,6. Reactions were quenched between 2.5 and 22 hours (SM). Most reactions were complete within 30 min (see below), conditions under which the catalyst remains highly effective[16]. [b] O = one-shot reaction; P = reagents were added portion by portion, each time bubble evolution ceased. [c] DCM contained 72.5 ppm water. Toluene was dry. [d] Fraction of D units in $D_3 + D_4 + D_5$ or PDMS based on integration in ^{29}Si NMR. [e] Mass % of non-volatiles. [f] Cold trap (volatiles) contained 23.9% (total mass balance 97.7%), which consisted of M^HM^H 50%, Me_2SiH_2 42%. [g] Cold trap contained 10.5% (total mass balance 99.6%), which consisted of M^HM^H 66%, Me_2SiH_2 26%.

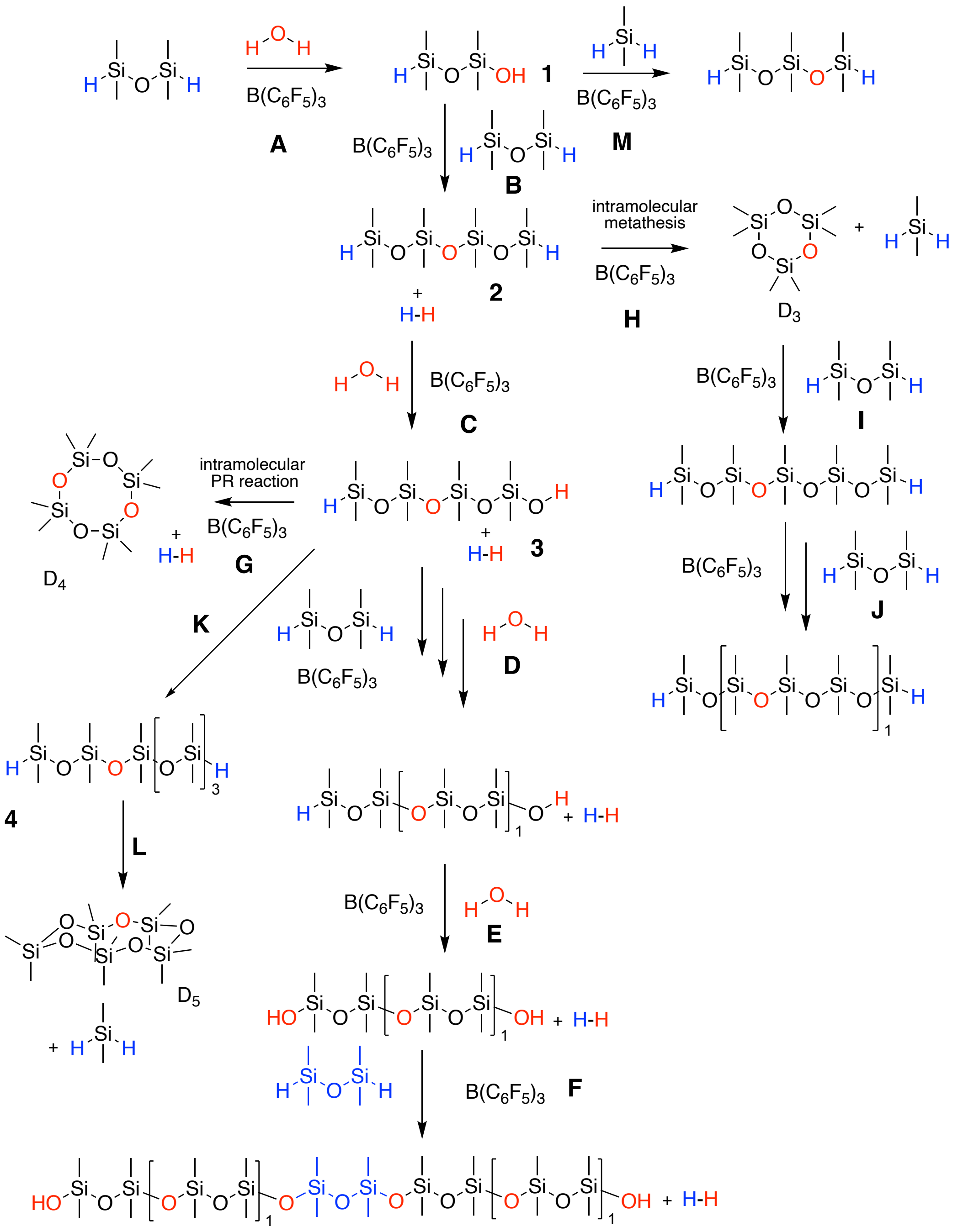
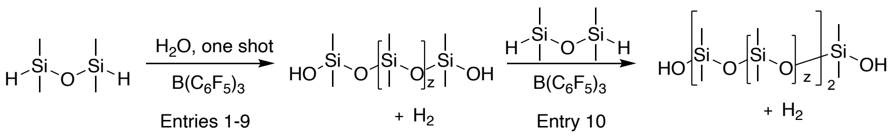


Figure 2.3. Proposed reactions for cyclooligosiloxane and polymer formation from M^HM^H.

2.4.1. High molecular weight PDMS preparation using hydrolysis

The preparation of telechelic PDMS polymers from M^HM^H, terminated with either SiOH or SiH groups, was straightforward by adding water in a one shot process in the presence of 0.02% $B(C_6F_5)_3$. The two-phase reaction water/silicone was surprisingly rapid; reaction times of less than 30 minutes led to polymers and concomitant formation of H_2. The hydrolysis/condensation reactions in 50wt% toluene were yet more rapid, as judged by the rate of build of polymer molecular weight (entries 1-9**, Table 2.2)**. We have not determined if the hydrolytic processes in toluene/water involve only homogeneous, or a mixture of homogeneous/heterogeneous steps. The efficiency of chain extension will decrease as the living polymer increases in size, particularly above the entanglement limit of about 29000 g mol^{-1} (Note: in the literature, reported entanglement limits ranges from about 15000-35000 g mol^{-1}. Here we use data from the seminal study of Mrozek et al.[38]). This was clearly observed here, as the final M_n were 31-45k g mol^{-1} (entry 9, **Table 2.2**); complete consumption of SiH groups at higher conversion terminates polymerization by forming HOSi-terminated polymers. Re-initiation of such 'dead' polymers is straightforward, however; addition of small quantities of M^HM^H caps the SiOH groups leading to dimerization or higher homologues of the existing polymer (entry 10, **Table 2.2**, **Figure 2.3**F). That is, a beneficial consequence of this process is that, if HSi-terminated polymers are desired, one need only add excess M^HM^H to cap (Silicone-Me_2SiOH → Silicone-$(Me_2SiO)_2Me_2SiH$) and, if desired, grow the polymers before quenching the catalyst. This observation demonstrates that the process is living (entry 10, **Table 2.2**)[26]. Note that, in some cases, these chain extensions are facilitated by removing using distillation the small quantities of low molecular weight materials present, including residual water.

Table 2.2. Molecular weight versus reaction time using hydrolysis of M^HM^H.



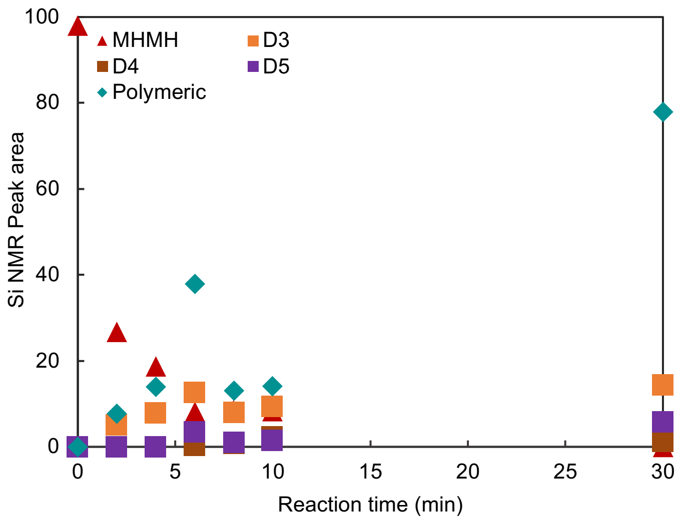
		neat				H_2O/toluene[a]			
Entry	Time(min)	M_n	MW	$Đ_M$	MW[b]	M_n	MW	$Đ_M$	MW[b]
1	0	-	-	-	134	-	-	-	134
2	2	-	-	-	240	-	-	-	250
3	4	-	-	-	300	-	-	-	310
4	6	-	-	-	520[c]	-	-	-	330
5	8	-	-	-	310	-	-	-	440
6	10	-	-	-	330	-	-	-	1030
7	30	21,600	54,000	2.50	-	39,000	69,700	1.79	-
8	60	21,800	63,000	2.90	- [a]	45,300	97,100	2.14	-
9	180	31,200	82,900	2.66	- [a]	45,500	79,900	1.76	-
		Chain	Extension[d]						
10		21,300	33,200	1.56	→	41,900	137,000	3.27	

[a] Reactions performed with 50 wt% M^HM^H dry toluene + liquid water. [b] Calculated based on Si*H* peak area versus SiC*H*3 (integrated to 100) region in the ^1H NMR. [c] The observation at 6 min. is considered an outlier. [d] Starting polymer entry 4, **Table 2.1** contained no cyclics, and none formed by ^{29}Si NMR; mass balance 99.9%.

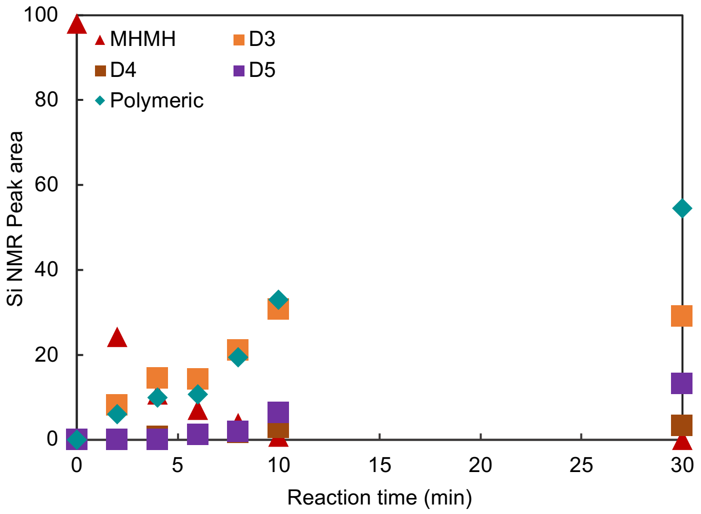
2.4.2. Managing Cyclics

Our objective was to develop simple, practicable polymer syntheses that avoided the need for inert gas blankets; a septum with a bubbler was used to control pressure. One of the challenges presented by M^HM^H is its high volatility, which was problematic with or without solvents. The evolution of cyclics was followed by a combination of gravimetric analysis for volatile products (trapped in a cold trap, that permitted cogenerated H_2 to escape) and, for the polymerization mixture, ^{29}Si NMR, which is particularly sensitive to subtle differences in the chemical environment of D units; it is straightforward to distinguish D_3 (-8.3 ppm), D_4 (-19.1 ppm) and D_5 (-21.5 ppm) from D units in linear polymers (-21.6 ppm)[39]. M^HM^H was the main constituent captured in a cold finger, with small amounts of M^HDM^H, Me_2SiH_2 and D_3 (entries 7,8, **Table 2.1**).

The hydrolysis/condensation of M^HM^H in dilute, homogenous toluene solution was very slow. However, two phase reactions – water/silicone or water/silicone+toluene – were very rapid reactions and complete in < 30 minutes. Reactions can occur at the interface, or within the organic fluid. In the case of the water/silicone mixture, the polymer yield was near 80%, with competing growth in D_3 and small amounts of D_5; D_4 was only inefficiently formed (**Figure 2.4**A). By contrast, even with the small dilution provided in the 50% water/silicone+toluene system, much less polymer was formed at the expense of D_3 and D_5 production, again with little D_4 (**Figure 2.4**B).



A



B

Figure 2.4. A: Conversion to polymer without solvent. B: Conversion to polymer in 50wt% toluene. Rate of reaction (loss of HSi) during hydrolysis of M^HM^H was monitored using ^{1}H NMR and silicone constituents using ^{29}Si NMR. Integrations assumed identical sensitivity for all D units and are normalized to 100%.

Cyclic monomers are important starting materials for silicone synthesis. As noted above, the ring strain in D_3 makes it an attractive starting material for ring opening polymerizations. On the other hand, there is an interest for a variety of reasons in making cyclic free silicones, particularly from an inexpensive starting material like M^HM^H that polymerizes so rapidly. We had hoped to be able to fine tune the polymerization to create high molecular polymers in the absence of cyclics.

After dimerization, $M^HM^H \rightarrow M^HDDM^H$ **2**, the tetramer can undergo hydrolysis to give **3** then further chain extension, or cyclization to give D_4 (**Figure 2.3**D vs G). The generation of D_4 during polymerization under equilibrating conditions is favored both enthalpically and entropically, possessing virtually zero ring strain, and the SiO bond strength in cyclics is similar to those in linear chains and larger number of molecules than in linear polymers[1]. In neither of the cases examined was D_4 a significant product (**Figure 2.4**, **Table 2.1**). Thus, under these conditions of chain extension of **3** outcompetes cyclization (D or K vs G). Adding small amounts of toluene led from an increase in D_4 product only from 1% to 3%.

More problematic, with respect to cyclics, was the formation of D_3 and, to a lesser extent, D_5. The most concentrated (neat) solution produced 13% D_3, but in the diluted sample 33% of the product mixture was D_3, in addition to linear polymer (entries 7,8, **Table 2.1**). These data show that, even in the presence of water, the Chojnowski metathesis to give D_3 and Me_2SiH_2 from **2** is highly competitive with hydrolysis (**Figure 2.3**H). The presence of D_5 in such high quantities is consistent with chain extension from **3** to **4** and then a different Chojnowski metathesis leading to D_5 and Me_2SiH_2 (e.g., **Figure 2.3**K,L)[40]. It is believed that the formation of M^HDM^H, found in the cold trap, can be ascribed to reactions with Me_2SiH_2 with disiloxanes in the presence of $B(C_6F_5)_3$ (**Figure 2.3**M).

Previous experience with polymer chain extension of HSi- telechelic polymers with water did not lead to the formation of cyclics. Under these conditions with low catalyst concentrations (0.02%)(BCF/H_2O and $B(C_6F_5)_3{\cdot}OH_2$[41]) redistribution reactions are similarly not efficient. While the reactions here were complete in 30 minutes, there was no change in the cyclics profile between 30-180 minutes (SM); redistribution would favor the formation of D_4 which, of the cyclics characterized, was formed in the lowest concentration. Under equilibration in the absence of solvents, the normal concentration of D_4 is ~15%[4]. Similarly, redistribution cannot explain the higher concentrations of D_3 and D_5.

The formation of cyclics vs linears is therefore a consequence of the kinetics of intra- vs intermolecular reactions within a silicone/organic solvent, or at the water interface. When done in 50wt% toluene, more cyclics, particularly D_3, were produced than when the only solvent for the silicone was M^HM^H and silicone products themselves, i.e., than when the system was more concentrated (**Figure 2.4**B vs A). This shows the power of Chojnowski metathesis. The conversion of **2** → D_3 (and **4** → D_5) effectively competes with hydrolysis of **2** → **5** when the reaction is slightly diluted, and is an important reaction even when done neat. The formation and then disappearance in the ^{29}Si NMR of a maximum of 1.4% of Me_2SiH_2 was observed based on D-units (for full details of all intermediates from **Figure 2.4**, see SM). M^HDM^H, observed in the cold trap, could arise from reaction of Me_2SiH_2 with **3** and there may be additional homologation reactions that consume this reactive material.

We cannot distinguish between polymerization involving hydrolysis/condensation (**Figure 2.3**B-E) vs the reaction between D_3 and hydrosiloxanes, as shown by Chojnowski et al. (**Figure 2.3**I,J)[35]. However, the rapid rate and high molecular weight support the hydrolytic/condensation process as dominant.

In part, the objectives of the work were met. It was possible to obtain rapid polymerization of M^HM^H with water to get medium molecular weight linear silicones terminated, if desired, with SiH groups. High concentrations facilitated the rates of polymerization. The process is living and any premature suppression of polymerization by complete hydrolysis to SiOH groups can be overcome by the addition of small amounts of M^HM^H, preferably after removing any residual water, a process that allows much longer polymers to form. However, unlike the hydrolytic process with starting materials that have a higher MW (e.g., DP > 6)[26], polymerization competed with undesired cyclic formation. Distinctions between these are previous studies are mostly related to concentrations. The important precedent work of Ganachaud showed that with very high water and higher catalyst concentrations, complex equilibration reactions occur under less controlled conditions[34]. On the other hand, with exceptionally low concentrations of water and catalysts, Chojnowski et al. showed metathesis of **2** dominates the process; one can elect to capture and then use D_3 for polymerization[21,22]. This work demonstrates the power of Chojnowski metathesis. Even without a solvent efficient formation of D_3 is observed, up to 33%, made worse even by small amounts of solvent.

2.5. Conclusions

The simple, efficient and mild process of hydrolyzing M^HM^H leads to high molecular weight PDMS (maximum 153,900 g mol^{-1}) a controllable and 'living' manner. The reactions can be completed in as short a time as 30 minutes, in two phase reactions using either bulk water with neat M^HM^H or M^HM^H in dry toluene (50wt%). Under either set of conditions, however, low D_4 (1-3%) content as produced and higher values of D_5 (2-10%) and particularly D_3 (13-33%). These outcomes are attributed to the particular efficiency of Chojnowski metathesis in organic solvents, even with high water content.

2.6. Acknowledgments

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada.

2.7. References

1. Chojnowski, J.; Cypryk, M. Synthesis of Linear Polysiloxanes. In *Silicon-Containing Polymers: The Science and Technology of Their Synthesis*, Jones, R.G., Ando, W., Chojnowski, J., Eds. Springer: 2000; pp. 1-42.
2. Kantor, S.W.; Grubb, W.T.; Osthoff, R.C. The Mechanism of the Acid- and Base-catalyzed Equilibration of Siloxanes. *J. Am. Chem. Soc.* **1954**, *76*, 5190-5197.
3. Chojnowski, J. Polymerization. In *Siloxane Polymers*, Clarson, S.J., Semlyen, J.A., Eds. Prentice Hall: Englewood Cliffs, NJ, 1993; pp. 1-71.
4. Wright, P.V.; Semlyen, J.A. Equilibrium ring concentrations and the statistical conformations of polymer chains: Part 3. Substituent effects in polysiloxane systems. *Polymer* **1970**, *11*, 462-471.
5. Franzen, A.; Greene, T.; Van Landingham, C.; Gentry, R. Toxicology of octamethylcyclotetrasiloxane (D4). *Toxic. Lett.* **2017**, *279*, 2-22.
6. Wang, D.-G.; Steer, H.; Tait, T.; Williams, Z.; Pacepavicius, G.; Young, T.; Ng, T.; Smyth, S.A.; Kinsman, L.; Alaee, M. Concentrations of cyclic volatile methylsiloxanes in biosolid amended soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada. *Chemosphere* **2013**, *93*, 766-773.
7. European Chemical Agency. Restriction proposal for siloxanes (D4, D5, D6) in personal care products. *ECHA* **2020**, *echa.europa.eu/-/echa-s-committees-conclude-on-five-restrictions*.
8. Environment Canada Regulation on D_4.
www.canada.ca/en/environment-climate-change/services/management-toxic-substances/list-canadian-environmental-protection-act/slioxane-d4.html,
9. Peters, M.A.; Belu, A.M.; Linton, R.W.; Dupray, L.; Meyer, T.J.; DeSimone, J.M. Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers. *J. Am. Chem. Soc.* **1995**, *117*, 3380-3388.
10. Frye, C.L.; Salinger, R.M.; Fearon, F.W.G.; Klosowski, J.M.; DeYoung, T. Reactions of organolithium reagents with siloxane substrates. *J. Org. Chem.* **1970**, *35*, 1308-1314.
11. Maschke, U.; Wagner, T.; Coqueret, X. Synthesis of high-molecular-weight poly(dimethylsiloxane) of uniform size by anionic polymerization, 1. Initiation by a monofunctional lithium siloxanolate. *Makromol. Chem.* **1992**, *193*, 2453-2466.
12. Fuchise, K.; Igarashi, M.; Sato, K.; Shimada, S. Organocatalytic controlled/living ring-opening polymerization of cyclotrisiloxanes initiated by water with strong organic base catalysts. *Chem. Sci.* **2018**, *9*, 2879-2891.
13. Brook, M.A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000.
14. Pesti, J.; Larson, G.L. Tetramethyldisiloxane: A Practical Organosilane Reducing Agent. *Org. Proc. Res. Devel.* **2016**, *20*, 1164-1181.

15. Larson, G.L. Silicon-Based Reducing Agents. *Gelest* **2004**.
16. Schneider, A.F.; Chen, Y.; Brook, M.A. Trace water affects tris(pentafluorophenyl)borane catalytic activity in the Piers–Rubinsztajn reaction. *Dalton Trans.* **2019**, *48*, 13599-13606.
17. Piers, W.E. The Chemistry of Perfluoroaryl Boranes. In *Adv. Organomet. Chem.*, Academic Press: 2004; Vol. 52, pp. 1-76.
18. Jacobsen, H.; Berke, H.; Doring, S.; Kehr, G.; Erker, G.; Frohlich, R.; Meyer, O. Lewis acid properties of tris(pentafluorophenyl)borane. Structure and bonding in L-B(C_6F_5)$_3$ complexes. *Organometallics* **1999**, *18*, 1724-1735.
19. Zheng, S.; Liao, M.; Chen, Y.; Brook, M.A. Dissolving used rubber tires. *Green Chem.* **2020**, *22*, 94-102, doi:10.1039/C9GC03545A.
20. Rubinsztajn, S.; Cella, J.A. A New Polycondensation Process for the Preparation of Polysiloxane Copolymers. *Macromolecules* **2005**, *38*, 1061-1063.
21. Chojnowski, J.; Rubinsztajn, S.; Cella, J.A.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kaźmierski, K. Mechanism of the B(C6F5)3-Catalyzed Reaction of Silyl Hydrides with Alkoxysilanes. Kinetic and Spectroscopic Studies. *Organometallics* **2005**, *24*, 6077-6084.
22. Chojnowski, J.; Fortuniak, W.; Kurjata, J.; Rubinsztajn, S.; Cella, J.A. Oligomerization of Hydrosiloxanes in the Presence of Tris(pentafluorophenyl)borane. *Macromolecules* **2006**, *39*, 3802-3807.
23. Zhou, D.; Kawakami, Y. Tris(pentafluorophenyl)borane as a Superior Catalyst in the Synthesis of Optically Active SiO-Containing Polymers. *Macromolecules* **2005**, *38*, 6902-6908.
24. Brook, M.A.; Grande, J.B.; Ganachaud, F. New Synthetic Strategies for Structured Silicones Using B(C_6F_5)$_3$. In *Silicon Polymers*, Muzafarov, A.M., Ed. Springer Berlin Heidelberg: Berlin, Heidelberg, 2011; 10.1007/12_2009_47pp. 161-183.
25. Brook, M.A. New Control Over Silicone Synthesis using SiH Chemistry: The Piers–Rubinsztajn Reaction. *Chem. Eur. J.* **2018**, *24*, 8458-8469.
26. Liao, M.; Schneider, A.F.; Laengert, S.E.; Gale, C.B.; Chen, Y.; Brook, M.A. Living synthesis of silicone polymers controlled by humidity. *Eur. Polym. J.* **2018**, *107*, 287-293.
27. Schneider, A.F.; Brook, M.A. High-Throughput Synthesis and Characterization of Aryl Silicones Using the Piers-Rubinsztajn Reaction. *Chem. Eur. J.* **2019**, *0*.
28. Schneider, A.F.; Lu, E.K.; Lu, G.; Brook, M.A. Facile synthesis of phenyl-rich functional siloxanes from simple silanes. *J. Polym. Sci.* **2020**, *n/a*.
29. Morgan, J.; Chen, T.; Hayes, R.; Dickie, T.; Urlich, T.; Brook, M.A. Facile synthesis of dendron-branched silicone polymers. *Polym. Chem.* **2017**, *8*, 2743-2746.
30. Thompson, D.B.; Brook, M.A. Rapid Assembly of Complex 3D Siloxane Architectures. *J. Am. Chem. Soc.* **2008**, *130*, 32-33.
31. Zheng, S.; Liang, S.; Chen, Y.; Brook, M.A. Hyperbranched Silicone MDTQ Tack Promoters. *Molecules* **2019**, *24*.

32. Kupareva, A.; Mäki-Arvela, P.; Grénman, H.; Eränen, K.; Murzin, D.Y. Base-Catalyzed Transformations of Tetramethyldisiloxane. *Ind. Eng. Chem. Res.* **2013**, *52*, 10080-10088.
33. Addis, D.; Das, S.; Junge, K.; Beller, M. Selective Reduction of Carboxylic Acid Derivatives by Catalytic Hydrosilylation. *Angew. Chem. Int. Ed.* **2011**, *50*, 6004-6011.
34. Longuet, C.; Joly-Duhamel, C.; Ganachaud, F. Copolycondensation of regular functional silane and siloxane in aqueous emulsion using $B(C_6F_5)_3$ as a catalyst. *Macromol. Chem. Phys.* **2007**, *208*, 1883-1892.
35. Chojnowski, J.; Rubinsztajn, S.; Fortuniak, W.; Kurjata, J. Oligomer and Polymer Formation in Hexamethylcyclotrisiloxane (D3) – Hydrosilane Systems Under Catalysis by tris(pentafluorophenyl)borane. *J. Inorg. Organomet. Polym. Mat.* **2007**, *17*, 173-187.
36. Babonneau, F.; Gualandris, V.; Maquet, J.; Massiot, D.; Janicke, M.T.; Chmelka, B.F. Newly Applied Two-Dimensional Solid-State NMR Correlation Techniques for the Characterization of Organically Modified Silicates. *J. Sol-Gel Sci. Technol.* **2000**, *19*, 113-117.
37. Taylor, R.B.; Parhboo, B.; Fillmore, D.M. Fillmore, D. M. Nuclear Magnetic Resonance Spectroscopy, In , Smith, A. L., Ed., Wiley, 1991, Chap. 12, . In *Analysis of Silicones*, Smith, A.L., Ed. Wiley: 1991; pp. 347-420.
38. Mrozek, R.A.; Cole, P.J.; Otim, K.J.; Shull, K.R.; Lenhart, J.L. Influence of solvent size on the mechanical properties and rheology of polydimethylsiloxane-based polymeric gels. *Polymer* **2011**, *52*, 3422-3430.
39. Williams, E.A. NMR Spectroscopy of Organosilicon Compounds. In *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z., Eds. John Wiley & Sons: Chichester, UK, 1989; Vol. 1, p. 511.
40. We thank a referee for this suggestion.
41. Rabanzo-Castillo, K.M.; Kumar, V.B.; Söhnel, T.; Leitao, E.M. Catalytic Synthesis of Oligosiloxanes Mediated by an Air Stable Catalyst, $(C_6F_5)_3B(OH_2)$. *Frontiers in Chemistry* **2020**, *8*.

2.8. Appendix 1- Supporting Information

2.8.1. Calculation of polymer molecular weight (M_n) using ^{1}H NMR

Here, we use the 4 min (50% wt. dry toluene) sample as an example (peak integration Si*H*: SiCH_3=7.65:100) for calculating MW using ^{1}H NMR.

We assume all the SiH functional groups are at the termini (**Figure S2.1**), then the Si*H* peak can be integrated into 2 (one SiH at each end) and if the number of silicon in SiCH_3 assigned to x (6 hydrogens attached to 1 silicon), we can write the equation as follow.

$$\frac{2}{7.65}=\frac{6x}{100}$$

$$x=4.357$$

The mass of the end group is 59 ($Si(CH_3)_2H$: 28+15*2+1=59 g mol^{-1}), two end group plus one oxygen (not containing in the repeating unit) should be as follows.

MW of two SiH end group and one oxygen atom=59*2+16=134 g mol^{-1}

Apart from 2 Si at the end, there are 2 Si left in the repeating unit (MW of the repeating unit $Si(CH_3)_2O$: 28+15*2+16=74 g mol^{-1})' thus, we can calculate the molecular weight as follow.

$$MW=(x-2)*74+134=308\approx310\ g\ mol^{-1}$$

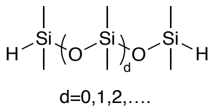


Figure S2.1. The proposed structure for low molecular weight silicones

2.8.2. 'Wet' toluene as the only water source ([OH]/[SiH]=1, [$B(C_6F_5)_3$]/[SiH]=0.02 mol%)

To a pre-dried 1.0 L three neck round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 0.23 g, 0.0017 mol) and 'wet' toluene (71.62 mL, 466.58 ppm water, 0.0016 mmol of water present) and then capped with a septum with a needle with a bubbler open to atmosphere to balance the pressure. The mixture was stirred for 5-10 minutes prior to the addition of $B(C_6F_5)_3$ stock solution in dry toluene (0.001 M, 0.06 mL, 0.0006 mmol). The $B(C_6F_5)_3$ stock solution was added by Eppendorf pipette into the flask through opening the septa. No obvious bubble formation was observed once catalyst was added. The mixture was stirred at room temperature for 24h and the aliquot was taken after 5h reaction time to run ^1H NMR. Finally, the reaction was quenched by alumina for 5h and the residual water droplet was removed by adding sodium sulfate.

5 h reaction time:

^1H NMR (600 MHz, chloroform-*d*): δ 4.71-4.75 (Si*H,* m, 8.35H), 3.76-3.80 ($Si(CH_3)_2H_2$, sep, *J* =4.1 Hz, 2.22H), 1.42 (H_2O, s, 1.42H), 0.09-0.22 ($Si-CH_3$, m, 100H) ppm.

24 h reaction time:

^1H NMR (600 MHz, chloroform-*d*): δ 4.70-4.74 (Si*H*, m, 8.35H), 3.76-3.79 ($Si(CH_3)_2H_2$, sep, *J* =4.1 Hz, 3.68H), 1.46 (H_2O, s, 2.12H), 0.08-0.21 ($Si-CH_3$, m, 100H) ppm.

2.8.3. Characterization of high molecular weight PDMS preparation using hydrolysis (Table 2.1, Entry 1-6)

Entry 1: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.54 (H_2O, s, 4.95H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.27 (*D$_3$*, s, 2.02Si), -21.50-(-) 22.49 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=43,700, M_w=129,200 g mol^{-1}, $Đ_M$: 2.97. (Yield: 70.1%).

Entry 2: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.55 (H_2O, s, 12.18H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.26 (*D$_3$*, s, 35.50Si), -21.93-(-) 22.16 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=52,700, M_w=105,400 g mol^{-1}, $Đ_M$: 2.00. (Yield: 71.3%).

Entry 3: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.54 (H_2O, s, 5.84H), 0.06-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.27 (*D$_3$*, s, 5.05Si), -19.06 (D_4, s, 1.29Si), -21.50-(-) 22.49 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=41,600, M_w=101,500 g mol^{-1}, $Đ_M$: 2.44. (Yield: 70.6%).

Entry 4: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.54 (H_2O, s, 1.62H), 0.07-0.17 (Si-CH_3, m, 100H) ppm.

^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.29 (*D$_3$*, s, 3.69Si), -10.36 (s, 1.55Si), -19.06 (D_4, s, 2.74Si), -21.50-(-) 22.50 (*D*, m, 100Si) ppm. (GPC, Toluene, before kugelrohr) M_n=20,700, M_w=32,500 g mol^{-1}, $Đ_M$: 1.57, (GPC, Toluene, after kugelrohr) M_n=20,700, M_w=32,500 g mol^{-1}, $Đ_M$: 1.57. (Yield: 79.3%).

Entry 5: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.54 (H_2O, s, 12.13H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.26 (D_3, s, 11.90Si), -19.06 (D_4, s, 2.87Si), -21.50-(-) 22.49 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=111,400, M_w=221,500 g mol^{-1}, $Đ_M$: 1.99. (Yield: 95.6%).

Entry 6: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.54 (H_2O, s, 2.82H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.26 (D_3, s, 3.07Si), -19.06 (D_4, s, 3.06Si), -21.49-(-) 22.48 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=152,500, M_w=314,000 g mol^{-1}, $Đ_M$: 2.06. (Yield: 82.9%).

Table S2.1. Summary of D_3, D_4 and D_5 formation in Entries 1-6 (**Table 2.1**).

Entry	End group	D_3 (%)	DM^{OH}	D_4 (%)	D_5 (%)	D (%)[a]
		-8.3 ppm	-10.4 ppm	-19.1 ppm	-21.5 ppm	-22ppm
1	SiOH	8.45	0	2.54	9.46	79.55
2	SiOH	12.93	0	0	10.78	76.29
3	SiOH	4.21	0	1.82	8.21	85.76
4	SiOH	3.74	0.88	2.27	3.82	89.29
5	SiOH	8.95	0	2.04	8.38	80.63
6	SiOH	3.88	0	3.38	5.4	87.34

[a] All peaks appeared at D unit are normalized to 100.

2.8.4. Characterization for hydrolysis reactions capturing volatiles using a cold trap condition (Table S2.1, Entry 7,8)

Table S2.2 The yield of different compounds formed from hydrolysis of M^HM^H under cold trap condition

Conditions	Actual starting material mass (g)[a]	D_3 (%)[b]	D_4 (%)	D_5 (%)	Polymeric (%)	M^HDM^H (%)	M^HDM^{OH} (%)	Me_2SiH_2 (%)
Neat	10.3236	13.32	0.76	2.32	67.96	1.11	0.59	11.31
50 wt% dry toluene	10.8532	33.01	2.81	10.23	49.89	0.43	0.25	2.95

[a] Calculation deduct the mass of the unreacted M^HM^H collected in the cold trap condenser. [b] The ratio of each component was identified by ^{29}Si NMR.

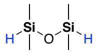
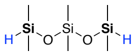
2.8.5. Neat (Table 2.1, Entry 7)

To a pre-dried 100.0 mL round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 10.38 g, 77.5 mmol) with distilled water (18 g mol^{-1}, 1.34 mL, 74.4 mmol). To the mixture was added $B(C_6F_5)_3$ stock solution in dry toluene (0.1 M, 0.298 ml, 0.0298 mmol). The cold trap condenser was submerged in dry ice/acetone with the addition of acetone and was directly connected to the round-bottomed flask through 6 mm O.D. Pyrex tubing. The mixture in the round bottle flask was stirred at room temperature for 3h and the reaction was quenched by alumina and the residual water droplet was removed by adding sodium sulfate with 5h quenching time. Before the work up procedures, the mixtures in the round bottle flask were weighted and characterized by ^{1}H, ^{29}Si NMR (SR) followed by filtration through Celite under reduced pressure.

Cold trap: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.70 (Si*H*, sep, *J* =2.8 Hz, 13.99H), 3.74-3.77 ($Si(CH_3)_2H_2$, sep, *J* =4.1 Hz, 1.89H), 1.52 (H_2O, s, 0.41H), 0.07-0.20 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -4.49 (M^HM^H, s, 21.91Si), -6.67 (M^HDM^H, s, 1.81Si), -8.35 (D_3, s, 1.00Si), -17.79 ($M^{H}\mathit{D}M^{OH}$, s, 0.96Si), -37.82 ($Me_2\underline{Si}H_2$, s, 18.38Si) ppm. Total Mass in trap: 2.798 g, 23.9%mass.

Polymeric material: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.63 (Si*H*, s, 0.04H), 1.54 (H_2O, s, 1.90H), 0.06-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -8.28 (D_3, s, 18.70Si), -19.07 (D_4, s, 1.12Si), -21.50 (D_5, S, 3.41Si), -21.95- (-)22.17 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=20,500, M_w=37,400 g mol^{-1}, $Đ_M$:1.82. Total Mass in reaction vessel: 8.646 g, 73.8%mass (total recovery, 97.7%).

Table S2.3 GC-MS data for volatile products collected in cold trap using hydrolysis of tetramethyldisiloxane in neat

Compound	Structures	Elution time (min)	MW (g mol^{-1})	GC-MS relative ratio (%)	Yield (%)[a]
M^HM^H		1.6	134.32	93.8	23.9
M^HDM^H		2.9	208.48	6.2	

[a] Yield was measured as mass balance before and after the reaction in the cold trap.

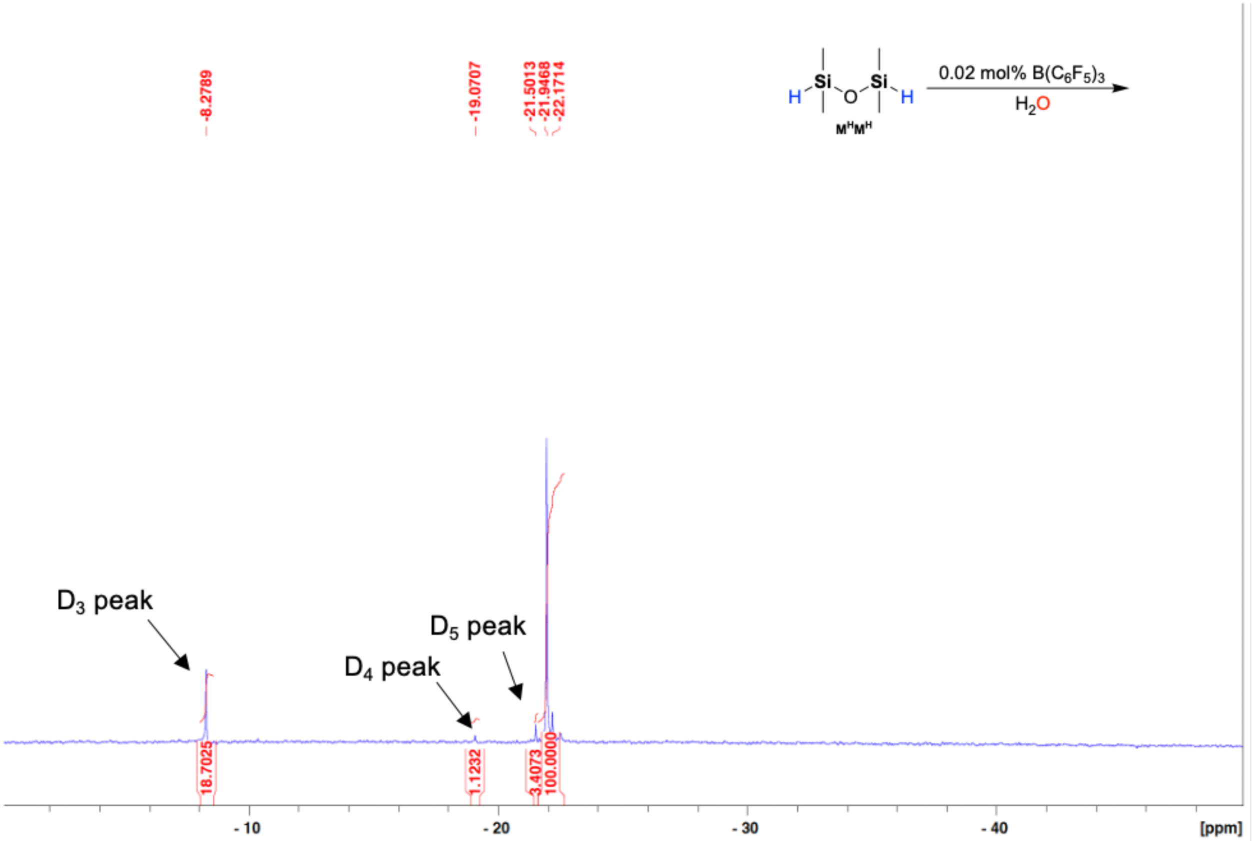


Figure S2.2. ^{29}Si NMR spectra of the cold-trap reaction using M^HM^H and water in the presence of $B(C_6F_5)_3$ catalyst (neat).

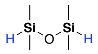
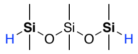
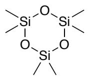
2.8.6. 50% wt. toluene (Table 2.1, Entry 8)

To a pre-dried 100.0 ml round-bottomed flask was added tetramethyldisiloxane (M^HM^H) (134 g mol^{-1}, 10.32 g, 77.0 mmol) with distilled water (18 g mol^{-1}, 1.34 mL, 74.4 mmol) and dry toluene (6.73 mL, 5.83 g, m_{MHMH}(g)/$V_{toluene}$ (mL)=1.53, m_{MHMH}+m_{H2O}=11.66 g). To the mixture was added $B(C_6F_5)_3$ stock solution in dry toluene (0.1 M, 0.298 ml, 0.0298 mmol). The cold trap condenser was submerged in dry ice/acetone with the addition of acetone and was directly connected to the round-bottomed flask through 6 mm O.D. Pyrex tubing. The mixture in the round bottle flask was stirred at room temperature for 3h and the reaction was quenched by alumina and the residual water droplet was removed by adding sodium sulfate with 5h quenching time. Before the work up procedures, the mixtures in the round bottle flask were weighted and characterized by ^{1}H, ^{29}Si NMR (SR) followed by filtration through Celite under reduced pressure.

Cold trap: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.68-4.71 (Si*H*, sep, *J* =2.8 Hz, 10.44H), 3.74-3.77 ($Si(CH_3)_2H_2$, sep, *J* =4.1 Hz, 8.42H), 1.53 (H_2O, s, 0.32H), 0.07-0.20 ($Si\text{-}CH_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -4.49 ($M^{H}M^{H}$, s, 42.30Si), -6.66 ($M^{H}DM^{H}$, s, 2.44Si), -8.33 (D_3, s, 1.00Si), -17.77 ($M^{H}DM^{OH}$, s, 1.40Si), -37.82 ($Me_2\underline{Si}H_2$, s, 16.67Si) ppm. Total Mass in trap: 1.224 g, 10.5%mass.

Polymeric material: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.70 (Si*H*, s, 0.01H), 1.50 (H_2O, s, 0.42H), 0.08-0.18 ($Si\text{-}CH_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -8.26 (D_3, s, 65.81Si), -19.02 (D_4, s, 5.63Si), -21.44 (D_5, s, 20.50), -22.11- (-) 22.43 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=40,000, M_w=63,100 g mol^{-1}, $Đ_M$: 1.58. Total Mass in reaction vessel: 10.393 g, 89.1%mass (total recovery, 99.6%).

Table S2.4. GC-MS data for volatile products collected in cold trap using hydrolysis of tetramethyldisiloxane in 50% wt. dry toluene

Compound	Structures	Elution time (min)	MW (g mol^{-1})	GC-MS relative ratio (%)	Yield (%)[a]
$M^{H}M^{H}$		1.6	134.32	85.6	10.5
$M^{H}DM^{H}$		2.9	208.48	11	
D_3		4.7	222.46	3.4	

[a] Yield was measured as mass balance before and after the reaction in the cold trap.

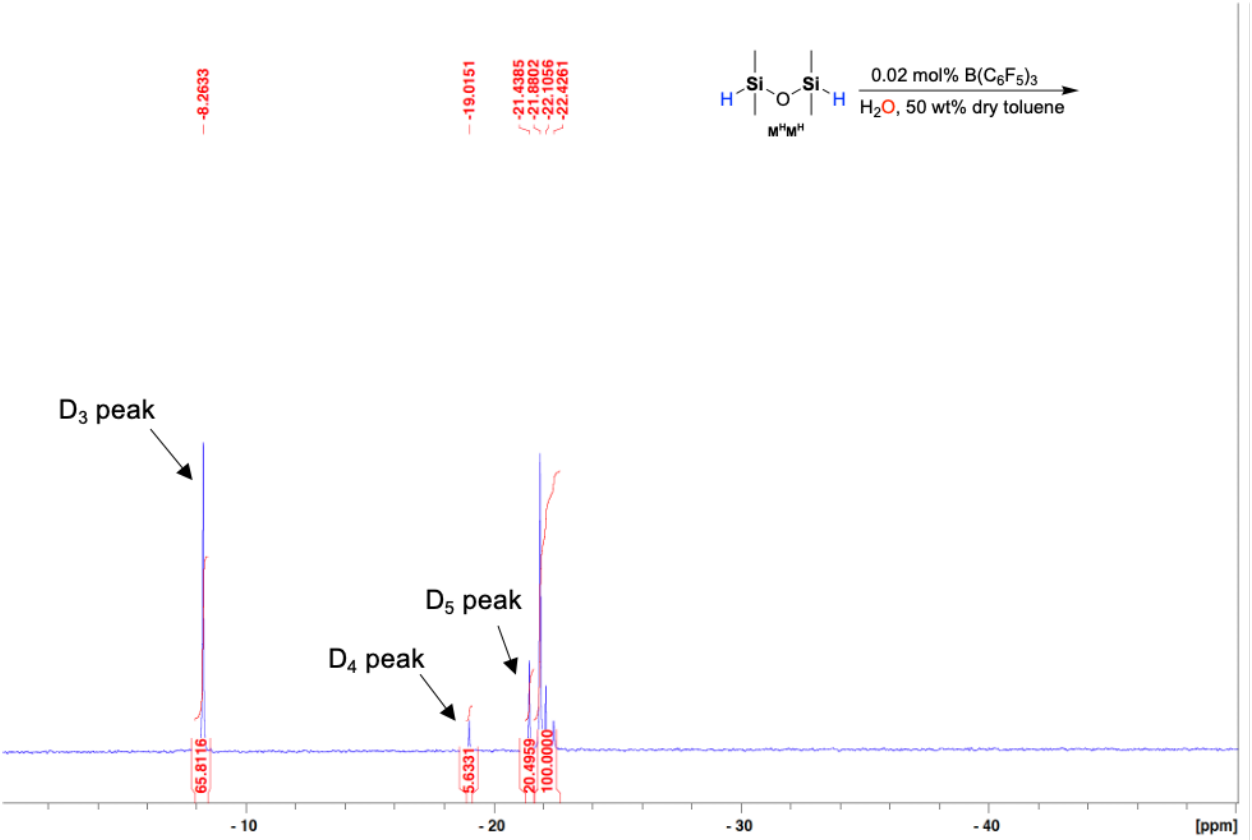
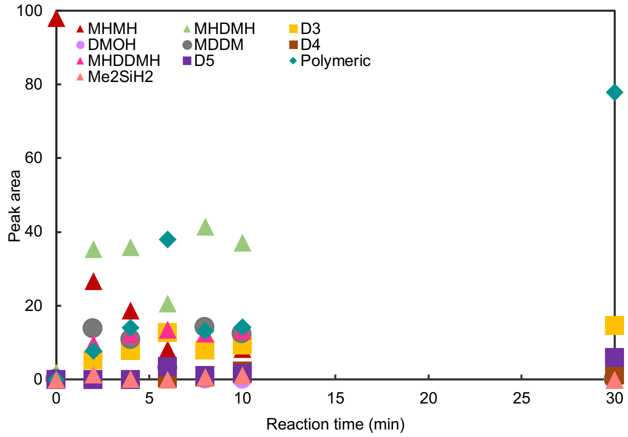
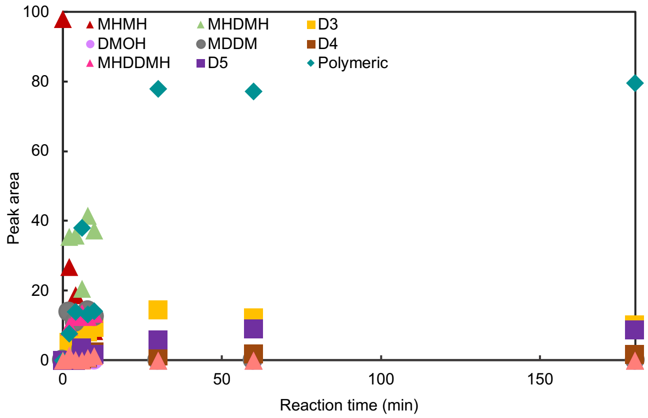


Figure S2.3. ^{29}Si NMR spectra of the cold-trap reaction using M^HM^H and water in the presence of $B(C_6F_5)_3$ catalyst (50 wt% dry toluene).

2.8.7. Monitoring hydrolysis/condensation processes neat (Table 2.2, Entries 1-9)



A



B

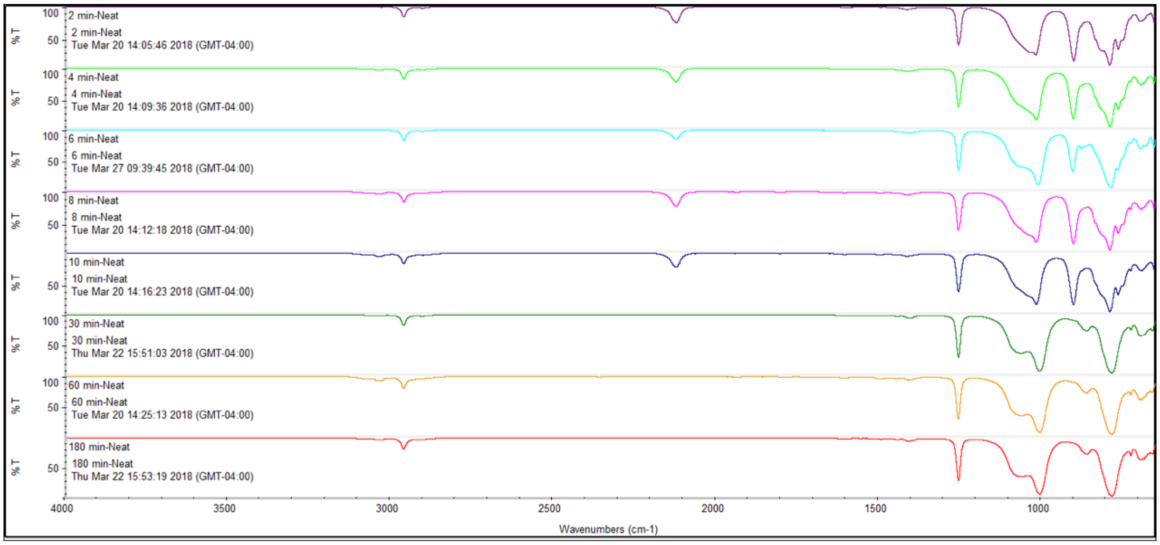


Figure S2.4. A: Plot of reaction constituents based on ^{29}Si NMR (neat). While small differences will exist in the sensitivity of the M vs D units (even in the presence of Cr(acac)$_3$) the presented data represents the Si monomer concentration normalized to 100% B: IR spectra at the same time points.

0 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.68 (Si*H*, sep, *J* = 2.8 Hz, 14.76H), 1.54 (*H*$_2$O, s, 0.26H), 0.19 (Si-C*H*$_3$, d, *J* =2.8 Hz, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.45 ($M^{\mathrm{H}}M^{\mathrm{H}}$, s, 98.04Si), -6.63 ($M^{\mathrm{H}}\mathrm{D}M^{\mathrm{H}}$, s, 1.96Si) ppm.

2 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.71 (Si*H*, m, 9.59H), 3.74-3.77 (Si(CH$_3$)$_2$*H*$_2$, sep, *J* =3.9 Hz, 0.09H), 1.53 (*H*$_2$O, s, 0.55H), 0.07-0.20 (Si-C*H*$_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.49 ($M^{\mathrm{H}}M^{\mathrm{H}}$, s, 26.80 Si), -6.66-(-)6.88 ($M^{\mathrm{H}}\mathrm{D}M^{\mathrm{H}}$, m, 35.36Si), -8.33 ($D_3$, s, 5.13Si), -17.76 ($\mathrm{M}^{\mathrm{H}}D\mathrm{M}^{\mathrm{OH}}$, s, 13.77Si), -19.72-(-) 19.83 ($\mathrm{M}^{\mathrm{H}}DD\mathrm{M}^{\mathrm{H}}$, 9.74), -21.69-(-)21.78 (*D*, m, 7.73Si), -37.85 (Me$_2$*Si*H$_2$, s, 1.46Si) ppm.

4 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.71 (Si*H*, m, 7.87H), 3.74-3.77 (Si(CH$_3$)$_2$*H*$_2$, sep, *J* =4.1 Hz, 0.12H), 1.53 (*H*$_2$O, s, 0.46H), 0.07-0.20 (Si-C*H*$_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -

4.49 ($M^{H}M^{H}$, s, 18.80 Si), -6.67-(-)6.90 ($M^{H}\mathrm{D}M^{H}$, m, 35.89Si), -8.33 (D_3, s, 7.88Si), -17.76 ($\mathrm{M^{H}}D\mathrm{M^{OH}}$, s, 10.85Si), -19.83-(-) 19.87 ($\mathrm{M^{H}}DD\mathrm{M^{H}}$, 12.40), -21.70-(-)21.91 (D, m, 14.01Si), -37.84 ($\mathrm{Me_2}Si\mathrm{H_2}$, s, 0.18Si) ppm.

6 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.71 (SiH, m, 4.58H), 3.74-3.77 ($\mathrm{Si(CH_3)_2}H_2$, sep, J =4.2 Hz, 0.02H), 1.54 ($H_2\mathrm{O}$, s, 0.44H), 0.07-0.20 ($\mathrm{Si\text{-}C}H_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $\mathrm{Cr(acac)_3}$): δ -4.48 ($M^{H}M^{H}$, s, 8.18 Si), -6.66-(-)6.90 ($M^{H}\mathrm{D}M^{H}$, m, 20.58Si), -8.32 (D_3, s, 12.68Si), -17.75 ($\mathrm{M^{H}}D\mathrm{M^{OH}}$, s, 3.17Si), -19.10 ($D_4$, s, 0.39Si), -19.72-(-) 19.88 ($\mathrm{M^{H}}DD\mathrm{M^{H}}$, 13.51), -21.53 ($D_5$, s, 3.49Si), -21.69-(-)22.52 (D, m, 38Si) ppm.

8 min: : ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.71 (SiH, m, 7.51H), 3.73-3.77 ($\mathrm{Si(CH_3)_2}H_2$, sep, J =4.1 Hz, 0.28H), 1.53 ($H_2\mathrm{O}$, s, 0.41H), 0.07-0.20 ($\mathrm{Si\text{-}C}H_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $\mathrm{Cr(acac)_3}$): δ -4.49 ($M^{H}M^{H}$, s, 8.40 Si), -6.66-(-)6.90 ($M^{H}\mathrm{D}M^{H}$, m, 41.50Si), -8.32 (D_3, s, 8.03Si), -17.75 ($\mathrm{M^{H}}D\mathrm{M^{OH}}$, s, 14.11Si), -19.10 ($D_4$, s, 0.75Si), -19.72-(-) 19.86 ($\mathrm{M^{H}}DD\mathrm{M^{H}}$, 12.45), -21.53 ($D_5$, s, 1.00Si), -21.69-(-)22.20 (D, m, 13.13Si), -37.84 ($\mathrm{Me_2}Si\mathrm{H_2}$, s, 0.63Si) ppm.

10 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.71 (SiH, m, 7.12H), 3.73-3.77 ($\mathrm{Si(CH_3)_2}H_2$, sep, J =4.1 Hz, 0.19H), 1.53 ($H_2\mathrm{O}$, s, 0.38H), 0.07-0.20 ($\mathrm{Si\text{-}C}H_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $\mathrm{Cr(acac)_3}$): δ -4.49 ($M^{H}M^{H}$, s, 8.35 Si), -6.66-(-)6.90 ($M^{H}\mathrm{D}M^{H}$, m, 37.22Si), -8.33 (D_3, s, 9.40Si), -17.75 ($\mathrm{M^{H}}D\mathrm{M^{OH}}$, s, 12.47Si), -19.10 ($D_4$, s, 2.25Si), -19.72-(-) 19.86 ($\mathrm{M^{H}}DD\mathrm{M^{H}}$, 13.33), -21.53 ($D_5$, s, 1.58Si), -21.78-(-)21.82 (D, m, 14.15Si), -37.84 ($\mathrm{Me_2}Si\mathrm{H_2}$, s, 1.25Si) ppm.

30 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.69-4.71 (Si*H*, m, 0.06H), 1.56 (H_2O, s, 7.49H), 0.06-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.27 (D_3, s, 14.52Si), -10.38 (M^{OH}D, 0.44Si), -19.07 (D_4, s, 1.20Si), -21.50 (D_5, s, 5.84Si), -21.94-(-)22.49 (*D*, m, 78.00Si) ppm. (GPC, Toluene) M_n=21,600, M_w=54,000 g mol^{-1}, $Đ_M$: 2.50.

60 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.62 (Si*H*, s, 0.03H), 1.56 (H_2O, s, 4.39H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.28 (D_3, s, 12.04Si), -19.07 (D_4, s, 1.77Si), -21.50 (D_5, s, 8.89Si), -21.95-(-)22.49 (*D*, m, 77.30Si) ppm. (GPC, Toluene) M_n=21,800, M_w=63,000 g mol^{-1}, $Đ_M$: 2.90.

180 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.53 (H_2O, s, 0.57H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -8.28 (D_3, s, 10.07Si), -19.07 (D_4, s, 1.64Si), -21.51 (D_5, s, 8.60Si), -21.95-(-)22.50 (*D*, m, 79.69Si) ppm. (GPC, Toluene) M_n=31,200, M_w=82,900 g mol^{-1}, $Đ_M$: 2.66.

2.8.8. Characterizations for monitoring hydrolysis process under 50% wt. dry toluene (Table 2.2, Entry 1-9)

0 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.67-4.68 (Si*H*, sep, *J* = 2.8 Hz, 14.76H), 1.54 (H_2O, s, 0.26H), 0.19 (Si-CH_3, d, *J* =2.8 Hz, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.45 (M^HM^H, s, 98.04Si), -6.63 (M^HDM^H, s, 1.96Si) ppm.

2 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.68-4.72 (Si*H*, m, 9.43H), 3.75-3.77 (Si(CH$_3$)$_2H_2$, sep, *J* =4.1 Hz, 0.10H), 1.52 (H_2O, s, 1.25H), 0.07-0.20 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.41 ($M^{H}M^{H}$, s, 24.18 Si), -6.58-(-)6.80 ($M^{H}\mathrm{D}M^{H}$, m, 36.67Si), -8.28 (D_3, s, 8.09Si), -17.70 ($\mathrm{M}^{H}D\mathrm{M}^{OH}$, s, 14.34Si), -19.66-(-) 19.76 ($\mathrm{M}^{H}DD\mathrm{M}^{H}$, 9.40), -21.63-(-)21.72 (*D*, m, 6.00Si), -37.85 ($\mathrm{Me_2}Si\mathrm{H_2}$, s, 1.32Si) ppm.

4 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.68-4.72 (Si*H*, m, 7.65H), 3.74-3.78 ($\mathrm{Si(CH_3)_2}H_2$, sep, *J* =4.1 Hz, 0.33H), 1.52 (H_2O, s, 2.60H), 0.07-0.21 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.38 ($M^{H}M^{H}$, s, 10.58 Si), -6.55-(-)6.77 ($M^{H}\mathrm{D}M^{H}$, m, 38.57Si), -8.23 (D_3, s, 14.40Si), -17.65 ($\mathrm{M}^{H}D\mathrm{M}^{OH}$, s, 12.86Si), -19.00 ($D_4$, s, 0.72Si), -19.61-(-) 19.72 ($\mathrm{M}^{H}DD\mathrm{M}^{H}$, 11.89), -21.58-(-)21.67 (*D*, m, 9.90Si), -37.73 ($\mathrm{Me_2}Si\mathrm{H_2}$, s, 1.08Si) ppm.

6 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.68-4.72 (Si*H*, m, 7.18H), 3.74-3.77 ($\mathrm{Si(CH_3)_2}H_2$, sep, *J* =4.1 Hz, 0.50H), 1.52 (H_2O, s, 1.39H), 0.06-0.21 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.42 ($M^{H}M^{H}$, s, 7.09 Si), -6.59-(-)6.83 ($M^{H}\mathrm{D}M^{H}$, m, 39.28Si), -8.28 (D_3, s, 14.30Si), -17.70 ($\mathrm{M}^{H}D\mathrm{M}^{OH}$, s, 13.11Si), -19.04 ($D_4$, s, 1.23Si), -19.66-(-) 19.80 ($\mathrm{M}^{H}DD\mathrm{M}^{H}$, 12.37), -21.46 ($D_5$, s, 1.11Si), -21.63-(-)22.13 (*D*, m, 10.70Si), -37.77 ($\mathrm{Me_2}Si\mathrm{H_2}$, s, 0.81Si) ppm.

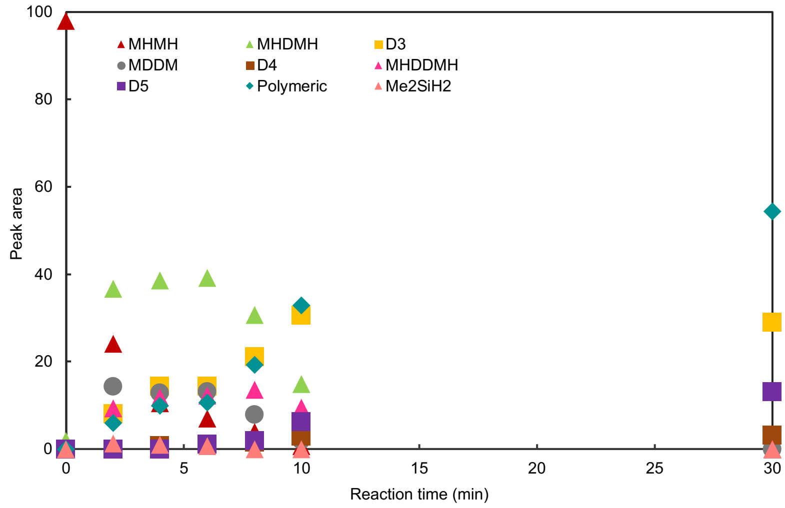
8 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.68-4.72 (Si*H*, m, 5.38H), 3.74-3.78 ($\mathrm{Si(CH_3)_2}H_2$, sep, *J* =4.1 Hz, 0.30H), 1.52 (H_2O, s, 1.06H), 0.07-0.21 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ -4.42 ($M^{H}M^{H}$, s, 3.92 Si), -6.59-(-)6.82 ($M^{H}\mathrm{D}M^{H}$, m, 30.69Si), -8.28 (D_3, s, 21.04Si), -17.70 ($\mathrm{M}^{H}D\mathrm{M}^{OH}$, s, 7.85Si), -19.04 ($D_4$, s, 1.66Si), -19.66-(-) 19.81 ($\mathrm{M}^{H}DD\mathrm{M}^{H}$, 13.59), -21.47 ($D_5$, s, 1.91Si), -21.63-(-)22.14 (*D*, m, 19.34Si) ppm.

10 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.68-4.73 (Si*H*, m, 2.36H), 3.75-3.78 ($Si(CH_3)_2H_2$, sep, *J* =4.2 Hz, 0.03H), 1.52 (H_2O, s, 0.98H), 0.07-0.20 ($Si\text{-}CH_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -4.42 (M^HM^H, s, 0.71 Si), -6.59-(-)6.84 ($M^H DM^H$, m, 14.99Si), -8.29 (D_3, s, 30.65Si), -17.71 ($M^H DM^{OH}$, s, 2.11Si), -19.05 (D_4, s, 2.88Si), -19.83 ($M^H DDM^H$, 9.46), -21.48 (D_5, s, 6.29Si), -21.64-(-)22.47 (*D*, m, 32.91Si) ppm.

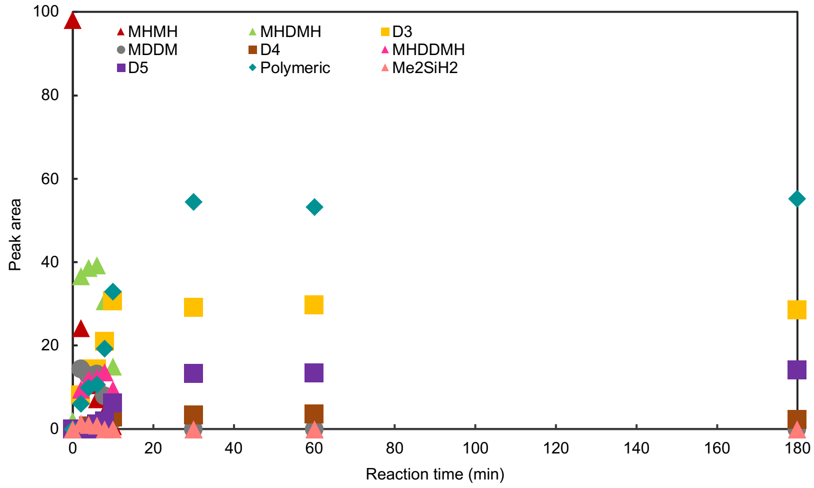
30 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.53 (H_2O, s, 1.89H), 0.07-0.19 ($Si\text{-}CH_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -8.28 (D_3, s, 29.04Si), -19.05 (D_4, s, 3.27Si), -21.47 (D_5, s, 13.24Si), -21.92-(-)22.46 (*D*, m, 54.45Si) ppm. (GPC, Toluene) M_n=39,000, M_w=69,700 g mol^{-1}, $Đ_M$:1.79.

60 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.52 (H_2O, s, 1.42H), 0.07-0.19 ($Si\text{-}CH_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -8.27 (D_3, s, 29.72Si), -19.04 (D_4, s, 3.58Si), -21.47 (D_5, s, 13.45Si), -21.91-(-)22.46 (*D*, m, 53.25Si) ppm. (GPC, Toluene) M_n=45,300, M_w=97,100 g mol^{-1}, $Đ_M$:2.14.

180 min: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.52 (H_2O, s, 1.09H), 0.08-0.18 ($Si\text{-}CH_3$, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -8.28 (D_3, s, 28.44Si), -19.06 (D_4, s, 2.30Si), -21.48 (D_5, s, 13.99Si), -21.93-(-)22.47 (*D*, m, 55.27Si) ppm. (GPC, Toluene) M_n=45,500, M_w=79,900 g mol^{-1}, $Đ_M$:1.76.



A



B

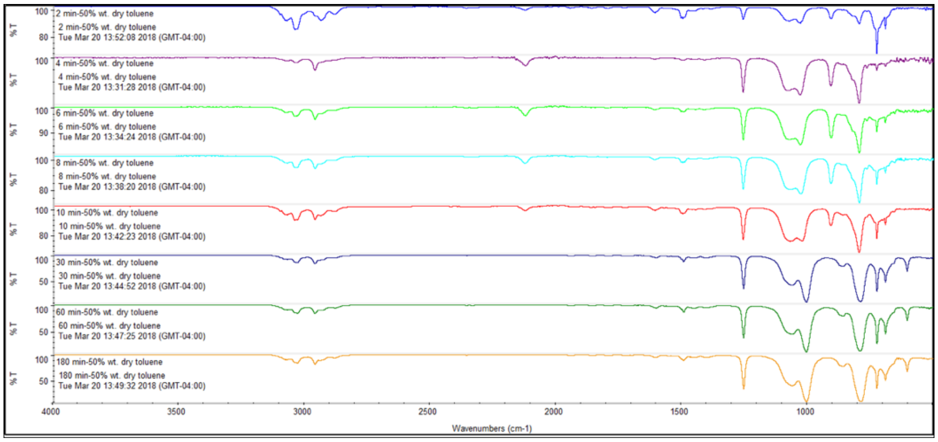


Figure S2.5. A: Plot of reaction constituents based on ^{29}Si NMR (with toluene). While small differences will exist in the sensitivity of the M vs D units (even in the presence of $Cr(acac)_3$) the presented data represents the Si monomer concentration normalized to 100% B: IR spectra at the same time points.

2.8.9. Characterizations for 'Living' reaction using hydrolysis of M^HM^H (Table 2.2, Entry 10)

Entry 10: ^{1}H NMR (600 MHz, chloroform-*d*): δ 1.53 (H_2O, s, 8.61H), 0.07-0.17 (Si-CH_3, m, 100H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ -21.95 (*D*, m, 100Si) ppm. (GPC, Toluene) M_n=41,900, M_w=137,000 g mol^{-1}, $Đ_M$: 3.27.

Chapter 3: Living Synthesis of Silicone Polymers Controlled by Humidity[&]

3.1. Abstract

The preparation of hydrophobic silicone (co)polymers generally requires acid- or base-catalyzed equilibration reactions that, in addition to polymer formation, generate undesired low molecular weight cyclic species. We report that living polymerization of hydrosiloxanes, controlled by the presence of water (bulk water/humidity/wet solvent) and 0.01-0.5mol% $B(C_6F_5)_3$, arises from facile SiH hydrolysis to the silanol and, subsequently, a more rapid reaction with remaining SiH groups leading to chain extension without significant accompanying cyclic monomer formation. The interaction between hydrophilic silicone and hydrophilic water plays a role in reaction rates. In the case of accidental introduction of excess water, polymerization of the 'dead' SiOH terminated polymers can be re-initiated using small quantities of telechelic HSi oligomers. This mild (room temperature and pressure in an open flask) method may be used to synthesize, in high yield, low molecular weight branched polymers, chain extended SiH telechelic silicones to give linear polymers, alternating silicone block copolymers with dispersities <2 and molecular weights ranging from ~2k - 250k g mol-^{1}, and resins or foams.

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Mengchen Liao performed all small molecule hydrolysis reactions, hydrolysis of DMS-H31, and was the lead author of the manuscript. Schneider performed hydrolysis reactions on DMS-H03 using different water sources and assisted with write-up of the manuscript. Laengert was responsible for all copolymerization reactions and Gale synthesized all foams.

3.2. Introduction

Silicones constitute a class of high value polymers that impact the efficacy of many technologies in industrial societies. They are used, particularly polydimethylsiloxanes (PDMS), in the form of fluids, oils, elastomers and resins due to their unusual properties, which include high thermal and electrical stability, optical transparency, low surface energy, high flexibility and low biological activity.[1]

The normal preparation of high molecular weight silicones involves acid or base-catalyzed equilibration of cyclic monomers such as D_4 ($(Me_2SiO)_4$) (D = Me_2SiO) and the desired end groups to grow linear polymers.[2] The process generally leads to silicones with high dispersities and a significant fraction (>10%) of cyclic monomers that must be stripped from the polymer product, a process that is increasingly difficult with increasing molecular weight. Additionally, it can be challenging to remove the catalysts.

Higher value silicones bear functional groups that can be used for crosslinking and/or organo-functionalization; vinyl and SiH groups are the most commonly used groups for these purposes. It has traditionally been difficult to control the location of functional groups that are pendant along a silicone chain.[3] However, it is straightforward to obtain silicones with SiH or SiVinyl groups at the termini of a telechelic silicone, and such materials are commercially available in a wide variety of molecular weights.[4]

Linear silicones of low dispersity may be prepared using kinetically controlled, ring-opening polymerization, normally of ring-strained D_3 ($(Me_2SiO)_3$). One may elect to have end groups in the product that are identical or different, for example, to prepare monofunctional polymers.[5] However, this process is disadvantageous because: access to cyclic trisiloxanes is limited aside from D_3; conversions cannot be high (or dispersity increases); low temperatures, scrupulously dry reactions and organic solvents are required. Thus, as with traditional polymerization routes, large quantities of cyclic monomers must be separated from the product.

Block copolymers, including alternating block copolymers, exhibit interesting properties due, in particular, to the way in which they self-assemble.[6,7] For example, epoxy/silicone copolymers undergo nanostructuring while forming thermosets and alternating block copolymers of silicones and polycarbonate exhibit excellent toughness while remaining highly transparent.[8,9] ABA triblock silicone copolymers can be prepared by initiating anionic polymerization with difunctional initiators; silicone-silicone alternating block copolymers (e.g., ($A_mC_nB_nBBB_nC_nA_m$) where A, B and C are Ph_2SiO, Me_2SiO, and PhMeSiO, respectively) were synthesized by the sequential addition of ring-strained cyclic trisiloxane monomers under anionic conditions.[10–14] However, these ring-opening polymerization (ROP) processes are frequently problematic, for the reasons noted above.

The Piers-Rubinsztajn reaction (PR) involves the condensation of hydrosilanes, including hydrosiloxanes (HSi compounds), with alkoxysilanes to give new siloxanes and an alkane.[15,16] The choice of precursors allows the preparation under mild conditions of silicone oils, including with precise comonomer sequence, dendrimers, elastomers, foams, and resins.[17–22] Analogous processes operate between HSi compounds and borates, phenols and alkoxybenzene derivatives, including lignin and silanols (***Figure 3.1***A).[23–28] The catalyst most commonly used for these processes is $B(C_6F_5)_3$, including a photoactivated version; Oestreich et al. have reviewed catalysts that can be used for these processes.[29,30]

Exquisite control over linear and network structures can arise by exploiting differences in relative reactivity of oxygen nucleophiles with this process. For example, Laengert et al. demonstrated that the order of reactivity of the 3 functional groups in the crosslinker eugenol (ArOH > ArOMe > Ar-$CH_2CH=CH_2$) could be used to create block copolymers or precise networks just by varying the order of addition of different SiH-telechelic silicones (***Figure 3.1***B).

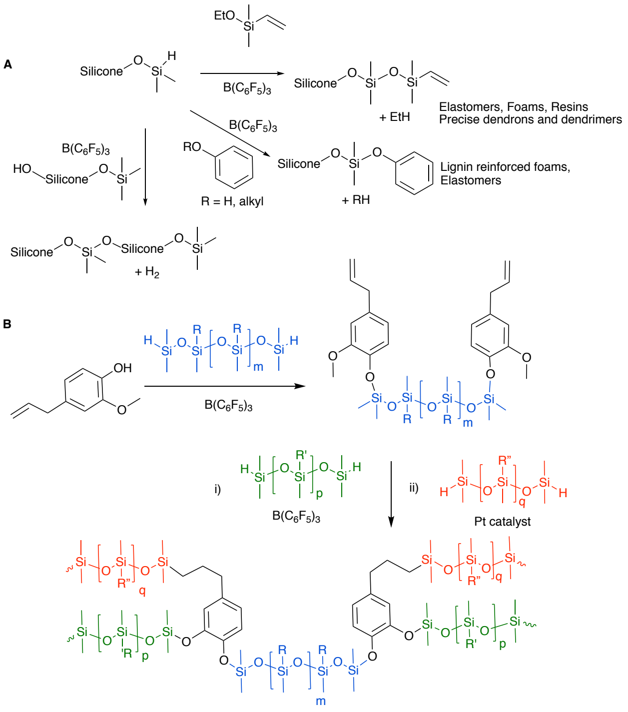


Figure 3.1. A: Selected Piers-Rubinsztajn type reactions; B: Sequential use of such reactions to assemble precise silicone networks.

We now report that excellent synthetic control over silicone homopolymer and block copolymer architecture arises simply from the controlled addition of water to hydrosiloxanes. The process is living, in that it depends on the availability of water. Resin, foam and elastomer syntheses are also described.

3.3. Experimental

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker Advance 600 MHz nuclear magnetic resonance spectrometer using deuterated solvent chloroform-*d*. Polymer molecular weights were established by gel permeation chromatography (GPC) using a Waters Alliance GPC System 2695 calibrated with a polystyrene calibration kit S-M-10 (Lot 85) from Polymer Laboratories.

GC-MS analyses were performed using an Agilent 6890N gas chromatograph (Santa Clara, CA, USA), equipped with a DB-17ht column (30 m × 0.25 mm i.d. x 0.15 μm film, J & W Scientific) and a retention gap (deactivated fused silica, 5 m x 0.53 mm i.d.), and coupled to an Agilent 5973 MSD single quadruple mass spectrometer. One microliter of sample was injected using Agilent 7683 autosampler with a 10:1 split and slit flow of 7.0 ml/min. The injector temperature was 250 °C and carrier gas (helium) flow was 0.7 ml/min. The transfer line was 280 °C and the MS source temperature was 230 °C. The column temperature started at 50 °C and raised to 300 °C at 8 °C /min, and then held at 300 °C for 10 min for a total run time of 41.25 min. Full scan mass spectra between m/z 50 and 800 were acquired after five min solvent delay.

FTIR data was collected on a Nicolet 6700 FTIR using Thermo Electron's OMNIC software. Shore OO measurements were taken using a Rex Durometer, Type OO, Model 1600 from Rex Gauge Co.

3.3.1. Monofunctional Hydrosiloxane Dimerization

3.3.1.1 Hydrolysis reaction with pentamethyldisiloxane MM^H + H_2O ([OH]/[SiH]=4; [BCF]/[SiH]=0.1 mol%)

Pentamethyldisiloxane (11.9 g, 0.08 mol) and H_2O droplets (2.88 ml, 0.16 mol) were placed in a 1L three-neck round-bottomed flask that was connected to a condenser under nitrogen protection and to which was added $B(C_6F_5)_3$ (0.1M, 0.72 ml, 0.072 mmol) diluted in toluene at room temperature. After 3 h the reaction was quenched by a small quantity of alumina, the product was collected by filtration through Celite under reduced pressure. The mass balance of the reaction is 86% 10.76 g due to volatility of some of the ingredients (**Table 3.1**).

Pentamethyldisiloxane: ^1H NMR (600 MHz, chloroform-*d*): δ 4.67 (sept, J = 2.8 Hz, 1H), 0.17 (d, J = 2.8 Hz, 6H), 0.09 (s, 9H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ 9.71 (s, 1Si), -6.76 (s, 1Si) ppm. GC-MS: $C_5H_{16}OSi_2$, calculated: 148, found: [M-15]=133.1 (100).

Hydrolysis products of pentamethyldisiloxane: ^1H NMR (600 MHz, chloroform-d): δ 1.54 (s, 0.2H), 0.09 (s, 6H), 0.05 (s, 4H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace $Cr(acac)_3$): δ 9.24 (s, 1 Si), -21.49 (s, 1Si) ppm. GC-MS: $C_{10}H_{30}O_3Si_4$, calculated: 310, found: [M-15]=295.1 (40), 207.1(100), 73.1 (30). $C_{12}H_{36}O_4Si_5$, calculated: 384, found: [M-15]= 369.2 (40), 281.1 (100), 147.1 (55), 73.2 (25). $C_{14}H_{42}O_5Si_6$, calculated: 458, found: [M-15]=443.2 (20), 355.1 (40), 281.1 (60), 221.1 (100), 207.1 (45), 147.1 (70), 91.1 (50), 73.1 (60). C16H48O6Si7, calculated: 532, found: [M-15]=517.2 (5), 341.0 (20), 207.1 (80), 91.2 (100).

3.3.1.2 Hydrolysis products of Bis(trimethylsiloxy)methylsilane - MD^HM + H_2O ([OH]/[SiH]=4; [BCF]/[SiH]=0.1 mol%)

Bis(trimethylsiloxy)methylsilane (17.8 g, 0.08 mol) and H_2O droplets (2.88 ml, 0.16 mol) were placed in a 1L three-neck round-bottomed flask which was connected to a condenser under nitrogen protection and to which was added $B(C_6F_5)_3$ (0.1M, 0.72 ml, 0.072 mmol) diluted in toluene at room temperature. After 3 h the reaction was quenched by alumina. The yield of the reaction is 95% (17.44 g, **Table 3.1**).

Bis(trimethylsiloxy)methylsilane: ^1H NMR (600 MHz, chloroform-*d*): δ 4.63 (d, *J* = 1.5 Hz, 1H), 1.54 (s, 0.3H), 0.12 (s, 18H), 0.10 (d, *J* = 1.6 Hz, 3H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119MHz, trace $Cr(acac)_3$): δ 9.36 (s, 2Si), -36.40 (s, 1Si) ppm. GC-MS: $C_7H_{22}O_2Si_3$, calculated: 222, found: [M-15]=207.2 (100), 73.1 (50)

Hydrolysis products of Bis(trimethylsiloxy)methylsilane: ^1H NMR (600 MHz, chloroform-*d*): δ 1.55 (s, 0.1H), 0.10 (s, 36H), 0.02 (s, 6H) ppm.^{29}Si NMR (600 MHz, chloroform-*d*, 119MHz, trace $Cr(acac)_3$): δ 7.59 (s, 4Si), -54.51 (s, 0.17Si), -65.93 (s, 2Si) ppm. GC-MS: compound insufficient sensitivity to characterize the peak to characterize the peak, [M-15]=355.0 (5), 207.1 (100), 106.1 (100), 77.1 (80), 51.1 (30). $C_{14}H_{42}O_5Si_6$, calculated: 458, found: [M-15]=443.2 (50), 355.1 (50), 281.1 (55), 221.1 (100), 147.1 (70), 73.1 (75).

3.3.1.3 Hydrolysis reaction using a mixture of pentamethyldisiloxane (MM^H) and bis(trimethylsiloxy)methylsilane (MD^HM)-MM^H + MD^HM + H_2O ([OH]/[SiH]=4; [BCF]/[SiH]=0.1 mol%)

Pentamethyldisiloxane (1.50 g, 0.01 mol), bis(trimethylsiloxy)methylsilane (2.24 g, 0.01 mol) and H_2O droplets (0.72 ml, 0.04 mol) were placed in a 50 ml plastic test tube that was connected to a condenser under nitrogen protection and to which was added $B(C_6F_5)_3$ (0.1M, 0.18ml, 0.018 mmol) diluted in toluene at room temperature. After 3h the reaction was quenched by alumina, the product was collected by filtration through Celite under reduced pressure.

Hydrolysis products using pentamethyldisiloxane with bis(trimethylsiloxy)methylsilane: ^{1}H NMR (600 MHz, Chloroform-*d*): δ 2.04 (s, 0.03H), 0.13 (s, 1H), 0.10 (d, *J* = 5.0 Hz, 15H), 0.05 (s, 3H), 0.03 (s, 2H) ppm. ^{29}Si NMR (600 MHz, Chloroform-*d*, 119MHz, trace $Cr(acac)_3$): δ 8.66 (s, 1Si), 7.58 (s, 20Si), 7.23 (s, 10Si), -21.50 (s, 9Si), -21.68 (s,1Si), -54.50 (s, 2Si), -65.37 (s, 2Si), -65.93 (s, 11Si) ppm. GC-MS: $C_{10}H_{30}O_3Si_4$, calculated: 310, found: [M-15]=295.1 (50), 207.1(100), 73.1 (50). $C_{12}H_{36}O_4Si_5$, calculated: 384, found: [M-15]=369.1 (30), 281.1 (100), 207.0 (90), 147.1 (40), 91.1 (25). $C_{14}H_{42}O_5Si_6$, calculated: 458, found: [M-15]=443.2 (60), 355.1 (60), 281.1 (70), 221.1 (100),147.1 (70), 73.1 (75).

3.3.1.4 Hydrolysis reaction using tris(trimethylsiloxy)silane - M_3T^H + H_2O ([OH]/[SiH]=4; [BCF]/[SiH]=0.1 mol%)

Tris(trimethylsiloxy)silane (23.7 g, 0.08 mol) and H_2O droplets (2.88 ml, 0.16 mol) were placed in a 1L three-neck round-bottomed flask that was connected to a condenser under nitrogen protection and to which was added $B(C_6F_5)_3$ (0.1M, 0.72

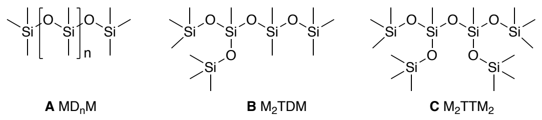
ml, 0.072 mmol) diluted in toluene at room temperature. After 3 h the reaction was quenched by alumina, the product was collected by filtration through Celite under reduced pressure. The characterizations are shown as below:

Tris(trimethylsiloxy)silane: ^{1}H NMR (600 MHz, chloroform-*d*): δ 4.23 (s, 1H), 1.51 (s, 0.20H), 0.12 (s, 27H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, 119 MHz, trace Cr(acac)$_3$): δ 9.41 (s, 3Si), -82.74 (s, 1Si) ppm. no reaction products were observed.

Table 3.1 GC-MS results for low cyclic-containing silicone oils by hydrolysis of monofunctional hydrosiloxanes.

MM^H +H$_2$O ([OH]/[SiH]=4)			
Structure[a]	Nomenclature	Relative ratio (%) GC	Product ratio by ^{29}Si NMR (% ± 5%)
A n=2	MD$_2$M	93	
A n=3	MD$_3$M	5	
A n=4	MD$_4$M	1	
A n=5	MD$_5$M	1	
MD^{H}M +H$_2$O ([OH]/[SiH]=4)			
Unknown low boiling compound[b]	-	3	
C	M$_2$TTM$_2$	97	
MM^H + MD^{H}M + H$_2$O ([OH]/[SiH]=4)			
A n=2	MD$_2$M	30	40
B	M$_2$TDM	9	14
C	M$_2$TTM$_2$	61	46

[a]



[b] Approximately a pentasiloxane, based on retention time.

3.3.2. Chain extension of telechelic H-terminated silicones

3.3.2.1 General procedure for chain extension using hydrolysis - water droplets (Table 3.2, 1-4, 7-9, Table S3.4, Entries 1-12)

To a mixture of hydride-terminated H-PDMS-H (M$_n$ 500 g mol^{-1} 2.03 g, 4.06 mmol) and distilled water (230 μl, 13 mmol) in a 100.0 ml round-bottomed flask that was connected to a condenser under a nitrogen blanket, was added tris(pentafluorophenyl)borane diluted in toluene (0.1M, 0.016 ml, 1.6 μmol). The mixture was stirred at room temperature. After 3 h, alumina (~0.5 g) was added to the mixture to quench the reaction. The product was collected by filtration through Celite under reduced pressure. M_n 46,000 M_w 86,200, $Đ_M$ 1.88, **Table 3.2**, entry 4. Note: ^{1}H NMR and ^{29}Si NMR are diagnostic for loss of SiH groups but are otherwise not helpful. Representative NMR data is provided; the other samples differ only in the relative magnitude of the $SiMe_2$ peak.

Entry 4, Table 3.2

^{1}H NMR (600 MHz, Chloroform-*d*): δ 1.54 (s, 20H), 0.17 (m, 6H), 0.14 (s, 1H), 0.07 (m, 258H), -0.03 (s, 1H) ppm. ^{29}Si NMR (600 MHz, chloroform -*d*, 119MHz, trace $Cr(acac)_3$): δ -21.94 (s, 1Si) ppm.

3.3.2.2 General procedure for chain extension using hydrolysis by moisture in an open flask (Table 3.2, 5, Table S3.4, Entries 13)

To a 10.0 ml round-bottomed flask was added hydride-terminated H-PDMS-H (500 g mol^{-1}, 2.05 g, 4.1 mmol) with $B(C_6F_5)_3$ diluted in toluene (0.1M, 0.040 ml, 4 μmol) ([BCF]/[SiH]=0.05 mol%, humidity: 15%). The mixture was stirred at room temperature open to atmosphere, and after 10 hours alumina (~0.5 g) was added to the mixture to quench the reaction. The product was collected by filtration through Celite under reduced pressure.

3.3.2.3 General procedure for chain extension using hydrolysis by moisture in an open flask augmented with wet toluene (Table 3.2, Table S3.4, Entries 14-16)

To a 100.0 ml round-bottomed flask was added hydride-terminated H-PDMS-H (500 g mol^{-1}, 1.53 g, 3.1 mmol) diluted in 15.0 ml toluene. The mixture was added tris(pentafluorophenyl)borane diluted in toluene (0.04 M, 0.020 ml, 0.77 μmol) ([BCF]/[SiH]=0.05 mol%, [OH]/[SiH]=0.08) and stirred at room temperature in an open vessel. After 24 h, alumina (~0.5 g) was added to the mixture to quench the reaction. The product was collected by filtration through Celite under reduced pressure.

3.3.2.4 Copolymerization of $HMe_2Si(OSiMe_2)_nSiMe_2H$ + $HOMe_2Si(OSiMe_2)_nSiMe_2OH$ (Table 3.2, entry 10, Table S3.4, Entry 17)

To a mixture of hydride-terminated H-PDMS-H (M_n 27,600 g mol^{-1} 1.23 g, 0.045 mmol) and hydroxyl-terminated HO-PDMS-OH (M_n 21,600 g mol^{-1} 1.05 g, 0.049 mmol) in a 100.0 ml round-bottomed flask that was connected to a condenser under a nitrogen blanket, was added tris(pentafluorophenyl)borane diluted in toluene (0.01M, 0.013 ml, 0.13 μmol). The mixture was stirred at room temperature. After 24 h, alumina (~0.5 g) was added to the mixture to quench the reaction. The product was collected by filtration through Celite under reduced pressure.

3.3.2.5 Copolymerization of $HMe_2Si(OSiMePh)_3SiMe_2H$ + $HOMe_2Si(OSiMe_2)_nSiMe_2OH$ (Table 3.2, entry 11, Table S3.4, Entries 18-23)

To an oven-dried 100.0 ml round-bottomed flask under nitrogen atmosphere was added dry toluene (5 ml). SiOH-terminated polysiloxane (MW: 1200 g mol^{-1}, 1.500 g, 1.25 mmol) was added, followed by addition of SiH-terminated polysiloxane (MW: 400, 0.500, 1.25 mmol). To this stirring mixture was added tris(pentafluorophenyl)borane (10^{-1} of a 25.6 mg ml^{-1} solution in toluene, 0.02 mol% relative to SiH) followed by the lowering of the flask into an oil bath preheated to 50 °C. Bubbling commenced quickly, tapering off over 10 min. Note: if catalyst concentrations higher than 0.02 mol% are used, it is advisable to add one of the reagents (SiH or SiOH) dropwise to safely control the rate of gas evolution. As reaction viscosity increased over the first 2 h, and additional 5-10 ml of dry toluene was added to allow stirring to continue. After 24 h, 0.500 g of neutral alumina was added to quench the catalyst. The reaction mixture was stirred for a further 2 h, filtered through Celite under reduced pressure, and concentrated to afford the product, a colorless oil.

Table 3.2. Polymerization of HSi-Telechelic Silicones Using Water or HOSi-Telechelic Silicones

Entry	n[a]	[OH]/[SiH]	[BCF]/[SiH][b]	t (h)	H_2O[c]	M_n	M_w	$Đ_M$	Copolymer
1	0	3	200	3	L	50,100	76,300	1.52	
2	5	3	200	3	L	27,800	52,600	1.89	
3	370	3	200	3	L	33400	50,900	1.53	
4	5	3	200	24	L	46,000	86,200	1.88	
5	5	NA	500	24	O	20,000	30,000	1.50	
6	5	0.08	500	24	S	183,000	349,000	1.91	
7	0	1	80	20	L	20,700	32,500	1.57	
8	0	3	200	3	L	50,100	76,300	1.52	
9	0	0.6	400	22	L	77,200	140,800	1.83	
10	370	1	500	24	NA	251,000	471,500	1.88	$HOSiMe_2O(SiMe_2O)_{371}H$
11	MePh[d]	1	200	24	NA	15,500	24,000	1.55	$HOSiMe_2O(SiMe_2O)_{16}H$

[a] n in $HSiMe_2O(SiMe_2O)_nSiMe_2H$. [b] in ppm: [BCF]/[SiH] x 10^6. [c] L = bulk liquid water (closed system), O open system 56% relative humidity, 230 ppm water in toluene and the flask was open to the atmosphere. [d] $HSiMe_2O(SiMePhO)_3SiMe_2H$, at 50°C.

3.3.3. Silicone resin preparation using hydrolysis

3.3.3.1 Procedure for silicone resin preparation using D^H_4 and water

D^H_4 (5.00 g, 20.8 mmol) was placed in a 100.0 ml round bottle flask with $B(C_6F_5)_3$ (0.078M, 0.625 ml, 0.049 mmol) iluted in toluene. The mixture was stirred at room temperature open to the atmosphere. A photo of the product and its characterization by IR, ^{29}Si NMR and ^{13}C solid state NMR spectra are shown in the Supporting Information (**Figure 3.2**A).

^{29}Si NMR (850 MHz): δ -35.78 (s, 5 Si), -56.87 (s, 1 Si), -65.79 (s, 5 Si) ppm. ^{13}C NMR (850 MHz): δ -2.12 (s, 1 C), -6.19 (s, 1 C) ppm.

3.3.3.2 General procedure for silicone elastomer/foam preparation using SiH compounds and water

Preparation of D^H_4 stock solution

D^H_4 (0.12 g, 0.48 mmol) was weighed in a 25.0 ml vial and dissolved in hexane (13.56 ml) to prepare a stock solution of D^H_4 (8.6 mg ml^{-1}).

Preparation of silicone foam using D^H_4 + DMS-H11 ([BCF]/[SiH]=0.02 mol%)

An oven dried round bottom flask was charged with D^{H}_{4} (2.00 g, 8.31 mmol), DMS-H11 (2.03 g, 1.818 mmol), distilled water (0.055 mol, 997 μl), $B(C_6F_5)_3$ (0.02 mol%, 0.0074 mmol, 73 μl). A water condenser was placed on top and a nitrogen balloon was used to maintain a positive pressure of nitrogen, the reaction was stirred for three hours. The resulting foam was removed from the flask and extracted using a Soxhlet extraction device.

Preparation of silicone foam using H-PDMS-H and $D_H{}^4$ with hexane ([BCF]/[SiH]=0.9 mol%)

DMS-H41 (1.53 g, 0.048 mmol) with D^{H}_{4} (142.7 mM, 34.3 mg ml^{-1}, 0.76 ml) were poured into a Teflon-coated 12 wellplate with $B(C_6F_5)_3$ (0.078M, 8 μl, 0.62 mmol). Once the $B(C_6F_5)_3$ was added, the mixture was vigorously stirred by hand (~30 s), then placed on the bench at room temperature overnight (**Figure 3.2**B,C).

Preparation of silicone elastomer ([BCF]/[SiH]=0.3 mol%)

To a mixture of DMS-H25 (1.53 g, 0.10 mmol), D^{H}_{4} (35.8 mM, 8.6 mg ml^{-1}, 1 ml) and hexane (1 ml) in a polystyrene Petri dish (10 mm thick 35 mm diameter), $B(C_6F_5)_3$ (0.078M, 15 μl, 1.17 mmol) was added. The contents were rapidly stirred at room temperature (~30 s), then moved to a 40 °C oven under vacuum (571 Torr) overnight. The Shore OO hardness of the silicone foam was 8.5 (**Figure 3.2**D).

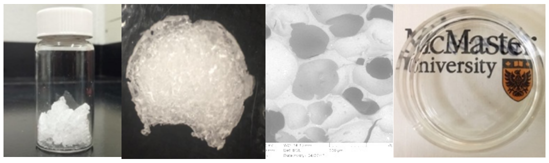


Figure 3.2. A: Silicone resin prepared using D^{H}_{4} and water. B: Silicone foam prepared using D^{H}_{4} and H-PDMS-H ([BCF]/[SiH]=0.9 mol%). C: The SEM

image of the silicone foam. D: Bubble-free silicone elastomer prepared using D^H_4 and H-PDMS-H ([BCF]/[SiH]=0.3 mol%)

3.4. Results and discussion

To better understand the reaction between water and hydrosilanes, we began with low molecular weight, monofunctional hydrosiloxanes that are commercially available, or can be readily synthesized.[31] In the presence of the Lewis acid catalyst $B(C_6F_5)_3$, exposure of $Me_3SiOSiMe_2H$ to water in the form of: atmospheric moisture; bulk water droplets; or water dissolved in an organic solvent led to dimerization in excellent yield without concomitant generation of silicone cyclics D_3-D_5 (**Figure 3.3**). The reaction was efficient at room temperature, with isolated yields after distillation of 85-95% using 0.1 mol% of BCF and water droplets as a source of water. *Note: hydrogen gas is a by-product of these reactions and appropriate caution must be exercised both with respect to flammability and buildup of pressure.*

Sterics affected the outcome of the process. Using water droplets (bulk water), the bulkiest silane **1** (M_3T^H) did not appreciably react within 3 hours, whereas the less branched analogues **2** and **3** underwent complete reaction in 2-3 hours to give homodimers; hydrogen bubble evolution was easily seen to occur at the water/silicone oil interface. A competition reaction between **2** and **3**, surprisingly, led mostly to the homodimers **4** and **5**, respectively, with about 10-20% formation of the crossproduct **6** as shown by GC/MS (**Figure 3.3**A-D, Supporting Information). Note that **6** is readily available using a standard Piers-Rubinsztajn reaction under the same conditions that combines MM^H + M_2D^{OMe} (**Figure 3.3**E).[32,33]

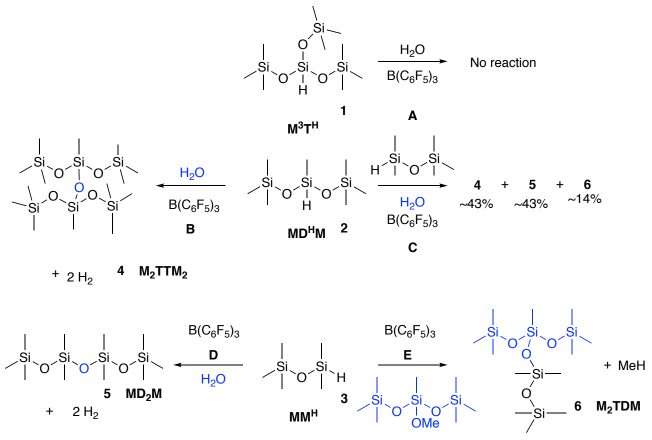


Figure 3.3. Dimerization reactions of monofunctional siloxanes.

HSi-telechelic silicone polymers are commercially available in many different molecular weights ranging from the disiloxanes to much higher homologues ($HSiMe_2O(SiMe_2O)_nSiMe_2H$, n = 0 to ~1000). The highest molecular weight SiH telechelic dimethylsiloxane sold by Gelest, for example, has a MW of 62,700 g mol^{-1}, n ~850. During preliminary experiments, it was discovered that the exposure of such polymers to a small stoichiometric excess of bulk water in the presence of 0.02mol% $B(C_6F_5)_3$ (200 ppm) led to chain extension (**Figure 3.4**A-C). Starting from three telechelic hydrosiloxanes ranging in molecular weight from 108 to ~26,600 g mol^{-1} we obtained three products with suspiciously similar molecular weights, near 35,000 g mol^{-1}, after 3 hours (**Table 3.2**, entries 1-3). Note that similar outcomes arose in the formation of higher molecular weight polymers when the only source of water was moisture that was allowed to enter an open flask; in these cases, reactions were slower (over 24 hours).

The processes leading to chain extension involve both hydrolysis and condensation. As with any step growth process, a stoichiometric imbalance between the reaction of two difunctional entities leads to lower molecular weight linear chains capped with the monomer in excess, OH in this case.[34] The first and slower of the two steps of the process involves hydrolysis (**Figure 3.4**A), followed by the faster condensation leading to dimers (**Figure 3.4**B); the ideal, stoichiometrically matched polymerization by iteration of these two steps leads to higher MW polymer (**Figure 3.4**C). The process is not associated with significant increases in cyclic monomer concentration and excellent dispersities were observed for a condensation process.

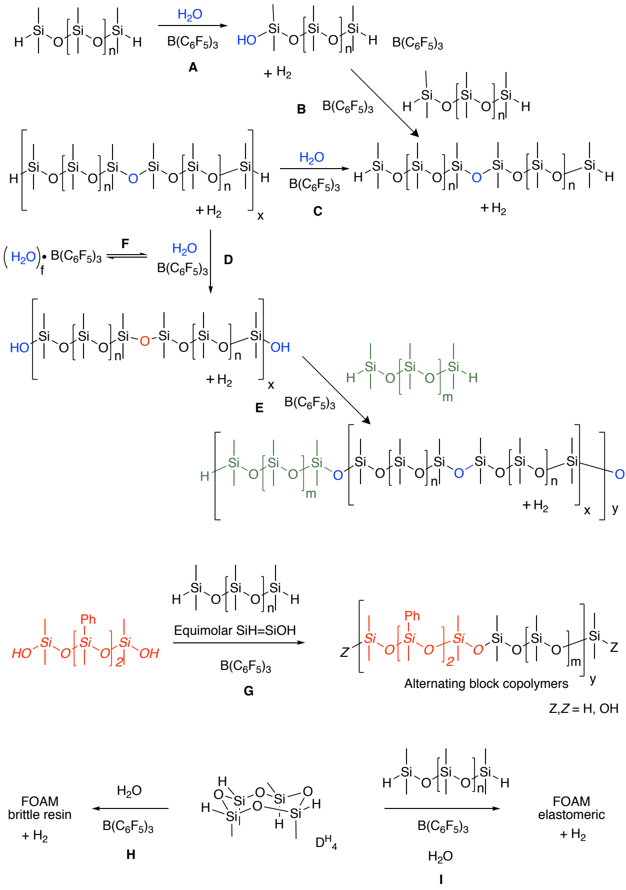


Figure 3.4. Hydrolysis and condensation reactions of: A-G telechelic siloxanes and H,I crosslinked siloxane polymers.

This model also explains why 3 starting materials of very different molecular weights led to product polymers of comparable molecular weight at a given time. As the reaction proceeds, the concentration of SiH groups decreases, while the concentration of water provided by the atmosphere (or excess bulk water) essentially remains constant. There will be a point at which the hydrolysis reaction will dominate because, even though it has a smaller rate constant than that for condensation, the concentration of water will be significantly higher than of residual SiH groups. In addition, as MW and viscosity of the product polymers increase, there will be an attendant reduction in the polymer/polymer condensation reaction rate. On the day of reaction, the concentration of water arising from room humidity won the battle at M_n ~35,000 (starting from a disiloxane) to give HO-telechelic polymers (**Figure 3.4**D); on humid days, much lower molecular weight polymers were obtained (data not shown).

A series of experiments was undertaken to establish optimal concentrations of both water and BCF. HSi-terminated silicone chains were produced in closed vessels using the process; the lengths of the product polymers could be controlled by slow introduction of bulk water, such that hydrolysis could not consume all the SiH groups (**Figure 3.4**A-C). Atmospheric moisture led to slower growth. The most convenient way to run these reactions was to add small quantities of wet toluene (water concentration 230 ppm, see below) in an open flask. Under these circumstances, PDMS polymers of up to 183,000 g mol^{-1} were readily attained (**Table 3.2**, entries 4-6, **Table S3.4**, Supporting Information). We infer that toluene acts to solubilize water, SiH-silicone and catalyst. While, in principle, alcohols such as ethanol or methanol should better dissolve in silicones than water, and lead to the same outcomes, our experience has been inconsistent.

If an excess of water is provided at the outset, or over time, silanol-terminate‘dead polymer’ forms (**Figure 3.4**D). The advantage of the current route over traditional processes for silicone polymerization is that reactivating 'dead' polymer simply requires addition of HSi-telechelic polymer of the same or different MW (**Figure 3.4**E, or if water is in deficit, by opening the flask to permit ingress of atmospheric moisture) in the same flask until the desired molecular weight is realized. In the absence of water, either no reaction was observed, or metathesis producing Me_2SiH_2 and shorter linear chains was observed, as has been previously reported.[35,36] Thus, the reaction is living, provided water is the limiting reagent.

Water is not benign in these reactions. Although it is possible to recover from addition of too much reagent water by adding additional SiH groups, it can be pernicious in other ways. As the water content increases, the amount of catalyst required also increases. $B(C_6F_5)_3$ forms a series of hydrates that are in equilibrium with free BCF. Additional water drags the equilibrium towards the hydrate (**Figure 3.4**F); at about 3% water neither the hydrolysis nor the condensation reactions function – polymerization shuts down. Note, however, that Ganachaud et al. have demonstrated the ability to polymerize $Me_2HSiOSiMe_2H$ into linear silicones using BCF in aqueous dispersions. In their case, possibly as a consequence of much higher concentrations of water used, they concluded that a different process was occurring, involving the formation, and then acid-catalyzed polymerization, of cyclic trisiloxanes in a process that they labelled, "non-controlled." Further research is therefore required to sort out the role of water in detail.[37]

Both reactions – hydrolysis and condensation – particularly the first, hydrolytic step, were much more sluggish than the PR reaction, for which 30-50 ppm catalyst is sufficient to lead relative reactivity is a consequence both of oxygen basicity and low solubility of water in the hydrophobic silicone medium. Given the differences in surface activity between water and silicone oils (~73 vs 16-22 mN m^{-1}), this may well be the key factor controlling reactivity with this oxygen nucleophile.[38]

Once it was recognized that hydrolysis was generating SiOH groups in situ, followed by chain extension by SiOH + SiH condensation processes, several opportunities presented themselves. First, commercially available HOSi-telechelic silicones could be converted to high molecular weight polydimethylsiloxanes simply by mixing commercial SiOH + SiH polymers in the presence of a small quantity of $B(C_6F_5)_3$ in the absence of water.[28] This condensation reaction is more efficient and rapid than the reactions that first hydrolysis, giving molecular weight polymers up to M_n = 251,000 g mol^{-1} with dispersities below 2 (R=Me, **Figure 3.4** F, **Table 3.2**, entry 10, **Table S3.4**). Second, there is no requirement to use only dimethylsiloxane polymers. We have prepared a series of alternating block copolymers by combining HOSi-terminated dimethylsiloxanes of different molecular weights and an HSi-terminated PhMe silicone (R = Ph, **Figure 3.4**G, **Table 3.2**, entry 11, **Table S3.4**); we are currently examining the potential of this process to incorporate other reactive organic functionalities into silicone blocks.[33] These products should be of interest because the behavior of block copolymers, particularly through self-association, depends highly on the fraction of a given polymer and, for alternating copolymers, the frequency of their distribution along the chain.[39] The ability to control block lengths and block frequency in pure silicones is straightforward using this condensation approach. The creation of such pure alternating silicone block polymers by traditional routes requires the use of use organic links.

Resins, elastomers and foams are readily prepared using the Piers-Rubinsztajn reaction.[19,20,22] When exposed to water under the same simple process conditions starting materials containing multifunctional SiH groups could be similarly utilized to prepare highly reticulated material whose properties depended on the M_c (that is, n in **Figure 3.4**I). For example, D^H_4 $(MeHSiO)_4$, in which each silicon atom is a potential crosslink site, rapidly foamed in the presence of water and $B(C_6F_5)_3$ to give a brittle resin (Supporting Information). The addition to this mixture of a short spacer (MW1,600) led to stiff elastomeric foams while the addition of a long spacer (MW=62,700) gave very soft elastomeric foams (Shore OO hardness 8.5). Note that these reactions can be capricious, in that small changes in reaction conditions affect the ability of bubbles to nucleate and coalesce, leading to differences in average bubble size and density in products made with the same starting materials.

The groups of Piers, and Gevorgyan established the general reactivities of different organic groups towards reduction by hydrosilanes in the presence of $B(C_6F_5)_3$.[40–45] To those rules we can begin to add rules for the relative reactivity of various oxygen nucleophiles towards the creation of siloxane bonds in silicones under similar conditions. Our experience has shown that the alkoxysilanes and alkyl phenyl ethers are more reactive than phenols or silanols. To that list can be added a slower reagent, water, that gives silanols from hydrosilanes.

The processes outlined here are mild (mostly at room temperature), facile and forgiving. Several advantages accrue from the PR by hydrolysis: a broad range of appropriately functional (telechelic SiOH, SiH silicones) are commercially available, including dimethyl- or methylphenylsilicones, and silicones bearing other organic functionalities may be readily synthesized; high molecular weight dimethylsilicone chains – up to 251,000 g mol^{-1} – can be readily created but, unlike traditional methods, dispersity values of the products are < 2; unlike most AA + BB condensation polymerizations, it is facile to overcome initial mismatches of stoichiometry; and, alternating or random block copolymers of different block length and functionality are readily synthesized with excellent control over final MW; cyclic content remains low, facilitating the isolation of clean polymers. It is rather unusual to observe a living condensation polymerization process controlled by the addition of water. We are examining other benefits that the process might provide.

3.5. Conclusions

The slow reaction between hydrosiloxanes and water can be used to control the assembly of silicone polymers. The living process, controlled by the available water concentration, permits large silicones of molecular weight up to 250 000 g mol^{-1} with low dispersity to be prepared. Alternating block copolymers are readily accessed from the reaction, without water, of telechelic SiOH polymers and telechelic SiH polymers, in the presence of $B(C_6F_5)_3$. An accidental excess of silanols is overcome simply by adding excess dihydrosilicones to restart the process. The process is mild, occurring at room temperature with low quantities of catalyst, and is not accompanied by the formation of significant quantities of low molecular weight byproducts.

3.6. Acknowledgements

We gratefully acknowledge the financial assistance of the Natural Sciences and Engineering Research Council of Canada.

3.7. References

(1) Noll, W. *Chemistry and Technology of Silicones*; Elsevier, 2012.

(2) Clarson, S. J.; Semlyen, J. A. *Siloxane Polymers*; Prentice Hall, 1993.

(3) Madsen, F. B.; Dimitrov, I.; Daugaard, A. E.; Hvilsted, S.; Skov, A. L. Novel Cross-Linkers for PDMS Networks for Controlled and Well Distributed Grafting of Functionalities by Click Chemistry. *Polym. Chem.* **2013**, *4* (5), 1700–1707.

(4) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; J. Wiley, 2000.

(5) Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M. Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers. *J. Am. Chem. Soc.* **1995**, *117* (12), 3380–3388.

(6) Mai, Y.; Eisenberg, A. Self-Assembly of Block Copolymers. *Chem. Soc. Rev.* **2012**, *41* (18), 5969–5985.

(7) Kim, H.-C.; Park, S.-M.; Hinsberg, W. D. Block Copolymer Based Nanostructures: Materials, Processes, and Applications to Electronics. *Chem. Rev.* **2010**, *110* (1), 146–177.

(8) Gong, W.; Zeng, K.; Wang, L.; Zheng, S. Poly (Hydroxyether of Bisphenol A)-Block-Polydimethylsiloxane Alternating Block Copolymer and Its Nanostructured Blends with Epoxy Resin. *Polymer (Guildf).* **2008**, *49* (15), 3318–3326.

(9) Vaughn, H. A. The Synthesis and Properties of Alternating Block Polymers of Dimethylsiloxane and Bisphenol-A Carbonate. *J. Polym. Sci. Part B Polym. Lett.* **1969**, *7* (8), 569–572.

(10) Gnanou, Y.; Rempp, P. Synthesis of Difunctional Poly (Dimethylsiloxane) s: Application to Macromonomer Synthesis. *Die Makromol. Chemie Macromol. Chem. Phys.* **1988**, *189* (9), 1997–2005.

(11) N.V. Gvozdic, J. Ibemesi, D.J. Meier. Triblock Copolymers of Diphenylsiloxane and Dimethylsiloxane. *Proc. 28th IUPAC Macromol. Symp.* **1982**, 168.

(12) J. Ibemesi, N. Gvozdic, M. Keumin, M.J. Lynch, D.J. Meier, Synthesis and properties of poly(diphenylsiloxane-b-dimethylsiloxane) copolymers, Polymer Preprints (American Chemical Society, Division of Polymer Chemistry 26(2) (1985) 18-19.

(13) E.E. Bostick, Polysiloxane block copolymers with ordered structures, US Patent (1968) 3378521 (to General Electric).

(14) E.E. Bostick, Polysiloxane block copolymers, US Patent (1967) 3337497 (to General Electric)

(15) S. Rubinsztajn, J. Cella, Formation of Siloxane Bonds via New Condensation Process, Polym. Prep. 45 (1) (2004) 635-6.

(16) Rubinsztajn, S.; Cella, J. A. A New Polycondensation Process for the Preparation of Polysiloxane Copolymers. *Macromolecules* **2005**, *38* (4), 1061–1063.

(17) Matsumoto, K.; Sajna, K. V.; Satoh, Y.; Sato, K.; Shimada, S. By-Product-Free Siloxane-Bond Formation and Programmed One-Pot Oligosiloxane Synthesis. *Angew. Chemie - Int. Ed.* **2017**, *56* (12), 3168–3171.

(18) Grande, J. B.; Urlich, T.; Dickie, T.; Brook, M. A. Silicone Dendrons and Dendrimers from Orthogonal SiH Coupling Reactions. *Polym. Chem.* **2014**, *5* (23), 6728–6739.

(19) Grande, J. B.; Fawcett, A. S.; McLaughlin, A. J.; Gonzaga, F.; Bender, T. P.; Brook, M. A. Anhydrous Formation of Foamed Silicone Elastomers Using the Piers–Rubinsztajn Reaction. *Polymer (Guildf).* **2012**, *53* (15), 3135–3142.

(20) Fawcett, A. S.; Grande, J. B.; Brook, M. A. Rapid, Metal-Free Room Temperature Vulcanization Produces Silicone Elastomers. *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51* (3), 644–652.

(21) Kurjata, J.; Fortuniak, W.; Rubinsztajn, S.; Chojnowski, J. $B(C_6F_5)_3$ Catalyzed Dehydrocarbon Polycondensation of PhSiH3 with (MeO)4Si as Model Polyfunctional Comonomers in New Route to Hydrophobic Silicone TQ Resins. *Eur. Polym. J.* **2009**, *45* (12), 3372–3379.

(22) Chojnowski, J.; Rubinsztajn, S.; Fortuniak, W.; Kurjata, J. Synthesis of Highly Branched Alkoxysiloxane-Dimethylsiloxane Copolymers by Nonhydrolytic Dehydrocarbon Polycondensation Catalyzed by Tris(Pentafluorophenyl)Borane. *Macromolecules* **2008**, *41* (20), 7352–7358.

(23) Rubinsztajn, S. New Facile Process for Synthesis of Borosiloxane Resins. *J. Inorg. Organomet. Polym. Mater.* **2014**, *24* (6), 1092–1095.

(24) Cella, J.; Rubinsztajn, S. Preparation of Polyaryloxysilanes and Polyaryloxysiloxanes by $B(C_6F_5)_3$ Catalyzed Polyetherification of Dihydrosilanes and Bis-Phenols. *Macromolecules* **2008**, *41* (19), 6965–6971.

(25) Kamino, B. A.; Grande, J. B.; Brook, M. A.; Bender, T. P. Siloxane− Triarylamine Hybrids: Discrete Room Temperature Liquid Triarylamines via the Piers− Rubinsztajn Reaction. *Org. Lett.* **2011**, *13* (1), 154–157.

(26) Zhang, J.; Chen, Y.; Brook, M. A. Reductive Degradation of Lignin and Model Compounds by Hydrosilanes. *ACS Sustain. Chem. Eng.* **2014**, *2* (8), 1983–1991.

(27) Zhang, J.; Chen, Y.; Sewell, P.; Brook, M. A. Utilization of Softwood Lignin as Both Crosslinker and Reinforcing Agent in Silicone Elastomers. *Green Chem.* **2015**, *17* (3), 1811–1819.

(28) Zhou, D.; Kawakami, Y. Tris (Pentafluorophenyl) Borane as a Superior Catalyst in the Synthesis of Optically Active SiO-Containing Polymers. *Macromolecules* **2005**, *38* (16), 6902–6908.

(29) Khalimon, A. Y.; Piers, W. E.; Blackwell, J. M.; Michalak, D. J.; Parvez, M. A Photo Lewis Acid Generator (PhLAG): Controlled Photorelease of B(C 6F 5) 3. *J. Am. Chem. Soc.* **2012**, *134* (23), 9601–9604.

(30) Oestreich, M.; Hermeke, J.; Mohr, J. A Unified Survey of Si-H and H-H Bond Activation Catalysed by Electron-Deficient Boranes. *Chem. Soc. Rev.* **2015**, *44* (8), 2202–2220.

(31) Morgan, J.; Chen, T.; Hayes, R.; Dickie, T.; Urlich, T.; Brook, M. A. Facile Synthesis of Dendron-Branched Silicone Polymers. *Polym. Chem.* **2017**, *25*, 2401–2406.

(32) Thompson, D. B.; Brook, M. A. Rapid Assembly of Complex 3D Siloxane

Architectures. *J. Am. Chem. Soc.* **2008**, *130* (1), 32–33.

(33) Grande, J. B.; Thompson, D. B.; Gonzaga, F.; Brook, M. A.; Thompson, D. B.; Brook, M. A.; Chojnowski, J.; Rubinsztajn, S.; Fortuniak, W.; Kurjata, J.; et al. Testing the Functional Tolerance of the Piers–Rubinsztajn Reaction: A New Strategy for Functional Silicones. *Chem. Commun.* **2010**, *46* (27), 4988.

(34) Flory, P. J. Fundamental Principles of Condensation Polymerization. *Chem. Rev.* **1946**, *39* (1), 137–197.

(35) Chojnowski, J.; Kurjata, J.; Fortuniak, W.; Rubinsztajn, S.; Trzebicka, B. Hydride Transfer Ring-Opening Polymerization of a Cyclic Oligomethylhydrosiloxane. Route to a Polymer of Closed Multicyclic Structure. *Macromolecules* **2012**, *45* (6), 2654–2661.

(36) Chojnowski, J.; Rubinsztajn, S.; Fortuniak, W.; Kurjata, J. Oligomer and Polymer Formation in Hexamethylcyclotrisiloxane (D_3) - Hydrosilane Systems under Catalysis by Tris(Pentafluorophenyl) Borane. *J. Inorg. Organomet. Polym. Mater.* **2007**, *17* (1), 173–187.

(37) Longuet, C.; Joly-Duhamel, C.; Ganachaud, F. Copolycondensation of Regular Functional Silane and Siloxane in Aqueous Emulsion Using $B(C_6F_5)_3$ as a Catalyst A. *Macromol. Chem. Phys.* **2007**, *208* (17), 1883–1892.

(38) Owen, M. J. Siloxane Surface Activity: Silicon-Based Polymer Science; a Comprehensive Resource. In *Advances in chemistry series*; 1990; Vol. 24.

(39) Zha, R. H.; Vantomme, G.; Berrocal, J. A.; Gosens, R.; De Waal, B.; Meskers, S.; Meijer, E. W. Photoswitchable Nanomaterials Based on Hierarchically Organized Siloxane Oligomers. *Adv. Funct. Mater.* **2018**, *28* (1), 1–8.

(40) Piers, W. E. The Chemistry of Perfluoroaryl Boranes. *Adv. Organomet. Chem.* **2004**, *52* (04), 1–76.

(41) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. $B(C_6F_5)_3$-Catalyzed Hydrosilation of Imines via Silyliminium Intermediates. *Org. Lett.* **2000**, *2* (7), 3921.

(42) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. $B(C_6F_5)_3$-Catalyzed Silation of Alcohols: A Mild, General Method for Synthesis of Silyl Ethers. *J. Org. Chem.* **1999**, *64* (9), 4887–4892.

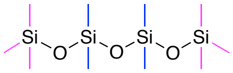
(43) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. A Novel Reduction of Alcohols and Ethers with a $HSiEt_3$catalytic $B(C_6F_5)_3$ System. *Tetrahedron Lett.* **1999**, *40* (50), 8919–8922.

(44) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. A Direct Reduction of Aliphatic Aldehyde, Acyl Chloride, Ester, and Carboxylic Functions into a Methyl Group. *J. Org. Chem.* **2001**, *66* (5), 1672–1675.

(45) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J. X.; Yamamoto, Y. A Novel $B(C_6F_5)_3$-Catalyzed Reduction of Alcohols and Cleavage of Aryl and Alkyl Ethers with Hydrosilanes. *J. Org. Chem.* **2000**, *65* (19), 6179–6186.

3.8. Appendix 2- Supporting Information

3.8.1. Hydrolysis products of pentamethyldisiloxane



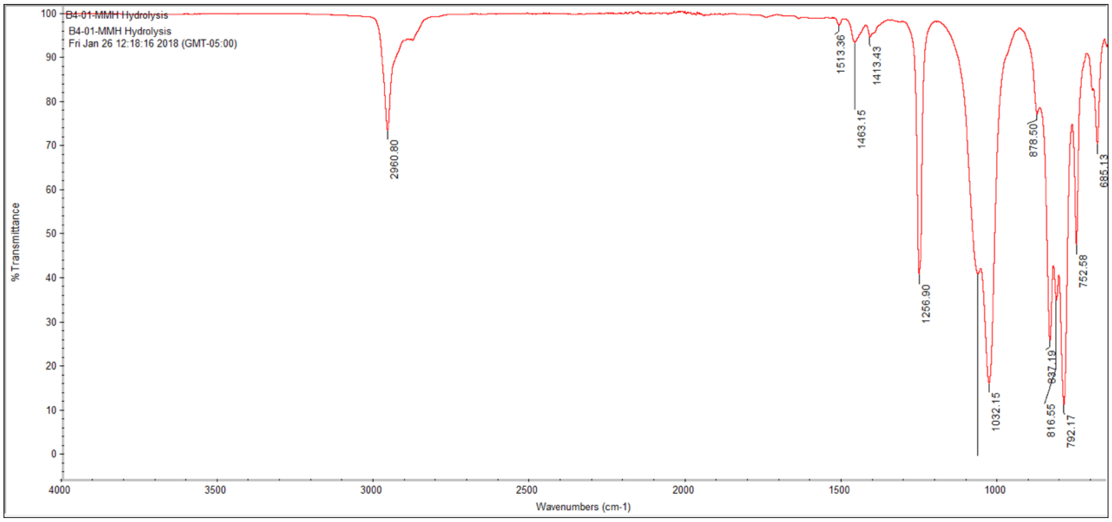
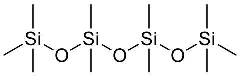
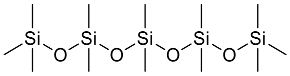
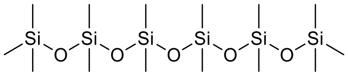
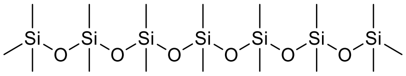
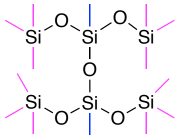


Figure S3.1. IR results for hydrolysis reaction using pentamethyldisiloxane (MM^H).

Table S3.1. GC-MS results for hydrolysis reaction using pentamethyldisiloxane (MM^H).

MM^H +H_2O ([OH]/[SiH]=4)			
Elution time (min)	M.W. (g/mol)	Structure	Relative ratio (%)
4.8	310		93
7.3	385		5
10.0	458		1
12.3	532		1

3.8.2. Hydrolysis products of Bis(trimethylsiloxy)methylsilane



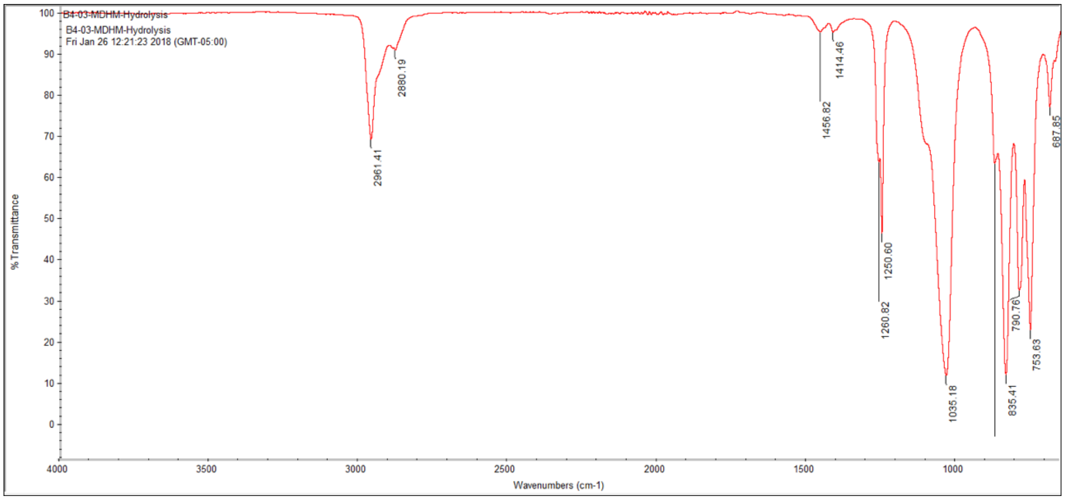
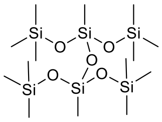


Figure S3.2. IR results for hydrolysis reaction using bis(trimethylsiloxy)methylsilane (MD^HM).

Table S3.2. GC-MS results for hydrolysis reaction using bis(trimethylsiloxy)methylsilane (MD^HM).

$MD^HM + H_2O$ ([OH]/[SiH]=4)			
Elution time (min)	M.W. (g/mol)	Structure	Relative ratio (%)
6.7	-[a]	-	3
9.3	458		97

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[a] Insufficient sensitivity to characterize the peak.

3.8.3. Hydrolysis reaction using a mixture of pentamethyldisiloxane (MM^H) and bis(trimethylsiloxy)methylsilane (MD^HM)

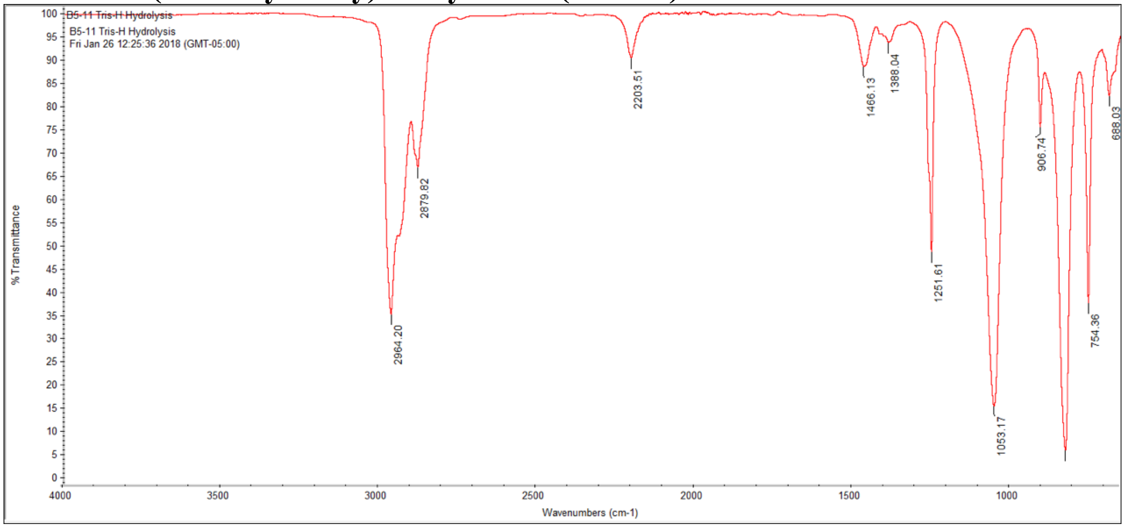
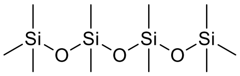
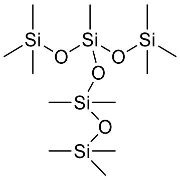
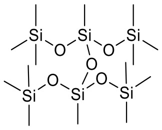


Figure S3.3. IR results for hydrolysis reaction using tris(trimethylsiloxy)silane.

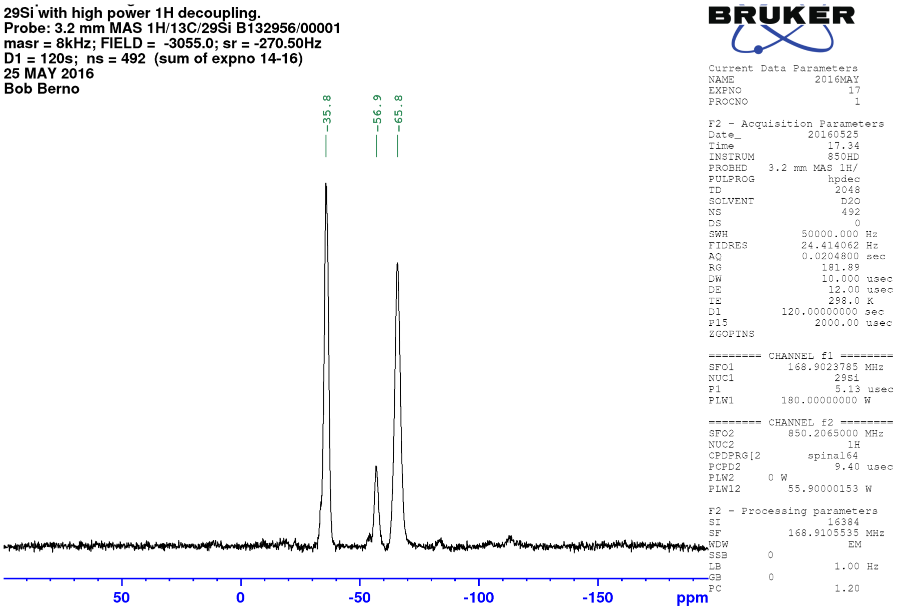
Table S3.3. GC-MS results for hydrolysis reaction using pentamethyldisiloxane (MM^H) and bis(trimethylsiloxy)methylsilane (MD^HM).

$MM^H + MD^HM + H_2O$ ([OH]/[SiH]=4)				
Elution time (min)	M.W. (g/mol)	Structure	Relative ratio (%)	Product ratio by ^{29}Si NMR (% ± 6%)
4.9	310		30	40
7.3	384		9	14
10.0	458		61	46

3.8.4. Silicone resin preparation using hydrolysis

Silicone resin preparation from D^H4 and water

Solid state NMR spectra for silicone resin



```
29Si with high power 1H decoupling.
Probe: 3.2 mm MAS 1H/13C/29Si B132956/00001
masr = 8kHz; FIELD = -3055.0; sr = -270.50Hz
D1 = 120s;  ns = 492  (sum of expno 14-16)
25 MAY 2016
Bob Berno
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Current Data Parameters
NAME              2016MAY
EXPNO                  17
PROCNO                  1

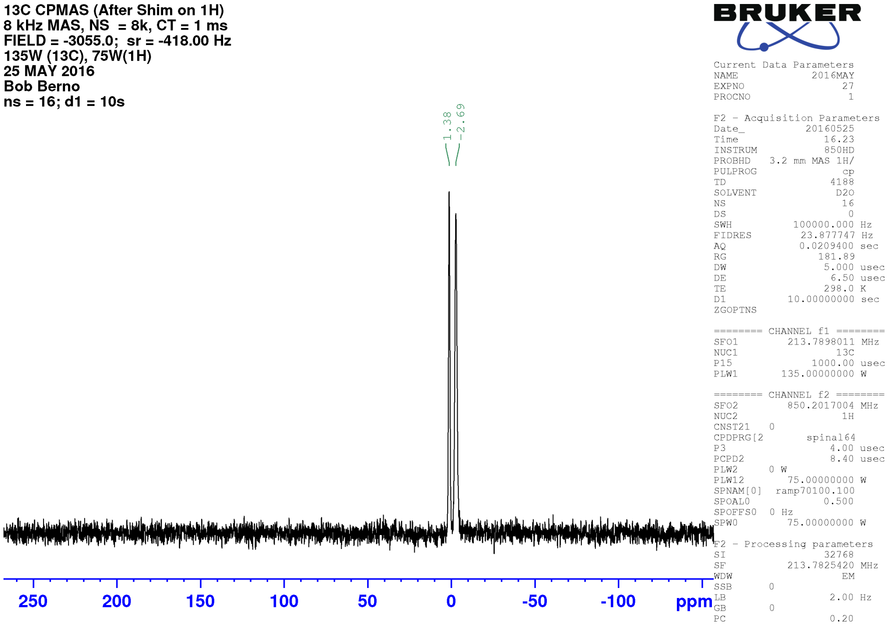
F2 - Acquisition Parameters
Date_            20160525
Time                17.34
INSTRUM             850HD
PROBHD   3.2 mm MAS 1H/
PULPROG             hpdec
TD                   2048
SOLVENT               D2O
NS                    492
DS                      0
SWH             50000.000 Hz
FIDRES          24.414062 Hz
AQ              0.0204800 sec
RG                 181.89
DW                 10.000 usec
DE                  12.00 usec
TE                  298.0 K
D1           120.00000000 sec
P15               2000.00 usec
ZGOPTNS

======== CHANNEL f1 ========
SFO1          168.9023785 MHz
NUC1                 29Si
P1                   5.13 usec
PLW1         180.00000000 W

======== CHANNEL f2 ========
SFO2          850.2065000 MHz
NUC2                   1H
CPDPRG[2         spinal64
PCPD2                9.40 usec
PLW2      0 W
PLW12         55.90000153 W

F2 - Processing parameters
SI                  16384
SF            168.9105535 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.20
```

Figure S3.4. ^{29}Si solid state NMR spectra for silicone resin preparation using $D^H{}_4$ and water.



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135W (13C), 75W(1H)
25 MAY 2016
Bob Berno
ns = 16; d1 = 10s
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Current Data Parameters
NAME              2016MAY
EXPNO                  27
PROCNO                  1

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AQ              0.0209400 sec
RG                 181.89
DW                  5.000 usec
DE                   6.50 usec
TE                  298.0 K
D1            10.00000000 sec
ZGOPTNS

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NUC1                  13C
P15               1000.00 usec
PLW1         135.00000000 W

======== CHANNEL f2 ========
SFO2          850.2017004 MHz
NUC2                   1H
CNST21    0
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PCPD2                8.40 usec
PLW2      0 W
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SPW0          75.00000000 W

F2 - Processing parameters
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SF            213.7825420 MHz
WDW                    EM
SSB       0
LB                   2.00 Hz
GB        0
PC                   0.20
```

Figure S3.5. ^{13}C solid state NMR spectra for silicone resin preparation using $D^H{}_4$ and water.

Table S3.4. Condensation polymerizations; homo- and copolymerization

Starting Materials		n	Mn	Mw	
$HSiMe_2O(SiMe_2O)_nSiMe_2H$	DMS-H31	360	26,600	39,300	1.48
	DMS-H11	5	1600	2700	1.68
	M^HM^H	0	110	110	1.00
$HOSiMe_2O(SiMe_2O)_{12}SiMe_2OH$	DMS-S14	12	1300	18,010	13.85
$HSiMe_2O(SiMePhO)_3SiMe_2H$	PMS-H03	3	370	400	1.08

Effect of [BCF]		n in $HSiMe_2O(SiMe_2O)_nSiMe_2H$	SM (g)	Reagent	water (g)	Open to air	[OH]/[SiH]	[BCF]/[SiH] mol%	conc BCF mg/ml	ml BCF	Solvent	solvent (mL)	rxn time (h)	Mn	Mw	Dispersity	
and chain	1	370	1.08	H_2O	0.002	N	3	0.01	0.52	0.007	NA	NA	3	41,900	65,500	1.56	
length	2	0	2.07	H_2O	0.858	N	3	0.02	51.2	0.06	NA	NA	3	50,100	76,300	1.52	
	3	5	2.14	H_2O	0.02	N	3	0.02	51.2	0.016	NA	NA	3	27,800	52,600	1.89	
	4	370	9.8	H_2O	0.02	N	3.2	0.02	51.2	1.4	NA	NA	3	33,400	50,900	1.53	
	5	370	1.1	H_2O	0.002	N	3	0.03	0.52	0.018	NA	NA	3	82,700	141,800	1.71	
	6	0	3.14	H_2O	0.4	N	1	0.02	51.2	0.09	NA	NA	3	52,700	105,400	2.00	
	7	0	5.01	H_2O	0.67	N	1	0.008	5.12	0.596	NA	NA	20	20,700	32,500	1.57	
	8	0	5.1	H_2O	0.402	N	0.6	0.04	5.12	2.98	NA	NA	22	77,200	140,800	1.82	
Reaction time	9	5	2.03	H_2O	0.23	N	3	0.02	51.2	0.016	NA	NA	24	46,000	86,200	1.88	
	10	5	2.14	H_2O	0.23	N	3	0.02	51.2	0.016	NA	NA	3	27,800	52,600	1.89	
	11	5	2.05	H_2O	0.72	N	1	0.02	51.2	0.016	NA	NA	1	2700	3100	1.15	
Water	12	5	2.03	H_2O	0.23	N	3	0.02	51.2	0.016	NA	NA	24	46,000	86,200	1.87	
source	13	5	3.01	humidity	56% RH	Y	NA	0.05	20	0.026	NA	NA	24	20,000	30,000	1.50	
	14	5	0.99	H_2O	230 ppm	Y	NA	0.07	20	0.012	toluene	10 ml	1	13,000	18,000	1.37	
	15	5	1.31	H_2O	230 ppm	Y	NA	0.05	10	0.023	toluene	15 ml	24	183,000	349,000	1.91	
	16	0	3.05	H_2O	0.3	N	0.75	0.004	5.12	0.18	DCM	1 g/ml	2.6	153,900	277,800	2.10	
Copolym-erization		n in $HSiMe_2O(SiMe_2O)_nSiMe_2H$												comonomer $HOSiMe_2O(SiMe_2O)_{370}SiMe_2OH$			SM (g)
	17	370	1.23	NA	NA	N	1	0.1	5.12	0.0126	NA		24	157,300	223,300	1.42	1
														$HOSiMe_2O(SiMe_2O)_{12}SiMe_2OH$			
	18	370	3.45	NA	NA	N	1	0.02	0.05	0.001	toluene	5+5+5	3	37,200	54,000	1.45	0.16
	19	370	3.45	NA	NA	N	1	0.02	0.05	0.001	toluene	5+5+5	24	45,100	70,600	1.57	0.16
	20	370	3.45	NA	NA	N	1	0.05	0.05	0.0025	toluene	5+5+5	3	180,000	363,200	2.02	0.16
	21	370	3.45	NA	NA	N	1	0.05	0.05	0.0025	toluene	5+5+5	24	251,000	471,500	1.88	0.16
		n in $HSiMe_2O(SiMePhO)_nSiMe_2H$												$HOSiMe_2O(SiMe_2O)_{12}SiMe_2OH$			
	22	3	0.5	NA	NA	N	1	0.02	0.05	0.01	toluene	5+5	3	14,400	21,200	1.47	1.5
	23	3	0.5	NA	NA	N	1	0.02	0.05	0.01	toluene	5+5	24	15,500	24,000	1.55	1.5

Chapter 4: Spatially Controlled Hyperbranched Vinylsilicones&

4.1. Abstract

Branched silicones possess interesting properties as oils, including their viscoelastic behavior, or as precursors to controlled networks. However, highly branched silicone polymers are difficult to form reliably using a “grafting to” strategy because functional groups may be bunched together preventing complete conversion for steric reasons. We report the synthesis of vinyl-functional highly branched silicone polymers based, at their core, on the ability to spatially locate functional vinyl groups along a silicone backbone at the desired frequency. Macromonomers were created and then polymerized using the Piers–Rubinsztajn reaction with dialkoxyvinylsilanes and telechelic HSi-silicones; molecular weights of the polymerized macromonomers were controlled by the ratio of the two reagents. The vinyl groups were subjected to iterative (two steps, one pot) hydrosilylation with alkoxysilane and Piers–Rubinsztajn reactions, leading to high molecular weight, highly branched silicones after one or two iterations. The vinyl-functional products can optionally be converted to phenyl/methyl-modified branched oils or elastomers.

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Mengchen Liao performed all experiments and was the lead author of the manuscript. Chen provided guidance for experiments.

4.2. Introduction

Macromolecules comprised of dendritic structures have been widely utilized in a variety of different areas both in academia and industry[1-3]. The introduction of, normally, randomly dispersed dendritic units with multi-functionalities along the polymeric backbone is key to the unique physiochemical properties they possess[4,5]. In comparison with their linear counterparts, highly branched materials exhibit low viscosity, enhanced solubility and the higher density branches can optionally possess functional groups to allow further modification[6]. The relative simplicity of the synthetic routes to dendritic branches differentiates them from the perfectly structured dendrimers that require laborious synthesis and work-up procedures; the higher the generation number, the more likely one is to generate defects. The former approach is therefore more suitable for industrial scale-up[7] . In light of their unique properties, highly branched and hyperbranched polymers have been commercialized for applications ranging from coatings, additives, and insulators to biomedical applications[8–12].

Dendritic moieties are, by definition, sterically demanding. As a consequence, when forming dendritic branches using a ‘grafting to’ process on a polymer backbone, it can be difficult to achieve complete reaction because: i) the backbone provides steric encumbrance that decreases the likelihood of successful grafting, a situation that, ii) is made worse when functional groups on the backbone are found in close proximity. The random dispersion of the dendritic units throughout the macromolecules leads to the formation of irregular structures[13]. Would a synthetic benefit be realized by controlling spatial location of the dendritic branches, and would spatial distribution contribute to useful properties?

Polysiloxanes are renowned for their flexibility, biocompatibility, gas permeability, low T_g, hydrophobicity and low surface energy[14–16]. The initial investigations of hyperbranched polysiloxanes were conducted by Muzafarov and co-workers through condensation of triethoxysilanol, catalyzed by ammonia, that yielded a transparent polymer[17,18]. In 2000, Paulasaari and Weber established lithium silanolate-initiated anionic polymerization (**Figure 4.1**A) for the preparation of a vinyl-containing hyperbranched polysiloxane with a molecular weight (MW) of 29,050 g mol^{-1} (vinyl = Vi = ~$HC{=}CH_2$)[19,20]. Chojnowski and co-workers further advanced this methodology with the synthesis from vinyl-substituted cyclotrisiloxanes of give vinyl-containing branched polysiloxanes of various topologies, including star- to dendritic-branched architectures (**Figure 4.1**B)[21].

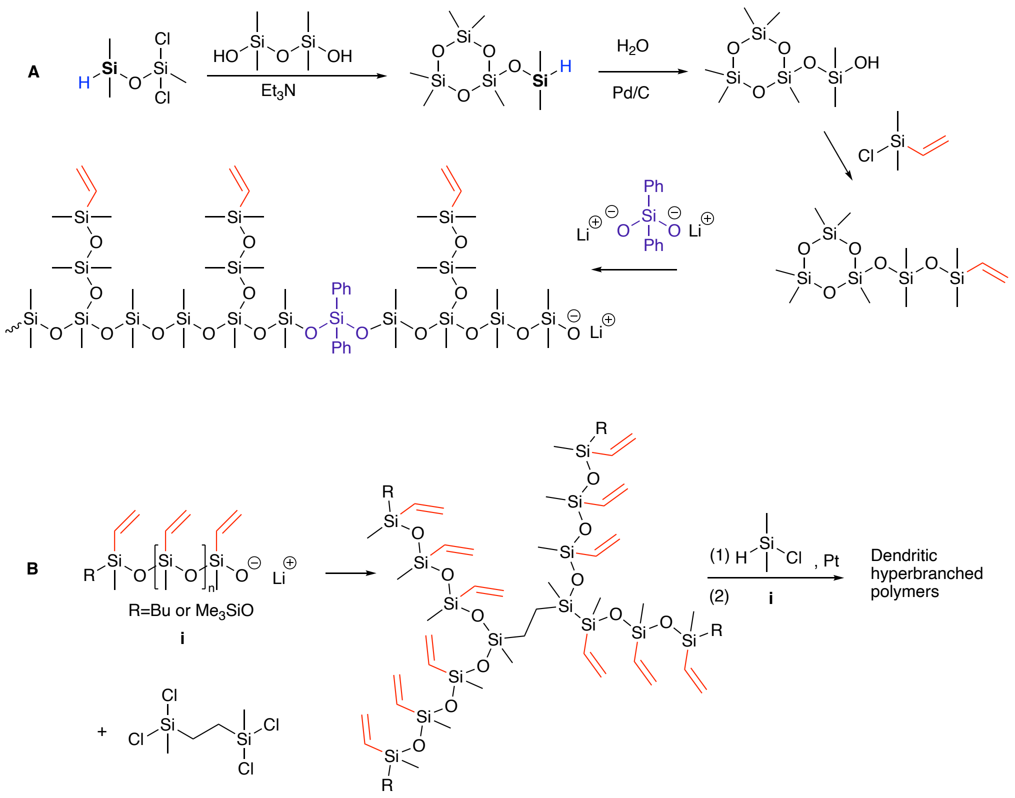


Figure 4.1. (**A**) The synthesis of hyperbranched polysiloxane using anionic ring-opening polymerizations[19]; (**B**) The synthesis of dendritic- branched polysiloxanes[21].

The Piers-Rubinsztajn reaction (PR), which provides a facile route to structural complex silicones, involves the reaction of hydrosilanes with the strong Lewis acid $B(C_6F_5)_3$ catalyst in the presence of appropriate nucleophiles[22]. We previously reported the use of this process combined with hydrosilylation reactions to synthesize precise silicone dendrimers with molar mass of up to 13,500 g mol^{-1} using iterative reactions of PR and platinum-catalyzed hydrosilylation in the absence of degradation (**Figure 4.2**A,C)[23]. Well-defined silicone resins with tunable branching degrees could also be prepared using this pair of reactions[24].

We wished to create highly branched linear silicone polymers with different branching densities, to take advantage of the benefits these polymers convey. While synthesis of the monomer branches was straightforward (**Figure 4.2**A,C), it was not always possible to achieve complete grafting of highly branched species onto randomly located SiH functional groups typically found on commercial silicones (unpublished data, **Figure 4.2**B); this inefficiency was ascribed to the steric hinderance in zones of high functional group density on the backbone (**Figure 4.2**D). Such inhomogeneity is unavoidable in functional silicones prepared by traditional redistribution reactions[25]. We reasoned two factors could be used to decrease sensitivity to steric issues: i) move the locus of reaction further away from the silicone backbone by use of vinyl groups on the backbone instead of SiH groups, and, ii) control the spatial distribution of vinyl groups to ensure adjacent functional groups are avoided (**Figure 4.2**E). In the dendrimeric vernacular, this refers to divergent rather than convergent growth or, ‘grafting from’ rather than ‘grafting to’.

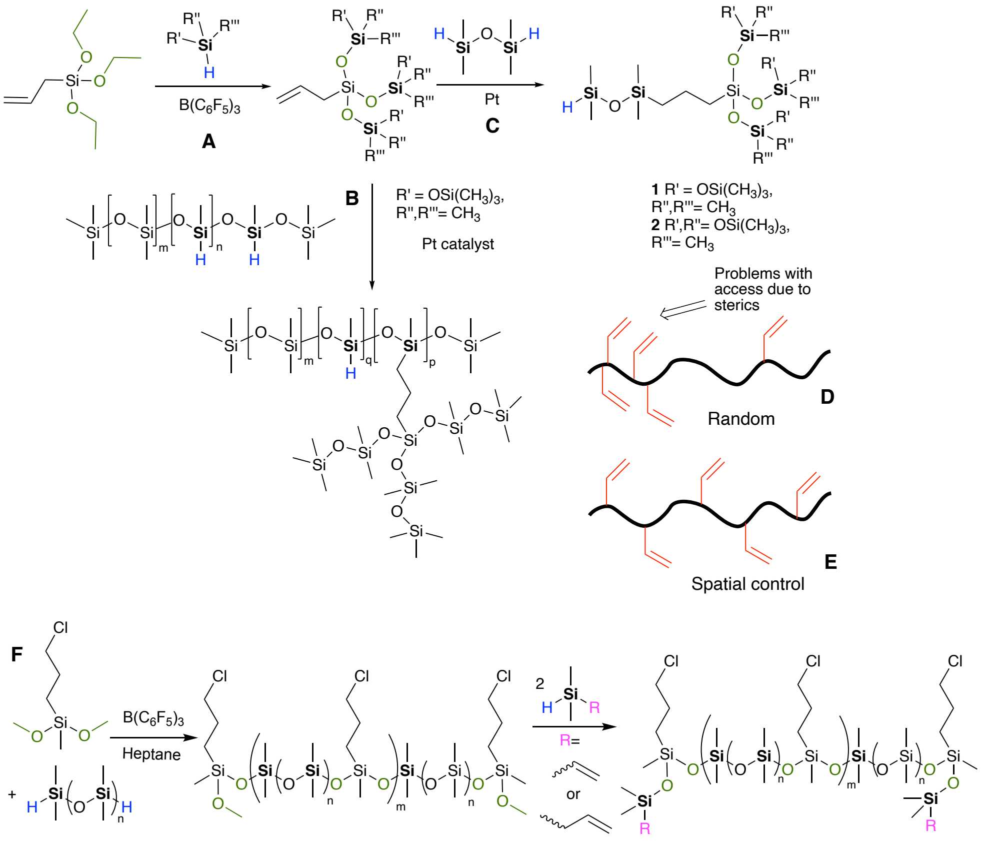


Figure 4.2. The preparation of (A, C): well-defined silicone dendrons *via* iterative process[24]. B: higher branched polymers. Model comparison of vinylsilicones. (D): random, (E). controlled locations. Using the Piers–Rubinsztajn reaction to prepare spatially controlled F: chloropropylsilicones[26].

The concept of properly controlling polymer synthesis using the perspective of synthetic organic chemists is gaining traction[27]. In the case of silicones, Skov and co-workers initially reported a strategy for synthesizing siloxane copolymer with spatially distributed pendent functional groups, including alkyl chloride and alkyl azide, using the PR reaction[26]. Such polymers should be less sensitive to steric issues during further functionalization because the sequence ensures functional groups maintain a constant distance along the backbone (**Figure 4.2**E,F). Using this strategy, we describe preparation of a hierarchical library of precisely spaced vinyl, or alkoxy, pendent linear silicones with either SiH or methoxy at the termini via iterative PR condensation and platinum-catalyzed hydrosilylation. The products include polymers bearing both SiH and SiVinyl groups, which are difficult to prepare by traditional routes. The polymers underwent self-crosslinking in a one-pot process to give soft elastomers possessing residual vinyl groups that, we show, can undergo secondary modification with different silicones. We expanded this concept to create a library of silicone crosslinkers possessing dendritic branches with different degrees of vinyl and alkoxy functionalization and show that, at lower generations, steric problems with functionalization are avoided.

4.3. Materials and Methods

4.3.1. Materials

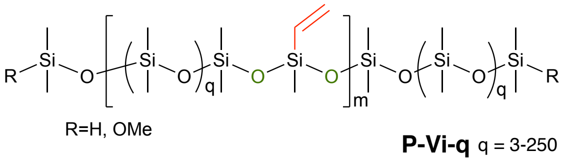
Pentamethyldisiloxane ($Me_3SiOSiMe_2H$, MM^H), bis(trimethylsiloxy)methylsilane ($(Me_3SiO)_2SiMeH$, MD^HM), tetramethyldisiloxane (**H-0-H** $HMe_2SiOSiMe_2H$, M^HM^H), phenyldimethylsilane and vinyltetramethyldisiloxane were purchased from Gelest and used as received. Hydride-terminated PDMS (**H-13-H** DMS-H03, MW=1,100 g mol^{-1}; **H-18-H** DMS-H11, MW=1,500 g mol^{-1}; **H-77-H** DMS-H21, MW=5,800 g mol^{-1}; **H-285-H** DMS-H25, MW=21,200 g mol^{-1}; DMS-H31, MW=24,400 g mol^{-1}) were purchased from Gelest and were vacuum distillation (kugelrohr) at 120 °C for 1 h prior to use. Hydride-terminated phenyl pendant PDMS (PMS-H03, 370 g mol^{-1}) was purchased from Gelest and used as received. Dimethoxymethylvinylsilane (97%), triethoxysilane and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst) in xylene (Pt 2%) were obtained from Sigma Aldrich and used as received. $B(C_6F_5)_3$ was purchased from Alfa Aesar. Toluene (solvent) received from Carleton (HPLC grade) was dried over activated alumina before use. Deuterated NMR solvent ($CDCl_3$) was obtained from Cambridge Isotope Laboratories. All glass apparatus were dried overnight at 120 °C and cooled under a dry nitrogen atmosphere for 30 min prior to use.

4.3.2. Methods

^1H NMR spectra were recorded on a Bruker AV600 MHz spectrometer using deuterated solvents ($CDCl_3$). Gel permeation chromatography (GPC), a Viscotek GPC Max (VE 2001 GPC Solvent/Sample Module) was used to determine molecular weights. The system was equipped with a Viscotek VE 3580 RI Detector, a Viscotek 270 Dual Detector, and a PolyAnalytik SupeRes PAS-101 (8 mm × 30 cm) column with a single pore, styrene-divinylbenzene gel, 6 μm particle size. Toluene was used as the eluent at a flow rate of 1.0 mL min^{-1}. Refractive index (R_f) measurement was carried out with a VEE GEE Scientific Abbe Refractometer Model C10.

4.3.3. Synthesis

General procedures for the preparation of vinylsilicones with controlled spacing. Shown for P-Vi-14



P-Vi-q q = 3-250

Hydride-terminated PDMS (**H-13-H**, 43.56 g, 39.60 mmol) was weighed into a 1.0 L three-neck round-bottomed flask with dry hexanes (218.0 mL). The flask was flushed with nitrogen before capping with a septum and left under a positive pressure of dry nitrogen. $B(C_6F_5)_3$ stock solution (0.079 mL, 51.2 mg mL^{-1} in dry toluene, 0.0079 mmol) was added before adding excess dimethoxymethylvinylsilane (6.29 g, 47.57 mmol). The mixture was stirred for 3h before neutral alumina was added to the flask to quench the $B(C_6F_5)_3$ catalyst, followed by filtration through Celite and rinsing with hexanes. **P-Vi-14** was obtained by removing hexanes under reduced pressure (rotavap at 60 °C) with yield of 83.8% (41.77 g) and vinyl conc. of 7% calculated based on the ^1H NMR data (sample calculation, see Supporting Information, SI).

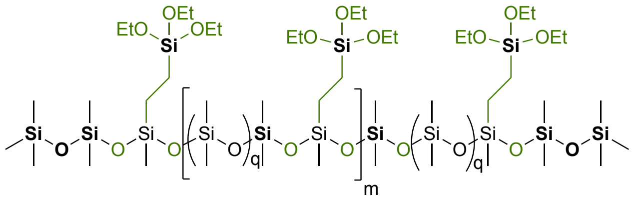
^1H NMR (600 MHz, chloroform-*d*): δ 5.77-6.02 (m, 3H, SiC*H*=C*H*$_2$), 3.47-3.48 (s, 0.10H, SiOC*H*$_3$), 0.05-0.13 (m, 83.55H, SiC*H*$_3$) ppm; GPC: M_n=37,400 g mol^{-1}; M_w=69,300 g mol^{-1}; $Đ_M$=1.85.

Capping OMe groups in P-Vi-14

P-Vi-14 (10.63 g, 0.28 mmol) and pentamethyldisiloxane (MM^H, 0.169 g, 1.15 mmol) were added to a pre-dried 25 0.0 mL round-bottomed flask together with dry hexanes (50.0 mL). The reaction flask was capped and flushed with dry nitrogen. $B(C_6F_5)_3$ stock solution (0.114 mL, 5.12 mg mL^{-1} in dry toluene, 0.00114 mmol) was added. The mixture was stirred for 3h before neutral alumina was added to the flask to quench the $B(C_6F_5)_3$ catalyst, followed by filtration through Celite and rinsing with hexanes. The capped product was obtained by removing hexanes under reduced pressure with yield of 97.6% (10.54 g) and vinyl conc. of 7% based on ^1H NMR data.

^1H NMR (600 MHz, chloroform-*d*): δ 5.77-6.04 (m, 3H, SiC*H*=C*H*$_2$), 0.05-0.19 (m, 84.62H, SiC*H*$_3$) ppm; GPC: M_n=39,000 g mol^{-1}; M_w=73,700 g mol^{-1}; $Đ_M$=1.89.

Synthesis of compound P-Vi-14-OR$_3$



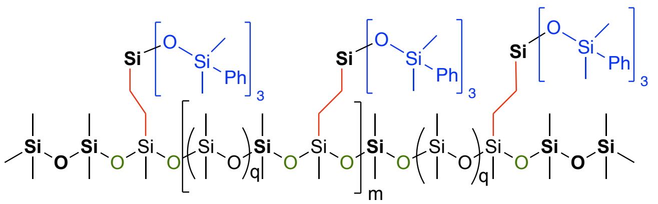
P-Vi-14-OR$_3$

q = 14

The capped compound from the previous step (10.38 g, 0.27 mmol) and triethoxysilane (4.88 g, 29.71 mmol) were added to a pre-dried 250.0 mL round-bottomed flask together with dry hexanes (30.0 mL). The reaction flask was capped and flushed with dry nitrogen. Karstedt's catalyst (0.015 mL, 2 wt% in xylene) was then directly added from the bottle. The mixture was stirred at room temperature for 24h before activated carbon was added to the flask to quench the Karstedt's catalyst followed by filtration through Celite and rinsing with hexanes. **P-Vi-14-OR$_3$** was obtained by removing hexanes under reduced pressure with yield of 75% (11.43 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ 3.79-3.83 (m, 6H, SiOCH_2CH$_3$), 1.20-1.23 (m, 9.04H, SiOCH$_2$CH_3), 0.50-0.59 (m, 3.43H, SiCH_2-CH_2-Si), 0.06-0.08 (m, 78.53H, SiCH_3) ppm; GPC: M_n=99,300 g mol^{-1}; M_w=185,400 g mol^{-1}; $Đ_M$=1.87.

Synthesis of compound P-Vi-14-OSi$_3$

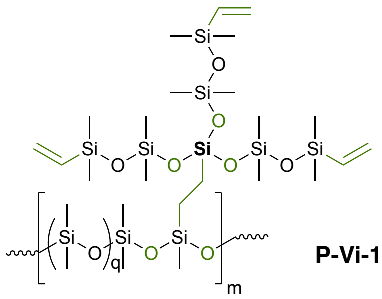


P-Vi-14-OSi$_3$

P-Vi-14-OR$_3$ (0.088 g, 0.0053 mmol) and phenyldimethylsilane (0.07 g, 0.514 mmol) were added to a pre-dried 25.0 mL round-bottomed flask together with dry hexanes (5.0 mL). The reaction flask was capped and flushed with dry nitrogen. $B(C_6F_5)_3$ stock solution (0.0197 mL, 5.12 mg mL^{-1} in dry toluene, 0.000197 mmol) was added. The mixture was stirred for 3h before neutral alumina was added to the flask to quench the $B(C_6F_5)_3$ catalyst followed by filtration through Celite and rinsing with hexanes. **P-Vi-14-OSi$_3$** was obtained by removing hexanes under reduced pressure with yield of 66% (0.11 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ 7.32-7.54 (m, 24.57H, aromatic H), 0.41-0.42 (m, 4H, SiCH_2-CH_2-Si), 0.02-0.08 (m, 118.36H, SiCH_3) ppm; GPC: M_n=55,000 g mol^{-1}; M_w=116,500 g mol^{-1}; Đ$_M$=2.12; R_I=1.383.

Synthesis of compound P-Vi-14-OVi$_3$

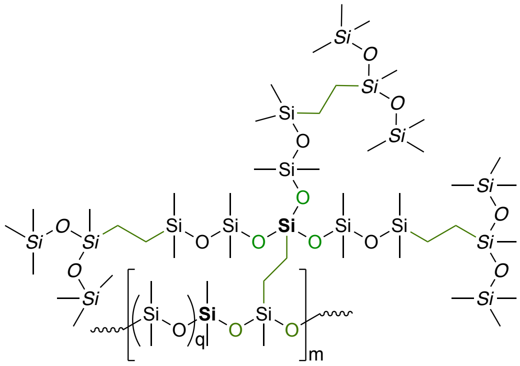


P-Vi-14-OVi$_3$

P-Vi-14-OR$_3$ (0.89 g, 0.053 mmol) and vinyltetramethyldisiloxane (1.38 g, 8.61 mmol) were added to a pre-dried 250.0 mL round-bottomed flask together in dry hexanes (25.0 mL). The reaction flask was capped and flushed with dry nitrogen. $B(C_6F_5)_3$ stock solution (0.127 mL, 5.12 mg mL^{-1} in dry toluene, 0.00127 mmol) was added. The mixture was stirred for 3h before neutral alumina was added to the flask to quench the $B(C_6F_5)_3$ catalyst followed by filtration through Celite and rinsing with hexanes. **P-Vi-14-OVi$_3$** was obtained by removing hexanes under reduced pressure with yield of 76% (1.73 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ 5.71-6.16 (m, 9H, SiC*H*=C*H*$_2$), 0.45-0.46 (m, 2.24H, SiC*H*$_2$-C*H*$_2$-Si), 0.06-0.16 (m, 93.34H, SiC*H*$_3$) ppm; GPC: M$_n$=278,800 g mol^{-1}; M$_w$=582,500 g mol^{-1}; $Đ_M$=2.09. We attribute this higher than expected increase in MW to adventitious hydrolysis/condensation of the polymers.

Synthesis of compound P-Vi-14-OSi$_3$OSi$_9$

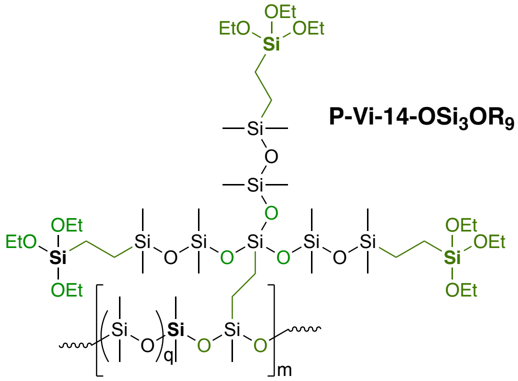


P-Vi-14-OSi$_3$OSi$_9$

P-Vi-14-OVi$_3$ (0.33 g, 0.0012 mmol) and bis(trimethylsiloxy)methylsilane (MD^{H}M, 0.37 g, 1.67 mmol) were added to a pre-dried 50.0 mL round-bottomed flask together with dry hexanes (25.0 mL). The reaction flask was capped and flushed with dry nitrogen. Karstedt's catalyst (0.0075 mL, 2 wt% in xylene) was then directly added. The mixture was stirred for 24h before activated carbon was added to the flask to quench the Karstedt's catalyst followed by filtration through Celite and rinsing with hexanes. **P-Vi-14-OSi$_3$OSi$_9$** was obtained by removing hexanes under reduced pressure with yield of 70% (0.49 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ 0.32-0.56 (m, 16H, SiC*H*$_2$-C*H*$_2$-Si), 0.01-0.09 (m, 178.59H, SiC*H*$_3$) ppm; GPC: M$_n$=310,500 mol^{-1}; M$_w$=609,200 g mol^{-1}; $Đ_M$=1.96.

Synthesis of compound P-Vi-14-OVi$_3$OR$_9$



P-Vi-14-OSi$_3$OR$_9$

P-Vi-14-OVi$_3$ (0.079 g, 0.000283 mmol) and triethoxysilane (0.083 g, 0.51 mmol) were added to a pre-dried 50.0 mL round-bottomed flask together with dry hexanes (10.0 mL). The reaction flask was capped and flushed with dry nitrogen. Karstedt's catalyst (0.0075 mL, 2 wt% in xylene) was then added. The mixture was stirred for 24h before activated carbon was added to the flask to quench the Karstedt's catalyst followed by filtration through Celite and rinsing with hexanes to give, after removing hexanes under reduced pressure, with a yield of 89% (0.14 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ 3.81-3.83 (m, 18H, SiOCH_2CH$_3$), 1.21-1.25 (m, 27.28H, SiOCH$_2$CH_3), 1.53 (s, 10.40H), 0.45-0.67 (m, 14.89H, SiCH_2-CH_2-Si), 0.04-0.08 (m, 113.63H, SiCH_3) ppm; GPC: M_n=56,400 g mol^{-1}; M_w=109,200 g mol^{-1}; $Đ_M$=1.94.

Attempted branching of compound P-Vi-14-OVi$_3$OR$_9$

P-Vi-14-OVi$_3$OR$_9$ (0.159 g, 0.0028 mmol) and bis(trimethylsiloxy)methylsilane (MD^{H}M, 1.779 g, 7.995 mmol) were added to a pre-dried 50.0 mL round-bottomed flask together in with dry hexanes (20.0 mL). The reaction flask was capped and flushed with dry nitrogen. B(C$_6$F$_5$)$_3$ stock solution (0.131 mL, 5.12 mg mL^{-1} in dry toluene, 0.00131 mmol) was added. The mixture was stirred for 24 h before neutral alumina was added to the flask to quench the $B(C_6F_5)_3$ catalyst. By ^1H NMR, the conversion of the ethoxy groups is < 20%.

^1H NMR (600 MHz, chloroform-*d*): δ 4.62-4.63 (m, 9.63H, Si*H*), 3.72-3.75 (m, 16.19H, $SiOCH_2CH_3$), 1.53 (s, 15.70H), 1.19-1.23 (m, 24.24H, $SiOCH_2CH_3$), 0.55-0.64 (m, 16H, $SiCH_2$-CH_2-Si), 0.02-0.12 (m, 2757.83H, $SiCH_3$) ppm.

The mixture from the above procedure was further heated at 50 °C for 24 h and based on the ^1H NMR, the maximum conversion of the ethoxy groups was 53%.

^1H NMR (600 MHz, chloroform-*d*): δ 4.62 (m, 0.61H, Si*H*), 3.72-3.81 (m, 9.43H, $SiOCH_2CH_3$), 1.19-1.23 (m, 15.21H, $SiOCH_2CH_3$), 0.54-0.56 (m, 16H, $SiCH_2$-CH_2-Si), 0.02-0.10 (m, 2090.55H, $SiCH_3$) ppm; GPC: M_n= 18,000 g mol^{-1}; M_w=49,300 g mol^{-1}; $Đ_M$=2.75. This low MW indicates that most of the material has been converted to a macroscopic resin, and only low MW materials remain in solution.

Synthesis of silicone elastomers using controlled spacing hydride-terminated vinyl-containing linear silicone

Step 1 (Table 4.2): **Synthesis of hydride-terminated, vinyl-pendant linear silicones (P-Vi-28)**

Hydride-terminated PDMS (**H-18-H**, 1,500 g mol^{-1}, 1.03 g, 0.94 mmol) was weighed into a 250.0 L three-neck round-bottomed flask with dry hexanes (5.0 mL). The flask was flushed with nitrogen before capped with a septum and left under positive nitrogen pressure. $B(C_6F_5)_3$ stock solution (0.133 mL, 51.2 mg mL^{-1} in dry toluene, 0.0133 mmol) was added before adding in dimethoxymethylvinylsilane (0.074 g, 0.560 mmol). The mixture was stirred for 3h before neutral alumina was added to the flask to quench the $B(C_6F_5)_3$ catalyst followed by filtration through Celite and rinsing with hexanes. The product **P-Vi-28** was obtained by removing hexanes under reduced pressure with yield of 84% (0.93 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ 5.78-6.03 (m, 3H, Si*C**H*=C*H*$_2$), 4.70-4.74 (Si*H*, m, 0.11H), 0.07-0.45 (m, 164.66H) ppm; GPC: M_n=65,700 g mol^{-1}; M_w=91,300 g mol^{-1}; $Đ_M$=1.39.

Step 2: **Synthesis of silicone elastomer using P-Vi-28 (entry 3, Table 4.2)**

The product obtained from **Step 1** (0.928 g, 0.014 mmol) and Karstedt's catalyst (0.260 mL, 5 mg mL^{-1} in dry toluene) were added into a 24-well plate. After stirring, the mixture was then placed under vacuum at 80 °C for 3h.

Step 3: Synthesis of silicone elastomer 2:1 SiH/SiVinyl from **P-Vi-28 (entry 5, Table 4.2)**

The as-prepared vinyl containing elastomer (0.078 g, 0.042 mmol for Si^{Vi}) was allowed to swell in toluene (2 mL) containing PMS-H03 (0.0158 g, 0.085 mmol for Si^{H}) for 24h in a 25 mL glass vial prior to the addition of Karstedt's catalyst (0.0188 mL, 5 mg mL^{-1} in dry toluene).

OR **Step 3**: **Synthesis of silicone elastomer 1:1 SiH/SiVinyl from P-Vi-28 (entry 6, Table 4.2)**

The as-prepared vinyl containing elastomer (0.07 g, 0.038 mmol for Si^{Vi}) was swollen in toluene (2 mL) and PMS-H03 (0.007 g, 0.038 mmol for Si^{H}) for 24h in a 25 mL glass vial prior to the addition of Karstedt's catalyst (0.0154 mL, 5 mg mL^{-1} in dry toluene). In either case, the vial was then paced at 80 °C oven for 24h; the longer reaction time for the evaporation of toluene (solvent).

4.4. Results

Spatial control of vinyl groups on a silicone backbone was provided by the PR reaction between the difunctional vinyl monomer vinyldimethoxymethylsilane and αω-hydride-terminated PDMS of various chain lengths ranging from the disiloxane to longer chain linear polymers (MW 134 to 21,200 g mol^{-1} **H-D$_n$-H** D = Me_2SiO, **H** = M^H = $Me_2HSiO_{2/2}$ Thus, **H-13-H** = $M^HD_{13}M^H$) in the presence of catalytic amount of $B(C_6F_5)_3$ (0.02 - 0.20 mol% (**Figure 4.3**A)[28]. Using ^1H NMR, the depletion of hydrosilane (SiH, ~4.7 ppm) or methoxy (SiOCH3, ~3.5 ppm) signals allowed one to demonstrate full consumption of reagents had occurred to give **P-Vi-q**, where q = spacing between adjacent vinyl groups. Thus, **P-Vi-3** = $((ViMeSiO)(Me_2SiO)_2)_m$).

The nature of the terminal functional groups were easily controlled simply by adjusting the [SiH]/[SiOMe] ratio (**Table 4.1**). Interestingly, at a stoichiometric [SiH]/[SiOMe] ratio, methoxy-terminated compounds were often obtained due to the occurrence of side reactions including metathesis that consumed some of the hydrosilanes ($2\ R_3SiOSiMe_2H \rightarrow R_3SiOSiMe_2OSiR_3 + Me_2SiH_2$, **Figure 4.4**A,B)[29]. Three factors controlled the precision of the spatial location of vinyl groups: the $Đ_M$ of the telechelic silicone; loss of functional groups due to undesired metathesis; and, the degree to which the reaction maintains a dry state[29]. Any defects are manifested in the differences, in some cases, between the expected vinyl frequency based on starting materials and the observed vinyl frequency in the product. For example, the expected vinyl% for the product of **H-13-H** should be about 7%, but in some cases was slower than expected due to chain extension from water (**Figure 4.4**A,B, entry 6 *vs* 2,10, **Table 4.1**)[29].

As with any AA + BB polymerization, the ultimate molecular weight was dependent on the precision with which the AA/BB stoichiometry was matched. One advantage with this chemistry is that, if water prematurely terminates the process, polymerization can be restarted using small quantities of a difunctional HSi compound (although, as noted above, this will lead to a defect in the vinyl spacing). Relatively high yields were obtained for these polymerizations (75-99%) except in the case of M^HM^H which, due to its high volatility, was partly lost once exposed to the heat released during the exothermic Piers–Rubinsztajn reaction[30]. The vinyl concentrations ($SiCH{=}CH_2$, ~5.8 ppm) in the resulting polymers varied from 0.4 to 29% in products with molecular weights ranging from 12,000 to 143,000 g mol^{-1} (^1H NMR and GPC data refer to **Table S4.1** and **Table S4.2** in the Supporting Information, SI).

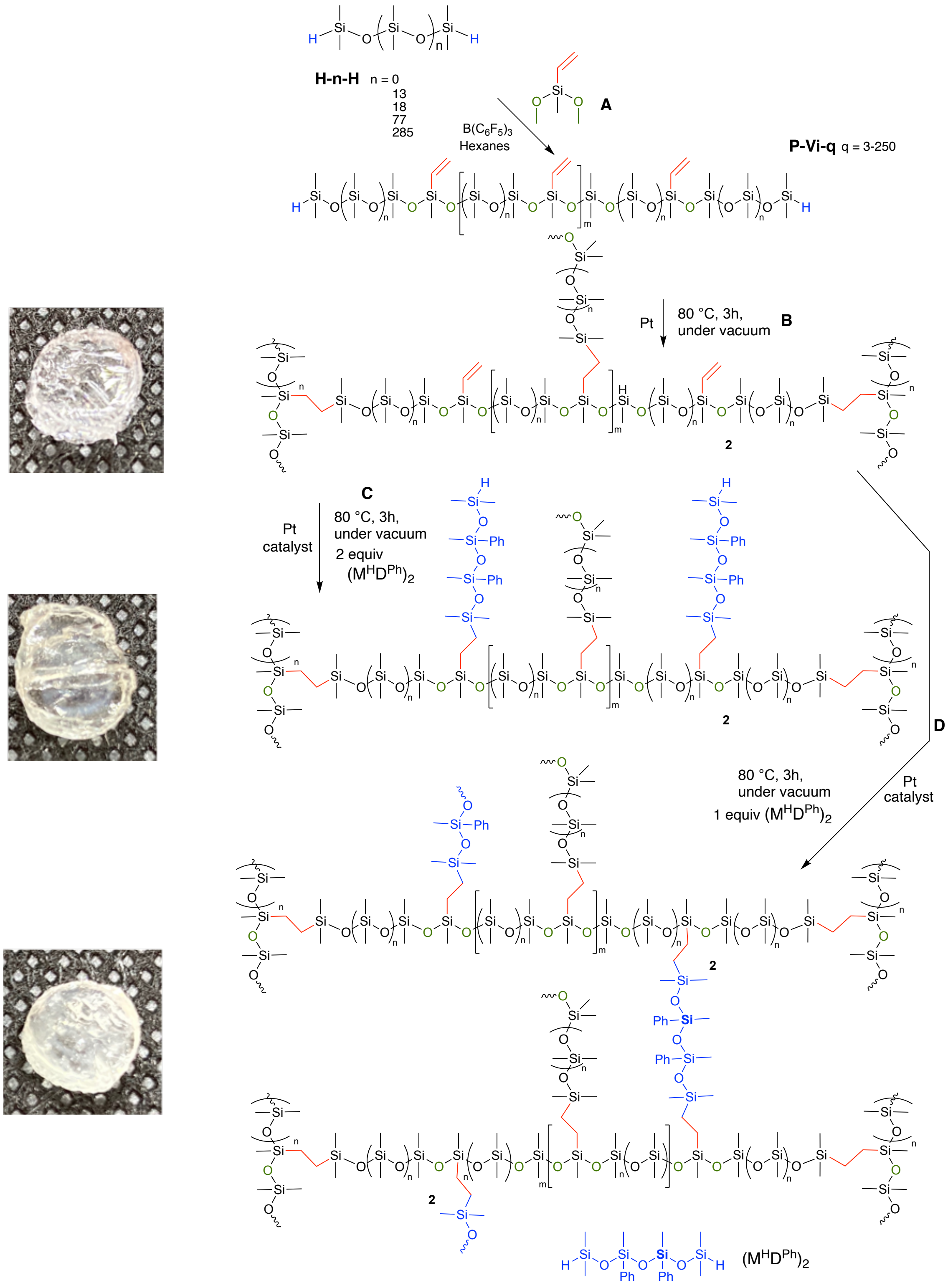


Figure 4.3. Synthesis of well-defined branched silicones using (A) Spatially controlled vinylsilicones using the Piers–Rubinsztajn reaction, shown for SiH terminated. (B) Self-curing of **P-Vi-n**. (C) Grafting of SiH branches using $(M^{H}D^{Ph})_2$. (D) Crosslinking using $(M^{H}D^{Ph})_2$.

Table 4.1. The synthesis of spatially controlled vinyl silicones with SiH or SiOMe as terminal functional groups

#	H-D$_n$-H[a]	M$_n$ (g mol^{-1})[b]	[SiH]/ [SiOMe]	M$_n$ (g mol^{-1})[c]	$Đ_M$	DP[d]	Product Name P-Vi-q	Vinyl conc. (%)	Yield (%)	Terminal groups
1	**H-0-H**	134	1	N/A[e]	N/A[e]	-	**P-Vi-3**	31.5	66	OMe
2	**H-13-H**	1,100	1	85,800	1.65	78	**P-Vi-16**	6.1	86	OMe
3	**H-18-H**	1,500	1	102,400	1.11	68	**P-Vi-26**	3.9	75	OMe
4	**H-77-H**	5,800	1	87,000	1.20	15	**P-Vi-200**	0.5	84	OMe
5	**H-0-H**	134	1.2	25,200	1.68	188	**P-Vi-4**	28.8	54	SiH
6	**H-13-H**	1,100	1.2	26,900	1.68	24	**P-Vi-29**	3.4	86	SiH
7	**H-18-H**	1,500	1.2	65,700	1.39	44	**P-Vi-28**	3.6	84	SiH
8	**H-77-H**	5,800	1.2	13,300	2.09	2	**P-Vi-111**	0.9	89	SiH
9	**H-0-H**	134	0.83	N/A[e]	N/A[e]	-	**P-Vi-3**	35.4	63	OMe
10	**H-13-H**	1,100	0.83	37,400	1.85	34	**P-Vi-14**	6.9	84	OMe
11	**H-18-H**	1,500	0.83	23,600	2.15	16	**P-Vi-17**	5.7	99	OMe
12	**H-77-H**	5,800	0.83	23,400	1.18	41	**P-Vi-83**	1.2	99	OMe
13	**H-285-H**	21,200	0.83	143,200	1.02	7	**P-Vi-250**	0.4	99	OMe

[a] D = Me_2SiO, M^H = $Me_2HSiO_{2/2}$ Thus, **H-0-H** = M^HM^H, **H-18-H** = $M^HD_{18}M^H$.

[b] M$_n$ of the starting material obtained by ^{1}H NMR end group analysis.

[c] M$_n$ obtained of the product obtained by GPC.

[d] macromonomer repeat units $[(ViMeSiO)_1(Me_2SiO)_n]_{DP}$.

[e] MW was too low to be detected by GPC.

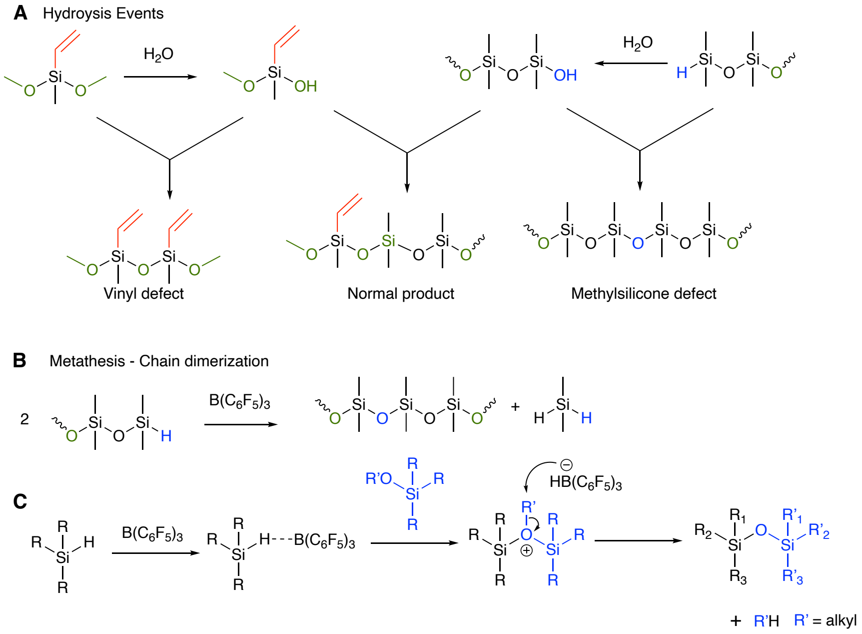


Figure 4.4. Origins of defects during chain extension. (A) Hydrolysis. (B) Metathesis. (C) Mechanism of the PR reaction.

The prevailing methodology for crosslinking in silicone elastomer synthesis is hydrosilylation, which involves the addition reaction between hydrosilane (SiH) and unsaturated bonds, in the presence of platinum catalyst, typically Karstedt's catalyst[31]. Normally, these systems are sold as two-part pre-elastomer kits in which one part contains vinylsilicone and catalyst, while in the other, hydrosiloxanes are found that are often the crosslinking partner. Polymers containing both functionalities are exceptionally rare, as neither traditional acid nor base catalyst technologies are compatible with both vinyl and HSi functionalities. The compounds fall in a convenient MW range of 10,000-60,000, within the 20,000-30,000 g mol^{-1} range that has been found to be convenient for many applications, once cured into elastomers[32]. These H/vinyl silicone polymers were able to self-cure to give bubble free elastomers by addition of Karstedt's catalyst (entries 1-4, **Table 4.2**, **Figure 4.3**B, ^{1}H NMR in ***Table S4.3***, Supplementary Information, SI). The Shore OO hardnesses of elastomers created from this homologous series ranged from 46 to 73 depending on overall MW and the spacing between vinyl groups.

Table 4.2. The synthesis of silicone elastomers using hydride-terminated, well-defined vinyl silicones via hydrosilylation.

	Self-crosslinked Elastomers			**Product**
	Starting polymer ^{a}	**Vinyl conc. (%)^{a}**	**MW (g mol^{-1})^{a}**	**Shore OO**
1	**P-Vi-4**	28.8	25,200	46±1
2	**P-Vi-29**	3.4	26,900	73±2
3	**P-Vi-28**	3.6	65,700	64±2
4	**P-Vi-111**	0.9	13,300	52±2
	Grafted copolymer networks			
#	**Starting elastomers**		**Eq^{a} M^{H} versus Si^{Vi}**	
5	entry 3		2	78±2^{b}
6	entry 3		1	82±1^{b}

[a] Compounds from **Table 4.1,** entries 5-8. [b] These materials are at the upper level of the Shore OO scale, but they were too brittle (they are unfilled) for measurement by Shore A - they cracked during measurement.

The elastomers prepared by self-hydrosilylation reactions possessed residual double bonds. These could be further modified to create new networks by swelling using different concentrations of the small telechelic hydrosilicone $(^{H}Me_2SiOSi^{Ph}Me)_2O(M^{H}D^{Ph})_2$ into the elastomers and then again curing with hydrosilylation (**Figure 4.3**C,D). Use of 2 equiv (based on SiH) led to SiH functional elastomers and a small increase in hardness; use of 1 equiv led to harder elastomers (entries 5-8, **Table 4.2**). Note: the materials were more highly crosslinked and much harder than the precursor elastomer but shattered during Shore A measurements. When an excess of SiH was used (2 equiv), all vinyl groups were consumed, while use of 1 equiv of SiH/vinyl, not all vinyl groups reacted, which is expected because of the lower degrees of freedom of mobility in a network (^{1}H NMR in **Table S4.3**, IR spectra in **Figure 4.5**). SiH groups were present in both products, suggesting that the limited degrees of freedom available to the short chains prohibits complete reaction.

The ultimate aim of this study was the creation of linear silicones with a spatially-controlled distribution of high density 3D branches. We hypothesized that spatial control would avoid clusters of functional groups, permitting full functionalization of the backbone. Spatially controlled vinyl-pendent linear silicone **P-Vi-14** with a molecular weight of 37,400 g mol-1, vinyl conc. of ~7% and spacing chain length of 1,100 g mol-1, DP~34 (that is, the macromonomer species is $\sim[(Me_2SiO)_{15}(MeSi^{Vi})]_n$) served as the starting material. Dense branches were created using a series of iterative processes, alternating between hydrosilylation and then PR with a variety of monomers bearing different functionalities including SiH, SiOEt and vinyl groups. Initially these reactions could be run neat. However, as the molecular weight increased, particularly above the entanglement limit of about 29,000 g mol^{-1} (reported entanglement limits for PDMS range from about 15,000-35,000 g mol^{-1}; here we use data from the seminal study of Mrozek et al.[25,33]) and branch density increased, it was necessary to dilute the system with hexanes[34] . Note that each iteration of PR then hydrosilylation could be undertaken in one pot, as the catalysts do not interfere with each other[35].

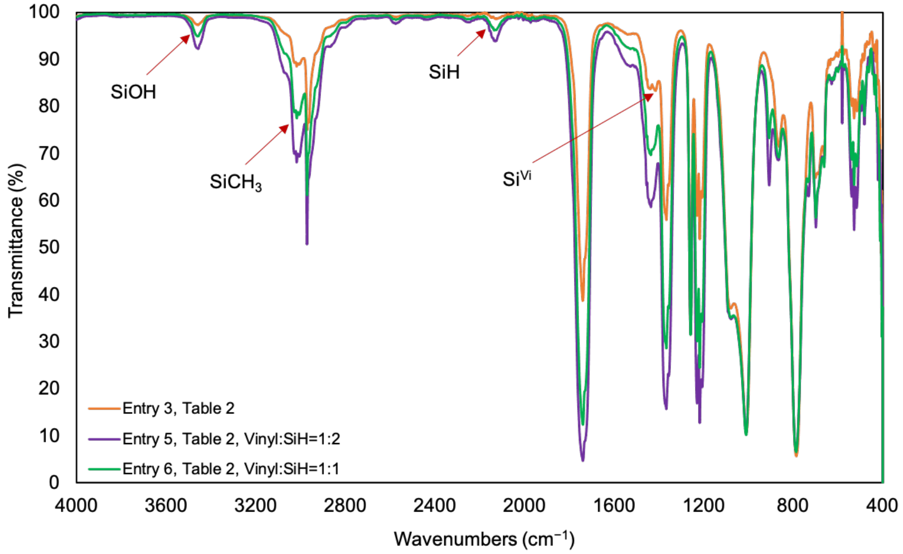


Figure 4.5. IR spectra for PMS-H03 modified elastomers using P-Vi-28 self-crosslinked elastomers (Table 2). The orange curve shows the IR spectra of precursor elastomer (Entry 3, **Table 4.2**), the purple curve shows the IR spectra of PMS-H03 (Vinyl:SiH = 1:2) modified elastomer (Entry 5, **Table 4.2**) and the green curve shows the IR spectra of PMS-H03(Vinyl:SiH = 1:1) modified elastomer (Entry 6, **Table 4.2**).

Selected examples of dendron-like branch growth are shown in **Figure 4.6**. The terminal methoxy groups on compound **P-Vi-14** were first capped using an excess of MM^H in the presence of $B(C_6F_5)_3$ catalyst; this process can be performed during workup of compound **P-Vi-14** and avoids adventitious PR side reactions.

Hydrosilylation with triethoxysilane in the presence of Karstedt's catalyst creates trifunctional branches in **P-Vi-14-OR$_3$** (**Figure 4.6**B,C). Note that, if desired, lower degrees of functionalization should be accessible by hydrosilylation with MeHSi(OEt)$_2$ or Me$_2$HSiOEt. ^{1}H NMR spectra showed the complete consumption of the vinyl group (SiC*H*=*CH*$_2$, ~5.8 ppm) and a newly emerged ethoxy peak (SiOC*H*$_2$CH$_3$, ~3.8 ppm). The alkoxygroups undergo ready silylation in a PR process, for example, with Me$_2$PhSiH to give highly branched, phenyl-rich compound **P-Vi-14-OSi$_3$**.

The iterative PR/hydrosilylation process can be repeated with compound **P-Vi-14-OR$_3$**, for example, using vinyltetramethyldisiloxane to give alkoxysilane-free compound **P-Vi-14-OVi$_3$**. The net effect is to convert single pendent vinyl groups in compound **P-Vi-14** into trivinyl-functional branches in compound **P-Vi-14-OVi$_3$**. These vinyl groups, in turn, were converted to more highly branched silicones **P-Vi-14-OSi$_3$OSi$_9$**, or new alkoxysilanes **P-Vi-14-OSi$_3$OR$_9$**. It was not possible, in our hands, to get clean products from a further PR reaction with **P-Vi-14-OSi$_3$OR$_9$**, which we ascribe to steric issues; a maximum efficiency of ~53% substitution was observed at 50 °C for 24 hours in an excess of MD^{H}M.

Some caveats must be attached to the synthetic sequence provided above. One must be exceptionally careful to store any of the alkoxysilane products completely dry. For example, although the conversion of **P-Vi-14 → P-Vi-14-OSi$_3$** led to the expected increase in molar mass, the analogous conversion of **P-Vi-14 → P-Vi-14-OVi$_3$** gave polymers with about 5x the expected molar mass. This is a consequence of very small amounts of water that lead to hydrolysis/condensation. Note that this problem is exacerbated at higher generations (researchers with better hands than ours are able to successfully manage this challenge[17-18]). Compound **P-Vi-14-OVi$_3$OR$_9$** has a molar mass by GPC that is appropriate based on its initial starting material **P-Vi-14** but lower than its immediate precursor **P-Vi-14-OVi$_3$**. The molecular weight didn't decrease. Instead, a fraction of the material became a resin that was no longer carried though the column. Note that, in addition at high branch density, GPC can underestimate molecular weight because the behavior of linear calibrating polymers is quite different from these highly branched polymers, which can take up a globular structure [25,36].

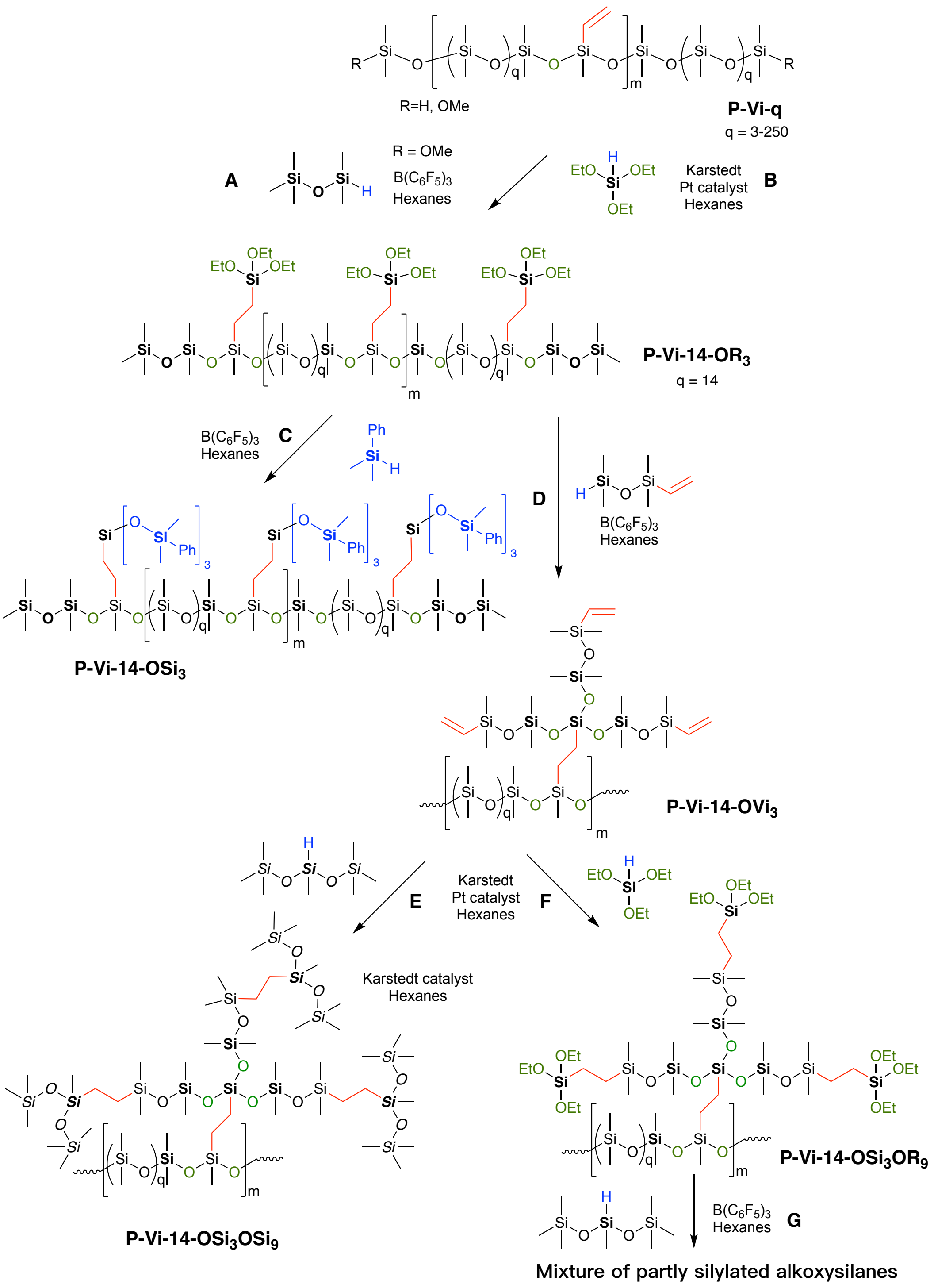


Figure 4.6. Synthesis of well-defined branched silicones by (A) capping residual SiOMe groups. (B) Hydrosilylation to introduce new SiOEt groups. (C) PR reaction to give branched siloxanes. (D) Chain extention to give trivinylbranches. (E) Dense silicone branches from hydrosilylation. (F) Dense alkoxysilane from hydrosilylation. (G) Failed attempt to extend the branches by hydrosilylation.

4.5. Discussion

The Piers-Rubinsztajn, combined with hydrosilylation, has previously been shown to be a valuable strategy to create structured networks[35]. Here we demonstrate that it similarly permits the preparation of highly functional, highly branched polymers and macro-crosslinkers. Use of Skov's technology permits precise spacing of vinyl functional groups between D units along a silicone backbone 1/3 to 1/250 (**Table 4.1**). The secondary level of control – DP of the macromer $[(MeViSiO)_1(Me_2Si)_n]_{DP}$ – was more difficult to manage; depending on the specific starting material ratios chosen, [SiOMe]/[SiH] DPs ranging from 2 to 188 were realized. As expected, the highest MW were achieved with a stoichiometric balance, that reduced the degree of premature termination.

The ideal spacing of vinyl groups was not always observed in these reactions. We attribute this observation to defects introduced by hydrolysis/condensation and metathesis; hydrolysis[29] and metathesis[28,37] reactions are promoted by $B(C_6F_5)_3$. In both cases, the first formed SiOH groups can undergo condensation to give chain extension. SiH groups in the presence of $B(C_6F_5)_3$ can also undergo metathesis reactions leading to longer polymers and coproduction of Me_2SiH_2. Either of these processes will lead to a defect in the chain with either a double or missing vinyl group (**Figure 4.4**A,B). Both of the processes leading to defects are less efficient/less rapid than the PR reaction. Thus, an advantage of the use of 1/1 [SiOMe]/[SiH] stoichiometry is a lower likelihood of defects. Note that we currently do not have the analytical capacity to detect these defects.

These reactions exhibit one unusual feature: low $Đ_M$[13]. Normally, one would expect ideal condensation polymer should normally have a dispersity approaching 2. Instead, the lower $Đ_M$ suggests the propagation has a kinetic/chain growth component. The mechanism for the PR reaction involves two nucleophilic substitutions. Either one could be the rate determining step of the overall process, similar to traditional chain processes rather than condensations (**Figure 4.4**C)2[22,38-40]. Chojnowski et al. have shown that related $B(C_6F_5)_3$-catalyzed reaction of cyclic hydrosiloxanes are kinetically controlled[41]. Regardless, this constitutes an advantage of the process.

Once vinyl groups were located in precise locations on a silicone chain, it was relatively straightforward to use iterative hydrosilylation/PR cycles to grow dense branches that terminated with functional groups or, as we showed here, capped to give branched silicones (**Figure 4.6**). As with dendrimers, at higher generations defects set in[42] and care must really be taken with the high density triethoxysilyl branches to convert them to hydrolytically stable analogues, either silyl or vinyl. However, even after one generation, high molecular weight, highly functional precise highly polymers are readily available.

Structure matters to all chemists. There is a paucity of data on the behavior of branched silicones. Charlesby created branched silicone by irradiation to create backbone radicals[43]. The method may have produced some lightly branched materials, but the author also recognized that their materials likely included crosslinked or uncontrollably branched components. The creation of these highly branched materials using a combination of PR and hydrosilylation reaction opens opportunities to fine tune the properties of both oils and elastomers. As the library of branched and highly branched[25] silicones is expanded, it will be possible to better identify the beneficial properties of both oils and elastomers that arise from precisely located vs. random branches.

4.6. Conclusions

A facile synthetic route to spatially controlled vinyl-pendent linear silicones, with vinyl spacing varying from 1/3 to 1/250 monomer units, low dispersities, and molecular weights of the obtained polymers ranging from 12,100 to 102,400 g mol^{-1} was reported. The terminal groups (SiH or SiOMe) of the polymers could by chosen by tuning the stoichiometry of the hydride-terminated PDMS and dimethoxymethylvinylsilane starting materials. The polymers with SiH termini underwent direct crosslinking using hydrosilylation to produce relatively soft elastomers containing residual vinyl groups that could be used for secondary functionalization or crosslinking. The vinyl groups were also used as loci from which dendritic branches were grown, eventually to make highly branched functional oils. The library of polymers produced, with precisely spaced mono- or dendritic multi-functional pendent groups, follows the paradigm of greater synthetic control to give narrower ranges of properties, and will permit an assessment of structure property relationships to allow the design of better silicone polymer fluids and elastomers.

4.7. Acknowledgements

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada.

4.8. References

(1) Wang, D.; Jin, Y.; Zhu, X.; Yan, D. Synthesis and applications of stimuli-responsive hyperbranched polymers. *Prog. Polym. Sci.* **2017**, *64*, 114–153, doi:10.1016/j.progpolymsci.2016.09.005.

(2) Konkolewicz, D.; Monteiro, M.J.; Perrier, S. Dendritic and Hyperbranched Polymers from Macromolecular Units: Elegant Approaches to the Synthesis of Functional Polymers. *Macromolecules* **2011**, *44*, 7067–7087, doi:10.1021/ma200656h.

(3) Abad, M.; Martínez-Bueno, A.; Mendoza, G.; Arruebo, M.; Oriol, L.; Sebastián, V.; Piñol, M. Supramolecular Functionalizable Linear–Dendritic Block Copolymers for the Preparation of Nanocarriers by Microfluidics. *Polymers* **2021**, *13*, 684, doi:10.3390/polym13050684.

(4) Chen, S.; Xu, Z.; Zhang, D. Synthesis and application of epoxy-ended hyperbranched polymers. *Chem. Eng. J.* **2018**, *343*, 283–302, doi:10.1016/j.cej.2018.03.014.

(5) Caminade, A.-M.; Yan, D.; Smith, D.K. Dendrimers and hyperbranched polymers. *Chem. Soc. Rev.* **2015**, *44*, 3870–3873, doi:10.1039/C5CS90049B.

(6) Mu, B.; Liu, T.; Tian, W. Long-Chain Hyperbranched Polymers: Synthesis, Properties, and Applications. *Macromol. Rapid Commun.* **2019**, *40*, 1800471, doi:10.1002/marc.201800471.

(7) Yates, C.R.; Hayes, W. Synthesis and applications of hyperbranched polymers. *Eur. Polym. J.* **2004**, *40*, 1257–1281, doi:10.1016/j.eurpolymj.2004.02.007.

(8) Gurunathan, T.; Mohanty, S.; Nayak, S.K. Hyperbranched Polymers for Coating Applications: A Review. *Polym. Plast. Technol. Eng.* **2016**, *55*, 92–117, doi:10.1080/03602559.2015.1021482.

(9) Emrick, T.; Chang, H.-T.; Fréchet, J.M.J.; Woods, J.; Baccei, L. Hyperbranched aromatic epoxies in the design of adhesive materials. *Polym. Bull.* **2000**, *45*, 1–7, doi:10.1007/s002890070049.

(10) Stumpe, K.; Eichhorn, K.-J.; Voit, B. Characterisation of Thin Composite Films from Hyperbranched Polyphenylene and Thermolabile Hyperbranched Polycarbonate. *Macromol. Chem. Phys.* **2008**, *209*, 1787–1796, doi:10.1002/macp.200800170.

(11) Zhou, Y.; Huang, W.; Liu, J.; Zhu, X.; Yan, D. Self-Assembly of Hyperbranched Polymers and Its Biomedical Applications. *Adv. Mater.* **2010**, *22*, 4567–4590, doi:10.1002/adma.201000369.

(12) Wang, Z.; Zhang, J.; Liu, J.; Hao, S.; Song, H.; Zhang, J. 3D Printable, Highly Stretchable, Superior Stable Ionogels Based on Poly(ionic liquid) with Hyperbranched Polymers as Macro-cross-linkers for High-Performance Strain Sensors. *ACS Appl. Mater. Interfaces* **2021**, *13*, 5614–5624, doi:10.1021/acsami.0c21121.

(13) Voit, B.I.; Lederer, A. Hyperbranched and Highly Branched Polymer Architectures—Synthetic Strategies and Major Characterization Aspects. *Chem. Rev.* **2009**, *109*, 5924–5973, doi:10.1021/cr900068q.

(14) Kamino, B.A.; Bender, T.P. The use of siloxanes, silsesquioxanes, and silicones in organic semiconducting materials. *Chem. Soc. Rev.* **2013**, *42*, 5119–5130, doi:10.1039/C3CS35519E.

(15) Zhang, H.; Cloud, A. The Permeability Characteristics of Silicone Rubber. In Proceedings of the SAMPE—Society for the Advancement of Material and Process Engineering, Fall Technical Conference, Dallas, TX, USA, November 6-9, 2006.

(16) Owen, M.J. Siloxane Surface Activity. In *Silicon-Based Polymer Science: A Comprehensive Resource*; Zeigler, J.M., Fearon, F.W.G., Eds.; American Chemical Society: Washington, DC, USA, 1990; pp. 705–739.

(17) Kazakova, V.V.; Rebrov, E.A.; Myakushev, V.B.; Strelkova, T.V.; Ozerin, A.N.; Ozerina, L.A.; Chenskaya, T.B.; Sheiko, S.S.; Sharipov, E.Y.; Muzafarov, A.M. From a Hyperbranched Polyethoxysiloxane Toward Molecular Forms of Silica: A Polymer-Based Approach to the Monitoring of Silica Properties. In *Silicones and Silicone-Modified Materials*, American Chemical Society: Washington, DC, USA, 2000; Volume 729, pp. 503–515.

(18) Jaumann, M.; Rebrov, E.A.; Kazakova, V.V.; Muzafarov, A.M.; Goedel, W.A.; Möller, M. Hyperbranched Polyalkoxysiloxanes via AB3-Type Monomers. *Macromol. Chem. Phys.* **2003**, *204*, 1014–1026, doi:10.1002/macp.200390067.

(19) Paulasaari, J.K.; Weber, W.P. Synthesis of Hyperbranched Polysiloxanes by Base-Catalyzed Proton-Transfer Polymerization. Comparison of Hyperbranched Polymer Microstructure and Properties to Those of Linear Analogues Prepared by Cationic or Anionic Ring-Opening Polymerization. *Macromolecules* **2000**, *33*, 2005–2010, doi:10.1021/ma991755x.

(20) Paulasaari, J.K.; Weber, W.P. Base catalyzed proton transfer polymerization of 1-hydroxypentamethylcyclotrisiloxane. Comparison of hyperbranched polymer microstructure and properties to those of highly regular linear analogs. *Macromol. Chem. Phys.* **2000**, *201*, 1585–1592, doi:10.1002/1521-3935(20000901)201:14<1585::AID-MACP1585>3.0.CO;2-3.

(21) Chojnowski, J.; Cypryk, M.; Fortuniak, W.; Ścibiorek, M.; Rózga-Wijas, K. Synthesis of Branched Polysiloxanes with Controlled Branching and Functionalization by Anionic Ring-Opening Polymerization. *Macromolecules* **2003**, *36*, 3890–3897, doi:10.1021/ma025920b.

(22) Brook, M.A. New Control Over Silicone Synthesis using SiH Chemistry: The Piers–Rubinsztajn Reaction. *Chem. Eur. J.* **2018**, *24*, 8458–8469, doi:10.1002/chem.201800123.

(23) Grande, J.B.; Urlich, T.; Dickie, T.; Brook, M.A. Silicone dendrons and dendrimers from orthogonal SiH coupling reactions. *Polym. Chem.* **2014**, *5*, 6728–6739, doi:10.1039/C4PY00680A.

(24) Zheng, S.; Liang, S.; Chen, Y.; Brook, M.A. Hyperbranched Silicone MDTQ Tack Promoters. *Molecules* **2019**, *24*, 4133, doi:10.3390/molecules24224133.

(25) Morgan, J.; Chen, T.; Hayes, R.; Dickie, T.; Urlich, T.; Brook, M.A. Facile synthesis of dendron-branched silicone polymers. *Polym. Chem.* **2017**, *8*, 2743–2746, doi:10.1039/C7PY00260B.

(26) Madsen, F.B.; Javakhishvili, I.; Jensen, R.E.; Daugaard, A.E.; Hvilsted, S.; Skov, A.L. Synthesis of telechelic vinyl/allyl functional siloxane copolymers

with structural control. *Polym. Chem.* **2014**, *5*, 7054–7061, doi:10.1039/C4PY00919C.

(27) van Genabeek, B.; Lamers, B.A.G.; Hawker, C.J.; Meijer, E.W.; Gutekunst, W.R.; Schmidt, B.V.K.J. Properties and applications of precision oligomer materials; where organic and polymer chemistry join forces. *J. Polym. Sci.* **2021**, *59*, 373–403, doi:10.1002/pol.20200862.

(28) Chojnowski, J.; Fortuniak, W.; Kurjata, J.; Rubinsztajn, S.; Cella, J.A. Oligomerization of Hydrosiloxanes in the Presence of Tris(pentafluorophenyl)borane. *Macromolecules* **2006**, *39*, 3802–3807, doi:10.1021/ma060080c.

(29) Liao, M.; Schneider, A.F.; Laengert, S.E.; Gale, C.B.; Chen, Y.; Brook, M.A. Living synthesis of silicone polymers controlled by humidity. *Eur. Polym. J.* **2018**, *107*, 287–293, doi:10.1016/j.eurpolymj.2018.07.023.

(30) Fawcett, A.S.; Grande, J.B.; Brook, M.A. Rapid, metal-free room temperature vulcanization produces silicone elastomers. *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51*, 644–652, doi:10.1002/pola.26414.

(31) Marciniec, B.; Gulinski, J.; Urbaniak, W.; Kornetka, Z.W. *Comprehensive Handbook on Hydrosilylation Chemistry*; Pergamon: Oxford, UK, 1992.

(32) Wang, D.; Klein, J.; Mejía, E. Catalytic Systems for the Cross-Linking of Organosilicon Polymers. *Chem. Asian J.* **2017**, *12*, 1180–1197, doi:10.1002/asia.201700304.

(33) Mrozek, R.A.; Cole, P.J.; Otim, K.J.; Shull, K.R.; Lenhart, J.L. Influence of solvent size on the mechanical properties and rheology of polydimethylsiloxane-based polymeric gels. *Polymer* **2011**, *52*, 3422–3430, doi:10.1016/j.polymer.2011.05.021.

(34) Stricher, A.M.; Rinaldi, R.G.; Barrès, C.; Ganachaud, F.; Chazeau, L. How I Met Your Elastomers: From Network Topology to Mechanical Behaviours of Conventional Silicone Materials. *RSC Adv.* **2015**, *5*, 53713–53725, doi:10.1039/C5RA06965C.

(35) Laengert, S.E.; Schneider, A.F.; Lovinger, E.; Chen, Y.; Brook, M.A. Sequential Functionalization of a Natural Crosslinker Leads to Designer Silicone Networks. *Chem. Asian J.* **2017**, *12*, 1208–1212, doi:10.1002/asia.201700160.

(36) Rogers, M.G. The structure of epoxy resins using NMR and GPC techniques. *J. Appl. Polym. Sci.* **1972**, *16*, 1953–1958, doi:10.1002/app.1972.070160809.

(37) Liao, M.; Chen, Y.; Brook, M.A. When Attempting Chain Extension, Even Without Solvent, It Is Not Possible to Avoid Chojnowski Metathesis Giving D_3. *Molecules* **2021**, *26*, 231, doi:10.3390/molecules26010231.

(38) Piers, W.E. The chemistry of perfluoroaryl boranes. *Adv. Organomet. Chem.* **2005**, *52*, 1–77.

(39) Chojnowski, J.; Rubinsztajn, S.; Cella, J.A.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kazmierski, K. Mechanism of the $B(C_6F_5)_3$-catalyzed reaction of silyl hydrides with alkoxysilanes. Kinetic and spectroscopic studies. *Organometallics* **2005**, *24*, 6077–6084.

(40) Rubinsztajn, S.; Cella, J.A. A new polycondensation process for the preparation of polysiloxane copolymers. *Macromolecules* **2005**, *38*, 1061–1063.

(41) Chojnowski, J.; Kurjata, J.; Fortuniak, W.; Rubinsztajn, S.; Trzebicka, B. Hydride Transfer Ring-Opening Polymerization of a Cyclic Oligomethylhydrosiloxane. Route to a Polymer of Closed Multicyclic Structure. *Macromolecules* **2012**, *45*, 2654–2661, doi:10.1021/ma202687u.

(42) van Dongen, M.A.; Desai, A.; Orr, B.G.; Baker, J.R.; Banaszak Holl, M.M. Quantitative analysis of generation and branch defects in G5 poly(amidoamine) dendrimer. *Polymer* **2013**, *54*, 4126–4133, doi:10.1016/j.polymer.2013.05.062.

(43) Charlesby, A. Viscosity measurements in branched silicones. *J. Polym. Sci.* **1955**, *17*, 379–390, doi:10.1002/pol.1955.120178506.

4.9.Appendix 3- Supporting Information

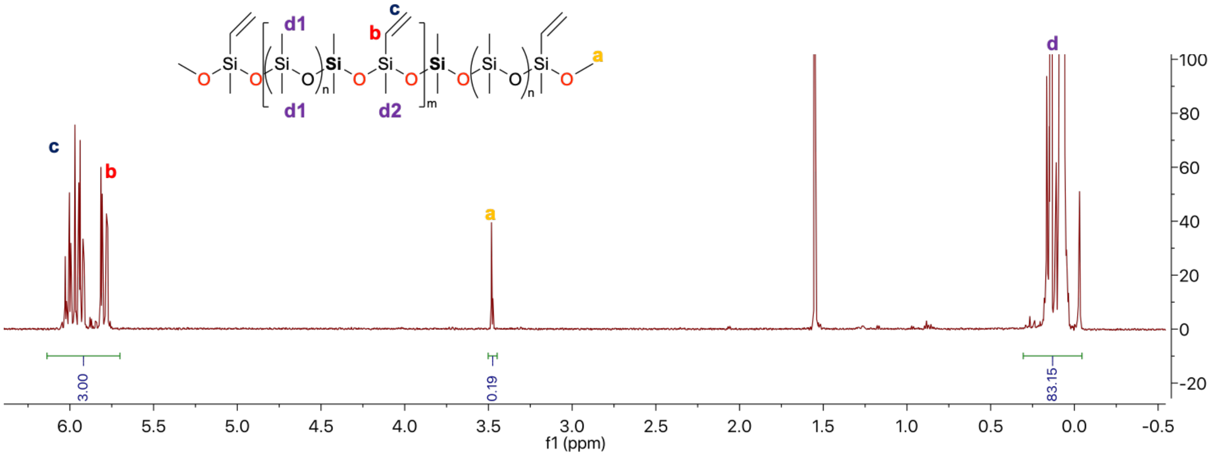
Table S4.1. The synthesis of well-defined vinyl silicones with SiH or SiOMe as terminal functional groups (**Table 4.1**) - ^{1}H NMR data

Entry	^{1}H NMR ($CDCl_3$, 600 MHz, δ)
1	5.78-6.05 (m, 3H), 3.46-3.47 (SiOCH_3, m, 0.48H), 0.07-0.23 (m, 16.08H) ppm.
2	5.78-6.03 (m, 3H), 3.47-3.48 (SiOCH_3, m, 0.18H), 1.54 (s, 1.74H), 0.07-0.27 (m, 94.68H) ppm.
3	5.77-6.02 (m, 3H), 3.46-3.47 (SiOCH_3, m, 0.27H), 1.54 (s, 0.88H), 0.06-0.26 (m, 149.35H) ppm.
4	5.77-6.04 (m, 3H), 3.47-3.48 (SiOCH_3, m, 3.13H), 1.54 (s, 12.12H), 0.07-0.16 (m, 1237.10H) ppm.
5	5.78-6.03 (m, 3H), 4.70-4.76 (Si*H*, m, 0.01H), 1.54 (s, 0.55H), 0.07-0.24 (m, 17.84H) ppm.
6	5.78-6.03 (m, 3H), 4.70-4.71 (Si*H*, m, 0.50H), 1.55 (s, 0.98H), 0.04-0.45 (m, 173.20H) ppm.
7	5.78-6.03 (m, 3H), 4.70-4.74 (Si*H*, m, 0.11H), 1.54 (s, 1.49H), 0.07-0.45 (m, 164.66H) ppm.
8	5.77-6.03 (m, 3H), 4.70-4.71 (Si*H*, m, 0.03H), 1.54 (s, 23.61H), 0.05-0.17 (m, 632.56H) ppm.
9	5.78-6.05 (m, 3H), 3.46-3.50 (SiOCH_3, m, 0.95H), 0.08-0.23 (m, 13.95H) ppm.
10	5.77-6.02 (m, 3H, SiC*H*=CH_2), 3.47-3.48 (s, 0.10H, SiOCH_3), 1.52 (s, 0.62H), 0.05-0.13 (m, 83.55H, SiCH_3) ppm
11	5.78-6.06 (m, 3H), 3.47-3.48 (SiOCH_3, m, 0.67H), 1.56 (s, 1.12H), 0.07-0.27 (m, 102.74H) ppm.
12	5.78-6.05 (m, 3H), 3.47-3.48 (SiOCH_3, m, 0.81H), 0.04-0.16 (m, 517.29H) ppm.
13	5.78-6.03 (m, 3H), 3.47-3.48 (SiOCH_3, m, 0.78H), 1.55 (s, 8.03H), 0.07-0.17 (m, 1621.13H) ppm.

Table S4.2. The synthesis of well-defined vinyl silicones with SiH or SiOMe as terminal functional groups (**Table 4.1**)- GPC data

Entry	M_n (g mol^{-1})	M_w (g mol^{-1})	$Đ_M$
1	N/A	N/A	N/A
2	85,800	141,700	1.65
3	102,400	113,100	1.11
4	87,000	104,800	1.20
5	25,200	42,400	1.68
6	26,900	45,000	1.68
7	65,700	91,300	1.39
8	13,300	27,800	2.09
9	N/A	N/A	N/A
10	37,400	69,300	1.85
11	23,600	50,600	2.15
12	23,400	27,600	1.18
13	143,200	146,200	1.02

Calculation of vinyl concentration based on ^{1}H NMR
Sample calculation for Entry 10 in Table 4.1



$$\text{\# of d1 silicon for every repeating unit}=\frac{(\text{The integration of siloxane region-3})}{6}=\frac{(83.15-3)}{6}\approx 13$$

$$\text{Vinyl conc. (\%)}=\frac{1}{[\frac{\text{The integration of siloxane region-3}}{6}+1]}*100\ \%=\frac{1}{[\frac{83.15-3}{6}+1]}=6.96\%$$

Table S4.3. The synthesis of silicone elastomers using hydride-terminated, well-defined vinyl silicones via hydrosilylation - ^{1}H NMR data (**Table 4.1**)

Entry	^{1}H NMR ($CDCl_3$, 600 MHz, δ)
1	5.80-6.01 (m, 98H, CH_2=CH-Si), 0.83 (m, 4H, CH_2-CH_2), 0.08-0.15 (m, 606H) ppm.
2	5.78-5.94 (m, 0.8H, CH_2=CH-Si), 0.80-0.86 (m, 4H, CH_2-CH_2), 0.07 (s, 44H) ppm.
3	5.77-6.00 (m, 5H, CH_2=CH-Si), 0.79-0.88 (m, 4H, CH_2-CH_2), 0.07-0.08 (m, 193H) ppm.
4	7.55-7.57 (m, 10H, aromatic H), 7.32-7.43 (m, 18H, aromatic H), 4.74-4.76 (m, 4H, SiH), 0.81-0.88 (m, 4H, CH_2-CH_2), 0.31-0.32 (m, 19H, Si(Ph)CH_3), 0.15-0.17 (m, 36H, Si(Ph)OSi(CH_3)$_2$), 0.07-0.08 (m, 117H) ppm. (Vinyl groups remain when only 1 equiv of SiH was used due to side reactions such as metathesis and hydrolysis that consume SiH groups)
5	7.55-7.58 (m, 7H, aromatic H), 7.32-7.39 (m, 12H, aromatic H), 5.94-5.97 (m, 0.16H, CH_2=CH-Si), 4.74-4.76 (m, 2H, SiH), 0.80-0.89 (m, 4H, CH_2-CH_2), 0.31-0.32 (m, 13H, Si(Ph)CH_3), 0.15-0.17 (m, 23H, Si(Ph)OSi(CH_3)$_2$), 0.07-0.08 (m, 98H) ppm.
6	5.77-6.03 (m, 0.90H, CH_2=CH-Si), 0.80-0.89 (m, 4H, CH_2-CH_2), 0.07 (s, 123H) ppm.

Chapter 5: Silylating disulfides and thiols with hydrosilicones catalyzed by $B(C_6F_5)_3$[&]

5.1. Abstract

Hydrosilanes and silicones, catalyzed with $B(C_6F_5)_3$, may be used to silylate thiols or cleave disulfides giving silyl thio ethers. Alcohols were found to react faster than thiols or disulfides, while alkoxysilanes (the Piers-Rubinsztajn reaction) were slower such that the overall order of reactivity was found to be HO > HS > SS > SiOEt. The resulting silane and silicone-protected thio ethers produced from the sulfur-based functional groups could be cleaved to thiols using alcohols or mild acid with rates that depend on the steric bulk of the siloxane.

5.2. Introduction

The utility of sulfur chemistry is intrinsic to materials science, historically via Goodyear vulcanization of rubber,[1] and more recently through practical, facile reactions that facilitate the assembly of complex materials, including thiol-ene reactions.[2] There has similarly been an expansion in the use of sulfur chemistry in synthetic organic methodology via sulfur anions, radicals, ylids, etc., because, in part, of the special reactivity of thiols when compared to alcohols.[3]

The reactivity of thiols, which is so beneficial in mediating organic chemistry can, however, be problematic because of the sensitivity of these groups to oxidation to disulfides, or further oxidation to sulfoxides, sulfones, etc.;[4] the biological redox

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[&] Submitted to *European Journal of Organic Chemistry*, **M. Liao**, S. Zheng and M.A. Brook (2021).
Mengchen Liao performed all experiments and was the lead author of the manuscript. Zheng performed experiments for the dodecanethiol model compound study.

partners cystamine/cysteamine, cysteine/cystine and glutathione/ glutathione disulfide[5] are emblematic of this oxidative sensitivity. There is, therefore, a need to protect thiols during synthetic sequences. For alcohol protection, one generally turns to silyl groups, because: deprotection with fluoride rarely affects other entities on the organic molecule; there is a well understood link between steric bulk at silicon and the difficulty of both introduction and cleavage processes, and organosilanes are perceived to be relatively benign.[6] Silyl groups have not found a similar place in synthesis involving thiols initially, in part we propose, because of early reports showing the Si-S bond is exquisitely sensitive towards hydrolysis, based on the reactivity of Me_3Si-S-$SiMe_3$.[7]

In a sense, disulfides are a vehicle to protect thiols. The reduction of SS bonds back to thiols is effectively managed by natural processes, as noted above. However, synthetic organic chemistry typically requires more vigorous conditions for this process.[8]

Many functional groups undergo reductions with hydrosilanes in the presence of $B(C_6F_5)_3$. Piers, in particular, has demonstrated the broad utility of these reducing conditions for organic functional groups.[9] It should be noted that the reduction of carbonyl groups may initially lead to silyl ethers but, under the same conditions with excess silane, further reduction to the alkane occurs. This latter reaction – a new reaction for making silicones – is the basis of the Piers-Rubinsztajn (PR) reaction.[10] An analogous PR process, via silyl thio ethers after reduction of thiobenzophenone, was described by Rosenberg's group[11] (**Figure 5.1**).

We recently described the reductive silylation of S-S linkages in automobile tires to facilitate removal of crosslinks and polymer recovery using $B(C_6F_5)_3$-

catalyzed silylation.[12] The process generates Si-S linkages that were far more robust than we had anticipated. We report here a preliminary examination of the degree to which this chemistry can be exploited with small organic molecules.

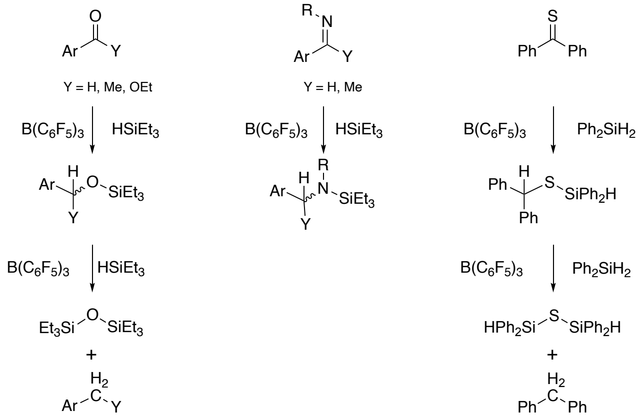


Figure 5.1. $B(C_6F_5)_3$-catalyzed silane reduction of organic groups.

5.3. Materials and Methods

5.3.1. Materials

Bis(triethoxysilylpropyl)disulfide (90%), bis(triethoxysilylpropyl)tetrasulfide (a mixture of oligosulfides, average S_4), bis(trimethylsiloxy)methylsilane **1** BisH (MD^HM) and pentamethyldisiloxane **2** (MM^H) were purchased from Gelest; dimethylphenylsilane **3** ($PhMe_2SiH$) was purchased from Sigma Aldrich and all were used after drying over molecular sieves overnight (Sigma Aldrich Molecular sieves, 4Å beads, 8-12 mesh). Benzyl thiol, octyl thiol, dodecyl thiol and tetrabutylammonium fluoride (TBAF) were purchased from Sigma Aldrich. Acetic acid was purchased from Caledon. Ultrapure water (18 MΩ-cm) was obtained using Easypure RF (Barnstead). $B(C_6F_5)_3$ was prepared by Grignard reaction following the literature procedure;[25] we acknowledge with gratitude Prof. David Emslie, McMaster University, for providing this sample. Naphthalene (internal standard) was purchased from Fisher. Toluene, hexanes and tetrahydrofuran (solvents) received from Caledon (HPLC grade) were dried over activated alumina before use. Isopropanol was purchased from Caledon and used as received. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories. Chromium (III) acetylacetonate was purchased from Sigma Aldrich and was used as received. All glassware was dried overnight at 120 °C and cooled under a dry nitrogen atmosphere for 30 min. However, reactions were generally run in an open flask, which accounts for the presence of water in some reactions.

5.3.2. Methods

^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using deuterated solvents chloroform-*d* and acetone-d_6. For ^{29}Si NMR, chromium (III) acetylacetonate was used as a paramagnetic relaxation agent.

GC-MS analyses were performed using an Agilent 6890N gas chromatograph (Santa Clara, CA, USA), equipped with a DB-17ht column (30 m × 0.25 mm i.d. x 0.15 µm film, J & W Scientific) and a retention gap (deactivated fused silica, 5 m x 0.53 mm i.d.) coupled to an Agilent 5973 MSD single quadruple mass spectrometer. A one microliter of sample was injected using an Agilent 7683 autosampler in splitless mode. The injector temperature was 250 °C and carrier gas (helium) flow was 1.1 mL/min. The transfer line was set at 280 °C and the MS source temperature was 230 °C. The column temperature started at 50 °C and was raised to 300 °C at 8 °C/min, and held at 300 °C for 15 min for a total run time of

46.25 min. Full scan mass spectra between m/z 50 and 800 were acquired with a solvent delay of 8 min.

LC-MS analysis utilized an Agilent Technologies 1200 LC coupled to an Agilent 6550 QTOF mass spectrometer. An injection of 2 μL was separated on a Phenomenex Luna C18(2) (150 mm×2.0 mm, 3 μm) column of a pore size of 100 Å (Phenomenex, CA, USA). The mobile phases were LCMS-grade 45/55 water/methanol with 0.5% acetic acid (A) and methanol with 0.5% acetic acid (B) at a flow rate of 300 μL/min. The column temperature was maintained at 40 °C, and the autosampler storage tray was set at 10 °C. The mobile phase gradient eluted isocratically with 10% B for 1.0 min followed by a gradient that led to 100% B over 17 min. The eluent was maintained at 100 % B for 2 min and then decreased to 10 % B over 0.1 min. A 5-min re-equilibration was utilized prior to the next injection. The total time for the HILIC gradient was 25 min.

Polymer molecular weights were established with gel permeation chromatography (GPC) using a Waters Alliance GPC System 2695 calibrated with a polystyrene calibration kit S-M-10 (Lot 85) from Polymer Laboratories using toluene as eluent.

5.3.3. Synthesis

General procedures are provided here. For complete details, please see the Supporting Information.

1.3.2.4. Stock solution preparation

Benzylthiol: A stock solution of benzyl thiol was prepared by adding solid naphthalene as internal standard (0.017 g, 0.133 mmol) to benzyl thiol (0.664 mL, 0.704 g, 5.67 mmol) in a dried 20.0 mL glass vial.

Bis(triethoxysilylpropyl)disulfide: A stock solution of bis(triethoxysilylpropyl)disulfide was prepared by adding solid naphthalene (0.056 g, 0.437 mmol) to bis(triethoxysilylpropyl)disulfide (2.21 mL, 2.27 g, 4.77 mmol) in a dried 20.0 mL glass vial.

Bis(triethoxysilylpropyl)tetrasulfide: A stock solution of bis(triethoxysilylpropyl)tetrasulfide was prepared by adding solid naphthalene (0.301 g, 2.35 mmol) into bis(triethoxysilylpropyl)tetrasulfide (11.77 mL, 12.89 g, 23.91 mmol) in a dried 20.0 mL glass vial.

Chloroform-*d* used for kinetic studies: A stock solution of chloroform-*d* was prepared by adding solid naphthalene (4 mg, 0.031 mmol) into chloroform-*d* (2 mL, 3.0 g, 24.92 mmol) in a dried 20.0 mL glass vial.

5.3.3.1. Comparative reactivities of benzyl thiol and benzyl alcohol

To a pre-dried 100.0 mL round-bottomed flask, the stock solution containing benzyl thiol (0.18 g, 1.45 mmol), benzyl alcohol (0.20 g, 1.85 mmol) and **1** (0.363 g, 1.63 mmol) were mixed together with dry toluene (2 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.258 mL, 0.026 mmol) after 5 min stirring. The total reaction time was 24h, then the reaction was quenched by adding neutral alumina. The final product was obtained using vacuum filtration. The NMR data is consistent with no change to the CH_2SH peaks, while substantial change occurred to the C*H*2OH peak leading to C*H*2OSi groups (**Figure S5.1**, **Table S5.1**, Supporting Information).

*Be*fore *(0 min)*: $PhCH_2SH$: $PhCH_2OH$: **1** = 1: 1.08: 0.75

^{1}H NMR (600 MHz, chloroform-*d*): $PhCH_2SH$ (1 eq) δ 1.76 (t, *J*=7.55 Hz, 1H, S*H*), 3.75 (d, *J*=7.55 Hz, 2H, SC*H*2Ph), 7.23-7.33 (m, aromatic 5H); $PhCH_2OH$ (1.08 eq) d 1.64 (t, *J*=5.97 Hz, 1H, O*H*), 4.71 (d, *J*=5.88 Hz, 2. H, OC*H*2Ph), 7.297.38 (m, 5H arom); $(Me_3SiO)_2SiMeH$ (0.75 eq) d 0.10-0.11 (m, 3H, $(Me_3SiO)_2$*Me*SiH)), 0.12 (s, 18H, (*Me*3SiO)2MeSiH)), 4.63 (q, *J*=1.54 Hz, 1H，Si*H*); Internal standard (naphthalene): 7.48 (q, *J*=3.16 Hz, 0.09H), 7.85 (q, *J*=3.15 Hz, 0.09H) ppm.

After (24h): $PhCH_2SH$: $PhCH_2OH$: $PhCH_2OSiMe(Me_3SiO)_2$: $PhCH_2SSiMe(Me_3SiO)_2$: 1: 0.70: 0.39: 0

$PhCH_2SH$ (1 eq) δ 1.76 (t, *J*=7.53 Hz, 1H, S*H*, partially overlapped with H_2O peak), 3.75 (d, *J*=7.54 Hz, 2H, SC*H*2Ph), 7.23-.733 (m, 5H arom); $PhCH_2OH$ (0.70 eq): d 1.63-1.65 (bs, 1H, O*H*), 4.70 (s, 2H, OC*H*2Ph) 7.23-.733 (m, aromatic 5H); $PhCH_2OSiMe(Me_3SiO)_2$ (0.39 eq): 0.08 (s, 1.22H), 0.11 (s. 6.59H), 4.77 (s, 0.74H, PhC*H*2OSiMe(Me3SiO)2); Silicone impurities: 0.01-0.06 (m, 0.51H), 0.08 (s, 1.22H), 0.13-0.21 (m, 1.48H); Impurity: 4.79 (s, 0.09H); Internal standard (naphthalene): 7.48 (quartet, *J*=3.16 Hz, 0.10H), 7.85 (quartet, *J*=3.16 Hz, 0.09H) ppm.

Aromatic peaks of benzyl alcohol and silylated benzyl alcohol overlapped, but are listed separately. Note: It can be seen that silylation of water is competitive with silylation of $PhCH_2OH$ (expected yield, 0.75 equiv. observed, 0.39 equiv.)

5.3.3.2. Silylation of Organic Thiols

Benzyl thiol: In a pre-dried 100.0 mL round-bottomed flask, benzyl thiol (3.05 g, 24.56 mmol) and **1** (5.39 g, 24.22 mmol) were mixed in dry hexanes (15.0 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.242 mL, 0.024 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **5** (7.71 g, contaminated with 4% silicone) was obtained using vacuum filtration (for full experimentals for **5-7** from benzyl thiol and **8-10** from octyl thiol, including NMR spectra and GC-MS data, see SI).

$PhC\mathit{H}_2SSiMe(Me_3SiO)_2$ (compound 5): $PhCH_2S\mathit{H}$=1:0.18

^{1}H NMR (600 MHz, chloroform-*d*): δ Compound 5 (*1 equiv.*): 0.12-0.14 (m, 18H, $PhCH_2SSiMe(\mathit{Me}_3SiO)_2$), 0.27 (s, 3H, $PhCH_2SSi\mathit{Me}(Me_3SiO)_2$), 3.75 (m, 2H, $PhC\mathit{H}_2SSiMe(Me_3SiO)_2$), 7.20-7.33 (m, 5H arom); $PhCH_2SH$ (*0.18 equiv.*): 1.76 (t, *J*=7.53 Hz, 1H, S*H*), 3.76 (s, 2H, $PhC\mathit{H}_2SH$) 7.20-7.33 (m, 5H arom); Impurity: 3.60 (s, 0.03H, from residual benzyl thiol starting material).

5.3.3.3. Reductive Cleavage of Organic Disulfides

Silylation of dibenzyl disulfide with Bis-H

In a pre-dried 100.0 mL round-bottomed flask dibenzyl disulfide (0.50 g, 2.03 mmol), Bis-H **1** (0.91 g, 4.09 mmol) with dry dichloromethane (3.81 g, 44.86 mmol) as solvent were added. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.167 mL, 0.033 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl disulfide product 5 was obtained (1.27 g) using vacuum filtration (for preparation and reductive silylation of dibenzyl disulfide to **6**, **7**, of didodecyl disulfide to **13** with **2**, and tetrasulfide **14** with **1** see SI). Due to the presence of water, an excess of the silane was required for complete conversion. Production of $PhCH_2SH$ is due to hydrolysis of **5**.

$PhCH_2SSiMe(Me_3SiO)_2$ (compound 5): $(PhCH_2S)_2$: $PhCH_2SH$ = 82.0: 4.1: 13.9 ^{1}H NMR (600 MHz, chloroform-*d*): δ Compound 5 (*1 equiv.*) see above; $(PhCH_2S)_2$ (*0.05 equiv.*) d 3.60 (s, 4H, $(PhCH_2)_2SS$), 7.16-7.34 (m, 5H, arom); $PhCH_2SH$ (*0.17 equiv.*) 1.76 (t, *J*= 7.56 Hz, 1H, S*H*), 3.76 (s, 2H, $PhCH_2SH$), 7.16-7.34 (m, 5H arom); Silicone impurity: 0.03 (s, 4H) ppm. (full spectrum in SI.)

5.3.3.4. Reduction of bis(triethoxysilylpropyl)disulfide S2 using dimethylphenylsilane 3 ([SiH]/[SiOEt]=8:6 to give S-OSi3

The process described above (Reductive Cleavage of Organic Disulfides) was followed to prepare silylated **S-OSi3**: bis(triethoxysilylpropyl)disulfide stock solution (0.50 g, 1.05 mmol); dimethylphenylsilane (1.15 g, 8.44 mmol); dry toluene (0.501 g, 5.44 mmol) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution (0.672 mL, 0.067 mmol)(recovered 1.44 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ **S-OSi3**: 0.35 (s, 24H, $PhSiMe_2CH_2CH_2CH_2Si((OSi(Me)_2Ph)_3)$, 0.60-0.71 (m, 2H, $CH_2CH_2CH_2Si((OSi(Me)_2Ph)_3)$, 1.60-1.88 (m, 2H, $CH_2CH_2CH_2Si((OSi(Me)_2Ph)_3)$, 2.44-2.82 (m, 2H, $CH_2CH_2CH_2Si((OSi(Me)_2Ph)_3)$, 7.16- 7.57 (m, 20H arom). Overlapped silicone (integration relative to **S-OSi3)**: 0.29 (s, 13H), 0.32 (s, 10H), 0.38-0.43 (m, 10H), 0.52-0.54 (m, 10H); Residual ethoxy: 1.07-1.14 (m, 0.71H, $SiOCH_2CH_3$), 3.60-3.73 (m, 0.52H, $SiOCH_2CH_3$)(full spectrum in the SI).

^{13}C NMR (600 MHz, chloroform-*d*): δ -0.22, 0.58, 0.65, 0.68, 0.97, 12.78, 13.56, 14.15, 14.58, 21.57, 26.97, 27.72, 28.07, 28.21, 30.13, 32.92, 125.42, 127.82, 128.35, 129.16, 129.36, 133.12, 137.99, 139.43, 139.94 ppm. ^{29}Si NMR (600 MHz, chloroform-*d*, trace Cr(acac)$_3$): δ -67.83 (s, 0.8Si), -66.10 (s, 0.6Si), -66.06 (s, 3Si), -56.14 (s, 1Si), -13.49 (s, 0.04Si), -11.94 (s, 0.3Si), -1.87-0.82 (m, 38Si), 0.83 (s, 1Si), 7.85 (s, 0.1Si), 8.99-9.05 (m, 4Si) ppm.

The evolution of silylated products, as shown in **Figure 5.4** to **Figure 5.5**, involved a separate reaction for each data point (see **Table S5.4**, **Figure S5.6** and **Figure S5.7**, SI), changing only the ratio of hydrosilane against disulfide [SiH]/[SiOEt].

5.3.3.5. Reduction of bis(triethoxysilylpropyl)disulfide S2 using BisH 1: ([SiH]/[SiOEt]=8:6 to give S-OSi3(Si)

To a pre-dried 200 mL round-bottomed flask purged with dry N$_2$ was added bis(triethoxysilylpropyl)disulfide stock solution (0.50 g, 1.05 mmol) and BisH (1.90 g, 8.54 mmol) together with dry toluene (0.730 g, 7.92 mmol) as solvent. Freshly prepared B(C$_6$F$_5$)$_3$ stock solution was added (0.345 mL, 0.067 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina (recovered 2.21 g). Note: for most reactions, bubble formation ceased within 30 min, but 3h was used to ensure complete reaction in all titrations.

S-OSi3(Si): δ 0.02-0.06 (m, 9H, CH$_2$Si((OSi*Me*(OSiMe$_3$)$_2$)$_3$), 0.09-0.13 (m, 72H, CH$_2$Si((OSiMe(OSi*Me*$_3$)$_2$)$_3$ and CH$_2$SSiMe(OSi*Me*$_3$)$_2$ overlapped), 0.27-0.29 (m, 3H, CH$_2$SSi*Me*(OSiMe$_3$)$_2$), 0.62-0.73 (m, 2H, SiC*H*$_2$CH$_2$CH$_2$S), 1.66-1.69 (m, 2H, SiCH$_2$C*H*$_2$CH$_2$S), 2.45-2.52 (m, 2H, SiCH$_2$CH$_2$C*H*$_2$S)(full spectrum in SI);^{13}C

NMR (600 MHz, chloroform-*d*): δ -1.86, 2.06, 5.16, 14.53, 21.81, 26.55, 30.07, 77.36, 126.16, 128.58, 138.21 ppm; ^{29}Si NMR (600 MHz, chloroform-*d*, trace Cr(acac)$_3$): δ -66.16- -65.90 (m, 1Si), -54.49 (s, 2Si), -30.67 (s, 1Si), 7.45-7.62 (m, 16Si), 9.40-9.53 (m, 4Si) ppm.

5.3.3.6. Complete reduction of bis(triethoxysilylpropyl)disulfide S2 using BisH 1: ([SiH]/[SiOEt]=9:6 to give S-OSi3(Si)

S-OSi3(Si): δ 0.03-0.07 (m, 9H, CH$_2$Si((OSi*Me*(OSiMe$_3$)$_2$)$_3$), 0.10-0.15 (m, 72H, CH$_2$Si((OSiMe(OSi*Me*$_3$)$_2$)$_3$ and CH$_2$SSiMe(OSi*Me*$_3$)$_2$ overlapped), 0.28-0.30 (m, 3H, CH$_2$SSi*Me*(OSiMe$_3$)$_2$), 0.64-0.74 (m, 2H, SiC*H*$_2$CH$_2$CH$_2$S), 1.69-1.72 (m, 2H, SiCH$_2$C*H*$_2$CH$_2$S), 2.50-2.54 (m, 2H, SiCH$_2$CH$_2$C*H*$_2$S); Silicone impurities (integration relative to **S-OSi3(Si))**: 0.03-0.07 (m, 13H, overlapped), 0.10-0.15 (m, 84H, overlapped), 0.37 (m, 0.3H) (full spectrum in the SI).

Each data point in **Figure 5.4** to **Figure 5.5** was obtained from a separate reaction conducted under identical reaction conditions, changing only the ratio of hydrosilane against disulfide [SiH]/[SiOEt] (see **Figure S5.8** to **Figure S5.10**, SI).

5.3.3.7. Reduction of bis(triethoxysilylpropyl)tetrasulfide S4 using BisH 1 ([SiH]/[SiOEt]=12:6 to give S-OSi3(Si)

The process described above was followed: bis(triethoxysilylpropyl)tetrasulfide **S4** stock solution (0.52 g, 0.96 mmol); BisH (2.48 g, 11.1 mmol); dry toluene (0.90 g, 9.77 mmol); B(C$_6$F$_5$)$_3$ stock solution was added (0.456 mL, 0.089 mmol)(recovered 2.69 g). A separate reaction was undertaken for each data point in **Figure S5.11** to **Figure S5.14**, changing only the ratio of hydrosilane against tetrasulfide [SiH]/[SiOEt].

^{1}H NMR (600 MHz, chloroform-*d*): δ 0.03-0.06 (m, 9H, $CH_2Si((OSi\mathit{Me}(OSiMe_3)_2)_3)$, 0.11-0.12 (m, 72H, $CH_2Si((OSiMe(OSi\mathit{Me}_3)_2)_3$ and $CH_2SSiMe(OSi\mathit{Me}_3)_2$ overlapped), 0.21-0.30 (m, 3H, $CH_2SSi\mathit{Me}(OSiMe_3)_2)$, 0.64-0.74 (m, 2H, $SiC\mathit{H}_2CH_2CH_2S$), 1.68-1.74 (m, 2H, $SiCH_2C\mathit{H}_2CH_2S$), 2.50-2.55 (m, 2H, $SiCH_2CH_2C\mathit{H}_2S$); Residual ethoxy: 1.19-1.21 (m, 0.12H, $SiOCH_2C\mathit{H}_3$), 3.80 (s, 0.08H, $SiOC\mathit{H}_2CH_3$); Silicone impurity (integration relative to S-OSi3(Si)): 0.07 (s, 4H), 0.37 (s, 4H)(full spectrum in the SI) ppm.

^{13}C NMR (600 MHz, chloroform-*d*): δ -1.86, 2.02, 5.16, 14.43, 21.81, 26.67, 28.29, 30.08, 77.36, 125.66, 128.58, 129.39, 138.21 ppm; ^{29}Si NMR (600 MHz, chloroform-*d*, trace $Cr(acac)_3$): δ -71.05 (s, 0.12 Si), -66.22 - -65.88 (m, 6Si), -30.66 (s, 1Si), -32.92 (s, 4Si), 7.46-7.64 (m, 25Si), 9.42-9.60 (m, 17Si) ppm.

Each data point in was obtained from a separate reaction conducted under identical reaction conditions, changing only the ratio of hydrosilane against disulfide [SiH]/[SiOEt] (see **Figure S5.8** to **Figure S5.10**, SI).

5.3.3.8. Characterization of Si-S-Si 15

Compound **15** was isolated after vacuum distillation (635 mmHg) at 110 °C from the previous reaction (recovered 1.39 g).

^{1}H NMR (600 MHz, chloroform-*d*): δ $((Me_3SiO)_2MeSi)_2S$: d 0.14 (s, 36H, $((\mathit{Me}_3SiO)_2MeSi)_2S$), 0.35 (s, 6H, $((Me_3SiO)_2\mathit{Me}Si)_2S$); Silicone impurities (integration relative to **15**): 0.10 (s, 3H), 0.02 (s, 0.51H) ppm. ^{29}Si NMR (600 MHz, chloroform-*d*): δ $((Me_3SiO)_2MeSi)_2S$: 9.55 (s, 4Si, $((Me_3\mathit{Si}O)_2MeSi)_2S$), -32.97 (s, 2Si, $((Me_3SiO)_2Me\mathit{Si})_2S$)(full spectrum in SI).

GC–MS: Sulfur containing compounds:

(1) $C_{14}H_{42}O_4SSi_6$ **15**, retention time (RT) 10.8 min, relative peak intensity (91%), MW: 474.14: $[M{-}15]^+$ = 459.2 (90), 371.1 (8), 297.1 (20), 249.0 (5), 221.1 (100), 147.1 (25), 73.1 (90).

Non-sulfur containing compounds (silicone compounds):

(2) Relative peak intensity (1%), RT) 28.3 min, MW: 327.3: $[M]^+$=327.3 (20), 283.3 (2), 242.2 (3), 201.2 (10), 158.1 (2), 127.2 (100), 98.1 (2), 57.2 (40).

(3) Relative peak intensity (6%), RT 29.7 min, MW 355.3: $[M]^+$=355.3 (40), 327.3 (37), 283.2 (2), 255.2 (5), 201.2 (15), 155.2 (40), 127.2 (100), 98.2 (10), 57.1 (50).

(4) Relative peak intensity (3%), RT 31.0 min, MW: 470.2: $[M]^+$=470.2 (1), 439.1 (2),383.3 (20), 355.3 (60), 311.2 (5), 283.2 (8), 229.2 (20), 201.2 (18), 155.2 (100), 127.2 (70), 98.1 (20), 71.2 (25), 57.2 (50).

5.3.3.9. Cleavage of SiS bonds: H_2O/IPA

In a pre-dried 100.0 mL round-bottomed flask containing **6** (0.50 g, 1.85 mmol) and distilled water (0.0333 mL, 0.0333 g, 1.85 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent. *No S-Si compounds were detected in the GC-MS*. For GC/MS data and analogous cleavage reactions **5-10**, and less effective desilylation methods using acid or TBAF, see the SI.

^{1}H NMR (600 MHz, chloroform-*d*): δ $PhCH_2SSiMe_2OSiMe_3$ (6): $PhCH_2SH$= 0: 1.0 $PhCH_2SH$ (*1 equiv.*): 1.76 (t, *J*=7.53 Hz, 1H, S*H*), 3.75 (d, *J*=7.56 Hz, 2H, $PhCH_2SH$), 7.23-7.33 (m, 5H, arom); Silicone impurity: 0.05-0.12 (m, 16H).

5.4. Materials and Methods

5.4.1. Silylating Thiols and Disulfides

To better understand the relative reactivity of thiols when compared to other organic groups, the competitive silylation of benzyl alcohol and benzyl thiol was attempted with less than one equivalent of the hydrosilane BisH (bis(trimethylsiloxy)methylsilane, $(Me_3SiO)_2SiMeH$ **1**) in the presence of low concentrations of $B(C_6F_5)_3$ (0.16 mol%). NMR studies clearly showed no change in the benzyl thiol ($C\mathit{H}_2SH$) but a change in chemical shift as benzyl alcohol was converted essentially quantitatively to silyl ether **4** ($C\mathit{H}_2OH \rightarrow C\mathit{H}_2OSi$ **Figure 5.2**A, Supporting Information, SI, **Figure S5.1**, **Figure S5.2**. Note that any trace water present undergoes preferential silylation over $PhCH_2OH$). This selectivity is unsurprising given the very high oxophilicity of silicon.[13] Thus, any $B(C_6F_5)_3$/silane chemistry at a sulfur functionality was initially anticipated to be unable to compete with oxygen-based groups.

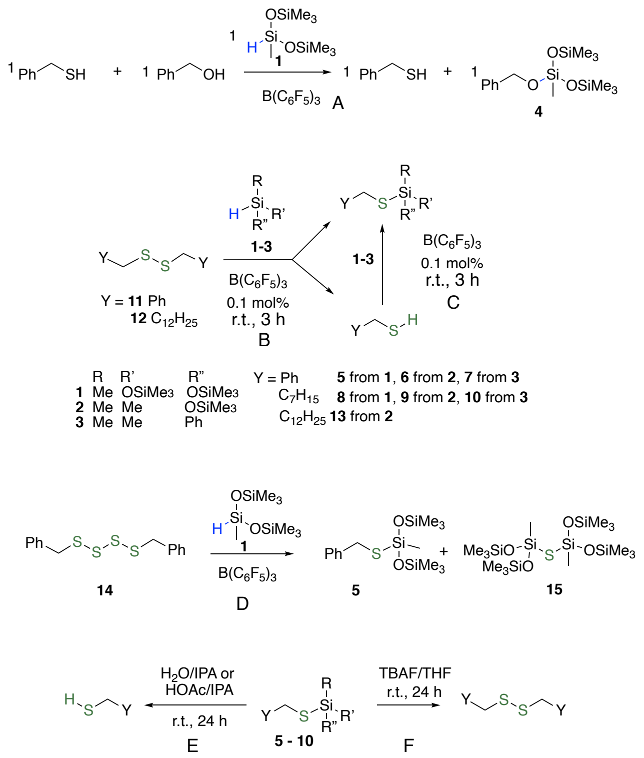


Figure 5.2. Reduction and desiliconization of simple organic disulfides.

The simple organic thiols benzyl thiol or octyl thiol were readily converted using **1**, pentamethyldisiloxane **2** or $PhMe_2SiH$ **3** to silyl thio ethers **4**, **5**, **6**, **7** or **8**, **9**, **10**, respectively (**Figure 5.2**C, SI).[14] Disulfides **11**, **12** were similarly reduced in high yields of 90% - 100% (SI) to the thio ethers **5**-**7**, **13** by the reaction of hydrosiloxanes in the presence of low concentrations of $B(C_6F_5)_3$ (0.8 mol% (SiH), **Figure 5.2**B, SI). While the reaction is straightforward to practice in toluene or dichloromethane, dibenzyl disulfide (and didodecyl disulfide, **Figure S5.3**, SI) could also be directly reduced in the absence of solvents, a convenient and Green protocol when the starting materials are sufficiently soluble in the silicone reagent. No thiols were observed if substoichiometric quantities of the hydrosiloxane were used. For example, when using 1 equiv. of **1** only about half of the starting disulfide

11 reacted (**Figure 5.2**B→C, **Figure S5.4**) indicating that the relative rates of reaction under these conditions is RS-H > RS-SR.

Polysulfides subjected to the same reaction conditions produced the same organic products (**Figure 5.2**D); starting from dibenzyl tetrasulfide **14** (SI), the sulfur not bound directly to carbon ended up as disilyl sulfide **15**, which was removed by evaporation. The ability to isolate the organic residue as a simple silyl thio ether was an unexpected benefit, as the "tetrasulfide" and "disulfide" compounds we purchased contained significant quantities of penta- and trisulfides, respectively. On the other hand, excess silane was required to remove the excess sulfur atoms in the form of **15**, which reflects an undesirable lack of atom efficiency of silanes just to create a waste product (for titration, see **Figure S5.5**, **Table S5.4**, SI).

5.4.2. Silylating Sulfur-based Coupling Agents

Sulfur-based alkoxysilane coupling agents are important commercial materials used, in particular, to modify silica to improve rolling resistance and, therefore, fuel economy in "Green Tires."[15] These molecules contain both S-S bonds and alkoxysilanes that can participate in Piers-Rubinsztajn reductions. Could these compounds be precursors to new sulfur-containing silicones?

As with simple disulfides, complete reduction of the **S2** and **S4** commercial coupling agents was straightforward, giving branched siloxanes with silylated thiols. In the case of **S2**, just over 8 equiv. of the corresponding SiH compound was required for complete reduction to the silicone **S-OSi3** (**Figure 5.3**A-F) **S4** required 12 equiv. (based on moles of starting material) to give the same product (**Figure**

5.3G). Note: water competes with these reductions (**Figure 5.3**H) to form bis(dimethylphenyl)disiloxane **16** from **3**.[16] Therefore, if performed in an open flask it will be necessary to use a slight excess of reducing agent. With exactly 8 equiv. of the silane in the reduction of **S2**, some residual ethoxysilane was isolated but with 9 equiv. conversion was 100% complete (SI). Thus, as with simple organic sulfides, a single organosiloxane was the product of mixtures of starting oligosulfides. The requirement for super-stoichiometric quantities to obtain complete conversion was a consequence of contamination of **S2** with small amounts of the trisulfide; **S4** was actually a complex mixture of the tri-, tetra-, penta- and hexasulfides.

Thiopropyl-modified silicones are commonly prepared in a messy S_N2 reaction of sodium sulfides with haloalkylsilanes or silicones. An alternative approach would involve silylating one of the alkoxy groups in a coupling agent to give a difunctional material **S-OSi1** that could be elaborated into linear polymers, as well as monoalkoxy compounds **S-OSi2** that could serve as polymer chain ends (**Figure 5.4**). This would require selective functionalization of the sulfur and of the alkoxysilane groups. While thermodynamics would predict the C-O cleavage to form SiO bonds over much weaker SiS bonds, as was seen with benzyl alcohol, kinetics favors S-S cleavage due to the very undemanding sterics of the sulfur center: S-S cleavage won. When one equiv. of **1** was added to **S2** the relative efficacy of the reaction with sulfur/SiOR was 95/5 (**Figure 5.4**A, [SiH]/[SS]=2); the analogous reaction with phenylsilane **3** was less selective, with a selectivity of sulfur/SiOR was 75/25 (**Figure 5.4**A, [SiH]/[SS]=2), as shown by the formation of disiloxanes right from the onset of reaction in the latter case. Lower selectivity with the phenylsilane may be a consequence of sterics,[5,6] but the higher electrophilicity of the silicon atom, as a consequence of the phenyl group, can also play a role.[5]

Mixed siloxy/alkoxysilanes were produced by titrating S2 until complete silylation had been achieved, with just over 8 equiv. of **3**, as noted. Clean preparation of the desired dialkoxy compound S-OSi1 would require that each sequential substitution proceed more slowly than the previous one, such that each homologue can be discreetly prepared and isolated. The rates of reaction were expected to be $Si(OEt)_3$ > $Si(OEt)_2OSi$ > $Si(OEt)(OSi)_2$ based on the known retardation in nucleophilic substitution at silicon that accompanies increased steric encumbrance at silicon.[6, 17]

The silylation process was followed with ^{29}Si NMR; chemical shifts are very sensitive to changes that occur as SiOEt → SiOSi (**Figure 5.4**(B), **Figure 5.5**; analogous ^{1}H and ^{13}C NMR for this and other reductive titrations **S2** + **3** and **S4** + **1** may be found in the SI). The relative reactivities of the alkoxysilanes followed a different profile than expected and were far less differentiated than desired. As a consequence, it was only possible to create mixtures of different alkoxy-functional compounds. For example, after adding 3 equiv. of silane, the product was a mixture of starting material **S2**+**S-OSi0** 23%, **S2-OSi1** 3% **S-OSi1** 45% and **S-OSi2** 29%; note, due to overlap of $Si(OEt)_3$ peaks in the ^{29}Si NMR, ^{1}H NMR was used to discriminate **S2-OSi1** from **S-OSi0**. We are examining if these mixtures can still serve as useful monomers and crosslinkers for thiopropyl-modified silicones.

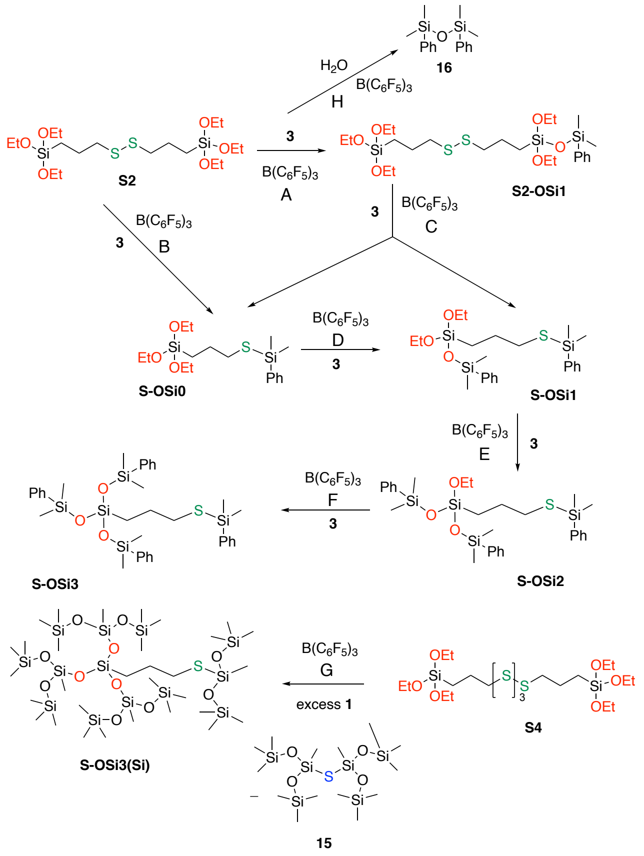


Figure 5.3. The structures of non-substituted (a), mono-substituted (b), di-substituted (c) and tri-substituted (d) S-Si products in commercial disulfide coupling system during titration with **3**.

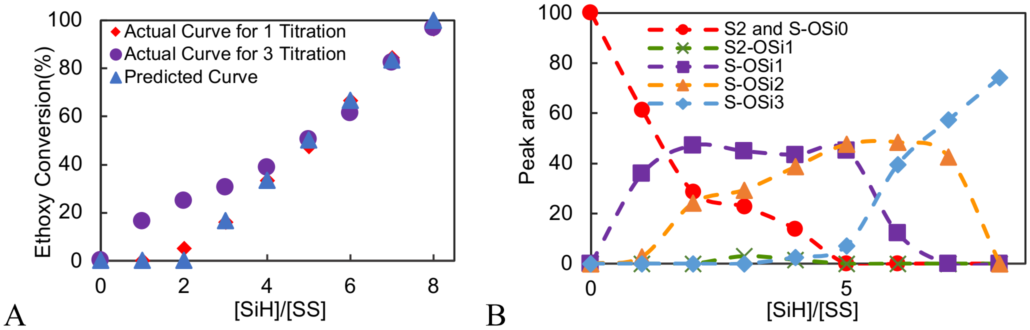


Figure 5.4. Reductive titration of **S2**: (A). Following EtO group loss, which occurs more selectively with **1** than **3**. (B). ^{29}Si NMR monitoring of the titration showing changes in product profile (**Figure 5.3**) as SS and SiOEt groups in **S2** are reduced with **3**.[18]

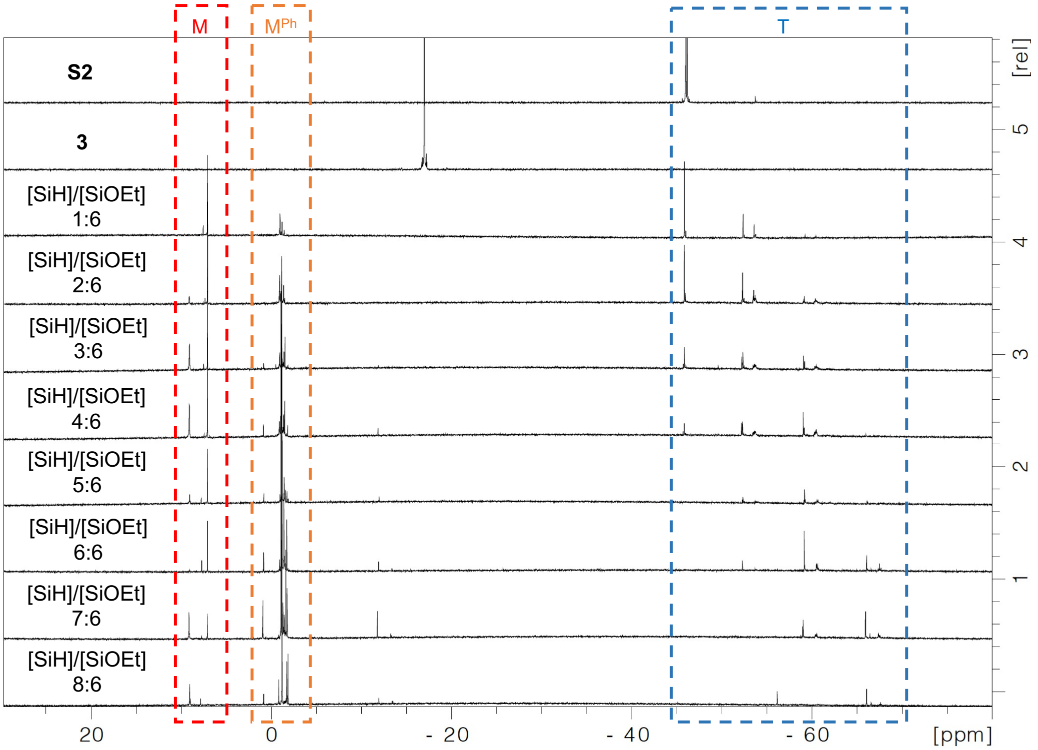


Figure 5.5. Reductive titration of **S2**: Stacked ^{29}Si NMR plot from which **Figure 5.4**(B) was produced. The red bracket (>5 ppm, left) shows the shift of M (Me_3SiO) units, the orange bracket (-5 - + 5 ppm, middle) shows the shift of M^{Ph} (Me_2PhSi-O) peak while the blue bracket (-40 - -75 ppm, right) shows the shift of T ($MeSiO_{3/2}$) units.

5.4.3. Lability of sulfur-silicon bonds (S-Si)

Having converted various sulfur moieties to a thio silyl ether, it remains to describe the processes to deprotect the sulfur. Much of the utility of silicon chemistry in organic synthesis hinges on reliable routes to silyl ethers, in particular, and then their clean deprotection, typically with fluoride that leaves other organic functionality untouched.[6] There are few reports of the reactivity of compounds containing Si-S bonds,[19] so thiol protection by silyl groups is not well understood. Early work by Boudjouk et al. showed that $Me_3SiSSiMe_3$ was extremely sensitive towards hydrolysis; the compounds hydrolyzed spontaneously in a moist atmosphere.[7] Rosenberg's group, however, prepared more hindered thio silyl ethers by the reduction of thiobenzophenone by mono- and disilanes with $B(C_6F_5)_3$ as catalyst.[20] The cleavage of these compounds in refluxing ethanol was, by comparison, relatively slow because of higher steric hinderance of the substituents near silicon, when compared to Me_3Si.[21]

$PhSiMe_2$ and $Me_3SiOSiMe_2$-based silyl thio ethers were readily cleaved simply by placing them in isopropanol (IPA)/water solutions. Deprotection with the more hindered trisiloxane derived from **1** was very sluggish under these conditions or with acetic acid/IPA (**Figure 5.2**E, **Table S5.4**, SI). That is, silyl protection groups for sulfur followed the same trend with respect to sterics as normal silyl ethers.[6] It was initially assumed that deprotection catalyzed by TBAF, to give the thiol, would be facile. Instead, the disulfide was the main product due (**Figure 5.2**F, SI). Analogous outcomes, oxidative conversion of thiols to disulfides, have been observed with the air oxidation of thiols catalyzed by ammonium salts,[22] for example, TBAF in CCl_4.[23]

Piers reduction shows broad applicability to many functional groups. When a silyl ether was desired from a carbonyl group, Piers provided a warning to avoid excess reagents or vigorous conditions that could lead to overreduction of an alkoxysilane to give alkanes and disiloxane.[24] The latter reaction, the Piers-Rubinsztajn reaction has become an important new route to silicones.[10] Rosenberg and team demonstrated that thioketones could similarly be reduced and, at least when reducing thiobenzophenone, overreduction is also possible.[11] In this particular case, it is likely the facility for overreduction may be in part attributed to the flanking phenyl groups.

Alkyl thiols were readily converted using this process with a variety of hydrosilanes to silyl thio ethers; overreduction was not observed. However, simple alcohols like benzyl alcohol were more reactive towards the silylation conditions than thiols because of the strong SiO bond formed and the lack of significant steric impediment to reaction at oxygen. Disulfides or tetrasulfides analogously underwent reductive cleavage, however, the intermediate thiol produced during reduction was not observed as, once formed, it outcompeted the disulfide starting material for reductive silylation (**Figure 5.2**B > C). Tetrasulfides similarly were reduced to the same organic thio silyl ether, with excess sulfur being lost as the silyl analog of water $R_3SiSSiR_3$ **15**. The use of so much silane might be justified when trying to recycle tires,[12] but otherwise only with very valuable organic residues.

Analogous outcomes were observed with sulfur-based coupling agents; surprisingly the disulfides and thiols were more reactive than alkoxysilanes in a PR reaction, but it was straightforward to reduce first the sulfur moieties and then the complete silylation of all alkoxysilane groups. These data allow us to conclude, with this range of compounds, that the relative rate of functional groups with hydrosilanes in the presence of $B(C_6F_5)_3$ follows the order ROH > RSH > RSSR > $ROSiR_3$. This simple strategy provides a method to reductively cleave and silylate a variety of sulfur-containing molecules and then later, depending on steric bulk of the groups on silicon, cleave the Si-S bond to reveal the organic thiol.

5.5. Conclusions

Thiols and disulfides are readily converted to silyl thio ethers by reduction with hydrosilanes and hydrosiloxanes in the presence of less than 1mol% $B(C_6F_5)_3$.

Alcohols react more rapidly than the thiols or disulfides, but alkoxysilanes react more slowly: the observed reactivity order was ROH > RSH > RSSR > SiOR. Reaction rates of the three alkoxy groups in coupling agents were only slightly different such that RSi(OR)(OSiR’3)2 and RSi(OR)2OSiR”3 could only be prepared as mixtures. TBAF, atypically, was not efficacious at deprotecting the silyl thio ether and led instead to reoxidation to the disulfide; alcoholysis with IPA was a convenient alternative to recover the thiol provided that the silane was not too bulky.

5.6. Acknowledgments

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada.

5.7. References

(1) C. Goodyear, *US Patent 3633* **1844**.

(2) M. J. Kade, D. J. Burke, C. J. Hawker, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 743-750.

(3) aP. Metzner, A. Thuillier, *Sulfur Reagents in Organic Synthesis*, Academic Press, **2013**; bS. Oae, *Organic Sulfur Chemistry*, CRC Press, **2018**.

(4) H. T. Abdel-Mohsen, K. Sudheendran, J. Conrad, U. Beifuss, *Green Chem.* **2013**, *15*, 1490-1495.

(5) F. Q. Schafer, G. R. Buettner, *Free Radical Biol. Med.* **2001**, *30*, 1191-1212.

(6) aP. Kocienski, *Protecting Groups* 3rd ed., Thieme, Stuttgart, **2005**; bP. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis*, 4th ed., Wiley-Interscience, New Jersey, **2006**.

(7) J.-H. So, P. Boudjouk, H. H. Hong, W. P. Weber, *Inorg. Synth.* **1992**, *29*, 30-32.

(8) I. V. Koval, *Russian Chemical Reviews* **1994**, *63*, 735-750.

(9) aW. E. Piers, in *Adv. Organomet. Chem., Vol. 52*, Academic Press, **2004**, pp. 1-76; bM. Oestreich, J. Hermeke, J. Mohr, *Chem. Soc. Rev.* **2015**, *44*, 2202-2220.

(10) M. A. Brook, *Chem. Eur. J.* **2018**, *24*, 8458-8469.

(11) P. T. K. Lee, M. K. Skjel, L. Rosenberg, *Organometallics* **2013**, *32*, 1575-1578.

(12) S. Zheng, M. Liao, Y. Chen, M. A. Brook, *Green Chem.* **2020**, *22*, 94-102.

(13) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, **2000**.

(14) J. B. Grande, D. B. Thompson, F. Gonzaga, M. A. Brook, *Chem. Commun.* **2010**, *46*, 4988-4990.

(15) aS. Uhrlandt, A. Blume, *Kautschuk Gummi Kunststoffe* **2001**, *54*, 520-527; bJ. T. Byers, *Rubber Chem. Tech.* **2002**, *75*, 527-547.

(16) M. Liao, A. F. Schneider, S. E. Laengert, C. B. Gale, Y. Chen, M. A. Brook, *Eur. Polym. J.* **2018**, *107*, 287-293.

(17) M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, **2000**, pp. 115-143.

(18) O. Paquet, M.-C. Brochier Salon, E. Zeno, M. N. Belgacem, *Mater. Sci. Eng. C* **2012**, *32*, 487-493.

(19) A. Haas, *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1014-1023.

(20) D. J. Harrison, R. McDonald, L. Rosenberg, *Organometallics* **2005**, *24*, 1398-1400.

(21) D. J. Harrison, D. R. Edwards, R. McDonald, L. Rosenberg, *Dalton Trans.* **2008**, 3401-3411.

(22) Y. He, D. Hang, M. Lu, *Phosphorus Sulfur Silicon Relat. Elem.* **2012**, *187*, 1118-1124.

(23) T. Maruyama, T. Ikeo, M. Ueki, *Tetrahedron Lett.* **1999**, *40*, 5031-5034.

(24) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090-3098.

(25) M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, *3*, 530-533.

5.8. Appendix 4- Supporting Information

5.8.1 Relative reactivity of silanes for benzyl alcohol and benzyl mercaptan

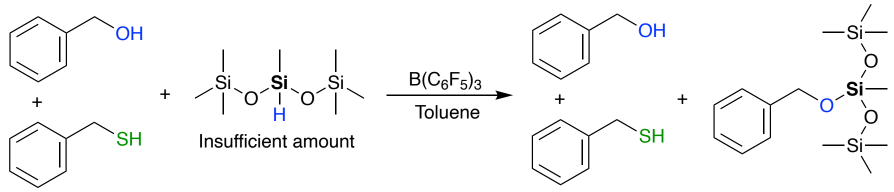


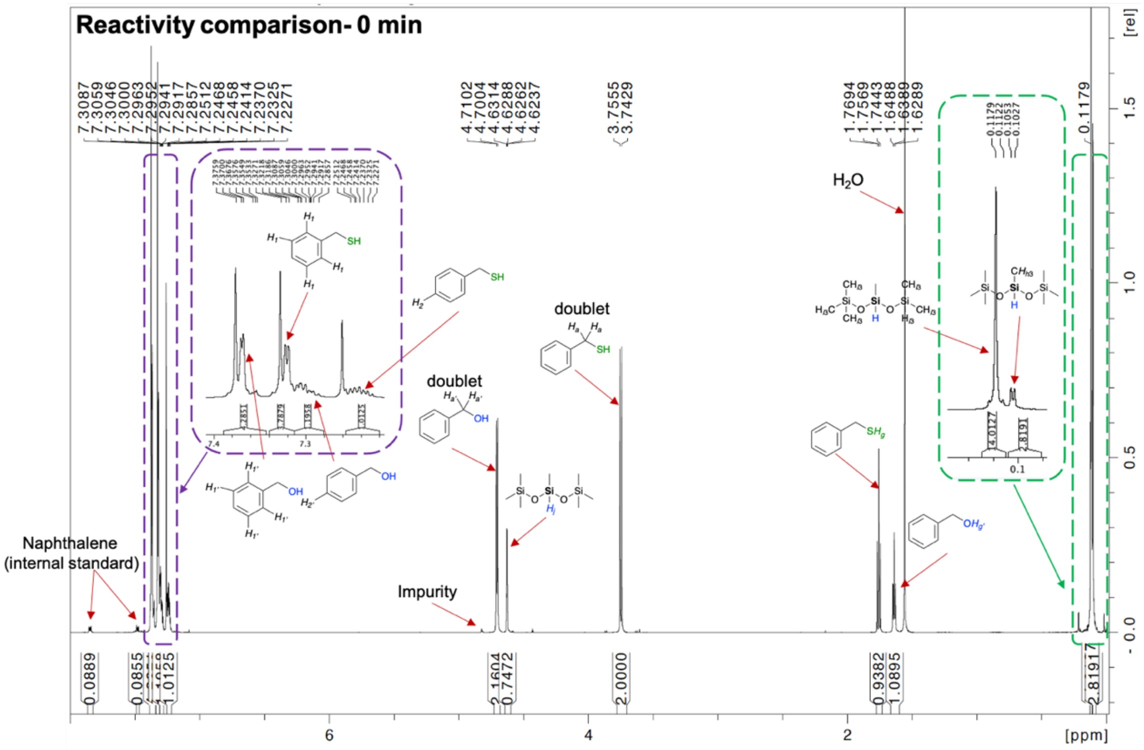
Figure S5.1. Competitive silylation of benzyl mercaptan and benzyl alcohol.

Table S5.1. Summary of the integration in ^{1}H NMR

Reaction time	~4.63 ppm (quartet)[a]	~3.74 ppm (doublet)	~4.70 ppm (doublet)	~4.77 ppm	7.85 ppm (internal standard)
	Si*H*	C*H*$_2$SH	C*H*$_2$OH	C*H*$_2$OSi	C$_5$*H*$_4$C$_5$H$_4$
0 min	0.75	2	2.16	0	0.0889
24 h	0	1.88[b]	1.32	0.74	0.0889

a. All integrations in ^{1}H NMR were obtained using naphthalene as an internal standard. **b**. There were no corresponding peaks for the SiS compound. Thus, the small deviation from 2H is within the normal range of sensitivity.

A



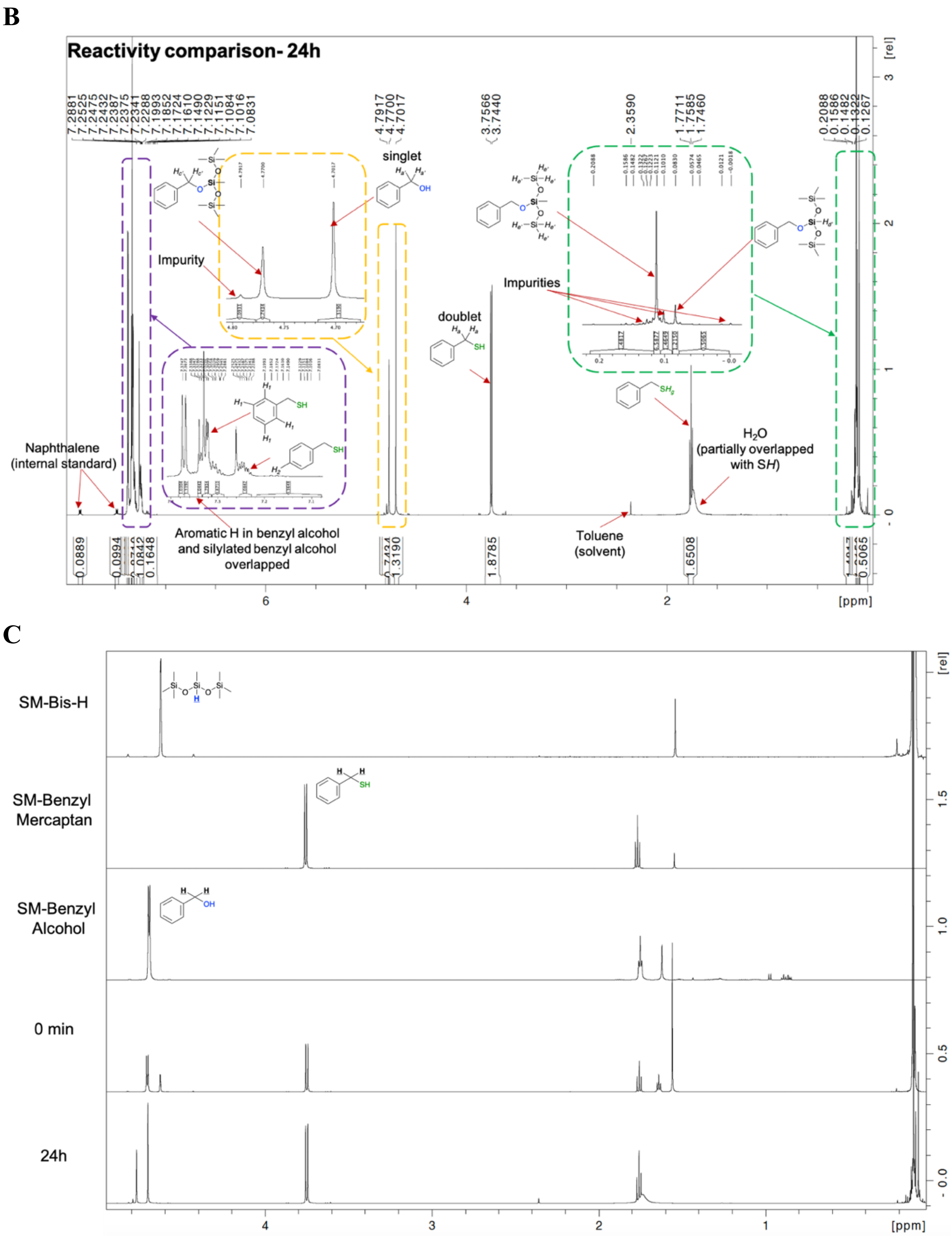
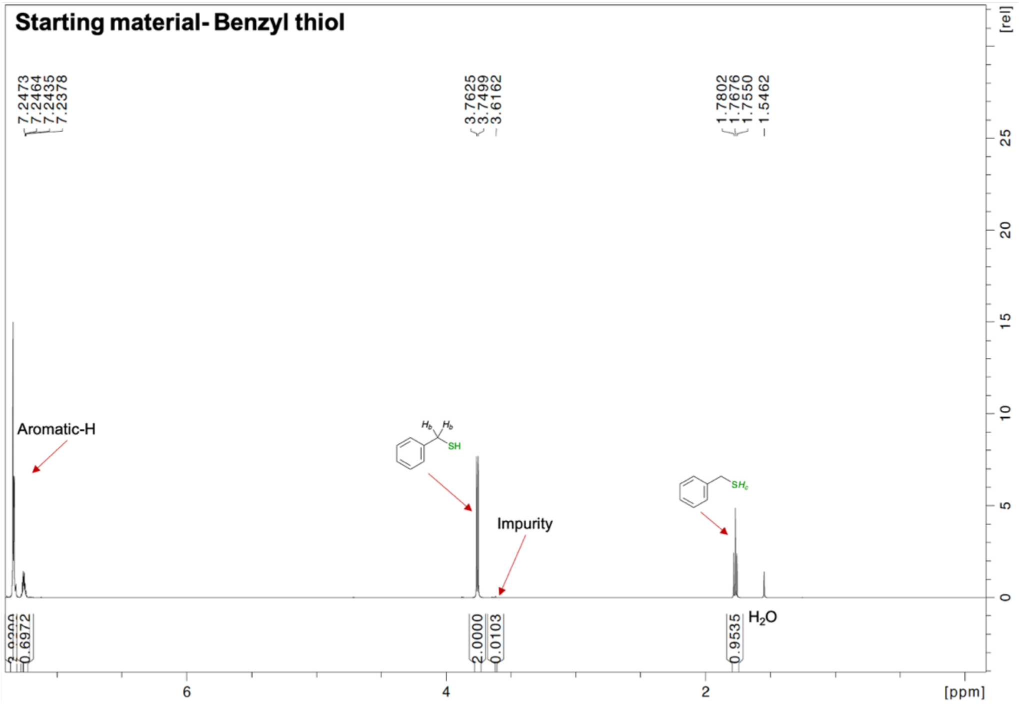


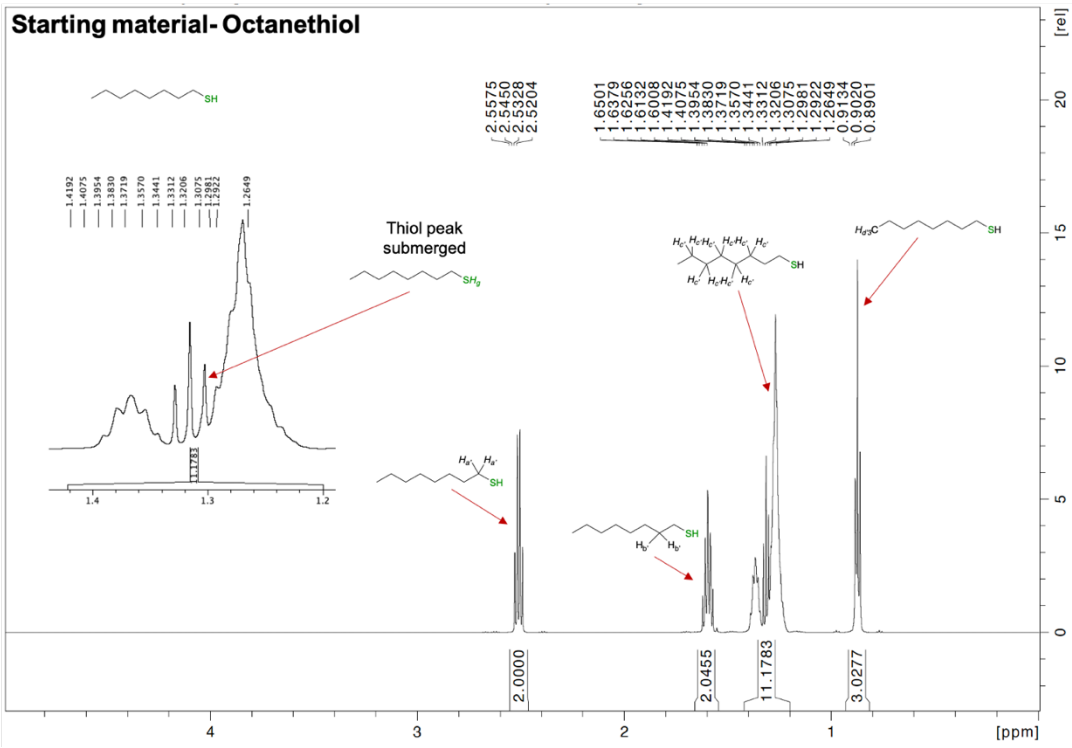
Figure S5.2. ^1H NMR spectra of the relative reactivities illustrated in **Figure S5.1**; (A) the ^1H NMR spectra at 0 min reaction time (**Table S5.1**); (B) the ^1H NMR spectra at 24h reaction time (**Table S5.1**); (C) stacked plot spectra. Note: in this spectrum only the SH and OH peaks overlap.

5.8.2 ^{1}H NMR of starting materials

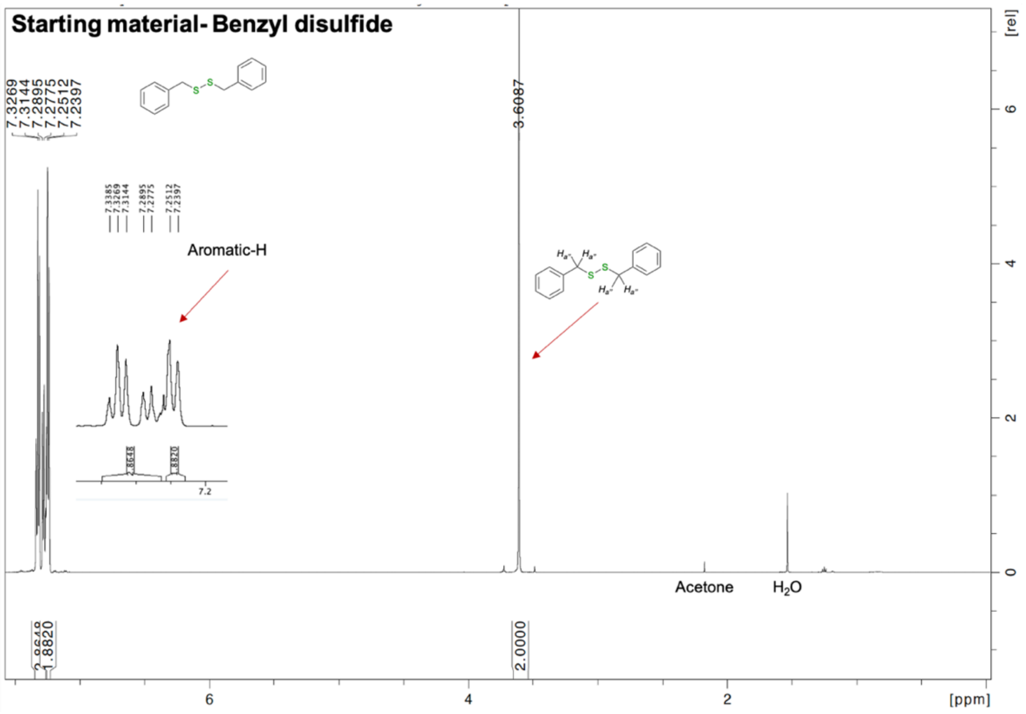
5.8.2.1 Benzyl thiol



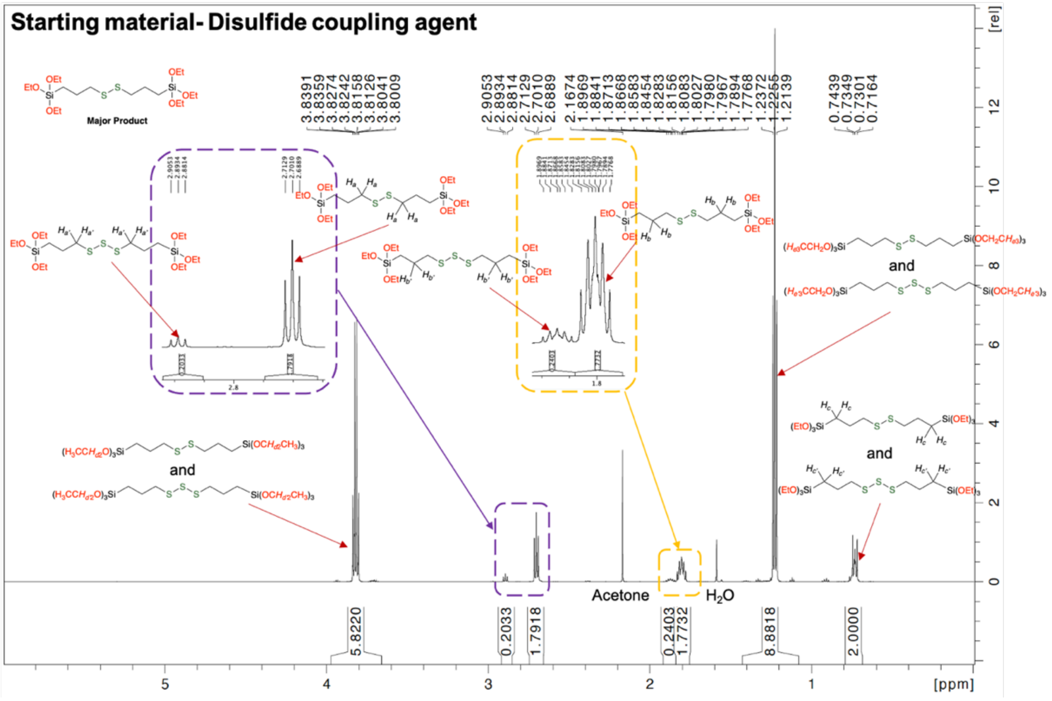
5.8.2.2 Octyl thiol



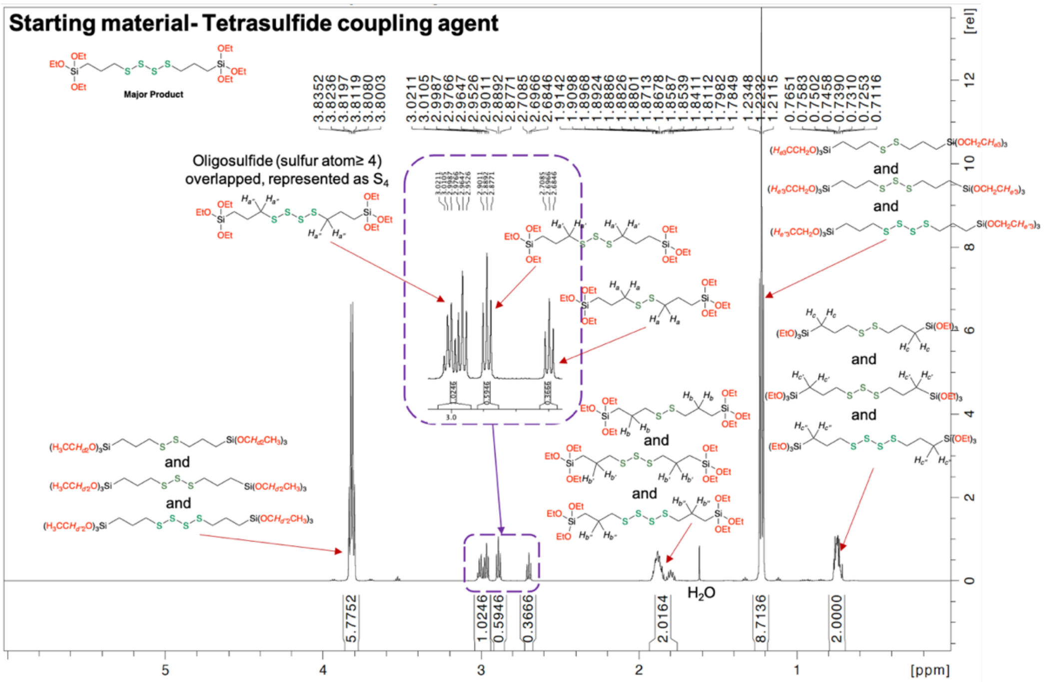
5.8.2.3 Dibenzyl disulfide



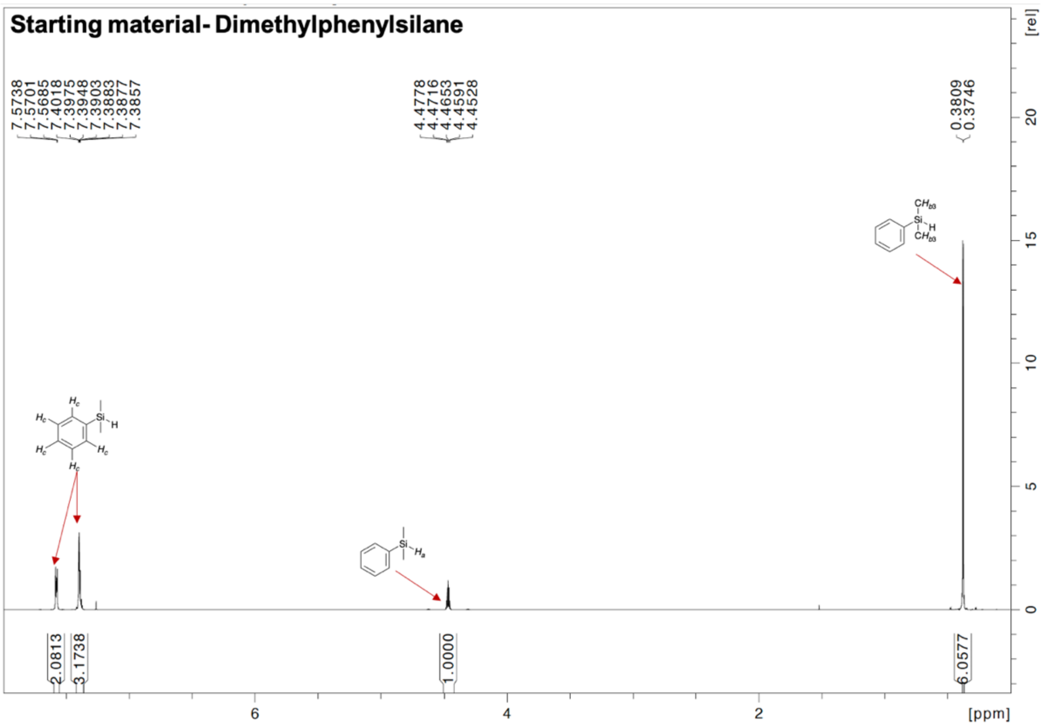
5.8.2.4 Disulfide coupling agent S2



5.8.2.5 Tetrasulfide coupling agent S4



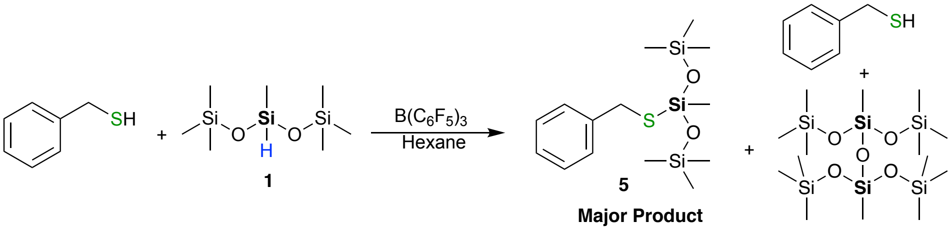
5.8.2.6 Dimethylphenylsilane 3



5.8.3 Silylation of organic thiols

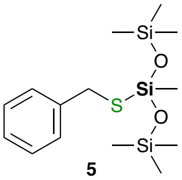
5.8.3.1 Silylation of benzyl thiol

Compound 5 (from **1**); incomplete reaction due to competitive silylation of water



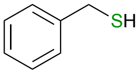
GC-MS: Compound 5: PhCH$_2$SH= 98.5: 1.5 (Relative peak intensity)

Sulfur-containing compounds:



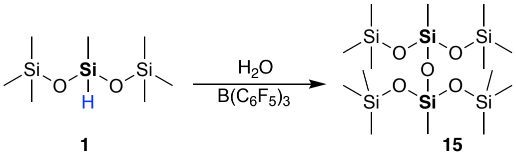
5

(1) $C_{14}H_{28}O_2SSi_3$, retention time 8.8 min, relative peak intensity (**95.0**%), MW: 344.11: $[M]^+$= 344.2 (18), 329.1 (10), 221.2 (100), 207.1 (15), 189.1 (4), 149.1 (5), 133.1 (11), 119.1 (1), 105.2 (1), 91.2 (99), 73.2 (20), 65.2 (10).

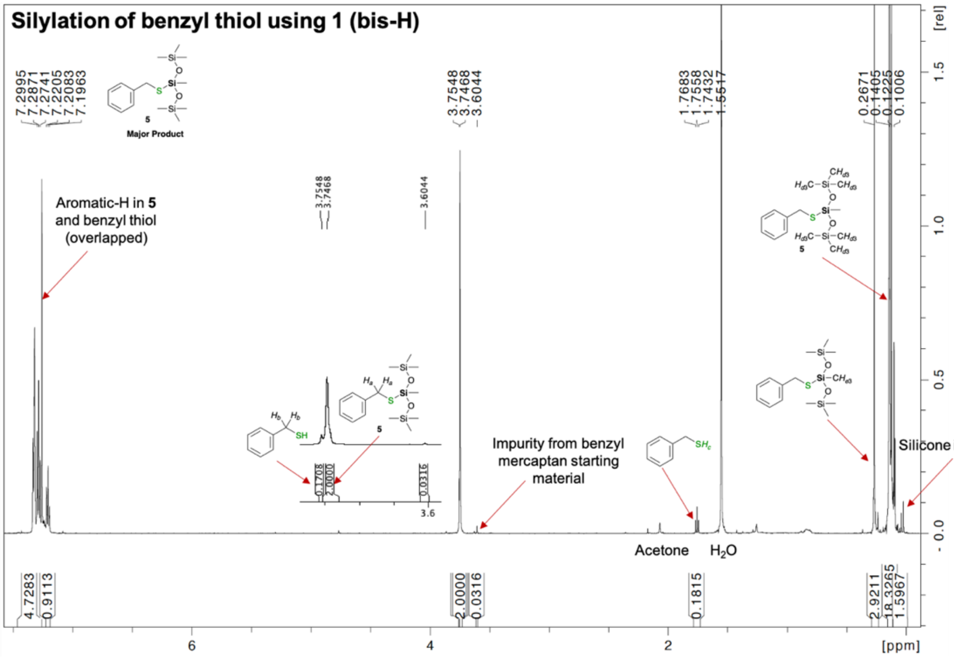


(2) C_7H_8S, retention time 5.2 min, relative peak intensity (**1.4**%), MW: 124.03: $[M]^+$= 124.1 (50), 91.2 (100), 77.1 (5), 69.1 (1), 65.2 (15), 51.2 (6).

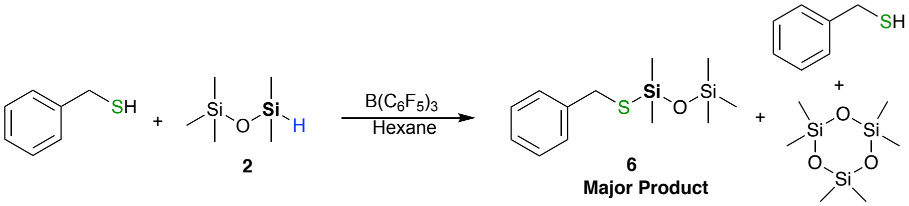
Non-sulfur containing compound (silicone compound):



(3) $C_{14}H_{42}O_5Si_6$, retention time 5.4 min, relative peak intensity (**3.6**%), MW: 458.16: $[M-15]^+$= 443.2 (30), 355.1 (42), 339.1 (6), 281.1 (55), 267.1 (40), 249.0 (3), 221.2 (80), 207.2 (7), 147.2 (75), 133.1 (3), 73.2 (100), 59.1 (5). Hydrolysis/condensation product of **1**, as illustrated above.



Compound 6 (from 2)



In a pre-dried 100.0 mL round-bottomed flask, benzyl thiol (2.00 g, 16.10 mmol) and **2** (2.40 g, 16.18 mmol) were mixed in dry hexanes (5.0 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (1.29 mL, 0.129 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **6** (3.74 g) was obtained using vacuum filtration.

The aromatic H in benzyl thiol and **6** are overlapped. The equivalents of benzyl thiol and **6** were determined using the PhC*H*$_2$ adjacent to S-Si and SH peak.

PhC*H*$_2$SSiMe$_2$OSiMe$_3$ (compound 6): PhCH$_2$S*H*= 90.9: 9.1

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **6** (*1 equiv.*): 0.13 (s, 9H, PhCH$_2$SSiMe$_2$OSi*Me*$_3$), 0.33 (s, 6H, PhCH$_2$SSi*Me*$_2$OSiMe$_3$), 3.77-3.79 (m, 2H, PhC*H*$_2$SSiMe$_2$OSiMe$_3$), 7.21-7.35 (m, 5H arom);

(2) PhCH$_2$SH (*0.10 equiv.*): δ 1.76 (t, *J*=7.53 Hz, 1H, S*H*), 3.76 (d, *J*=7.56 Hz, 2H, PhC*H*$_2$SH), 7.21-7.35 (m, 5H arom);

(3) Impurity: 3.60 (s, 0.02H, in the benzyl mercaptan starting material);

(4) Silicone impurity: 0.10-0.12 (m, 0.60H) ppm.

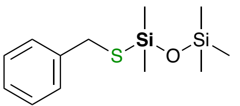
Starting material (Benzyl thiol): δ

(1) PhCH$_2$SH (*1 equiv.*): 1.77 (t, *J*=7.55 Hz, 1H, S*H*), 3.76 (d, 2H, PhC*H*$_2$SH), 7.23-7.34 (m, 5H arom)(for ^{1}H NMR see p. 171)

(2) Impurity: 3.61 (s, 0.01H) ppm.

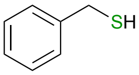
GC-MS: Compound 6: PhCH$_2$SH= 95.7: 4.3 (Relative peak intensity of product and SM)

Sulfur-containing compounds:



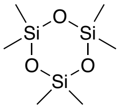
6

(1) C$_{12}$H$_{22}$OSSi$_2$, retention time 16.4 min, relative peak intensity (**84.5%**), MW: 270.09: [M]$^+$= 270.2 (50), 147.2 (80), 91.2 (100).



(2) C_7H_8S, retention time 10.4 min, relative peak intensity (**3.8%**), MW: 124.03: $[M]^+$= 124.1 (30), 91.1 (100), 65.1 (15).

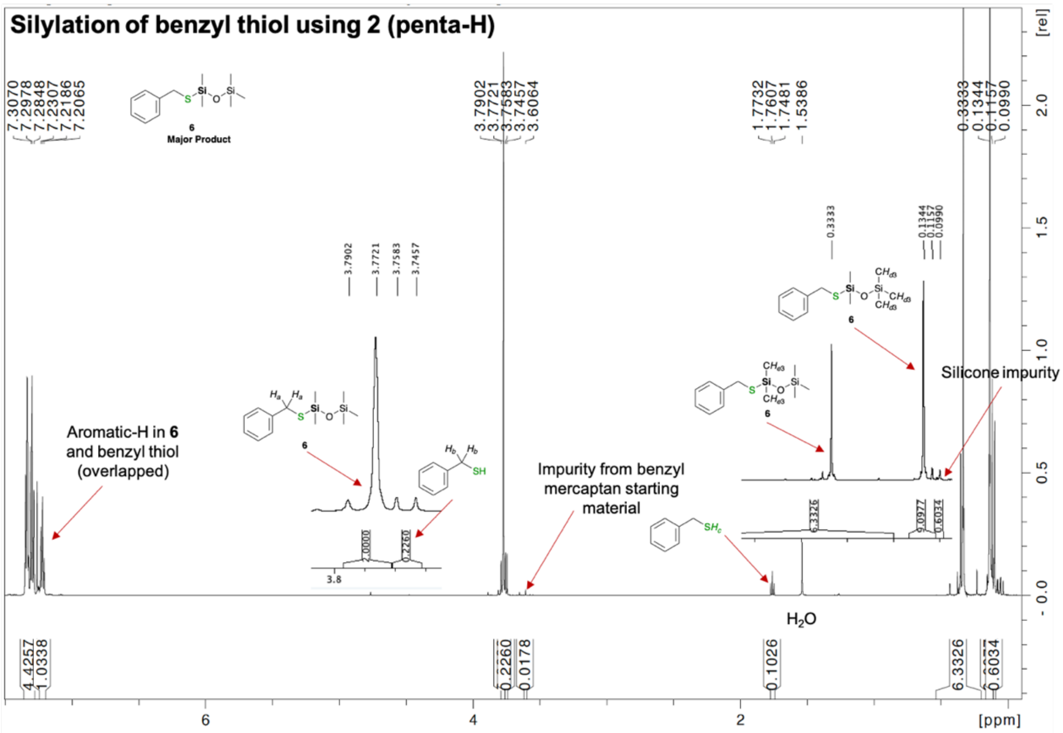
Non-sulfur containing compounds (silicone compounds):



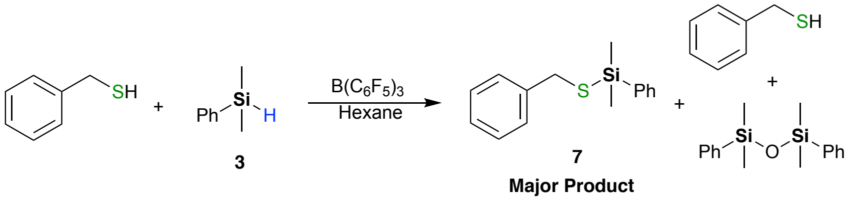
(3) D_3, $C_6H_{18}O_3Si_3$ $(Me_2SiO)_3$ retention time 18.2 min, relative peak intensity (**10.1%**), MW: 222.06: $[M]^+$= 221.1 (100), 133.1 (5), 91.1 (80), 73.1 (20).

(4) Relative peak intensity (**0.6%**), retention time 12.5 min, MW: 254.20: $[M]^+$= 254.2 (10), 91.1 (100), 65.1 (5).

(5) Relative peak intensity (**1.0%**), retention time 20.0 min, MW: 403.2: $[M]^+$= 403.2 (3), 295.2 (50), 270.1 (90), 133.0 (1), 91.1 (100), 73.1 (40).



Compound 7 (from **3**):



In a pre-dried 100.0 mL round-bottomed flask, benzyl thiol (1.01 g, 8.13 mmol) and **3** (1.10 g, 8.07 mmol) were mixed in dry hexanes (5.0 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.644 mL, 0.0644 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **7** (recovered 1.78 g) was obtained using vacuum filtration.

The aromatic H in benzyl thiol, **3** and **7** are overlapped. The equivalents of benzyl thiol and **7** were determined using the $PhCH_2$ adjacent to S-Si and SH peak.

$PhCH_2SSiMe_2Ph$ (compound 7): $PhCH_2SH$= 83.3: 16.7

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **7** (*1 equiv.*): 0.45 (s, 6H, $PhCH_2SSiMe_2Ph$), 3.52 (s, 2H, $PhCH_2SSiMe_2Ph$), 7.11-7.58 (m, 5H arom);

(2) $PhCH_2SH$ (*0.2 equiv.*): 1.69 (t, *J*=7.55 Hz, 1H, S*H*), 3.68 (d, *J*=7.55 Hz, 2H, $PhCH_2SH$), 7.11-7.58 (m, 5H arom);

(4) Silicone impurities: 0.01 (s, 0.2H), 0.26 (s, 1H), 0.35 (s, 0.5H) ppm.

Starting material (Benzyl thiol): δ

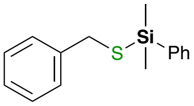
(1) $PhCH_2SH$ (*1 equiv.*): 1.77 (t, *J*=7.55 Hz, 1H, S*H*), 3.76 (d, 2H, $PhCH_2SH$), 7.23-7.34 (m, 5H arom)(for ^{1}H NMR see p. 171)

(2) Impurity: 3.61 (s, 0.01H) ppm.

Starting material (Dimethylphenylsilane): δ 0.38 (d, *J*=3.76 Hz, 6H, SiC*H*$_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm (for ^{1}H NMR see p. 173)

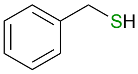
GC-MS: Compound 7: PhCH$_2$SH= 90.7: 9.3 (Relative peak intensity)

Sulfur-containing compounds:



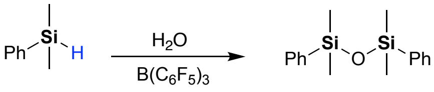
7

(1) $C_{15}H_{18}SSi$, retention time 11.9 min, relative peak intensity (**69.2%**), MW: 258.09: $[M]^+$= 258.2 (5), 243.1 (1), 209.2 (20), 180.1 (50), 165.1 (55), 151.1 (5), 135.1 (55), 121.1 (1), 91.1 (100), 77.1 (3), 65.1 (5).



(2) C_7H_8S, retention time 5.0 min, relative peak intensity (**7.1%**), MW: 124.03: $[M]^+$ = 124.1 (30), 91.1 (100), 77.1 (5), 65.1 (12).

Non-sulfur containing compounds (silicone compounds):



3

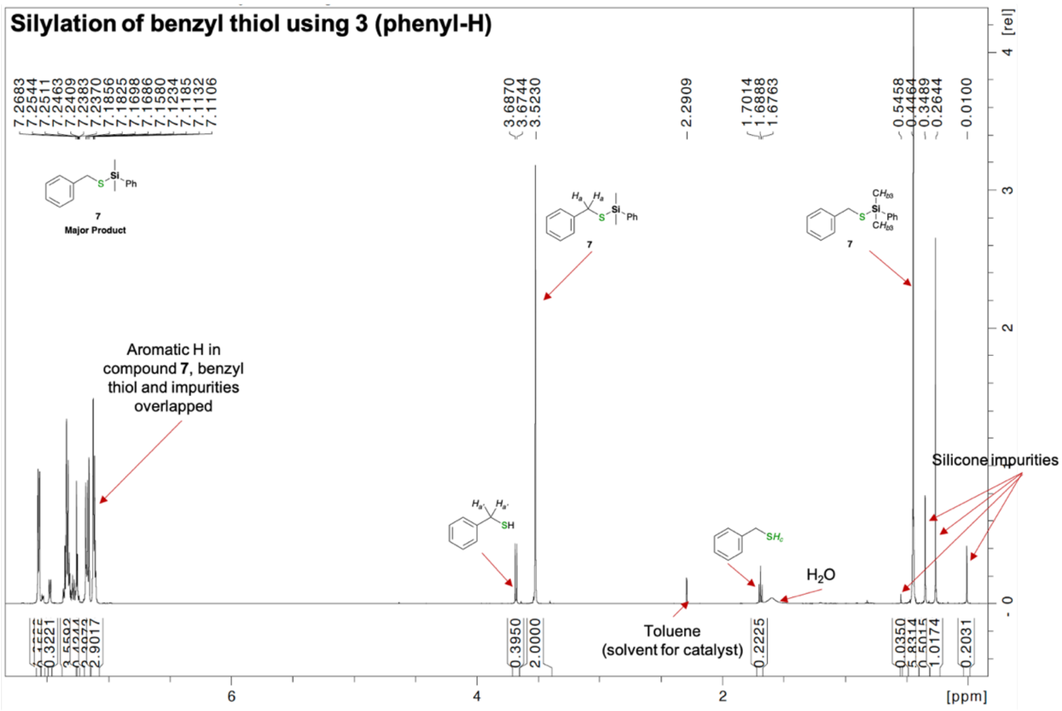
(3) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**23.0%**), MW: 286.12: $[M]^+$ = 286.2 (10), 271.2 (100), 255.1 (5), 193.1 (60), 179.1 (5), 165.1 (5), 135.2 (10), 105.1 (5), 89.1 (15). Hydrolysis/condensation product of **3**.

(4) Relative peak intensity (**0.3%**), retention time 4.9 min, MW: 152.20: $[M]^+$= 152.2 (10), 137.1 (100), 119.1 (1), 91.5 (5), 78.1 (5).

(5) Relative peak intensity (**0.1%**), retention time 7.5 min, MW: 318.10: $[M]^+$= 318.1 (25), 303.0 (15), 283.0 (1), 269.0 (1), 219.2 (1), 203.1 (1), 175.1 (40), 156.0 (1), 135.1 (100), 107.2 (5), 91.1 (15), 77.1 (10), 65.1 (1).

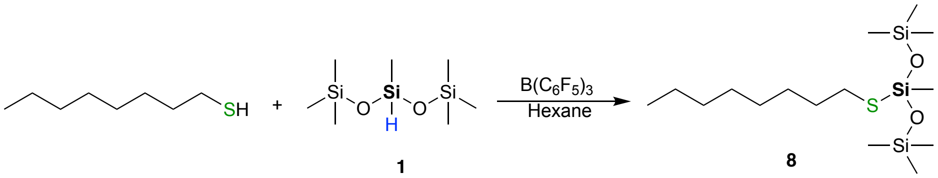
(6) Relative peak intensity (**0.1%**), retention time 11.6 min, MW: 214.10: $[M]^+$= 214.1 (40), 123.1 (30), 91.1 (100), 77.1 (5), 65.1 (15).

(7) Relative peak intensity (**0.2%**), retention time 13.4 min, MW: 377.10: $[M]^+$= 377.1 (5), 315.0 (5), 246.1 (20), 181.1 (15), 121.1 (5), 91.1 (100), 77.1 (1), 65.2 (20).



5.8.3.2 Silylation of octanethiol

Compound 8 (from 1)



In a pre-dried 100.0 mL round-bottomed flask octanethiol (5.00 g, 34.18 mmol) and **1** (7.61 g, 34.20 mmol) were mixed in dry hexanes (25.0 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (2.73 mL, 0.273 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **8** (recovered 11.07 g) was obtained using vacuum filtration.

The alkyl H peaks in octanethiol and **8** overlap; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

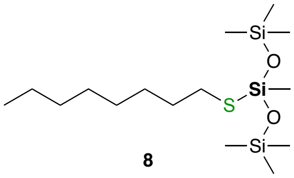
^{1}H NMR (600 MHz, chloroform-*d*): δ Compound **8** (*1 equiv.*): 0.13 (s, 18H, $C_8H_{17}SSiMe(OSi\mathit{Me}_3)_2$), 0.30 (s, 3H, $C_8H_{17}SSi\mathit{Me}(OSi\mathit{Me}_3)_2$), 0.88 (t, *J*=6.93 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2SSi$), 1.27-1.38 (m, 10H, $CH_3C_5\mathit{H}_{10}CH_2CH_2SSi$), 1.60 (quint, *J*=7.47 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SSi$), 2.51 (t, *J*=7.44 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SSi$) ppm.

Starting material (octanethiol): δ

0.87 (t, *J*=6.99 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2SH$), 1.26-1.38 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2SH$ and $C_8H_{17}S\mathit{H}$, overlapped), 1.60 (quint, *J*=7.42 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SH$), 2.51 (t, *J*=7.41 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SH$) ppm.

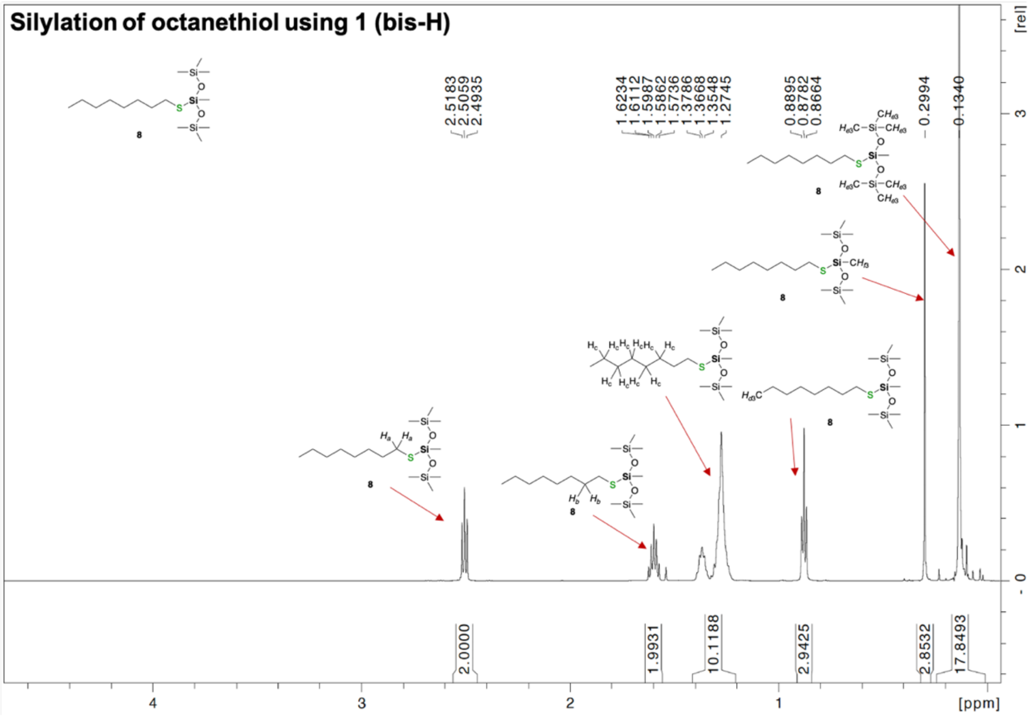
GC-MS: Compound 8: $C_8H_{17}SH$= 100: 0 (Relative peak intensity)

Sulfur-containing compound:

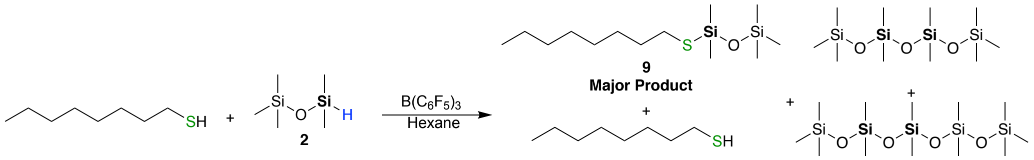


8

$C_{15}H_{38}O_2SSi_3$, retention time 15.2 min, relative peak intensity (**100%**), MW: 366.19: $[M]^+$= 366.2 (10), 351.2 (30), 239.1 (20), 221.1 (100), 133.1 (6), 73.1 (25), 57.2 (5).



Compound 9 (from 2)



In a pre-dried 100.0 mL round-bottomed flask octanethiol (5.00 g, 34.18 mmol) and **2** (5.07 g, 34.18 mmol) were mixed in dry hexanes (25.0 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (2.73 mL, 0.273 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **9** (recovered 9.20 g) was obtained using vacuum filtration.

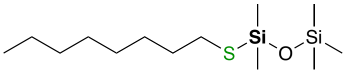
The alkyl H peaks in octanethiol and **9** overlap. $C_7H_{15}CH_2SH$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **9**: 0.11 (s, 9H, $C_8H_{17}SSiMe_2OSi\mathit{Me}_3$), 0.33 (s, 6H, $C_8H_{17}SSi\mathit{Me}_2OSiMe_3$), 0.87 (t, *J*=7.02 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$,), 1.26-1.37 (m, 10H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$), 1.60 (quint, *J*=7.51 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2S$), 2.53 (t, *J*=7.46 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2S$) ppm.

(2) **Octanethiol**, 0.87 (t, *J*=6.99 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2SH$), 1.26-1.38 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2SH$ and $C_8H_{17}S\mathit{H}$, overlapped), 1.60 (quint, *J*=7.42 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SH$), 2.51 (t, *J*=7.41 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SH$) ppm (for ^{1}H NMR see p. 171).

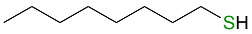
GC-MS: Compound 9: $C_8H_{17}SH$= 97.2: 2.8 (Relative peak intensity)

Sulfur-containing compounds:



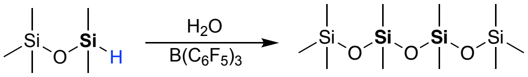
9

(1) $C_{13}H_{32}OSSi_2$, retention time 15.3 min, relative peak intensity (**88.4%**), MW: 292.17: $[M]^+$ = 292.2 (1), 277.2 (60), 165.1 (60), 147.1 (100), 73.1 (10), 57.2 (5).

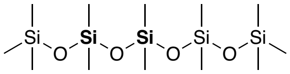


(2) $C_8H_{18}S$, retention time 9.1 min, relative peak intensity (**2.5%**), MW: 146.11: $[M]^+$ =146.2 (70), 112.2 (12), 70.2 (75), 56.2 (100).

Non-sulfur containing compounds (silicone compounds):



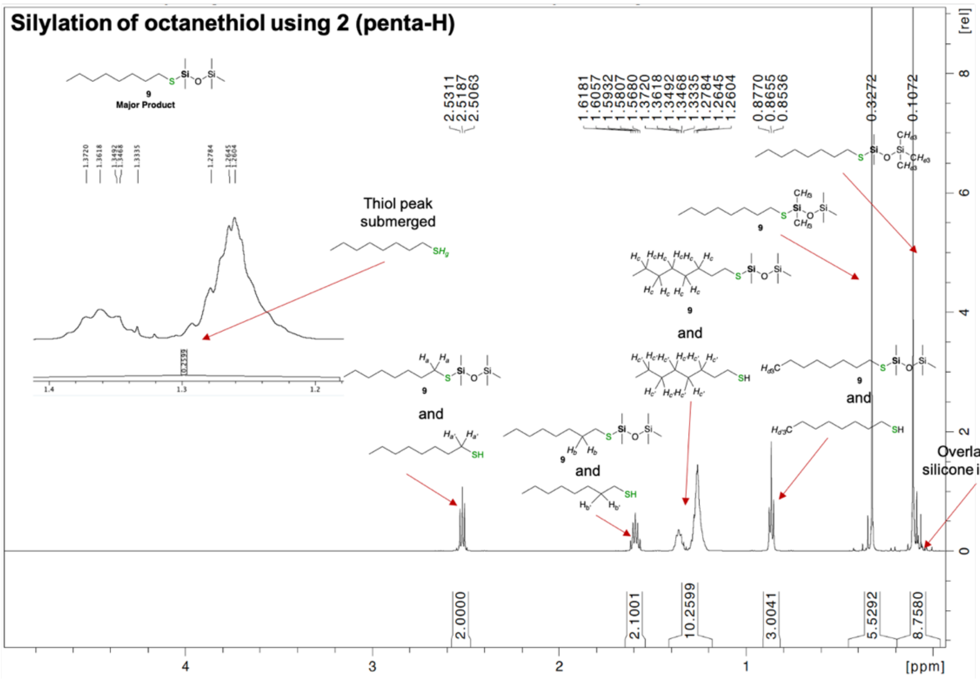
(3) $C_{10}H_{30}O_3Si_4$, retention time 5.5 min, relative peak intensity (**0.7%**), MW: 310.13: $[M-15]^+$= 295.1 (30), 207.1 (100), 131.1 (1), 73.1 (20), 59.1 (1).



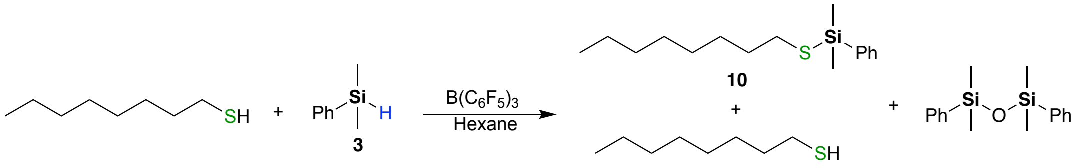
(4) $C_{12}H_{36}O_4Si_5$, retention time 9.0 min, relative peak intensity (**0.2%**), MW: 384.15: $[M-15]^+$= 369.2 (40), 281.1 (100), 207.0 (5), 147.1 (75), 73.1 (50), 59.0 (1).

(5) Relative peak intensity (**7.8%**), retention time 17.2 min, MW: 351.20: $[M]^+$= 351.2 (5), 221.1 (100), 73.1 (10), 57.2 (1).

(6) Relative peak intensity (**0.4%**), retention time 19.0 min, MW: 425.30: $[M]^+$= 425.3 (5), 295.1 (60), 207.1 (100), 73.1 (30), 57.1 (5).



Compound 10 (from **3**):



In a pre-dried 100.0 mL round-bottomed flask, octanethiol (1.02 g, 6.97 mmol) and **3** (0.95 g, 6.97 mmol) were mixed in dry hexanes (5.0 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.547 mL, 0.0547 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **10** (recovered 1.70 g) was obtained using vacuum filtration.

The alkyl H peaks in octanethiol and **10** are overlapped, not distinguishable by ^{1}H NMR. The $C_7H_{15}CH_2S\mathit{H}$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture. The equivalents of compound **10** and octanethiol were calculated based on the $C\mathit{H}_2$ peak besides sulfur.

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **10** (*1 equiv.*): 0.57 (s, 6H, $C_8H_{17}SSi(\mathit{Me})_2Ph$), 0.87-0.90 (m, 3H, $C\mathit{H}_3C_7H_{14}S$), 1.22-1.40 (m, 10H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$), 1.62 (quintet, *J*=7.38 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SSiMe_2Ph$), 2.53 (q, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SSiMe_2Ph$), 7.34-7.64 (m, 5H arom);

(2) $C_8H_{17}SH$ (*0.94 equiv.*): 0.87-0.90 (m, 3H, $C\mathit{H}_3C_7H_{14}S$), 1.22-1.40 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$, and $C_8H_{17}S\mathit{H}$ submerged), 1.51 (quintet, *J*=7.44 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SH$), 2.39 (t, *J*=7.36 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SH$);

(3) Silicone impurities: 0.08 (s, 0.11H), 0.23 (s, 0.03H), 0.34 (s, 4H), 0.42 (s, 1H) ppm.

Starting material (Octanethiol): δ

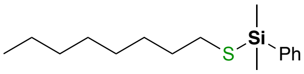
0.87 (t, *J*=6.99 Hz, 3H, $CH_3C_5H_{10}CH_2CH_2SH$), 1.26-1.38 (m, 11H, $CH_3C_5H_{10}CH_2CH_2SH$ and $C_8H_{17}SH$, overlapped), 1.60 (quint, *J*=7.42 Hz, 2H, $CH_3C_5H_{10}CH_2CH_2SH$), 2.51 (t, *J*=7.41 Hz, 2H, $CH_3C_5H_{10}CH_2CH_2SH$) ppm (for ^{1}H NMR see p. 171)

Starting material (Dimethylphenylsilane): δ

0.38 (d, *J*=3.76 Hz, 6H, $SiCH_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm (for ^{1}H NMR see p. 173)

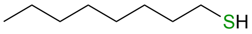
GC-MS: Compound 10: $C_8H_{17}SH$= 80.7: 19.3 (Relative peak intensity)

Sulfur-containing compounds:



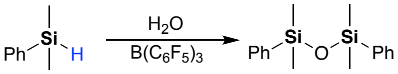
10

(1) $C_{16}H_{28}SSi$, retention time 11.1min, relative peak intensity (**39.2%**), MW: 280.17: $[M]^+$= 280.2 (25), 265.2 (65), 168.1 (2), 153.1 (60), 135.1 (100), 75.1 (1).



(2) $C_8H_{18}S$, retention time 4.4 min, relative peak intensity (**9.4%**), MW: 146.11: $[M]^+$= 146.2 (60), 112.2 (20), 83.2 (60), 70.2 (70), 56.2 (100).

Non-sulfur containing compounds (silicone compounds):



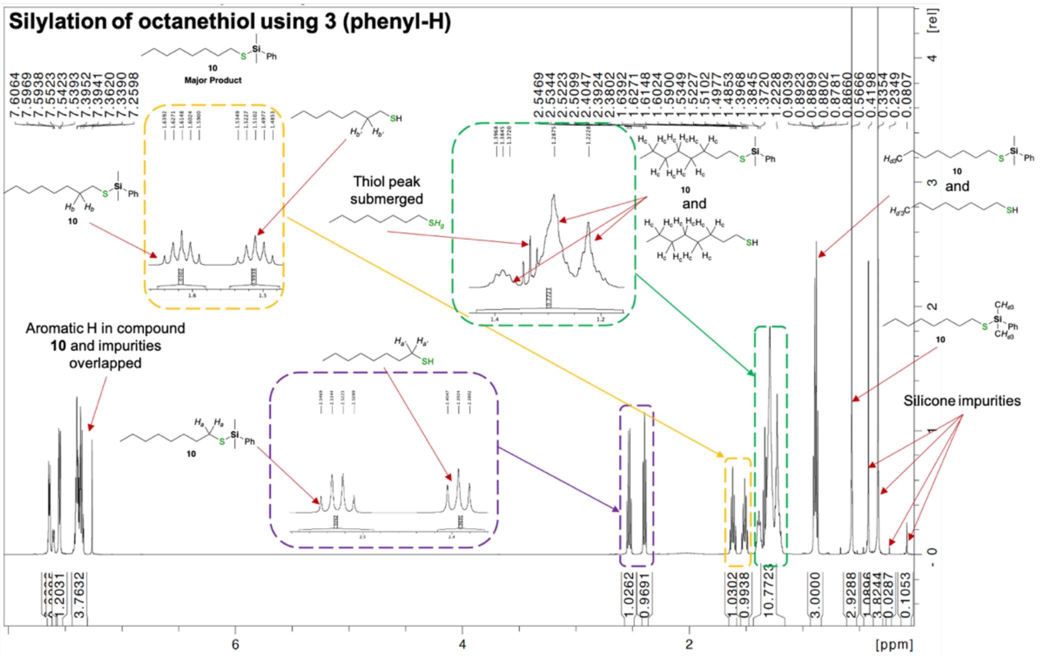
(3) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**50.6%**), MW: 286.12: $[M]^+$= 286.2 (15), 271.2 (100), 255.1 (8), 193.1 (60), 165.1 (3), 135.2 (10), 89.1 (15), 73.1 (1). Hydrolysis/condensation product of **3**.

(4) Relative peak intensity (**0.5%**), retention time 4.9 min, MW: 137.10: $[M]^+$= 137.1 (100), 119.1 (1), 91.1 (3), 77.1 (1).

(5) Relative peak intensity (**0.1**%), retention time 10.4 min, MW: 345.2: $[M]^+$= 345.2 (100), 315.2 (5), 267.1 (27), 197.1 (25), 165.1 (20), 135.1 (30), 91.1 (5), 73.1 (5).

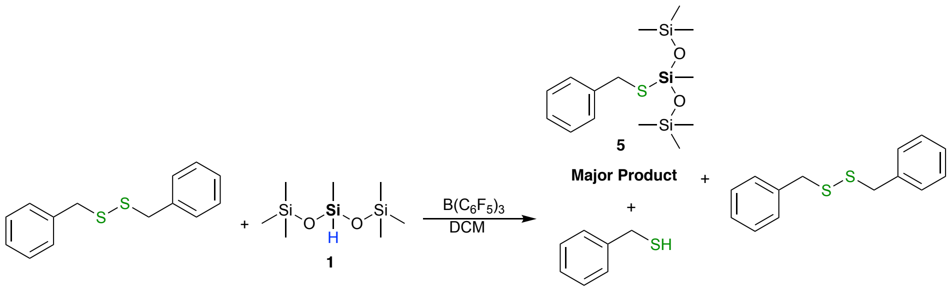
(6) Relative peak intensity (**0.1**%), retention time 11.3 min, MW: 512.60: $[M]^+$= 512.6 (1), 455.1 (5), 419.2 (40), 393.0 (10), 377.1 (20), 315.9 (5), 269.1 (60), 253.1 (30), 197.1 (60), 135.1 (100), 91.1 (25), 73.1 (20).

(7) Relative peak intensity (**0.1**%), retention time 11.9 min, MW: 529.20: $[M]^+$= 529.2 (1), 467.3 (1), 439.2 (5), 373.1 (5), 317.2 (3). 290.2 (90), 253.0 (3), 207.1 (8), 178.1 (40), 145.2 (50), 87.2 (20), 71.2 (100).



5.8.4 Silylation of organic disulfides

5.8.4.1 Benzyl disulfide



Compound 5 (from **1**):

The aromatic H in benzyl disulfide, benzyl thiol and **5** overlapped. The equivalents of benzyl disulfide, benzyl thiol and **5** were determined using the PhC*H*$_2$ adjacent to SS, S-Si and SH peaks.

PhC*H*$_2$SSiMe(OSiMe$_3$)$_2$ (compound 5): (PhC*H*$_2$S)$_2$: PhCH$_2$S*H*= 82.0: 4.1: 13.9

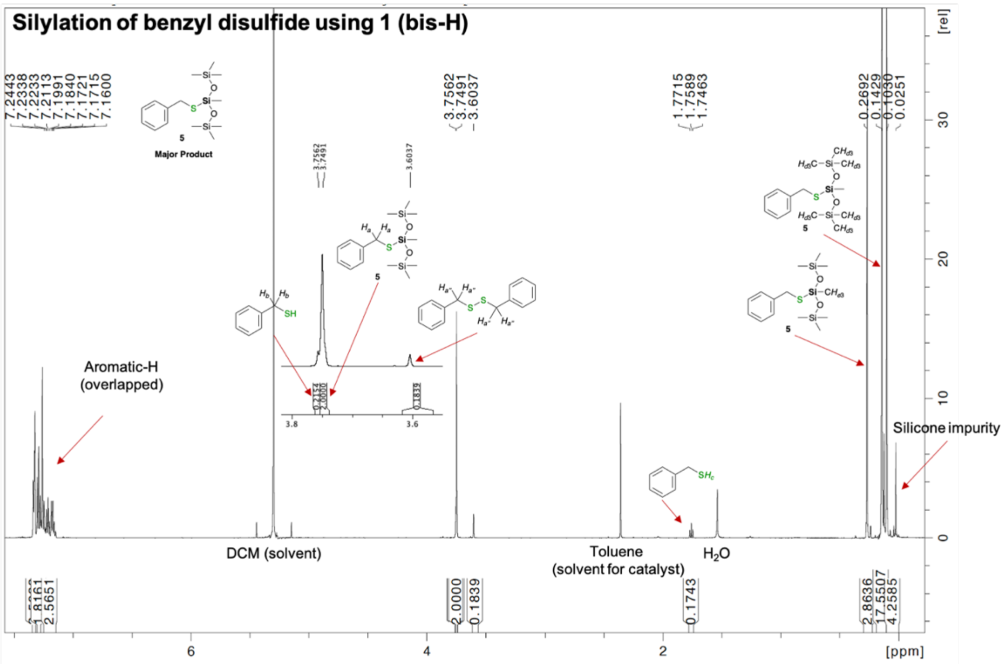
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **5** (*1 equiv.*) 0.10-0.14 (m, 18H, PhCH$_2$SSiMe(*Me*$_3$SiO)$_2$), 0.27 (s, 3H, PhCH$_2$SSi*Me*(Me$_3$SiO)$_2$), 3.75 (s, 2H, PhC*H*$_2$SSiMe(Me$_3$SiO)$_2$) 7.16-7.34 (m, 5H arom);

(2) (PhCH$_2$S)$_2$ (*0.05 equiv.*) 3.60 (s, 2H, (PhC*H*$_2$)$_2$SS) 7.16-7.34 (m, 5H arom);

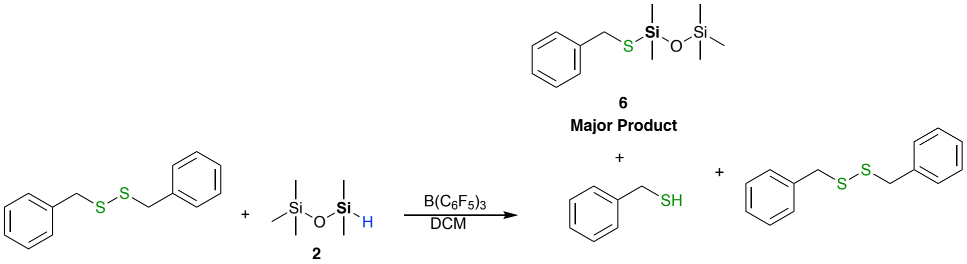
(3) PhCH$_2$SH (*0.17 equiv.*) 1.76 (t, *J*= 7.56 Hz, 1H, S*H*), 3.76 (s, 2H, PhC*H*$_2$SH); 7.16-7.34 (m, 5H arom);

(4) Silicone impurity: 0.03 (s, 4H) ppm.

Starting material ((PhCH$_2$S)$_2$): **δ** (PhCH$_2$S)$_2$: 3.61 (s, 2H, (PhC*H*$_2$)$_2$SS), 7.24-7.25 (m, 2H arom), 7.28-7.34 (m, 3H arom) ppm (for ^{1}H NMR see p. 172).



Compound 6 (from **2**):



To a pre-dried 100.0 mL round-bottomed flask, benzyl disulfide (0.50 g, 2.03 mmol) and **2** (0.66 g, 4.45 mmol) were mixed in dry DCM (3.21 g, 2.41 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.182 mL, 0.0355 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **6** (recovered 1.02 g) was obtained using vacuum filtration.

The aromatic H in benzyl disulfide and **6** had overlapping peaks. The equivalents of benzyl disulfide and **6** were determined using PhCH_2 adjacent to SS, S-Si and SH peak.

$PhC\mathit{H}_2SSiMe_2OSiMe_3$ (compound 6): $(PhC\mathit{H}_2S)_2$: $PhCH_2S\mathit{H}$= 75.2: 7.5: 17.3

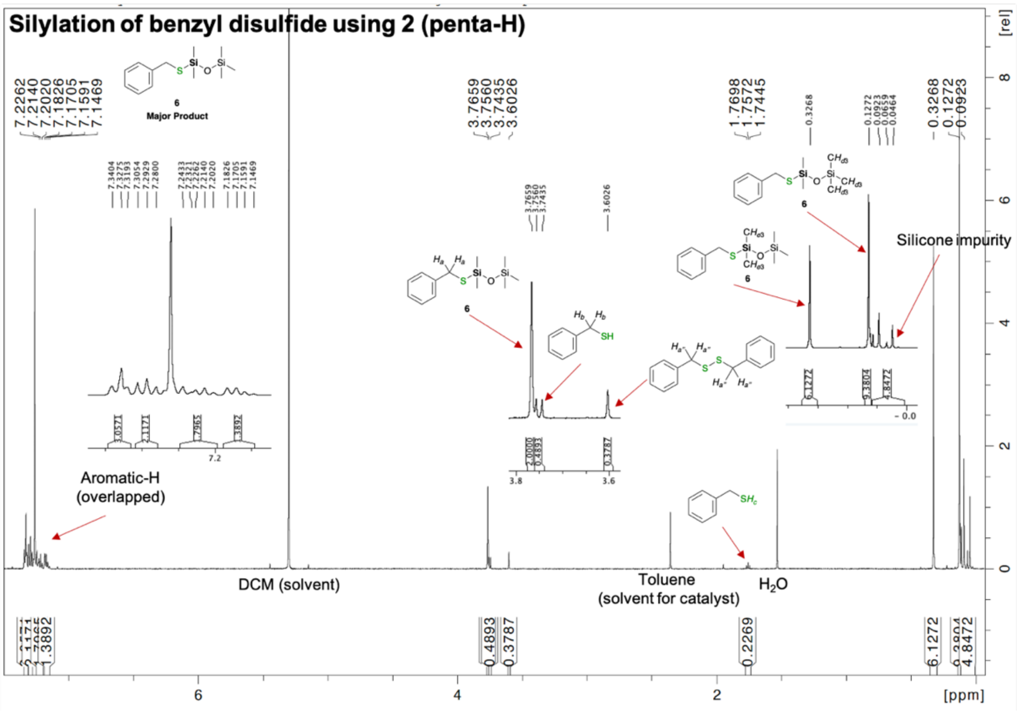
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **6** (*1 equiv.*) δ 0.13 (s, 9H, $PhCH_2SSiMe_2OSi\mathit{Me}_3$), 0.33 (s, 6H, $PhCH_2SSi\mathit{Me}_2OSiMe_3$), 3.77 (s, 2H, $PhC\mathit{H}_2SSiMe(Me_3SiO)_2$),7.15-7.34 (m, 5H arom);

(2) $(PhCH_2S)_2$ (*0.10 equiv.*) δ 3.60 (s, 2H, $(PhC\mathit{H}_2)_2S_2$), 7.15-7.34 (m, 5H arom);

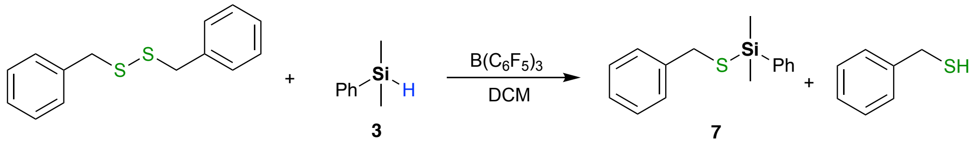
(3) $PhCH_2SH$ (*0.23 equiv.*): 1.76 (t, *J*=7.58 Hz, 1H, S*H*), 3.75 (d, *J*=7.50 Hz, 2H, $PhC\mathit{H}_2SH$), 7.15-7.34 (m, 5H arom);

(4) Silicone impurity: 0.05-0.09 (m, 5H) ppm.

Starting material ($(PhCH_2S)_2$): **δ** 3.61 (s, 2H, $(PhC\mathit{H}_2)_2SS$), 7.24-7.25 (m, 2H arom), 7.28-7.34 (m, 3H arom) ppm (for ^{1}H NMR see p. 172).



Compound 7 (from 3): $PhCH_2SSiMe_2Ph$



To a pre-dried 100.0 mL round-bottomed flask, benzyl disulfide (0.51 g, 2.05 mmol) and **3** (0.56 g, 4.10 mmol) were mixed in dry DCM (2.85 g, 2.14 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.325 mL, 0.0325 mmol) after 5 min stirring. The total reaction time was 3h, then the reaction was quenched by adding neutral alumina. The silylated benzyl thiol product **7** (recovered 0.91 g) was obtained using vacuum filtration.

The aromatic Hs in benzyl thiol, **7** and the impurity overlapped. The equivalents of benzyl thiol (produced by adventitious hydrolysis) and **7** are determined using the $PhCH_2$ adjacent to S-Si and SH peaks.

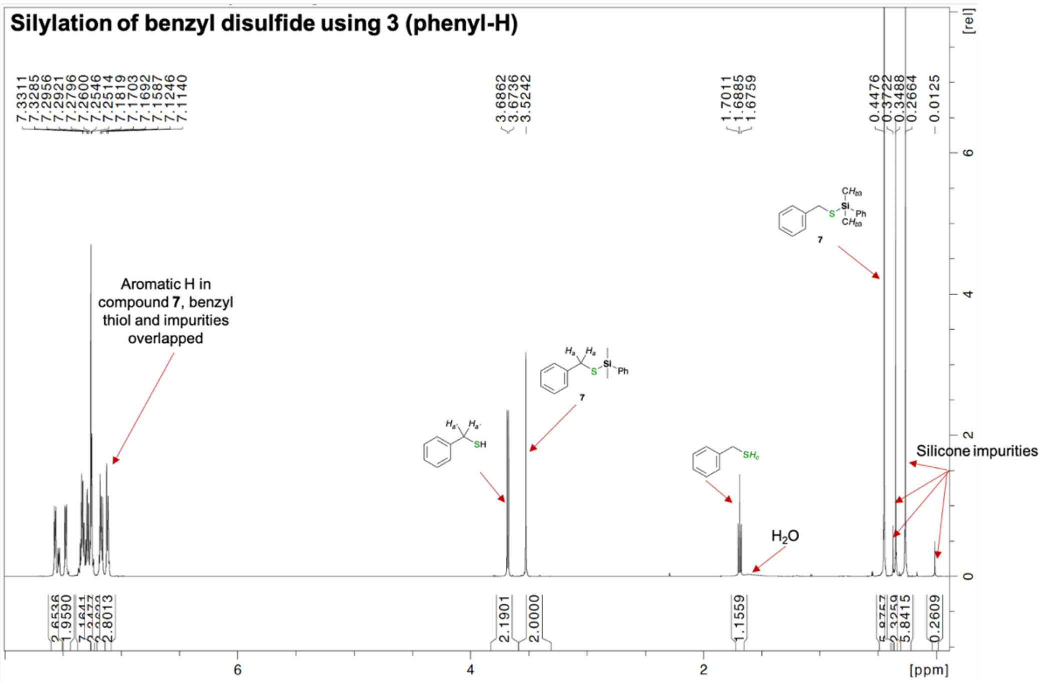
$PhCH_2SSiMe_2Ph$ (compound 7): $(PhCH_2S)_2$: $PhCH_2SH$= 46.3: 0: 53.7

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **7** (*1 equiv.*): 0.45 (s, 6H, $PhCH_2SSiMe_2Ph$), 3.52 (s, 2H, $PhCH_2SSiMe_2Ph$), 7.11-7.57 (m, 5H arom);

(2) $PhCH_2SH$ (*1.16 equiv.*): 1.69 (t, *J*=7.56 Hz, 1. H, S*H*), 3.68 (d, *J*=7.56 Hz, 2H, $PhCH_2SH$), 7.11-7.57 (m, 5H arom) ppm.

Starting material ($(PhCH_2S)_2$): **δ** 3.61 (s, 2H, $(PhCH_2)_2SS$), 7.24-7.25 (m, 2H arom), 7.28-7.34 (m, 3H arom) ppm (for ^{1}H NMR see p. 172).

Starting material (Dimethylphenylsilane): δ 0.38 (d, *J*=3.76 Hz, 6H, $SiCH_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm (for ^{1}H NMR see p. 173).


Silylation of benzyl disulfide using 3 (phenyl-H)
7.3311
7.3285
7.2956
7.2921
7.2796
7.2600
7.2546
7.2514
7.1819
7.1703
7.1692
7.1587
7.1246
7.1140
3.6862
3.6736
3.5242
1.7011
1.6885
1.6759
0.4476
0.3722
0.3488
0.2664
-0.0125
Aromatic H in compound 7, benzyl thiol and impurities overlapped
$H_{a'}$
$H_{a'}$
SH
H_a
H_a
S
Si
Ph
7
SH_c
H_2O
CH_{b3}
Si
Ph
CH_{b3}
S
7
Silicone impurities
2.6536
1.9590
2.8013
2.1901
2.0000
1.1559
5.8415
0.2609
[rel]
6
4
2
0
6
4
2
[ppm]

5.8.4.2 Didodecyl disulfide

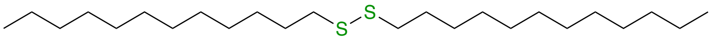
Oxidation of dodecanethiol with NaOCl (bleach)[1]

Dodecanethiol (1.0g, 1.183mL, 5mmol) was added to a 100 mL round-bottomed flask to which was added diluted NaOCl solution (18.4ml, concentration:0.16mmol/ml, 3.0mmol). The mixture was vigorously stirred for 18 h at room temperature. Hexanes (30mL) were added to extract didodecyl disulfide product from the aqueous phase. The hexanes phase was centrifuged (Thermo Electron, 4000rpm) to remove the precipitated byproduct sodium 1-dodecanesulfonate. Hexanes were then removed by evaporation to give **12** (yield 97.5%, 0.97 g).

^{1}H NMR (600 MHz, chloroform-*d*) δ 0.88 (t, *J*= 7.0 Hz, 3H, $(CH_3C_9H_{18}CH_2CH_2S)_2$), 1.19 - 1.42 (m, 18H, $(CH_3C_9H_{18}CH_2CH_2S)_2$), 1.61 (p, *J*= 7.3 Hz, 2H, $(CH_3C_9H_{18}CH_2CH_2S)_2$), 2.51 (q, *J*= 7.4 Hz, 2H, $(CH_3C_9H_{18}CH_2CH_2S)_2$) ppm.

GC-MS:

Sulfur-containing compounds:

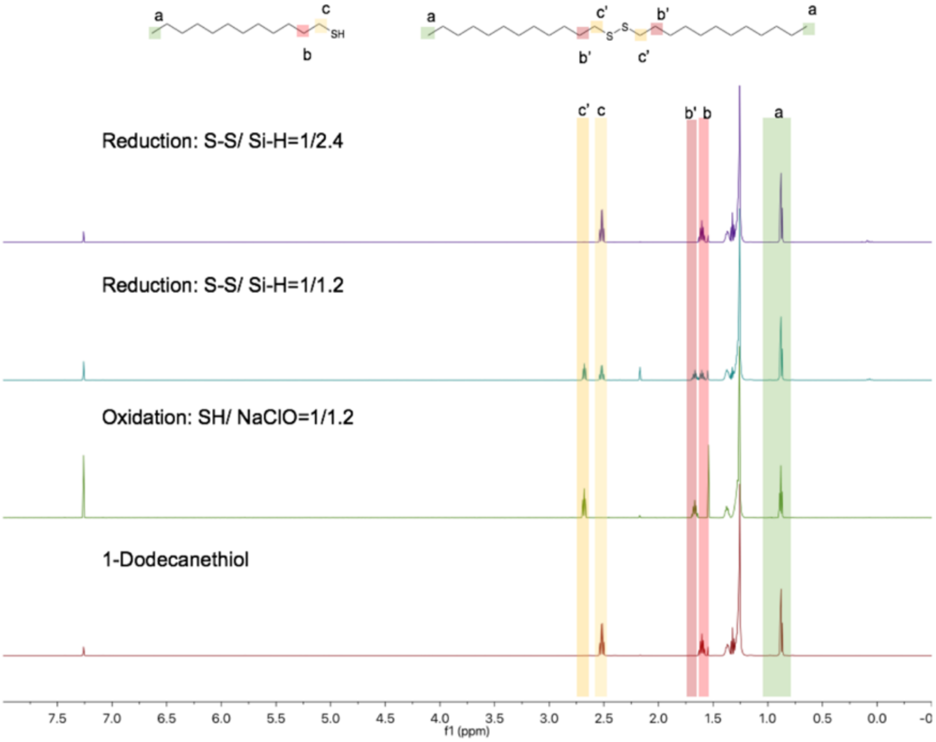


$C_{14}H_{14}S_2$, relative peak intensity (**100%**), MW: 402.34: $[M]^+$ = 402.4 (60), 234.2 (30), 201.2 (35), 85.2 (40), 71.2 (60), 57.2 (100).

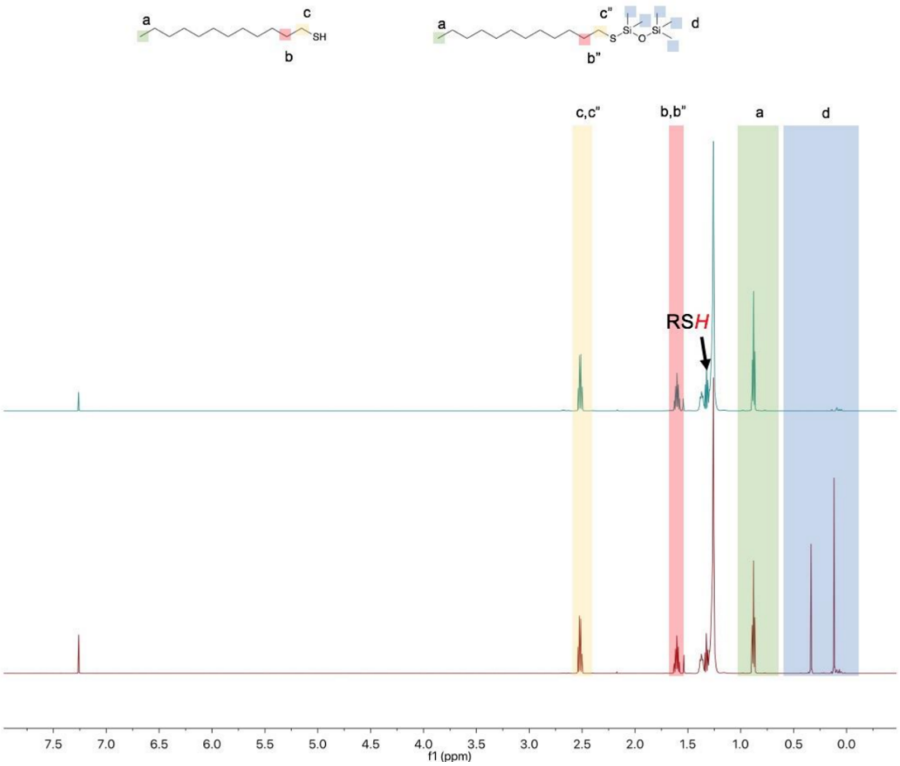
Reductive cleavage of didodecyl disulfide (to give 13)[1]

To a pre-dried 100 mL round-bottomed flask was added didodecyl disulfide (0.3 g, 0.75 mmol) and pentamethyldisiloxane **2** (0.22g, 1.79 mmol) in dry toluene (10 mL) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.364 mL, 0.0356 mmol) after the starting materials had dissolved. After 3 h, the reaction was quenched by the addition of neutral alumina (~ 0.5 g). The reaction mixture, which contained silylated thiols (silyl thio ethers), was then filtered through a layer of Celite using a sintered glass funnel. The solution was concentrated using rotary evaporation.

Hydrolysis of the S-Si compound to thiol was carried out by stirring the product in isopropanol/H_2O (80/20 v/v, in 5 mL) overnight, followed by purging with N_2. S-Si cleavage was shown by the disappearance of peaks near 0 ppm in the ^{1}H NMR, consistent with recovery of dodecanethiol (recovered 0.2553 g, **Figure S5.3**).[1]



A



B

Figure S5.3. A: ^{1}H NMR spectra of oxidation preparation of didodecyl disulfide and B: desilylation of S-Si bonds using H_2O/IPA (80/20 v/v).

5.8.5 Dibenzyl tetrasulfide preparation and reduction using Bis-H (1)

5.8.5.1 Titration of benzyl disulfide using BisH: ([SiH]/[SS]=4:1 for complete reduction)

To a pre-dried 200 mL round-bottomed flask purged with dry N_2 gas, was added dibenzyl disulfide (0.50 g, 2.04 mmol) and Bis-H (0.91 g, 4.09 mmol) together with dry DCM (3.81 g, 44.86 mmol) as solvent. Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.167 mL, 0.0326 mmol) after 5 min stirring. The total reaction time was 3 h, then the reaction was quenched by adding neutral alumina. Each datapoint in **Figure S5.4** was obtained using the identical reaction protocol, only changing the ratio of hydrosilane to disulfide [SiH]/[SS]. The peak area of the hydrogens on the carbon adjacent to disulfide bond in ^1H NMR were plotted against different ratio of hydrosilane (SiH) input. The predicated curved was plotted based on the assumption that the SS reacted faster than thiol (only half equivalent of the disulfide was converted when exposed to one equivalent of hydrosilane).

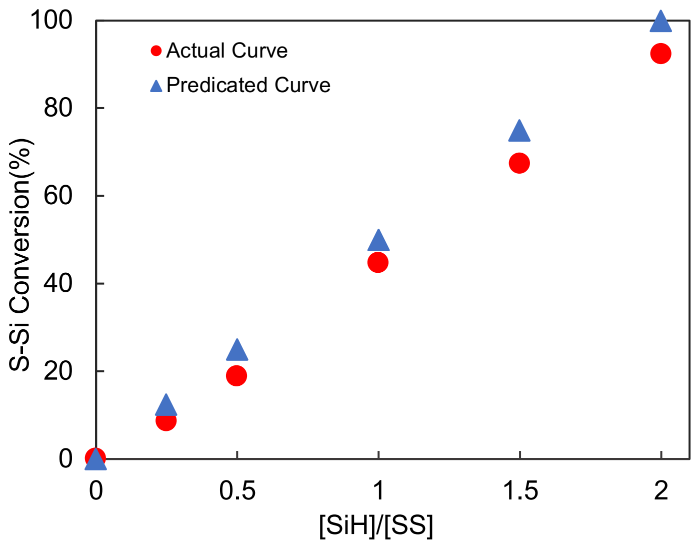


Figure S5.4. Polysulfide conversion in the benzyl disulfide system versus [SiH]/[SS] using Bis-H (**1**). Peak area refers to integration of CH_2 signals (**Table S3**).[2] Note: no benzyl thiol was observed in these experiments.

Table S5.2. ^{1}H NMR Integration data used to plot **Figure S5.4**.

Ratio [SiH]/[SS]	Benzyl disulfide (g)	Bis-H (g)	DCM (g)	$B(C_6F_5)_3$ (mL)^a
0.25	0.50	0.12	1.68	0.021
0.5	0.50	0.24	2.05	0.042
1	0.50	0.46	2.59	0.084
1.5	0.50	0.68	3.20	0.125
2	0.50	0.91	3.81	0.167

^{a}: 100 mg mL^{-1} $B(C_6F_5)_3$ stock solution.

5.8.5.2 Preparation of dibenzyl tetrasulfide

To a pre-dried 200 mL round-bottomed flask purged with dry N_2 were added sodium tetrasulfide (0.098 g, 0.562 mmol), benzyl bromide (0.209 g, 1.22 mmol) and dry THF (50 mL, 44.45 g, 0.616 mol) as solvent. The mixture was stirred for 23 d (without catalyst) and collected by vacuum filtration. The mixture was purified using column chromatography; the low polarity impurity (S_8) was removed using hexanes, after which the elution solvent was switched to dichloromethane, to give a recovery of 137 mg, a mixture of polysulfides as assigned by ^{1}H NMR.[2]

The aromatic H overlapped in the phenyl oligosulfide compounds. Note: it was not possible to detect tetrasulfide or higher polysulfide linkages in the GC-MS, which may be due to thermal degradation of polysulfide bond when n > 3 (n= the number of sulfur atoms in the oligosulfide). The oligosulfide compounds (n>3) were therefore identified by ^{1}H NMR using the assignment in the literature.[3]

^{1}H NMR (600 MHz, acetone-*d*6): δ (1) $PhCH_2S_2$ (0.05 equiv.): 3.72 (s, 4H, $SS(PhCH_2)_2$), 7.28–7.40 (m, 10H arom);

(2) $PhCH_2S_3$ (1 equiv.): 4.11 (s, 4H, $SSS(PhCH_2)_2$), 7.28–7.40 (m, 10H arom);

(3) $PhCH_2S_4$ (0.59 equiv.): 4.24 (s, 4H, $SSSS(PhCH_2)_2$), 7.28–7.40 (m, 10H arom);

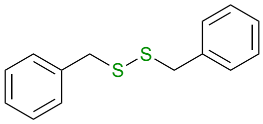
(4) $PhCH_2S_5$ (0.33 equiv.): 4.30 (s, 4H, $SSSSS(PhCH_2)_2$), 7.28–7.40 (m, 0H arom) ppm.

^{13}C NMR (600 MHz, acetone-d_6): δ 29.85 (acetone- d_6), 43.55 ($SSS(PhCH_2)_2$), 43.99 ($SSSS(PhCH_2)_2$)), 44.54 ($SSSSS(PhCH_2)_2$)); Aromatic C: 128.36, 129.42, 130.33, 137.54, 137.80 ppm.

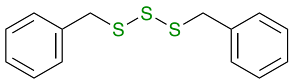
Note: Unlike ^{1}H NMR, ^{13}C NMR sensitivity was not sensitive enough to detect the small amount of $(SCH_2Ph)_2$, but the existence of $(SCH_2Ph)_2$ was proven by ^{1}H NMR and GC-MS.

GC-MS:

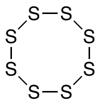
Sulfur-containing compounds:



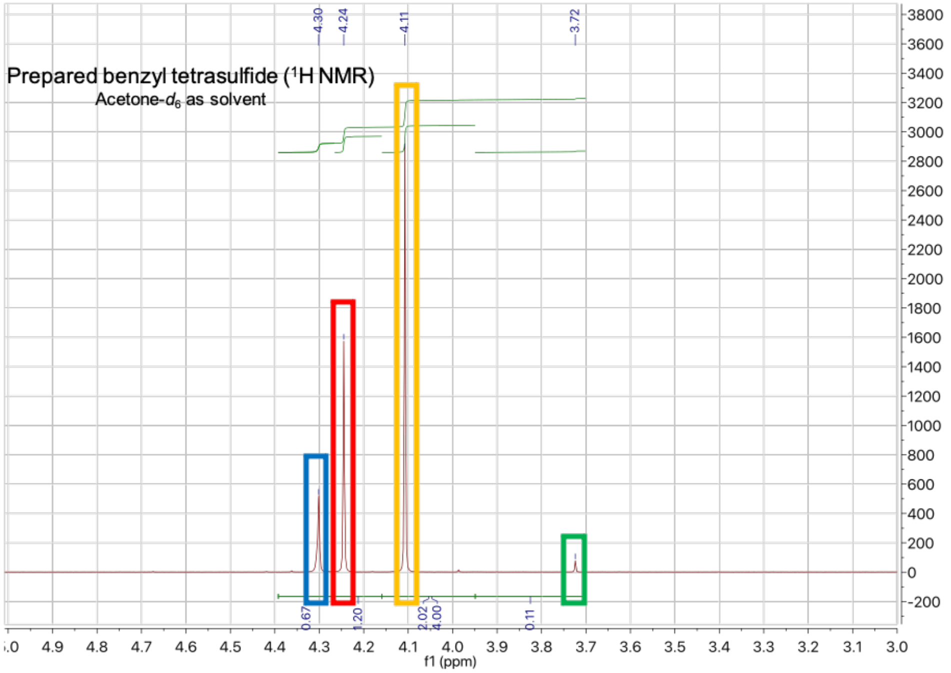
(1) $C_{14}H_{14}S_2$, relative peak intensity (**6.6%**), MW: 246.05: $[M]^+$ = 246.1 (20), 181.2 (18), 121.1 (5), 91.1 (90), 77.2 (8), 65.2 (18).



(2) $C_{14}H_{14}S_3$, relative peak intensity (**92.5%**), MW: 278.03: $[M]^+$= 278.1 (13), 213.1 (56), 181.2 (2), 123.1 (3), 91.2 (100), 77.1 (3), 65.2 (13).



(3) S_8, relative peak intensity (**0.9%**), MW: 255.78: $[M]^+$= 255.8 (98), 223.9 (7), 207.1 (5), 191.9 (53), 160.0 (66), 127.9 (60), 91.1 (66), 77.1 (7), 64.1 (100).



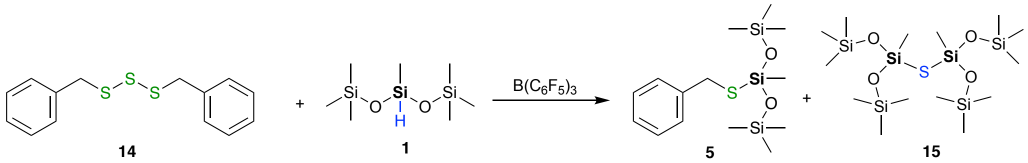
^{1}H NMR data

Product (C**H**$_2$SSSS)	4.24 ppm	***30.0***%
Impurity1 (C**H**$_2$SS)	3.72 ppm	2.7%
Impurity2 (C**H**$_2$SSS)	4.11 ppm	50.5%
Impurity3 (C**H**$_2$SSSSS)	4.30 ppm	16.8%

5.8.5.3 Titration of dibenzyl tetrasulfide 14 using BisH 1: ([SiH]/[SSSS]=5:1 for complete reduction)

To a dried glass NMR tube (7×5 mm) purged with dry N_2, dibenzyl tetrasulfide (0.055 g, 0.185 mmol, **14** (a mix of oligosulfides centered near n = 4, $PhCH_2S_nCH_2Ph$) and Bis-H **1** (0.048 g, 0.216 mmol) were added together with chloroform-*d* stock solution (0.6 mL). Freshly prepared $B(C_6F_5)_3$ stock solution was added (0.023 mL, 0.0045 mmol) after 5 min sonication. Each point on **Figure S5.5**

Figure S5.5.. was obtained by adding **1** (0.048 g, 0.216 mmol) and $B(C_6F_5)_3$ stock solution (0.023 mL, 0.0045 mmol) in aliquots portion by portion with 3h time interval between additions. The peak area of the hydrogens on the carbon adjacent to polysulfide bonds including pentasulfide (-CH_2SSSSS), tetrasulfide (-CH_2SSSS), trisulfide (-CH_2SSS) and disulfide (-CH_2SS) in ^{1}H NMR were plotted against different ratio of hydrosilane (SiH) input.



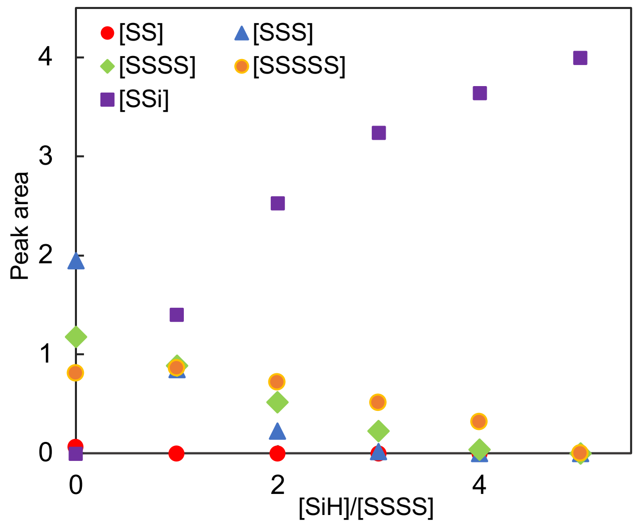


Figure S5.5. Polysulfide conversion in the benzyl tetrasulfide system **14** versus [SiH]/[SSSS] using Bis-H **1**. Peak area refers to integration of CH_2 signals **Table S5.3**).[2]

Table S5.3. ^{1}H NMR Integration data used to plot

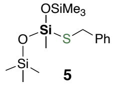
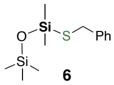
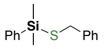
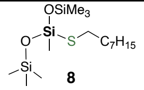
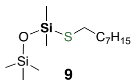
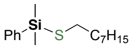
Ratio [SiH]/[SSSS][a]	CH_2SS	CH_2SSS	CH_2SSSS	CH_2SSSSS	CH_2SSi
0	0.06	1.95	1.18	0.81	0.00
1	0.00	0.85	0.89	0.86	1.40
2	0.00	0.23	0.52	0.72	2.53
3	0.00	0.02	0.23	0.51	3.24
4	0.00	0.00	0.04	0.32	3.64
5	0.00	0.00	0.00	0.00	4.00

[a] The tetrasulfide is actually a complex mixture of oligosulfides, with the tetrasulfide as major constituent. In this case, naphthalene was used an internal standard. The total integration of the CH_2-S groups all constituents was normalized to 4H.

5.8.6 Deprotection of silylated thiols

The efficiency of deprotection of silylated thiols is collated in **Table S5.1**. Note that use of TBAF led mostly to recovery of the disulfide. See the spectral and chromatographic data for each compound.

Table S5.4. Conversion (%) of silyl thio ethers **5-10** to thiols.[a]

Starting Material	H_2O/IPA		HOAc/IPA	
	NMR	GC	NMR	GC
 **5**	35	n/a	21	n/a
 **6**	100	100[b]	100	100[b]
 **7**	100	100[b]	100	100[b]
 **8**	[c]	1	[c]	0
 **9**	[c]	64	[c]	9
 **10**	[c]	99	[c]	100[b]

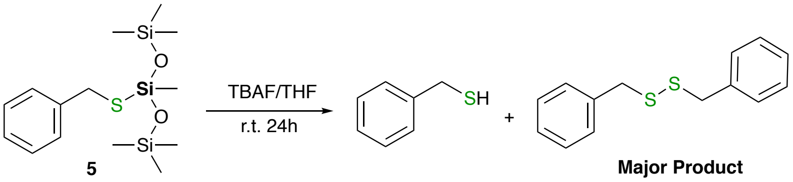
[a] Integration of ^{1}H NMR signals and relative intensity of peaks on GC MS (SI) were used to evaluate the efficiency of Si-S cleavage. [b] No silylated products were detected in the GC-MS. [c] An NMR yield of the recovered thiol compounds could not be reliably determined due to the overlap of thiol peak with the CH_2 peaks.

5.8.7 Deprotection of silylated benzyl thiol

5.8.7.1 Cleavage of SiS bonds: Attempts with TBAF/THF

Compound 5 (TBAF/THF)

In a pre-dried 100.0 mL round-bottomed flask, silylated product **5** (0.53 g, 1.54 mmol) (obtained from reduction of benzyl thiol with **1**) and tetrabutylammonium fluoride (TBAF, 0.41 g, 1.57 mmol) were mixed together with dry tetrahydrofuran (THF 5.0 mL) as solvent. The mixture was stirred for 24h then solvent was removed under a stream of nitrogen. After the removal of THF, 4.0 mL of methanol together with 12.0 mL of distilled water were added and stirred for 24h under a nitrogen blanket. The liquid was extracted three times with hexanes (15.0 mL). The combined hexanes extracts were dried over sodium sulfate. Solvents were removed by rotary evaporation after filtration.



The aromatic H in the major product and **5** are overlapped.

(PhC*H*$_2$S)$_2$: C$_6$H$_5$C*H*$_2$SH: PhCH$_2$SSiMe(*Me*$_3$SiO)$_2$ (compound 5)= 100: 0: 0

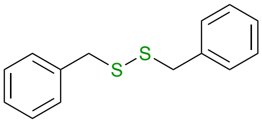
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) (PhCH$_2$S)$_2$: 3.60 (s, 2H, (PhC*H*$_2$S)$_2$), 7.23-7.25 (m, 3H arom), 7.31-7.57 (m, 7H arom);

(2) Silicone impurity: 0.07-0.12 (m, 3H based on integration of 2H in **(PhC*H*$_2$S)$_2$**);

(3) Impurity: 4.33 (s, 0.26H), 4.50 (s, 0.13H), 4.60 (s, 0.41H), 7.96-8.01 (m, 0.66H) ppm.

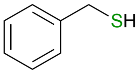
GC-MS: $(PhCH_2S)_2$ (Major product): $C_8H_{17}SH$: compound 5 = 98.25: 1.75 (Relative peak intensity)

Sulfur-containing compounds:



Major Product

(1) $C_{14}H_{14}S_2$, retention time 13.4 min, relative peak intensity (**50.4%**), MW: 246.05: $[M]^+$=246.1 (5), 181.1 (3), 121.1 (1), 91.1 (100), 77.1 (1), 65.1 (5).



(2) C_7H_8S, retention time 5.1 min, relative peak intensity (**0.9%**), MW: 124.03: $[M]^+$= 124.1 (35), 105.1 (2), 91.1 (100), 77.1 (5), 65.1 (8).

Non-sulfur containing compounds (silicone compounds):

(3) Relative peak intensity (**0.6%**), retention time 3.9 min, MW: 106.10: $[M]^+$= 106.1 (100), 77.1 (99), 63.2 (5).

(4) Relative peak intensity (**13.8%**), retention time 12.9 min, MW: 228.10: $[M]^+$= 228.1 (15), 121.1 (1), 105.1 (100), 91.1 (10), 77.1 (20), 65.1 (5).

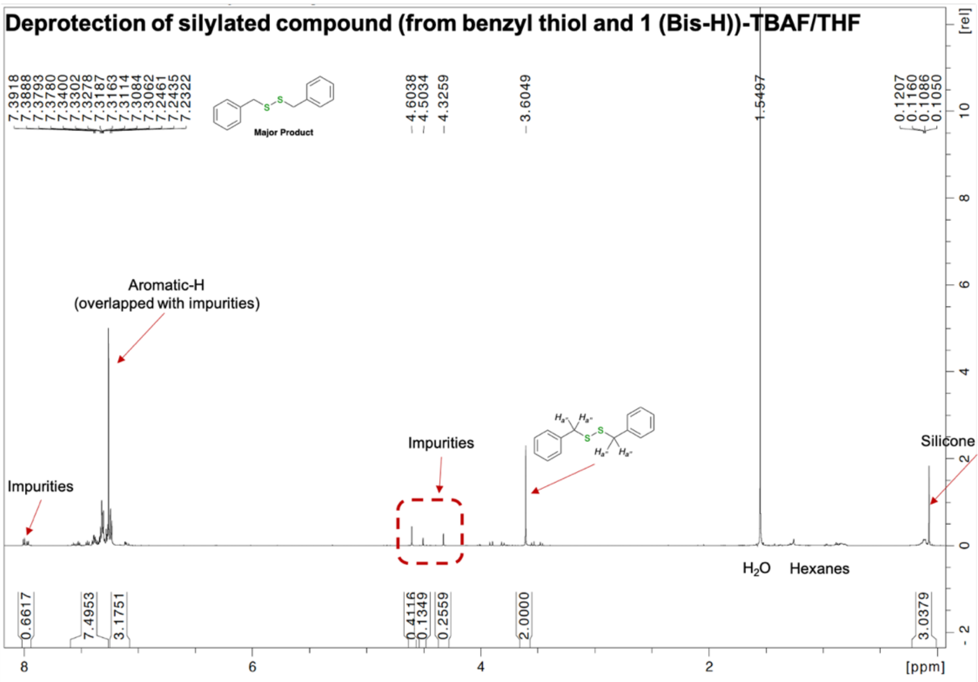
(5) Relative peak intensity (**1.6%**), retention time 13.1 min, MW: 224.10: $[M]^+$= 224.1 (10), 159.1 (100), 131.1 (30), 115.1 (4), 103.1 (3), 91.1 (15), 77.1 (10).

(6) Relative peak intensity (**27.7%**), retention time 14.5 min, MW: 244.10: $[M]^+$= 244.1 (30), 211.1 (15), 180.2 (1), 153.0 (2), 121.1 (100), 91.1 (90), 77.1 (30), 65.1 (13).

(7) Relative peak intensity (**1.7%**), retention time 14.6 min, MW: 121.10: $[M]^+$= 121.1 (1), 105.1 (100), 91.1 (15), 77.1 (30), 65.1 (10).

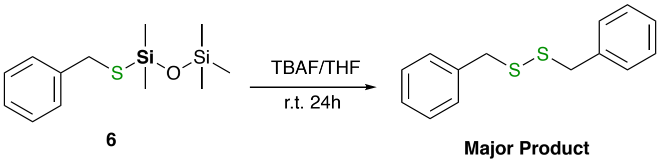
(8) Relative peak intensity (**1.1%**), retention time 15.1 min, MW: 315.10: $[M]^+$= 315.1 (1), 278. 1 (3), 213.1 (30), 123.1 (3), 91.1 (100), 77.1 (3), 65.1 (10).

(9) Relative peak intensity (**2.2%**), retention time 17.4 min, MW: 245.10.10: $[M]^+$= 245.1 (1), 213.1 (60), 181.1 (3), 135.1 (1), 121.1 (10), 91.1 (100), 77.1 (3), 65.1 (5).



Compound 6 (TBAF/THF)

In a pre-dried 100.0 mL round-bottomed flask, the silylated product **6** (0.50 g, 1.85 mmol) (obtained from reduction of benzyl thiol with **2**) and tetrabutylammonium fluoride (TBAF, 0.48 g, 1.85 mmol) were mixed together with dry tetrahydrofuran (THF 5.0 mL) as solvent. The mixture was stirred for 24h then solvent was removed under a stream of nitrogen. After the removal of THF, 4.0 mL of methanol together with 12.0 mL of distilled water were added and stirred for 24h under a nitrogen blanket. The liquid was extracted three times with hexanes (15.0 mL). The combined hexanes extracts were dried over sodium sulfate. Solvents were removed by rotary evaporation after filtration. *No residual S-Si compounds were detected in the GC-MS.*



$(PhC\mathit{H}_2S)_2$: $C_6H_5C\mathit{H}_2SH$: $PhC\mathit{H}_2SSiMe_2OSiMe_3$ (compound 6)= 100: 0: 0

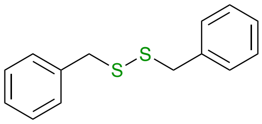
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $(PhCH_2S)_2$: 3.61 (s, 2H, $(PhC\mathit{H}_2S)_2$), 7.24-7.57 (m, 5H arom);

(2) Silicone impurity: 0.06-0.18 (m, 0.37H based on integration of 2H in **$(PhC\mathit{H}_2S)_2$**);

(3) Impurities: 4.33 (s, 0.17H), 4.51 (s, 0.03H), 4.61 (s, 0.39H), 7.97-8.01 (m, 0.57H) ppm.

GC-MS: $(PhCH_2S)_2$ (Major product): $C_8H_{17}SH$: compound 6=100: 0: 0 (Relative peak intensity)

Sulfur-containing compound:



(1) $C_{14}H_{14}S_2$, retention time 22.5 min, relative peak intensity (**62.0%**), MW: 246.05: $[M]^+$= 246.1 (12), 181.2 (5), 91.1 (100), 65.1 (10).

Non-sulfur containing compounds:

(2) MW: 443.20, retention time 8.6 min, relative peak intensity (**0.5%**): $[M]^+$= 443.2 (10), 355.1 (25), 281.1 (40), 221.2 (100), 147.1 (60), 73.1 (77).

(3) MW: 214.10, retention time 19.3 min, relative peak intensity (**1.0%**): $[M]^+$= 214.1 (30), 123.1 (20), 91.1 (100), 65.1 (13).

(4) MW: 228.10, retention time 21.8 min, relative peak intensity (**9.0%**): $[M]^+$= 228.1 (18), 105.1 (100), 91.1 (15), 77.1 (30), 51.1 (13).

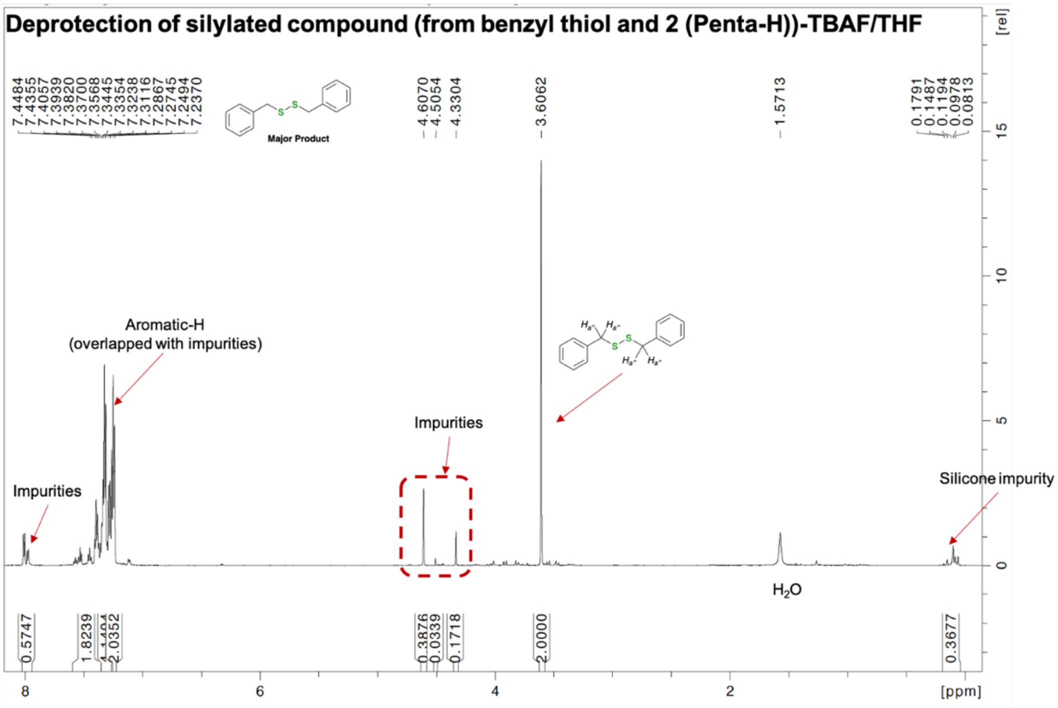
(5) MW: 224.10, retention time 21.9 min, relative peak intensity (**1.0%**): $[M]^+$= 224.1 (10), 159.1 (100), 131.2 (30), 91.2 (20), 77.2 (10), 51.2 (8).

(6) MW: 393.10, retention time 24.3 min, relative peak intensity (**0.5%**): $[M]^+$= 393.1 (50), 315.1 (100), 253.1 (15), 195.1 (7), 165.1 (8), 121.1 (5), 91.1 (15).

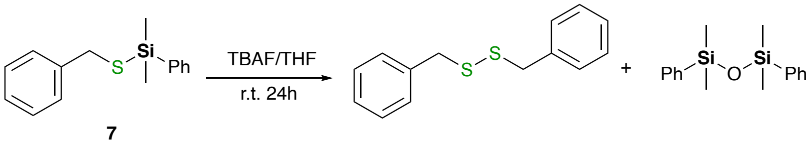
(7) MW: 244.10, retention time 24.6 min, relative peak intensity (**24.0%**): $[M]^+$= 244.1 (40), 211.1 (15), 153.0 (2), 121.1 (100), 91.1 (95), 77.1 (35), 65.1 (10).

(8) MW: 105.10, retention time 24.9 min, relative peak intensity (**1.0%**): $[M]^+$= 105.1 (100), 91.1 (20), 77.1 (35), 51.1 (10).

(9) MW: 253.10, retention time 29.9 min, relative peak intensity (**1.0%**): $[M]^+$= 253.1 (3), 213.1 (50), 181.1 (5), 121.1 (10), 91.1 (100), 65.1 (8).



Compound 7 (TBAF/THF)



In a pre-dried 100.0 mL round-bottomed flask, the silylated product **7** (0.21 g, 0.81 mmol) (obtained from reduction of benzyl thiol with **3**) and tetrabutylammonium fluoride (TBAF, 0.21 g, 0.81 mmol) were mixed together with dry tetrahydrofuran (THF 2.0 mL) as solvent. The mixture was stirred for 24h then the solvent was removed under a stream of nitrogen. After the removal of THF, 4.0 mL of methanol together with 12.0 mL of distilled water were added and stirred for 24h under a nitrogen blanket. The liquid was extracted three times with hexanes (15.0 mL). The combined hexanes extracts were dried over sodium sulfate. Solvents were removed by rotary evaporation after filtration. *No residual S-Si compounds were detected in the GC-MS.*

The aromatic H in benzyl disulfide and impurity are overlapped. The equivalents of benzyldisulfide benzyl thiol and **7** are determined using the $PhCH_2$ adjacent to S-S, S-Si and SH peak.

$(PhCH_2S)_2$: $C_6H_5CH_2SH$: $PhCH_2SSiMe_2Ph$ (compound 7)= 100: 0: 0

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $(PhCH_2S)_2$ (*1 equiv.*): 3.61 (s, 2H, $(PhCH_2S)_2$), 7.23-7.57 (m, 5H arom);

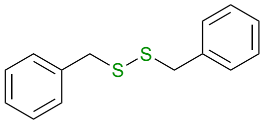
(2) Silicone impurities: 0.05-0.13 (m, 0.2H), 0.33 (s, 6H), 0.41 (s, 2H);

(3) Impurities: 4.33 (s, 0.03H), 4.50 (s, 0.05H), 4.60 (s, 0.17H) ppm.

Starting material (Dimethylphenylsilane): δ 0.38 (d, *J*=3.76 Hz, 6H, $SiCH_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom)(the ^{1}H NMR spectrum is shown on p. 173) ppm.

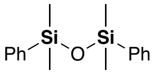
GC-MS: $(PhCH_2S)_2$: $C_8H_{17}SH$: compound 7= 1: 0: 0 (Relative peak intensity)

Sulfur-containing compound:



(1) $C_{14}H_{14}S_2$, retention time 13.4 min, relative peak intensity (**21.2%**), MW: 246.05: $[M]^+$= 246.1 (20), 181.2 (10), 121.1 (1), 91.1 (100), 77.1 (5), 65.1 (15).

Non-sulfur containing compounds:



(2) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**58.2%**), MW: 286.12: $[M]^+$= 286.2 (25), 271.2 (100), 255.1 (10), 193.1 (90), 165.1 (5), 135.2 (10), 89.1 (25), 73.1 (1).

(3) MW: 166.10, retention time 4.4 min, relative peak intensity (**0.5%**): $[M]^+$= 166.1 (5), 151.1 (100), 135.1 (5), 121.1 (45), 105.1 (5), 91.2 (8), 77.1 (1), 59.1 (8).

(4) MW: 228.10, retention time 4.5 min, relative peak intensity (**0.5%**): $[M]^+$= 228.1 (1), 213.1 (100), 197.1 (20), 183.1 (1), 151.1 (1), 135.1 (5), 121.1 (1), 106.9 (1), 99.1 (1), 91.1 (5), 77.2 (5).

(5) $C_8H_{12}OSi$ ($HOSiMe_2Ph$), retention time 4.9 min, MW: 152.10, relative peak intensity (**10.4%**): $[M]^+$= 152.1 (10), 137.1 (100), 91.1 (8), 77.1 (1).

(6) MW: 211.10, retention time 6.1 min, relative peak intensity (**0.5%**): $[M]^+$= 211.1 (90), 195.1 (15), 181.1 (1), 165.1 (1), 149.1 (1), 133.1 (100), 119.1 (5), 98.1 (10), 89.1 (15), 75.1 (10).

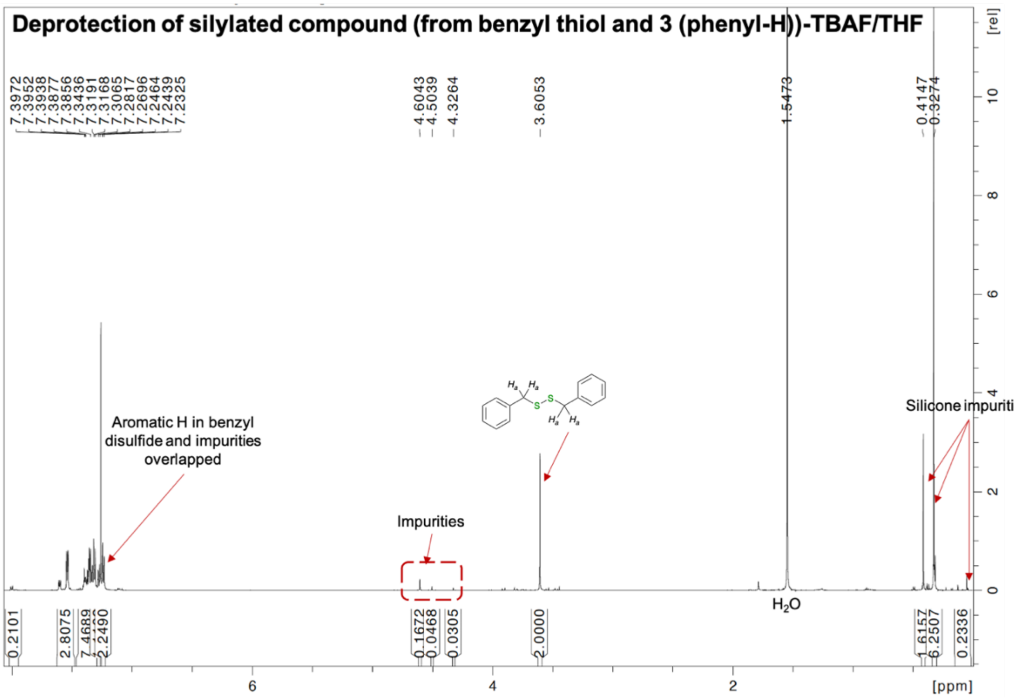
(7) MW: 345.20, retention time 10.4 min, relative peak intensity (**3.8%**): $[M]^+$= 345.2 (100), 313.1 (1), 267.1 (20), 197.2 (15), 165.1 (10), 135.1 (20), 107.1 (1), 91.1 (1), 73.2 (1).

(8) MW: 419.10, retention time 11.3 min, relative peak intensity (**0.2%**): $[M]^+$= 419.1 (40), 377.2 (1), 325.2 (1), 269.1 (60), 253.1 (25), 197.2 (60), 155.3 (1), 135.1 (100), 107.2 (1), 73.2 (10).

(9) MW: 214.10, retention time 11.6 min, relative peak intensity (**0.1%**): $[M]^+$= 214.1 (35), 123.1 (30), 91.1 (100), 65.1 (15).

(10) MW: 228.10, retention time 12.9 min, relative peak intensity (**0.8%**): $[M]^+$= 228.1 (10), 121.1 (1), 105.1 (100), 91.1 (10), 77.1 (30), 65.1 (5).

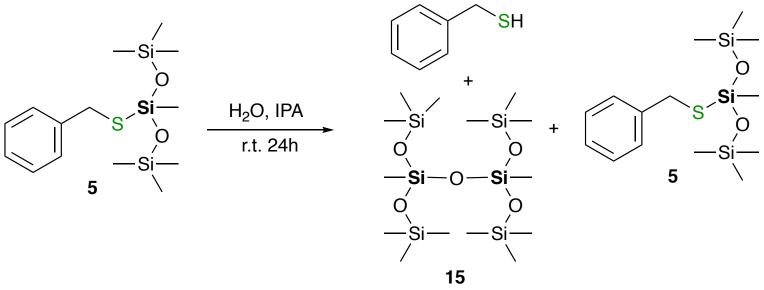
(11) MW: 244.10, retention time 14.5 min, relative peak intensity (**3.8%**): $[M]^+$= 244.1 (40), 211.1 (25), 180.2 (1), 153.1 (1), 121.1 (100), 91.1 (85), 77.1 (30), 65.1 (10).



Deprotection of silylated compound (from benzyl thiol and 3 (phenyl-H))-TBAF/THF

5.8.7.2 Cleavage of SiS bonds: Attempts with H_2O/IPA

Compound 5 (H_2O/IPA)



To a pre-dried 100.0 mL round-bottomed flask **5** (0.50 g, 1.45 mmol) (obtained from reduction of benzyl thiol with **1**) and distilled water (0.0263 mL, 0.0263 g, 1.45 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The aromatic H in **5** and benzyl thiol peaks were overlapped. The equivalents of benzyl thiol and **5** in the product mixture were determined using PhCH_2 adjacent to S-Si and SH peak.

$PhCH_2SSiMe(\mathit{Me}_3SiO)_2$ (compound 5): $C_6H_5C\mathit{H}_2SH$= 65.4: 34.6

^{1}H NMR (600 MHz, chloroform-*d*): **δ** (1) Compound **5** (*1 equiv.*): 0.14 (s, 18H, $PhCH_2SSiMe(\mathit{Me}_3SiO)_2$), 0.30 (s, 3H, $PhCH_2SSi\mathit{Me}(Me_3SiO)_2$), 3.75 (s, 2H, $PhC\mathit{H}_2SSiMe(Me_3SiO)_2$), 7.20-7.33 (m, 5H arom);

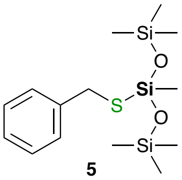
(2) $PhCH_2SH$ (*0.53 equiv.*): 1.76 (t, *J*=7.55 Hz, 1H, S*H*), 3.74 (s, 2H, $PhC\mathit{H}_2SH$), 7.20-7.33 (m, 5H arom);

(3) Impurity: 3.60 (s, 0.06H, in the benzyl mercaptan starting material);

(4) Silicone impurity: 0.02-0.12 (m, 15H) ppm.

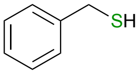
GC-MS: Compound 5: $PhCH_2SH$= 91.5: 8.5 (Relative peak intensity)

Sulfur-containing compounds:



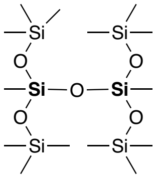
5

(1) $C_{14}H_{28}O_2SSi_3$, retention time 8.7 min, relative peak intensity (**86.2%**), MW: 344.11: $[M]^+$= 344.2 (10), 221.2 (99), 133.1 (5), 91.2 (100), 73.1 (25).



(2) C_7H_8S, retention time 5.0 min, relative peak intensity (**8.0%**), MW: 124.03: $[M]^+$= 124.1 (40), 91.1 (100), 65.1 (15), 51.2 (6).

Non-sulfur containing compounds (silicone compounds) **15**:

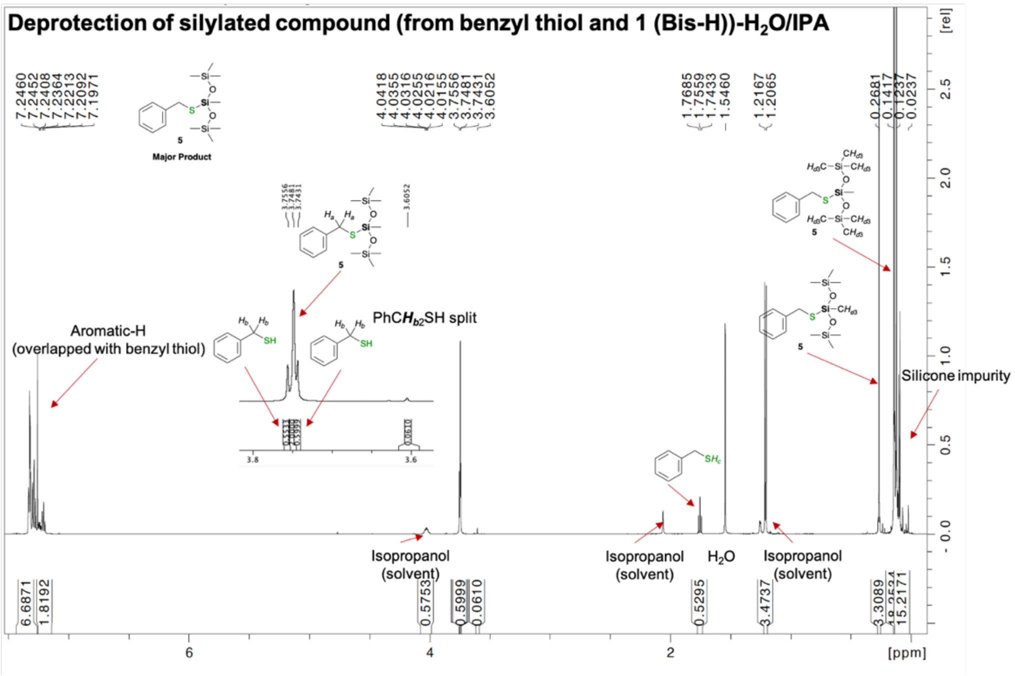


(3) $C_{14}H_{42}O_5Si_6$, retention time 5.1 min, relative peak intensity (**4.2%**), MW: 459.00: $[M-15]^+$= 443.2 (10), 355.1 (20), 323.0 (2), 281.1 (40), 249.0 (1), 221.1 (80), 147.1 (60), 73.1 (100), 59.1 (1).

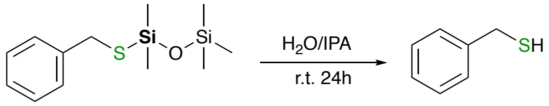
(4) Relative peak intensity (**0.6%**), retention time 4.8 min, MW: 355.10: $[M]^+$= 355.1 (30), 323.1 (1), 281.1 (15), 267.1 (60), 193.0 (3), 147.1 (2), 73.1 (100), 59.1 (2).

(5) Relative peak intensity (**0.7%**), retention time 6.9 min, MW: 328.20: $[M]^+$= 328.2 (1), 207.1 (3), 133.1 (1), 91.1 (100), 73.1 (3).

(6) Relative peak intensity (**0.3%**), retention time 13.4 min, MW: 470.20: $[M]^+$= 470.2 (1), 439.1 (1), 377.1 (2), 246.1 (5), 181.1 (2), 121.1 (2), 91.1 (100), 65.1 (6).



Compound 6 (H_2O/IPA)



6 **Major Product**

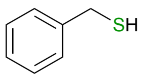
PhC*H*$_2$SSiMe$_2$OSiMe$_3$ (compound 6): PhCH$_2$S*H*= 0: 100

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) PhCH$_2$SH (*1 equiv.*): 1.76 (t, *J*=7.53 Hz, 1H, S*H*), 3.75 (d, *J*=7.56 Hz, 2H, PhC*H*$_2$SH), 7.23-7.33 (m, 5H arom);

(2) Silicone impurity: 0.05-0.12 (m, 16H) ppm.

GC-MS: Compound 6: C_8H_{17}SH=0: 100

Sulfur-containing compound:



(1) C_7H_8S, retention time 5.0 min, relative peak intensity (**94.7%**), MW: 124.03: $[M]^+$= 124.1 (40), 91.2 (100), 77.1 (8), 65.1 (15).

Non-sulfur containing compounds (silicone compounds):

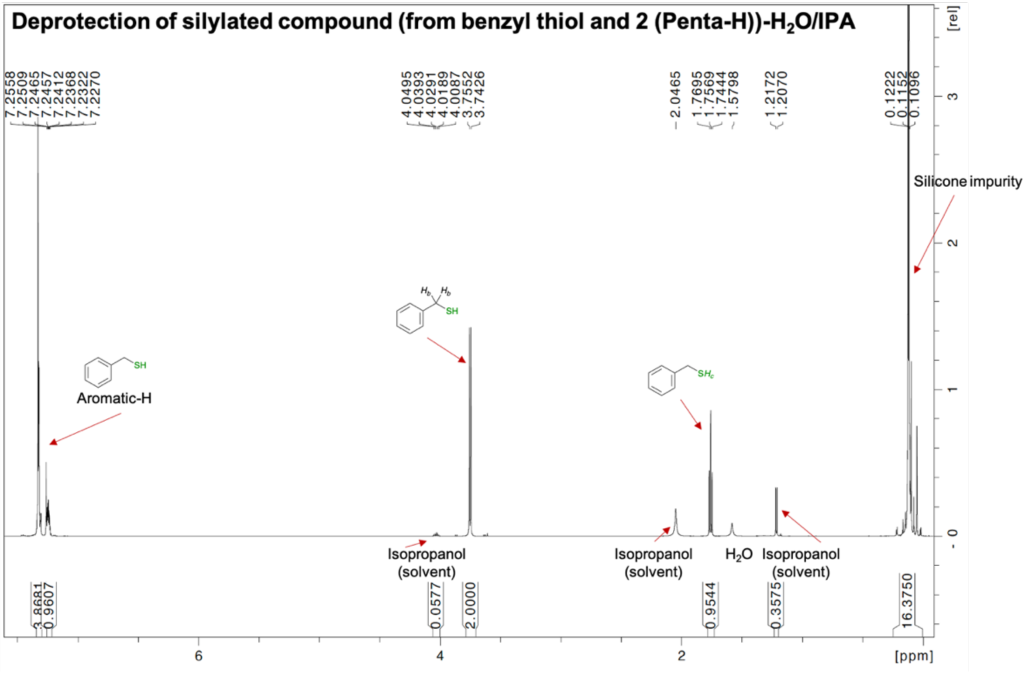
(2) Relative peak intensity (**2.6%**), retention time 3.7 min, MW:281.10: $[M]^{+}$= 281.1 (100), 265.1 (5), 243.0 (3), 207.1 (8), 133.1 (3), 73.1 (10).

(3) Relative peak intensity (**1.0 %**), retention time 4.0 min, MW:369.20: $[M]^{+}$= 369.2 (10), 281.1 (100), 265.1 (8), 249.0 (5), 207.1 (5), 191.1 (2), 147.2 (60), 117.0 (2), 73.1 (30).

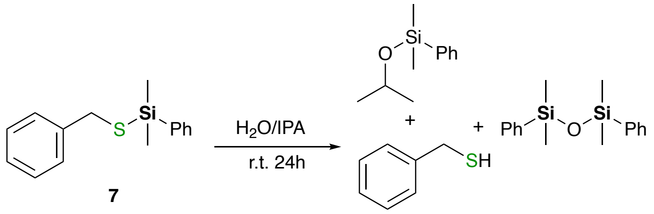
(4) Relative peak intensity (**0.6%**), retention time 5.4 min, MW:443.10: $[M]^{+}$= 443.1 (2), 355.1 (8), 338.8 (1), 323.1 (1), 281.1 (40), 249.2 (1), 221.1 (100), 147.1 (70), 91.1 (1), 73.1 (80).

(5) Relative peak intensity (**0.5%**), retention time 11.6 min, MW:451.30: $[M]^{+}$= 451.3 (1), 378.2 (1), 214.1 (30), 123.1 (10), 91.2 (100), 77.1 (1), 65.2 (10).

(6) Relative peak intensity (**0.6%**), retention time 13.4 min, MW:377.10: $[M]^{+}$= 377.1 (1), 315.1 (2), 246.2 (5), 197.0 (1), 181.2 (2), 121.0 (1), 91.2 (100), 77.1 (1), 65.1 (8).



Compound 7 (H_2O/IPA)

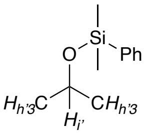


In a pre-dried 100.0 mL round-bottomed flask **7** (0.50 g, 1.94 mmol) (obtained from reduction of benzyl thiol with **3**) and distilled water (0.0348 mL, 0.0348 g, 1.94 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The aromatic H peaks in benzyl thiol, **3** and the impurity overlapped. The relative equivalents of benzyl thiol and **7** were determined using the PhC*H*$_2$ adjacent to S-Si and SH peak.

PhC*H*$_2$SSiMe$_2$Ph (compound 7): PhCH$_2$S*H*= 0: 100

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) PhCH$_2$SH (*1 equiv.*): 1.76 (t, *J*= 7.55 Hz, 1H, S*H*), 3.75 (d, *J*=7.55 Hz, 2H, PhC*H*$_2$SH), 7.23-7.61 (m, 5H arom);



(2) $C_{11}H_{18}OSi$ (*0.03 equiv.*): 0.33-0.42 (m, 6H, SiC*H*$_3$), 1.14 (d, *J*= 6.08 Hz, 6H, $H_{h'3}$), 3.97- 4.01 (m, 1H, $H_{i'}$, overlapped with isopropanol peak), 7.23-7.61 (m, 5H arom);

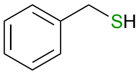
(3) Silicone impurities: 0.33 (s, 3H), 0.42 (s, 5H);

(4) Impurity: 1.82 (s, 0.8H) ppm.

Starting material (Dimethylphenylsilane): δ 0.38 (d, *J*=3.76 Hz, 6H, SiC*H*$_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm.

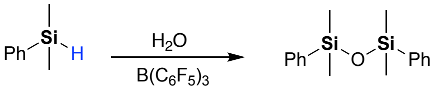
GC-MS: Compound 7: PhCH$_2$SH= 0: 100 (Relative peak intensity)

Sulfur-containing compound:



(1) C_7H_8S, retention time 5.0 min, relative peak intensity (**27.0%**), MW: 124.03: $[M]^+$ = 124.1 (30), 91.1 (100), 77.1 (5), 65.1 (10).

Non-sulfur containing compounds (silicone compounds):



3

(2) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**37.6%**), MW: 286.12: $[M]^+$ = 286.2 (10), 271.2 (100), 255.1 (1), 193.1 (70), 179.1 (1), 165.1 (1), 135.2 (10), 105.1 (1), 89.1 (15). Hydrolysis/condensation product of **3**.

(3) $C_8H_{12}OSi$ (HOSiMe$_2$Ph), retention time 4.9 min, relative peak intensity (**34.7%**), MW: 152.20: $[M]^+$ =152.2 (8), 137.1 (100), 119.1 (1), 91.2 (5), 77.1 (1).

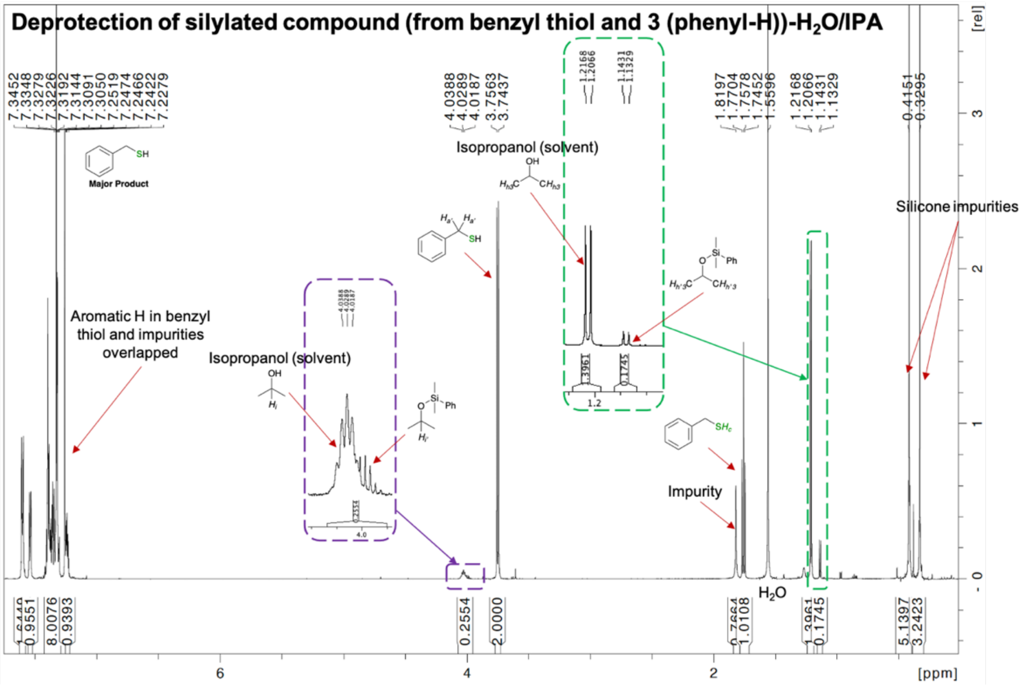
(4) Relative peak intensity (**0.1%**), retention time 9.2 min, MW: 327.00: $[M]^+$ =327.0 (1), 228.2 (50), 213.1 (100), 197.2 (1), 152.0 (1), 135.2 (25), 106.3 (1), 91.2 (20), 77.1 (10), 65.1 (1).

(5) Relative peak intensity (**0.2%**), retention time 10.0 min, MW: 227.20: $[M]^+$ = 227.2 (40), 197.2 (70), 164.1 (85), 149.1 (40), 135.1 (20), 91.1 (100), 65.2 (15).

(6) Relative peak intensity (**0.1%**), retention time 10.4 min, MW: 377.00: $[M]^+$ = 377.0 (1), 345.2 (100), 312.9 (1), 267.1 (25), 197.2 (20), 165.1 (10), 135.2 (25), 91.1 (1), 73.0 (1).

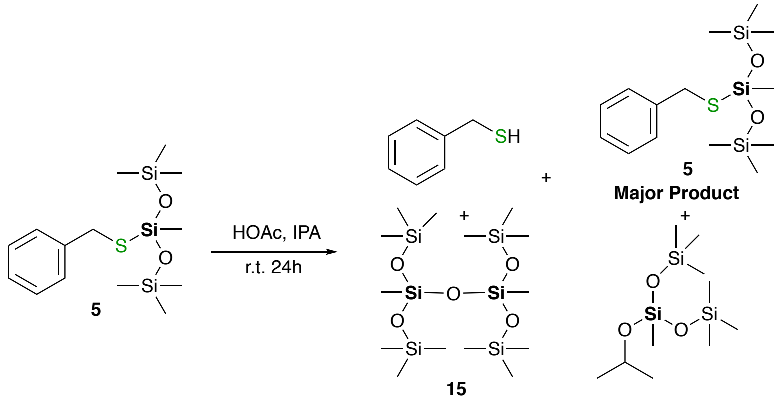
(7) Relative peak intensity (**0.1%**), retention time 11.6 min, MW: 470.10: $[M]^+$ = 470.1 (1), 377.1 (1), 214.2 (30), 197.0 (1), 123.1 (20), 91.1 (100), 65.2 (15).

(8) Relative peak intensity (**0.2%**), retention time 13.4 min, MW: 471.10: $[M]^+$ = 471.1 (1), 377.1 (1), 316.1 (1), 246.1 (15), 218.0 (1), 181.1 (1), 157.1 (1), 121.1 (1), 91.1 (100), 65.1 (15).



5.8.7.3 Cleavage of SiS bonds: Attempts with HOAc/IPA

Compound 5 (HOAc/IPA)



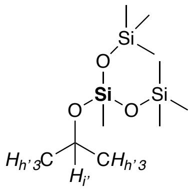
In a pre-dried 100.0 mL round-bottomed flask **5** (0.53 g, 1.53 mmol) (obtained from reduction of benzyl thiol with **1**) and acetic acid (0.093 g, 1.54 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The aromatic H in **5** and benzyl thiol were overlapped, and the $SiCH_3$ within $C_{10}H_{28}O_3Si_3$ overlapped with silicone impurity. The equivalents of benzyl thiol and **5** present in the mixture were determined using $PhCH_2$ adjacent to S-Si and SH peaks.

$PhC\mathit{H}_2SSiMe(Me_3SiO)_2$ (compound 5): $PhCH_2S\mathit{H}$= 78.7: 21.3

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **5** (*1 equiv.*): 0.14 (s, 18H, $PhCH_2SSiMe(\mathit{Me}_3SiO)_2$), 0.27 (s, 3H, $PhCH_2SSi\mathit{Me}(Me_3SiO)_2$), 3.75 (s, 2H, $PhC\mathit{H}_2SSiMe(Me_3SiO)_2$), 7.20-7.33 (m, 5H arom);

(2) $PhCH_2SH$ (*0.27 equiv.*) δ 1.76 (t, *J*=7.55 Hz, 1H, S*H*), 3.74 (s, 1H, $PhC\mathit{H}_2SH$), 3.76 (s, 1H, $PhC\mathit{H}_2SH$), 7.20-7.33 (m, 5H arom);



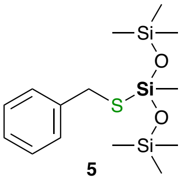
(3) $C_{10}H_{28}O_3Si_3$ (*0.03 equiv.*): 1.17 (d, *J*=6.11 Hz, 0.19H, $H_{h'}$), 4.13 (sept, *J*=6.10 Hz, 0.03H, $H_{i'}$);

(4) Overlapped silicone impurities and $SiCH_3$ within $C_{10}H_{28}O_3Si_3$: 0.02- 0.13 (m, 8H), 0.37 (s, 0.02H);

(5 Impurity: 3.60 (s, 0.05H, in the benzyl mercaptan starting material) ppm.

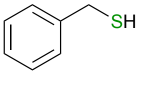
GC-MS: Compound 5: $PhCH_2SH$= 96.1: 3.9 (Relative peak intensity)

Sulfur-containing compounds:



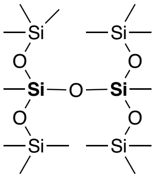
5

(1) $C_{14}H_{28}O_2SSi_3$, retention time 8.8 min, relative peak intensity (**91.8%**), MW: 344.11: $[M]^+$= 344.1 (30), 221.2 (98), 207.1 (20),133.1 (10), 105.1 (1), 91.2 (100), 73.1 (35).



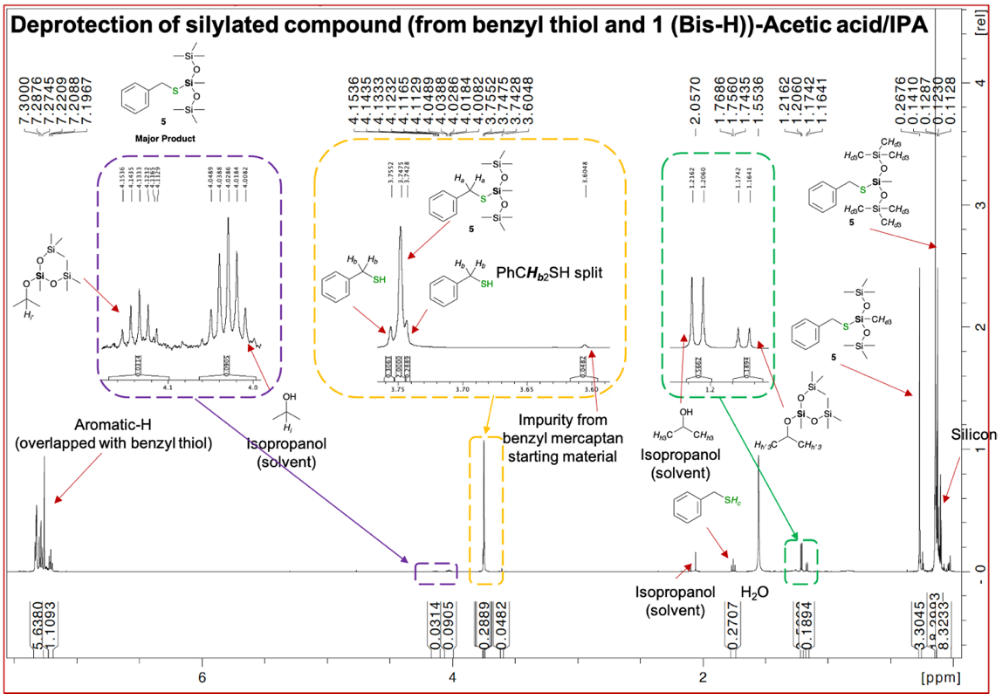
(2) C_7H_8S, retention time 5.0 min, relative peak intensity (**3.8%**), MW: 124.03: $[M]^+$= 124.1 (32), 91.1 (100), 65.1 (15).

Non-sulfur containing compounds (silicone compounds):



15

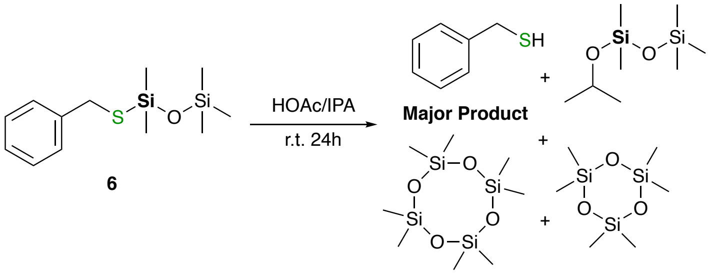
(3) $C_{14}H_{42}O_5Si_6$, retention time 5.1 min, relative peak intensity (**4.4%**), MW: 459.00: $[M-15]^+$= 443.1 (25), 355.1 (30), 323.0 (2), 281.1 (65), 287.0 (30), 249.0 (1), 221.1 (75), 147.1 (70), 117.1 (1), 73.1 (100), 59.1 (2).



Compound 6 (HOAc/IPA)

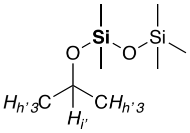
In a pre-dried 100.0 mL round-bottomed flask **6** (0.50 g, 1.85 mmol) and acetic acid (0.11 g, 1.85 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent. *No S-Si compounds were detected in the GC-MS*. For GC/MS data, see SI. ^{1}H NMR (600 MHz, chloroform-*d*): δ **PhC*H*$_2$SSiMe$_2$OSiMe$_3$ 6: PhCH$_2$S*H* = 0: 1.0**

PhCH$_2$SH (*1 equiv.*): δ 1.76 (t, *J*=7.53 Hz, 1H, S*H*), 3.75 (d, *J*=7.55 Hz, 2H, PhC*H*$_2$SH), 7.24-7.33 (m, 5H arom); **$C_8H_{22}O_2Si_2$** (*0.03 equiv.*): 1.17-1.19 (m, 15H, $H_{h'}$), 4.08-4.15 (m, 2H, $H_{i'}$); **Silicone impurity**: 0.05-0.18 (m, 1H); **Impurity**: 3.60 (s, 0.04H, from benzyl thiol starting material) ppm.



PhC*H*$_2$SSiMe$_2$OSiMe$_3$ (compound 6): PhCH$_2$S*H*= 0: 100

^{1}H NMR (600 MHz, chloroform-*d*): (1) PhCH$_2$SH (*1 equiv.*): δ 1.76 (t, *J*=7.53 Hz, 1H, S*H*), 3.75 (d, *J*=7.55 Hz, 2H, PhC*H*$_2$SH), 7.24-7.33 (m, 5H arom);



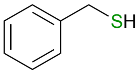
(2) $C_8H_{22}O_2Si_2$ (*0.03 equiv.*): 1.17-1.19 (m, 0.10H, $H_{h'}$), 4.08-4.15 (m, 0.014H, $H_{i'}$)

(4) Silicone impurity: 0.05-0.18 (m, 1H);

(5) Impurity: 3.60 (s, 0.04H, in the benzyl mercaptan starting material) ppm.

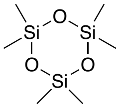
GC-MS: Compound 6: $C_8H_{17}SH$=0: 100

Sulfur-containing compound:

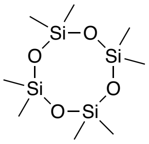


(1) C_7H_8S, retention time 10.5 min, relative peak intensity (**84.3%**), MW: 124.03: $[M]^+$= 124.1 (45), 91.1 (100), 65.1 (15).

Non-sulfur containing compounds (silicone compounds):



(2) D_3, retention time 4.8 min, relative peak intensity (**2.2%**), MW:222.06: $[M-15]^+$= 207.1 (100), 133.1 (10), 196.1 (5), 75.1 (5).



(3) D_4, retention time 8.8 min, relative peak intensity (**2.3%**), MW:296.08: $[M-15]^+$= 281.1 (100), 207.1 (20), 73.1 (14).

(4) Relative peak intensity (**3.2%**), retention time 5.4 min, MW:265.10: $[M]^+$= 265.1 (13), 207.1 (100), 133.1 (5), 103.1 (5), 73.1 (8).

(5) Relative peak intensity (**1.5%**), retention time 8.0 min, MW:281.10: $[M]^+$= 281.1 (100), 207.1 (18), 133.1 (5), 73.1 (15).

(6) Relative peak intensity (**2.0%**), retention time 9.0 min, MW:369.20: $[M]^+$= 369.2 (30), 281.1 (100), 207.1 (15), 147.1 (65), 73.1 (40).

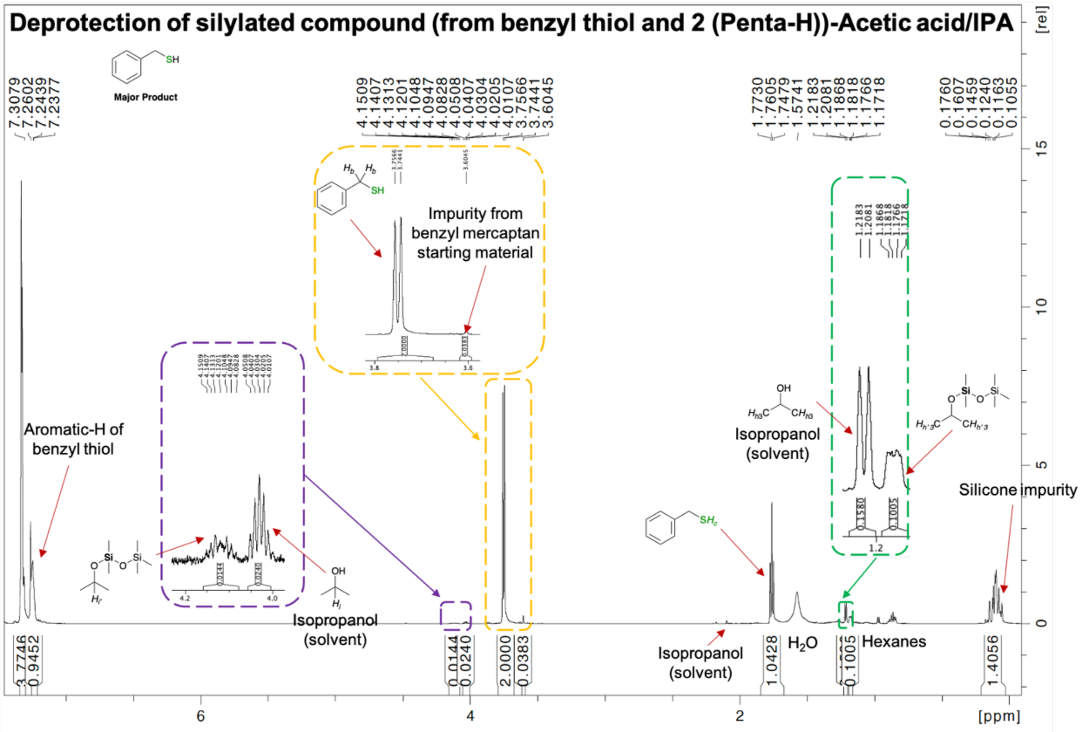
(7) Relative peak intensity (**1.2%**), retention time 11.7 min, MW: 355.10: $[M]^+$= 355.1 (55), 281.1 (100), 191.1 (25), 147.1 (23), 73.1 (70).

(8) Relative peak intensity (**0.9 %**), retention time 11.9 min, MW: 443.20: $[M]^+$= 443.2 (15), 355.1 (20), 323.0 (5), 281.1 (45), 221.1 (100), 147.1 (70), 73.1 (75).

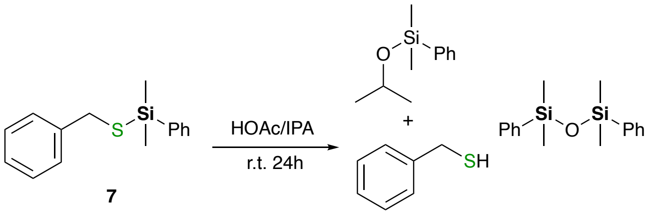
(9) Relative peak intensity (**0.9%**), retention time 12.5 min, MW: 254.10: $[M]^+$= 254.1 (10), 147.1 (5), 119.2 (10), 91.1 (100), 73.1 (5).

(10) Relative peak intensity (**0.7%**), retention time 14.3 min, MW: 429.10: $[M]^+$= 429.1 (5), 355.1 (100), 281.1 (23), 221.1 (40), 191.1 (23), 147.1 (30), 73.1 (80).

(11) Relative peak intensity (**0.8%**), retention time 33.4 min, MW: 245.1: $[M]^+$= 245.1 (5), 213.1 (65), 181.1 (10), 121.1 (20), 91.1 (100), 65.1 (10).



Compound 7 (HOAc/IPA)

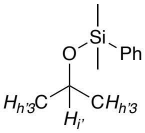


In a pre-dried 100.0 mL round-bottomed flask **7** (0.21 g, 0.81 mmol) (obtained from reduction of benzyl thiol with **3**) and acetic acid (0.05 g, 0.83 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The aromatic H in benzyl thiol, **3** are overlapped. The equivalents of benzyl thiol were determined from the SH peak. No Si-S compounds remained.

^{1}H NMR (600 MHz, chloroform-*d*): δ PhCH_2SSiMe$_2$Ph:PhCH$_2$S*H*= 0:100

(1) PhCH$_2$SH (*1 equiv.*) 1.76 (t, *J*=7.55 Hz, 1H, S*H*), 3.75 (d, *J*=7.55 Hz, 2H, PhCH_2SH), 7.23-7.61 (m, 5H arom);



(2) $C_{11}H_{18}OSi$ (*0.03 equiv.*): 0.33-0.57 (m, 6H, SiCH_3), 1.13 (d, *J*=6.08 Hz, 6H, $H_{h'3}$), 4.01 (m, 1H, overlapped with isopropanol peak), 7.23-7.61 (m, 5H arom);

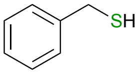
(3) Silicone impurities: 0.33 (s, 3H), 0.38-0.42 (m, 5H), 0.57 (s, 0.11H) ppm.

Starting material (Dimethylphenylsilane): δ

0.38 (d, *J*=3.76 Hz, 6H, SiCH_3), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm (for the ^{1}H NMR, see p. 173).

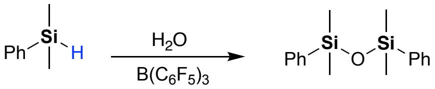
GC-MS: Compound 7: $PhCH_2SH$= 0: 100 (Relative peak intensity)

Sulfur-containing compounds:



(1) C_7H_8S, relative peak intensity (**24.8%**), retention time 5.0 min, MW: 124.03: $[M]^+$=124.1 (30), 91.1 (100), 77.1 (1), 65.1 (5).

Non-sulfur containing compounds (silicone compounds):



3

(2) $C_{16}H_{22}OSi_2$, relative peak intensity (**39.1%**), retention time 9.6 min, MW: 286.12: $[M]^+$ = 286.2 (10), 271.2 (100), 255.1 (5), 193.1 (60), 179.1 (5), 165.1 (5), 135.2 (10), 105.1 (5), 89.1 (15). Hydrolysis/condensation product of **3**.

(3) Relative peak intensity (**22.2%**), retention time 4.9 min, MW: 179.20: $[M]^+$= 179.2 (50), 137.1 (100), 116.1 (20), 91.1 (5), 75.1 (10).

(4) Relative peak intensity (**12.1%**), retention time 4.9 min, MW: 137.10: $[M]^+$= 137.1 (100), 91.1 (5), 77.1 (1).

(5) Relative peak intensity (**1.3%**), retention time 6.1 min, MW: 179.10: $[M]^+$= 179.1 (90), 137.1 (100), 117.1 (30), 91.1 (10), 75.1 (20).

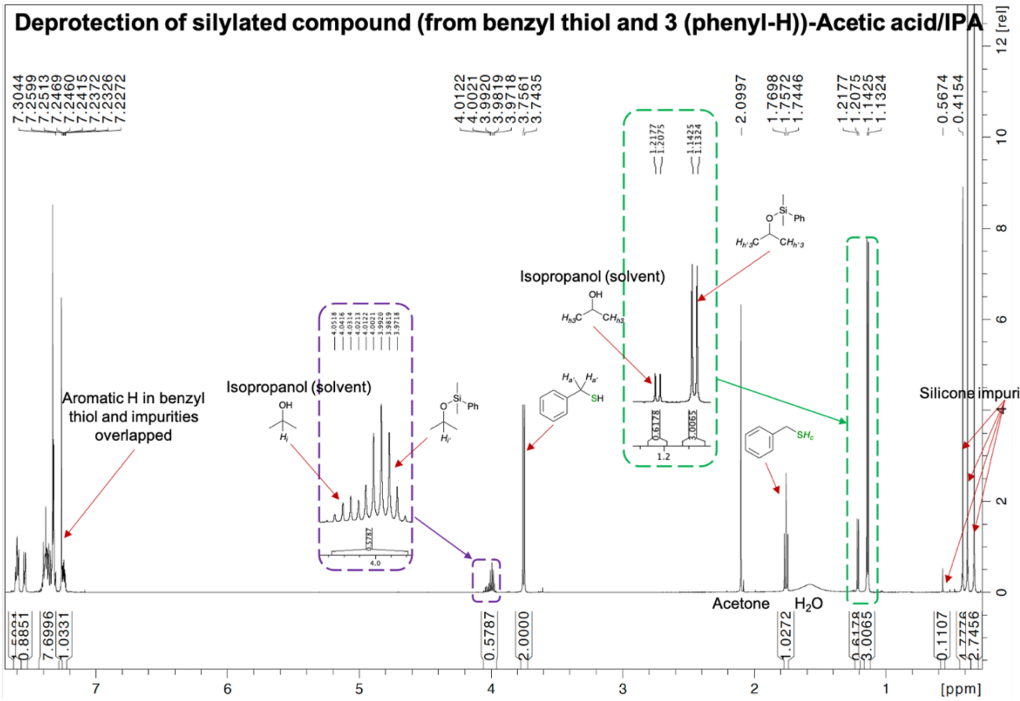
(6) Relative peak intensity (**0.1%**), retention time 9.2 min, MW: 252.90: $[M]^+$= 252.9 (1), 228.2 (40), 213.1 (100), 197.0 (5),135.0 (25), 91.2 (20), 77.1 (10), 65.1 (5).

(7) Relative peak intensity (**0.1%**), retention time 10.0 min, MW: 376.80: $[M]^+$= 376.8 (1), 315.0 (1), 227.1 (45), 197.2 (70), 164.2 (90), 149.1 (45), 91.2 (100), 77.1 (5), 65.1 (10).

(8) Relative peak intensity (**0.1%**), retention time 10.4 min, MW: 345.20: $[M]^+$= 345.2 (100), 313.1 (1), 267.0 (20), 251.1 (5), 197.1 (15), 165.0 (15), 135.1 (25), 107.0 (5), 73.1 (5).

(9) Relative peak intensity (**0.1%**), retention time 11.6 min, MW: 377.00: $[M]^+$= 377.0 (100), 316.0 (5), 253.1 (1), 214.1 (50), 197.2 (1), 123.0 (60), 91.1 (100), 77.1 (10), 65.2 (25).

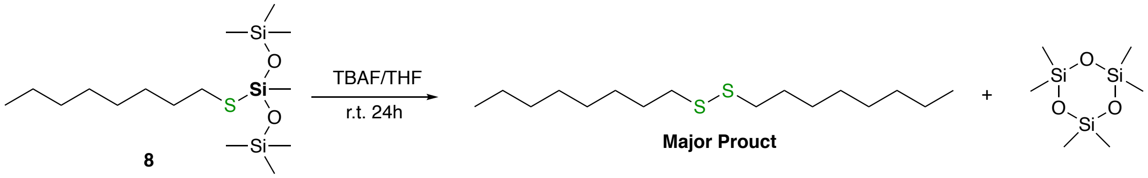
(10) Relative peak intensity (**0.1%**), retention time 13.4 min, MW: 315.10: $[M]^+$= 315.1 (1), 246.1 (10), 181.2 (5), 121.2 (1), 91.1 (100), 77.1 (5), 65.1 (10).


Deprotection of silylated compound (from benzyl thiol and 3 (phenyl-H))-Acetic acid/IPA
7.3044
7.2599
7.2513
7.2469
7.2460
7.2415
7.2372
7.2326
7.2272
4.0122
4.0021
3.9920
3.9819
3.9718
3.7561
3.7435
2.0997
1.7698
1.7572
1.7446
1.2177
1.2075
1.1425
1.1324
0.5674
0.4154
Aromatic H in benzyl thiol and impurities overlapped
Isopropanol (solvent)
OH
H_i
O
Si
Ph
$H_{i'}$
4.0
0.5787
$H_{a'}$
$H_{a'}$
SH
Isopropanol (solvent)
OH
$H_{h3}C$
CH_{h3}
$H_{h'3}C$
$CH_{h'3}$
0.6178
3.0065
1.2
SH_c
Acetone
H_2O
Silicone impurities
0.8851
7.6996
1.0331
0.5787
2.0000
1.0272
0.6178
3.0065
0.1107
4.7776
2.7456
7
6
5
4
3
2
1
[ppm]
0
2
4
6
8
10
12 [rel]

5.8.8 Deprotection of silylated octanethiol

5.8.8.1 Cleavage of SiS bonds: Attempts with TBAF/THF

Compound 8 (TBAF/THF)



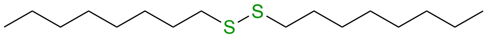
To a pre-dried 100.0 mL round-bottomed flask, the silylated product **8** (0.51 g, 1.39 mmol) (obtained from reduction of octanethiol with **1**) and tetrabutylammonium fluoride (TBAF, 0.37 g, 1.40 mmol) were mixed together with dry tetrahydrofuran (THF 5.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent. After the removal of THF, 4.0 mL of methanol together with 12.0 mL of distilled water were added and stirred for 24h under nitrogen blanket. The liquid extraction was performed three times for the obtained mixture by adding 15.0 mL of hexanes followed by the addition of sodium sulfate to absorb the residual water. *No residual S-Si compounds were detected in the GC-MS.*

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $C_{16}H_{34}S_2$ (*1 equiv.*): 0.88 (t, *J*=6.83 Hz, 3H, $(CH_3C_5H_{10}CH_2CH_2S)_2$), 1.27-1.39 (m, 10H, $(CH_3C_5H_{10}CH_2CH_2S)_2$), 1.67 (quint, *J*=7.43 Hz, 2H, $(CH_3C_5H_{10}CH_2CH_2S)_2$), 2.68 (t, *J*=7.38 Hz, 2H, $(CH_3C_5H_{10}CH_2CH_2S)_2$);

(2) Silicone impurity: 0.07-0.12 (m, 7H) ppm.

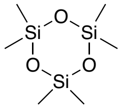
GC-MS: $C_{16}H_{34}S_2$ (major product): $C_8H_{17}SH$: compound 8=100: 0: 0 (Relative peak intensity)

Sulfur-containing compound:



(1) $C_{16}H_{34}S_2$, retention time 23.6 min, relative peak intensity (**93.0%**), MW: 290.21: $[M]^+$ = 290.3 (80), 178.1 (40), 145.2 (40), 57.2 (100).

Non-sulfur containing compounds (silicone compounds):



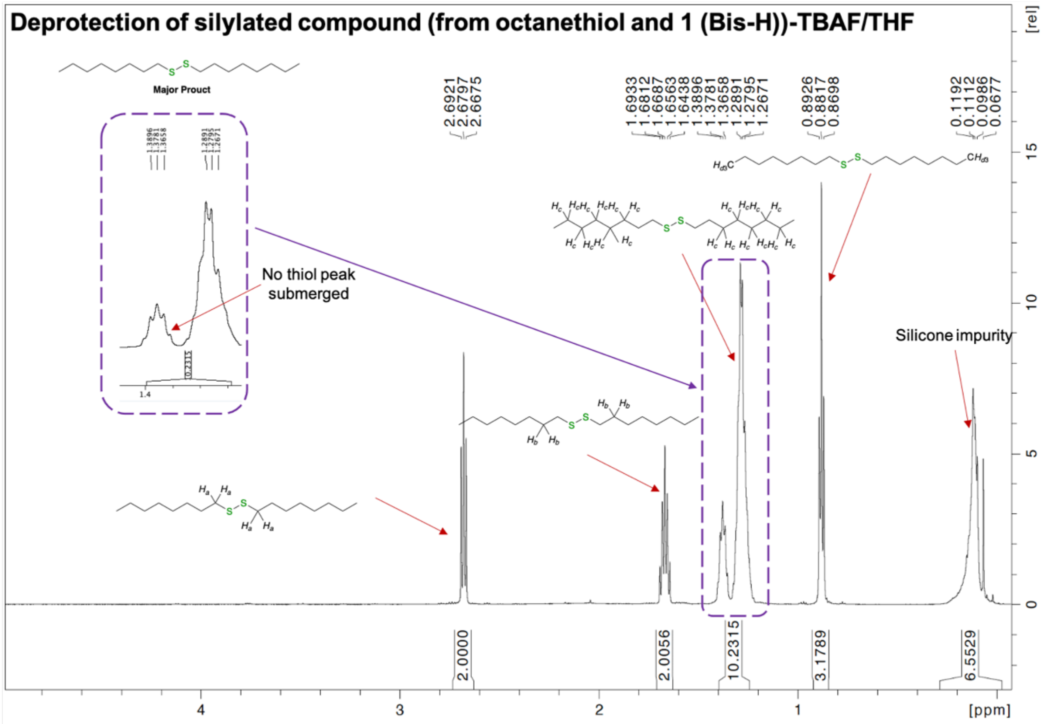
(2) D_3, retention time 4.9 min, relative peak intensity (**1.0%**), MW:222.06: $[M-15]^+$= 207.1 (100), 133.1 (2), 84.0 (3), 51.1 (1).

(3) Relative peak intensity (**1.0%**), retention time 10.7 min, MW:355.10: $[M]^+$= 355.1 (55), 267.1 (90), 207.0 (2), 147.1 (1), 73.1 (100).

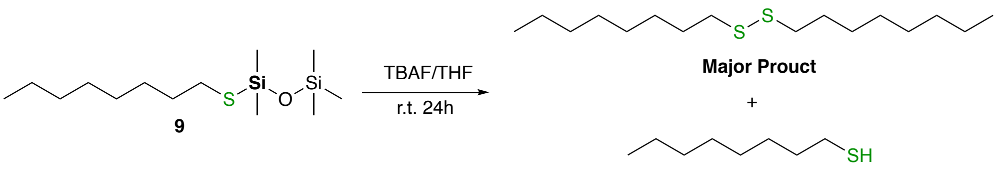
(4) Relative peak intensity (**2.0%**), retention time 11.4 min, MW:443.20: $[M]^+$= 443.2 (20), 355.1 (30), 323.0 (1), 281.1 (40), 221.1 (80), 147.1 (75), 73.1 (100).

(5) Relative peak intensity (**1.0%**), retention time 17.7 min, MW:597.00: $[M]^+$= 597.0 (100), 507.0 (7), 460.9 (1), 327.0 (5), 283.0 (90), 246.0 (7), 207.0 (5), 73.3 (5).

(6) Relative peak intensity (**2.0%**), retention time 31.8 min, MW:257.20: $[M]^+$= 257.3 (100), 143.2 (5), 69.1 (35).



Compound 9 (TBAF/THF)



To a pre-dried 100.0 mL round-bottomed flask, the silylated product **9** (0.51 g, 1.74 mmol) (obtained from reduction of octanethiol with **2**) and tetrabutylammonium fluoride (TBAF, 0.45 g, 1.72 mmol) were mixed together with dry tetrahydrofuran (THF 5.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent. After the removal of THF, 4.0 mL of methanol together with 12.0 mL of distilled water were added and stirred for 24h under nitrogen blanket. The liquid extraction was performed three times for the obtained mixture by adding 15.0 mL of hexanes followed by the addition of sodium sulfate to absorb the residual water. *No residual S-Si compounds were detected in the GC-MS.*

The alkyl H peaks in octanethiol and **9** overlapped. The $C_7H_{15}CH_2S\mathit{H}$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture by ^{1}H NMR.

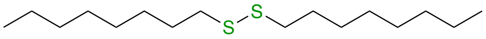
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $C_{16}H_{34}S_2$: 0.87-0.89 (m, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.28-1.43 (m, 10H, $(CH_3C_5\mathit{H}_{10}CH_2CH_2S)_2$ 10H), 1.67 (quint, *J*=7.44 Hz, 2H, $(CH_3C_5H_{10}C\mathit{H}_2CH_2S)_2$), 2.68 (t, *J*=7.41 Hz, 2H, $(CH_3C_5H_{10}CH_2C\mathit{H}_2S)_2$);

(2) $C_8H_{17}SH$: 0.87-0.89 (m, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.28-1.43 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$, overlapped with S*H*), 1.61 (quint, *J*=7.38 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SH$), 2.52 (t, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SH$);

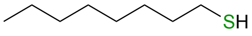
(3) Silicone impurity: 0.02-0.20 (m, 8H) ppm.

GC-MS: $C_{16}H_{34}S_2$ (major product): $C_8H_{17}SH$: compound 9=93.6: 6.4: 0 (Relative peak intensity)

Sulfur-containing compound:



(1) $C_{16}H_{34}S_2$, retention time 12.0 min, relative peak intensity (**90.1%**), MW: 290.21: $[M]^+$ = 290.3 (90), 176.2 (50), 145.2 (50), 87.2 (20), 71.2 (90), 57.2 (100).

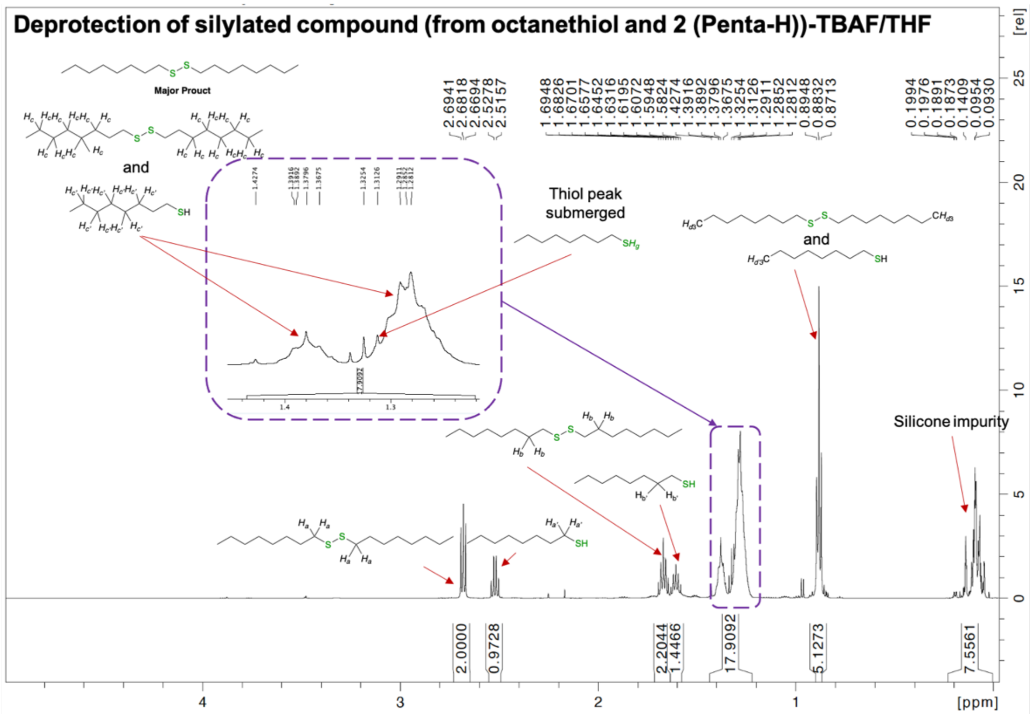


(2) $C_8H_{18}S$, retention time 4.5 min, relative peak intensity (**6.2%**), MW: 146.11: $[M]^+$= 146.2 (60), 112.2 (8), 83.2 (60), 70.2 (70), 58.2 (100).

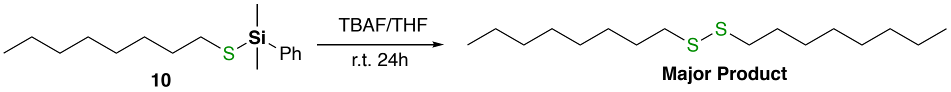
Non-sulfur containing compounds (silicone compounds):

(3) Relative peak intensity (**2.5%**), retention time 15.0 min, MW: 529.20: $[M]^+$= 529.2 (1), 470.1 (15), 377.1 (2), 340.3 (30), 317.0 (1), 284.2 (2), 218.0 (2), 177.2 (100), 127.1 (6), 91.2 (5), 57.2 (2).

(4) Relative peak intensity (**1.2%**), retention time 16.5 min, MW: 544.10: $[M]^+$= 544.1 (1), 513.0 (5), 470.2 (20), 440.1 (25), 378.1 (25), 331.1 (5), 281.2 (1), 257.3 (100), 219.1 (10), 181.1 (10), 143.2 (5), 69.2 (30).



Compound 10 (TBAF/THF)



To a pre-dried 100.0 mL round-bottomed flask, the silylated product **10** (0.21 g, 0.75 mmol) (obtained from reduction of octanethiol with **3**) and tetrabutylammonium fluoride (TBAF, 0.19 g, 0.73 mmol) were mixed together with dry tetrahydrofuran (THF 5.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent. After the removal of

THF, 4.0 mL of methanol together with 12.0 mL of distilled water were added and stirred for 24h under nitrogen blanket. The liquid extraction was performed three times for the obtained mixture by adding 15.0 mL of hexanes followed by the addition of sodium sulfate to absorb the residual water. *No residual S-Si compounds were detected in the GC-MS.*

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $C_{16}H_{34}S_2$ (*1 equiv.*): 0.89 (t, *J*=7.02 Hz, 3H, $(C\mathit{H}_3C_5H_{10}CH_2CH_2S)_2$), 1.27-1.41 (m, 10H, $(CH_3C_5\mathit{H}_{10}CH_2CH_2S)_2$), 1.68 (quintet, *J*=7.44 Hz, 2H, $(CH_3C_5H_{10}C\mathit{H}_2CH_2S)_2$), 2.69 (t, *J*=7.38 Hz, 2H, $(CH_3C_5H_{10}CH_2C\mathit{H}_2S)_2$);

(2) Silicone impurities: 0.05 (s, 0.1H), 0.09-0.39 (m, 4H), 0.41 (s, 1H), 0.49-0.51 (m, 0.07H);

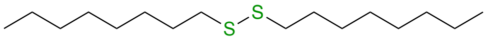
(3) Impurities: 1.79 (s, 0.14H), 3.44 (s, 0.03H), 7.33-7.61 (m, 4H) ppm.

Starting material (Dimethylphenylsilane): δ

0.38 (d, *J*=3.76 Hz, 6H, $SiC\mathit{H}_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm.

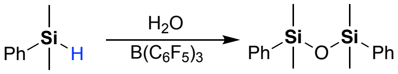
GC-MS: $(C_8H_{17}S)_2$: $C_8H_{17}SH$: compound 10 = 100: 0: 0 (Relative peak intensity)

Sulfur-containing compound:



(1) $(CH_3C_5H_{10}CH_2CH_2S)_2$, retention time 11.9 min, relative peak intensity (**35.7%**), MW: 290.21: $[M]^+$= 290.3 (100), 178.2 (40), 145.2 (40), 87.1 (15), 71.2 (80), 57.2 (80).

Non-sulfur containing compounds (silicone compounds):



(2) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**48.6%**), MW: 286.12: $[M]^+$= 286.2 (15), 271.2 (100), 255.1 (5), 193.1 (70), 165.1 (5), 135.2 (10), 89.1 (15).

(3) $C_8H_{12}OSi$ ($HOSiMe_2Ph$), retention time 4.9 min, relative peak intensity (**11.0%**), MW: 152.10: $[M]^+$= 152.1 (1), 137.1 (100), 91.1 (5), 77.1 (5).

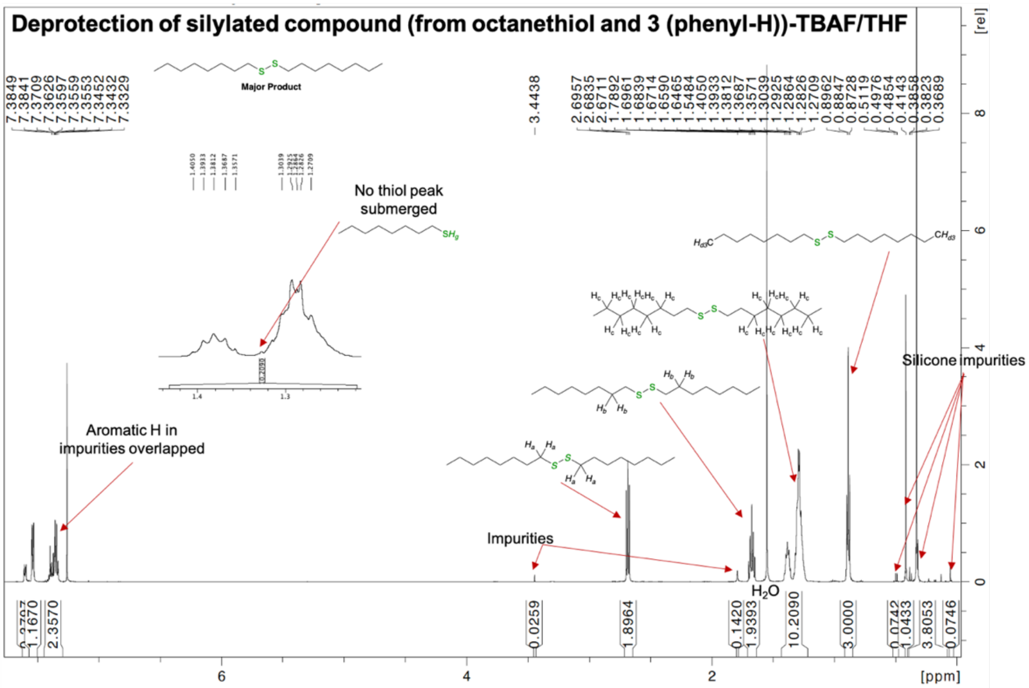
(4) Relative peak intensity (**0.6%**), retention time 4.4 min, MW: 166.10: $[M]^+$= 166.1 (5), 151.1 (100), 135.2 (1), 121.1 (40), 105.1 (5), 91.1 (8), 77.1 (1), 59.1 (8).

(5) Relative peak intensity (**0.4%**), retention time 4.5 min, MW: 228.10: $[M]^+$= 228.1 (1), 213.1 (100), 197.0 (20), 183.1 (1), 151.1 (1), 135.2 (5), 121.1 (1), 99.1 (1), 91.1 (5), 77.1 (5).

(6) Relative peak intensity (**0.3%**), retention time 6.1 min, MW: 211.10: $[M]^+$= 211.1 (100), 195.1 (15), 179.1 (5), 165.0 (1), 149.1 (5), 133.1 (99), 115.0 (5), 98.2 (1), 89.1 (20), 75.1 (5), 61.1 (1).

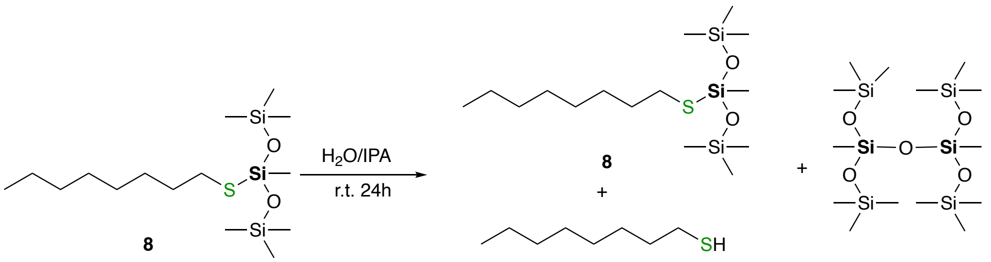
(7) Relative peak intensity (**3.3%**), retention time 10.4 min, MW: 345.20: $[M]^+$= 345.2 (100), 313.2 (1), 267.1 (18), 197.2 (15), 165.1 (10), 135.2 (25), 107.1 (1), 91.1 (1), 73.1 (1).

(8) Relative peak intensity (**0.1%**), retention time 11.3 min, MW: 471.00: $[M]^+$= 471.0 (1), 451.4 (1), 419.3 (40), 377.8 (1), 325.1 (1), 269.1 (60), 197.2 (90), 155.2 (1), 135.1 (100), 91.1 (3), 73.2 (10).


Deprotection of silylated compound (from octanethiol and 3 (phenyl-H))-TBAF/THF
Major Product
No thiol peak submerged
Aromatic H in impurities overlapped
Impurities
Silicone impurities
H2O
[rel]
[ppm]

5.8.8.2 Cleavage of SiS bonds: Attempts with H2O/IPA

Compound 8 (H_2O/IPA)



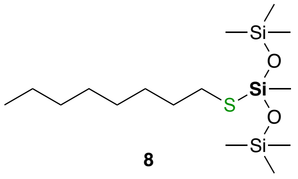
To a pre-dried 100.0 mL round-bottomed flask **8** (0.50 g, 1.37 mmol) (obtained from reduction of octanethiol with **1**) and distilled water (0.0246 mL, 0.0246 g, 1.37 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The alkyl H peaks in octanethiol and **8** were overlapped. The $C_7H_{15}CH_2S\mathit{H}$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **8**: 0.14 (s, 18H, $C_8H_{17}SSiMe(\mathit{Me}_3SiO)_2$), 0.30 (s, 3H, $C_8H_{17}SSi\mathit{Me}(Me_3SiO)_2$), 0.88 (t, *J*=7.02 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.27-1.38 (m, 10H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$), 1.60 (quint, *J*=7.47 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2S$), 2.51 (t, *J*=7.47 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2S$); (2) $C_7H_{15}CH_2SH$: 0.88 (t, *J*=7.02 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.27-1.38 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$ and $C_8H_{17}S\mathit{H}$ overlapped), 1.60 (quint, *J*=7.47 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2S$), 2.51 (t, *J*=7.47 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2S$);
(3) Silicone impurity: 0.02- 0.12 (m, 0.41H) ppm.

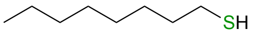
GC-MS: Compound 8: $C_8H_{17}SH$= 99.1: 0.9 (Relative peak intensity)

Sulfur-containing compounds:



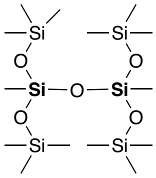
8

(1) $C_{15}H_{38}O_2SSi_3$, retention time 8.2 min, relative peak intensity (**97.2%**), MW: 366.19: $[M]^+$= 366.3 (8), 351.2 (30), 239.1 (20), 221.2 (100), 207.1 (10), 133.1 (5), 73.1 (30).



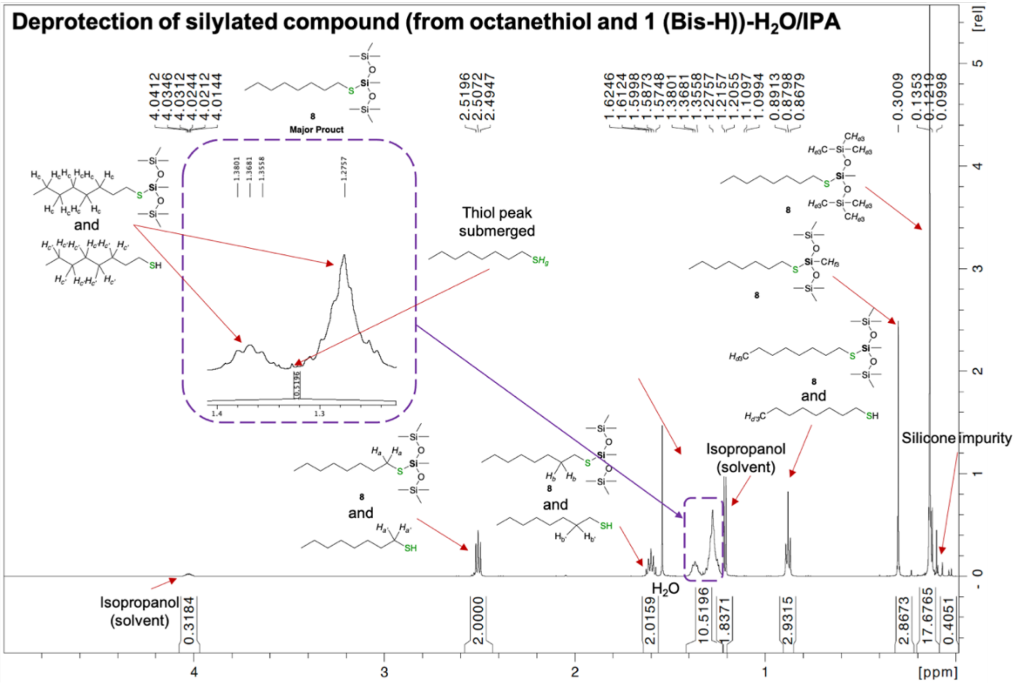
(2) $C_8H_{18}S$, retention time 4.4 min, relative peak intensity (**0.9%**), MW: 146.11: $[M]^+$= 146.2 (70), 112.2 (20), 83.2 (85), 70.1 (100).

Non-sulfur containing compound (silicone compound):

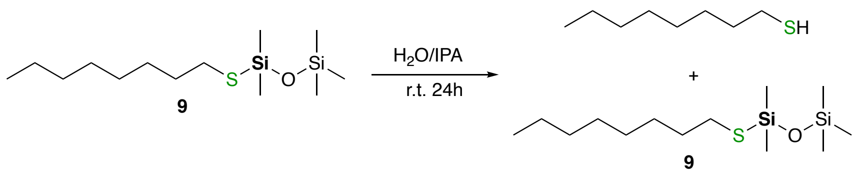


15

(3) $C_{14}H_{42}O_5Si_6$, retention time 5.1 min, relative peak intensity (**1.9%**), MW: 459.00: $[M-15]^+$= 443.2 (20), 355.1 (30), 323.1 (5), 281.1 (45), 267.1 (30), 249.0 (5), 221.2 (70), 147.1 (60), 73.1 (100), 59.1 (5).



Compound 9 (H_2O/IPA)



To a pre-dried 100.0 mL round-bottomed flask **9** (0.50 g, 1.71 mmol) (obtained from reduction of octanethiol with **2**) and distilled water (0.0308 mL, 0.0308 g, 1.71 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The alkyl H peaks in octanethiol and **9** are overlapped. The $C_7H_{15}CH_2S\mathit{H}$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

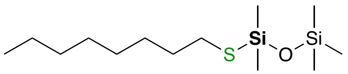
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **9**: 0.01-0.33 (m, 15H, $CH_3C_5H_{10}CH_2CH_2SSi\mathit{Me}_2OSi\mathit{Me}_3$), 0.88 (t, *J*=7.04 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.25-1.39 (m, 10H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$), 1.61 (quint, *J*=7.39 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2S$), 2.52 (t, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2S$);

(2) $C_7H_{15}CH_2SH$: 0.88 (t, *J*=7.04 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.25-1.39 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$ and $C_8H_{17}S\mathit{H}$ overlapped), 1.61 (quint, *J*=7.39 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2S$), 2.52 (t, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2S$);

(3) Overlapped silicone H in compound **9** and silicone impurity: 0.01-0.08 (m, 1H), 0.09-0.12 (m, 13H), 0.33 (s, 0.70H), ppm.

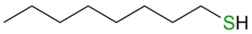
GC-MS: Compound 9: $C_8H_{17}SH$=36.1: 63.9 (Relative peak intensity)

Sulfur-containing compounds:



9

(1) $C_{13}H_{32}OSSi_2$, retention time 7.4 min, relative peak intensity (**33.5%**), MW: 292.17: $[M]^+$ = 292.2 (10), 277.2 (30), 165.1 (35), 147.1 (100), 117.1 (5), 73.1 (10).



(2) $C_8H_{18}S$, retention time 4.4 min, relative peak intensity (**59.3%**), MW: 146.11: $[M]^+$ = 146.2 (80), 112.2 (20), 83.2 (80), 70.2 (100).

Non-sulfur containing compounds (silicone compounds):

(3) Relative peak intensity (**3.7%**), retention time 4.0 min, MW: 369.20: $[M]^+$= 369.2 (20), 281.1 (100), 265.1 (10), 207.1 (10), 147.2 (70), 117.1 (2), 73.1 (50), 59.1 (2).

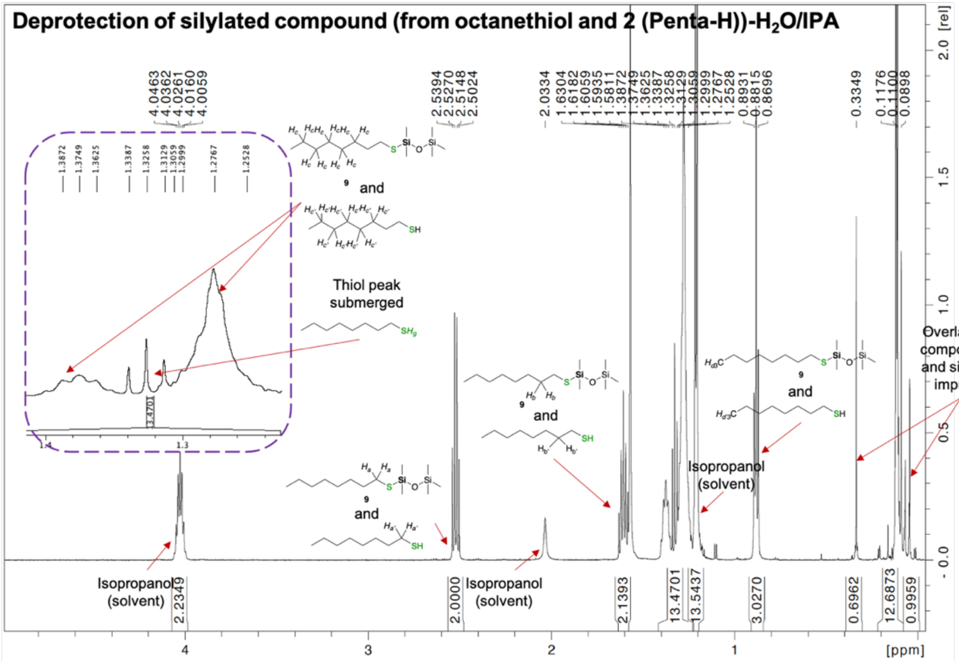
(4) Relative peak intensity (**1.5%**), retention time 5.4 min, MW: 443.20: $[M]^+$= 443.2 (10), 355.1 (30), 323.1 (5), 281.1 (40), 267.1 (30), 249.1 (5), 221.2 (100), 191.1 (5), 147.1 (60), 73.1 (75), 59.2 (1).

(5) Relative peak intensity (**0.8%**), retention time 6.7 min, MW: 429.20: $[M]^+$= 429.2 (5), 341.1 (20), 295.2 (30), 281.1 (10), 221.1 (100), 207.1 (30), 147.1 (40), 131.0 (5), 112.2 (1), 73.2 (70).

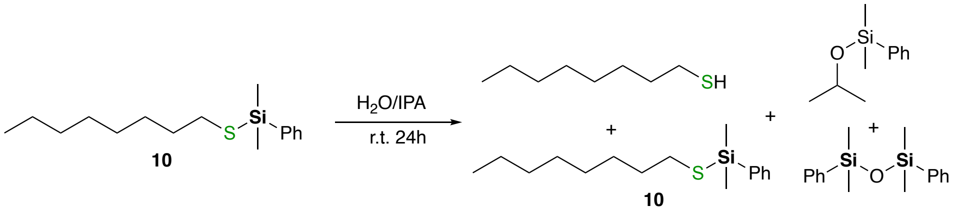
(6) Relative peak intensity (**0.5%**), retention time 7.8 min, MW: 497.20: $[M]^+$= 497.2 (1), 458.6 (1), 428.9 (1), 399.2 (5), 369.1 (15), 341.0 (20), 295.1 (30), 254.0 (15), 221.1 (100), 207.0 (50), 147.2 (60), 73.1 (80), 59.1 (10).

(7) Relative peak intensity (**0.4%**), retention time 8.2 min, MW: 404.7: $[M]^+$= 404.7 (1), 351.3 (20), 315.2 (1), 293.0 (1), 221.2 (100), 149.0 (5), 73.0 (20).

(8) Relative peak intensity (**0.3%**), retention time 8.4 min, MW: 351.20: $[M]^+$= 351.2 (5), 269.2 (1), 221.1 (100), 147.0 (5), 118.9 (1), 73.2 (10).



Compound 10 (H_2O/IPA)

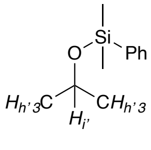


In a pre-dried 100.0 mL round-bottomed flask **10** (0.50 g, 1.78 mmol) (obtained from reduction of octanethiol with **3**) and distilled water (0.0321 mL, 0.0321 g, 1.78 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The alkyl H peaks in octanethiol and **10** were overlapped. The $C_7H_{15}CH_2SH$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **10**: 0.33-0.41 (m, 6H, $C_8H_{17}SSiMe_2Ph$), 0.89 (t, *J*=7.05 Hz, 3H, $CH_3C_7H_{14}S$), 1.26-1.39 (m, 10H, $CH_3C_5H_{10}CH_2CH_2S$), 1.61 (quintet, *J*=7.38 Hz, 2H, $CH_3C_5H_{10}CH_2CH_2S$), 2.52 (quartet, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2CH_2S$) 7.33-7.61 (m, 5H arom);

(2) $C_8H_{17}SH$: 0.89 (t, *J*=7.05 Hz, 3H, $CH_3C_7H_{14}S$), 1.26-1.39 (m, 11H, $CH_3C_5H_{10}CH_2CH_2S$ and $C_8H_{17}SH$ submerged), 1.61 (quintet, *J*=7.38 Hz, 2H, $CH_3C_5H_{10}CH_2CH_2S$), 2.52 (quartet, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2CH_2S$);



(3) $C_{11}H_{18}OSi$: 0.33-0.41 (m, 6H, $SiCH_3$), 1.14 (d, *J*= 6.06 Hz, 6H, $H_{h'3}$), 3.97- 4.01 (m, 1H, $H_{i'}$, overlapped with isopropanol peak), 7.33-7.61 (m, 5H arom);

(4) Silicone impurities: 0.33 (s, 3H), 0.41 (s, 3H);

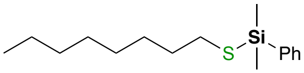
(5) Impurity: 1.80 (s, 0.48H) ppm.

Starting material (Dimethylphenylsilane): δ

0.38 (d, *J*=3.76 Hz, 6H, SiC*H*$_3$), 4.47 (sept, *J*=3.75 Hz, 1H, Si*H*), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm (see the ^{1}H NMR on p. 173).

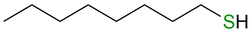
GC-MS: Compound 10: $C_8H_{17}SH$ = 1.2: 98.8 (Relative peak intensity)

Sulfur-containing compounds:



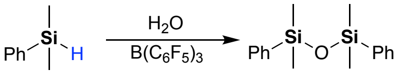
10

(1) $C_{16}H_{28}SSi$, retention time 11.1 min, relative peak intensity (**0.3%**), MW: 280.17: $[M]^+$= 280.3 (20), 265.2 (70), 207.0 (1), 168.1 (15), 153.1 (60), 135.2 (100), 91.1 (10), 75.1 (10), 56.2 (5).



(2) $C_8H_{18}S$, retention time 4.4 min, relative peak intensity (**23.9%**), MW: 146.11: $[M]^+$= 146.2 (60), 112.2 (20), 97.2 (5), 83.2 (70), 70.2 (75), 56.2 (100).

Non-sulfur containing compounds (silicone compounds):

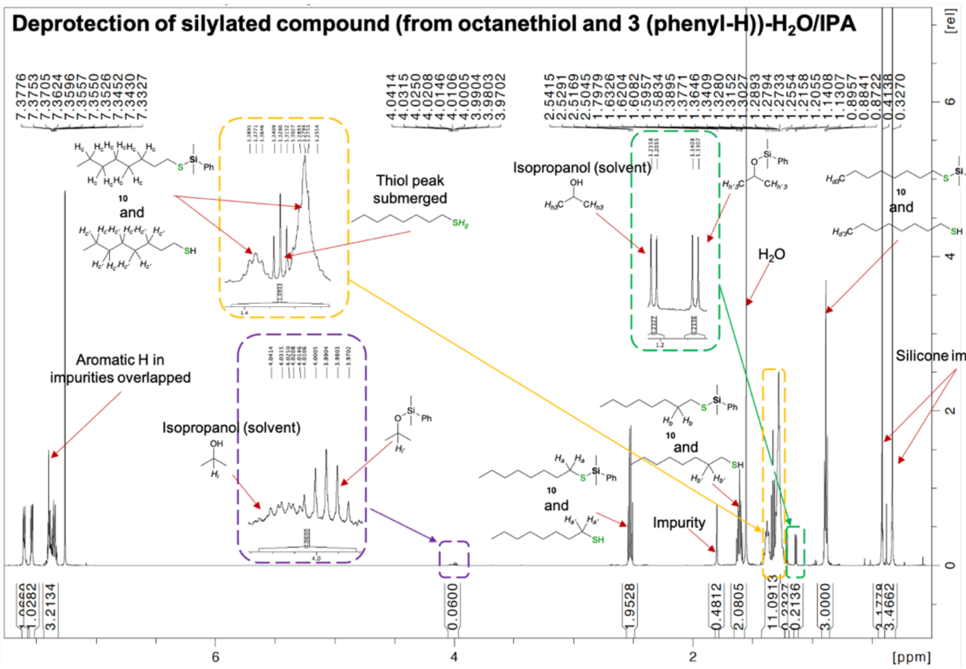


(3) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**46.8%**), MW: 286.12: $[M]^+$= 286.2 (10), 271.2 (100), 255.1 (5), 193.1 (70), 165.1 (1), 135.2 (10), 105.1 (1), 89.1 (15).

(4) $C_8H_{12}OSi$ ($HOSiMe_2Ph$), retention time 4.9 min, relative peak intensity (**26.0%**), MW: 152.20: $[M]^+$= 152.2 (10), 137.1 (100), 119.1 (1), 91.1 (5), 77.1 (1).

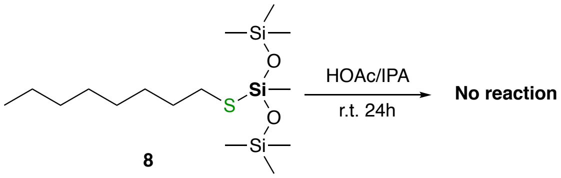
(5) Relative peak intensity (**2.9%**), retention time 4.9 min, MW: 179.20: $[M]^+$= 179.2 (70), 137.1 (100), 116.2 (25), 105.1 (10), 91.1 (5), 75.1 (10), 53.1 (1).

(6) Relative peak intensity (**0.1%**), retention time 10.4 min, MW: 455.00: $[M]^+$= 455.0 (1), 377.0 (1), 345.2 (100), 315.3 (1), 267.1 (25), 251.0 (10), 197.1 (20), 165.1 (15), 135.1 (25), 106.9 (1), 73.1 (5), 56.1 (1).



5.8.8.3 Cleavage of SiS bonds: Attempts with HOAc/IPA

Compound 8 (HOAc/IPA)



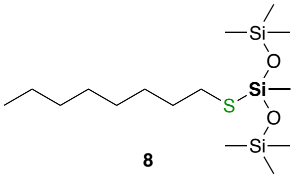
8

To a pre-dried 100.0 mL round-bottomed flask **8** (0.51 g, 1.39 mmol) (obtained from reduction of octanethiol with **1**) and acetic acid (0.083 g, 1.38 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

^{1}H NMR (600 MHz, chloroform-*d*): δ Compound **8** (*1 equiv.*): 0.13 (s, 18H, $C_8H_{17}SSiMe(\mathit{Me}_3SiO)_2$), 0.30 (s, 3H, $C_8H_{17}SSi\mathit{Me}(Me_3SiO)_2$), 0.88 (t, *J*=6.89 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2SSiMe(Me_3SiO)_2$), 1.27-1.38 (m, 10 H, $CH_3C_5\mathit{H}_{10}CH_2CH_2SSiMe(Me_3SiO)_2$), 1.60 (quint, *J*=7.48 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SSiMe(Me_3SiO)_2$), 2.51 (t, *J*=7.45 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SSiMe(Me_3SiO)_2$) ppm.

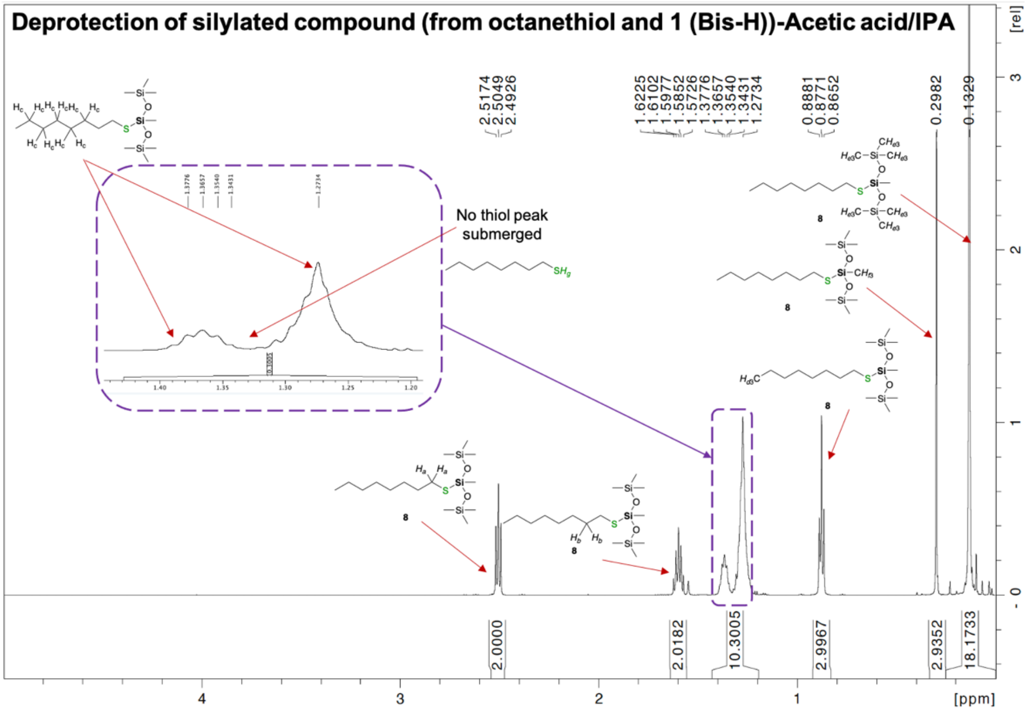
GC-MS: Compound 8: $C_8H_{17}SH$= 100: 0 (Relative peak intensity)

Sulfur-containing compound:

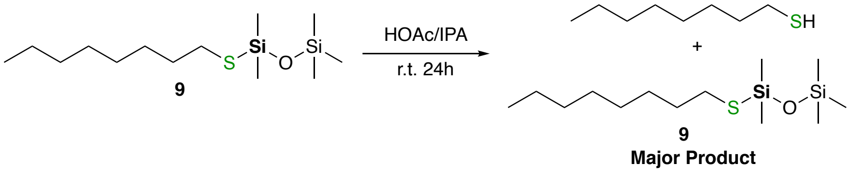


8

$C_{15}H_{38}O_2SSi_3$, retention time 16.8 min, relative peak intensity (**100%**), MW: 366.19: $[M]^+$= 366.2 (5), 351.2 (20), 221.1 (100), 133.1 (10), 73.1 (20).



Compound 9 (HOAc/IPA)



In a pre-dried 100.0 mL round-bottomed flask **9** (0.50 g, 1.71 mmol) (obtained from reduction of octanethiol with **2**) and acetic acid (0.105 g, 1.74 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The alkyl H peaks in octanethiol and **9** are overlapped. The$C_7H_{15}CH_2S\mathit{H}$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

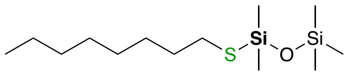
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) Compound **9**: 0.12-0.33 (m, 15H, $CH_3C_5H_{10}CH_2CH_2SSi\mathit{Me_2}OSi\mathit{Me}_3$), 0.88 (t, *J*=6.89 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.28-1.39 (m, 10H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$), 1.61 (quint, *J*=7.44 Hz, 2H, $CH_3C_5H_{10}C\mathit{H_2}CH_2S$), 2.53 (t, *J*=7.44 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H_2}S$);

(2) $C_8H_{17}SH$: 0.88 (t, *J*=6.89 Hz, 3H, $C\mathit{H}_3C_5H_{10}CH_2CH_2S$), 1.28-1.39 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2S$ and $C_8H_{17}S\mathit{H}$), 1.61 (quint, *J*=7.44 Hz, 2H, $CH_3C_5H_{10}C\mathit{H_2}CH_2S$), 2.53 (t, *J*=7.44 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H_2}S$);

(3) Overlapped silicone H in compound **9** and silicone impurity: 0.12 (s, 7H), 0.33 (s, 4H) ppm.

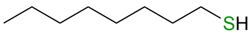
GC-MS: Compound 9: $C_8H_{17}SH$= 91.1: 8.8 (Relative peak intensity)

Sulfur-containing compounds:



9

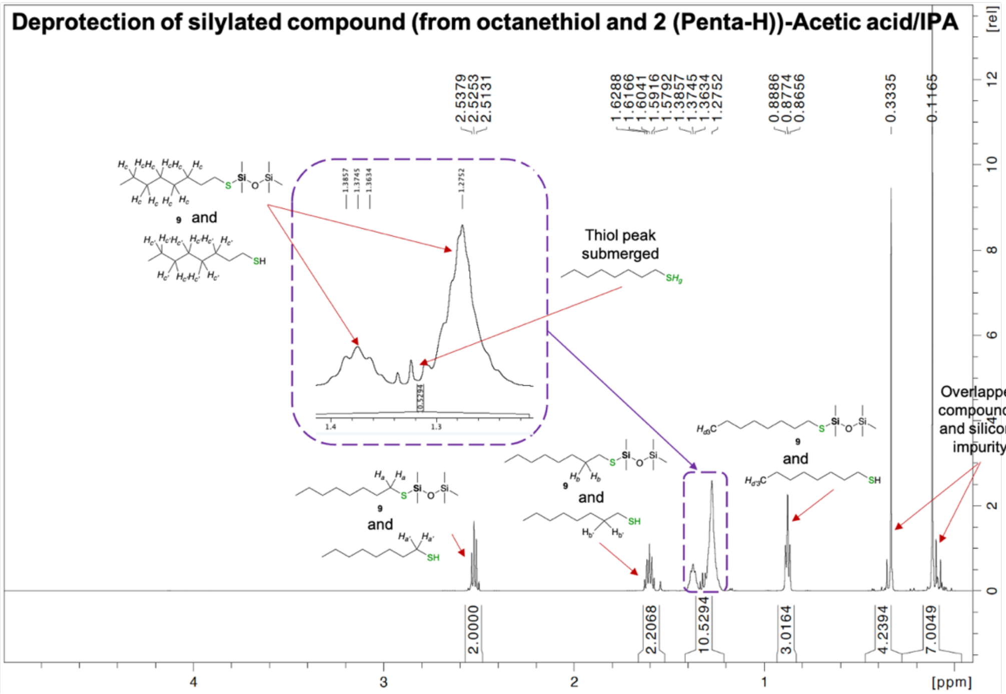
(1) $C_{13}H_{32}OSSi_2$, retention time 15.3 min, relative peak intensity (**82.0%**), MW: 292.17: $[M]^+$ = 292.2 (10), 277.2 (60), 165.1 (60), 147.1 (100), 131.1 (10), 73.1 (10), 57.2 (10).



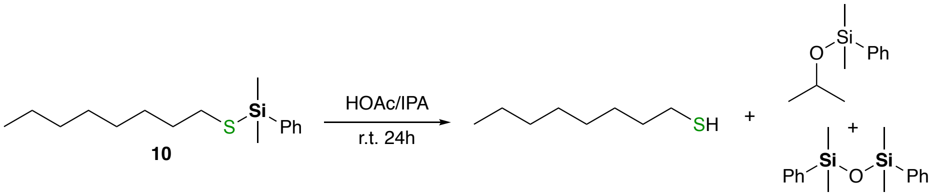
(2) $C_8H_{18}S$, retention time 9.1 min, relative peak intensity (**8.0%**), MW: 146.11: $[M]^+$ = 146.2 (60), 112.2 (20), 83.2 (60), 70.2 (80), 56.2 (100).

Non-sulfur containing compound (silicone compound):

(3) Relative peak intensity (**10.0%**), retention time 17.1 min, MW: 221.10: $[M]^+$= 221.1 (100), 73.1 (10).



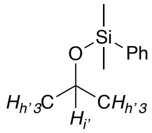
Compound 10 (HOAc/IPA)



To a pre-dried 100.0 mL round-bottomed flask **10** (0.22 g, 0.79 mmol) (obtained from reduction of octanethiol with **3**) and acetic acid (0.044 g, 0.73 mmol) were mixed together with isopropanol (3.0 mL) as solvent. The mixture was stirred for 24h followed by a continuous nitrogen flow to remove the solvent.

The $C_7H_{15}CH_2S\mathit{H}$ peak was located in a cluster of peaks between 1.2-1.4 ppm; it is not therefore possible by NMR to assign the fraction of unreacted thiol in the product mixture.

^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $C_8H_{17}SH$: 0.89 (t, *J*=7.02 Hz, 3H, $C\mathit{H}_3C_7H_{14}SH$), 1.26-1.39 (m, 11H, $CH_3C_5\mathit{H}_{10}CH_2CH_2SH$, overlapped and $C_8H_{17}S\mathit{H}$ submerged), 1.60 (quintet, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}C\mathit{H}_2CH_2SH$), 2.53 (quartet, *J*=7.40 Hz, 2H, $CH_3C_5H_{10}CH_2C\mathit{H}_2SH$);



(2) $C_{11}H_{18}OSi$: 0.07-0.42 (m, 6H, $SiC\mathit{H}_3$), 1.13 (d, *J*= 6.06 Hz, 6H, $H_{h'3}$), 3.96 - 4.03 (m, 1H, $H_{i'}$, overlapped with isopropanol peak), 7.33-7.61 (m, 5H, arom H);

(3) Silicone impurities: 0.07 (s, 0.05H), 0.33 (s, 3H), 0.38 (s, 2H), 0.42 (s, 1H);

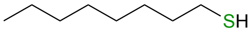
(4) Impurity: 7.33-7.61 (m, 5H arom) ppm.

Starting material (Dimethylphenylsilane): δ

0.38 (d, *J*=3.76 Hz, 6H, $SiC\mathit{H}_3$), 4.47 (sept, *J*=3.75 Hz, 1H, $Si\mathit{H}$), 7.39-7.40 (m, 3H arom), 7.57-7.58 (m, 2H arom) ppm.

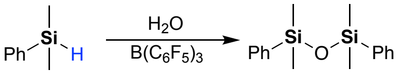
GC-MS: Compound 10: $C_8H_{17}SH$ = 0: 100 (Relative peak intensity)

Sulfur-containing compound:



(1) $C_8H_{18}S$, retention time 4.4 min, relative peak intensity (**21.6%**), MW: 146.11: $[M]^+$= 146.2 (80), 112.2 (40), 83.2 (80), 70.2 (85), 56.2 (100).

Non-sulfur containing compounds (silicone compounds):

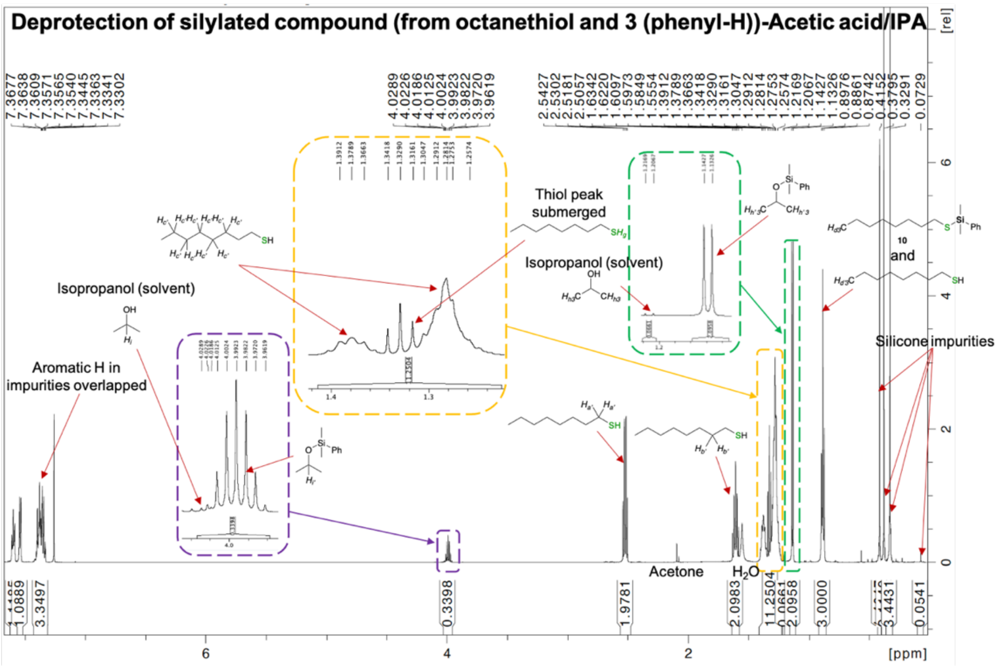


(2) $C_{16}H_{22}OSi_2$, retention time 9.6 min, relative peak intensity (**39.2%**), MW: 286.12: $[M]^+$= 286.2 (15), 271.2 (100), 255.1 (1), 193.1 (80), 179.1 (1), 165.1 (3), 135.2 (5), 105.1 (1), 89.1 (15).

(3) $C_8H_{12}OSi$ ($HOSiMe_2Ph$), retention time 4.9 min, relative peak intensity (**12.4%**), MW: 152.10: $[M]^+$= 152.1 (10), 137.1 (100), 91.1 (5), 77.1 (1).

(4) Relative peak intensity (**26.6%**), retention time 4.9 min, MW: 179.20: $[M]^+$= 179.2 (50), 137.1 (100), 116.1 (10), 105.1 (1), 91.1 (1), 75.1 (3).

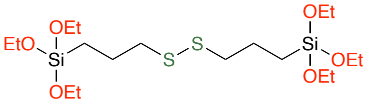
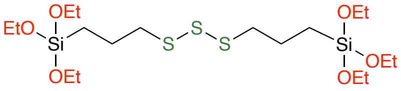
(5) Relative peak intensity (**0.2%**), retention time 6.2 min, MW: 179.10: $[M]^+$= 179.1 (75), 137.1 (100), 117.1 (30), 105.2 (5), 91.1 (10), 75.1 (20).



5.8.9 Titration of sulfur-based coupling agents using different silane sources

Characterization of starting materials - coupling agents

Table S5.5. GC-MS for commercial TESPD S2 starting material

Elution time (min)	M.W (g mol^{-1})	Structures	Relative ratio (%)
23.6	474		89.3
25.8	506		10.7

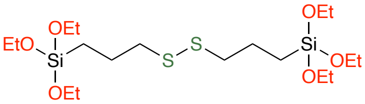
Starting material S2: $((SiOEt)_3(CH_2)_2C\mathit{H}_2)_2S_2$: $((SiOEt)_3(CH_2)_2C\mathit{H}_2)_2S_3$= 1: 0.1

The alkyl H and SiOEt overlapped in disulfide and trisulfide coupling agents and the integration of peaks were assigned using naphthalene as internal standard. The equivalents of disulfide coupling agent and tetrasulfide coupling agent were determined using the $C\mathit{H}_2$ adjacent to sulfur atom.

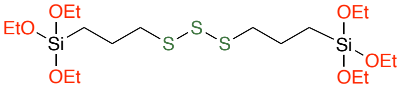
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $((SiOEt)_3(CH_2)_2CH_2)_2S_2$ (*1 equiv.*): 0.72-0.74 (m, 2H, $(SiOEt)_3(C\mathit{H}_2CH_2CH_2))_2S$), 1.23 (t, *J*=7.00 Hz, 9H, $SiOCH_2C\mathit{H}_3$), 1.78-1.83 (m, 2H, $(SiOEt)_3(CH_2C\mathit{H}_2CH_2))_2S$)), 2.70 (t, *J*=7.19 Hz, 2H, $((SiOEt)_3(CH_2)_2C\mathit{H}_2)_2S_2$), 3.82 (quartet, *J*=7.00 Hz, 6H, $SiOC\mathit{H}_2CH_3$);

(2) $((SiOEt)_3(CH_2)_2CH_2)_2S_3$ (*0.1 equiv.*): 0.72-0.74 (m, 2H, $((SiOEt)_3(C\mathit{H}_2CH_2CH_2))_2S$), 1.23 (t, *J*=7.00 Hz, 9H, $SiOCH_2C\mathit{H}_3$), 1.85-1.90 (m, 0.24H, $(SiOEt)_3(CH_2C\mathit{H}_2CH_2))_2S$)), 2.90 (t, *J*= 7.19 Hz, 0.20H, $((SiOEt)_3(CH_2)_2C\mathit{H}_2)_2S_3$), 3.82 (quartet, *J*=7.00 Hz, 6H, $SiOC\mathit{H}_2CH_3$) ppm.

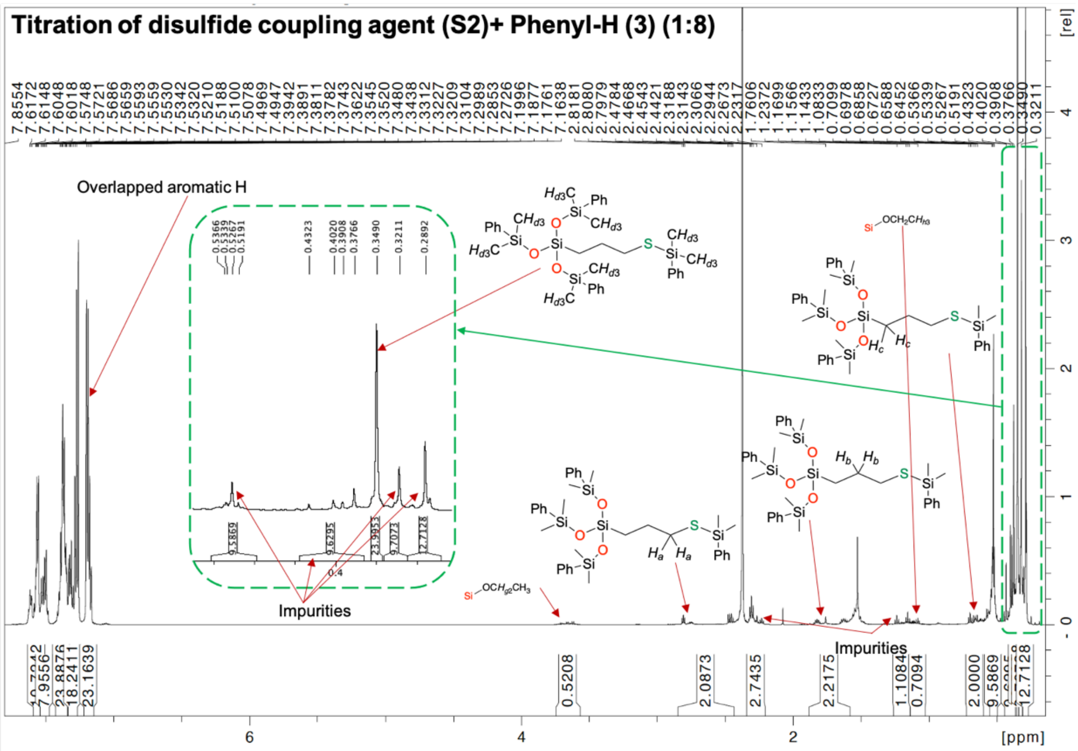
GC-MS: $((SiOEt)_3(CH_2)_3)_2S_2$: $((SiOEt)_3(CH_2)_3)_2S_3$ = 89.3: 10.7 (Relative peak intensity)

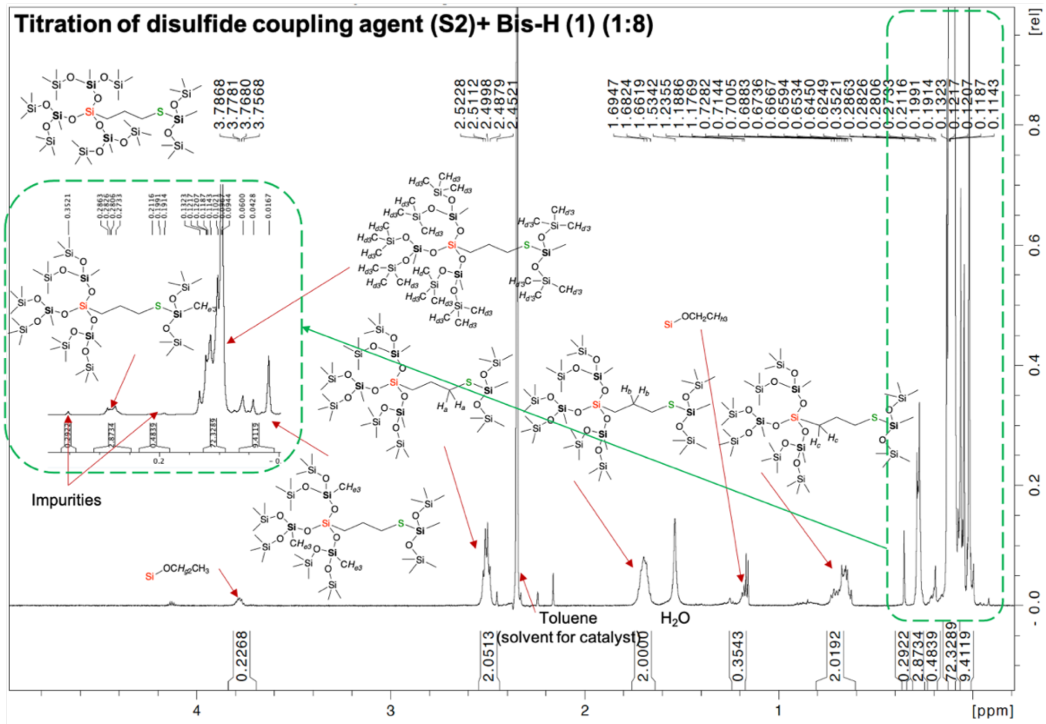


(1) $C_{18}H_{42}O_6S_2Si_3$, retention time 23.6 min, relative peak intensity (**89.3%**), MW: 474.20: $[M]^+$ = 474.2 (30), 429.2 (15), 395.2 (5), 355.1 (10), 313.0 (10), 281.1 (15), 253.0 (1), 224.0 (15), 205.1 (60), 192.1 (30), 163.1 (100), 135.1 (25), 107.1 (20), 91.1 (15), 79.0 (25), 63.1 (15).



(2) $C_{18}H_{42}O_6S_3Si_3$, , retention time 25.8 min, relative peak intensity (**10.7%**), MW: 506.17: $[M]^+$ = 506.1 (1), 281.0 (1), 191.1 (100), 119.1 (30), 79.0 (20).




Titration of disulfide coupling agent (S2)+ Bis-H (1) (1:8)
3.7868
3.7781
3.7680
3.7568
2.5228
2.5112
2.4998
2.4879
2.4521
1.6947
1.6824
1.6619
1.5342
1.3555
1.1886
1.1769
0.7282
0.7144
0.7005
0.6883
0.6736
0.6667
0.6594
0.6534
0.6450
0.6249
0.3521
0.2863
0.2826
0.2806
0.2733
0.2116
0.1991
0.1914
0.1323
0.1217
0.1207
0.1187
0.1143
Impurities
Si–OCH$_2$CH$_3$
Toluene (solvent for catalyst)
H$_2$O
H$_a$
H$_b$
H$_c$
0.2268
2.0513
2.0000
0.3543
2.0192
0.2922
2.8734
0.4839
72.3289
9.4119
[rel]
[ppm]

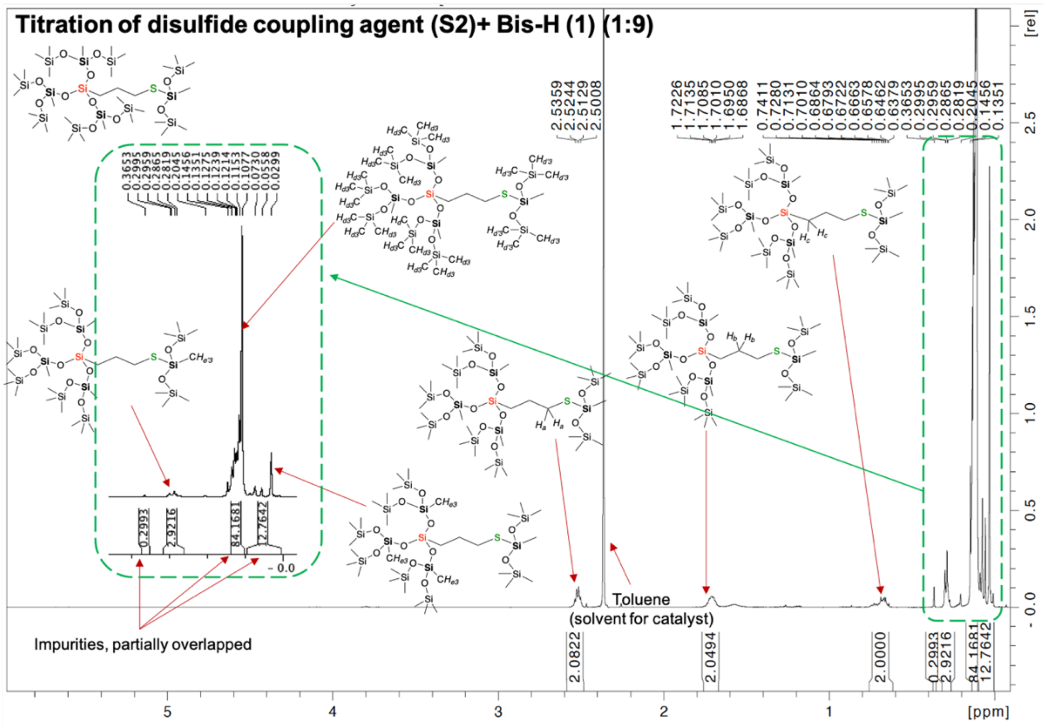
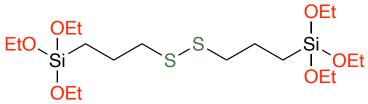
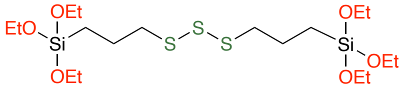
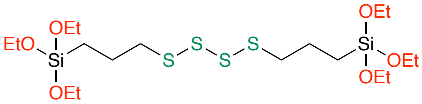
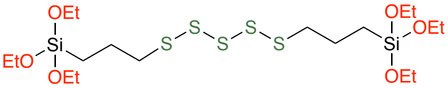
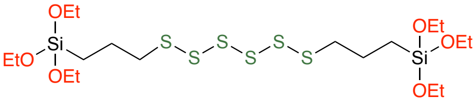

Titration of disulfide coupling agent (S2)+ Bis-H (1) (1:9)
2.5359
2.5244
2.5129
2.5008
1.7226
1.7135
1.7085
1.7010
1.6950
1.6868
0.7411
0.7280
0.7131
0.7010
0.6864
0.6793
0.6722
0.6663
0.6578
0.6462
0.6379
0.3653
0.2995
0.2959
0.2865
0.2819
0.2045
0.1456
0.1351
Impurities, partially overlapped
Toluene (solvent for catalyst)
H$_a$
H$_b$
H$_c$
2.0822
2.0494
2.0000
0.2993
2.9216
84.1681
12.7642
[rel]
[ppm]

Table S5.6. LC-MS for commercial TESPT starting material

Elution time (min)	M.W (g mol^{-1})	Structures	Relative ratio (%)
18.07	474		20.1
18.97	506		33.4
19.63	538		27.3
20.31	570		14.7
20.94	602		4.5

Starting material TESPT:

The equivalents are calculated based on the CH_2 peaks besides to oligosulfur. The number of sulfur atoms in the oligosulfide coupling agent denoted as **n**, for **n** >3, the CH_2 peaks overlapped, thus represented as n=4 (S_4).

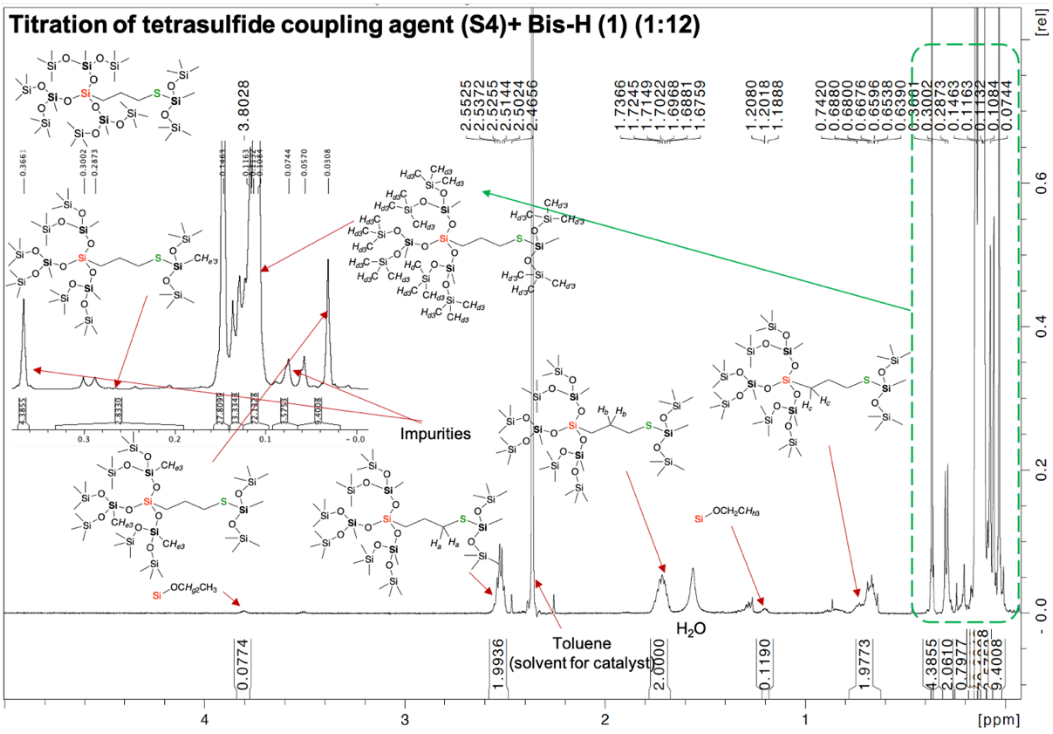
^{1}H NMR (600 MHz, chloroform-*d*): δ (1) $((SiOEt)_3(CH_2)_2CH_2)_2S_2$ (*0.36 equiv.*): 2.69 (t, *J*=7.18 Hz, 0.37H, $((SiOEt)_3(CH_2)_2CH_2)_2S_2$);

(2) $((SiOEt)_3(CH_2)_2CH_2)_2S_3$ (*0.58 equiv.*): 2.89 (t, *J*=7.19 Hz, 0.59H, $((SiOEt)_3(CH_2)_2CH_2)_2S_3$);

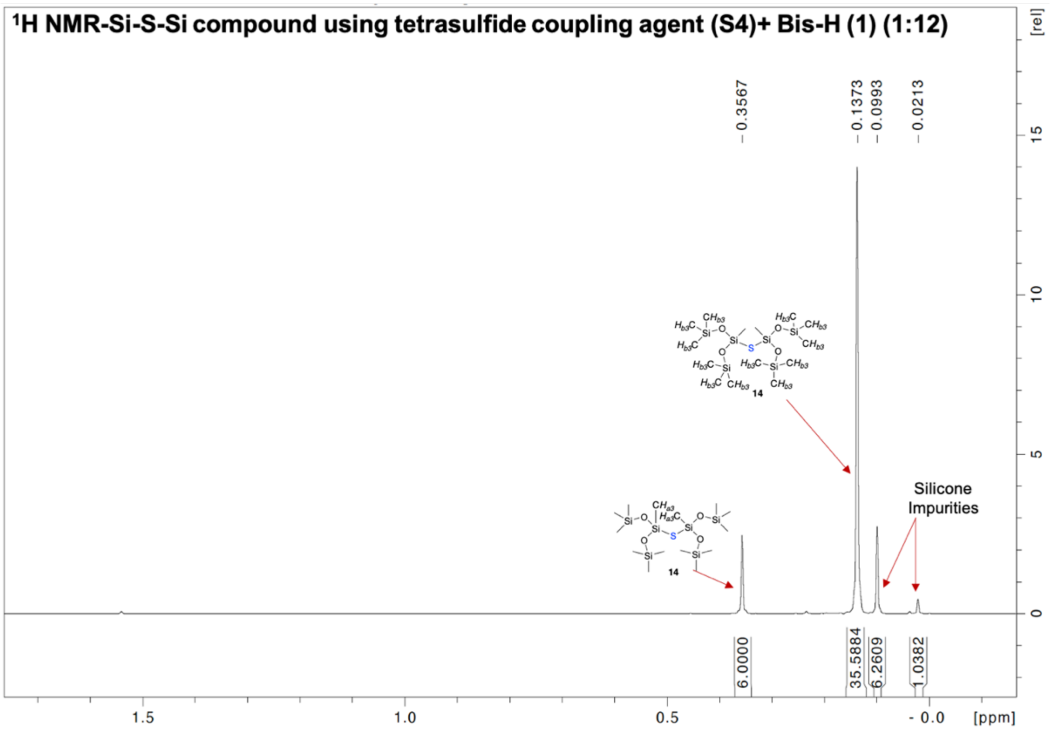
(3) $((SiOEt)_3(CH_2)_2CH_2)_2S_4$ (*1 equiv.*): 2.95-3.02 (m, 6H, $((SiOEt)_3(CH_2)_2CH_2)_2S_4$);

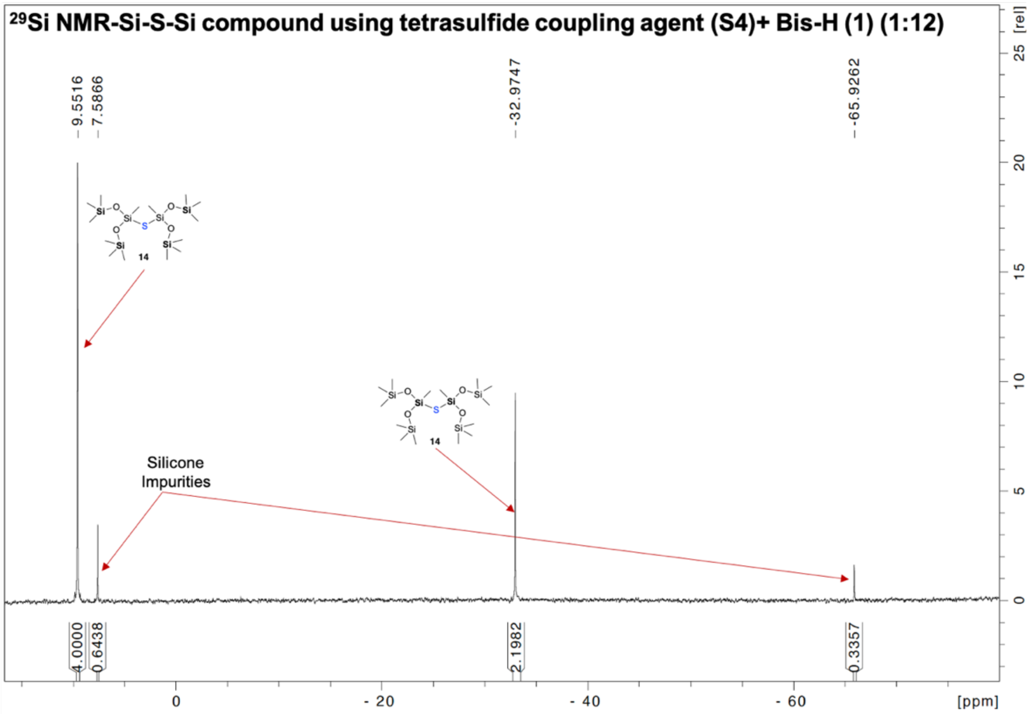
(4) Overlapped alkyl H: 0.71-0.77 (m, 2H, $((SiOEt)_3(CH_2CH_2CH_2))_2S$), 1.78-1.91 (m, 2H, $((SiOEt)_3(CH_2CH_2CH_2))_2S$);

(5) Overlapped ethoxy H: 1.23 (t, *J*=7.00 Hz, 9H, $SiOCH_2CH_3$), 3.80-3.84 (m, 6H, $SiOCH_2CH_3$) ppm.



5.8.10 Characterizations of the Si-S-Si compound 15 using commercial tetrasulfide coupling agent (S4) and Bis-H (1)




²⁹Si NMR-Si-S-Si compound using tetrasulfide coupling agent (S4)+ Bis-H (1) (1:12)
9.5516
7.5866
-32.9747
-65.9262
14
14
Silicone Impurities
4.0000
0.6438
2.1982
0.3357
0
- 20
- 40
- 60
[ppm]
0
5
10
15
20
25
[rel]

5.8.11 Following the titration process using commercial disulfide coupling agent (S2) and PhSiMe$_2$H (3)

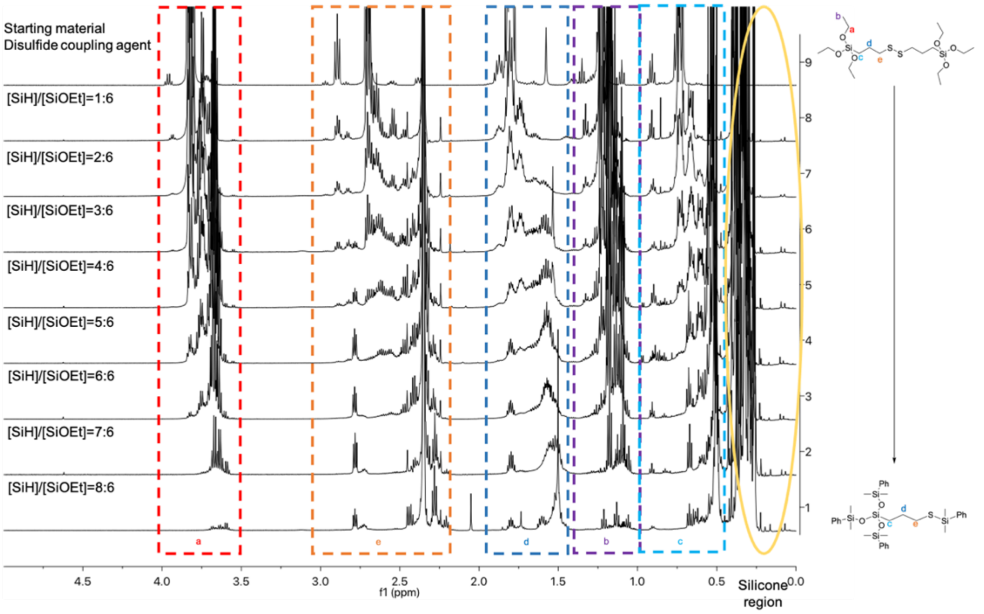


Figure S5.6. Titration of S2 reaction with PhSiMe$_2$H 3 monitored by ^{1}H NMR.

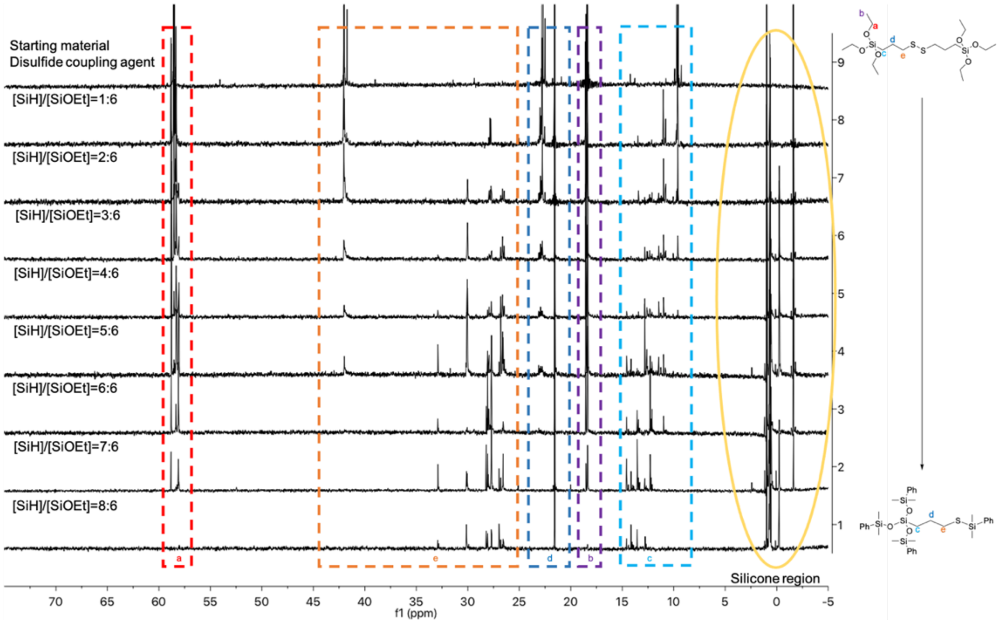


Figure S5.7. Titration of S2 reaction with PhSiMe$_2$H 3 monitored by ^{13}C NMR.

5.8.12 Characterizations of the titration process using commercial disulfide coupling agent (S2) and Bis-H (1)

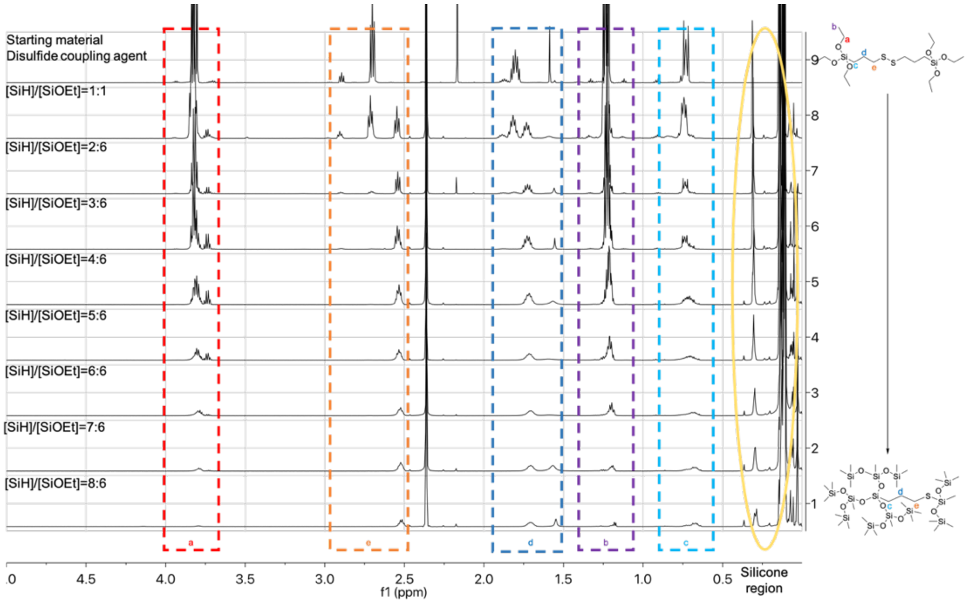


Figure S5.8. Titration of **S2** reaction with Bis-H **1** monitored by ^{1}H NMR.

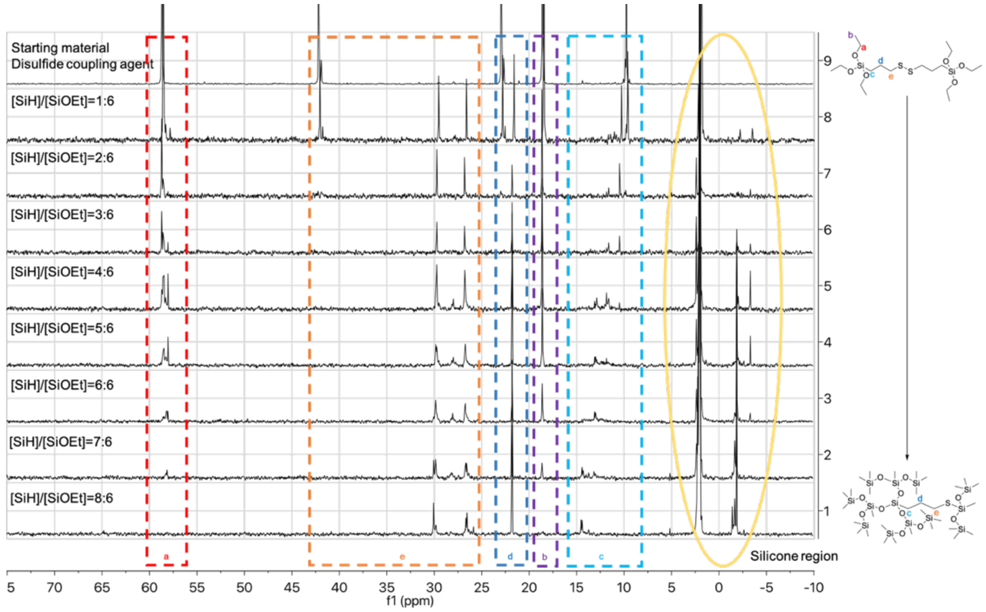


Figure S5.9. Titration of **S2** reaction with Bis-H **1** monitored by ^{13}C NMR.

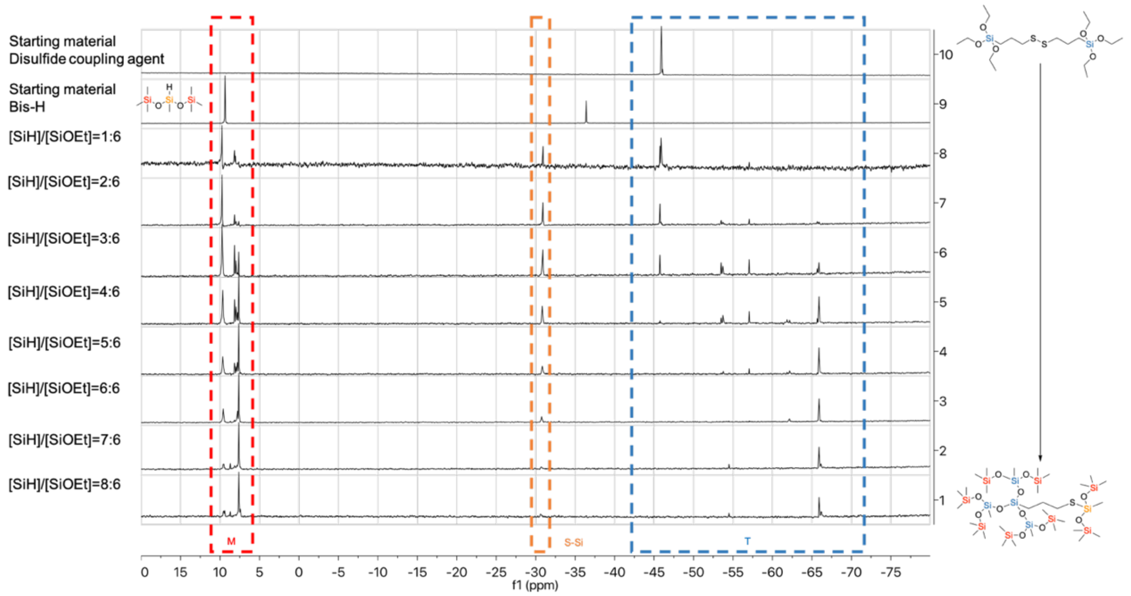


Figure S5.10. Titration of **S2** reaction with Bis-H **1** monitored by ^{29}Si NMR.

5.8.13 Characterizations of the titration process using commercial tetrasulfide coupling agent (S4) and Bis-H (1)

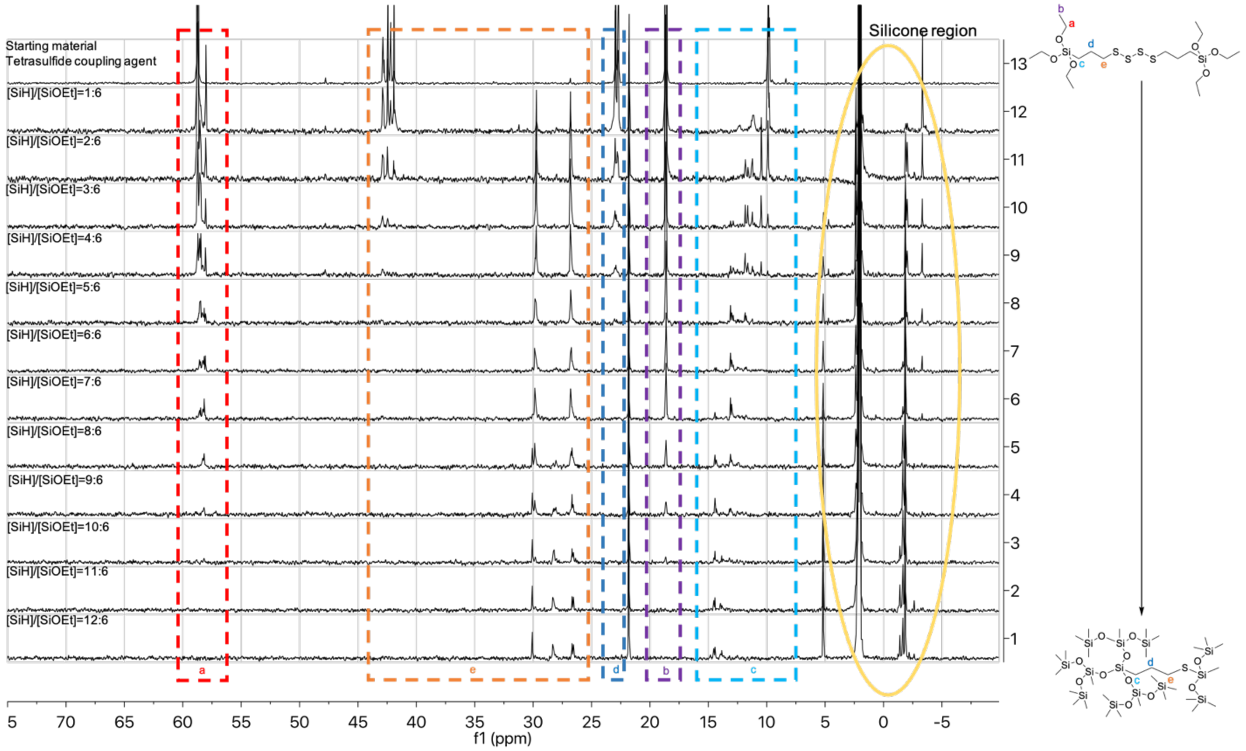


Figure S5.11. Titration of **S4** reaction with Bis-H **1** monitored by ^{1}H NMR.

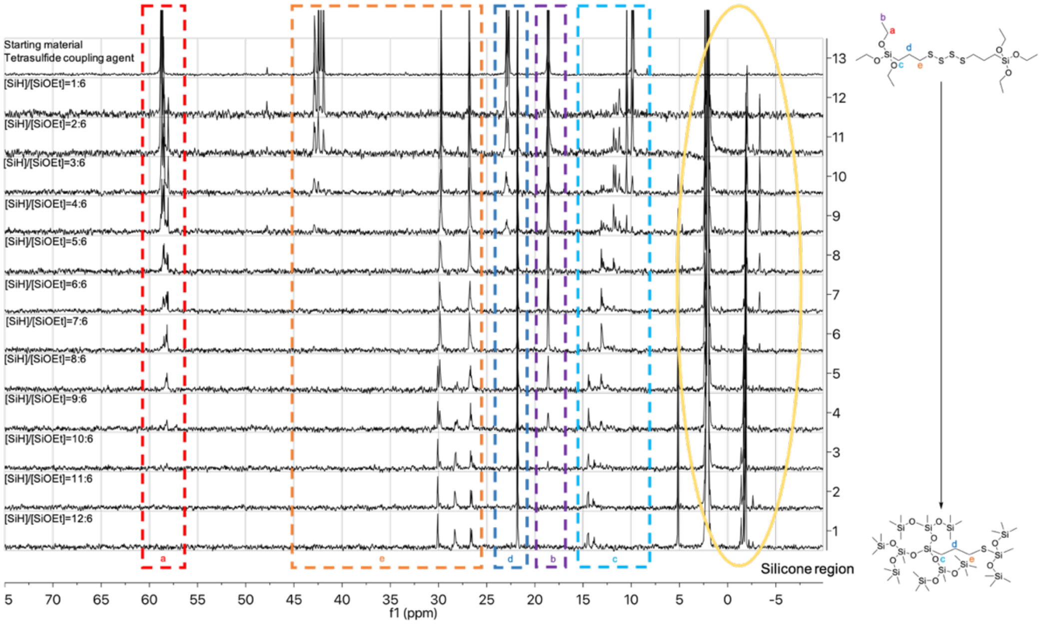


Figure S5.12. Titration of **S4** reaction with Bis-H **1** monitored by ^{13}C NMR.

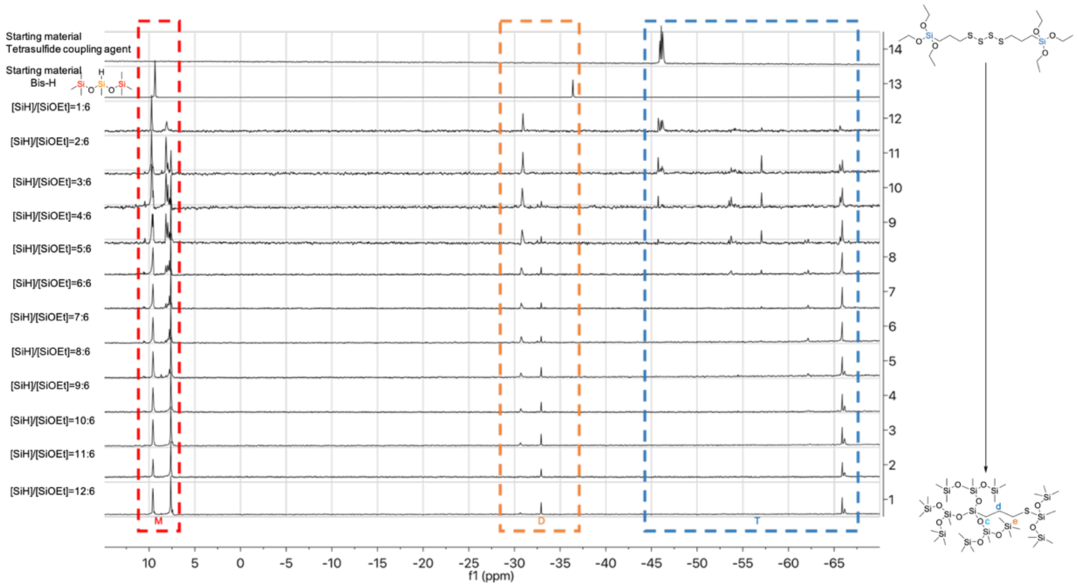


Figure S5.13. Titration of reaction with Bis-H **1** monitored by ^{29}Si NMR.

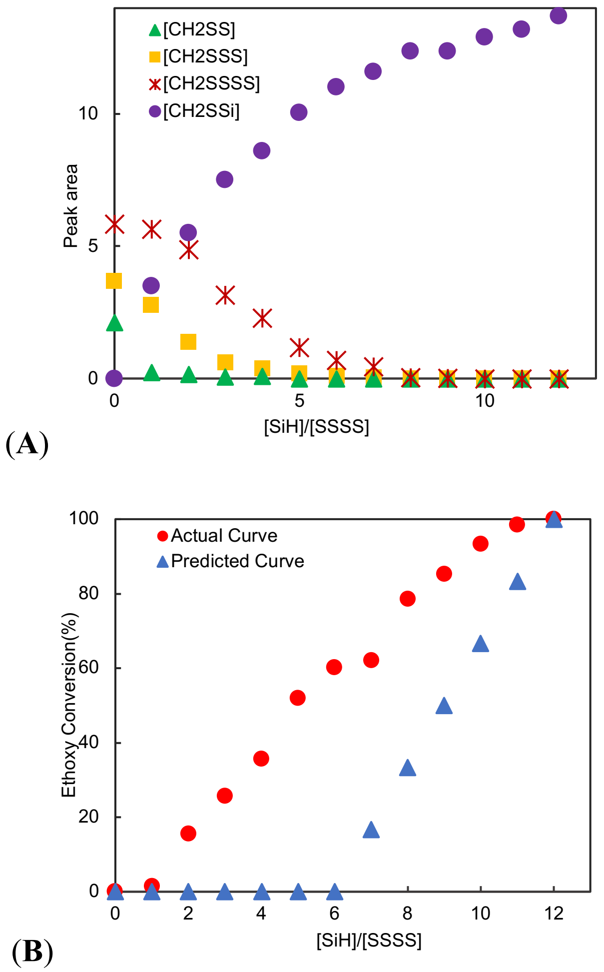


Figure S5.14. Complete reduction of using BisH ([SiH]/[SiOEt]=12:6; (**A**). Polysulfide reduction monitored using CH_2S_n in ^1H NMR. (B). Ethoxy conversion in commercial tetrasulfide coupling agent S4 (average sulfur atoms) versus [SiH]/[SS] using BisH, the predicted curve assumes complete reaction of SS bonds before reactions occur with alkoxysilanes.

Chapter 6: Conclusions

In Chapter **2**, we have developed an facile and efficient method to synthesis high molecular weight PDMS with maximum 153,900 g mol^{-1} from cheap, commercially available hydrosilane, tetramethyldisiloxane with water catalyzed by $B(C_6F_5)_3$ in a controlled and 'living' manner. The reactions in two phase reactions using either bulk water with neat M^HM^H or M^HM^H in dry toluene (50wt%) can be completed within only 30 minutes. Under either set of conditions, however, low D_4 (1-3%) content as produced and higher values of D_5 (2-10%) and particularly D_3 (13-33%). The method provides an alternative for the preparation of high molecular weight PDMS with valuable D_3 as the by-product.

In Chapter **3**, we have further investigated the mechanism and the control assembly of silicone polymers using this slow reaction of hydrosiloxanes with water in the presence of catalytic amount of $B(C_6F_5)_3$. The 'living' character of this process, controlled by the available water concentration, leads to silicones of molecular weight up to 250 000 g mol^{-1} with low dispersity. The facile method further implemented to the preparation of alternating block copolymers by reacting telechelic SiOH polymers and telechelic SiH polymers in the absence of water. An accidental excess of silanols is overcome simply by adding excess dihydrosilicones to restart the process. Conclusively, we have explored the scope of this mild and simple method for the preparation of a versatile of silicone in a controlled manner.

In Chapter **4**, we have further advanced the PR reaction in the preparation of spatially controlled vinyl-pendent linear silicones, with vinyl spacing varying from 1/3 to 1/250 monomer units, low dispersities, and molecular weights of the obtained polymers ranging from 12,100 to 102,400 g mol^{-1}. The tunable terminal groups (SiH or SiOMe) of the vinyl-pendent polymers could by chosen by tuning the stoichiometry of the hydride-terminated PDMS and dimethoxymethylvinylsilane starting materials. Moreover, the SiH termini polymers underwent self-crosslinking with the pendant vinyl groups in the presence of Pt catalyst to give soft silicone elastomers containing residual vinyl groups which allows secondary modification to form harder silicone elastomers. The vinyl groups were also used as loci from which dendritic branches were grown, eventually to make highly branched functional oils. The library of polymers produced, with precisely spaced mono- or dendritic multi-functional pendent groups, follows the paradigm of greater synthetic control to give narrower ranges of properties, and will permit an assessment of structure property relationships to allow the design of better silicone polymer fluids and elastomers.

In Chapter **5**, we investigated into the reaction of hydrosilane as reducing agent for disulfide cleavage in the presence of $B(C_6F_5)_3$. We found that thiols and disulfides are readily converted to silyl thio ethers by reduction with hydrosilanes and hydrosiloxanes in the presence of less than 1mol% $B(C_6F_5)_3$. Alcohols react more rapidly than the thiols or disulfides, but alkoxysilanes react more slowly: the observed reactivity order was ROH > RSH > RSSR > SiOR. Reaction rates of the three alkoxy groups in coupling agents were only slightly different such that RSi(OR)(OSiR'3)2 and RSi(OR)2OSiR"3 could only be prepared as mixtures. TBAF, atypically, was not efficacious at deprotecting the silyl thio ether and led instead to reoxidation to the disulfide; alcoholysis with IPA was a convenient alternative to recover the thiol provided that the silane was not too bulky.